Scuola di Dottorato di Ricerca in Ingegneria Industriale
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Dipartimento di Ingegneria Industriale
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Nicola Gemo

ENGINEERING THE CATALYTIC
BATCHWISE SYNTHESIS OF H₂O₂
FROM ITS ELEMENTS

Direttore della Scuola: Ch.mo Prof. Paolo Colombo
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Sede Amministrativa: Università degli Studi di Padova

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Preface

The present work was carried out at the Dipartimento di Principi ed Impianti di Ingegneria Chimica (DIPIC), Università di Padova, between 2009 and 2012. Financial support from the Cariparo Foundation is gratefully acknowledged. This research would not have been possible without the supervision and guidance of Prof. Paolo Canu, to whom my deepest esteem goes. His clever ideas and stimulating scientific discussions were, and still are, sincerely appreciated. Experimental studies were also performed at the Laboratory of Industrial Chemistry and Reaction Engineering, Department of Chemical Engineering at Åbo Akademi University, Finland, under the guidance of Academy Prof. Tapio Salmi, whose support and precious advices were fundamental to this work. Financial support during the period spent in Finland from Åbo Akademi Foundation (Johan Gadolin Scholarship) is gratefully acknowledged.

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Last but not least, I would like to thank Sabrina for her immense patience and support.
Abstract

Hydrogen peroxide is a versatile oxidizing agent with several industrial applications. It is also one of “greenest”, since its oxidation by-product is only water. The global demand of the peroxide is increasing, due to its recent usage in new large scale oxidation processes, such as the epoxidation of propylene to propylene oxide and the synthesis of caprolactam. Nowadays most of the world production of H$_2$O$_2$ is carried out by the anthraquinone autoxidation process. Though very safe (H$_2$ and O$_2$ are never in direct contact), the costs related to the high energy consumption for the extraction and purification of the peroxide produced, together with the usage and periodic replacement of toxic and expensive solvents, stimulated the interest in new production paths. Among the several alternatives proposed, the most fascinating one is the direct synthesis (DS) from H$_2$ and O$_2$. It is a environmentally friendly process that would be economically profitable for an in-situ production, requiring lower investments and operating costs. During the last thirty years this system has been under intensive study both by industries as well as academia. However, it has not been commercialized yet, mainly because of poor selectivity and safety concerns.

While most of the efforts on improving DS must address the catalyst, there are reaction engineering aspects that deserve attention. DS is frequently carried out in solvents other than water, both to improve H$_2$ solubility and isolate the undesired product (H$_2$O). Further, CO$_2$ is used for safety, H$_2$ solubility and H$_2$O$_2$ stability. However, the lack of information about the solubility of the reagents makes it difficult to develop a realistic kinetic description of the reactions involved in the DS process. Hence, the first step of the research presented herein dealt with solubility measurements, at temperatures in the range 268-288 K and pressures between 0.37 and 3.5 MPa. Measurements were focused on H$_2$, i.e. the limiting reagent during the reaction. At all conditions investigated a linear relation between hydrogen partial pressure and concentration was observed. Increasing the temperature resulted in an enhanced H$_2$ solubility at the same H$_2$ partial pressure. At constant H$_2$ fugacity, the presence of CO$_2$ favored the dissolution of hydrogen in the liquid phase. Correlation and generalization of the measurements were provided through an EoS-based thermodynamic model for the estimation of H$_2$ solubility at reaction conditions.
A batch apparatus for the direct synthesis of hydrogen peroxide was developed, to carry out activity measurements on new catalysts and develop a quantitative model of the kinetics. Hydrogenation, disproportionation and direct synthesis reactions were studied on a commercial 5 wt.% Pd/C catalysts at temperatures in the range 258-313 K and pressure up to 2 MPa. Separate experiments were performed to highlight the role of each reaction. An enhanced H$_2$O$_2$ production was obtained adopting different H$_2$ feeding policies, although selectivity did not exceeded 30%.

A model of the gas bubbling, batch slurry reactor for H$_2$O$_2$ direct synthesis was developed. A sensitivity analysis on the mass transfer coefficients excluded any limitations occurring at experimental conditions. Comparable temperature dependence was observed for H$_2$O production, hydrogenation and disproportionation (activation energies close to 45 kJ mol$^{-1}$), while H$_2$O$_2$ synthesis had a much lower activation energy (close to 24 kJ mol$^{-1}$), suggesting that a higher selectivity is achievable at low temperature. Disproportionation reaction had a very limited influence on the overall peroxide production rate, while hydrogenation was the most rapid side reaction. Water formation was significant, prevailing at higher temperatures.

Following these results, Pd and PdAu catalysts supported on SBA15 were prepared and investigated for H$_2$O$_2$ direct synthesis. Catalysts were doped with bromine, a promoter in the H$_2$O$_2$ direct synthesis. Productivity and selectivity decreased when bromine was incorporated in the catalysts, suggesting a possible poisoning due to the grafting process. A synergetic effect between Pd and Au was observed both in presence and absence of bromopropylsilane grafting on the catalyst. Three modifiers of the SBA15 support (Al, CeO$_2$ and Ti) were chosen to elucidate the influence of the surface properties on metal dispersion and catalytic performance. Higher productivity and selectivity were achieved incorporating Al into the SBA15 framework, whereas neither Ti nor CeO$_2$ improved H$_2$O$_2$ yields. The enhanced performance observed for the PdAu/Al-SBA15 catalysts was attributed to the increased number of Brønsted acid sites.

Supported catalysts were also synthesized depositing Pd on a highly acidic, macroporous PS-DVB resin (Lewtit K2621). Catalysts with active metal content in the range 0.3-5 wt.% were tested batchwise for the direct synthesis of H$_2$O$_2$. Preliminary H$_2$O$_2$ measurements and X-ray photoelectron spectroscopy (XPS) analysis revealed that the reduced form of Pd was more selective than PdO towards the peroxide. Transmission electron microscopy (TEM) images
showed that smaller nanoclusters favored the production of \( \text{H}_2\text{O} \), likely due to their O-O bond breaking aptitude.
Il perossido di idrogeno è un potente agente ossidante, molto usato nella pratica industriale. È uno dei meno tossici, dal momento che l’unico sottoprodotto della sua ossidazione è l’acqua.

A livello mondiale, la domanda di H\textsubscript{2}O\textsubscript{2} è in costante aumento, non da ultimo grazie a recenti usi in nuovi processi ossidativi, quali l’eossidazione del propilene e la sintesi del caprolattame. Attualmente l’acqua ossigenata viene prodotta quasi esclusivamente attraverso l’auto-ossidazione dell’antrachinone. Sebbene molto sicuro (non vi è mai contatto diretto tra idrogeno ed ossigeno), questo processo presenta alcuni svantaggi, quali ad esempio gli alti costi di esercizio, dovuti in particolare all’alta richiesta energetica per la separazione e la purificazione del perossido prodotto. Si tratta inoltre di un processo potenzialmente inquinante, in quanto fa uso di costosi solventi tossici, e dagli alti costi d’investimento, essendo economicamente vantaggioso solo per grandi produzioni (>4*10\textsuperscript{4} tonnellate all’anno). Pertanto l’H\textsubscript{2}O\textsubscript{2} è attualmente prodotta in pochi grandi impianti e trasferita per grandi distanze all’utente finale. Il trasporto aggiunge costi e rischi, in quanto soluzioni concentrate di H\textsubscript{2}O\textsubscript{2} possono decomporre violentemente. Nelle ultime decadi vi è stato un notevole interesse nella ricerca di nuovi processi di produzione del perossido di idrogeno, che fossero contemporaneamente meno costosi ed inquinanti. Tra le varie alternative proposte, la più affascinante è sicuramente la sintesi diretta a partire da H\textsubscript{2} ed O\textsubscript{2}. Si tratta di un processo “verde”, che si propone di eliminare i sottoproducti inquinanti e, allo stesso tempo, ridurre i costi di produzione, rendendo economicamente vantaggiosa la produzione in situ presso l’utilizzatore finale. Nonostante il grande interesse sia industriale che accademico suscitato da tale processo negli ultimi trent’anni, a tutt’oggi non vi è nessuna applicazione industriale. Il motivo di ciò è da ricercarsi principalmente nei problemi di sicurezza e selettività che a tutt’ora restano irrisolti.

La mancanza di informazioni sulla solubilità dei reagenti alle condizioni di reazione rende difficoltoso ottenere una descrizione cinetica precisa delle reazioni coinvolte nella sintesi diretta. Pertanto i pri\textsuperscript{...}mo passi della ricerca qui presentata sono stati mossi con l’obiettivo di raccogliere dati di solubilità alle condizioni di reazione (temperatura compresa tra i 268 e i 288 K e pressione tra 0.37 e 3.5 MPa). In particolare, si era interessati all’H\textsubscript{2}, in quanto reagente limitante del processo. A tutte le condizioni indagate, è stata riscontrata una
relazione lineare tra la pressione parziale e la concentrazione di H₂. Contrariamente a quanto normalmente avviene, l’incremento di temperatura ha avuto l’effetto di aumentare la solubilità nella fase liquida (a parità di pressione parziale). Inoltre, a parità di fugacità di H₂, la presenza di CO₂ ha favorito la concentrazione dell’H₂ nel liquido. I risultati ottenuti sono stati generalizzati sviluppando un modello per stimare la solubilità dell’H₂ alle condizioni di reazione.

E’ stato poi realizzato un apparato batch per la sintesi diretta di acqua ossigenata. Un catalizzatore commerciale a base di Pd (5 wt.%) su carbone è stato utilizzato per studiare le reazioni di idrogenazioni, dismutazione e sintesi a temperature comprese tra 258 e 313 K e pressioni fino a 2.0 MPa. Il ruolo di ciascuna reazione è stato studiato attraverso esperimenti specifici. Appropriate politiche di alimentazione dell’H₂ hanno permesso di realizzare un aumento di produzione rispetto a condizioni tipicamente batch. Tuttavia il catalizzatore testato ha rivelato limiti di selettività, non superando valori del 30% ca.

Per studiare le cinetiche di reazione, è stato sviluppato un modello per il reattore batch. Un’analisì di sensitività sui coefficienti di trasporto di materia (sia dalla fase gassosa alla liquida che dalla liquida al catalizzatore) ha permesso di escludere ogni limitazione tra le fasi coinvolte nelle reazioni. Le reazioni indesiderate (formazione di H₂O, dismutazione ed idrogenazione) hanno rivelato una simile dipendenza dalla temperatura (con un’energia di attivazione di circa 45 kJ mol⁻¹). Una minore energia di attivazione è stata ottenuta per la reazione di sintesi diretta di H₂O₂ (24 kJ mol⁻¹), il che suggerisce che la selettività è favorita alle basse temperature. Un confronto tra le velocità delle reazioni coinvolte ha permesso di identificare la dismutazione come la reazione più lenta di distruzione del perossido. Inoltre, la formazione di acqua era sempre significativa, compromettendo la selettività.

A seguito di questi risultati, si è deciso di focalizzare l’attenzione sul catalizzatore. Catalizzatori mono e bi-metallici sono stati realizzati depositando Pd e PdAu su SBA15, una silice macroporosa e strutturata. Tali catalizzatori sono stati anche dopati con l’aggiunta di bromo, un noto promotore della reazione di sintesi diretta. Sia la selettività che la produttività sono diminuite modificando i catalizzatori con l’alogenio, probabilmente a causa di un avvelenamento durante la procedura di innesto del bromo. Una sinergia tra i metalli Pd e Au è stata osservata sia nei catalizzatori con e che senza bromo. Tre modifiche sono state apportate al miglior catalizzatore sviluppato (PdAu/SBA15) per evidenziare l’influenza delle proprietà superficiali sulla reazione di sintesi diretta. Tre modificatori sono stati incorporati nel
supporto: Al, CeO₂ e Ti. Un aumento sia di selettività che di produttività è stato riscontrato solo con l’aggiunta di Al. Tale risultato è stato attribuito al maggior numero di siti acidi di Brønsted riscontrati su questo catalizzatore.

Un'altra famiglia di catalizzatori, con un contenuto di metallo attivo variabile tra lo 0.3 ed il 5 wt.%, è stata sintetizzata depositando del Pd su una resina acida e macroporosa, miscela di PS e DVB. I risultati preliminari dei test catalitici e delle analisi di spettroscopia fotoelettronica a raggi X (XPS) hanno rivelato che lo stato di ossidazione del palladio più selettivo verso il perossido è quello ridotto, mentre il PdO porta più facilmente alla formazione di H₂O. Le immagini al microscopio elettronico a trasmissione (TEM) hanno mostrato che i nanocluster di Pd più piccoli portato alla formazione preferenziale di H₂O, il che è probabilmente legato alla loro propensione alla rottura del legame O-O.
List of publications

The thesis consists of an extended summary and the following publications for a detailed description of the work. Throughout the text, the publications are referred to by their roman numbers.


List of related contributions

1. CAMURE-8 (Catalysis in Multiphase Reactors) & ISMR-7 (International Symposium on Multifunctional Reactors), Naantali, Finland, May 22nd – 25th 2011, Oral presentation

2. GLS10 (Gas-Liquid and Gas-Liquid-Solid reactor Engineering), Braga, Portugal, June 26th -29th 2011, Poster presentation

3. APCRE’11 (The 6th Asia Pacific Chemical Reaction Engineering Symposium), Beijing, China, 18th -21st September 2011, participant

4. The 15th Nordic Symposium on Catalysis, Mariehamn, Åland (Finland), 10th – 12th June 2012, Oral presentation

5. ISCRE22 (International Symposium on Chemical Reaction Engineering), Maastricht, The Netherlands, September 2th – 5th 2012, Oral presentation


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1 Introduction

1.1 General

Hydrogen peroxide is an attractive, non-polluting oxidizing agent with several industrial applications. It is considered one of the most efficient oxidant by virtue of the high oxygen content and its oxidation potential (1.78 eV), comparable to that of ozone (2.07 eV). It is also one of the greenest since its oxidation by-products comprise water and oxygen only. The current global \( \text{H}_2\text{O}_2 \) production is approximately 2.7 mln tons per year and its demand is increasing by 4\% per annum\(^1\). This growth is mainly due to its recent usage in new large scale oxidation processes (Figure 1.1), such as the epoxidation of propylene to propylene oxide and the synthesis of caprolactam (Sumitomo).

![Chemical Synthesis](image1.png)

Figure 1.1. Main uses of hydrogen peroxide

\( \text{H}_2\text{O}_2 \) is also widely used in the waste and wastewater treatments, textile, pulp and paper bleaching industries (as an environmentally friendly alternative to chlorine), in mining and processing of metals and in the production of stain free detergents. Large amounts of low concentration \( \text{H}_2\text{O}_2 \) solution are consumed by the cosmetic and pharmaceutical industries for its disinfecting properties, whereas highly pure \( \text{H}_2\text{O}_2 \) is used for etching and purification of electronic materials.

Hydrogen peroxide was first discovered by the French chemist Louis Jacques Thénard in 1818, reacting barium peroxide with nitric acid. Once produced mainly via the electrolysis of...
ammonium sulfate, nowadays H$_2$O$_2$ is almost exclusively manufactured by the anthraquinone autoxidation process (1936). This process involves a catalytic hydrogenation, followed by an oxidation reaction to yield H$_2$O$_2$. Anthraquinone is used as a H$_2$ carrier to avoid the H$_2$/O$_2$ direct contact, so that the process is very safe. However, several drawbacks are involved, such as the use and periodic replacement of toxic and expensive solvents (anthraquinone, ester, hydrocarbons, octanol/methyl-naphthalene) and the high energy cost for the extraction and purification of the H$_2$O$_2$ produced. Moreover, it is profitable only for large-scale production. The transportation to the final consumer creates additional costs and safety issues since concentrated H$_2$O$_2$ can violently decompose and explode. For all these reasons, in the last decades there have been many efforts to develop cost-effective and greener processes to obtain the peroxide. Different solution were proposed, such as fuel cell technology and H$_2$/O$_2$ non-equilibrium plasma reaction. However, the most fascinating alternative to the anthraquinone route is the direct synthesis (DS) from H$_2$ and O$_2$. It is an environmentally friendly process (no toxic solvents are required) that would be profitable also for small scale plants, reducing the investments and operating costs for an economically viable in-situ production. During the last thirty years the direct synthesis of hydrogen peroxide has been under intensive study both by industry as well as academia\textsuperscript{1-3}. However, despite many efforts, selectivity is still an obstacle to the industrial feasibility. Although the reaction H$_2$+O$_2$→H$_2$O$_2$ is in principle very simple, the complete reaction pathway is more complex (Scheme 1.1).

\begin{center}
\begin{tikzpicture}
\node[draw, thick, circle, fill=blue!10] (H2O2) at (0,0) {H$_2$O$_2$};
\node (H2) at (-1.5,-1) {H$_2$};
\node (O2) at (-1.5,-2) {O$_2$};
\node (0.5O2) at (-1.5,-3) {0.5 O$_2$};
\node (H2O) at (-1.5,-4) {H$_2$O};
\draw [->, thick] (H2O2) -- (H2) node [midway, above] {+H$_2$};
\draw [->, thick] (H2O2) -- (O2) node [midway, above] {+O$_2$};
\draw [->, thick] (H2O2) -- (0.5O2) node [midway, above] {+0.5 O$_2$};
\draw [->, thick] (H2O2) -- (H2O) node [midway, above] {H$_2$O + 0.5 O$_2$};
\draw [->, thick] (H2O2) -- (2H2O) node [midway, above] {2 H$_2$O};
\end{tikzpicture}
\end{center}

Scheme 1.1. Reactions involved in the direct synthesis of H$_2$O$_2$.

All the reactions involved are thermodynamically favored and highly exothermic. Moreover, the contribution of each reaction differs with the conditions (i.e. temperature, pressure, promoters, stabilizers, reactant medium, etc). Two consecutive (hydrogenation and disproportionation) and one parallel reaction (H$_2$O formation) competing with the selective H$_2$ oxidation to H$_2$O$_2$ are involved. All the undesired reactions are promoted by the same catalyst active for the selective hydrogenation to the peroxide, severely limiting the selectivity. The DS process also imply the direct contact between H$_2$ and O$_2$, raising safety concerns\textsuperscript{3,4}. The
flammability limits of H$_2$ in O$_2$ are quite narrow (4-94%), so that safe mixtures must be highly
diluted. Unfortunately, operations with mixtures outside flammability limits showed a drop of
the H$_2$O$_2$ production to industrially unacceptable values\(^2\). For all these reasons,
notwithstanding the efforts of several companies (BASF, EniChem S.p.A., Dow Chemical,
DuPont, Solvay Interox, Mitsubishi Gas Chemical Co.), the direct synthesis process has yet
not been commercialized. The development of this approach for the industrial production of
H$_2$O$_2$ would be a real breakthrough in the oxidation process technology.

1.2 Approaches to the direct synthesis

H$_2$O$_2$ direct synthesis is normally carried out in a three phase system. Basically, hydrogen and
oxygen are dissolved in a proper reaction medium (i.e. alcoholic solution or water) and react
over a solid catalyst. Since the early 90’s, the DS process attracted interests of many research
groups, trying to develop new catalyst concepts, reactor design and operation conditions\(^1,2,5-16\). Despite results of different works are difficult to compare, mainly because of the different
reaction conditions adopted, a comparison of literature studies can give important insights
about the different approaches to the direct synthesis. Batch reactors are usually adopted for
catalytic tests\(^6,7,11-13\), semi-batch reactors to investigate the operation conditions and enhance
the production of H$_2$O$_2$\(^7,11,12,14\), membrane reactors and microreactors\(^5,10,17\) to operate safely
within flammability limits and, therefore, try to enhance both productivity and selectivity.

Methanol is often chosen as the reactant medium\(^5,8,11-13\), in view of an integration with the
propylene oxide synthesis, where the propylene reacts with the hydrogen peroxide in
methanol. Water is instead chosen for safety reasons and for its lower cost\(^9,10,14\).

Temperatures between -263 and 278 K are suitable to avoid the consecutive reactions
(hydrogenation and disproportionation)\(^6,13\). Operations at temperatures up to 313 K
necessarily require the addition of stabilizers in the reaction medium\(^9,14\).

An inert gas is usually required to dilute the gas mixture outside flammability limit. At the
same time, the inert enhances the total pressure in the system, increasing the rather low
solubility of the reagent gases and hence the H$_2$O$_2$ production rate. Carbon dioxide is often
used for these scopes. Systems involving CO$_2$-expanded liquids (such as methanol) are a
current topic in modern chemical synthesis. Besides advantages due to the mixture physical
properties, mainly related to marked modifications of the vapor-liquid equilibrium, CO$_2$
brings about a reduced impact on environment and minimization of safety issues\(^4,18\). Both
homogeneously and heterogeneously catalyzed reactions have been tested in CO$_2$ expanded solvents. Research interest is especially focused on reactions limited by a poor solubility of reactant gas, such as hydrogenations and oxidations, making this gas particularly appealing for the DS process.

1.3 Catalysts

Most of the catalysts for the hydrogen peroxide direct synthesis are based on Pd, supported on a great variety of substrates such as C, SiO$_2$, ZrO$_2$ and Al$_2$O$_3$. Enhanced productivity and selectivity were observed upon addition of a second metal, specifically Au. Although Au-only catalysts are generally less effective than Pd-only catalysts, a synergetic effect was observed combining these two metals. An Au-rich core, Pd shell structure was suggested for the Au-Pd nanoclusters, with the Au acting as an electronic promoter for the surface Pd atoms. Other authors proposed that isolated Pd atoms are the most efficient for the H$_2$O$_2$ direct synthesis, with Au playing a fundamental role in the isolation of Pd atoms within a gold matrix. Acid are often added to the reaction medium to prevent the hydrogenation/disproportionation reactions. Several papers report the beneficial effect of the H$^+$ ion in promoting the selectivity towards the peroxide. Although different explanation have been proposed, including a possible influence on the electronic state of the Pd surface, the specific role of the proton remains unclear. Halide are also known to increase the selectivity towards H$_2$O$_2$, especially bromide and chlorine. However, highly concentrated acid solutions requires special equipments. Moreover, the presence of proton and halides ions favor the leaching of the active metal, compromising the stability of the catalyst. Solid acid supports are an interesting solution to minimize the presence of inorganic acid in the reaction medium.

1.4 Reaction kinetics

Despite numerous studies, a general understanding of the reaction mechanism involved in the DS process has not yet been achieved. The unwanted reactions (Scheme 1.1) could be minimized acting on the operating conditions, in addition to designing a suitable catalyst, but kinetics and mass transfer limitation must be known. Most of the researches concentrate on the catalyst design, where different metals or combination of metals and supports were studied to minimize the unwanted reactions. However, results are difficult to compare mainly because of the different catalysts and reaction conditions involved. Recently
contributions on the kinetics are growing in the Literature\textsuperscript{8, 9, 39, 51, 52}. The main efforts were spent in rationalizing the effect of different reaction conditions on the catalyst and develop models to study the actual mechanism, for further optimization of selectivity and production rate. Still, there is no agreement on the mechanism and conditions favoring the synthesis and the kinetic remains mostly empirical.

1.5 Research strategy

In a context where efforts to develop DS appear to concentrate exclusively on the search for a breakthrough catalyst, we addressed the engineering of the reaction, trying to exploit the potential of the ever improving catalysts.

The determination of H\textsubscript{2} solubility at reaction condition was the starting point of the research. Up to now, the lack of information on vapor-liquid equilibria makes it difficult to obtain a precise kinetic description of this process, where solubility modifications confuse with kinetics. Under H\textsubscript{2} poor conditions, often prevailing in H\textsubscript{2}–O\textsubscript{2} mixtures to operate outside the (lower) flammability limit, H\textsubscript{2} solubility is the key information required. In Publication I, solubility data for hydrogen in methanol, in CO\textsubscript{2} + CH\textsubscript{3}OH and in CO\textsubscript{2} + CH\textsubscript{3}OH + O\textsubscript{2} were collected and critically compared with available literature data, in the range 268 < T/K < 288 and total pressures between 1 and 3.5 MPa (H\textsubscript{2} partial pressure varied between 0 and 1 MPa). A thermodynamic model was also proposed, developing an equation for the estimation of a pseudo Henry constant of H\textsubscript{2}.

A proper apparatus was design to study the optimal reaction conditions, as documented in Publication II. Methanol was chosen as the reaction medium. CO\textsubscript{2} diluted the H\textsubscript{2}/O\textsubscript{2} mixture outside flammability limits. A 5% Pd on carbon catalyst (Evonik) was used both for its commercial availability and for its stable performance. Hydrogenation, disproportionation and direct synthesis experiments were independently carried out to elucidate the role of each reaction. The presence of promoters was deliberately avoided to focus on the catalyst performance solely. Special attention was given to dissolved hydrogen measurements, as they can provide important information on the reaction mechanism. Different H\textsubscript{2} feeding polices were implemented, trying to enhance both the H\textsubscript{2}O\textsubscript{2} selectivity and productivity.

A precise kinetic description of the reaction involved in the H\textsubscript{2}O\textsubscript{2} direct synthesis is a crucial step for the correct description of the process. Publication III deals purely with theoretical speculation on the kinetics and transport limitations. The knowledge gather with the work on
kinetics experiments (Publication II) was essential to perform the calculations, together with our previous research on hydrogen solubility (Publication I). Extensive modeling was carried out both on direct synthesis, disproportionation and hydrogenation reactions, highlighted in separate experiments. A multiphase reactor model was developed including the influence of transport limitations. The simulations revealed the controlling factors that limits the selective hydrogenation to the peroxide.

The results of the kinetic study encouraged us to investigate the properties of the catalyst to gain more insights on the selectivity performance (Publication IV). Monometallic (Pd) and bi-metallic (Pd and Au) catalysts with different surface properties were synthesized and investigated for H_2O_2 direct synthesis. SBA15 mesoporous material was chosen as support because it promotes a high dispersion and stability of metal nanoparticles^{11,48,53}, also acting as a template to control the nanocluster size. Three modifications of the parent SBA15 support material (incorporation of Al, CeO_2 and Ti) were chosen to elucidate the influence of surface properties (such as Bronsted and Lewis acidity) on the metal dispersion and the overall performance of the catalysts. Br-doped catalysts were obtained by grafting bromine on SBA15-based catalysts, so that the presence of the free ions in the solution was avoided.

Catalysts with Pd content in the range 0.3-5 wt.% were synthesis by ion exchange method. A highly acidic, macroporous PS-DVB resin (Lewtit K2621) was adopted as support. Large pore structure and the swelling in polar media facilitate the access of H_2 and O_2 to the active sites, as well as the removal of the peroxide produced. The sulfonic groups in the resin contribute to stabilize the H_2O_2, at the same time avoiding the presence of acid in the reaction environment. Results suggested some interesting features of the catalyst to enhance the selectivity toward the selective hydrogenation to H_2O_2.
2 Experimental & methods

2.1 H$_2$O$_2$ direct synthesis experiments

The direct synthesis experiments were carried out in a stainless steel, fixed volume autoclave (Parr Instrument, accessible volume 636 cm$^3$) equipped with a mechanical stirrer. The apparatus is schematically described in Scheme 2.1.

![Scheme 2.1. Schematic of the experimental apparatus. 1 – Reactor. 2-3 Gas bottles. 4-5 – Hydrogen vessel and MFC, respectively. 6-7 Valve system for gas loading. 8 – Safety valve. 9-10 Pressure and temperature measurements, respectively. 11 – Liquid sampling valve. 12 - HP pump. 13 – Degasser. 14-15 - Liquid solvent supply and balance, respectively. 16 – Fugatron HYD-100. 17 – Cooling/heating system.]

Temperature in the range 258-313 K was controlled with an external flow of heating/cooling fluid and monitored with a thermocouple. Pressure was monitored with a pressure transducer. The reactor was operated batchwise, hydrogen being the limiting reagent. This way it was possible to study the direct synthesis process with a gas mixture always outside flammability limits. In a typical experiment, the catalyst was introduced first. The reactor was then flushed with CO$_2$ four times to remove air and moisture. Carbon dioxide and oxygen were loaded into the reactor directly from the cylinders, followed by the injection of the methanol via a high
pressure pump. After both pressure and temperature were stable, hydrogen was fed as the limiting reagent. \( \text{H}_2 \) flow during the introduction was tightly controlled for reproducibility with a mass flow controller. In addition, a constant volume (59 cm\(^3\)) vessel was used between the \( \text{H}_2 \) bottle and the mass flow controller. Loaded with \( \text{H}_2 \) at a pressure higher than the measuring cell, it double checks the amount of \( \text{H}_2 \) fed to the reactor, determined from pressure difference inside the \( \text{H}_2 \) vessel before and after the loading and the quantity fed through the mass flow controller. Methanol was degassed and then introduced in the system via a high pressure pump. Hydrogenation and disproportionation experiments were carried out using \( \text{N}_2 \) instead of \( \text{O}_2 \) and \( \text{H}_2 \), respectively. Liquid samples were withdrawn through an external loop, fitted with a six-way GC valve. The liquid sampling probe was equipped with a 7 \( \mu \text{m} \) filter to prevent any block of the sampling valve and pump by small catalyst particles.

Water and \( \text{H}_2\text{O}_2 \) contents were determined by volumetric Karl Fischer and iodometric titration, respectively. Hydrogen dissolved in the liquid phase was measured via an in situ technique, using Fugatron HYD-100. The same instrument was adopted to perform \( \text{H}_2 \) solubility measurements, as described in the following section.

### 2.2 Hydrogen solubility measurements

Measurements of hydrogen solubility in binary (\( \text{H}_2 + \text{CH}_3\text{OH} \)), ternary (\( \text{CO}_2 + \text{CH}_3\text{OH} + \text{H}_2 \)) and quaternary (\( \text{CO}_2 + \text{CH}_3\text{OH} + \text{O}_2 + \text{H}_2 \)) systems were performed in the same apparatus developed for the DS experiments (Scheme 2.1). The external recirculation loop for the liquid phase was removed to perform the measurements. An in situ technique using Fugatron HYD-100 was adopted to measure the hydrogen solubility. The instrument allows continuous, in situ measurements of \( \text{H}_2 \) solubilized in a liquid phase\(^{54,55} \). It is based on a probe immersed in the liquid phase, with a rigid, dense membrane internally purged with a carrier gas (nitrogen) flowing at 10 Nml min\(^{-1} \). Hydrogen permeates the membrane and is brought to a gas detector by the carrier gas. The instrument has been coupled to gas absorption measurements for calibration, the latter remaining the reference technique used. Comparison between the hydrogen concentration measured via gas absorption technique (\( C_{\text{H}_2} \)) and reading of the Fugatron instrument provides the calibration constant of the instrument \(^{54, f:} \)

\[
f = C_{\text{H}_2}/q
\]  
2.1
where \( q \) is the instrument reading, i.e. mole fraction of hydrogen in the carrier gas behind the membrane, reaching the gas detector in the instrument. The calibration constant \( f \) is indeed quite sensitive to temperature, so that \( f(T) \) has actually been determined.

Equilibrium configurations at different temperatures, pressures and composition were studied with sequential additions of a given species (\( \text{H}_2 \), \( \text{CO}_2 \), and \( \text{O}_2 \)), suitably adjusting the procedure to minimize uncertainties. Whenever compatible with the procedure, methanol was fed last, after each gas, to prevent solubility disturbing the gas quantification by pressure.

### 2.3 Catalysts preparation

Mesoporous silica SBA15 was synthesized according to a modification of the procedure reported by Zhao et al.\(^{56} \). Metal substituted M-SBA15 with Si/M ratio of 25 (where M= Al and Ti) were synthesized by the addition of an appropriate amount of metal precursors. Aluminium isopropoxide and titanium tetraisopropoxide were used as the sources of Al and Ti, respectively. \( \text{CeO}_2 \) modified SBA15 (20 wt.% theoretical loading) was prepared by means of deposition-precipitation method from the calcined SBA15 material.

PdAu/SBA15 catalyst was synthesized supporting Pd and Au (1:4 mole ratio) on SBA15 by wet impregnation method. HAuCl\(_4\)-H\(_2\)O and PdCl\(_2\) were used as precursors, added to the solution at the same time. The impregnated catalyst was dried at 378 K overnight and then reduced at 573 K for 8 hours with a 30 ml/min flow of hydrogen and then passivated for 24 h under a 2 vol% \( \text{O}_2/\text{N}_2 \) mixture at room temperature. The final metal content observed was 0.3 wt% of Pd and 2.2 wt% of Au, respectively. The synthesis of two Pd/SBA15 (0.3 and 2.5 wt.%) catalysts was carried out following the same procedure, but impregnating the support with Pd only. The active metals were supported on M-SBA15 (M = Al, Ti and \( \text{CeO}_2 \)) also by impregnation method.

Modified mono and bi-metallic catalysts were obtained grafting the reduced form of the original catalysts with 3-bromopropyl-trimethoxy-silane. The active metal contents of the catalysts were 0.19 wt.% and 1 wt.% for Au and Pd, respectively. The catalysts were suspended in dry toluene. Then the 3-bromopropyl-trimethoxy-silane (5 mmol per gram of catalyst) was slowly added to the suspension. The mixture was fluxed at 353 K in inert atmosphere for 24 h. After completion, the catalyst was washed with an excess of dry toluene and dried at 373 K for 24 h in air. A PdAu-Br/SBA15 catalyst was prepared reversing the
order of the described procedures, first grafting the support and then impregnating the active metals.

Pd/Si and PdAu/Si catalysts were prepared using a commercial SiO$_2$ (Akzo, 329 m$^2$/g of surface area). The support was impregnated by incipient wetness with H$_2$PdCl$_4$ and/or HAuCl$_4$ aqueous solutions (addition of the two precursor solutions was simultaneous for the bimetallic catalyst) to give the desired metal loading (0.5 wt.% Pd for Pd/Si and 1.5 wt% Pd and Au for PdAu/Si). Samples were calcined at 773 K in flowing air for 3 hours.

Pd was also supported on a macroporous resin (Lewatit K2621) by ion exchange method. An aqueous solution of the precursor Pd(NO$_3$)$_2$ and the support was let react overnight. The amount of Pd(NO$_3$)$_2$ was adjusted to match 0.3, 0.5, 1, 2.5 and 5 wt.% nominal Pd loadings. Less than 0.1 mol% of the initial amount of Pd was found in the mother liquor (ICP-MS analysis), confirming that the metal loading was essentially equal to the nominal value. The synthesized catalysts were reduced in THF under hydrogen flux at room temperature for 5 hours. After recovery by vacuum filtration, the materials were dried in oven at 383 K overnight.

### 2.4 Catalyst characterizations

#### 2.4.1 Nitrogen adsorption and CO chemisorption measurements

Surface area and pore size distribution measurements were obtained from N$_2$ adsorption/desorption isotherms at 77 K (using a Carlo Erba Sorptomatic 1900). Prior to the measurements, the samples were outgassed at 573 K for 2 h under vacuum. The surface area was calculated from the N$_2$ adsorption isotherm by the Brunauer, Emmett, and Teller (BET) equation, and pore size distribution was determined by the Barrett, Joyner, Halenda and Dollimore/Heal method.

CO chemisorption measurements were performed at 298 K with a Micromeritics pulse flow system. Prior to the measurements, samples were subjected to a pretreatment involving exposure to hydrogen flow for 1 h at 298 K, followed by He purge for 2 h at the same temperature of reduction.
2.4.2 Surface analysis

X-ray photoelectron spectroscopy (XPS) analysis were performed in a Perkin-Elmer 5400 ESCA spectrometer with monochromatized Al Kα radiation (photon energy 1486.6 eV) and a pass energy value of 35 eV. Samples were transferred to the XPS system in an ethanol solvent to protect them from oxidation in ambient air. A low energy electron gun (flood gun) was used to stabilize the charging that arises from loss of photoelectrons during X-ray bombardment. FitXPS software by D. Adams, University of Aarhus, was used in the line fitting procedure. Pd 3d lines were found on a non-linear background and parabolic background was used in the line fitting.

Particle size and distribution, as well as the structure of the support, were assessed by energy filtered transmission electron microscopy (EFTEM, LEO 912 OMEGA, LaB6 filament, 120 kV).

2.4.3 Induced current plasma - mass spectroscopy (ICP-MS)

Active metal content in the reaction medium was accessed by a PerkinElmer Sciex ICP Mass Spectrometer Elan 6100 DRC Plus.

2.4.4 Acidity measurements

For selected catalysts, the nature of the acid sites was determined by Fourier transform infrared (FT-IR) spectroscopy of adsorbed pyridine. The analysis were carried out according to literature procedure. Lewis and Brønsted acid sites were calculated from the IR band area at 1450 and 1545 cm⁻¹, respectively. The integrated molar extinction coefficients were assumed as 1.67 cm/µmol for Brønsted acidity and 2.22 cm/µmol for Lewis acidity.

2.4.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were carried out on the grafted SBA15-based catalysts. Samples were heated up to 1173 K with a heating rate of 15 K min⁻¹ in air. Prior to the analysis, the samples were pretreated in an oven at 393 K for 2h to eliminate the water eventually present. Weight loss during TGA measurements was due to the loss of the organic part carrying the bromine. Hence, bromine content was estimated from the weight loss upon heating.
3 Results and discussion

3.1 Hydrogen solubility

We investigated hydrogen solubility in three different (binary, ternary and quaternary) species combinations: $H_2 + \text{CH}_3\text{OH}$, $\text{CO}_2 + \text{CH}_3\text{OH} + H_2$ and $\text{CO}_2 + \text{CH}_3\text{OH} + \text{O}_2 + H_2$. The quaternary data are completely original, while the other combinations have been already investigated in literature, as well binary combinations of the four species other than $H_2 + \text{CH}_3\text{OH}$, that we did not investigate experimentally. Literature data provide the opportunity to calibrate a thermodynamic model (estimation of binary interaction parameters) to correlate ternary and quaternary data, in addition of validating our experimental methods.

$H_2 + \text{CH}_3\text{OH}$

Figure 3.1 shows hydrogen liquid phase concentrations measured at 278 K.

![Figure 3.1. CH₃OH + H₂ binary system. Concentration of hydrogen in liquid methanol as a function of its partial pressure above the liquid, at 278 K. ■, this work; *, Descamps et al.⁵⁸; ○, calculated from data of Katayama et al.⁵⁹.](image)

Plotting experimental $C_{H_2}$ against $P_{H_2}$ allows determining the average Henry’s constant as the slope of the resulting linear interpolating function (i.e. Henry’s law, $C_{H_2} = H_{H_2} \cdot P_{H_2}$), including
the origin for physical consistency. The determined value of the Henry’s constant is $30.14 \pm 1.02$ (MPa m$^3$ kmol$^{-1}$), where the error is one standard deviation of the error between calculated $H_{H_2}$ and individual values. This value is quite close to 29.36 (MPa m$^3$ kmol$^{-1}$) calculated from data reported by Katayama et al.$^59$ at the same temperature. It also compares well to 28.39 (MPa m$^3$ kmol$^{-1}$) measured by Descamps et al.$^58$, who carried out a thorough analysis of literature studies on this system. They already reported that literature estimates differ, even at comparable conditions, concluding that discrepancies are likely due to the analytical techniques and to the small amount of water always present in methanol. At any rate, Figure 3.1 shows that our measurements compare well with those of Descampes$^58$ and Katayama$^59$. Our data for CH$_3$OH - H$_2$ provide the opportunity to validate our procedures and the analytical technique.

$CO_2 + CH_3OH + H_2$

Experimental results for $CO_2 + CH_3OH + H_2$ ternary system at 268, 278 and 288 K are shown in Figure 3.2. At each temperature, a number of combinations of H$_2$ partial pressure were screened, by sequential additions of hydrogen.

![Figure 3.2 CO$_2$ + CH$_3$OH + H$_2$ ternary system. Solubility data of hydrogen: ♦, 288 K; ▲, 278 K; ●, 268 K; solid line, Peng-Robinson EoS after tuning $k_{ij}$; △, H$_2$ + CH$_3$OH binary at 278 K.](Image)

Average Henry’s law constants calculated as above with the collected data are $16.7 \pm 0.43$, $18.9 \pm 0.67$ and $20.1 \pm 0.95$ (MPa m$^3$ kmol$^{-1}$), respectively at 288 K, 278 K and 268 K. A
linear interpolation of the \( H_{\text{H}_2}(T) \) dependency yields \( H_{\text{H}_2}(\text{MPa m}^3 \text{ kmol}^{-1}) = 65.8 - 0.17 \cdot T(K) \). The hydrogen solubility increases with temperature (lower \( H_{\text{H}_2} \)), as typical of \( \text{H}_2 \) in \( \text{CH}_3\text{OH} \). It is also apparent that the hydrogen solubility increases compared to binary system, at the same hydrogen partial pressure. This is attributed to the presence of carbon dioxide: enhancements of \( \text{H}_2 \) solubility by \( \text{CO}_2 \) up to 80% has been reported in many organic solvent\(^5\), including methanol. In our conditions, comparing data at 278K we have an increment of 37% due to the use of \( \text{CO}_2 \). Figure 3.3 compares our data (liquid phase mole fractions calculated with PR-EoS tuned on our measurements, as explained below) with those reported by Bezahehtak et al.\(^6\) at the same temperature and total pressure, showing quite a good agreement.

![Figure 3.3](image)

**Figure 3.3.** \( \text{CO}_2 + \text{CH}_3\text{OH} + \text{H}_2 \) ternary system. Comparison of \( \text{H}_2 \) solubility measurements with Literature data at 2 MPa (a, 278 K; b, 288 K): ♦, Bezahehtak et al.\(^6\); *, this work.

Interestingly, their data show a decreasing \( \text{H}_2 \) liquid mole fraction with that of \( \text{CO}_2 \) increases, against the known evidence that \( \text{CO}_2 \) increases \( \text{H}_2 \) solubility. According to the authors, this is an apparent contradiction due to their experimental protocol, where a larger \( \text{CO}_2 \) amount in the whole V-L cell causes a smaller partial pressure of \( \text{H}_2 \) in the vapor phase, also lowering its amount in the liquid.

\[ \text{CO}_2 + \text{CH}_3\text{OH} + \text{O}_2 + \text{H}_2 \]

Figure 3.4 shows the experimental data of hydrogen solubility as a function of hydrogen partial pressure in the quaternary \( \text{CO}_2 + \text{CH}_3\text{OH} + \text{O}_2 + \text{H}_2 \) system, measured at 268 and 278 K. Calculated Henry’s law constants are 18.24 ± 0.89 and 20.88 ± 1.71 (\( \text{MPa m}^3 \text{ kmol}^{-1} \)) at
278 and 268 K, respectively. Being that CO$_2$ liquid phase molar fraction is always the one used in the ternary case, we conclude that the addition of quite a significant amount of O$_2$ does not lead to any significant modification of the H$_2$ solubility. For sake of completeness, the composition of both phases according to PR EoS VLE calculations, result $x_{CO_2} = 0.11$ and $0.43 < y_{O_2} < 0.53$, depending on temperature and total pressure.

![Figure 3.4. CO$_2$ + CH$_3$OH + O$_2$ + H$_2$ quaternary system. Solubility data of hydrogen: ●, 278 K; ♦, 268 K; solid line, Peng-Robinson EoS after tuning $k_{ij}$.](image)

The linear interpolation of $H_{H_2}(T)$ with quaternary data at the temperature investigated resulted in $H_{H_2} (MPa \ m^3 \ kmol^{-1}) = 68.3 - 0.18\cdot T(K)$. Again, hydrogen solubility increases with increasing temperature, as known.

### 3.1.1 Modeling

Besides the experimentally measured data and corresponding Henry’s constants, any equilibrium state, at predefined combinations of species amount and temperature (including early steps of filling), has been characterized by a flash calculation, using a φ-φ approach ($K_i = y_i/x_i = \phi_i^L/\phi_i^V$) and the Peng-Robinson Equation of State (PR-EoS). Standard routines has been used, through a well established commercial code (Aspen Plus). Calculations provide the vapor and liquid phase properties, and we focused on molar fractions. Total available amount of species is known from experiments, as well as temperature and total pressure given as input conditions. The calculations become predictive once EoS parameters are tuned on
experimental data. van der Waals mixing rules were adopted, linear for the co-volume $b$ and quadratic for the attractive interaction parameter $a$. Due to the presence of supercritical species ($\text{H}_2$ and $\text{O}_2$), a Boston-Mathias alpha function was chosen. Binary interaction parameters $k_{ij}$ have to be tuned. They were assumed to vary with temperature alone; while estimated at any temperature investigated, results (reported in Table 3.1) were fit by the expression:

$$k_{ij} = k_{ij}^1 + k_{ij}^2 \cdot T$$  \hspace{1cm} (3.1)

We predicted $\text{H}_2$ solubility in ternary and quaternary systems using only binary interaction parameters $k_{ij}$ calibrated on literature binary phase equilibrium, selected to be as close as possible to our experimental conditions ($T$, $P$ and liquid phase composition). The objective function to be minimized by manipulating $k_{ij}(T)$ was based on departures between calculated and experimental liquid phase compositions. We assumed that oxygen and hydrogen interaction in the liquid phase are negligible, i.e. $k_{\text{O}_2,\text{H}_2} = 0$, according to experimental indications. Comparison of optimization results in term of $\text{H}_2$ solubility prediction accuracy was quantified through the mean absolute percentage error (MAPE):

$$MAPE = \frac{100}{n} \sum_{j=1}^{n} \frac{C_{\text{H}_2,j}^{\text{calc}} - C_{\text{H}_2,j}^{\text{exp}}}{C_{\text{H}_2,j}^{\text{exp}}}$$  \hspace{1cm} (3.2)

where $n$ is the number of measurements. The model first tuned on literature binary data agrees quite well with all binary literature data. While $\text{H}_2$ liquid phase composition dependence on temperature and pressure in ternary and quaternary systems was reasonable, dissolution of $\text{H}_2$ was systematically underestimated, with a MAPE errors as high as 20%, especially at the higher temperature and pressure. Using also ternary measurements to fit $k_{ij}$ values for $\text{H}_2 + \text{CH}_3\text{OH}$, the model was significantly improved as compared to ternary experimental data. The prediction of $C_{\text{H}_2}$ in quaternary $\text{CO}_2 + \text{CH}_3\text{OH} + \text{O}_2 + \text{H}_2$ configurations was also remarkably improved. All the final binary interaction parameters estimated are reported in Table 3.1, along with MAPE errors for all the investigated configurations and temperatures. Their correlation with temperature according to equation (3.1) leads to the coefficients reported in Table 3.2. The actual comparison with our experimental data is reported in Figure 3.2 and Figure 3.4, for ternary and quaternary systems, respectively. MAPE values are quite satisfactory. The calculated hydrogen liquid phase concentration of $\text{H}_2$ for $\text{CO}_2 + \text{CH}_3\text{OH} +$
H₂ system was always in an excellent agreement with experimental data, the highest MAPE error being 7% at 268 K. Predictions for CO₂ + CH₃OH + O₂ + H₂ quaternary system are also remarkably good, with MAPE errors below 7.6% (Table 3.1).

Table 3.1. Mean Absolute Percentage Error and binary interaction parameters for the Peng-Robinson Equation of State in ternary and quaternary systems.

<table>
<thead>
<tr>
<th>System</th>
<th>T (K)</th>
<th>MAPE (%)</th>
<th>k₁₂</th>
<th>k₁₃</th>
<th>k₂₃</th>
<th>k₁₄</th>
<th>k₂₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH(1) + CO₂(2) + H₂(3)</td>
<td>268</td>
<td>7.2</td>
<td>0.036</td>
<td>-0.459</td>
<td>0.147</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>3.0</td>
<td>0.041</td>
<td>-0.476</td>
<td>0.129</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>2.4</td>
<td>0.046</td>
<td>-0.493</td>
<td>0.109</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CH₃OH(1) + CO₂(2) + H₂(3) + O₂(4)</td>
<td>268</td>
<td>7.6</td>
<td>0.036</td>
<td>-0.459</td>
<td>0.147</td>
<td>-0.046</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>5.4</td>
<td>0.041</td>
<td>-0.476</td>
<td>0.129</td>
<td>-0.028</td>
<td>0.100</td>
</tr>
</tbody>
</table>

Table 3.2. Coefficients for temperature correlation of binary interaction parameters (equation 3.1)

<table>
<thead>
<tr>
<th></th>
<th>O₂-MeOH</th>
<th>CO₂-MeOH</th>
<th>CO₂-O₂</th>
<th>CO₂-H₂</th>
<th>MeOH-H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k'_{ij} )</td>
<td>-5.338E-01</td>
<td>-9.251E-02</td>
<td>6.968E-02</td>
<td>6.568E-01</td>
<td>0.000E+00</td>
</tr>
<tr>
<td>( k^2_{ij} )</td>
<td>1.820E-03</td>
<td>4.803E-04</td>
<td>1.091E-04</td>
<td>-1.900E-03</td>
<td>-1.711E-03</td>
</tr>
</tbody>
</table>

The developed model allows estimating the CO₂ effect on the hydrogen solubility. Figure 3.5 shows calculated Henry’s constants of hydrogen as a function of temperature and total CO₂/CH₃OH molar ratio, \( \gamma = \frac{n_{CO_2}}{n_{CH_3OH}} \), according to PR-EoS tuned on literature and our experimental data.
Figure 3.5. Predicted Henry’s constants of hydrogen as a function of temperature and 
\[ \gamma = \frac{n_{CO_2}}{n_{CH_3OH}} \] calculated from PR-EoS tuned on literature and our experimental data: □, 
\[ \gamma = 0.3; \Delta, \gamma = 0.25; \circ, \gamma = 0.15; \times, \gamma = 0.09; \bullet, \text{experimental data (Results & discussion, } CO_2 + CH_3OH + O_2 + H_2). \]

Though predicted \( H_{H_2}(T) \) appears slightly curved upwards, linear interpolations are 
acceptable, leading to the correlation:

\[
H_{H_2} = \alpha(\gamma) + \beta(\gamma) \cdot T \\
\alpha(\gamma) = -91.96 + 114.09 \\
\beta(\gamma) = 0.26\gamma - 0.33
\]

We already mentioned the significant H\(_2\) solubility enhancement due to CO\(_2\) by comparing 
binary and ternary data, also shown in Figure 3.2, confirming literature data\(^{60,61}\) measured 
in different conditions. The enhancement factor (EF) was adopted to quantitatively measure the 
advantage given by CO\(_2\), comparing H\(_2\) solubility without (H\(_2\) + CH\(_3\)OH ) and with CO\(_2\) (CO\(_2\) 
+ CH\(_3\)OH + O\(_2\) + H\(_2\) ). EF is defined as the ratio of hydrogen composition in methanol ( 
x\(_{H_2}^{\text{Binary}}\) ) and CO\(_2\) + CH\(_3\)OH + O\(_2\) systems (x\(_{H_2}^{\text{Quaternary}}\) ) at the same conditions of temperature and 
hydrogen fugacity:

\[
EF = \frac{x_{H_2}^{\text{Quaternary}}}{x_{H_2}^{\text{Binary}}} 
\]
Values higher than 1 indicate an increased hydrogen dissolution in the liquid phase caused by carbon dioxide, and thus are desirable. According to the predictions based on this model, EF can approach 2.1 at 278 K and $\gamma = 0.3$.

### 3.2 H$_2$O$_2$ synthesis: hydrogen feeding policies

The reactor was operated batchwise, with H$_2$ as the limiting reagent, to keep the gas mixture outside (lower) flammability limit. Due to the small amount of H$_2$ introduced, a low concentration of H$_2$O$_2$ is expected. In order to overcome this drawback and in view of a potential industrial application, the same amount of hydrogen was fed into the reactor with different strategies. Experiments were carried out at 283 K and 1.8 MPa, also measuring H$_2$ in the liquid phase. Two H$_2$ feeding polices were implemented: four equal hydrogen fillings were introduced 1) after each complete hydrogen conversion and 2) as soon as hydrogen concentration in the liquid phase started to decrease. Results are reported in Figure 3.6.

![Graph](image_url)

**Figure 3.6.** H$_2$O$_2$ direct synthesis at 283 K and 1.8 MPa with different hydrogen feeding policies: 1) Hydrogen amount fed after its complete conversion (dashed line) and 2) hydrogen subsequently fed as it decreases in the liquid phase (solid line). H$_2$O$_2$ concentration (a) and selectivity (b) under feeding policy 1 (■) and 2 (▲).
In experiment type 1) the amount of hydrogen dissolved in the liquid rapidly reached a peak after each introduction, slowly decreasing afterwards. 29% maximum selectivity was observed and \( \text{H}_2\text{O}_2 \) production increased each time \( \text{H}_2 \) was fed. Interestingly, as soon as hydrogen decreased in the liquid phase, the selectivity towards hydrogen peroxide was also reduced, and the formation of water prevailed. However, every time hydrogen was fed into the reactor, the selectivity increased, although smaller values were achieved. This result is interesting as it suggests a possible relationship between the amount of hydrogen in the liquid phase and the quantity of \( \text{H}_2\text{O}_2 \) produced. It appears that keeping the hydrogen conversion below 100% (i.e. 60%) favors the selectivity. Possibly, the presence/absence of \( \text{H}_2 \) influenced the oxidation state of the active metal, thus changing the reaction kinetic. In that sense, the presence of \( \text{H}_2 \) would favor the selectivity towards the peroxide. Hence an experiment was performed avoiding the complete depletion of hydrogen in the liquid phase (feeding policy 2). A higher selectivity could be achieved, reaching a peak around 33%, compared to 29% of the previous experiment. In both cases, after \( \text{H}_2 \) complete depletion the selectivity reached a similar value, i.e. 20%. Interestingly, the hydrogen peroxide production was similar with the two \( \text{H}_2 \) feeding policies. These results seem to confirm that the presence of \( \text{H}_2 \) in the liquid phase favors the production of the peroxide.

### 3.3 Kinetics identification

#### 3.3.1 \( \text{H}_2\text{O}_2 \) synthesis, hydrogenation and disproportionation: effect of temperature

Kinetic experiments of the hydrogen peroxide direct synthesis were carried out varying the temperature. The \( \text{H}_2: \text{O}_2 \) ratio was set to 1:10, i.e. hydrogen was the limiting reagent. Results of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) production are reported in Figure 3.7.
Overall, the water production during the experiments increased constantly and prevailed over the hydrogen peroxide formation, reaching higher concentrations than the peroxide. The H$_2$O$_2$ formation increased rapidly in the very beginning, reaching a maximum and gradually decreasing afterwards. The complete consumption of H$_2$ corresponded to the maximum concentration of H$_2$O$_2$: after H$_2$ was no longer present in the liquid phase, and the direct synthesis as well as the hydrogenation were suppressed. Thus, the only possible reaction was the disproportionation, resulting in a drop of the peroxide formation. Experimental results confirmed that the direct synthesis reaction was very fast at the beginning, but hydrogenation and disproportionation reactions increased as hydrogen concentration in the liquid phase decreases. Interestingly the direct synthesis is favored at lower temperatures.

Palladium based catalysts are well known for being suitable for the direct synthesis of hydrogen peroxide. Unfortunately, they also promote H$_2$O$_2$ disproportionation and hydrogenation. To quantify the degree of H$_2$O$_2$ loss by disproportionation and hydrogenation, kinetic experiments were carried out with the same catalyst and under the same operation conditions as the direct synthesis. Results are shown in Figure 3.8, as a percentage of the H$_2$O$_2$ loss.
Qualitatively, both degradation paths (with/without H₂) were similarly affected by the temperature. However it is apparent that in presence of H₂ the destruction of the peroxide was much faster (min vs hours).

3.3.2 Modeling

Several surface mechanisms on palladium can give the overall process described in Scheme 1.1. In our study, very small surface coverage was assumed, so that pseudo-homogeneous rate equations could be assumed. With the purpose of investigating the multiphase nature of the reaction, the reactions in Scheme 1.1 were assumed elementary and irreversible, occurring on the surface of a non-porous powder catalyst. Accordingly, the following rate expressions for each step are valid:

\[
R_{ds} = k_{ds} C_{H_2}^s C_{O_2}^s 
\]

\[
R_{wf} = k_{wf} C_{H_2}^s \left( C_{O_2}^s \right)^{1/2} 
\]

\[
R_d = k_d C_{H_2O_2}^s 
\]

\[
R_h = k_h C_{H_2O_2}^s C_{H_2}^s 
\]

with temperature dependent, Arrhenius-type kinetic constants:
\[ k_i = A_i e^{-\frac{E_{ai}}{RT}} \]  

3.9

Pre-exponential factor \((A_i)\) and activation energy \((E_{ai})\) of each reaction are determined from our experimental data. According to the stoichiometry, the production rates of each species to be used in individual mass balances are:

\[
r_{H_2O_2} = R_{ds} - R_d - R_h
\]
\[3.10\]

\[
r_{H_2O} = R_{wf} + R_d + 2R_h
\]
\[3.11\]

\[
r_{H_2} = -R_{ds} - R_{wf} - R_h
\]
\[3.12\]

\[
r_{O_2} = -R_{ds} - 0.5R_{wf} + 0.5R_d
\]
\[3.13\]

Two mass transfer resistances were considered, dissolution of gases into the liquid phase and reactant transport in the liquid to the catalyst surface. Coefficients were calculated according to best available correlation for the reactor used, considering that gas was bubbling in the liquid and catalyst was in the form of fine powder, suspended in the liquid. The species mass balances were written in each phase, i.e. vapor and liquid, the solid being assumed non-porous reduce to a flux balance at its interface. Balances are based on the following assumptions:

a) both liquid and vapor phase are well mixed;

b) carbon dioxide and methanol are not involved in any reaction;

c) any increment of liquid volume due to the accumulation of H\(_2\)O\(_2\) and H\(_2\)O is neglected, while the change caused by sampling is taken into account.

d) species cannot accumulate on the catalyst surface, nor in the liquid boundary layer surrounding the catalyst particles.

According to these assumptions, the mass balances in the gas and liquid phases can be written as:

\[
V^G \frac{dC_{i}^{G}}{dt} = a^{LG} K_{i}^{L} \left( C_{i}^{L} - C_{i}^{L,*} \right) \quad i = H_2, O_2
\]
\[3.14\]

\[
V^L \frac{dC_{i}^{L}}{dt} = a^{LG} K_{i}^{L} \left( C_{i}^{L,*} - C_{i}^{L} \right) - d^{LS} K_{i}^{S} \left( C_{i}^{L} - C_{i}^{S} \right) \quad i = H_2, O_2, H_2O_2, H_2O
\]
\[3.15\]

At the catalyst surface interface the material balances under assumption d) becomes:
where the production rates \( r_i \) appears, which are functions of the species concentration facing the catalyst surface, \( C_i^S \). At the gas-liquid interface equilibrium holds. The equilibrium constants were estimated from an equation of state tuned on specific experimental data (Publication I).

The proposed model is given by a total of ten equations: 2 ODEs for the gas phase, 4 ODEs for the liquid phase and 4 algebraic equations for the catalyst surface, resulting in a low index ADEs system. Its integrations yields the evolution in time of the concentration of reactants (i.e. \( \text{H}_2 \) and \( \text{O}_2 \)) in the gas and liquid phases and at the catalyst surface (6 unknown functions), and the concentration of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) in the liquid phase and at the catalytic surface (4 unknowns).

According to the experimental procedure (Publication II), the following ten initial conditions are assumed:

\[
\begin{align*}
a) C_{\text{O}_2}^G \bigg|_{t=0} &= C_{\text{O}_2}^{G,0} \\
b) C_{\text{H}_2}^G \bigg|_{t=0} &= \frac{n_{\text{H}_2}}{V^L} \\
c) C_{\text{O}_2}^L \bigg|_{t=0} &= C_{\text{O}_2}^{L,0} \\
d) C_{\text{H}_2\text{O}_2}^L \bigg|_{t=0} &= C_{\text{H}_2\text{O}_2}^{L,0} \\
e) C_{\text{H}_2}^L \bigg|_{t=0} = C_{\text{H}_2\text{O}_2}^L \bigg|_{t=0} = 0 \\
f) C_{\text{O}_2}^S \bigg|_{t=0} = C_{\text{O}_2}^{S,0} \\
g) C_{\text{H}_2\text{O}}^S \bigg|_{t=0} = C_{\text{H}_2\text{O}}^{S,0} \\
h) C_{\text{H}_2}^S \bigg|_{t=0} = C_{\text{H}_2\text{O}}^S \bigg|_{t=0} = 0
\end{align*}
\]

3.17

Primarily, hydrogen (the limiting reagent) was introduced after all the other species, when stable values of pressure and temperature were reached inside the reactor (filled with \( \text{O}_2 \), \( \text{CO}_2 \) and methanol). Since the \( \text{H}_2 \) feeding was fast compared to the reaction time, hydrogen is assumed not to dissolve in the liquid phase while introduced (conditions 3.17b and 3.17e). The initial concentration of water in the reaction medium (condition 3.17d) was measured prior the introduction of hydrogen.

The material balances equations (3.14-3.16), together with initial conditions (3.17) have been efficiently solved using Matlab’s ode15s ADEs solver, also suitable for stiff equations, being based on a multistep, variable order method based on the numerical differentiation formulas. Values of the activation energy and the pre-exponential factor of each reaction were determined by a sequence of isothermal experimental data fitting, providing the four irreversible reaction rate constants \( k_{ds}, \ k_{wf}, \ k_d \) and \( k_h \) at the given temperature. Then an
Arrhenius plot was assembled for each reaction, and the relative activation energy and pre-exponential factors determined by fitting $k(T)$. The following error function was used for each experiment (i.e. a given temperature) to fit the experimental data:

$$
err = \sqrt{\frac{1}{n_{H_2O}^{\exp}} \sum_{i=1}^{n_{H_2O}^{\exp}} (C_{S, Exp}^{H_2O_2, i} - C_{S, Calc}^{H_2O_2, i})^2} + w \sqrt{\frac{1}{n_{H_2O}^{\exp}} \sum_{i=1}^{n_{H_2O}^{\exp}} (C_{S, Exp}^{H_2O, i} - C_{S, Calc}^{H_2O, i})^2}
$$

Note that errors between experimental and calculated concentrations were rescaled. In pure disproportionation and hydrogenation experiments, where water concentration was not measured, we set the parameter $w=0$; in all other cases, $w=1$. A Nelder-Mead simplex algorithm with positivity constraints on the parameters (fminsearchbnd function) was used to minimize the error by adjusting the four parameters of the model ($k_{ds}, k_{ws}, k_d$ and $k_h$).

**Direct synthesis**

Each isothermal run has been simulated and a set of $k$’s estimated, for each step in the mechanism; results are shown in Figure 3.7. The model is always in very good agreement with experimental results. Experimental measurements of H$_2$O are less precise, due to the different analytical procedure, slightly decreasing the goodness of fit. The kinetic constants calculated at each temperature are collected in Figure 3.9 in the form of Arrhenius plots, and the resulting activation energies and pre-exponential factor are reported in Table 3.3.
Figure 3.9. Arrhenius plots for the kinetic constants of each individual step in the mechanism.

Table 3.3. Arrhenius constants for the rate equations 3.5-3.8 (direct synthesis experiments).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pre-exponential factor</th>
<th>Activation energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct synthesis</td>
<td>4.18 ± 0.15 x 10(^{12})</td>
<td>23.84 ± 2.45</td>
</tr>
<tr>
<td>Water formation</td>
<td>4.27 ± 0.20 x 10(^{14})</td>
<td>45.31 ± 3.61</td>
</tr>
<tr>
<td>Disproportionation</td>
<td>2.61 ± 0.45 x 10(^{10})</td>
<td>45.06 ± 9.60</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>5.65 ± 0.22 x 10(^{17})</td>
<td>46.58 ± 3.72</td>
</tr>
</tbody>
</table>

The temperature dependence of water formation, disproportionation and hydrogenation are all comparable (activation energies close to 45 kJ mol\(^{-1}\)). However, the kinetics of these reactions is quite different. \(k\) values can differ by orders of magnitude, but they are not really comparable, because refer to different overall reaction orders. The most appropriate comparison must inspect the values of the reaction rates during the course of each experiments, as shown in Figure 3.10.
Each reaction rate has been related to the one of direct synthesis, $R_{wf}/R_{ds}$, $R_d/R_{ds}$ and $R_h/R_{ds}$. Both disproportionation and hydrogenation rates are null at the beginning, requiring the presence of the peroxide (i.e. they are reactions consecutive to the direct synthesis). Their rates increase during the reactions course, at a different pace. Disproportionation reaction is very slow compared to the direct synthesis and becomes important only at a high $H_2$ conversion, when the direct synthesis reaction slows down. A strong effect of the temperature is also observed on this reaction, where lower temperature is confirmed to stabilize the $H_2O_2$ produced. The preferred path of $H_2O_2$ degradation is the hydrogenation reaction: its rate rapidly increases as $H_2O_2$ becomes available, limiting the $H_2O_2$ production. However this reaction is always slower than the direct synthesis ($R_h/R_{ds} < 1$) and it can be limited by decreasing the temperature, up to $R_h/R_{ds} < 0.5$ at 258 K. Unfortunately, the $R_{wf}/R_{ds}$ is always significant because the formation of water really competes with the direct synthesis, prevailing ($R_{wf}/R_{ds} > 1$) at higher temperature, whereas lower temperature favors the direct synthesis ($R_{wf}/R_{ds} < 1$). At a given temperature, the rate of $H_2O$ formation remains very close to that of the direct synthesis (constant $R_{wf}/R_{ds}$) except for a short initial transient favoring the direct synthesis.

Due to the intrinsic nature of the interconnected reaction mechanism, a correlation between the estimates of reaction rate constants has to be expected. A quantitative evaluation is given
in Figure 3.11 as contour plots for the parameter estimates, at \( T = 268 \) K. A small correlation is indicated by contours approaching circles.

![Contour plots of regressed kinetic parameters (T = 268 K).](image)

A strong correlation is observed between most reaction constants, and remarkably among direct \( \text{H}_2\text{O}_2 \) synthesis and the other reactions. The lowest correlation occurs between disproportionation and water formation, as expected. The same analysis was carried out for all isothermal data with similar results. In order to improve or double check our estimates and suppress the correlation among the parameters, we studied the disproportionation and hydrogenation rate constants independently, with dedicated experiments.

**Disproportionation**

Rate expression (3.7) was used to fit the \( \text{H}_2\text{O}_2 \) concentration profiles during disproportionation experiments, to isolate this step. Since in these experiments \( \text{H}_2 \) was replaced with \( \text{N}_2 \), calculations were carried out neglecting rate expressions (3.5), (3.6) and (3.8) and hydrogen mass balance (eq. 3.12). Figure 3.8 (a) shows the results as measured and calculated isothermal data of \( \text{H}_2\text{O}_2 \) concentration. Arrhenius plot for disproportionation reaction is reported in Figure 3.12.
Figure 3.12. Arrhenius plot for disproportionation reaction.

Predictions were in good agreement ($r^2$ very close to 1) with experimental observations at any temperature considered, confirming that disproportionation is a first order reaction with respect to $\text{H}_2\text{O}_2$ concentration. The calculated kinetic parameters are reported in Table 3.4.

<table>
<thead>
<tr>
<th>Pre-exponential factor ($\text{cm}^3 \text{s}^{-1}$)</th>
<th>Activation energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.11 \pm 0.21 \times 10^{11}$</td>
<td>$50.43 \pm 4.28$</td>
</tr>
</tbody>
</table>

A comparison of the Arrhenius constants obtained by fitting all the rate constant in eqs. (3.5-3.8) together, using the direct synthesis experimental data, shows that the activation energy for $k_d$ obtained here for the disproportionation reaction (50.43 kJ mol$^{-1}$) compares well with the above value (45.06 kJ mol$^{-1}$, Table 3.3), being that their confidence intervals overlap substantially. A higher deviation is observed in the pre-exponential factors. However, the deviation on the isothermal kinetic constants $k_d$ is less than 10% ($T < 273$ K), confirming the results reported in Table 3.3.
**Hydrogenation**

H$_2$O$_2$ hydrogenation experiments were performed substituting O$_2$ with N$_2$. Hence, direct synthesis and water formation reactions do not occur. Accordingly, when regressing these data the mass balance of O$_2$ (eq. 3.13) and rates (3.5) and (3.6) were ignored. Disproportionation rate constants were not regressed and the parameters previously obtained (Table 3.4) were introduced in the model and kept fixed. Only rate expression (3.8) was considered and isothermal hydrogenation reaction constants regressed. The deviation between experimental H$_2$O$_2$ concentration measured during pure hydrogenation and the best fit predictions is rather high, as shown in Figure 3.8 (b). Apparently, the kinetic model in this case is not adequate. The decay of H$_2$O$_2$ concentration in time is only approximately exponential, as clearly perceivable from Figure 3.8 (b). In the first minutes of reaction, and more clearly at lower temperature, the H$_2$O$_2$ concentration decreases more slowly than later on. At higher H$_2$ conversion, the decay is very rapid, in a way that a second-order rate equation, linearly proportional to each reagent concentration, cannot fit. Consequently, the model switch from under- to overestimation of the measured H$_2$O$_2$ concentration, when approx. 70% of the introduced H$_2$O$_2$ is consumed. The effect of temperature, within the approximation discussed above, is well described by a linear Arrhenius plot. The calculated activation energy and pre-exponential factor are respectively $17.85 \pm 1.00$ (kJ mol$^{-1}$) and $7.47 \pm 0.11 \times 10^{12}$ (cm$^6$ mol$^{-1}$ s$^{-1}$ mol$_{Pd}^{-1}$). However, the $k_h$ values are much higher compared to the ones reported in Figure 3.9, also reflected in a significantly lower activation energy. We explain both results, a 2-steps H$_2$O$_2$ consumption and its higher rate, in terms of differences in the catalyst oxidation state. Synthesis and hydrogenation experiments use a different experimental condition: the former were carried out in large excess of O$_2$, the latter did not include any O$_2$, but H$_2$ was the only reactant present. Accordingly, the active metal on the catalyst can be mostly oxidized in excess of O$_2$ (synthesis conditions), and reduced in excess of H$_2$ (hydrogenation conditions). The reduced form of the catalyst can be more effective for the hydrogenation reaction, enhancing its rate, consistently with literature observations$^{23,52}$ that the production of hydrogen peroxide is favored by the oxidized form of Pd. In addition, the H$_2$O$_2$ hydrogenation on reduced Pd may occur with a non-elementary mechanism, involving a complex model also accounting for competitive adsorption of H$_2$ and O$_2$. According to the discussion above, we rely on the kinetic model and values of Table 3.3 to describe the reaction network at synthesis (i.e. O$_2$ dominated) conditions. Further, we question the significance of independently estimating the H$_2$O$_2$ hydrogenation kinetics in case the catalyst is vulnerable to oxidation/reduction at conditions of the experiments, which is quite
common. Also, in case of non-elementary mechanism, a competitive adsorption on the catalyst sites between H\textsubscript{2} and O\textsubscript{2} is expected in the synthesis experiments, which is not the case for hydrogenation experiments.

**Parametric sensitivity on mass transfer coefficients**

Values of $K_i^L a^L$ (mass transfer between gas and liquid) for H\textsubscript{2} was calculate in the range 960-1880 h\textsuperscript{-1}, at 258 and 297 K, respectively. The coefficients of mass transfer resistance at the catalyst surface, $K_i^S$, were in the range $1.4 \cdot 10^{-2}$ - $3.5 \cdot 10^{-2}$ cm s\textsuperscript{-1} at 258 K and 297 K, respectively, for all components. Since we tried to predict the mass transfer rates a priori, using the best available correlations, we expect that the chemical kinetics was properly identified, with the results given in Table 3.3. Would the mass transfer actually control the process, or part of it, we should expect the chemical kinetics to be inaccurately determined. We actually used this reasoning to evaluate the extent of mass transfer control at our experimental conditions. The values of $K_i^L a^L$ and $K_i^S$ were increased or decreased by up to one order of magnitude and the kinetic parameters (activation energy and pre-exponential factors) re-estimated. Different simulations were carried out changing each individual mass transfer coefficients, one at a time. As expected, no influence on the kinetic parameters was observed varying $K_i^L a^L$ and $K_i^S$ values of O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O, the only critical species being hydrogen, the limiting reagent in all the performed experiments. Further, disproportionation reaction was not affected by hydrogen concentration because of its rate law expression, and it was excluded from this analysis. The sensitivities of the reaction rate constants $k$ to $K_{H_2}^L a^L$ are shown in Figure 3.13.
Figure 3.13. Effect of $K_{H2}^L$ on the reaction rate constants of direct synthesis, water formation and hydrogenation. The value given by correlation 10 has been multiplied by: 0.0035 (□), 0.08 (☉), 0.15 (○), 0.5 (*), 1 (△), 5 (+), 10 (x).

Decreasing H2 mass transfer coefficients from gas to liquid affects the estimated rate constants of any reaction; the reduced H2 transfer rate to the liquid phase (and hence to the catalyst) must be balanced by the increased reaction kinetics. Interestingly, limitations in the H2 mass transfer rate cause an apparent increase in the estimated activation energy, as can be observed in Figure 3.14, recalling the importance of accounting for mass transfer to properly identify the kinetics.
However, some mass transfer effect was only evident at temperatures above 283 K, by artificially lowering $K_{H_2}^L a^L$ at least by one order of magnitude (from 1880 h$^{-1}$ to 140 h$^{-1}$). Accordingly, we conclude that limitations due to the dissolution rate of hydrogen can be excluded at the experimental conditions, even accounting for uncertainties in the correlations, that could not be as high as 1 order of magnitude.

Figure 3.15 shows the effect of the mass transfer rate from the liquid to the solid surface ($K_{H_2}^S$) on the reaction rate constants of direct synthesis, water formation and hydrogenation.
3.4 SBA15-based doped supported catalysts

3.4.1 Non-ordered and ordered mesoporous Si-based catalysts

We investigated the role of Au and incorporated-bromine over five different SBA15-based catalysts. Figure 3.16 illustrates H$_2$O$_2$ concentration as a function of time observed with these catalysts.
Among the synthesized catalysts, PdAu/SBA15 was the most active one. Figure 3.16 clearly distinguishes the differences in mono- and bimetallic catalysts, where the latter ones always show a much higher H$_2$O$_2$ productivity upon short contact time. Monometallic Pd/SBA15 catalyst had a productivity 50% reduced compared to the bimetallic PdAu/SBA15. Its grafted parent (Br-Pd/SBA15) demonstrated a poor H$_2$O$_2$ productivity also, i.e. five times lower compared to the bimetallic Br-PdAu/SBA15. Upon testing the monometallic Br-Pd/SBA15 catalyst, H$_2$O concentration was within the measurement error and, consequently, H$_2$ conversion and selectivity could not be calculated. The comparison of mono- and bimetallic catalysts (either grafted or not) confirms the synergetic effect between Pd and Au reported in the literature$^{26,62}$. The grafting process had a two-fold effect on the bimetallic catalyst, clearly seen when comparing the performance of the PdAu/SBA15 and Br-PdAu/SBA15. The selectivity was reduced by 15% in the presence of bromine attached on the catalyst. Moreover, the productivity was three times lower over Br-PdAu/SBA15 and also the H$_2$ conversion was reduced by a factor of 80%. The grafting process could induce poisoning of the catalyst by pore blocking (bromoalkyl species) and/or causing migration and sintering of the metal nanocluster outside the mesoporous of the support. Neither H$_2$O$_2$ nor H$_2$O were observed when the SBA15 was grafted before Pd and Au deposition. The reduction performed at 573 K after the grafting process could induce a partial disproportionation of the bromopropyl groups, leading to coke formation and poisoning of the catalyst. Thermogravimetric Analysis (TGA) measurements confirmed this hypothesis. Weight loss upon heating of the catalyst reduced after Br grafting was 37% lower compared to the
catalysts obtained with the reverse procedure, i.e. grafting the catalysts after active metals deposition, suggesting that partial decomposition of the organic chains occurred during reduction of the PdAu-Br/SBA15 catalyst.

Performances of SBA15-based catalysts were also compared to non-ordered SiO$_2$-based catalysts, Figure 3.16. The synergetic effect of Pd and Au observed with SBA15 supported catalysts was not observed when using silica as support. Compared to the PdAu/Si, the monometallic Pd/Si catalyst displayed both higher selectivity and productivity, though at lower H$_2$ conversion. However, the performance of these catalysts was generally lower than that shown by the non-grafted SBA15 supported one, confirming the advantage of using an ordered mesoporous support.

### 3.4.2 Al, Ti and CeO$_2$-SBA15 modified catalysts

Starting from the consolidated knowledge that an acid environment favors the H$_2$O$_2$ direct synthesis$^{1, 2, 37, 63}$, the catalyst displaying the best performance (PdAu/SBA15) was further modified. Three different surface modifiers were chosen: incorporation of Al into the framework is known to give Brønsted acidity$^{64}$, CeO$_2$ adds Lewis acidity$^{65, 66}$ while Ti gives mild oxidizing property$^{67, 68}$. H$_2$O$_2$ concentrations obtained in batch experiments with PdAu/M-SBA15 (M = Al, Ti and CeO$_2$) are reported in Figure 3.17.

![Figure 3.17 H$_2$O$_2$ concentration in batch reactor: PdAu/Al-SBA15 (■), PdAu/CeO$_2$-SBA15 (*), PdAu/Ti-SBA15 (+), Br-PdAu/Al-SBA15 (x). Conditions: T = 283 K, P = 1.75 MPa.](image)

Modifying the support with Al gave the best results, both in terms of productivity and selectivity. Compared with the corresponding unmodified catalyst, the productivity was increased by 37% with comparable selectivity and H$_2$ conversion. Modification of the support
with CeO$_2$ or Ti impaired the catalytic performances, decreasing both selectivity and productivity values. A catalytic test was also carried out with the best catalyst (PdAu/Al-SBA15) modified by an addition of bromine (Br-PdAu/Al-SBA15). Bromine was grafted after the deposition of the active metals on the support, whereas the reverse procedure revealed the deactivation of the catalyst. However, doping the catalyst decreased the selectivity and resulted in a drop of productivity by one order of magnitude, confirming the poisoning already observed with the unmodified SBA15-based catalysts. Different surface analysis techniques were carried out on the catalysts to explain these results. All except the Br-PdAu/Al-SBA15 catalysts demonstrated comparable particle size distributions where most of the nanoclusters had a diameter close to that of the support pores (i.e. 6-7 nm) and only occasionally showing diameters up to 25 nm. This confirms that a good control of the nanocluster size was achieved using SBA15 as support. The particle size distributions were almost unchanged in the spent catalysts, confirming the stability of the metal nanoclusters at reaction conditions. A comparison of PdAu/Al-SBA15 with Br-PdAu/Al-SBA15 demonstrated that a broader particle size distribution was obtained after bromine doping (clusters between 6 and 22 nm). The metal nanoparticles possibly migrated on the catalyst surface and agglomerate into larger clusters upon bromine modification. The bromine also caused a noticeable sintering of metal nanoclusters after use. The broader nanocluster size distribution and the poorer stability of the metal nanoclusters are deemed responsible for the lower activity of the bromine containing catalyst. Compared to the other catalysts, the PdAu/CeO$_2$-SBA15 revealed a more homogeneous surface, where the support channels were less clearly distinguishable. This difference in the surface structure is possibly due the presence of CeO$_2$. All SBA15-based catalysts were prepared via a direct synthesis method$^{56}$, except CeO$_2$ modification, carried out by a post-synthesis method. The high CeO$_2$ loading (20 wt%) may have caused partial pore blocking. To verify this hypothesis, nitrogen physisorption (BET method) measurements were carried out on the catalysts. The specific surface area of the PdAu/M-SBA15 (M = Al and Ti) catalysts resulted in 600 m$^2$/g. Only the CeO$_2$-modified catalyst had a lower area of 430 m$^2$/g, confirming partial pore blocking caused by the CeO$_2$ doping. The decreased available surface area can also be responsible for the lower activity of this particular catalyst.

FT-IR spectroscopy by means of pyridine adsorption was performed on these catalysts to characterize the Lewis and Brønsted acidity present. The presence of Brønsted and/or Lewis acid sites was confirmed in the modified supports. The enhanced performance of the
PdAu/Al-SBA15 catalyst can be explained by the presence of Brønsted acid sites: hydrogenation of \( \text{H}_2\text{O}_2 \) is suppressed when the peroxide is surrounded by protons\(^2\),\(^63\), and hence the increased Brønsted acidity as a result of increased Al (modifier) enhanced the peroxide productivity.

### 3.5 Pd/K2621 catalysts

Another series of catalysts was synthesized supporting Pd on an acidic, macroporous resin (Lewatit K2621). Two series of experiments were carried out batchwise at 283 K, using catalyst amounts in the range 0.075-0.5 g (Pd content 1 wt.%) and catalysts with Pd content in the range 0.3-5 wt.% (catalysts quantity 0.15 g). A careful analysis excluded any mass transfer limitation. Results of the former series of experiments are shown in Figure 3.18, whereas Figure 3.19 reports the results of the latter series.

![Figure 3.18. \( \text{H}_2\text{O}_2 \) concentration and selectivity in batch experiments with different amount of 1 wt.% Pd/K2621 catalyst: * 0.075 g; ● 0.11 g; ♦ 0.15 g; ■ 0.3 g; ▲ 0.5 g.](image-url)
Figure 3.19. \( \text{H}_2\text{O}_2 \) concentration and selectivity in batch experiments with different Pd loading on K2621 support: * 0.3 wt.%; ● 0.5 wt.%; ♦ 1 wt.%; ■ 2.5 wt.%; ▲ 5 wt.% Catalyst amount: 0.15 g.

Enhancing the catalyst quantity had a two-fold effect (Figure 3.18). \( \text{H}_2\text{O}_2 \) production rate increased with the catalyst amount, i.e. the \( \text{H}_2\text{O}_2 \) peak was reached more rapidly. More surprisingly, the maximum peroxide concentration decreased enhancing the catalyst quantity in the reactor. The selectivity was also impaired enhancing the catalyst quantity. This is unexpected, since the amount of catalyst should similarly affect all the reactions involved in the direct synthesis process, with unchanged selectivity. Enhancing the Pd wt.% had a similar effect (Figure 3.19), resulting in an increased \( \text{H}_2\text{O}_2 \) production rate and in a decreased maximum peroxide concentration. Accordingly, the lower the Pd content, the higher the selectivity. Interestingly, value as high as 60% were obtained with 0.3-0.5 wt.% Pd at short contact time. Average particle size and surface oxidation state of the used catalysts were accessed by TEM and XPS analysis, respectively. Both \( \text{H}_2\text{O}_2 \) selectivity and productivity increased increasing the nanocluster diameter, as shown in Figure 3.20 (a).
Small Pd particles, containing highly energetic defects, edges and corners, likely favored the cleavage of the O-O bonding, hence favoring the undesired formation of H$_2$O$^{41, 51}$. XPS analysis of the catalysts after reaction reveled that catalysts with lower Pd loading were poorer in surface Pd oxide and favored the H$_2$O$_2$ formation (Figure 3.20 (b)). Difference of surface Pd oxide are likely due to the different H$_2$/Pd ratio in the catalytic test. This could also explain the results shown in Figure 3.18: decreasing the amount of catalyst also lowers the H$_2$/Pd ratio. However, at the time of writing, analysis on these results were still in progress.

Figure 3.20. Performance of Pd/K2621 catalysts with different Pd loadings: H$_2$O$_2$ selectivity at 15 min of reaction as a function of Pd nanocluster size (a) and PdO amount (b).
4 Conclusions

Hydrogen solubility was investigated in three different systems: pure methanol, CO$_2$ + CH$_3$OH and CO$_2$ + CH$_3$OH + O$_2$ at temperatures between 268 K and 288 K and for pressure up to 3.49 MPa. For all studied conditions, the solubility of hydrogen in the liquid phase increased with H$_2$ partial pressure, as expected. A linearity of hydrogen concentration with hydrogen partial pressure was confirmed, likely due to the low solubility of H$_2$. In both ternary CO$_2$ + CH$_3$OH + H$_2$ and quaternary CO$_2$ + CH$_3$OH + O$_2$ + H$_2$ systems, increasing the temperature resulted in an enhanced hydrogen solubility at the same H$_2$ partial pressure. In the presence of CO$_2$, concentration of hydrogen in the liquid phase was significantly larger than in pure methanol at the same H$_2$ fugacity, with an enhancement factor as high as 2.1 (at CO$_2$/CH$_3$OH molar ratio = 0.3). A model based on Pr-EoS was proposed for the estimation of H$_2$ Henry’s constant as a function of temperature and CO$_2$/CH$_3$OH molar ratio, useful to predict H$_2$ solubility in H$_2$O$_2$ direct synthesis kinetic studies, where hydrogen is introduced as the limiting reagent, due to safety reasons.

A batch apparatus for the direct synthesis of hydrogen peroxide was developed to safely operate outside flammability limits. A 5% Pd on carbon commercial catalyst was used for direct synthesis experiments. An enhanced H$_2$O$_2$ production was obtained adopting different H$_2$ feeding policies, although selectivity did not exceed 30%. A relation between selectivity and the hydrogen dissolved in the liquid phase was suggested.

A kinetic analysis was performed to identify the role of each reaction involved in the complex reaction mechanism. Batchwise direct synthesis, hydrogenation and disproportionation data were collected at temperatures in the range 258 – 297 K and pressure between 1.4 and 2.0 MPa (depending on the temperature) using a commercial 5% Pd on carbon catalyst in a methanolic solution and in the absence of halides and acids. A model of a gas bubbling, batch slurry reactor for H$_2$O$_2$ direct synthesis was formulated, including mass transfer resistances between gas and liquid and bulk of the liquid-catalyst surface. A sensitivity analysis on the mass transfer coefficients to allow for uncertainties in the correlations proved that no resistances in the liquid occur, while gas-liquid H$_2$ transfer rate may be limiting, although unlikely, requiring that literature coefficients overestimate the real transfer rate by an order of
magnitude. Comparable activation energies close to 45 kJ mol\(^{-1}\) were observed for H\(_2\)O production, hydrogenation and disproportionation, while H\(_2\)O\(_2\) synthesis had a different temperature dependence (23 kJ mol\(^{-1}\)), suggesting that a higher selectivity is achievable at low temperature. Disproportionation had a very limited influence on the overall peroxide production rate, with \(R_{d}/R_{ds} > 0.5\) only at high H\(_2\) conversion, when the direct synthesis reaction slows down. Hydrogenation was the preferred path of H\(_2\)O\(_2\) degradation as its reaction rate rapidly increased with H\(_2\) conversion. Water formation was always significant, prevailing (\(R_{wf}/R_{ds} > 1\)) at higher temperature, whereas lower temperature favors the direct synthesis (\(R_{wf}/R_{ds} < 1\)). Independent investigations on disproportionation in the absence of H\(_2\) confirmed the results, whereas H\(_2\)O\(_2\) hydrogenation experiments (carried out in the absence of O\(_2\)) highlighted significant difference in the kinetics. This observation seems to confirm the influence of dissolved H\(_2\) in the direct synthesis process, apparently due to different oxidation states of the catalyst.

Further investigations on the catalyst properties were carried out. Pd and PdAu catalysts supported on mesoporous ordered SBA15 and doped M-SBA15 (M = Al, Ti and CeO\(_2\)) were synthesized. A good control of both the catalysts dispersion and nanoparticle stability was achieved using SBA15. A synergetic effect between Pd and Au was observed when comparing mono- and bimetallic SBA15-based catalysts, both bromine-grafted and unmodified. However, the selectivity decreased when bromine was incorporated in the catalysts. Possibly the introduction of relatively bulky bromoalkyl–species caused the blocking/poisoning of the catalyst. The performance of the unordered SiO\(_2\) based catalysts was inferior compared to the ordered mesoporous ones, confirming the advantage of using the latter support. The catalyst showing the best performance (PdAu/SBA15) was modified to gain more surface acidity. Higher productivity and slightly higher selectivity were achieved incorporating Al into the framework, likely due to the increased number of Brønsted acid sites including Al into the support framework.

Catalysts supported on a strongly acidic, macroporous resin (Lewatit K2621) were prepared by ion-exchange method. Different active metal (Pd) contents, as well as different amounts of catalyst, were tested batchwise. Results revealed that smaller nanoclusters favor the production of H\(_2\)O, likely due to their O-O bond breaking aptitude. Further, preliminary analysis suggest that the reduced form of Pd is more active than the oxidized form in promoting the selective hydrogenation to H\(_2\)O\(_2\).
Many paths have been opened as logical continuation of this work. More investigations are suggested to identify the most suitable surface mechanism describing the overall process. A semi-batch apparatus, with a continuous gas phase bubbling through a static liquid, is being considered to study the dependence of the reaction rates on H₂ and O₂ partial pressures, and hence access the partial reaction orders. Literature density functional theory calculations could help to developed a reaction mechanism also accounting for adsorption of reagents (ether associative or dissociative), desorption of products and reaction intermediates.

A relation between selectivity and the oxidation state of the active metal has been proposed. Different reaction conditions could help to better understand the role of the Pd oxide, for instance using O₂ as the limiting reagent. The reduced state of the catalyst would be this way maintained during the reaction, possibly favouring a higher selectivity.

An experimental study on Pd single crystals with different surface structures could help to identify the best catalyst structure and optimize the selectivity. Moreover, Pd is well known to form hydride in the presence of H₂, whose catalytic properties are still little known. An investigation on model catalysts (where the surface/volume ratio is very small) is encouraged to understand the role that the bulk of the active metal has in the DS process. These tasks will provide useful insights to developed a better catalyst.

This work has shown that the direct synthesis of hydrogen peroxide is a feasible process and the results achieved are very promising. The ultimate goal should be the implementation and optimization of a continuous process, for a cost-effective in situ production. In that sense, a microreactor is being considered to operate safely even within flammability limits at high H₂ concentrations.
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6 Publications
Review

H₂ solubility in methanol in the presence of CO₂ and O₂

Nicola Gemo a, b, Pierdomenico Biasi b, Tapio O. Salmi b, Paolo Canu a, *

a Dipartimento di Princìpi e Impianti di Ingegneria Chimica “I. Sorgato” (DIPIC), University of Padova, via Marzolo 9, 35131 Padova, Italy
b Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi, Biskopsgatan 8, 20500 Turku, Finland

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Abstract

Hydrogen solubility in methanol, (methanol + carbon dioxide) and (methanol + carbon dioxide + oxygen) was measured and correlated at different temperatures (268 < T/K < 288) and pressures (0.37 < P/MPa < 3.5). Hydrogen content in the liquid phase was measured using a gas absorption method and Fugatron HYD-100 instrument. Experiments were performed in a fixed volume cell at constant temperature and hydrogen content was varied with subsequent loadings in the cell environment. At all conditions investigated a linear relation between hydrogen partial pressure and concentration was observed. Results were correlated and generalized as Henry’s constants for H₂, as a function of temperature and CO₂/methanol overall ratio. Correlation and generalization of the measurements was provided through a thermodynamic model, based on Peng–Robinson equation of state with van der Waals mixing rules and Boston–Mathias x-function. H₂ solubility in methanol was confirmed to grow with temperature and amount of CO₂; at constant H₂ partial pressure, O₂ does not affect H₂ solubility.

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1. Introduction

Systems involving CO₂-expanded liquids are a current topic in modern chemical synthesis. Besides advantages due to the mixture physical properties, mainly related to marked modifications of the vapour–liquid equilibrium (VLE), CO₂ brings about a reduced impact on environment and minimization of safety issues [1,2]. Both homogeneously and heterogeneously [1–4] catalyzed reactions have been tested in CO₂ expanded solvents. Research interest is especially focused on reactions limited by a poor solubility of reactant gas, such as hydrogenations [5–7] and oxidations [8–10]. Reaction rates may also take advantage of CO₂ enhanced transport properties [1] (i.e., diffusivities and viscosity) in addition to the
increased solubility of reactant gases. Chen et al. [6], while studying the hydrogenation of p-chloronitrobenzene in CO2-expanded methanol, found a conversion enhancement when operating with CO2 that they referred to an increase in hydrogen solubilization. Musie et al. [9,10] carried out homogeneous oxidations in CO2-expanded solvents; they measured reaction rates 1 to 2 orders or magnitude larger than with a pure organic solvent as reaction medium, suggesting that a larger O2 solubility due to CO2 was the cause. Other authors [11–13] explained the enhancement of H2 and O2 solubility by the increased free volume in the solution caused by dissolved CO2. Our motivation is specifically based on the interest in H2O2 direct synthesis reaction, where proper estimation of the phase equilibria of H2, O2, CO2 and methanol, is crucial in optimizing the reaction conditions and determining the intrinsic reaction kinetics.

A significant number of vapour–liquid equilibrium data is available for binary systems involving the four species (H2, O2, CO2, and CH3OH) of our interest [14–24]. Only few data were published for ternary systems including both CO2 and CH3OH, i.e., (CO2 + CH3OH + H2) and (CO2 + CH3OH + O2). Measurements of the (CO2 + CH3OH + H2) system at T = 313 K were reported by Xie et al. [25] and Lopez-Castillo et al. [11] The same combination was also investigated by Bezanehtak et al. [26] at T = 278, 288 and 298 K. Vapour–liquid equilibrium data for the (CO2 + CH3O–H + O2) ternary system are available only at T = 313 K[12]. No data were found for the quaternary mixture (CO2 + CH3OH + O2 + H2). The latter system has crucial importance on hydrogen peroxide direct synthesis [27–31], whereas the above mentioned gases are dissolved in a liquid phase (i.e., methanol) with H2 acting as the limiting reagent. Up to now, the lack of information on vapour-liquid equilibria makes it difficult to obtain a precise kinetic description of the reactions involved in this process, where solubility modifications confuse with kinetics. Under H2 poor conditions, often prevailing in H2–O2 mixtures to operate outside the (lower) flammability limit, H2 solubility is the key information required. In this work, solubility data for hydrogen in methanol, in (CO2 + CH3OH) and in (CO2 + CH3OH + O2) are collected and critically compared with available literature data, within the range 268 < T / K < 288 and total pressures between 1 and 3.5 MPa (H2 partial pressure, P(H2) varied between 0 and 1 MPa). Measurements of hydrogen solubility were carried out in a fixed volume cell. In addition to the standard gas absorption method, we also used the Fugatron HYD-100 instrument, which allows measuring hydrogen concentration in the liquid phase in the reactor environment [32,33].

2. Experimental

2.1. Materials

The chemicals used in the present work (see table 1) were carbon dioxide and oxygen with a certified purity of 0.9999 in mole fraction (Oy AGA Ab, Espoo, Finland), hydrogen with a mole fraction certified purity of 0.99999 (Oy AGA Ab, Espoo, Finland) and methanol (0.998 mol fraction purity, J.T. Baker). All materials were used as received.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Source</th>
<th>Certified purity/mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>AGA</td>
<td>0.9999</td>
</tr>
<tr>
<td>Oxygen</td>
<td>AGA</td>
<td>0.9999</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>AGA</td>
<td>0.99999</td>
</tr>
<tr>
<td>Methanol</td>
<td>J.T. Baker</td>
<td>0.998</td>
</tr>
</tbody>
</table>

* No further purification was done before use.

2.2. Apparatus

Measurements of hydrogen solubility in binary (H2 + CH3OH), ternary (CO2 + CH3OH + H2) and quaternary (CO2 + CH3O-H + O2 + H2) systems were performed using the experimental set-up schematically described in scheme 1.

The equilibrium cell is a stainless steel, fixed volume autoclave (Parr Instrument) equipped with a mechanical stirrer (Heidolph RZR 2021). The accessible gas volume was 636 cm3, including piping, precisely measured according to the procedure described below. Temperature inside the equilibrium cell was controlled with an external flow of heating/cooling fluid (B. Braun, Thermomix UB/Frigomix) and monitored with a K-type thermocouple (accuracy ±1 K) connected to a digital temperature indicator. Pressure was monitored with a Keller PA-21R pressure transducer (accuracy ±0.01 MPa). CO2 and O2 were transferred to the system directly from the cylinders via a throttle valve. H2 flow during each sequential injection was tightly controlled for reproducibility with mass flow meters (Brooks Instruments 5850 E Series). In addition, a constant volume (59 cm3) vessel was used between the H2 bottle and the mass flow controller (scheme 1). Loaded with H2 at a pressure higher than the measuring cell, it double checks the amount of H2 fed to the reactor, determined from pressure difference inside the H2 vessel before and after the loading and the quantity fed through the mass flow controller.

Methanol was degassed using an Agilent 1100 series degasser and then introduced in the system via a high pressure piston metering pump (Eldeox Laboratories, Inc).

2.3. H2 solubility measurements

An in situ technique using Fugatron HYD-100 was adopted to measure the hydrogen solubility, in view of its use to monitor and control hydrogenation reactions at comparable conditions. The instrument has been coupled to gas absorption measurements for calibration, the latter remaining the reference technique used. Fugatron HYD-100 allows continuous, in situ measurements of H2 solubilized in a liquid phase [32,33]. It is based on a probe immersed in the liquid phase, with a rigid, dense membrane internally purged with a carrier gas (nitrogen) flowing at 10 Ncm3 min−1. Hydrogen permeates the membrane and is brought to a gas detector by the carrier gas. Hence, a small amount of hydrogen continuously flows through the probe to the detector. Hydrogen loss for the analysis was evaluated by integrating the instrument measurement and the amount loss was less than 0.2% of the total H2 introduced during each experiment. Accordingly, pressure in the equilibrium vessel within the experimental time does not show any detectable loss due to the instrument uptake. The instrument reading also reached a very stable value after any hydrogen addition to the equilibrium cell. Both evidences confirm that the H2 loss for the analysis was not detectable and had no significant influence on measurements.

Prior to the experimental campaign, the cross-sensitivity with methanol, oxygen and carbon dioxide was explored. No signal was observed when the probe was immersed in the mixture without H2 being present, proving the selectivity of the membrane and excluding any interference with others species.

The instrument provides a measurement linearly proportional to the H2 concentration in the liquid. While this could be enough to monitor H2 consumption in hydrogenation reactions [32], relating actual H2 concentration to the initial value, here we need an absolute measure. Accordingly, we calibrated the instrument with the gas absorption method.

The method is based on the estimation of the amount of H2 in a given liquid mixture volume (i.e., its liquid phase concentration), from experimental measurements. These are the total amount of H2 in the cell and that in the vapour phase above the liquid. Besides...
the simple case of binary H\textsubscript{2}/CH\textsubscript{3}OH mixtures, the estimation is not obvious, due to the non-ideal behaviour of the gas phase that includes CO\textsubscript{2}, at the temperature and pressure domain investigated. Accordingly, the estimation strategies vary for binary, ternary and quaternary systems, as explained in the Procedures section.

Comparison between the hydrogen concentration (\(c_{\text{H}_2}\)) measured and reading of the Fugatron instrument provides the calibration constant \(f\):

\[
f = \frac{c_{\text{H}_2}}{q},
\]

where \(q\) is the instrument reading, i.e., mole fraction of hydrogen in the carrier gas behind the membrane, reaching the gas detector in the instrument. The calibration constant \(f\) is indeed quite sensitive to temperature, so that \(f(T)\) has actually been determined. On the other hand, it is not affected by total pressure and liquid phase composition, as mentioned above.

### 2.4. Procedures

Precise knowledge of net available volumes (equilibrium cell and H\textsubscript{2} vessel) is mandatory for an accurate estimation of gas amounts. Connection pipes and internals, such as stirring system and Fugatron probe, make the accessible volume different from the nominal. Accurate volume measurements before the experimental campaign were carried out using an auxiliary vessel with a precisely determined volume (1000 cm\(^3\)), connected to the equilibrium cell through an on/off valve, thus assembling an overall volume only partially known. Air inside both vessels was evacuated pressuring and depressurizing with N\textsubscript{2} up to 0.3 MPa, repeated three times. Then, the equilibrium cell alone was filled with N\textsubscript{2} up to 2 MPa and equilibrated at \(T = 293\) K. The valve connecting the two vessels was then opened to slowly transfer N\textsubscript{2} inside the secondary vessel, of known volume. Once stabilized, pressure and temperature were measured again. Using the ideal gas law, volume of the equilibrium cell was calculated from the initial and final pressures and temperature measurements, given that the amount of N\textsubscript{2} remains constant. The same procedure was adopted to measure the volume of the H\textsubscript{2} reservoir. The procedure was repeated four times with a standard deviation < 1.5%.

Then, equilibrium configurations at different temperatures, pressures and composition were studied with sequential additions of a given species (H\textsubscript{2}, CO\textsubscript{2}, and O\textsubscript{2}), suitably adjusting the procedure to minimize uncertainties, as specified below. Whenever compatible with the procedure, methanol was fed last, after each gas, to prevent solubility disturbing the gas quantification by pressure.

#### 2.4.1. Binary system

The liquid phase concentration of hydrogen in (CH\textsubscript{3}OH + H\textsubscript{2}) system was evaluated at \(T = 278\) K and variable pressure, up to 1.56 MPa with the purpose of validating our procedures and methods against literature data. Equilibrium vessel and piping were swept first by cycling (three times) pressurization (0.3 MPa) and evacuation (0.1 MPa) with argon. The procedure was repeated 3 times with H\textsubscript{2} to evacuate argon and set the initial amount of H\textsubscript{2} in the equilibrium cell, precisely determined by pressure, temperature, available cell volume and ideal gas law. An accurately weighed amount of methanol (typically 330 g) was introduced later, with a metering pump. Stirring (1000 rpm) was turned on; after approx. one hour the pressure and Fugatron reading were definitely stable, proving that VLE and instrument steady-state were fully set.

Hydrogen was further introduced with several additions of approx. 0.4 MPa from the dedicated vessel, to investigate the composition space. After each H\textsubscript{2} addition, its amount in the vapour phase of the equilibrium vessel was recalculated by the ideal gas equation, using the equilibrium temperature and pressure, and the net gas phase volume (total accessible vessel volume subtracted the volume of the methanol initially loaded). We assumed that the partial pressure of methanol in the gas phase was negligible, at the relatively low temperature investigated. Based on available correlations for pure methanol vapour pressure, in the worst case \((T/K = 278\) and \(P/\text{MPa} = 0.37\)) the mole fraction of methanol in the vapour phase is less than 1.5%, decreasing below 0.35% at the highest pressure. The imbalance between moles of H\textsubscript{2} added (\(n_{\text{H}_2}^{\text{added}}\)) and moles in the gas phase (\(n_{\text{H}_2}^{\text{gas}}\)) gives the amount of H\textsubscript{2} in the liquid phase, \(n_{\text{H}_2}^{\text{L}}\):

\[
SCHEME 1. Experimental apparatus: 1, Equilibrium vessel; 2, hydrogen reservoir; 3, hydrogen mass flow controller; 4, temperature control; 5, methanol pump; 6, Degasser; 7, Fugatron HYD-100 H\textsubscript{2} analyzer; 8, precision balance.
2.4.2. Ternary systems

molar density of pure methanol at the temperature of interest [34]. Measured CH₃OH also provide valuable data to calibrate the Fugatron instruments, i.e., f(T) identification, to reliably use it in other conditions.

### 2.4.3. Quaternary systems

The liquid phase concentration of hydrogen in (CO₂ + CH₃OH + H₂) ternary system was measured at T = 268 and 278 K varying hydrogen partial pressure, while keeping the same CO₂/CH₃OH overall ratio. Before each experiment, the empty vessel and piping were purged three times by cycling pressure (up to 0.3 MPa) with CO₂. The vessel was thermally equilibrated at T = 293 K and pressure continuously logged. Eventually, the measuring vessel was filled with CO₂ up to a pressure of 3.9 MPa. The total amount of CO₂ in the cell was evaluated with its gas density, calculated with the Peng–Robinson equation of state [35] (PR-EoS) and the available vessel volume. Though the initial amount of CO₂ is estimated by way of a calculated property, thus not exactly a measurement, the accuracy of the PR-EoS for a single phase/single component calculation of gas density sufficiently far from supercritical conditions is quite good. Methanol was then introduced in the equilibrium cell as explained for binary systems. It should be noticed that loading CO₂ as a gas, before any liquid is present in the cell, allows to accurately dose its amount as well as that of methanol; the reverse (feeding the liquid before the gas) does not allow to calculate the CO₂ fed by pressure measurements in the cell, because of its rapid and extensive solubilization.

The vessel was then brought to the desired temperature (268 < T < 288) and stirring (1000 rpm). After less than 10 min temperature and pressure were stable, confirming the faster dissolution rate of CO₂.

Methanol is known as a CO₂ expanding solvent [1,3,4,11] especially approaching supercritical conditions [1]. The volume expansion depends only on CO₂ dissolved in the liquid phase [13–17], and it can be significant. At given pressure, temperature and total amount of each species (CO₂ and CH₃OH) inside the cell, both phases thermodynamic state (including composition and densities) has been determined with a binary flash calculation, using a ϕ–ϕ approach and PR-EoS. Further details on the thermodynamic model are given below. The volume increment due to CO₂ swelling was calculated as +10% by PR-EoS. Estimates from available experimental data [14] at our CO₂ liquid phase mole fraction suggest a larger volume increment of +18% compared to pure methanol.

We trusted the measurements, using the 18% increment for further calculation, assuming the EoS estimation of liquid volume to be less reliable. Keeping the CO₂ and CH₃OH constant, CO₂ liquid phase composition varied less that 3.3%, within the investigated temperature range, because of H₂ (and then pressure) increments, resulting in a negligible variation in methanol volume enhancement, according to literature [13–17].

After equilibrating methanol and CO₂, known amounts of H₂ were introduced from its storage vessel, with consecutive additions, up to a maximum H₂ partial pressure of 1.27 MPa (gas phase mole fraction up to 57%). The amount of H₂ in the gas phase of the cell after each addition was estimated by the increment of pressure in the cell after equilibration and consequently the amount of H₂ in the liquid phase by difference with the amount fed. As above, we assumed that H₂ does not affect the liquid phase volume [14].

Due to the broader temperature range investigated in the (CO₂ + CH₃OH + H₂) combination, solubility measurements supply the single temperature binary data to calibrate the Fugatron instrument, using H₂ liquid phase concentration obtained with gas absorption method, as previously described.

3. Results and discussion

We investigated hydrogen solubility in three different (binary, ternary and quaternary) species combinations: (H₂ + CH₃OH), (CO₂ + CH₃OH + H₂) and (CO₂ + CH₃OH + O₂ + H₂). The quaternary data are completely original, while the other combinations investigated are reported in the literature, as well binary as combinations of the four species other than (H₂ + CH₃OH) that we did not investigate experimentally. Literature data provide the opportunity to

![Figure 1](image-url)
TABLE 2
CH3OH + H2 binary system. Liquid phase H2 concentration measured at different hydrogen partial pressures, at T = 278 K.

<table>
<thead>
<tr>
<th>( P_{H2} ) (MPa)</th>
<th>( 10^{-3} C_{H2} ) (mol cm(^{-3}))</th>
</tr>
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<tbody>
<tr>
<td>0.37</td>
<td>1.31</td>
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<tr>
<td>0.37</td>
<td>1.27</td>
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<tr>
<td>0.39</td>
<td>1.27</td>
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<tr>
<td>0.40</td>
<td>1.23</td>
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<td>0.79</td>
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<td>0.81</td>
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<td>0.82</td>
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<tr>
<td>1.55</td>
<td>5.10</td>
</tr>
<tr>
<td>1.56</td>
<td>5.21</td>
</tr>
</tbody>
</table>

Error in \( C_{H2} \) is 0.01 \( 10^{-3} \) mol cm\(^{-3}\).

FIGURE 2. CH3OH + H2 binary system. Plot of concentration of hydrogen in liquid methanol as a function of its partial pressure above the liquid, at T = 278 K. ■ This work; ✨ Descamps et al. [23]; ○, calculated from data of Katayama et al. [24].

calibrate a thermodynamic model (estimation of binary interaction parameters) to correlate ternary and quaternary data, in addition of validating our experimental methods.

Before presenting and discussing each single set of data, we show in figure 1 all the original data of H2 partial pressure in the gas phase vs. H2 mole fractions in the carrier gas behind the membrane (Fugatron HYD-100 readings). Linearity is evident for all systems, at the conditions investigated, notwithstanding the wide range of H2 concentration in the gas phase investigated (up to 57%). In addition, the data confirm the insensitivity of the permeation instrument to the total pressure, whose effect should cause a significant curvature, which is clearly not the case. Since Fugatron readings are themselves proportional to \( C_{H2} \) [32], the observed linearity also confirms the validity of Henry’s law at all examined conditions, caused by a rather small solubility of H2 in the liquid.

We can also anticipate from figure 1 that the H2 solubility at given partial pressure of hydrogen in the gas and temperature is extremely close, whether O2 is present or not, suggesting that no H2–O2 interactions occurs in the liquid phase.

In the following, raw instrument measurements, \( q \), will be converted to \( C_{H2} \) given the calibration function \( f(T) \) determined above, by absorption measurements, for the purpose of calculating the Henry’s constant and its dependencies.

3.1. H2 + CH3OH

Table 2 reports values of hydrogen liquid phase concentrations measured at \( T = 278 \) K according to the procedure described above, i.e., progressively increasing the amount of hydrogen in the atmosphere above methanol.

Plotting experimental \( C_{H2} \) against \( P_{H2} \) (figure 2) allows determining the average Henry’s constant as the slope of the resulting linear interpolating function (i.e., Henry’s law, \( C_{H2} = P_{H2} \cdot k_{ij} \)), including the origin for physical consistency. The determined value of the Henry’s constant is \( (30.14 ± 1.02) \) (MPa m\(^{-3}\)kmol\(^{-1}\)), where the error is one standard deviation of the error between calculated \( H_{ij} \) and individual values. This value is quite close to 29.36 (MPa m\(^{-3}\)kmol\(^{-1}\)) calculated from data reported by Katayama et al. [24] at the same temperature. It also compares well to 28.39 (MPa m\(^{-3}\)kmol\(^{-1}\)) measured by Descamps et al. [23], who carried out a thorough analysis of literature studies on this system. They already reported that literature estimates differ [14–16], even at comparable conditions, concluding that discrepancies are likely due to the analytical techniques and to the small amount of water always present in methanol. At any rate, figure 2 shows that our measurements compare well with those of Descamps [23] and Katayama [24]. Our data for CH3OH–H2 provide the opportunity to validate our procedures and the analytical technique.

3.2. CO2 + CH3OH + H2

Experimental results for the (CO2 + CH3OH + H2) ternary system at \( T = 268, 278 \) and 288 K are listed in table 3. At each temperature, a number of combinations of H2 partial pressure were screened, by sequential additions of hydrogen.

Hydrogen concentration in the liquid phase as a function of its partial pressure is shown in figure 3. Average Henry’s law constants calculated as above with the collected data are \( (16.7 ± 0.43) \), \( (18.9 ± 0.67) \) and \( (20.1 ± 0.95) \) (MPa m\(^{-3}\)kmol\(^{-1}\)), respectively at \( T = 268 K, 278 K \) and 268 K. A linear interpolation of the \( H_{ij}(T) \) dependency yields \( H_{ij} \) (MPa m\(^{-3}\)kmol\(^{-1}\)) = 65.8–0.17 T /K. The hydrogen solubility increases with temperature (lower \( H_{ij} \)) as typical of H2 in CH3OH. It is also apparent that the hydrogen solu-
bility increases compared to binary system, at the same hydrogen partial pressure. This is attributed to the presence of carbon dioxide: enhancements of H2 solubility by CO2 up to 80% has been reported in many organic solvent [24], including methanol. In our conditions, comparing data at $T = 278$ K we have an increment of 37% due to the use of CO2.

Figure 4 compares our data (liquid phase mole fractions calculated with PR-EoS tuned on our measurements, as explained below) with those reported by Bezanehtak et al. [26] at the same temperature and total pressure, showing quite a good agreement. Interestingly, their data show a decreasing H2 liquid mole fraction with that of CO2 increases, against the known evidence that CO2 increases H2 solubility. According to the authors, this is an apparent contradiction due to their experimental protocol, where a larger CO2 amount in the whole V−L cell causes a smaller partial pressure of H2 in the vapour phase, also lowering its amount in the liquid.

Table 4 reports the experimental data of hydrogen solubility for the quaternary (CO2 + CH3OH + O2 + H2) system, measured at $T = 268$ and 278 K. Figure 5 shows the experimental values as a function of hydrogen partial pressure. Calculated Henry's law constants are (18.24 ± 0.89) and (20.88 ± 1.71) (MPa m3·mol−1) at $T = 278$ and 268 K, respectively. Being that CO2 liquid phase molar fraction is always the one used in the ternary case, we conclude that the addition of quite a significant amount of O2 does not lead to any significant modification of the H2 solubility. For sake of

We point out that the data reported by Bezanehtak et al. [26] were measured at 2 MPa. Since our data were measured at slightly different pressure, H2 concentrations shown in figure 4b were linearly interpolated from data at 1.87 and 2.16 MPa (see Table 3).

3.3. CO2 + CH3OH + O2 + H2

Table 4 reports the experimental data of hydrogen solubility for the quaternary (CO2 + CH3OH + O2 + H2) system, measured at $T = 268$ and 278 K. Figure 5 shows the experimental values as a function of hydrogen partial pressure. Calculated Henry's law constants are (18.24 ± 0.89) and (20.88 ± 1.71) (MPa m3·mol−1) at $T = 278$ and 268 K, respectively. Being that CO2 liquid phase molar fraction is always the one used in the ternary case, we conclude that the addition of quite a significant amount of O2 does not lead to any significant modification of the H2 solubility. For sake of

![Figure 4](image-url) CO2 + CH3OH + H2 ternary system. Comparison of H2 solubility measurements with literature data at 2 MPa (a, $T = 278$ K; b, 288 K): †, Bezanehtak et al. [26]; ‡, this work.

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$P_{H2}$/MPa</th>
<th>$10^{-5}$ $C_{H2}^{Exp}$/mol cm$^{-3}$</th>
<th>$10^{-5}$ $C_{H2}^{Calc}$/mol cm$^{-3}$</th>
<th>$\Delta C_{H2}$/%</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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<td>1.92</td>
<td>1.79</td>
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<td>1.09</td>
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<td>4.84</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Error in $C_{H2}^{Exp}$ is 0.01 $10^{-5}$ mol cm$^{-3}$.
TABLE 4
CO\textsubscript{2} + CH\textsubscript{3}OH + O\textsubscript{2} + H\textsubscript{2} quaternary system. Measured and calculated liquid phase concentration of hydrogen at different hydrogen partial pressure and temperatures.

<table>
<thead>
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<th>T /K</th>
<th>P /MPa</th>
<th>(P_{li}/\text{MPa} )</th>
<th>(10^{-5} \frac{C_{H_2,li}}{\text{mol cm}^{-3}} )</th>
<th>(10^{-5} \frac{C_{H_2,calc}}{\text{mol cm}^{-3}} )</th>
<th>(\Delta C_{H_2} /% )</th>
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</table>

Error in \(c_{li}^{exp}\) is 0.01 \(10^{-5}\) mol cm\(^{-3}\).

FIGURE 5. CO\textsubscript{2} + CH\textsubscript{3}OH + O\textsubscript{2} + H\textsubscript{2} quaternary system. Solubility data of hydrogen: ●, \(T = 278\) K; ○, 268 K; solid line, Peng–Robinson EoS after tuning \(k_0\).

completeness, the composition of both phases according to PR EoS VLE calculations, result \(x_{CO2} = 0.11\) and 0.43 < \(y_{O2} < 0.53\), depending on temperature and total pressure.

The negligible effect of O\textsubscript{2} on H\textsubscript{2} solubility was already anticipated, see figure 1. Accordingly, we can improve the linear interpolation of \(H_{li} (T)\) including quaternary data at the temperature investigated, resulting in \(H_{li} (/\text{MPa·m}^{-3}·\text{kmol}^{-1}) = 68.3–0.18\, T /K\). Again, hydrogen solubility increases with increasing temperature, as known. We could not find any literature data to compare with.

FIGURE 6. Dependence of hydrogen solubility on hydrogen partial pressure at 278 K. Solid line, Peng–Robinson EoS after tuning \(k_0\).

TABLE 5

<table>
<thead>
<tr>
<th>Components</th>
<th>T /K</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}–H\textsubscript{2}</td>
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<td>[14]</td>
</tr>
<tr>
<td>CH\textsubscript{3}OH–H\textsubscript{2}</td>
<td>298.15–323.15–373.15</td>
<td>[17]</td>
</tr>
<tr>
<td>CH\textsubscript{3}OH–CO\textsubscript{2}</td>
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<td>[18]</td>
</tr>
<tr>
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<td>[19]</td>
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<td>O\textsubscript{2}–CO\textsubscript{2}</td>
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<tr>
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<td>[21]</td>
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</table>

4. Modelling

Besides the experimentally measured data and corresponding Henry’s constants, any equilibrium state, at predefined combinations of species amount and temperature (including early steps of filling), has been characterized by a flash calculation, using a \(\phi–\phi\) approach (\(K_i = y_i/x_i = \phi_i^L/\phi_i^V\)) and the Peng–Robinson equation of state (PR-EoS):

\[
P = \frac{RT}{V_m - b} \frac{a}{V_m(V_m + b) + b(V_m - b)}
\]

Here \(V_m\) refers to the molar volume. Standard routines have been used, through a well established commercial code [36]. Calculations provide the vapour and liquid phase properties, and we focused on mole fractions. The total available amount of species is known from experiments, as well as temperature and total pressure and are given as input conditions. The calculations become predictive once EoS parameters are tuned on experimental data. Typical mixing rules of pure species parameters have been used; linear for the co-volume \(b\) and quadratic for the attractive interaction parameter \(a\):

\[
b = \sum_{i=1}^{NC} x_i b_i,
\]

\[
a = \sum_{i=1}^{NC} x_i \sqrt{\bar{a}_i \bar{a}_j (1 - k_{ij})},
\]

\[
k_{ij} = \frac{b_{ij}}{b_i b_j},
\]

Here \(x_i\) represent the mole fraction, while subscript \(i\) and \(c\) indicate species and critical property, respectively. Due to the presence of supercritical species (H\textsubscript{2} and O\textsubscript{2}), a Boston–Mathias alpha function [37] was chosen for \(\alpha_i(T)\):

\[
\begin{align*}
T_{c,i} &\leq 1, \quad \alpha_i(T) = [1 + m_i (1 - \sqrt{T_{c,i}})]^2, \\
T_{c,i} &> 1, \quad \alpha_i(T) = \exp[(1 - T_{c,i})], \quad c = 1 + m_i/2, \quad d = m_i/2, \\
T_{c,ij} &\leq 1, \quad k_{ij} = k_{ij}^c + k_{ij}^d, \quad T_{c,ij} < T_{c,i}, \quad T_{c,ij} < T_{c,j},
\end{align*}
\]

where subscript \(r\) indicates a reduced property and \(c\) the acentric factor. Binary interaction parameters \(k_{ij}\) have to be tuned. They are assumed to vary with temperature alone; while estimated at any temperature investigated, results (reported in table 6) were fit by the expression:

\[
k_{ij} = k_{ij}^c + k_{ij}^d, \quad T.
\]
We predicted H2 solubility in ternary and quaternary systems using only binary interaction parameters \(k_{ij}\) calibrated on literature binary phase equilibrium data (Table 5), selected to be as close as possible to our experimental conditions (\(T, P\) and liquid phase composition).

The objective function to be minimized by manipulating \(k_{ij}(T)\) was based on departures between calculated and experimental liquid phase compositions. We assumed that oxygen and hydrogen interaction in the liquid phase are negligible, i.e., \(k_{O2-H2} = 0\), according to experimental indications. Comparing the optimization results in term of H2 solubility prediction, the accuracy was quantified through the mean absolute percentage error (MAPE):

\[
\text{MAPE} = \frac{100}{n} \sum_{j=1}^{n} \left| \frac{C_{\text{exp}}^{H2}_{j} - C_{\text{calc}}^{H2}_{j}}{C_{\text{calc}}^{H2}_{j}} \right|
\]

where \(n\) is the number of measurements.

The model first tuned on literature binary data agrees quite well with all binary literature data. While \(H2\) liquid phase composition dependence on temperature and pressure in ternary and quaternary systems was reasonable, dissolution of \(H2\) was systematically underestimated, with a MAPE errors as high as 20%, especially at the higher temperature and pressure. Using also ternary measurements to fit \(k_{ij}\) values for \((H2 + CH3OH)\), the model was significantly improved as compared to ternary experimental data. The prediction of \(C_{H2}\) in quaternary \((CO2 + CH3OH + O2 + H2)\) configurations was also remarkably improved. All the final binary interaction parameters estimated are reported in Table 6, along with MAPE errors for all the investigated configurations and temperatures.

The developed model allows estimating the CO2 effect on the hydrogen solubility. Figure 6 shows calculated Henry's constants of hydrogen as a function of temperature and total \(CO2/CH3OH\) mole ratio, \(\gamma = nCO2/nCH3OH\), according to PR-EoS tuned on literature and our experimental data.

Though predicted \(H_{B2}(T)\) appears slightly curved upwards, linear interpolations are acceptable, leading to the correlation:

\[
H_{B2}/(\text{MPa} \cdot \text{m}^3/\text{kmol}) = \alpha(\gamma) + \beta(\gamma)T/K
= -91.96\gamma + 114.09
\]

\[
\beta(\gamma) = 0.26\gamma - 0.33
\]

We already mentioned the significant H2 solubility enhancement due to CO2 by comparing binary and ternary data, also shown in Figure 3, confirming literature data [11,26] measured under different conditions. To measure quantitatively the advantage given by CO2, we used the enhancement factor (EF) [12], comparing H2 solubility without \((H2 + CH3OH)\) and with \((CO2 + CH3OH + O2 + H2)\). EF is defined as the ratio of hydrogen composition in methanol \((X_{H2}^{\text{binary}})\) and \((CH3OH + CO2)\) systems \((X_{H2}^{\text{quaternary}})\) at the same conditions of temperature and hydrogen fugacity:

\[
\text{EF} = \frac{X_{H2}^{\text{quaternary}}}{X_{H2}^{\text{binary}}}
\]

Values higher than 1 indicate increased hydrogen dissolution in the liquid phase caused by carbon dioxide, and thus are desirable. According to the predictions based on this model, EF can approach 2.1 at \(T = 278 K\) and \(\gamma = 0.3\).

5. Conclusions

We investigated hydrogen solubility in three different systems: pure methanol, \((CO2 + CH3OH)\) and \((CO2 + CH3OH + O2)\) at temperatures between 268 and 288 K and for pressure up to 3.49 MPa. A gas absorption method was adopted along with an in situ technique using Fugatron HYD-100 instrument. Whenever possible, results were compared with available literature data, showing good agreement. For all conditions studied, the solubility of hydrogen in the liquid phase increased with \(H2\) partial pressure, as expected.

**Table 6**

<table>
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<th>System</th>
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<td>/</td>
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<td>278</td>
<td>3.0</td>
<td>0.041</td>
<td>-0.476</td>
<td>0.129</td>
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<td>7.6</td>
<td>0.036</td>
<td>-0.459</td>
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<td>278</td>
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<td>-0.476</td>
<td>0.129</td>
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**Table 7**

Coefficients for temperature correlation of binary interaction parameters (equation (8)).

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<td>(MeOH-H2)</td>
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</tbody>
</table>

**Figure 6.** Predicted Henry's constants of hydrogen as a function of temperature and liquid phase composition. D: calculated from PR-EoS tuned on literature and our experimental data, C: \(\gamma = 0.3\); A: \(\gamma = 0.25\); O: \(\gamma = 0.15\); x, \(\gamma = 0.09\); ●, experimental data (see Section 3, \(CO2 + CH3OH + O2 + H2\)).
The linearity of hydrogen concentration with hydrogen partial pressure was confirmed by the solubility measurements (Fugatron HYD-100) and is likely due to the low solubility of H₂, in any case. In both ternary (CO₂ + CH₃OH + H₂) and quaternary (CO₂ + CH₃OH + H₂ + O₂ + H₂) systems, increasing the temperature resulted in an enhanced hydrogen solubility at the same H₂ partial pressure. In the presence of CO₂, the concentration of hydrogen in the liquid phase was significantly larger than in pure methanol at the same H₂ fugacity, with an enhancement factor as high as 2.1 (at CO₂/CH₃OH molar ratio = 0.3). The experimental data were modelled with the Peng–Robinson equation of state with van der Waals mixing rules and Boston–Mathias correction; binary interaction parameters were tuned with binary data from the literature, together with our ternary measurements. The EoS-based correlation allowed development maps and the equation for H₂ Henry’s constant as a function of temperature and CO₂/CH₃OH mole ratio, useful to predict the H₂ solubility in H₂O₂ direct synthesis kinetic studies, where hydrogen is introduced as the limiting reagent, due to safety reasons. This work identifies the lack of information on vapour–liquid equilibria hindering a correct description of the reaction mechanism and kinetics of the direct synthesis of hydrogen peroxide.

Acknowledgments

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References

Kinetics and Mechanism of H\textsubscript{2}O\textsubscript{2} Direct Synthesis over a Pd/C Catalyst in a Batch Reactor

Pierdomenico Biasi,*,†,‡ Nicola Gemo,*,† José Rafael Hernández Carucci,*,§ Kari Eränen,† Paolo Canu,‡ and Tapio O. Salmi†

†Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering Åbo Akademi, Biskopsgatan 8, 20500, Turku, Finland
‡Dipartimento di Ingegneria Industriale, University of Padova, via Marzolo 9, 35131 Padova, Italy
§BiCHEM Technology BV, High Tech Campus 48-2, 5656 AE, Eindhoven, The Netherlands

ABSTRACT: Kinetic experiments of the decomposition, hydrogenation, and direct synthesis of hydrogen peroxide were performed on a commercial Pd/C catalyst. Temperature effects and subsequent hydrogen addition were investigated without using promoters. The hydrogen amount in the liquid phase was measured online by using a Fugatron Instrument to investigate the effect of the gas on the direct synthesis. Decomposition and hydrogenation reactions were affected differently by the temperatures used during the experiments. The formation of hydrogen peroxide showed different behaviors with different hydrogen feeding policies. The hydrogen dissolved in the liquid phase measured experimentally was correlated with the hydrogen peroxide production. As the amount of dissolved hydrogen increases in the liquid phase the direct synthesis rate increases, while the reaction slows down as the hydrogen pressure is decreased. The selectivity is also affected by the H\textsubscript{2} recharges. Every time that hydrogen is recharged in the reactor (during the direct synthesis) the selectivity toward H\textsubscript{2}O\textsubscript{2} increases. Two different methods to recharge H\textsubscript{2} during the reaction were analyzed. The first method consists in feeding the hydrogen when it is totally consumed, the second one in refilling hydrogen in the reactor before its total consumption. The hydrogen solubility was found as an important parameter for the direct synthesis. An explanation on hydrogen peroxide formation was given taking into account the H\textsubscript{2}/Pd ratio.

1. INTRODUCTION

Hydrogen peroxide is an attractive oxidizing agent and its direct synthesis has been studied for many decades. Despite the efforts to find an innovative process to manufacture hydrogen peroxide from the elements, such technology has not been accomplished yet, due to problems related to flammability limits\textsuperscript{2−4} between hydrogen and oxygen and consecutive/parallel reactions.\textsuperscript{3,5,6} The direct synthesis consists principally in one reaction: hydrogen and oxygen are dissolved in a liquid phase and react on a solid catalyst. Although this process seems to be so simple, two consecutive reactions (i.e., decomposition and hydrogenation of hydrogen peroxide) take place over the same catalyst used for the direct synthesis.\textsuperscript{7,8} Moreover, a parallel reaction forming water from hydrogen and oxygen can take place over the catalyst surface. Despite numerous studies on the direct synthesis of H\textsubscript{2}O\textsubscript{2}, a general understanding of the mechanism, solubility problems, and how to avoid consecutive and parallel reactions without promoters has not been achieved.\textsuperscript{9,10} The studies on the direct synthesis have mainly been focused on the catalyst design and screening; however, such tests are almost impossible to compare due to different conditions used (i.e., solvent, halides, acids, inert gases, pressure, temperature, and many others).\textsuperscript{2,4,5,11−15} Numerous catalysts based on Pd and PdAu have been investigated\textsuperscript{12,15−18} and different ideas have been published on the reaction mechanism and the role of each promoter, including halides and acids.\textsuperscript{8,13,19−23} Still there is no agreement on the mechanism and conditions favoring the synthesis due to the complicated character of the system. This is the reason why a precise kinetic analysis is needed to understand the real mechanism of the direct synthesis. Kinetic studies are important to improve the operation conditions in continuous reactors, for which a complete understanding of the regimes and mechanism is needed to enhance the catalyst performance.\textsuperscript{21,24,25} Kinetic analyses have lately started to appear in the field of direct synthesis of hydrogen peroxide.\textsuperscript{21,24−26} However, these studies remain scarce, and more effort has to be focused on this area if the correct mechanism of the direct synthesis is to be understood.

To understand better the difficult to analyze results of different groups on hydrogen peroxide direct synthesis we report a table (Table 1) where a comparison of different works\textsuperscript{2,12,15,23,27−32} is done. In this table, catalysts, reactors, operative conditions, additives, and results are compared. Batch reactors are adopted for catalytic tests,\textsuperscript{12,13,29−31} for semibatch reactors to investigate the operation conditions and enhance the quantity of H\textsubscript{2}O\textsubscript{2} obtained,\textsuperscript{15,29,30,32} membrane reactors and microreactors\textsuperscript{2,27,28} to operate safely within flammability and,

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Table 1. Comparison between This Work and Different Reactor Systems

<table>
<thead>
<tr>
<th>ref</th>
<th>catalyst</th>
<th>reactor</th>
<th>liquid phase</th>
<th>gas composition</th>
<th>temperature (°C)</th>
<th>pressure bar</th>
<th>additives</th>
<th>productivity</th>
<th>selectivity (%)</th>
<th>H₂ conversion (%)</th>
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<td>5% Pd/C</td>
<td>batch</td>
<td>CH₃OH</td>
<td>H₂O:CO₂ = 9.6:22:68.2</td>
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<td>//</td>
<td>146 a</td>
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<td>100</td>
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<td></td>
<td>2% Pd/SiO₂</td>
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<td>H₂O</td>
<td>9.1% H₂ in air</td>
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<td>21</td>
<td>1% (w/w) H₂SO₄, 10 ppm NaBr</td>
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<td>50</td>
<td>25</td>
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<tr>
<td></td>
<td>5% Pd/C</td>
<td>microreactor</td>
<td>H₂O</td>
<td>D₂/O₂ 2/3</td>
<td>20</td>
<td>21</td>
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<td>D₂/O₂ 2/3</td>
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<td>H₂O₂ = 4.96</td>
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<td>amb</td>
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<td>10</td>
<td>0.01 M H₂SO₄</td>
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<td>100</td>
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<tr>
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<td>20</td>
<td>//</td>
<td>//</td>
<td>70</td>
<td>60</td>
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<td>30</td>
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<td>160 f</td>
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</table>

"For the productivity: a) mol H₂O₂/(h*molPd), b) gH₂O₂/(gPd*h), c) molH₂O₂/(gcat*h), d) mmolH₂O₂/(gcat*h), e) mgH₂O₂/(mgPd*h) (at 1 h reaction), f) molH₂O₂/(kgcat*h)."
therefore, try to enhance both productivity and selectivity. The temperature adopted varies from −10 to 40 °C. Temperatures between −10 and 5 °C are suitable to avoid the consecutive reactions (hydrogenation and decomposition), although in an industrial perspective they would probably imply production costs that are too high. Most of the works are actually carried out around 20 °C, a suitable temperature from an industrial point of view. Higher temperatures, reaching values of 40−50 °C, are used with the addition of additives to make the direct synthesis faster and to avoid consecutive reactions as well. Pressure is an important parameter to control the direct synthesis. A higher dissolution of the gases (i.e., reagents), obtained with pressure higher than ambient, enhance the production rate of the hydrogen peroxide formed due to the higher concentration of the reagents in the liquid phase. Pressure varies from 1 bar to 80 bar, more specific, 1 bar, 5−10 bar, 20−30 bar, and up to 80 bar. Another way to obtain a higher selectivity is to operate in acidic conditions: it is widely recognized that low pH stabilizes hydrogen peroxide, limiting the hydrogenation and decomposition reactions. H₂SO₄ and H₃PO₄ are normally used to keep stable the pH between 3 and 5. Carbon dioxide is also used as a possible substitute of the acidic compounds is the carbon dioxide: it dissolves in the liquid phase and in the presence of water forms carbonic acid, reducing the pH of the liquid phase where the H₂O₂ is formed. Moreover carbon dioxide in methanol enhances hydrogen solubility, which is desired as specified above. Carbon dioxide is also used in the direct synthesis to expand the solvent (i.e., methanol), but to make more feasible the process in an industrial scale nitrogen is preferred. Indeed, for cost reasons the use of air (i.e., a mixture of oxygen and nitrogen) would be much better than carbon dioxide. Halogens are also known to influence the selectivity to the peroxide, but their presence in the solution is undesired and thus their use is limited. Methanol was chosen as the reactant medium in many cases, in view of an integration with the propylene oxide synthesis, where the propylene reacts with the hydrogen peroxide in methanol. Water was chosen instead for safety reasons and for its low cost. It is interesting that with a catalyst containing acidic functions on the support the direct synthesis can achieve 98% of selectivity.

The analysis of the reaction conditions reported above show the difficult to compare results obtained by different research groups. For example it is hard to compare studies carried out at different temperatures, because a general understanding of the reaction mechanism has not yet been reached, and therefore the temperature dependence of the consecutive/parallel reactions (see Scheme 1) remains uncertain. The presence of 4 additives could also be responsible for the differences within the reported literature data, although an enhancement of selectivity could be observed in the presence of acids and bromine together. A comparison of the literature results can give important information on the studies and the trends on direct synthesis research, but works carried out by different research groups are in so different operative condition that is very difficult to analyze them together. For instance, reaction rate depends not only on temperature, pressure, and additive type/concentration but also on liquid composition, which in turn is influenced by solvent type, total composition of the gases, temperature, and pressure. Although almost all the reported works were carried out outside flammability limits (using CO₂ to dilute the gas mixture), the ranges of gas composition were rather broad.

In the present study, experimental kinetics for the hydrogenation, decomposition and direct synthesis in the absence of halides and acids were determined over a 5% Pd on carbon catalyst. The catalyst used for the experiments was chosen both for its commercial availability and for its stable performance. Special attention has been paid on the hydrogen measurements in the liquid phase. A Fugatron instrument was used to constantly monitor, during the reaction, the amount of hydrogen dissolved and consumed in the liquid phase. Online measurements of dissolved hydrogen can provide important information on the reaction mechanism and thanks to this, hypothesis can be proposed for further kinetic and reactor modeling. The work shows that by measuring the hydrogen amount in the liquid phase and relating it with the selectivity and the production rate of hydrogen peroxide, critical information about the direct synthesis reaction can be obtained. Moreover, by monitoring and controlling the hydrogen solubility (mass transfer) the selectivity and the hydrogen peroxide formation can be enhanced.

2. EXPERIMENTAL SECTION

Materials. 5% Pd/C catalyst (Degussa) was used as received. Methanol for HPLC was used as reaction medium (J.T. Baker 99.99%), H₂ and O₂ as reagents and CO₂ as inert were used for the direct synthesis (AGA high purity), H₂O₂ 30% w/w (Merck) for the decomposition and hydrogenation experiments, potassium iodide (Sigma-Aldrich), hydramul- composite 2 (Fluka), dry methanol for KFT (Fluka), acetic acid (Sigma-Aldrich), sodium thiosulfate penta-hydrate 99.5% (Sigma-Aldrich), starch (Sigma-Aldrich), potassium dichromate (Riedel de Haën), and ammonium molybdate tetrahydrate (Fluka) were used in the chemical analyses.

Reactor Setup for the Experiments. The apparatus used to perform the direct synthesis experiments is schematically described in Figure 1. The experiments were performed in a tailored batch reactor (1), i.e., a stainless steel autoclave reactor (Parr) with a volume of 600 mL and a maximum working pressure of 200 bar. The mixing was done by a Heidolph RZR 2021 rotor operating at 1000 rpm. The reactor was fitted with a K-type thermocouple (10) connected to a computer that allowed registering the temperature during the experiments. CO₂ and O₂ (2) were loaded into the reactor directly from gas cylinders. Hydrogen (3) was fed by a Brooks mass flow controller (5) to avoid overpressure in the reactor and to ensure a constant and reproducible flow. A 35 mL vessel (4) coupled with a pressure transducer and a heating jacket was placed before the mass flow controller (MFC) for hydrogen.
feeding. This was used to precisely calculate the amount of hydrogen fed into the reactor. A system of on/off valves (6) was arranged after the gas cylinders to ensure a separation between the cylinders and the reactor. A regulation valve was used to dose the gas from the cylinders (7). Each cylinder was also equipped with a one-way valve to avoid backmixing from the reactor environment to the pipelines. A safety valve (8) ensured to avoid overpressure inside the reactor. The pressure was constantly monitored through a pressure transducer (9) and registered by a computer. A mechanical pressure gauge was also used to monitor the pressure in the vessel.

Liquid samples were withdrawn through a six-way GC valve (11). An HP (high pressure) pump (12) ensured the liquid recirculation and dosed the solvent inside the reactor before and during the experiments. Methanol was degassed using an Agilent 1100 series degasser (13) and introduced into the system directly from a glass bottle (14). A precision balance (15) allowed the exact quantification of the methanol fed into the reactor. The liquid sampling probe was equipped with a 7 μm filter to prevent any block of the sampling valve and pump by small catalyst particles. A cooling/heating system was included (17) in order to control the temperature and to maintain it constant during the experiments.

Hydrogen dissolved in the liquid phase was measured with Fugatron HYD-100 (16). Its signal is proportional to the partial pressure of the dissolved gas. The instrument is provided with a probe to be immersed in the liquid, with a rigid membrane internally purged with a carrier gas and connected to an electrochemical detector: hydrogen permeates the membrane and reaches the detector with the carrier gas. Experiments were performed batchwise, and the hydrogen flowing to the instrument was evaluated by time integral of the instrument response: during the experiments less than 0.2% was subtracted from the reaction environment for analysis.

\( \text{H}_2\text{O}_2 \) Experiments and Analyses. Before the experimental campaign started, a four hour passivation treatment was performed on the reactor, using 30 wt.% nitric acid at 40 °C. The reactor was then tested for both decomposition and hydrogenation of hydrogen peroxide. A solution of 0.5 wt.% \( \text{H}_2\text{O}_2 \) in methanol was loaded inside the batch vessel. A \( \text{CO}_2 \)-\( \text{O}_2 \) mixture (75–25 vol.% respectively) was introduced until reaching a pressure of 10 bar. The percentage of \( \text{O}_2 \) was substituted with a mixture consisting of \( \text{N}_2 \) (85 vol%) and \( \text{H}_2 \) (15%) in the hydrogenation tests. The experiments were carried out at 10 °C varying the stirring rate (0, 500, and 1000 rpm). After four hours of operation, no \( \text{H}_2\text{O}_2 \) decomposition or hydrogenation was detected.

The protocol developed for the experiments was as follows: 0.15 g of a 5% Pd/C catalyst was loaded in the reactor. The reactor was then flushed with \( \text{CO}_2 \) four times to remove air and moisture present in the reactor. Carbon dioxide (18.4 bar) and oxygen (6 bar) were loaded into the reactor directly from the cylinders at 25 °C, followed by the injection of 400 mL of methanol by an HPLC pump. After the desired methanol amount was fed, the pump was then set to recirculate the liquid phase. The stirrer was turned on, and the desired temperature was fixed (−5 °C, 0 °C, 10 °C, and 40 °C). After both pressure and temperature were stable, the stirrer and pump were turned off. The vessel (4) before MFC (5) was loaded with pure hydrogen at a higher pressure than the reactor. Hydrogen was always the limiting reagent, fed from the vessel into the reactor through the mass flow controller. The moles of hydrogen introduced were calculated with the ideal gas law by the pressure difference in the loading vessel, knowing its temperature and volume. Immediately after the hydrogen loading had been completed, stirring was turned on again at 1000 rpm, along with the recirculation pump. A fast hydrogen introduction compared to the reaction rates was implemented (seconds vs minutes). Hence, the reaction was assumed to start when both stirrer and pump were turned on.

Hydrogenation and decomposition experiments were carried out following the same procedure, but using \( \text{N}_2 \) instead of \( \text{O}_2 \) and \( \text{H}_2 \) respectively.

The decomposition, hydrogenation, and direct synthesis experiments were performed at −5 °C, 0 °C, 10 °C, and 40 °C at 18 bar using methanol as a reaction medium. Temperatures between −5 and 40 °C were chosen because 1) the decomposition and hydrogenation of \( \text{H}_2\text{O}_2 \) are slower, while the synthesis is less affected by the temperature, 2) the solubility of \( \text{CO}_2 \) in methanol rises, thus increasing the hydrogen solubility in the mixture, 3) it is a low temperature industrially feasible without significant increase of costs, and 4) the catalyst and mixture stability increase.

Figure 1. Schematic of the experimental apparatus. 1 — Reactor. 2—3 Gas bottles. 4—5 — Hydrogen vessel and MFC, respectively. 6—7 Valve system for gas loading. 8 — Safety valve. 9—10 Pressure and temperature measurements, respectively. 11 — Liquid sampling valve. 12 — HP pump. 13 — Degasser. 14—15 — Liquid solvent supply and balance, respectively. 16 — Fugatron HYD-100. 17 — Cooling/heating system.
During each single experiment, the liquid phase was sampled from the batch reactor and analyzed as follows: the water and H2O2 contents were determined by volumetric Karl Fischer and iodometric titration, respectively. The concentrations are given on weight basis. The selectivity is defined as 100[H2O2]/([H2O2] + [H2O2]prod); it is equal to the moles of H2O2 produced, divided by the moles of hydrogen consumed.

**Catalyst and Catalyst Characterization Methods.** The catalyst used was a 5% Pd/C commercial catalyst from Degussa (Evonik). The surface area and the pore size distribution were obtained from N2 adsorption/desorption isotherms at −196 °C (using a Carlo Erba Sorptomatic 1900). Samples (300 mg) were outgassed at 300 °C for 2 h under vacuum. The surface area was calculated from the N2 adsorption isotherm by the BET equation, and pore size distribution was determined by the BJH method. Total pore volume was taken at P/P0 = 0.99.

CO chemisorption measurements were performed at 25 °C by a Micromeritics pulse flow system. Prior to the measurements, samples were subjected to a pretreatment involving exposure to hydrogen flow for 1 h at 25 °C, followed by He purge for 2 h at the same temperature of reduction.

XPS measurements were performed in a Perkin-Elmer 5400 ESCA spectrometer with monochromatized Al Kα radiation (photon energy 1486.6 eV) and a pass energy value of 35 eV. Samples were transferred to the XPS system in an ethanol solvent to protect them from oxidation in ambient air. A low energy electron gun (flood gun) was used to stabilize the charging that arises from loss of photoelectrons during X-ray bombardment. To calibrate the binding energy (BE) axis accurately, carbon 1s line at 284.6 eV was used as BE reference. In the line fitting procedure, the intensity ratios of Pd 3d5/2:2:3d3/2 lines were kept fixed at their theoretical values (3:2) and a Doniach-Šunjic line shape was used. The sensitivity factors used in determining the atomic concentration ratios for Pd 3d, C 1s, Cl 2p, and O 1s were 4.642, 0.296, 0.770, 0.711, respectively. FitXPS software by D. Adams, University of Aarhus, was used in the line fitting procedure. Pd 3d lines were found on a nonlinear background, and a parabolic background was used in the line fitting.

3. RESULTS AND DISCUSSION

**Catalyst Characterization Results.** The BET results revealed that the surface area was 792.8 m²/g and the specific pore volume was 0.887 cm³/g. The chemisorptions measurements revealed that the average particle size of Pd was 2.62 nm with a dispersion of 42.8%.

Regarding the XPS results, it is generally observed that Pd peaks for the Pd(3d5/2) and Pd(3d3/2) spin–orbit doublet reported for bulk Pd occur at about 334.9 and 340.1 eV, respectively. PdO peaks occur at about 336.5 and 341 eV. In our samples, however, the binding energies of the Pd(3d) peaks for Pd nanoparticles on C are about 1 eV higher and were located at 337.6 and 342.3 eV, respectively (Table 1) . The larger binding energies of the supported Pd have been reported for bulk Pd have been reported at about 334.9 and 340.1 eV, respectively. PdO peaks occur at about 336.5 and 341 eV. In our samples, however, the binding energies of the Pd(3d) peaks for Pd nanoparticles on C are about 1 eV higher and were located at 337.6 and 342.3 eV, respectively (Table 1). The larger binding energies of the supported Pd have been reported previously. Our results, in fact, are very close to those reported by Campbell et al., who obtained the XPS of small Pd nanoparticles (2–10 nm) on an α-Al2O3 (0001) single crystal under different conditions. Also Liu et al. reported a shift of 1 eV for palladium nanoparticles on silica. They also found that the binding energies of the Pd(3d) peaks increased about 1 eV compared to bulk palladium and suggested that the shift to higher binding energies for the Pd nanoparticles compared to the bulk Pd metal is mainly a result of final-state screening by conduction electrons. The catalyst presents an oxidized surface as explained. No changes occurred on the catalyst after a 4 h reaction (Table 2).

| Table 2. XPS Results for the Catalyst Pd/C |
| catalyst | C ls (eV) | Pd 3d5/2 (eV) | 0 ls (eV) | Cl2p (eV) |
| fresh | 284.60 | 337.6 | 531.2 (34%) | 198.6 |
| used | 284.60 | 337.6 | 531.5 (45%) | 198.6 |

**H2O2 Hydrogenation and Decomposition.** Palladium based catalysts are well-known for being suitable for the direct synthesis of hydrogen peroxide. Unfortunately, they enhance H2O2 decomposition and hydrogenation too (reactions 3 and 4 of Scheme 1). To quantify the degree of H2O2 loss by decomposition and hydrogenation, kinetic experiments were carried out with the same catalyst and under the same operation conditions as the direct synthesis. The results in the batch reactor at different temperatures are shown in Figures 2 and 3, as a percentage of the H2O2 loss. Qualitatively, both degradation paths (with/without H2) were similarly affected by the temperature. At low temperatures, the decomposition was almost suppressed due to the low activity of palladium, and less degradation of H2O2 occurred. Figure 2 shows the kinetics of the hydrogen peroxide decomposition. At 40 °C, a fast H2O2 decomposition was observed, with a 50% loss after 1 h operation, and almost a total decomposition after 3 h of reaction. The decomposition experiments carried out at −5, 0, and 10 °C showed a similar trend (Figure 2). The H2O2 decomposition was around 10% after 1 h and between 12 and 18% after 4 h. Stirring speeds up to 1000 rpm did not decompose hydrogen peroxide in the solution as reported above. Figure 3 shows the hydrogenation kinetics at different temperatures. Even if the presence of H2 enhanced the hydrogen peroxide degradation, the time scale of the experiments was much smaller compared to the decomposition experiments. Surprisingly, the temperature did not seem to
hydrogen peroxide as limited reagent, went really fast. At 10 and 40 °C H2 lim (i.e., hydrogen as limited reagent), the hydrogenation rates seemed to be rather similar. After 15 min, the H2O2 degradation was almost 90% of the total hydrogen peroxide introduced. On the other hand, at −5 °C after 15 min, the hydrogen peroxide that remained in the solution was around 40% of the total amount introduced. The hydrogenation and decomposition reactions affected differently the direct synthesis. The decomposition at low temperatures did not largely affect the direct synthesis, whereas hydrogenation did. It seemed that the palladium catalyst was activated very fast by hydrogen at low temperatures, while during the decomposition experiments the catalyst was activated at high temperatures only. This implies that the hydrogenation was not affected in great extent by the temperature but by the hydrogen feeding into the reactor. The decomposition reaction was most probably controlled by kinetics while the hydrogenation was first kinetically controlled and when the hydrogen concentration was decreasing in the liquid phase, it entered into the mass transfer limited regime.

Hydrogenation at 40 °C H2 lim was performed by using H2 as a limiting reagent. The data collected by the Fugatron instrument gave important information about kinetic and mass transfer regimes during the reaction. After three minutes of reaction the hydrogen dissolved in the liquid phase reached a maximum (peak). After such peak the H2O2 degradation rate starts to decrease. Eight minutes after the peak, hydrogen was completely consumed, and the hydrogenation of H2O2 becomes slower (Figure 3 and Figure A Supporting Information). In the absence of dissolved hydrogen, the only possible reaction was the H2O2 decomposition. In the first three minutes the hydrogenation reaction appears to be very fast; H2O2 decreased rapidly in the solution and the H2 amount in the solution was quite high. This situation is a classical kinetically controlled regime. Between four and ten minutes, mass transfer begins to be of importance as hydrogen started to be the limiting reagent in the liquid phase. Hydrogen disappeared after ten minutes of reaction where mass transfer limitations become evident. After this time, H2O2 decreased slowly compared to the first minutes, because no more available hydrogen was present in the liquid phase and only the decomposition reaction took place. In the experiment at 0 °C, H2O2 was the limiting reagent. The slope of hydrogenation in this case was linear, and it was not characterized by different regimes (Figure 3). A comparison of the collected information gave the opportunity to define the mass transfer and kinetic regimes.

**H2O2 Synthesis: Effect of Temperature.** Kinetic experiments of the hydrogen peroxide direct synthesis were carried out by varying the temperature. The H2:O2 ratio was set to 1:10, i.e., hydrogen was the limiting reagent. In Figure 4 the production of hydrogen peroxide is reported at 18 bar and temperatures between −5 and 40 °C. Water production measurements for the same experiments are reported in Figure 5. Overall, the water production during the experiments increased constantly and, moreover, prevailed over the hydrogen peroxide formation, reaching higher concentrations than the peroxide. The H2O2 formation increased rapidly in the very beginning, reaching a maximum and gradually decreasing afterward. A complete consumption of H2 corresponded to the maximum concentration of H2O2: after H2 was no longer present in the liquid phase, the direct synthesis as well as the hydrogenation were suppressed. Thus, only the decomposition of H2O2 took place, resulting in a drop of the peroxide formation and consequently in a slower water production rate. At 0 °C, the maximum H2O2 concentration was 0.02 wt.% after 60 min of reaction, and the maximum concentration of water reached 0.06 wt.% after 300 min. At 10 °C, the maximum H2O2 concentration was 0.03% wt. after 40 min and 0.07 wt % for water after 300 min. At −5 °C, the maximum hydrogen peroxide production was about 0.03 wt % after 70 min, and the maximum water production reached 0.05 wt % after 300 min. At 40 °C, the water formation was highly favored, as the H2O2 formation increased constantly and the H2O2 concentration only reached 0.15 wt %, while H2O raised up to 0.13 wt % (Figures 4 and 5). The peak in H2O2 concentration was shifted with temperature: at 40 °C it appeared after 5 min of reaction, while at 10 °C the maximum of H2O2 production occurred after 40 min. When working at −5 °C, such peak
H2O2 formation (Figures 4-6). Moreover, the maximum in the system was found (i.e., direct synthesis, hydrogenation and combination between the three reactions involved in the reaction) compared to faster at 10 °C, slower at −5 °C. This could be explained with the following considerations: 1) hydrogenation and decomposition were slower at −5 °C compared to 10 °C; 2) the direct synthesis was faster at 10 °C due to the higher solubility of hydrogen compared to −5 °C. For such reasons a convenient combination between the three reactions involved in the system was found (i.e., direct synthesis, hydrogenation and decomposition) resulting in a similar overall reaction rate for H2O2 formation (Figures 4-6). Moreover, the maximum in the hydrogen peroxide production at −5 °C was reached 15 min later compared to the experiment conducted at 10 °C, which is in agreement with our considerations. In summary, the direct H2O2 direct synthesis reaction as well as decomposition and hydrogenation are faster at 10 °C compared to a temperature of −5 °C. A combination of the three reactions produces similar trends and similar values for the selectivity toward hydrogen peroxide.

The hydrogen peroxide selectivity data at different temperatures is presented in Figure 6. At temperatures equal or lower than 10 °C, the selectivity toward H2O2 was high at the beginning of the reaction and further decreased sharply during the first hour of reaction. Thereafter, only the decomposition reaction took place, and the final selectivity was found to be between 10 and 20%. Similar trends were observed at 40 °C, but the absolute values were much lower and the decrease on selectivity seemed somewhat faster. Taking into account the results of both the H2O2 production and selectivity it is reasonable to state that 1) the reaction of the direct synthesis of hydrogen peroxide is very fast at the beginning with a high selectivity; 2) hydrogenation and decomposition reactions increase as hydrogen peroxide is produced; 3) H2O2 production decreases and water formation is favored as hydrogen concentration in the liquid phase decreases; and 4) direct synthesis is highly unfavorable at higher temperatures, as the side reactions prevail over the H2O2 production.

A maximum selectivity of 80% at 0 °C was reached, compared to a maximum of 60% at −5 °C and 40% at 10 °C. That implies that without stabilizers in the media, both temperature and reaction time played an important role on the selectivity. Furthermore, a short contact time is necessary to achieve such extraordinarily high selectivity, even if this highest selectivity corresponded to low productivity rates.

H2O2 Synthesis: Hydrogen Feeding. The Fugatron instrument allowed us to measure the hydrogen dissolved in the liquid phase (Figure 7). The experiments were conducted at 10 and 10 °C. Gas and liquid feeding was done in the same way as in the former experiments. Three different experiments were conducted: 1) synthesis of hydrogen peroxide with one hydrogen filling at the beginning of the reaction; 2) synthesis of hydrogen peroxide with four hydrogen fillings along the reaction, after the totality of the hydrogen dissolved in the liquid phase was completely consumed; and 3) synthesis of hydrogen peroxide with four hydrogen fillings, as soon as the hydrogen concentration in the liquid phase started to decrease. Figure 7 shows a typical experiment of the direct synthesis, in which information about the amount of hydrogen dissolved in the liquid phase plus the hydrogen peroxide and water production are displayed. Hydrogen dissolved in the liquid phase was consumed rapidly as the narrow peak in Figure 7 shows. Additionally, this experiment showed how the hydrogen peroxide concentration started to decrease after hydrogen was no longer present in the liquid phase. The amount of hydrogen dissolved in the liquid reached a peak during the first minutes of the reaction, decreasing slowly afterward. The peak of H2 in the liquid phase corresponded with the maximum in selectivity (i.e., max H2O2/H2O + H2O ratio). After such peak, hydrogen decreased slowly. The increase of hydrogen in the liquid was faster then its decrease. As soon as hydrogen decreased in the liquid phase, the selectivity toward hydrogen peroxide was also reduced, and the formation of water prevailed. Additionally, as the hydrogen concentration in the liquid started to increase, the amount of water in the system increased drastically. After hydrogen was completely consumed from the liquid phase the concentration of hydrogen peroxide decreased slowly. These results were in line with our decomposition experiments presented in this work (Figure 2). A relationship between the
amount of hydrogen in the liquid phase and the quantity of hydrogen peroxide produced could be found. It appears that there is an optimum amount of hydrogen in the liquid phase that enhances the selectivity of the direct synthesis reaction. Plausible hypotheses for this reaction are as follows: 1) before hydrogen was introduced oxygen covers catalyst surface;\textsuperscript{13,15,17} 2) as soon as hydrogen was dissolved in the liquid phase, it reacted with oxygen on the catalyst surface;\textsuperscript{15,17} 3) when hydrogen started to decrease some changes in catalyst surface happened;\textsuperscript{13,15,17} and 4) probably the $\text{H}_2/\text{Pd}$ ratio was changing and hydrogenation was favored compared to the direct synthesis reaction. In order to confirm these hypotheses, experiments refilling hydrogen were needed as well as measurements of hydrogen solubility.

The subsequent experiment was performed in order to find a relationship between the selectivity, the production rate, and the amount of hydrogen fed into the reactor (Figures 8 and 9).

![Figure 8](image_url) Production of $\text{H}_2\text{O}_2$ at 10 °C and 18 bar with different hydrogen feeding policies: 1) Hydrogen amount fed after its complete depletion in the liquid phase (solid line) and 2) hydrogen subsequently fed as it decreases in the liquid phase (dashed line). $\text{H}_2\text{O}_2$ production under feeding policy 1 (□) and under feeding policy 2 (▲).

![Figure 9](image_url) Selectivity of $\text{H}_2\text{O}_2$ at 10 °C and 18 bar with different hydrogen feeding policies: 1) Hydrogen amount fed after its complete depletion in the liquid phase (solid line) and 2) hydrogen subsequently fed as it decreases in the liquid phase (dashed line). $\text{H}_2\text{O}_2$ selectivity under feeding policy 1 (□) and under feeding policy 2 (▲).

The same amount of hydrogen was fed into the reactor straight after the gas dissolved in the liquid was completely consumed. Both the hydrogen peroxide and water concentrations increased during the reaction. The selectivity had different behavior though: every time that fresh hydrogen was fed into the reactor, the selectivity toward hydrogen peroxide increased; when hydrogen started to decrease, such selectivity decreased as well. The results prove that the amount of hydrogen plays an important role in the direct synthesis. A maximum selectivity toward hydrogen peroxide was found to be close to 30%. However, as hydrogen was consumed, this selectivity dropped to 20%. It was interesting to notice that when hydrogen was refilled into the reactor, the selectivity level of 27% was regained. This same result was reproduced with consecutive hydrogen loadings. Moreover, the hydrogen peroxide production increased with this hydrogen feeding policy (Figure 8). As hydrogen was already depleted from the liquid phase, the concentration of hydrogen peroxide remained stable, and, more importantly, no decomposition was detected as seen during former decomposition experiments (Figures 2 and 3). This experiment confirms all four hypotheses made above.

Regarding the importance of the $\text{H}_2/\text{Pd}$ ratio, experiments were conducted avoiding the complete depletion of hydrogen in the liquid phase. In that sense, equal amounts of hydrogen were reloaded into the reactor after certain time after the $\text{H}_2$ peak was recorded with the Fugatron. Such subsequent hydrogen feeding policy demonstrated how a higher selectivity could be achieved compared to the former experiments when the hydrogen was refilled before its complete consumption. The selectivity toward hydrogen peroxide in this case reached a peak around 33%, compared to only 27% in the previous case, i.e., when hydrogen was completely consumed (Figure 9). Moreover, the hydrogen peroxide concentration increased constantly until soluble hydrogen was consumed. After this point, the concentration of $\text{H}_2\text{O}_2$ remained quite stable. It is interesting to notice that the hydrogen peroxide production was pretty much equal to the former experiments, but the selectivity reached a higher value (Figures 8 and 9). Hydrogen peroxide formed faster in such experiments due to the amount of hydrogen present in the liquid phase.

Comparing the two experiments performed with the hydrogen refilling, an obvious observation concerns the selectivity, which remained stable around a value of 20% after hydrogen depletion. Moreover, in both cases (Figure 8 and 9), the highest selectivity was reached during the first minutes of the reaction.

These results allow to arrive to the following considerations: 1) hydrogen dissolved in the liquid phase is consumed rapidly (during the first 30 min of reaction time); 2) when hydrogen was not present in the liquid phase, the hydrogen peroxide formed decreased slowly and so did the selectivity; 3) the hydrogen refilled in the reactor enhanced the selectivity; 4) hydrogen refilling before its complete depletion gave better results compared to the case when hydrogen was refilled after its complete consumption; and finally 5) hydrogen peroxide production could be increased by regulating the amount of hydrogen dissolved in the reaction medium.

**Remarks on Conversion and Selectivity.** Another general observation regards the correlation between selectivity and hydrogen conversion: low hydrogen conversions corresponded a high selectivity,\textsuperscript{12,27,28,31,32} while a high conversion led to low selectivity.\textsuperscript{15,25,29,30} In this work following the kinetics of hydrogen peroxide formation we saw that at the beginning of the reaction with low $\text{H}_2$ conversion selectivity was high, while when hydrogen was consumed (more than 40%) selectivity started to drop. With the refilling method was
possible to see that there was the same trend of conversion vs selectivity. H₂O₂ formation and selectivity started to rise again when hydrogen was fed in the reactor, and when a specific amount of hydrogen was consumed (i.e., 40%) H₂O₂ formation and selectivity dropped again. It seems that keeping the hydrogen conversion below 100% (i.e., 60%) inside the reactor gives an enhancement on the selectivity. Most probably there is an effect of the hydrogen on the metal nanocluster surface that allows to reduce unwanted reactions like hydrogenation and decomposition. We want to underline that thanks to the measurements of the hydrogen dissolved in the liquid phase we were able to compare hydrogen solubilized in the liquid phase with the selectivity obtained finding that hydrogen consumption and selectivity are strictly interlinked. This correlation between conversion and selectivity can also be found in some of the works reported in Table 1.

In general, the final selectivity obtained in this work was lower than most of the studies reported in Table 1, but we remark that our aim was to study the H₂O₂ direct synthesis, decomposition, and hydrogenation only with respect to the temperature, the time, and in the absence of promoters and stabilizers. Usually in the literature most of the efforts are focused on the development of the catalyst, and we were focusing on the reactor development trying to understand how it is possible to enhance hydrogen peroxide selectivity and productivity changing the operation conditions.

4. CONCLUSIONS

Hydrogen peroxide direct synthesis was studied deeply taking into account decomposition and hydrogenation reactions. Moreover a relationship between selectivity and the hydrogen dissolved in the liquid phase was found.

Temperatures between −5 and 10 °C did not decompose hydrogen peroxide in large amounts. Hydrogenation of H₂O₂ was fast, and its kinetics were similar in the range of 0 to 40 °C while at −5 °C showed to be slower than in the former cases. When trying the direct synthesis of hydrogen peroxide at high temperatures (i.e., 40 °C) without promoters, both decomposition and hydrogenation seemed too fast to allow a high production of hydrogen peroxide. Regarding hydrogenation and decomposition, experiments conducted at −5 and 10 °C showed similar production of H₂O₂. At −5 °C, hydrogenation was suppressed, while at 10 °C, the production of hydrogen peroxide was overcome by its hydrogenation. Experiments conducted at 0 °C showed that such temperature was not the best for hydrogen peroxide direct synthesis compared to −5 and 10 °C. The Fugatron instrument allowed monitoring hydrogen dissolved in the liquid phase during the experiments. Different policies of H₂ feeding gave the possibility to enhance the hydrogen peroxide production rate and selectivity. An enhanced selectivity was achieved by refilling hydrogen before its complete consumption. Experiments gave the further direction of investigation on the role of hydrogen dissolved in the liquid phase, in the direct synthesis reaction. Kinetic and reactor modeling will be performed with the obtained data in order to tune and engineer the reaction. Further kinetic analyses are needed to fully understand the reaction mechanism.

ASSOCIATED CONTENT

Supporting Information

Hydrogen in liquid phase vs hydrogenation of hydrogen peroxide is provided at 40 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bpierdem@abo.fi.

Notes

The authors declare no competing financial interest.

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Mass transfer and kinetics of H$_2$O$_2$ direct synthesis in a batch slurry reactor

Nicola Gemo$^a$, Pierdomenico Biasi$^b$, Paolo Canu$^{a,*}$, Tapio O. Salmi$^b$

$^a$Dipartimento di Ingegneria Industriale, University of Padova, via Marzolo 9, 35131 Padova, Italy
$^b$Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi, Biskopsgatan 8, 20500 Turku, Finland

HIGHLIGHTS

- Modeling of H$_2$O$_2$ direct synthesis, decomposition and hydrogenation experiments.
- Gas to liquid and liquid to solid mass transfer limitation analysis.
- Estimation of activation energies and pre-exponential factors.

ABSTRACT

A model of a gas bubbling, batch slurry reactor for H$_2$O$_2$ direct synthesis is presented. Experimental measurements were carried out in the absence of halides and acids at temperatures between 258 and 297 K (pressures 14–20 bar, depending on temperature) with H$_2$ and O$_2$ diluted in CO$_2$, outside flammability limits (gas phase composition of CO$_2$, O$_2$ and H$_2$ was 77%, 21% and 2%, respectively). Kinetic experiments performed on a commercial 5% Pd/C catalyst (0.15 g in 400 ml methanolic solution) have been used to identify the intrinsic kinetics and assess the influence of mass transfer. The simplest rate equations compatible with the acknowledged reaction network has been included in a reactor model, which accounts for mass transfer resistances between gas and liquid and bulk of the liquid-catalyst surface. The corresponding Arrhenius parameters were estimated from direct synthesis experiments for all the reactions. Comparable temperature dependence was observed for H$_2$O production, hydrogenation and decomposition (activation energies close to 45 kJ mol$^{-1}$), while H$_2$O$_2$ synthesis has a much lower activation energy (close to 24 kJ mol$^{-1}$), suggesting that a higher selectivity is achievable at low temperature. Decomposition had a very limited influence on the overall peroxide production rate, being quite slow (its rate is approx. 40% the direct synthesis rate at H$_2$ full conversion). Hydrogenation was the most rapid side reaction, depressing H$_2$O$_2$ production as H$_2$ conversion increased. Independent investigation on the H$_2$O$_2$ hydrogenation in the absence of O$_2$ highlighted significant difference in the kinetics, apparently due to a different oxidation state of the catalyst.

A sensitivity analysis on the mass transfer coefficients to allow for uncertainties in the correlations proved that no resistances in the liquid occur, while gas–liquid H$_2$ transfer rate may be limiting, although unlikely, requiring that literature coefficients overestimates the real transfer rate by an order of magnitude.

1. Introduction

Hydrogen peroxide is the simplest peroxide and is commercially available in aqueous solution over a wide concentration range. The main uses of hydrogen peroxide are in the preparation

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of other peroxides, as an oxidizing agent and to substitute chlorine in the waste treatment, textile industries and pulp and paper bleaching. The major manufacturing process (anthraquinone autoxidation) involves a catalytic hydrogenation, followed by an oxidation reaction to yield H$_2$O$_2$. Anthraquinone (Q) is used as a H$_2$ carrier.

Nowadays the interest on hydrogen peroxide direct synthesis (DS) is growing due to its constantly increasing demand. Moreover the possibility to couple the DS with already existent processes (i.e. synthesis of caprolactame and propene oxide) would allow reducing operations and transportations costs as well as the hazard of handling H$_2$O$_2$ solution.

The direct synthesis of hydrogen peroxide is a thermodynamically favored process, but selectivity and safety are still an obstacle to the industrial feasibility. The major limits of the DS process are selectivity (the same catalyst active for the DS is also promoting the competitive reactions, i.e. decomposition and hydrogenation) and safety, because of the wide flammability limits of hydrogen. Lately the DS has attracted interests of both the Academia and Industries, trying to develop new catalyst concepts, reactor design and operation conditions [1,2]. Unfortunately, due to the interconnected reaction mechanism shown in Scheme 1 and the difficulty of analyzing the real mechanism of each reaction at the catalytic surface, the kinetic is still mostly empirical. In Scheme 1 all the reactions are catalyzed by Pd, and the contribution of each one differs with the reaction conditions (i.e. temperature, pressure, promoters, stabilizers, reactant medium, etc.). The four reactions involved are the direct formation of H$_2$O$_2$ (ds), the formation of H$_2$O (wf) and two consecutive reactions

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Greek letters

| \( \alpha \) | Hurter number, \( \alpha = 1 - \frac{R_{cat}}{r_c} \) |
| \( \beta \) | dimensionless catalyst porosity |
| \( \phi \) | gas hold-up |
| \( \phi \) | Thiele modulus |
| \( \kappa \) | equilibrium rate constant of reaction \( i \) (units depend on reaction) |
| \( \kappa'_i \) | apparent equilibrium rate constant of reaction \( i \) (units depend on reaction) |
| \( \xi \) | energy dissipation rate per unit mass (W kg$^{-1}$) |
| \( \rho \) | density (kg m$^{-3}$) |
| \( \rho_{cat} \) | catalyst density (mol_Pd cm$^{-3}$) |
| \( \sigma \) | interfacial tension (N m$^{-1}$) |

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Scheme 1. Reactions involved in the direct synthesis of H$_2$O$_2$. 

![Scheme 1. Reactions involved in the direct synthesis of H$_2$O$_2$.](image-url)
The experiments were performed batchwise in a 600 ml unbaflled reactor with standard geometry (Buchi) and equipped with a self-sucking 6 blade impeller. Experimental apparatus and procedures are described elsewhere [18]. Shortly, 0.15 g of a 5% Pd/C catalyst were loaded in the reactor, that was then flushed four times with CO₂ to remove air and moisture. Carbon dioxide (18.4 bar) and oxygen (6 bar) were introduced in the vessel (298 K), followed by the injection of 400 ml of methanol. After pressure and temperature were stable at the desired values, hydrogen was fed as the limiting reagent. The reaction was assumed to start immediately after hydrogen loading. The gas mixture was carefully kept outside flammability limits (composition was 77%, 21% and 2% of CO₂, O₂ and H₂ respectively). A stirring rate of 1000 rpm was conservatively adopted to ensure a good mixing of the liquid phase, as verified in dedicated experiments. Hydrogenation and decomposition experiments were carried out following the same procedure, with N₂ replacing O₂ or H₂, respectively. The liquid phase was sampled at different times and water and H₂O₂ contents were determined by volumetric Karl Fischer and iodometric titration, respectively. The amount of liquid subtracted for each analysis was 0.7 ml, so that the total uptake never exceeded 8% of the initial liquid volume. Errors on H₂O₂ and H₂O measurements were estimated analyzing a methanol solution with a known water and hydrogen peroxide content (0.8% and 1.6% respectively), sampled from the reactor at experimental conditions. Estimated error on H₂O₂ was 0.8%, whereas on H₂O it was 2%.

3. Model

3.1. Chemical kinetics

Several surface mechanisms on palladium can give the overall process described in Scheme 1. Voloshin et al. [16] screened some mechanisms to describe kinetic data obtained from microstructured reactors and concluded that a Langmuir–Hinshelwood-type mechanism, with the surface reaction steps as rate determining ones, gave the best agreement with experimental data. Dissociative adsorption of the reactant species was also proposed by Deguchi et al. [10]. Some mechanistic studies have given information about the reaction mechanism. For instance, Dissanayake and Lunsford [19] proposed that the O–O bond does not dissociate during the H₂O₂ synthesis process and Sivadarayana et al. [20] confirm the species HO⁻ on a gold catalyst surface. However, it is clear that water formation requires the rupture of the O–O bond on the catalyst surface.

All the reactions involved in the series–parallel network (Scheme 1) are exothermic and thermodynamically favored [21] and Pd is known to promote all of them. Some basic assumptions are used here to describe the rate equations for the overall reactions in as simple as possible manner. The reaction mechanism proposed is summarized in Table 1.

The mechanism is based on the hypotheses that hydrogen and oxygen adsorb simultaneously and dissociatively on the metal catalyst surface, and surface hydroxyls are formed leading to the formation of hydrogen peroxide and water. The hydrogen peroxide decomposition and hydrogenation are described with the simplest possible mechanisms. Homogeneous reactions in the liquid phase are neglected, as experimentally demonstrated [18]. The adsorption and desorption steps are assumed to be rapid enough to reach quasi-equilibria, while the surface reaction steps IV, V, VI and VII are assumed to limit the rates.

For hydrogen and oxygen, the quasi-equilibrium hypothesis yields:
of the rate-limiting steps can now be written as:

\[
R = k_7 \left( \frac{C_{H_2}^2 - C_{H_2O}^2}{C_{H_2O}^2} \right) / k_7
\]

The concentrations of the surface species are expressed with the quasi-equilibria and the concentration of vacant sites. After inserting all these expressions, the rate equations can be rearranged. The constants can be merged, so that just a forward rate constant and an equilibrium constant is used for each step (the merged constants \(k\) and \(k'\) are products of surface rate and adsorption equilibrium constants):

\[
R_4 = k_4 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) D^{-2}
\]

\[
R_5 = k_5 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) / k_5
\]

\[
R_6 = k_6 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) D^{-2}
\]

\[
R_7 = k_7 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) / k_7
\]

Assuming that the steps are practically irreversible under the actual conditions and neglecting the adsorption contribution in the denominator because of low concentrations \((D = 1)\), gives the simplest rate equations:

\[
R_4 = R_{\text{H}_2} = k_{\text{H}_2} C_{H_2O}^2, \quad k_{\text{H}_2} = k_4
\]

\[
R_5 = R_{\text{H}_2} = k_{\text{H}_2} C_{H_2O}^2, \quad k_{\text{H}_2} = k_5
\]

\[
R_6 = R_d = k_d C_{H_2O}, \quad k_d = k_6
\]

\[
R_7 = R_n = k_n C_{H_2O}^2, \quad k_n = k_7
\]

with temperature dependent, Arrhenius-type kinetic constants:

\[
k_i = A_i e^{-E_i/RT}
\]

Pre-exponential factor \(A_i\) and activation energy \(E_i\) of each reaction are determined from our experimental data, as described below. The generation rates are formulated with the aid of the rate-limiting steps IV–VII. The following expressions are obtained:

\[
r_{H_2O_2} = R_{\text{H}_2} - R_d - R_n
\]

\[
r_{H_2O} = R_{\text{H}_2} + 2R_d
\]

\[
r_{H_2} = -R_{\text{H}_2} - R_{\text{H}_2O} + R_n
\]

\[
r_{O_2} = -R_{\text{H}_2} - 0.5R_d + 0.5R_n
\]

3.2. Mass transfer

Mass transfer resistances are always involved in a multiphase reacting environment, hence, their role should be taken into account in a kinetic study. Here we consider two mass transfer resistances, dissolution of gases into the liquid phase and reactant transport in the liquid to the catalyst surface. For sake of clarity, a schematic representation is given in Fig. 1.

The gas phase is assumed well mixed so that the mass transfer between gas and liquid is controlled by the liquid side resistance (Fig. 1). At the gas–liquid interface, equilibrium holds. Vapor pressure of \(H_2O\) and \(H_2O_2\) are neglected \((258 < T(K) < 297)\) so that gradients occur only near the solid interface and species cumulate in the liquid phase.

Species fluxes are described in terms of mass transfer coefficients times concentration differences. Coefficients are calculated according to best available correlation for the reactor used, considering

\[
R_4 = k_4 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) / k_4
\]

\[
R_5 = k_5 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) / k_5
\]

\[
R_6 = k_6 \left( C_{H_2O}^2 - C_{H_2O}^2 \right) / k_6
\]
that gas is bubbling in the liquid and catalyst is in the form of fine powder, suspended in the liquid.

3.3. Gas–liquid mass transfer coefficients

The gas–liquid mass transfer coefficient depends on several factors (fluids considered, apparatus, agitation rate, temperature) and a suitable correlation for their estimation should be carefully chosen. The reactor used for the kinetics experiments was equipped with a self-suction turbine. Stirring causes a negative pressure at the impeller that induces suction of gas from the atmosphere above the liquid, through the hollow shaft, continuously yielding fine bubbles in the liquid phase. Therefore, the liquid mass transfer coefficients for O₂ and H₂ are estimated with a correlation for sparged stirred tank reactors [22]:

\[
K_i^L \cdot d^i = \frac{2}{\sqrt{\pi}} \sqrt{\frac{3}{8}} \frac{1}{P^i} a^i \tag{27}
\]

Values of the diffusion coefficients \( (\kappa_i) \) are calculated with the Wilke–Chang equation [23] assuming pure methanol, because it largely dominates the liquid composition. Assuming that energy at gas–liquid interface is consumed at the gas bubbles surface, the energy dissipation rate per unit mass \( (\varepsilon) \) can be evaluated with the correlation proposed by Garcia-Ochoa et al. [24]:

\[
\varepsilon = \frac{p}{\rho^i \left(\pi/4\right)N_p} \tag{28}
\]

where the power input \( (P) \) is calculated as:

\[
P = 0.783 \left( \frac{p^i N_p d^i}{Q^i} \right)^{0.459} \tag{29}
\]

We used the gas flow rate recirculated through the hollow shaft for \( Q \). The value of \( Q \) was 5 cm³ s⁻¹, estimated with dedicated experiments. \( P_0 \) is the power consumption in an un-aerated system. Its values depends on the power number, \( N_p \), that can be considered constant assuming turbulent regime [24]. According to the definition of the dimensionless power number, \( P_0 \) is given by:

\[
N_p = \frac{P_0}{\rho^i N_p d^i} \tag{30}
\]

The power number depends on the impeller type and geometry and is estimated using the correlation proposed by Rutherford et al. [25]:

\[
N_p = 6.405 - 55.673(t/d) \tag{31}
\]

For the correct evaluation of the mass transfer resistance, also the gas–liquid interfacial area \( (a^i) \) has to be estimated. Assuming spherical bubbles, \( a^i \) can be calculated from the average bubble size, \( d_b \), and the gas hold-up, \( \phi \), by the following correlations [24]:

\[
a^i = \frac{6 \phi}{d_b} \tag{32}
\]

\[
\frac{\phi}{1 - \phi} = 0.5 \left( \frac{Q/(\pi z^2)}{(9.81/l)^{1.3}} \left( \rho^i / \rho^g \right) \right) \tag{33}
\]

where

\[
l = 2 \left( \frac{\sigma}{0.4 \rho^i} \right)^{3/5} \left( \frac{h^i/6}{(\pi N_p d^i)^{0.5}} \right) \left( \frac{p^i}{\rho^i} \right)^{0.1} \tag{34}
\]

For Newtonian fluids, the estimation of the average bubble size \( (d_b) \) is given by [26]:

\[
d_b = 0.7 \left( \frac{\sigma^{0.6}}{10^9 p^i V^i} \right)^{0.4} \left( \frac{\rho_L}{\rho^i} \right)^{0.1} \tag{35}
\]

The density \( (\rho) \) and the viscosity \( (\mu) \) of liquid and gas phases, as well as the interfacial tension \( (\sigma) \), required in Eqs. (10)–(18), are estimated with an equation of state [17] at experimental conditions.

3.4. Liquid–solid mass transfer coefficients

The catalyst effectiveness factor is initially considered equal to one because of the small particle size (the average diameter is 30 μm) and slow reaction rate, so that mass transfer limitation inside the catalyst is likely to be negligible. This assumption will be discussed later. The external mass transfer coefficients at the catalyst surface are evaluated assuming no relative velocity between the liquid and the catalyst. This assumption is justified because of the small dimension of the catalyst particles. In this condition the Sherwood number can be approximated to 2, and the \( K_i^L \) values are essentially the diffusion coefficients \( (\kappa_i) \):

\[
Sh = 2 = K_i^L \cdot d_{cat} \cdot 10^5 \tag{36}
\]

The liquid–solid interface area \( (a^i) \) is evaluated from the catalyst amount \((0.15 \text{ g})\) and its specific surface area, according to BET measurements (Sorbomatic 1900, Carlo Erba Instruments) resulted in 855 m² g⁻¹, which implies \( a^i = 128 \text{ m}^2 \).

3.5. Reactor model

The reactor and operating procedures have been described elsewhere [18]. Shortly, it is a batch, slurry reactor with a gas entraining stirrer that continuously creates gas bubbles in the bulk of the liquid, drawing gas from the atmosphere above the liquid. The species mass balances have been written in each phase, i.e. gas and liquid, the solid being assumed non-porous reduce to a flux balance at its interface. Balances are based on the following assumptions:

(a) both liquid and gas phase are well mixed;
(b) carbon dioxide and methanol are not involved in any reaction;
(c) any increment of liquid volume due to the accumulation of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) is neglected, while the change caused by sampling is taken into account;
(d) species cannot accumulate on the catalyst surface, nor in the liquid boundary layer surrounding the catalyst particles.

According to these assumptions, the mass balances in the gas and liquid phases can be written as:
\[
V^d \frac{dC}{dt}^C = d^C K_i^C (C^C_i - C^C_{i-1}), \quad i = H_2, O_2
\]

(37)

\[
V^d \frac{dC}{dt}^C = d^C K_i^C (C^C_i - C^C_{i-1}) - d^A K_i^A (C^A_i - C^A_{i-1})
\]

\[
i = H_2, O_2, H_2O_2, H_2O
\]

At the catalyst surface interface the material balances under assumption (d) becomes:

\[
0 = d^S K_i^S (C^S_i - C^S_{i-1}) - r_i \text{ mol} \quad i = H_2, O_2, H_2O_2, H_2O
\]

(39)

where the production rates \( r_i \) appears, which are functions of the species concentration facing the catalytic surface, \( C^S_i \). At the gas-liquid surface interface equilibrium holds:

\[
C^C_i = H_k^C_i
\]

(40)

The equilibrium constants \( H_k \) depends on total composition, pressure and temperatures. \( H_k \) values are only needed for oxygen and hydrogen, due to assumptions (b) and (c), and are estimated from an equation of state [17] tuned on specific experimental data.

The proposed model is given by a total of ten equations: two ODEs for the gas phase, four ODEs for the liquid phase and four algebraic equations for the catalyst surface, resulting in a low index ADEs system. Its integrations yields the evolution in time of the concentration of reactants (i.e. \( H_2 \) and \( O_2 \)) in the gas and liquid phases and at the catalyst surface (six unknown functions), and the concentration of \( H_2O_2 \) and \( H_2O \) in the liquid phase and at the catalytic surface (four unknowns).

According to the experimental procedure [18], the following ten initial conditions are assumed:

(a) \( C_{O_2}^{C,|t=0} = C_{O_2}^{C,|t=0} = 0.0 \)

(b) \( C_{H_2}^{C,|t=0} = C_{H_2}^{C,|t=0} = 0 \)

(c) \( C_{H_2O_2,|t=0} = C_{H_2O_2,|t=0} = 0 \)

(d) \( C_{O_2}^{C,|t=0} = C_{O_2}^{C,|t=0} = 0 \)

Primarily, hydrogen (the limiting reagent) was introduced after all the other species, when stable values of pressure and temperature were reached inside the reactor (filled with \( H_2O_2, CO_2 \) and methanol). Since the \( H_2 \) feeding was fast compared to the reaction time [18], hydrogen is assumed not to dissolve in the liquid phase while introduced (conditions 41b and 41e). Initial compositions of the gas and liquid phases were evaluated with an equation of state [17]. The initial concentration of water in the reaction medium (condition 41d) was measured [18] prior the introduction of hydrogen.

The material balances Eqs. (37)-(39), together with initial conditions (41) have been efficiently solved using MatLab’s ode15s ADEs solver, also suitable for stiff equations, being based on a multistep, variable order method based on the numerical differentiation formulas.

3.6. Kinetics identification

The kinetic model has been formulated above. To complete its definition, values of the activation energy and the pre-exponential factor of the reactions involved in the catalytic process must be calculated. They have been determined by a sequence of isothermal experimental data fitting, providing the four irreversible reaction rate constants \( k_{\text{dil}}, k_{\text{shp}}, k_d \) and \( k_b \) at the given temperature. Then an Arrhenius plot is assembled for each reaction, and the relative activation energy and pre-exponential factors determined by fitting \( k(T) \).

To fit the experimental data, the following error function was used for each experiment (i.e. a given temperature):

\[
\text{err} = \sqrt{\sum_{i=1}^{n_{\text{exp}}} \left( C_{\text{exp},i}^{H_2O_2,j} - C_{\text{calc},i}^{H_2O_2,j} \right)^2} \quad + \quad \sqrt{\sum_{i=1}^{n_{\text{exp}}} \left( C_{\text{exp},i}^{H_2O,j} - C_{\text{calc},i}^{H_2O,j} \right)^2} \quad + \quad w \sqrt{\sum_{i=1}^{n_{\text{exp}}} \left( C_{\text{exp},i}^{H_2O_2,j} - C_{\text{calc},i}^{H_2O_2,j} \right)^2}
\]

(42)

Note that errors between experimental and calculated concentrations have been rescaled. In pure decomposition and hydrogenation experiments, where water concentration was not measured, we set the parameter \( w = 0 \); in all other cases, \( w = 1 \). A Nelder–Mead simplex algorithm with positivity constraints on the parameters (fminsearchbnd function) is used to minimize the error by adjusting the four parameters of the model (\( k_{\text{dil}}, k_{\text{shp}}, k_d \) and \( k_b \)).

The results were critically analyzed by preparing sensitivity plots, in which the objective function was plotted as a function of a single parameter at a time, while the other parameter values were kept fixed, which gave the objective function minimum. The correlation between the parameters were visualized evaluating a contour plots for each pair, that is plotting couples of parameter values that result in the same value of the error function (42), with the other parameters kept constant.

The goodness of the fit in each experiment is measured with the squared correlation between predicted and experimental concentrations:

\[
r^2_{\text{H}_2\text{O}_2} = 1 - \frac{\sum_{i=1}^{n_{\text{exp}}} \left( C_{\text{exp},i}^{H_2O_2,j} - C_{\text{calc},i}^{H_2O_2,j} \right)^2}{\sum_{i=1}^{n_{\text{exp}}} \left( C_{\text{exp},i}^{H_2O_2,j} - C_{\text{calc},i}^{H_2O_2,j} \right)^2}
\]

(43)

Whenever experimental concentrations of \( H_2O \) are available, Eq. (43) is also used to check the fit to those data.

The slope and the intercept of the Arrhenius plots are fitted in a least-square sense using linear fitting. The errors on activation energy and pre-exponential factors of each reaction are calculated [27] as standard deviations of slope (\( m_i \)) and intercept (\( q_i \)) of the fitted lines, respectively:

\[
s_{m_i} = \frac{1}{m_i} \left( \frac{n_{\text{exp}} \sum_{i=1}^{n_{\text{exp}}} \left[ \ln(k_i) - \left( m_i + \frac{q_i}{T} \right) \right]^2}{n_{\text{exp}} - 2} \right) \frac{1}{n_{\text{exp}} \sum_{i=1}^{n_{\text{exp}}} \left( \frac{1}{T_i} \right)^2} \quad 100
\]

(44)

\[
s_{q_i} = \frac{n_i}{q_i} \left( \frac{n_{\text{exp}} \sum_{i=1}^{n_{\text{exp}}} \left( \frac{1}{T_i} \right)^2}{n_{\text{exp}}} \right) \quad \frac{n_{\text{exp}} \sum_{i=1}^{n_{\text{exp}}} \left( \frac{1}{T_i} \right)^2}{n_{\text{exp}}}
\]

(45)

The goodness of the fitting to the Arrhenius plot is also checked by the degree of explanation (\( r^2 \), analogous of Eq. (43)).

4. Results and discussion

The kinetics has been formulated above; assuming pseudo-elemetary reactions, the partial reaction orders have been taken from the stoichiometry. Experimental data were then used to estimate the parameters in the Arrhenius constant for each step in the mechanism. Experiments of direct synthesis, \( H_2O_2 \) decomposition and hydrogenation have been analyzed independently.

4.1. Direct synthesis experiments

Fig. 2 shows the whole set of experimental data used, \( H_2O \) and \( H_2O_2 \) mol concentration in the liquid have been collected along the time in isothermal, batch experiments, at different temperatures. A
minimum of 30 samples was collected at each temperature; a total of 174 data was used for the regression of the eight parameters, i.e. activation energy and pre-exponential factors. Each isothermal run has been simulated and a set of $k$'s estimated, for each step in the mechanism; results are reported in Table 2, along with the coefficients of determination $r^2$ measuring the agreement of model predictions with both $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$ concentration profiles, qualitatively shown in Fig. 2.

The model is always in very good agreement with experimental results, with $r^2$ values for $\text{H}_2\text{O}_2$ very close to 1. Experimental measurements of $\text{H}_2\text{O}$ are less precise, due to the different analytical procedure, slightly decreasing the goodness of fit.

With the calculated isothermal rate constants the assumption of unitary effectiveness factor can be checked. The Thiele modulus, $\phi$, is estimated as [28]:

$$\phi = \frac{R_{\text{cat}}}{\frac{3}{5} \left( k_{\text{d}} C_{\text{O}_2}^2 + k_{\text{wf}} (C_{\text{O}_2})^{1/2} + k_{\text{h}} C_{\text{H}_2\text{O}_2} \right) \rho_{\text{cat}}}$$  \hspace{1cm} (46)

where $D_{\text{H}_2}$ (effective diffusivity of $\text{H}_2$) is computed as $D_{\text{H}_2} = \frac{\varepsilon_{\text{cat}}^2}{\delta_{\text{cat}}}$, where $\varepsilon_{\text{cat}} = 0.6$ is the porosity of the catalyst. The effectiveness factor is calculated as follows:

$$\eta = \frac{1}{\phi} \left( \coth 3\phi - \frac{1}{3\phi} \right)$$  \hspace{1cm} (47)

For a typical particle size $R_{\text{cat}} = 15$ $\mu$m and at the highest temperature (i.e. highest reaction rates), $\phi$ is in the order of $10^{-3}$ and $\eta \approx 1$, so that recalculation of the mass transfer coefficients and rate constants is unnecessary.

The kinetic constants calculated at each temperature are collected in Fig. 3 in the form of Arrhenius plots, and the resulting activation energies and pre-exponential factor are reported in Table 3.

The temperature dependence of water formation, decomposition and hydrogenation are all comparable (activation energies close to 45 kJ mol$^{-1}$). However, the kinetics of these reactions is quite different. Table 2 shows that $k$ values can differ by orders of magnitude, but they are not really comparable, because refer to different overall reaction orders. The most appropriate comparison must inspect the values of the reaction rates during the course of each experiments, as shown in Fig. 4.

Each reaction rate has been related to the one of direct synthesis, $R_{\text{wf}}/R_{\text{ds}}$, $R_{\text{h}}/R_{\text{ds}}$ and $R_{\text{h}}/R_{\text{ds}}$. Both decomposition and hydrogenation rates are null at the beginning, requiring the presence of the peroxide (i.e. they are reactions consecutive to the direct synthesis). Their rates increase during the reactions course, at a different pace. Decomposition reaction is very slow compared to the direct synthesis and becomes important only at a high $\text{H}_2$ conversion, when the direct synthesis reaction slows down. A strong effect of the temperature is also observed on this reaction, where lower temperature is confirmed to stabilize the $\text{H}_2\text{O}_2$ produced. The preferred path of $\text{H}_2\text{O}_2$ degradation is the hydrogenation reaction: its rate rapidly increases as $\text{H}_2\text{O}_2$ becomes available, limiting the $\text{H}_2\text{O}_2$ production. However this reaction is always slower than the direct synthesis ($R_{\text{ds}}/R_{\text{ds}} < 1$) and it can be limited by decreasing the temperature, up to $R_{\text{ds}}/R_{\text{ds}} < 0.5$ at 258 K. Unfortunately, the $R_{\text{h}}/R_{\text{ds}}$ is always significant because the formation of water really competes with the direct synthesis, prevailing ($R_{\text{h}}/R_{\text{ds}} > 1$) at higher temperature, whereas lower temperature favors the direct synthesis ($R_{\text{h}}/R_{\text{ds}} < 1$). This explains the increased selectivity at lower temperature reported in the Literature, including our previous work [18]. At a given temperature, the rate of $\text{H}_2\text{O}$ formation remains very close to that of the direct synthesis (constant $R_{\text{h}}/R_{\text{ds}}$) except for a short initial transient favoring the direct synthesis.

Due to the intrinsic nature of the interconnected reaction mechanism, a correlation between the estimates of reaction rate constants has to be expected. A quantitative evaluation is given in Fig. 5 as contour plots for the parameter estimates, at $T = 268$ K. A small correlation is indicated by contours approaching circles.

A strong corelation is observed between most reaction constants, and remarkably among direct $\text{H}_2\text{O}_2$ synthesis and the other reactions. The lowest corelation occurs between decomposition and water formation, as expected. The same analysis was carried out for all isothermal data with similar results. In order to improve or validate check our estimates and suppress the correlation among the parameters, we studied the decomposition and hydrogenation rate constants independently, with dedicated experiments.

### 4.2. Decomposition experiments

Rate expression (20) was used to fit the $\text{H}_2\text{O}_2$ concentration profiles during decomposition experiments, to isolate this step. At each temperature a minimum of 10 samples was collected; a total of 45 data was used to calculate the two parameters, i.e. activation energy and pre-exponential factor. Since in these experiments $\text{H}_2$ was replaced with $\text{N}_2$, calculations were carried out neglecting rate expressions (18) and (19) and hydrogen mass balance (Eq. (25)).

Fig. 6 shows the results, both as measured and calculated isothermal data of $\text{H}_2\text{O}_2$ concentration as a function of time, and in terms of Arrhenius plot. Predictions are in good agreement ($r^2$ very close to 1) with experimental observations at any temperature considered, confirming that decomposition is a first order reaction with respect to $\text{H}_2\text{O}_2$ concentration. The calculated reaction rate constants are
shown in Fig. 6b and the corresponding kinetic parameters are reported in Table 4.

A comparison of the Arrhenius constants obtained by fitting all the rate constant in Eqs. (18)–(21) together, using the direct synthesis experimental data, shows that the activation energy for $k_d$ obtained here for the decomposition reaction (50.43 kJ mol$^{-1}$) compares well with the above value (45.06 kJ mol$^{-1}$, Table 3), being that their confidence intervals overlap substantially. A higher deviation is observed in the pre-exponential factors. However, the deviation on the isothermal kinetic constants $k_d$ is less than 10% ($T < 273$ K), confirming the results reported in Table 3.

### 4.3. Hydrogenation experiments

H$_2$O$_2$ hydrogenation experiments were carried out collecting a minimum of 10 samples; a total of 36 data was used to calculate the two parameters, i.e. activation energy and pre-exponential factor. The experiments were performed substituting O$_2$ with N$_2$. Hence, direct synthesis and water formation reactions do not occur. Accordingly, when regressing these data the mass balance of O$_2$ (Eq. (26)) and rates (18) and (19) are ignored. Decomposition rate constants are not regressed this time and the parameters previously obtained (Table 4) are introduced in the model and kept fixed. Only rate expression (21) is considered and isothermal hydrogenation reaction constants regressed. The deviation between experimental H$_2$O$_2$ concentration measured during pure hydrogenation and the best fit predictions is rather high, as shown in Fig. 7a.

Apparently, the kinetic model in this case is not adequate. The decay of H$_2$O$_2$ concentration in time is only approximately exponential, as clearly perceivable from Fig. 7a. In the first minutes of reaction, and more clearly at lower temperature, the H$_2$O$_2$ concentration decreases more slowly than later on. At higher H$_2$ conversion, the decay is very rapid, in a way that a second-order rate equation, linearly proportional to each reagent concentration, cannot fit. Consequently, the model switch from under- to over-estimation of the measured H$_2$O$_2$ concentration, when approx. 70% of the introduced H$_2$O$_2$ is consumed. The effect of temperature, within the approximation discussed above, is well described by a linear Arrhenius plot, shown in Fig. 7b. The calculated activation energy and pre-exponential factor are respectively 17.85 ± 1.00 kJ mol$^{-1}$ and 7.47 ± 0.11 $\times 10^{12}$ cm$^6$ mol$^{-1}$ s$^{-1}$ mol$_{Pd}$.$^{-1}$. However, the $k_0$ values are much higher compared to the ones reported in Fig. 3, also reflected in a significantly lower activation energy. We explain both results, a 2-steps H$_2$O$_2$ consumption and its higher rate, in terms of differences in the catalyst oxidation state. Synthesis and hydrogenation experiments use a different experimental condition: the former are carried out in large excess of O$_2$, the latter does not include any O$_2$, but H$_2$ is the only reactant present. Accordingly, the

### Table 2

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$k_d$/10$^7$ (cm$^6$ mol$^{-1}$ s$^{-1}$ mol$_{Pd}$)</th>
<th>$k_{wf}$/10$^5$ (cm$^9$ s$^{-1}$ mol$_{Pd}$)</th>
<th>$k_d$/10 (cm$^3$ s$^{-1}$ mol$_{Pd}$)</th>
<th>$k_{th}$/10$^8$ (cm$^6$ mol$^{-1}$ s$^{-1}$ mol$_{Pd}$)$^8$</th>
<th>$r^2$H$_2$O$_2$ (-)</th>
<th>$r^2$H$_2$D (-)</th>
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<td>48.78</td>
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<td>17</td>
<td>2.30</td>
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<td>0.9716</td>
</tr>
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**Fig. 3.** Arrhenius plots for the kinetic constants of each individual step in the mechanism.

### Table 3

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pre-exponential factor (see Table 2 for units)</th>
<th>Activation energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct synthesis</td>
<td>4.18 ± 0.15 $\times 10^{12}$</td>
<td>23.84 ± 2.45</td>
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<td>Water formation</td>
<td>4.27 ± 0.20 $\times 10^{14}$</td>
<td>45.31 ± 3.61</td>
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<td>Decomposition</td>
<td>2.61 ± 0.45 $\times 10^{10}$</td>
<td>45.06 ± 9.60</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>5.65 ± 0.22 $\times 10^{17}$</td>
<td>46.58 ± 3.72</td>
</tr>
</tbody>
</table>
active metal on the catalyst can be mostly oxidized in excess of O₂ (synthesis conditions), and reduced in excess of H₂ (hydrogenation conditions). The reduced form of the catalyst can be more effective for the hydrogenation reaction, enhancing its rate, consistently with literature observations [21,12] that the production of hydrogen peroxide is favoured by the oxidized form of Pd. In addition, the H₂O₂ hydrogenation on reduced Pd may occur with a non-elementary mechanism, involving a complex model also accounting for competitive adsorption of H₂ and O₂. According to the discussion above, we rely on the kinetic model and values of Table 2 to describe the reaction network at synthesis (i.e. O₂ dominated) conditions. Further, we question the significance of independently estimating the H₂O₂ hydrogenation kinetics in case the catalyst is vulnerable to oxidation/reduction at conditions of the experiments, which is quite common. Also, in case of non-elementary mechanism, a competitive adsorption on the catalyst sites between H₂ and O₂ is expected in the synthesis experiments, which is not the case for hydrogenation experiments.

Unfortunately, the kinetic parameters determined here are difficult to compare numerically with other studies in the Literature, because of the different rate laws, catalysts, and assumptions in describing the reacting environment. Menegazzo et al. [13] studied the kinetics on a bimetallic Pd/Au catalyst, in a semi-batch reactor (batch liquid phase and flowing gas), at ambient conditions. Being the concentration of H₂ and O₂ constant (albeit not specified), they were included in the kinetic parameters, making a quantitative comparison with our results quite difficult. In addition, material balances differ in the stoichiometry and reaction orders as well. Voloshin et al. [15] measured the kinetics of H₂O₂ hydrogenation reaction over a Pd/SiO catalyst in a microreactor; they determined an activation energy of 43.71 kJ mol⁻¹, close to our estimate using synthesis experiments (46.58 kJ mol⁻¹), but not the pure hydrogenation ones, as discussed above. In another study [9], the same Authors reported the activation energy for the direct synthesis as...
well, in a similar apparatus; they found 22.34 kJ mol$^{-1}$/C$^0_1$, a value that compare well to 23.84 kJ mol$^{-1}$/C$^0_1$ that we calculated here.

5. Parametric sensitivity on mass transfer coefficients

Values of $K_{i g}^j a^i$ (mass transfer between gas and liquid) for $H_2$ was calculate in the range 960–1880 h$^{-1}$/C$^0_1$, at 258 and 297 K, respectively. Similar values were obtain for $O_2$. Our calculations compare well with 1080 h$^{-1}$/C$^0_1$ measured by Meyberg et al. [29] for $H_2$ in liquid alkyn in a similar apparatus. Deguchi et al. [30] observed smaller values for $H_2$ dissolution in water at 303 K in a 300 ml flask equipped with a magnetic stirrer (149–560 h$^{-1}$/C$^0_1$ varying the stirring speed from 1000 to 1350 rpm). Andersson et al. [31] performed $H_2$ dissolution experiments in anthraquinones at different temperatures in a two liters autoclave with two turbine impeller, reporting a $K_{i g}^j a^i$ value of 1400 h$^{-1}$/C$^0_1$ at 298 K. The deviations observed among these works are likely due to differences in the geometry of the equipment used, stirring and operative conditions adopted.

The coefficients of mass transfer resistance at the catalyst surface, $K_i^j$, estimated by Eq. (36), are in the range $1.4 \times 10^{-2}$–$3.5 \times 10^{-2}$ cm s$^{-1}$ at 258 K and 297 K, respectively, for all components.

Since we tried to predict the mass transfer rates a priori, using the best available correlations, we expect that the chemical kinetics was properly identified, with the results given in Table 3. Would the mass transfer actually control the process, or part of it, we should expect the chemical kinetics to be inaccurately determined. We actually used this reasoning to evaluate the extent of mass transfer control at our experimental conditions. The values of $K_{i g}^j a^i$ and $K_i^j$, first calculated by Eqs. (27)–(36), have been increased or decreased by up to one order of magnitude and the kinetic parameters (activation energy and pre-exponential factors) re-estimated. Different simulations were carried out changing each individual mass transfer coefficients, one at a time. As expected, no influence on the kinetic parameters was observed varying $K_{i g}^j a^i$ and $K_i^j$ values of $O_2$, $H_2O_2$ and $H_2O$, the only critical species being hydrogen, the limiting reagent in all the performed experiments. Further, decomposition reaction is not affected by hydrogen concentration because of its rate law expression, and it is excluded from this analysis. The sensitivities of the reaction rate constants $k$ to $K_{i g}^j a^i$ are shown in Fig. 8.

Decreasing $H_2$ mass transfer coefficients from gas to liquid affects the estimated rate constants of any reaction; the reduced $H_2$ transfer rate to the liquid phase (and hence to the catalyst) must be balanced by the increased reaction kinetics. Interestingly, limitations in the $H_2$ mass transfer rate cause an apparent increase in the estimated activation energy, as can be observed in Fig. 9, recalling the importance of accounting for mass transfer to properly identify the kinetics.

However, some mass transfer effect was only evident at temperatures above 283 K, by artificially lowering $K_{H_2} a^i$ at least by

---

**Fig. 6.** $H_2O_2$ decomposition experiments in a batch reactor: (a) normalized experimental and calculated $H_2O_2$ concentration and r-square values: □, 313 K; ◦, 283; ○, 273 K; ■, 268 K; solid line, model. (b) Arrhenius plot for $k$.

**Fig. 7.** $H_2O_2$ hydrogenation experiments in batch reactor: (a) normalized experimental and calculated $H_2O_2$ concentration: □, 313 K; ◦, 283; ○, 273 K; solid line, model. (b) Arrhenius plot.

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one order of magnitude (form 1880 h⁻¹ to 140 h⁻¹). Accordingly, we conclude that limitations due to the dissolution rate of hydrogen can be excluded at the experimental conditions, even accounting for uncertainties in the correlations, that could not be as high as 1 order of magnitude.

At the highest temperature (i.e., 297 K), where the effect is expected to be more evident, \( K_{H_2}^{L} \) were varied from 3.01 \( \times 10^{-4} \) cm s⁻¹ to 8.61 \( \times 10^{-4} \) cm s⁻¹. As can be seen, predicted values of reaction rate constants do not significantly change, even varying the resistance by two orders of magnitude. Accordingly, the activation energy of the three reaction remains constant (Fig. 9). This proves that any restriction due to the mass transfer limitation to the catalyst surface is negligible at the experimental conditions.
6. Conclusions

Direct synthesis of \( \text{H}_2\text{O}_2 \) is mainly limited by the identification of a selective catalyst, but fully exploiting the potential of the most promising ones requires knowledge of the reaction kinetics. Among the many studies on commercial and innovative catalysts, we perceived controversial indications about the role of mass transfer in either limiting the conversion or affecting the selectivity. Due to the parallel and consecutive structure of the mechanism, simple method based on a single reaction cannot be used to easily assess the mass transfer contribution. In addition, without any information about the controlling regime, a kinetic study is inevitably connected to an appropriate account of the transport limitations. In the present study we formulated a model of a gas bubbling, batch slurry reactor for \( \text{H}_2\text{O}_2 \) direct synthesis. Direct synthesis data were collected at temperatures in the range 258–297 K and pressure between 14 and 20 bar (depending on the temperature) using a commercial 5% Pd on carbon catalyst (0.15 g) in a methanolic solution (400 ml). The reagents \( \text{H}_2 \) and \( \text{O}_2 \) were diluted with \( \text{CO}_2 \) outside flammability limits. Our experimental measurements, carried out batchwise in the absence of halides and acids, have been used to identify the intrinsic kinetics and assess the influence of mass transfer. The simplest rate equations compatible with the acknowledged reaction network has been included in a reactor model accounting for mass transfer resistance between gas and liquid and bulk of the liquid-catalyst surface.

The corresponding Arrhenius parameters were estimated from direct synthesis experiments for all the reactions. Comparable activation energies close to 45 kJ \( \text{mol}^{-1} \) were observed for \( \text{H}_2 \text{O} \) production, hydrogenation and decomposition, while \( \text{H}_2\text{O}_2 \) synthesis had a different temperature dependence (23 kJ \( \text{mol}^{-1} \)), suggesting that a higher selectivity is achievable at low temperature. Decomposition had a very limited influence on the overall peroxide production rate, with \( \frac{R_d}{R_{ds}} \geq 0.5 \) only at high \( \text{H}_2 \) conversion, when the direct synthesis reaction slows down. Hydrogenation was the preferred path of \( \text{H}_2\text{O}_2 \) degradation as its reaction rate rapidly increased with \( \text{H}_2 \) conversion. Water formation was always significant, prevailing \( \left( \frac{R_{wf}}{R_{ds}} > 1 \right) \) at higher temperature, whereas lower temperature favors the direct synthesis \( \left( \frac{R_{wf}}{R_{ds}} < 1 \right) \). Independent investigations on decomposition in the absence of \( \text{H}_2 \) confirmed the results, whereas \( \text{H}_2\text{O}_2 \) hydrogenation experiments (carried out in the absence of \( \text{O}_2 \)) highlighted significant difference in the kinetics, apparently due to a different oxidation state of the catalyst.

A sensitivity analysis on the mass transfer coefficients to allow for uncertainties in the correlations proved that no resistances in the liquid occur, while gas–liquid \( \text{H}_2 \) transfer rate may be limiting, although unlikely, requiring that literature coefficients overestimates the real transfer rate by an order of magnitude.

Acknowledgments

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Reactivity aspects of SBA15-based doped supported catalysts: H$_2$O$_2$ direct synthesis and disproportionation reactions

Nicola Gemo$^{1,*}$, Pierdomenico Biasi$^{2,*}$, Paolo Canu$^{1}$, Federica Menegazzo$^{3}$, Francesco Pinna$^{3}$, Ajaikumar Samikannu$^{4}$, Krisztián Kordás$^{4}$, Tapio O. Salmi$^{2}$, Jyri-Pekka Mikkola$^{3,4}$

$^1$Dipartimento di Ingegneria Industriale University of Padova, via Marzolo 9, 35131, PADOVA, Italy

$^2$Department of Chemical Engineering, Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering Åbo Akademi University, Biskopsgatan 8, ÅBO-TURKU, 20500, Finland

$^3$Department of Molecular Science and Nanosystems, Ca’ Foscari Venice University and Consortium INSTM UdR Ve, Dorsoduro 2137, Venezia, Italy;

$^4$Department of Chemistry, Chemical-Biochemical Centre (KBC), Technical Chemistry, Umeå University, UMEÅ, SE-90187, Sweden

*To whom correspondence should be addressed. E-mail: bpierdom@abo.fi, Jyri-Pekka.Mikkola@chem.umu.se

‡ The first two authors contributed equally to the present work
1. Abstract

Pd and PdAu catalysts supported on SBA15 and SiO$_2$ were prepared and investigated for H$_2$O$_2$ direct synthesis in a batch autoclave (10°C and 17.5 bar) and in the absence of halides and acids. The SiO$_2$ supported catalysts exhibited inferior performances compared to the mesoporous ordered-SBA15. A good control of both the catalysts dispersion and nanoparticle stability was achieved using SBA15. Catalysts were doped with bromine, a promoter in the H$_2$O$_2$ direct synthesis. Productivity and selectivity decreased when bromine was incorporated in the catalysts, thus indicating a possible poisoning due to the grafting process. A synergetic effect between Pd and Au was observed both in presence and absence of bromopropylsilane grafting on the catalyst surface. Three modifiers of the SBA15 support (Al, CeO$_2$ and Ti) were chosen to elucidate the influence of the surface properties on metal dispersion and catalytic performance. Higher productivity and selectivity were achieved incorporating Al into the SBA15 framework, whereas neither Ti nor CeO$_2$ improved H$_2$O$_2$ yields. The enhanced performance observed for the PdAu/Al-SBA15 catalysts was attributed to the increased number of Brønsted acid sites. A modification of this catalyst with bromine was confirmed to impair both productivity and selectivity, possibly due to the broader particle size distribution and the poor stability of the metal nanoparticles, as demonstrate by Transmission Electron Microscopy (TEM) images. H$_2$O$_2$ disproportionation was also investigated. A much slower reaction rate was observed compared to the H$_2$O$_2$ production, suggesting that the major contributor in the process of H$_2$O$_2$ destruction must be connected to the hydrogenation reaction.

Hydrogen peroxide, direct synthesis, SBA15, silica, palladium
2. Introduction

The global demand of hydrogen peroxide is increasing due to its recent usage in new large scale oxidation processes, such as the epoxidation of propylene to propylene oxide[1] and the synthesis of caprolactam (Sumitomo)[2] Since the early 90’s, many research groups have tried to develop new alternatives for the production of this peroxide[3-5]. The most attractive one is the direct synthesis (DS process), due to its atom-efficient nature and the costs savings that can be achieved[3]. Basically, hydrogen and oxygen are dissolved in a proper reaction medium (i.e. alcoholic solution or water) and react over a solid catalyst. This three phase system has been under intensive study during the last thirty years both by industries as well as academia[3, 4, 6-15]. The main obstacles to industrial feasibility are selectivity and safety issues[4]. The reaction pathway for the direct synthesis of hydrogen peroxide is depicted in Scheme 1.

![Scheme 1. Reactions involved in the direct synthesis of \( \text{H}_2\text{O}_2 \).](image)

Two consecutive (hydrogenation and disproportionation) and one parallel reaction (\( \text{H}_2\text{O} \) formation) competing with the formation of the hydrogen peroxide are involved. Recent progress in terms of kinetic studies[16-21] aim at elucidating the specific role of each of these reactions. However, the results are often difficult to compare because of the different approaches, reactors and reaction conditions adopted. In the present study, we focused on identifying a suitable support to limit the undesired reactions. Monometallic (Pd)[17, 22-25] and bi-metallic (Pd and Au)[26, 27] catalysts with different surface properties were
synthesized and investigated for H$_2$O$_2$ direct synthesis in the absence of halides and acids at identical reaction conditions, to facilitate a consistent comparison. Kinetic studies were carried out in a batch, laboratory scale slurry autoclave with H$_2$ as the limiting reagent. SBA15 mesoporous material was chosen as support because of its interesting characteristics: it has a high specific surface area, it promotes a high dispersion and stability of metal nanoparticles[28-30] and it also acts as a template to control the nanocluster size. A good control of the catalysts dispersion is fundamental: very small metal nanoclusters are not desired because of their O-O bond breaking aptitude, hence leading to H$_2$O formation[11], whereas low dispersion catalysts are less active[30]. On the other hand, an acidic environment is known to promote the peroxide formation[3, 4, 31, 32]. Consequently, three modifications of the parent SBA15 support material (incorporation of Al, CeO$_2$ and Ti) were chosen to elucidate the influence of surface properties (such as Brønsted and Lewis acidity) on the metal dispersion and the overall performance observed upon H$_2$O$_2$ direct synthesis. Halide ions are also known to increase the selectivity towards H$_2$O$_2$, especially bromide[26, 33-35], but their presence in the solution is undesired. Hence, Br-doped catalysts were obtained by grafting bromine on SBA15-based catalysts, so that presence of the free ions in the solution was avoided. The performances of these SBA15 supported catalysts were also compared to unordered, classic silica[11]. After complete conversion of H$_2$, the disproportionation reaction was also investigated.

3. Materials

SiO$_2$ (Akzo), tetraethyl orthosilicate (purity ≥ 99.0%), poloxamer (pluronic P-123), hydrochloric acid (37%), urea (purity ≥ 98%), aluminium isopropanoxide, titanium tetraisopropoxide and PdCl$_2$ (all purchased from Sigma-Aldrich) were used for the catalyst preparations as received, as well as Ce(NO$_3$)$_3$.6H$_2$O (purity 99.5%, Alfa Aesar), ammonia solution (25%, Fisher Scientific) and HAuCl$_4$ (ABCR).
Methanol was the reaction medium (J.T. Baker 99.99% purity). H₂, O₂ and CO₂ were used in the direct synthesis experiments as received (AGA 99.999% mol/mol purity).

4. Catalysts preparation

A total of eleven catalysts were synthesized according to the following procedures.

4.1 Preparation of the supports

Preparation of SBA15 and M-SBA15 (M = Al and Ti) by hydrothermal method

Mesoporous silica SBA15 was synthesized according to a modification of the procedure reported by Zhao et al.[36]. In a typical synthesis, 10 g of the structure directing agent, a triblock copolymer Pluronic P-123 (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), EO₂₀-PO₂₀-EO₂₀, Mₙ ≈5,800) was dissolved in a polypropylene bottle using 75 ml of distilled water, followed by an addition 300 ml of 2M of hydrochloric acid and stirred at 40°C for 2 h. Then, 21.25g of the silica source, tetraethyl orthosilicate (TEOS) was slowly added to the above mixture, stirred for 24 h at 40°C and aged for 48 h at 90 °C under static conditions. The resultant solid product was filtered, washed thoroughly with deionized water to reach neutral pH, dried at 90 °C in an oven and, finally, the organic template in the synthesized material was removed by calcination under air flow at 550°C for 6 h.

Metal substituted M-SBA15 with Si/M ratio of 25 (where M= Al and Ti) were synthesized by hydrothermal incorporation method using tetraethyl orthosilicate (TEOS), aluminium isopropoxide and titanium tetraisopropoxide as the sources of Si, Al and Ti, respectively. These materials were obtained following the procedure described for SBA15, expect that the addition of tetraethyl orthosilicate (TEOS) was followed by the addition of an appropriate amount of metal precursors (dissolved in ethanol).
Preparation of CeO$_2$-SBA15

CeO$_2$ modified SBA15 was prepared by means of deposition-precipitation method. About 6 gram of the calcined SBA15 was dispersed in 300 ml of urea (0.372M). Under stirring, an appropriate amount of Ce(NO$_3$)$_3$·6H$_2$O (dissolved in deionized water) was added to the above suspension to yield a theoretical loading of 20 wt.% CeO$_2$. The temperature of the suspension was raised to 70 °C and stirred for 5 h enabled slow disproportionation of the urea to ammonia, increasing the pH and, consequently, giving a slow precipitation of metal precursors. The pH of the suspension was then increased to 9 by addition of 25% aqueous ammonia to ensure complete precipitation. After stirring for 1 h, the solids were recovered by filtration and washed thoroughly with deionized water. Finally, the solids were dried overnight in an oven at 100 °C and calcined in a furnace under normal air at 500 °C for 5 hours.

4.2 Metal loading

Br-modified PdAu/ and Pd/SBA15 catalysts

PdAu/SBA15 catalyst was synthesized supporting Pd and Au (1:4 mole ratio) on SBA15 by wet impregnation method. HAuCl$_4$·H$_2$O and PdCl$_2$ were used as precursors, added to the solution at the same time. The impregnated catalyst was dried at 100°C overnight and then reduced at 300°C for 8 hours with a 30 ml/min flow of hydrogen. The furnace was allowed to cool down to room temperature and the catalyst was passivated for 24 h under a 2 vol% O$_2$/N$_2$ mixture. The final metal content observed was 0.3 wt% of Pd and 2.2 wt% of Au, respectively.

A bromopropyl-PdAu/SBA15 (Br-PdAu/SBA15) catalyst was obtained grafting the reduced form of this catalyst with 3-bromopropyl-trimethoxy-silane. The catalyst was suspended in
dry toluene. Then the 3-bromopropyl-trimethoxy-silane (5 mmol per gram of catalyst) was slowly added to the suspension. The mixture was fluxed at 80 °C in inert atmosphere for 24 h. After completion, the catalyst was washed with an excess of dry toluene and dried at 100°C for 24 h in air. The synthesis and the grafting process of the Pd/SBA15 (2.5 wt.% and Br-Pd/SBA15 (0.3 wt.%) catalysts were carried out following the same procedure, but impregnating the support with Pd only. PdAu-Br/SBA15 (0.3 wt% Pd and 2.2 wt% Au) was prepared reversing the order of the described procedures, first grafting the support and then impregnating the active metals.

PdAu/M-SBA15 (M = Al, Ti and CeO$_2$)

The active metals were supported on M-SBA15 (M = Al, Ti and CeO$_2$) by impregnation method using aqueous methanol solutions. About 2.0 grams of the pre-dried M-SBA15 support was dispersed in 30 ml of methanol. Then, the required amount of metal precursors (HAuCl$_4$ and PdCl$_2$) were dissolved separately in water (1M HCl in the case of PdCl$_2$) and added simultaneously to the above stirred suspension of the support. Stirring was continued for 5 hours. The solid product was recovered by evaporation of the solvent under reduced pressure using a rotary evaporator and dried overnight in an oven at 100 °C. Finally, the material was calcined at 400 °C for 3 h in air and reduced at 300 °C for 3 h in 30 ml/min H$_2$ flow. The active metal content of the catalysts were 0.19 wt.% and 1 wt.% for Au and Pd, respectively.

Br-PdAu/Al-SBA15

About 1.0 gram of the above prepared PdAu/Al-SBA15 was dispersed in 20 ml of dry methanol. An appropriate amount of ammonium bromide (5mmol per gram of catalyst) was dissolved in 5 ml of methanol and added to the stirred suspension of the base-catalyst. Stirring was continued for 2 h. The solid product was recovered by evaporation of the solvent under
reduced pressure using rotary evaporator and dried in an oven at 80 °C. Finally, the material was calcined at 400 °C for 1 h under nitrogen atmosphere (flow 30 ml/min) and reduced at 300 °C flowing hydrogen (30 ml/min) for 3 h. (NOTE: Care must be taken while adding methanol to the reduced form of the catalyst due to a possibility of explosion. Self ignition of the catalyst was observed in our laboratory during this procedure).

**Pd/Si and PdAu/Si**

A commercial SiO$_2$ (Akzo, 329 m$^2$/g of surface area) was used as received for samples synthesis. It was impregnated by incipient wetness with H$_2$PdCl$_4$ and/or HAuCl$_4$ aqueous solutions (addition of the two precursor solutions was simultaneous for the bimetallic catalyst) to give the desired metal loading (0.5 wt.% Pd for Pd/Si and 1.5 wt% Pd and Au for PdAu/Si). Samples were finally calcined at 500 °C in flowing air for 3 hours.

5. **Experimental section**

A recent study highlighted how carbon dioxide can reduce the flammability region of the hydrogen/oxygen mixture[37]. Moreover, CO$_2$ is also known to enhance H$_2$ solubility in many solvents[38-40]. For these particular reasons, in this study CO$_2$ was chosen as a dilutant for the H$_2$/O$_2$ mixture residing outside the flammability limits. The experiments were performed in a 600 ml laboratory-scale batch reactor, described elsewhere[23]. Briefly, after the introduction of the catalyst (0.15 g), CO$_2$ (18.4 bar at 23°C) and O$_2$ (up to 24.7 bar at 23°C) were introduced into the reactor, followed by methanol (400 ml). The temperature was decreased to 10°C and stirring (1000 rpm) for 30 min allowed to reach the equilibrium (17.5 bar). Hydrogen (0.0183 mol) was fed as the limiting reagent from a dedicated vessel. The reaction started immediately after H$_2$ was introduced to the reaction zone and the stirring turned on. Several liquid samples were withdrawn through a GC-valve during each experiment. H$_2$O$_2$ concentration was determined by iodometric titration whereas H$_2$O content
was measured by Karl-Fischer analysis. The selectivity and H₂ conversion were calculated as follows: 

\[
\text{H}_2\text{O}_2 \text{ selectivity} = \frac{\text{moles H}_2\text{O}_2 \text{ produced}}{\text{moles H}_2\text{O} + \text{H}_2\text{O}_2 \text{ produced}} \times 100;
\]

\[
\text{H}_2 \text{ conversion} = \frac{\text{moles H}_2\text{O} + \text{H}_2\text{O}_2 \text{ produced}}{\text{moles H}_2 \text{ introduced}} \times 100.
\]

Specific \( \text{H}_2\text{O}_2 \) productivity was calculated as: 

\[
\text{Specific H}_2\text{O}_2 \text{ productivity} = \frac{\text{moles H}_2\text{O}_2 \text{ produced}}{\text{time} \cdot \text{moles of active metal}}.
\]

\( \text{N}_2 \) adsorption measurements were performed with a Carlo Erba Sorptomatic 1900. Specific surface area was evaluated according to the BET equation, whereas pore size distribution of the bulk supports was estimated according to Dollimore/Heal method.

The nature of the acid sites of the catalysts was determined by Fourier transform infrared (FT-IR) spectroscopy of adsorbed pyridine. The analysis were carried out according to literature procedure[41]. Lewis and Brønsted acid sites were calculated from the IR band area at 1450 and 1545 cm\(^{-1} \), respectively. The integrated molar extinction coefficients were assumed as 1.67 cm/µmol for Brønsted acidity and 2.22 cm/µmol for Lewis acidity. Particle size and structure was assessed by energy-filtered transmission electron microscopy (EFTEM, LEO 912 OMEGA, LaB6 filament, 120 kV).

TGA measurements were carried out on the grafted catalysts. Weight loss was due to the loss of the organic part carrying the bromine. Hence, bromine content was estimated from the weight loss upon heating. The bromine content of the catalysts obtained grafting the support after active metals deposition was 4.5 wt.%. The catalyst obtained with the reversed procedure, i.e. grafting the support before the deposition of the active metals (PdAu-Br/SBA15), revealed a lower bromine content (2.8 wt.%).

6. Results and discussion

Table 1 summarizes \( \text{H}_2\text{O}_2 \) productivity, selectivity and \( \text{H}_2 \) conversion after 15 min of reaction for all the catalysts. For selected catalysts, acid sites concentration of the support is also reported.
Table 1. \( \text{H}_2\text{O}_2 \) synthesis with SBA15 and Si supported catalysts: acidity, \( \text{H}_2 \) conversion after 15 min of reaction, productivity and selectivity (after 15 min of reaction and at complete \( \text{H}_2 \) conversion). Conditions: \( T = 10 \ ^\circ \text{C} \), \( P = 17.5 \text{ bar} \).

<table>
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<th>Catalyst</th>
<th>Acidity</th>
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<td>78</td>
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</tr>
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<td>74</td>
<td>67</td>
<td>62</td>
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<td>50</td>
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</tbody>
</table>

Legend: Reacted
It is important to compare the different catalysts in similar reaction conditions, that is before
H\textsubscript{2} was completely consumed. We observed that 15 min were enough to obtain a significant
quantity of H\textsubscript{2}O\textsubscript{2} with H\textsubscript{2} still present in the liquid phase. Thus, the catalysts were compared
while the direct synthesis of H\textsubscript{2}O\textsubscript{2} was still increasing. For sake of completeness, selectivity
and H\textsubscript{2}O\textsubscript{2} productivity values at complete H\textsubscript{2} consumption are also included. The selectivity
measured at different H\textsubscript{2} conversions are quite close, whereas the H\textsubscript{2}O\textsubscript{2} productivity spread
displays bigger differences. However, caution should be taken comparing the productivity at
complete H\textsubscript{2} conversion, as it occurs at different reaction time. The selectivities reported in
Table 1 are generally lower compared to the values obtained by other authors with nominally
similar catalysts[11, 29, 30, 42]. However, in these papers an acidic medium was adopted to
stabilize the peroxide formed, hence drastically increasing the selectivity. In our study the
presence of promoters and stabilizers was deliberately avoided to focus on the catalysts
performance solely. Experimental results are discussed below.

6.1 Non-ordered and ordered mesoporous Si-based catalysts: Au and incorporated-bromine
effect

We investigated the role of Au and incorporated-bromine over five different SBA15-based
catalysts. Selectivity, H\textsubscript{2} conversion and H\textsubscript{2}O\textsubscript{2} productivity after 15 min of reaction are
reported in Table 1, entries 1 to 5.

Figure 1 illustrates H\textsubscript{2}O\textsubscript{2} concentration as a function of time observed with these catalysts.
Figure 1. $\text{H}_2\text{O}_2$ concentration in batch reactor: PdAu/SBA15 (□), Br-PdAu/SBA15 (△), Pd/SBA15 (●), Br-Pd/SBA15 (○), PdAu-Br/SBA15 (♦), Pd/Si (▲), PdAu/Si (○). Conditions: $\text{T} = 10 \, ^\circ\text{C}$, $\text{P} = 17.5 \text{ bar}$

Typically, $\text{H}_2\text{O}_2$ formation increased rapidly in the beginning, reaching a maximum and gradually decreasing afterwards. The exceptions were Br-PdAu/SBA15, Br-Pd/SBA15 and PdAu-Br/SBA15, showing low or negligible activity (Table 1). The $\text{H}_2\text{O}_2$ concentration profile is closely related to the $\text{H}_2$ consumption, as discussed in the next section.

Among the synthesized catalysts, PdAu/SBA15 was the most active one. Figure 1 clearly distinguishes the differences in mono- and bimetallic catalysts, where the latter ones always show a much higher $\text{H}_2\text{O}_2$ productivity upon short contact time. Monometallic Pd/SBA15 catalyst had a productivity 50% reduced compared to the bimetallic PdAu/SBA15. Its grafted parent (Br-Pd/SBA15) demonstrated a poor $\text{H}_2\text{O}_2$ productivity also, i.e. five times lower
compared to the bimetallic Br-PdAu/SBA15. Upon testing the monometallic Br-Pd/SBA15 catalyst, H2O concentration was within the measurement error and, consequently, H2 conversion and selectivity could not be calculated. The comparison of mono- and bimetallic catalysts (either grafted or not) confirms the synergetic effect between Pd and Au reported in the literature[26, 27]. The grafting process had a two-fold effect on the bimetallic catalyst, clearly seen when comparing the performance of the PdAu/SBA15 and Br-PdAu/SBA15. The selectivity was reduced by 15% in the presence of bromine attached on the catalyst. Moreover, the productivity was three times lower over Br-PdAu/SBA15 and also the H2 conversion was reduced by a factor of 80%. The grafting process could induce poisoning of the catalyst by pore blocking (bromoalkyl species) and/or causing migration and sintering of the metal nanocluster outside the mesoporous of the support, as shown by the TEM images discussed below. Neither H2O2 nor H2O were observed when the SBA15 was grafted before Pd and Au deposition. The reduction performed at 300 °C after the grafting process could induce a partial disproportionation of the bromopropyl groups, leading to coke formation and poisoning of the catalyst. Thermogravimetric Analysis (TGA) measurements confirmed this hypothesis. Weight loss upon heating of the catalyst reduced after Br grafting was 37% lower compared to the catalysts obtained with the reverse procedure, i.e. grafting the catalysts after active metals deposition, suggesting that partial decomposition of the organic chains occurred during reduction of the PdAu-Br/SBA15 catalyst.

Performances of SBA15-based catalysts were also compared to non-ordered SiO2-based catalysts, Figure 1 and Table 1, entries 6 to 7, respectively. The synergetic effect of Pd and Au observed with SBA15 supported catalysts was not observed when using silica as support. Compared to the PdAu/Si, the monometallic Pd/Si catalyst displayed both higher selectivity and productivity, though at lower H2 conversion. However, the performance of these catalysts
was generally lower than that shown by the non-grafted SBA15 supported one, confirming the advantage of using an ordered mesoporous support.

6.2 Al, Ti and CeO$_2$-SBA15 modified catalysts

Starting from the consolidated knowledge that an acid environment favors the H$_2$O$_2$ direct synthesis[3, 4, 31, 32], the catalyst displaying the best performance (PdAu/SBA15) was further modified. Three different surface modifiers were chosen: incorporation of Al into the framework is known to give Brønsted acidity[43], CeO$_2$ adds Lewis acidity[44, 45] while Ti gives mild oxidizing property[46, 47]. H$_2$O$_2$ concentrations obtained in batch experiments with PdAu/M-SBA15 (M = Al, Ti and CeO$_2$) are reported in Figure 2.

Figure 2. H$_2$O$_2$ concentration in batch reactor: PdAu/Al-SBA15 (■), PdAu/CeO$_2$-SBA15 (*), PdAu/Ti-SBA15 (+), Br-PdAu/Al-SBA15 (x). Conditions: T = 10 °C, P = 17.5 bar.

Again, H$_2$O$_2$ concentration goes through a maximum and then slowly decreases, except for Br-PdAu/Al-SBA15 catalyst, that demonstrates a lower reaction rate. The performance of these catalysts are reported in Table 1, entries 8 to 11. Modifying the support with Al gave the
best results, both in terms of productivity and selectivity. Compared with the corresponding unmodified catalyst (Table 1, entry PdAu/SBA15), the productivity was increased by 37% with comparable selectivity and H₂ conversion. Modification of the support with CeO₂ or Ti impaired the catalytic performances, decreasing both selectivity and productivity values. A catalytic test was also carried out with the best catalyst (PdAu/Al-SBA15) modified by an addition of bromine (Br-PdAu/Al-SBA15). Bromine was grafted after the deposition of the active metals on the support, whereas the reverse procedure revealed the deactivation of the catalyst (Table 1). However, doping the catalyst decreased the selectivity and resulted in a drop of productivity by one order of magnitude (entry Br-PdAu/Al-SBA15, Table 1), confirming the poisoning already observed with the unmodified SBA15-based catalysts. Different surface analysis techniques were carried out on the catalysts to explain these results.

Figure 3 shows TEM images of PdAu/M-SBA15 (M = Al, Ti and CeO₂) catalysts, before and after use.
Figure 3. TEM images of SBA15 modified catalysts: a) PdAu/Ti-SBA15, b) PdAu/Al-SBA15, c) Br-PdAu/Al-SBA15, d) PdAu/CeO$_2$-SBA15; 1) fresh catalyst (left), 2) used catalyst (right).
Pore size diameters of the bulk support were estimated from TEM images, and the calculations suggested that approx. 6 nm is a realistic estimate for all of the catalysts. This result was confirmed by nitrogen physisorption measurements as well (Dollimore/Heal method). This also compares well with values reported in the literature[28, 29, 36]. The analyses were repeated before and after the reaction. No significant changes were found, confirming the stability of the support during the reaction. Particle size distributions of the bimetallic (PdAu) nanoclusters obtained from the TEM images on fresh and spent catalysts are summarized in Figure 4.

![Particle size distribution of modified SBA15-based catalyst](image)

Figure 4. Particle size distribution of modified SBA15-based catalyst (the modifier is indicated in the legend): a) fresh catalyst; b) spent catalyst.
All except the Br-PdAu/Al-SBA15 catalysts demonstrated comparable particle size distributions where most of the nanoclusters had a diameter close to that of the support pores (i.e. 6-7 nm) and only occasionally showing diameters up to 25 nm. This confirms that a good control of the nanocluster size was achieved using SBA15 as support. The particle size distributions were almost unchanged in the spent catalysts (Figure 4b), confirming the stability of the metal nanoclusters at reaction conditions. A comparison of PdAu/Al-SBA15 with Br-PdAu/Al-SBA15 (Figure 4a) clearly demonstrated that a broader particle size distribution was obtained after bromine doping (clusters between 6 and 22 nm). The metal nanoparticles possibly migrated on the catalyst surface and agglomerate into larger clusters upon bromine modification. The bromine also caused a noticeable sintering of metal nanoclusters after use, as shown in Figure 4b. The broader nanocluster size distribution and the poorer stability of the metal nanoclusters are deemed responsible for the lower activity of the bromine containing catalyst. Compared to the other catalysts, TEM images of the PdAu/CeO$_2$-SBA15 (Figure 3d) revealed a more homogeneous surface, where the support channels are less clearly distinguishable. This difference in the surface structure is possibly due the presence of CeO$_2$. All SBA15-based catalysts were prepared via a direct synthesis method[36], except CeO$_2$ modification, carried out by a post-synthesis method. The high CeO$_2$ loading (20 wt%) may have caused partial pore blocking. To verify this hypothesis, nitrogen physisorption (BET method) measurements were carried out on the catalysts. The specific surface area of the PdAu/M-SBA15 (M = Al and Ti) catalysts resulted in 600 m$^2$/g. Only the CeO$_2$-modified catalyst had a lower area of 430 m$^2$/g, confirming partial pore blocking caused by the CeO$_2$ doping. The decreased available surface area can also be responsible for the lower activity of this particular catalyst (Table 1).

FT-IR spectroscopy by means of pyridine adsorption was performed on these catalysts to characterize the Lewis and Brønsted acidity present. IR spectra were recorded at 250, 350 and
450 °C, respectively. Adsorbed pyridine was detected only at 250 °C. No peaks were observed at higher temperatures. Measured acid sites concentrations are reported in Table 1 (entries 8 to 11). The presence of Brønsted and/or Lewis acid sites was confirmed in the modified supports. The enhanced performance of the PdAu/Al-SBA15 catalyst can be explained by the presence of Brønsted acid sites: hydrogenation of H$_2$O$_2$ is suppressed when the peroxide is surrounded by protons[4, 31], and hence the increased Brønsted acidity as a result of increased Al (modifier) enhanced the peroxide productivity.

6.3 $H_2$ conversion and disproportionation reaction

$H_2$ conversion has a key role on the H$_2$O$_2$ concentration profiles shown in Figure 1 and Figure 2. The moment of complete $H_2$ conversion is particularly important, implying a significant change in the ongoing reactions: initially, $H_2$ is present and all the reactions (see Scheme 1) occur simultaneously. After complete $H_2$ conversion, disproportionation is the only possible reaction. Interestingly, complete $H_2$ conversion was found to occur simultaneously to the peroxide peak (Figure 1 and Figure 2), meaning that the experimental data collected afterwards are representative only of the disproportionation reaction. It has to be mentioned that Br-Pd/SBA15, PdAu-Br/SBA15, Br-PdAu/SBA15 and Br-PdAu/Al-SBA15 catalysts demonstrated a low productivity (Figure 1 and Table 1) and did not reach complete $H_2$ conversion within experimental time. Hence these catalysts are excluded from this discussion. In general, it is apparent that the H$_2$O$_2$ disproportionation occurs at a different time scale compared to the other reactions: H$_2$O$_2$ concentration is rapidly increased in less than 50 min, while the subsequent disproportionation took several hours. Thus, the major step for the peroxide destruction is to be assigned to the hydrogenation reaction, regardless the support and the active metal content of the catalyst. Assuming disproportionation is a first order
reaction with respect to $\text{H}_2\text{O}_2$, its rate constant ($k_d$) can be estimated with the experimental data collected after $\text{H}_2\text{O}_2$ peak by integration of Equation 1:

$$\frac{d[H_2O_2]}{dt} = k_d \cdot [H_2O_2] \cdot \frac{n_{\text{metal}}}{V_L}$$

Note that the decomposition kinetic constant is scaled to the total moles of metal on the catalyst ($n_{\text{metal}}$).

Figure 5 depicts the experimental disproportionation data collected after complete $\text{H}_2$ consumption along with their fit, for a few catalysts. $k_d$ values estimated accordingly are reported in Table 2.

![Figure 5. Elaboration of disproportionation data (i.e. collected after complete H₂ conversion) according to Eq. 1: PdAu/Si (○), PdAu/Al-SBA15 (■), PdAu/CeO₂-SBA15 (*); solid line, model.](image-url)
Table 2. Disproportionation rate constants based on Eq. 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_d$ $l^{-1} min^{-1} n_{metal}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdAu/Si</td>
<td>3.7</td>
</tr>
<tr>
<td>Pd/SBA15</td>
<td>4.6</td>
</tr>
<tr>
<td>PdAu/SBA15</td>
<td>4.3</td>
</tr>
<tr>
<td>PdAu/Al-SBA15</td>
<td>9.4</td>
</tr>
<tr>
<td>Pd/Si</td>
<td>18.1</td>
</tr>
<tr>
<td>PdAu/CeO$_2$-SBA15</td>
<td>19.6</td>
</tr>
<tr>
<td>PdAu/Ti-SBA15</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Values in the range 4-20 $l^{-1} min^{-1} n_{metal}^{-1}$ were obtained. Three groups of catalysts are recognized: PdAu/Si, Pd/SBA15 and PdAu/SBA15 with $k_d \sim 4$ $l^{-1} min^{-1} n_{metal}^{-1}$, PdAu/Al-SBA15 with $k_d \sim 9$ $l^{-1} min^{-1} n_{metal}^{-1}$ and Pd/Si, PdAu/CeO$_2$-SBA15 and PdAu/Ti-SBA15 $k_d \sim 18-20$ $l^{-1} min^{-1} n_{metal}^{-1}$. For sake of clarity, one representative catalyst per group is depicted in Figure 5. A good linear relationship was obtained, confirming that the disproportionation is a first order reaction with respect to H$_2$O$_2$. Calculated rates are close to the values reported by Moreno et al.[18] (3.5 $l^{-1} min^{-1} n_{metal}^{-1}$) and Lunsford et al.[48] (53 $l^{-1} min^{-1} n_{metal}^{-1}$), though in these papers different reactors and reaction conditions were adopted. Modifying the SBA15 support with Ti and CeO$_2$ resulted in an enhancement (approx. x 5) of the disproportionation rate with respect to the unmodified catalysts (PdAu/SBA15). This enhancement could be responsible for the decreased selectivity and productivity observed for these catalysts (Table 1). Modification with Al doubled the disproportionation rate but also enhanced the peroxide productivity (Table 1), suggesting that the direct formation of H$_2$O and H$_2$O$_2$ hydrogenation were successfully decreased by the Al (modifier), likely due to the increased Brønsted acidity[31]. The PdAu/Si catalyst had the lowest disproportionation rate, but also the lowest selectivity, which implies a high hydrogenation and water production activity.
7. Conclusions

Pd and PdAu catalysts supported on mesoporous ordered SBA15 and doped M-SBA15 (M = Al, Ti and CeO₂) were synthesized. All samples were tested for the direct synthesis and disproportionation of hydrogen peroxide. A good metal dispersion was achieved using SBA15 as support, with the majority of the metal nanoparticles in the range 5-7 nm. TEM images also confirmed that both the support structure and the metal nanoparticles size were almost unchanged before and after the reaction, revealing the stability of these catalysts at experimental conditions. Two techniques were applied for the incorporation of bromine onto the catalyst surface. Grafting of the metal containing catalysts and grafting the support before the deposition of active metal, respectively.

A synergetic effect between Pd and Au was observed when comparing mono- and bimetallic SBA15-based catalysts, both grafted and unmodified. However, the selectivity decreased when bromine was incorporated in the catalysts. Possibly the introduction of relatively bulky bromoalkyl–species caused the blocking/poisoning of the catalyst, especially when performed on the support before the active metal deposition. Ordered mesoporous SBA15 catalysts were compared to unordered SiO₂ based catalysts under identical experimental conditions. The performance of the latter catalysts was inferior compared to the SBA15-based ones, confirming the advantage of using an ordered mesoporous support. The catalyst showing the best performance (PdAu/SBA15) was modified to gain more surface acidity. Higher productivity and slightly higher selectivity were achieved incorporating Al into the framework, whereas the other modifiers (i.e. Ti and CeO₂) did not improve H₂O₂ productivity. The improved performance of the PdAu/Al-SBA15 catalysts were attributed to the increased number of Brønsted acid sites including Al into the support framework. Modification of this catalyst with bromine was confirmed to impair both productivity and
selectivity, possibly due to the broader particle size distribution and the poor stability of the metal nanoparticles.

After complete $\text{H}_2$ conversion, the disproportionation reaction was also investigated. Assuming a first order reaction rate, disproportionation kinetic constants were calculated from the experimental data. The values calculated were in the range of $4-20 \, l\text{min}^{-1} \text{m}^{-1}$. It was apparent that this reaction had a remarkably slower time scale compared to the $\text{H}_2\text{O}_2$ formation, suggesting that the peroxide destruction mainly occurs upon the hydrogenation step, regardless of the support and the active metal content of the catalyst.

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