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INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI

*Investigation of H<sub>2</sub>O<sub>2</sub> direct synthesis on model catalysts*

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*A Gabriele, per avermi insegnato  
il valore della Vita e delle relazioni.*





*'Was sagt dein Gewissen?' - 'Du sollst der werden, der du bist.'*  
*'Che cosa dice la tua Coscienza?' - 'Tu devi diventare ciò che sei.'*

— Friedrich Nietzsche, *La Gaia Scienza*



## ABSTRACT

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The present work investigate the direct synthesis of hydrogen peroxide catalyzed by a model catalyst made of pure palladium, the most suitable active metal for the studied reaction. The latter is carried out in a batch autoclave of ca. 100 ml made of AISI136 and stirred at 1500 rpm; reaction conditions are atmospheric temperature and moderate pressure (higher than 20 bar), with methanol as the solvent in which gaseous hydrogen and oxygen dissolve, with carbon dioxide acting as inert, and no bromides or acids as promoters. Iodometric titration is employed to analyzed the  $H_2O_2$  produced.

First of all the study verified if, as suggested in literature, a well ordered superficial structure of the catalyst, a peculiar characteristic of the model catalyst, leads to higher productivities toward  $H_2O_2$ ; this is done by comparing different catalysts, that is a commercial pellet, a polycrystalline disk and a monocrystalline one.

Further, taking advantage of the surface science's techniques, a catalyst design is planned to be carried out, in a way to engineer the direct synthesis reaction: such a design is preliminary investigate by treating the catalyst surface with different gases, namely hydrogen, to perform a reduction cycle, and oxygen, to let oxides being formed on the Pd surface. The effect of these treatments are investigated both from a surface science point of view, employing XPS analysis, and from a chemical engineering one, by comparing the results in terms of  $H_2O_2$  produced.

Finally attention is given to the comparison of results coming from different types of catalysts, such as disk catalysts and commercial pellet: the different figures of merit available are analyzed and compared, identifying, in the end, the turn over frequency (TOF) in its original definition as the most suitable one.



## SOMMARIO

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Il presente lavoro indaga la sintesi diretta di acqua ossigenata catalizzata da un catalizzatore modello, costituito da puro palladio, il metallo attivo più adeguato per la reazione studiata. Quest'ultima è condotta in un reattore batch in AISI136 da 100 ml circa di volume, agitato a 1500 rpm; le condizioni operative sono temperatura atmosferica e una pressione superiore ai 20 bar, con metanolo a costituire l'ambiente di reazione in cui i gas reagenti, ossigeno e idrogeno, si dissolvono, in presenza di anidride carbonica come inerte, e in assenza di bromuri (o altri alogenuri) e acidi come promotori. L'acqua ossigenata prodotta è quindi analizzata con titolazione iodometrica.

In primo luogo lo studio verifica se, come suggerito in letteratura, una struttura superficiale ordinata del catalizzatore, garantita dal catalizzatore modello, porti a una maggiore selettività e produttività verso  $H_2O_2$ , attraverso il confronto tra tre tipi di catalizzatore diversi, i.e. un pellet commerciale, un disco di Pd policristallino e uno monocristallino, il catalizzatore modello appunto.

In secondo luogo mira a operare un effettivo 'catalyst design' sfruttando gli strumenti forniti dalla surface science nella caratterizzazione superficiale del catalizzatore modello, in modo da poter successivamente ingegnerizzare la reazione studiata. In quest'ottica vengono testati differenti trattamenti della superficie del catalizzatore, verificandone gli effetti sulla produzione di acqua ossigenata; tali trattamenti sono ottenuti esponendo il catalizzatore a un'atmosfera di puro idrogeno, per ottenere un ciclo riduttivo, e di puro ossigeno, al fine di permettere la formazione di uno strato superficiale di ossidi di palladio, ritenuti responsabili dell'attività catalitica.

Utilizzare un catalizzatore perfettamente caratterizzato (e caratterizzabile) in superficie consente di conoscere quantità e disposizione superficiale degli atomi, così da poter effettuare studi fondamentali nonché ottenere una migliore comprensione del network reattivo, finora poco conosciuto e, inoltre, fortemente condizionato dal tipo di catalizzatore utilizzato. Le tecniche della surface science, in più, promettono di poter selettivamente posizionare atomi di altri metalli nobili, in particolare oro, in modo da formare leghe PdAu che dovrebbero, secondo quanto dimostrato da studi teorici, garantire alta produttività e, allo stesso tempo, alta selettività verso  $H_2O_2$ .

Infine si pone l'accento sulle difficoltà che caratterizzano il confronto tra risultati di catalizzatori diversi, come i catalizzatori impiegati nel presente studio: differenti quantità notevoli sono investigate nei loro pro e contro e comparate, andando così a identificare nell'originaria definizione di 'turn over frequency' (TOF), cioè basata sul numero

effettivo di siti attivi, la figura di merito da impiegare per operare tale confronto.

Infatti uno dei problemi che si incontrano leggendo diversi lavori pubblicati in letteratura è proprio la mancanza di omogeneità nella presentazione dei risultati, che rispecchia la moltitudine di catalizzatori, a volte perfino esoterici, creati con lo scopo ultimo di trovare, con operazioni più di alchimia che di vero 'catalyst design', quella formula che permetta di fare il grande salto e rendere commerciale un processo basato sulla sintesi diretta, finora più volte annunciato ma mai raggiunto in realtà.

Analogo problema si è posto quando si sono dovuti confrontare risultati provenienti da un pellet altamente poroso e dal contenuto nominale di 0.5 % wt di palladio con un catalizzatore 2-D come i dischi, costituiti da puro palladio, che però espongono appunto solo una superficie piana e praticamente impenetrabile ai gas reagenti.

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Grazie al **Prof. Paolo Canu** per avermi dato l'opportunità di lavorare nuovamente assieme a lui, per le discussioni in cui sento di non dover mai mettere freno alla mia immaginazione, per il 'gossip' che non manca mai nelle nostre riunioni, per gli attestati di stima: un suo complimento andrebbe incorniciato.

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## INTRODUCTION

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Green chemistry is a term coined by Paul Anastas in the 1991 that describes the philosophy of chemical research and engineering aimed to design products and processes that minimize their impact on the nature, by avoiding the use and, mainly, the production of hazardous substances. Moreover, another focus of green chemistry is to maximize the efficiency of processes, from an atomic level (with the concept of atomic efficiency) to the whole efficiency of the industrial plant, introducing concepts like process integration and encouraging in situ synthesis.

To explain what green chemistry means in practice, [Anastas and Warner \[2000\]](#) developed the 12 principles of green chemistry, among which concepts like avoiding by-products and the advise to use catalytic reagents appear of primary importance. In that sense hydrogen peroxide is a completely green compound: it leaves, in fact, no by-products when reacting, apart from water, and allowed the extensive employment of the TS-1 catalyst discovered by Enichem in the 1990s, forming a couple of oxidant-catalyst able to increase the greenness of several synthesis of widely commercialized compounds, by allowing their production with a new, greener reaction pathway.

As a proof, in fact, [Noyori \[2005\]](#) identified three key developments in green chemistry, that is:

1. use of  $\text{scCO}_2$  as green solvent;
2. use of hydrogen in asymmetric synthesis;
3. aqueous  $\text{H}_2\text{O}_2$  for clean oxidations.

In [Chapter 1](#), therefore, the hydrogen peroxide molecule is presented, as well as few examples of newer and greener industrial synthesis, not avoiding, however, to underline the safety concerns regarding this highly reactive species.

Although  $\text{H}_2\text{O}_2$  itself is the ideal molecule searched by the green chemistry, it is not possible to state the same thing regarding its most common way of production, the so called anthraquinone autoxidation route: as explained in [§ 1.3.1](#) it allows to safely produce hydrogen peroxide in commercial amount and concentrations, but is far from being a sustainable process, producing important amounts of wastes and being characterized by high energy requests.

That is why since the 1980s a strong research has been made in investigating a different and more sustainable way to produce  $\text{H}_2\text{O}_2$ , i. e. the direct synthesis from its elements ([Chapter 2](#)): it takes advantages of the reaction between hydrogen and oxygen in presence of a

selective catalyst (usually with Pd as the active metal) and can lead directly to hydrogen peroxide without wastes production and with no purification steps required, thus minimizing the energy demand for the process.

However, despite the great efforts made by researchers all around the world, still several issues need to be overcome to make this process commercially available, among which the most important are:

- the direct contact between the two reactant gases can be carried only outside the explosive limits, forcing to operate with large excess of oxygen and low concentrations of hydrogen, with resulting difficulties in achieving commercial concentrations of  $\text{H}_2\text{O}_2$  in the products stream;
- the reaction toward hydrogen peroxide is just one of the four of the reaction network, with a strongly competitive reaction of water formation, as well as two important decomposition reactions, namely the disproportionation and the hydrogenation: these features help to reduce both selectivity and productivity of  $\text{H}_2\text{O}_2$ ;
- there is still a poor comprehension of several parameters affecting the reaction, although the presence of a great speculation in literature. In particular both experimental and theoretical works suggest that a more well-ordered surface of the catalyst would lead to higher selectivity and activity toward  $\text{H}_2\text{O}_2$ , even if no solid proof are still available.

The last concept is one of the motivation behind this thesis work, since the choice of the catalyst has been done in order to make possible to work with well-ordered catalyst surface, with the aim to demonstrate whether a more defective structure of the active metal is less suitable for the direct synthesis or not.

Two of the three catalyst tested, in fact, are disk catalysts, also called 2-D catalyst, since they only expose a 2-D surface to the reactants; among them, also, one is characterized by having a well-defined order in the atomic arrangement of the surface: as explained in [Chapter 3](#), such a catalyst is called model, and its peculiar structure allows to employ common surface science technique to investigate it.

The research presented in this thesis, in fact, has been carried out in a collaboration between two departments of the Università degli Studi di Padova, namely the Dipartimento di Ingegneria Industriale (formerly Dipartimento di Impianti e Principi di Ingegneria Chimica 'I. Sorgato') and the Dipartimento di Scienze Chimiche. The latter has provided the model catalyst and mainly led the analysis and treatments of the catalysts, whereas all the catalytic experiments (which results are presented in [Chapter 4](#)) has been conducted at the DII, as well as the analysis of the  $\text{H}_2\text{O}_2$ .

Therefore this work has also the aim to bridge chemical engineering and surface science, demonstrating that model catalyst can be effective in industrial synthesis, strictly because its well-defined atomic structure of the surface. Moreover this peculiar feature of the model catalyst allows to carry out reaction in which the catalyst have a completely characterized surface, an unthinkable situation with commercial catalysts, either obtained by impregnation or precipitation. In these the structure of active metal particles is completely random, making really hard to operate fundamental studies of, among the other, chemical reaction engineering.

Besides this, the fully characterized structure also allows to place a milestone that acts as reference in the sea of different catalysts employed in the direct synthesis, by making it clear that the comparison should be carried out using the turn over frequency (TOF) in its real definition, that is:

$$\text{TOF} = \frac{\text{grams or moles of product}}{\text{number of active sites} \cdot \text{time}}$$

Moreover, surface science techniques seem to allow to modify the catalyst's surface in a very precise and fully designable way, a real catalyst design, difficult to realize with common supported catalyst. One of the most attractive future development of this preliminary work, as pointed out in [Chapter 5](#), is to employ a bimetallic catalyst made by alloying Au and Pd, taking advantage of the characteristics of both these noble metals.

Finally [Appendix A](#) collects the technical material and, in particular, the procedures used in the experiments, as well as in the preparation of the reactants employed in the sample analysis.



## THE HYDROGEN PEROXIDE

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The aim of this chapter is to introduce the hydrogen peroxide and its properties, problematics, commercial uses as well as the ways of production.

It is fundamental to clearly understand the peculiarities of this widely used compound, in particular the problems connected with usage and production, as well as transport and storage, to subsequently be able to appreciate why the direct synthesis is such an investigated route to hydrogen peroxide. Thus a general view of its chemistry is first given, followed by a punctual explanation of the production pathways nowadays used, focusing on the so called 'anthraquinone process', the dominating way of production of  $\text{H}_2\text{O}_2$  on large scale. Finally the safety issues in the transport and storage of hydrogen peroxide are presented and discussed.

### 1.1 GENERALITIES OF THE $\text{H}_2\text{O}_2$

Hydrogen peroxide (or, according to the IUPAC nomenclature, dihydrogen dioxide) has been synthesized for the first time in the 1818 by Louis Jacques Thénard [[Thénard, 1818](#)] by reacting barium peroxide with nitric acid (later substituted with hydrochloric acid to optimize the reaction), using sulfuric acid to precipitate by product (barium sulfate). This process has been employed until the middle of the 20th century, when the anthraquinone process has taken the lead.

Hydrogen peroxide is the simplest peroxide, a class of compounds characterized by having an oxygen-oxygen single bond, a feature that makes the peroxides very reactive:  $\text{H}_2\text{O}_2$ , in fact, can be employed as both strong oxidizing and reducing agent, depending on the reaction environment.

Pure  $\text{H}_2\text{O}_2$  appears as a pale blue liquid, slightly more viscous of water and colorless when in diluted solutions. Its oxidizing capacity is so strong that it is considered a highly reactive oxygen species, making it an often used bleaching or cleaning agent. However  $\text{H}_2\text{O}_2$  can act also as a strong reducing agent, mainly with other stronger oxidizing compounds such as  $\text{NaClO}$  and  $\text{Cl}_2$ .

The  $\text{H}_2\text{O}_2$  molecule has two structural forms, the *anti* (characterized by minimum steric repulsion) and the *syn* (best hybridization between *p*-orbitals of an oxygen atom and its neighbor): the resulting anticlinal structure is a compromise between these two conformers.

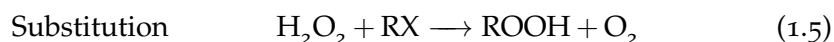
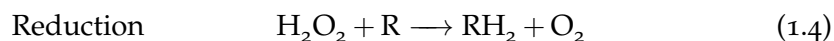
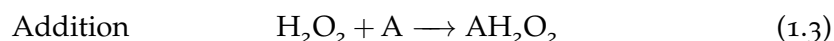
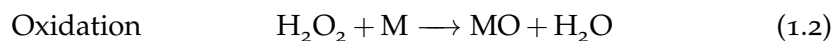
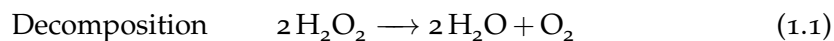
Data pertaining to molecular structure of both gaseous [[Wikipedia, 2011](#)] and solid [[Goor, Kunkel, and Weiberg, 1989](#)]  $\text{H}_2\text{O}_2$  are listed

**Table 1.1:** Molecular structure of H<sub>2</sub>O<sub>2</sub>.

Dimension	Solid	Gaseous
Bond length, O–O	0.14531 ± 0.0007 nm	147.4 pm
Bond length, O–H	0.0998 ± 0.0005 nm	95.0 pm
Bond angle, O–O–H	102.7 ± 0.3°	94.8°
Azimuthal angle	90.2 ± 0.6°	111.5°

in [Table 1.1](#). The differences between the two aggregation status are mainly due to the hydrogen bonds, that can actually influence the bond angles.

From a general point of view the reactions that H<sub>2</sub>O<sub>2</sub> can undergo are [[Campos-Martin, Blanco-Brieva, and Fierro, 2006](#)]:



The decomposition reaction occurs with disproportionation and must be carefully controlled due to its high exothermicity<sup>1</sup> and the production of gaseous oxygen, thus leading to safety concerns. The rate of decomposition depends on temperature, pH (that should be lower than 5, that is why acid is used as stabilizer), concentration of peroxide and presence of stabilizers or impurities: in fact, even few ppm of, for example, transition metals salts can negatively affect the shelf-life of H<sub>2</sub>O<sub>2</sub>. Historically this has been the reason why in the 19th century there was the belief that hydrogen peroxide was an unstable compound; nowadays the use of stabilizers avoids the risks in the commercialized products (see [Section 1.4](#) for further details).

## 1.2 APPLICATIONS

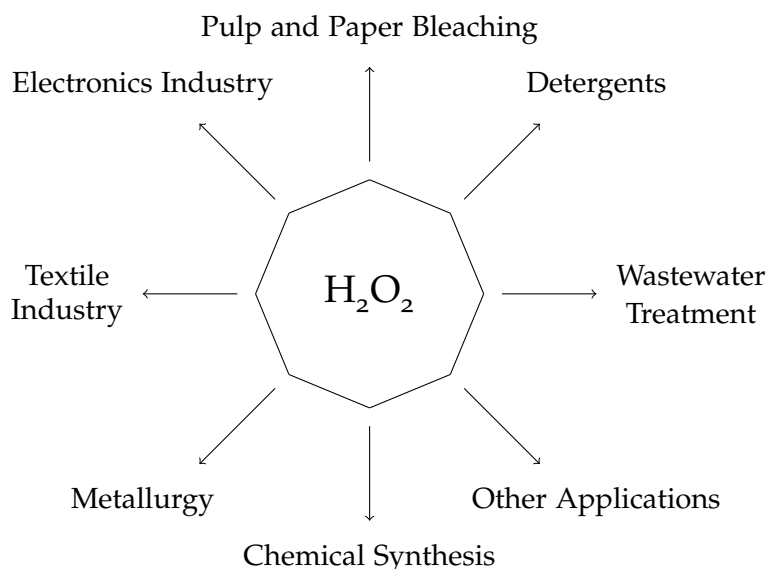
Hydrogen peroxide has a broad spectrum of everyday applications, as presented in [Figure 1.1](#): this is mainly due to its non-polluting nature, since the only by-product of its reactions is water.

The most important areas of application of H<sub>2</sub>O<sub>2</sub> are:

**BLEACHING:** as oxidizing agent mainly employed in pulp and paper industry.

<sup>1</sup>  $\Delta H_{298}^0 = -105.8 \text{ kJ/mol}$





**Figure 1.1:** Principal uses of hydrogen peroxide. Adapted from [Campos-Martin, Blanco-Brieva, and Fierro \[ivi\]](#)

**WASTEWATER TREATMENT:** used in the removal of  $\text{H}_2\text{S}$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$  and other organic compounds. Moreover  $\text{H}_2\text{O}_2$  can be used in the biological treatment of sludges and to avoid denitrification in the settling basin.

**DETERGENTS AND DISINFECTANTS:** used in the color-safe laundry bleaches, that have increasingly replaced the previously used bleaches containing hypochlorite, and in detergents in association with sodium percarbonate or sodium perborate.

**CHEMICAL SYNTHESIS:** employed in the manufacture of many organic and inorganic chemicals, such as hydrazine, bromine, cyanogen, perborates, etc. In the last decades it has been also used in the alternative ways of synthesis of propene oxide (HPPO process) and caprolactam (Sumitomo process).

**OTHER:**  $\text{H}_2\text{O}_2$  is used in electronics industry (where high purity is needed), as well as in the extraction and purification of several metals, such as uranium, copper, chromium and others.

As reported by [Centi, Perathoner, and Abate \[2009\]](#), up to 2009 the hydrogen peroxide market was in expansion, with a global consumption expected of over 4 millions of metric tons per year in the 2012, almost doubling that expected for the 2009 (equals to ca. 2.2 millions of metric tons per year). However, since the market is dominated by two companies (as reported in [Table 1.2](#)), it is actually difficult to find out updated and trusted informations about global consumption of  $\text{H}_2\text{O}_2$ .

Even if the pulp and paper industry is still the dominant demanding

**Table 1.2:** Worldwide capacity of the main producers of H<sub>2</sub>O<sub>2</sub>, adapted from Centi, Perathoner, and Abate [2009]

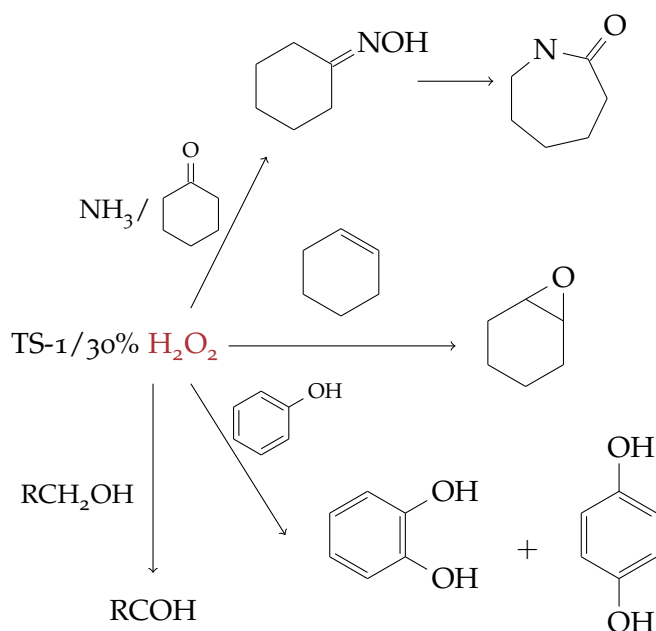
Company	Capacity	
	10 <sup>3</sup> · t/y	%
Solvay	676	27.7
Degussa	456	18.7
Arkema	306	12.5
FMC	291	11.9
Kemira	186	7.6
Eka Chemicals	175	7.2
Mitsubishi Gas Chem.	126	5.2
EkO Peroxide	64	2.6
DC Chemical	60	2.5
Degussa-Headwaters	50	2.0
Hansol	40	1.6
Ecros	12	0.5

sector, the request of H<sub>2</sub>O<sub>2</sub> in new application is rising, mainly for the production of fine chemicals. In particular the development of the TS-1 zeolite by Enichem (now Polimeri Europa) in the early 1990s has lead to greener and less complex route to the production of several commercial intermediates (see [Figure 1.2](#)), all of them using H<sub>2</sub>O<sub>2</sub> as the oxidizing agent.

Among all these processes three particularly important examples have been chosen and are explained in details in the following.

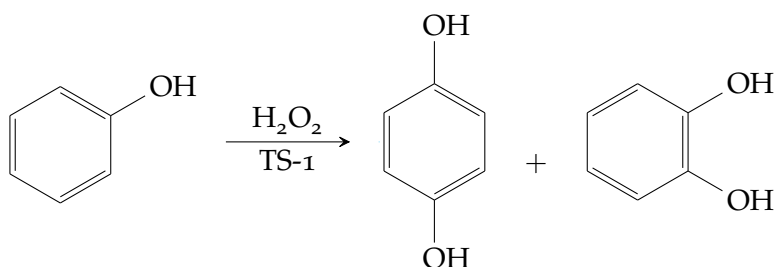
#### 1.2.1 *Production of fine chemicals using H<sub>2</sub>O<sub>2</sub>*

In the last decades the growing research for greener processes in the manufacture of fine chemicals has individuated in the couple made by TS-1 as catalyst and H<sub>2</sub>O<sub>2</sub> as oxidizing agent one of the most important tool in the green chemistry field. From that moment, in fact, a lot of well established processes for the manufacture of chemicals has begun to be re-think using a greener approach, among which the most important steps has been made in the production of hydroquinone/catechol from phenol, the ammonoxidation of cyclohexanone to cyclohexanoxime in the caprolactam manufacture and the oxidation of propene to propene oxide.



**Figure 1.2:** Possible applications of TS-1 catalyst developed by EniChem. Adapted from Lancaster [2002]

**HYDROXYLATION OF PHENOL.** Nowadays there are three processes in Europe that uses  $\text{H}_2\text{O}_2$  in the synthesis of mixtures of hydroquinone (para-isomer) and catechol (ortho-isomer), two of the three dihydroxybenzene isomers, both commercially employed as intermediates in different applications (pesticides, photography, etc.): the Rhône-Poulenc process (acid as catalyst), the Brichima process (catalyzed by radical  $\text{Fe}_2^+$ ) and the EniChem process, which employs the TS-1 zeolite. Approximately half of the diphenols produced in the world (more than 50000 t/y) are synthesized using these three processes [Centi, Cavani, and Trifirò, 2001]. In particular a 10000 t/y plant for the production of the two isomers with the EniChem process (see Scheme 1.1) began operating at Ravenna, Italy, in 1986. The EniChem process guarantees higher yield (around 90%) and selectivities (with the para isomer being favoured) com-



**Scheme 1.1:** Reaction scheme of the hydroxylation of phenol to catechol and hydroquinone. Adapted from Lancaster [2002].

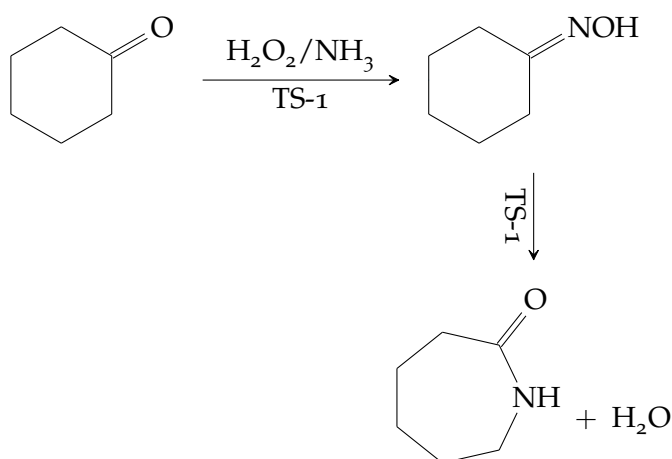
pared to the others: this is mainly related to the fact that the molecular size of the two isomers is very close to that of the catalyst's pores (i. e. shape selectivity of TS-1 zeolite), thus preventing further oxidations and maintaining high selectivities.

**AMMONOXIDATION OF CYCLOHEXANONE.** Cyclohexanone oxime, an intermediate in the production of the caprolactam (one of the two monomers for Nylon 6), is manufactured following a number of different processes, all characterized by similar drawbacks, such as the production of an important amount of wastes (e.g. ammonium sulfate). Therefore researchers have tried to find a more sustainable way of production, eventually developing a one step route using again TS-1 as catalyst and  $\text{H}_2\text{O}_2$  as the oxidizing agent (the so called EniChem-Sumitomo process, see [Scheme 1.2](#)).

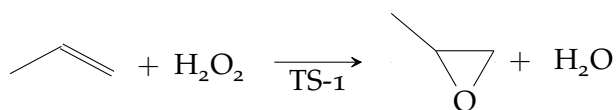
The process performances can be very high, with conversion up to 100% and a selectivity to cyclohexanoxime of 98%, but the simplification connected with the use of a single step ammonoxidation is the major advantage.

**OXIDATION OF PROPENE.** Propene oxide (PO) is one of the most important starting material in the chemical industry, being used as a precursor for the production of polyurethanes, which annual worldwide growth was, in the 2007, between 5 and 6% according to [Ullrich, Kolbe, and Bredemeyer \[2007\]](#): therefore advantages in the PO manufacturing could lead to some kind of revolution in its market (that had, by itself, an annual growth of  $\simeq 4 - 5\%$  [[Nijhuis \*et al.\*, 2006](#)]).

An important step in this sense has been made by the commercialization of the so called HPPO (Hydrogen Peroxide Propene Oxide) process from a series of company (BASF-Dow and Solvay, Uhde-Degussa): the epoxidation of propylene to propylene ox-



**Scheme 1.2:** Ammonoxidation of cyclohexanone according to the EniChem-Sumitomo process.



**Scheme 1.3:** Production of PO using  $\text{H}_2\text{O}_2$  and TS-1, adapted from Centi, Cavani, and Trifirò [2001].

ide is reached in the presence of  $\text{H}_2\text{O}_2$ , with TS-1 as catalyst, as shown in Scheme 1.3.

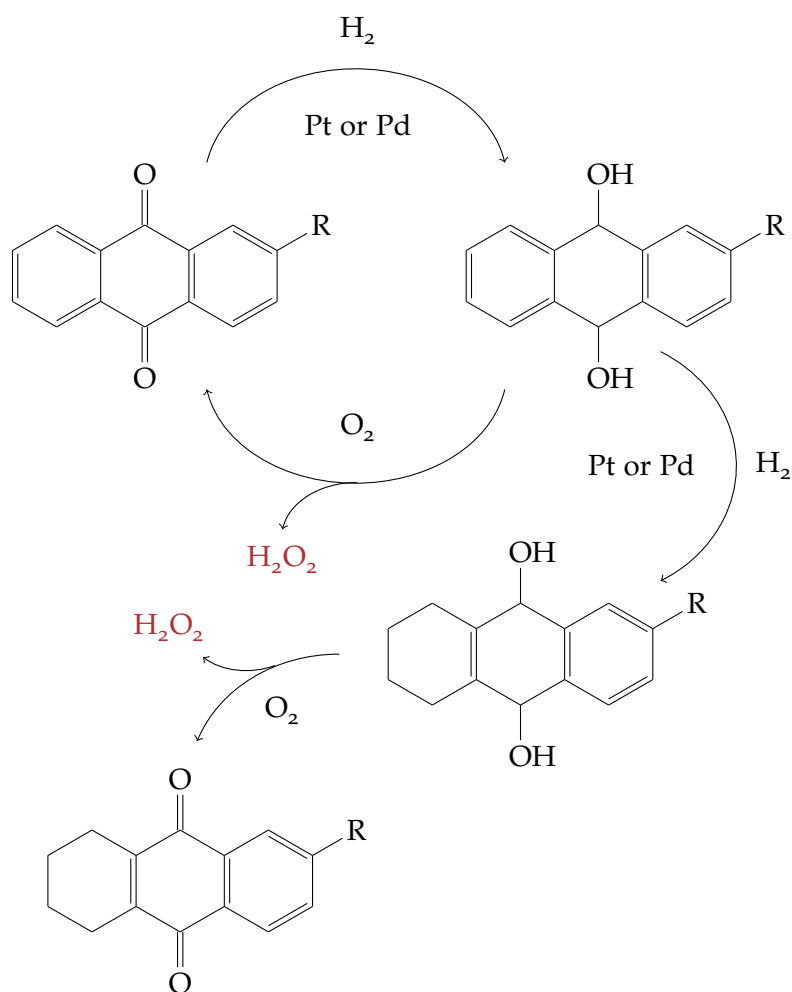
The main problem in this synthesis is the fact that, on a molar basis, propene oxide and hydrogen peroxide have comparable market values, making this process unprofitable. Therefore to make a breakthrough there is the need for:

- large plant and process integration: this is the idea followed by BASF-Dow and Solvay, that have established a partnership to build a 230000 t/y  $\text{H}_2\text{O}_2$  supply plant in Antwerp [Tullo, 2004], close to the BASF-Dow HPPO plant (*in situ* production of  $\text{H}_2\text{O}_2$ ), that has started operations in November 2008 [Cavani and Gaffney, 2009], and have announced another HPPO plant in Map Ta Phut, Thailand with a capacity of 390000 t/y of PO, with a coupled 330000 t/y  $\text{H}_2\text{O}_2$  plant next to it, the latter being the largest plant of that type worldwide [ivi].
- simpler technology, i.e. direct synthesis of  $\text{H}_2\text{O}_2$  from its elements (DSHP). Degussa-Evonik and Headwaters Nanokinetix have built a demonstration unit able to produce thousand of metric tons per year of diluted  $\text{H}_2\text{O}_2$  in 2006 [ivi] and have announced the construction of a 200000 t/y plant that should have been completed in 2010 [Centi, Perathoner, and Abate, 2009], based on the NxCat<sup>TM</sup> from Headwaters Nanokinetix; moreover, once the commercialization of the first DSHP process has been completed, there is aim to shift the supply of the SKC's HPPO plant (100000 t/y), built in the 2008 in South Korea, from  $\text{H}_2\text{O}_2$  obtained with the traditional AO process with hydrogen peroxide from the DSHP [ivi].

Therefore there is, under the push of the green chemistry, an increasing number of industrial processes that uses  $\text{H}_2\text{O}_2$  as a crucial reagent, leading to a higher hydrogen peroxide demand, that is at the same time a strong demand for a greener, simpler and more economical way to produce it.

### 1.3 PRODUCTION

Almost all of the currently produced hydrogen peroxide is obtained with the anthraquinone autoxidation process, in which hydrogen, oxy-



**Scheme 1.4:** Reaction scheme for the anthraquinone autoxidation, according to the cyclic Riedel-Pfleiderer process. Adapted from [Campos-Martin, Blanco-Brieva, and Fierro \[2006\]](#).

gen and an anthraquinone derivative (typically the 2-ethylanthraquinone) are employed in the reaction cycle, with the latter acting as the 'reaction carrier'. Other ways of production are the so called 2-propanol route, i.e. obtaining H<sub>2</sub>O<sub>2</sub> from the oxidation of alcohols, and the electrochemical synthesis. Further there are few emerging alternatives, among which the direct synthesis appears to be the most promising one.

In this section the AO process will be introduced and described, as well as the other large scale production pathways, with the aim of demonstrate how desired and attractive can be the direct synthesis route to H<sub>2</sub>O<sub>2</sub>.

### 1.3.1 The AO process

The anthraquinone autoxidation is exemplified in [Scheme 1.4](#), in which a 2-alkylanthraquinone (AQ) is hydrogenated to give a 2-alkylanthrahydroquinone (AHQ), that can undergo two pathways:

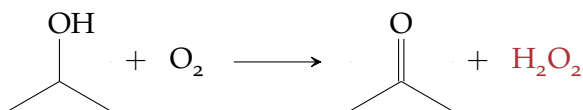
- an oxidation to give back to the initial 2-alkylanthraquinone and hydrogen peroxide, with a molar ratio 1 : 1;
- an ulterior hydrogenation to a 5,6,7,8-tetrahydroanthrahydroquinone (THAHQ, a side product of the first hydrogenation), that can in its turn be oxidized to a tetrahydroanthraquinone (THAQ), with again  $\text{H}_2\text{O}_2$  formed as co-product, still in equimolar amount.

$\text{H}_2\text{O}_2$  is then stripped from the mixture of solvent used as the reaction medium (i.e. the working solution) with demineralized water, to form a 30%wt solution, with a maximum recover around 95% of the theoretical amount of hydrogen peroxide; this aqueous  $\text{H}_2\text{O}_2$  is then distilled to remove impurities and concentrate the product up to 70%, whereas the solvent/anthraquinone mixture is recycled.

The proposed [Scheme 1.4](#) is only a simplified description of the reaction system, since a series of side reactions can occur in the process, all of them contributing to a net consumption of anthraquinone, as well as in the production of an important amount of byproducts and wastes.

The main advantages of this process are the high yield of  $\text{H}_2\text{O}_2$  for cycle and the fact that hydrogen peroxide is continuously produced without direct contact of  $\text{O}_2$  and  $\text{H}_2$  at mild conditions: this is the reason why more than 95% of the consumed  $\text{H}_2\text{O}_2$  is produced with this method. However the AO process has still important drawbacks:

- difficulties in controlling key factors like the  $\text{H}_2/\text{AQ}$  ratio and the AQ residence time in the first hydrogenation step lead to a huge amount of by-products (mainly due to overhydrogenation of AQ and solvent), that must be removed from the reaction medium continuously;
- cross-contamination of phases due to the contact between water and working solution during the liquid-liquid extraction (aqueous  $\text{H}_2\text{O}_2$  is contaminated by organic compounds);
- considerable energy consumption in the distillation of both concentrated and purified  $\text{H}_2\text{O}_2$ ;
- purification of the working solution leads to production of wastes;
- mass-transport limitations in both hydrogenation and oxidation reactors;



**Scheme 1.5:** The Shell process, adapted from [Goor, Kunkel, and Weiberg \[1989\]](#)

- process complexity.

Therefore the AO process is far from being a sustainable and green one, thus making reasonable to look for a more environmental friendly method of production; moreover the complexity of the anthraquinone route makes it suitable only for large-scale productions, whereas nowadays there is an increasing need for small onsite ones [[Centi, Perathoner, and Abate, 2009](#)], in order to minimize risks connected with transport of concentrated  $\text{H}_2\text{O}_2$  and to avoid the use of stabilizers to inhibit the decomposition reaction.

### 1.3.2 Other processes and future perspectives

Besides the AO process there are some alternatives for manufacturing hydrogen peroxide, even if only few of them have been commercially applied.

The so called Shell process [[Goor, Kunkel, and Weiberg, 1989](#)] is based on the discover made by Harry in the 1945 that secondary alcohols react with oxygen to give  $\text{H}_2\text{O}_2$  and an aldehyde or ketone; in particular, when the alcohol is the 2-propanol there is an industrial interest, since the co-product is acetone, as shown in [Scheme 1.5](#).

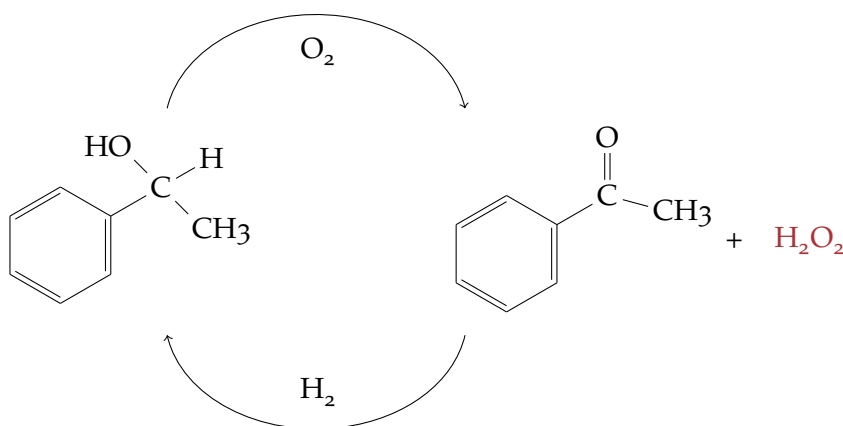
This reaction needs no catalyst, since it is catalyzed by the hydrogen peroxide produced, and is carried out with low conversion of 2-propanol to reduce by-products (e.g. acetic acid). Between 1957 and 1980 Shell Chemical used this route in Norco (United States), but made only a small contribution to the hydrogen peroxide production (annual production capacity of around 15000 t).

Lyondell Chemical and Repsol Química have developed (in parallel) a process that leads to  $\text{H}_2\text{O}_2$  via oxidation of a methylbenzylalcohol (MBA), a coproduct of the PO/styrene process, following the scheme shown in [Scheme 1.6](#). The patent claims a MBA conversion of 32% and a selectivity toward hydrogen peroxide up to 97%, leading to a content of the latter in the liquid phase of approximately 7.5%, higher than the one achieved in the AO process. Further details can be found in literature [[Campos-Martin, Blanco-Brieva, and Fierro, 2006](#)].

Electrochemical production of hydrogen peroxide can follow different ways:

- electrolysis of a dilute solution of NaOH in an electrochemical cell (Dow process);





**Scheme 1.6:**  $\text{H}_2\text{O}_2$  synthesis by oxidation of MBA. Adapted from [Campos-Martin, Blanco-Brieva, and Fierro \[ivi\]](#).

- oxidation of sulfuric acid in the Degussa-Weissenstein process;
- electrolysis of ammonium hydrogen sulfate solutions in the Münchner and Riedel-Loewenstein processes.

This productive alternative is of minor industrial importance, even if used in past (mainly in the first half of the last century).

Emerging alternatives are photocatalysis, in which  $\text{H}_2\text{O}_2$  is formed at the surface of semiconductor oxides under UV irradiation, direct and continuous production in inexpensive fuel cells (that do not require electrical energy unlike electrolytic devices), and direct synthesis from its elements, that are gaseous hydrogen and oxygen. The latter will be described in details in [Chapter 2](#).

#### 1.4 SAFETY

Hydrogen peroxide is usually available on the market as aqueous solutions at concentration of 35, 50 and 75% wt or in solutions at lower concentrations (from 3 to 6% wt), like those available in the pharmacies as disinfectants. High concentrations are desired since lead to lower transport costs (due to the handling of hazards), but, on the other hand, the production costs increase due to the difficult purification steps necessary.

Great care must be taken in every operation connected with hydrogen peroxide to prevent impurities from entering the  $\text{H}_2\text{O}_2$  solutions and to ensure that the storage tanks and transport containers, usually made of Al, Al–Mg alloys, stainless steel or polyethylene<sup>2</sup>, are perfectly clean, since few ppm of impurities can act as catalyst for the decomposition reaction. That is the reason why stabilization of

<sup>2</sup> Usually employed for solution with concentrations up to 50% wt, due to its corrosion resistance.

commercial solutions (that always contain traces of impurities) is extremely important, as well as to counter unavoidable impacts during transport: stabilizers (usually sodium pyrophosphate, sodium stannate or tin-based compound for high concentrated solutions, acetanilide or other organic compounds for low concentrated) have the function of inhibit the decomposition reaction, that is not only a concern for the product integrity, but also a safety issue, since it can produce gaseous oxygen and free a high amount of heat.

In fact even common domestic products based on  $H_2O_2$ , such as disinfectants, detergents or solutions for contact lenses, can cause damages to clothes (bleaching to a pink color), surfaces and persons: for example, if a solution containing hydrogen peroxide is ingested, it may decompose in the stomach giving molecular oxygen, thus highly increase the pressure (ten times the ingested volume for a solution at 3%), causing internal emorragies.

Other important risks are those connected to the fact that  $H_2O_2$  solutions, although being nonflammable, can still cause ignition of flammable material, leading to an immediate fire, further fed by the oxygen deriving from the decomposition; moreover hydrogen peroxide vapours can cause a bleve even at atmospheric pressure.

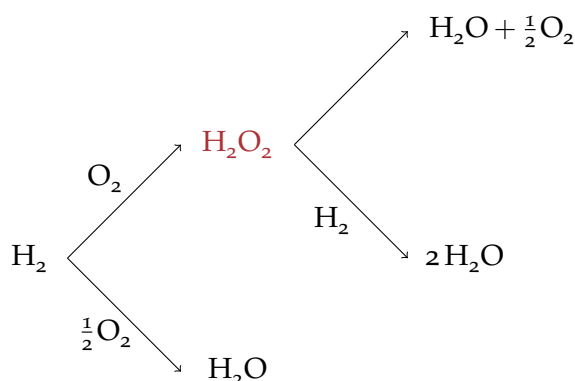
Therefore hydrogen peroxide must be handle with care: its R-phrases are R5, R8, R20/22, R35, whereas the S-phrases are S1/2, S17, S26, S28, S36/37/39, S45. All of them are listed in the [Appendix A](#).

DIRECT SYNTHESIS OF  $\text{H}_2\text{O}_2$ 

The direct synthesis of hydrogen peroxide from gaseous hydrogen and oxygen is a well-known reaction since 1914 [Henkel and Weber, 1914], as well as its drawbacks: the main reaction, in fact, is always accompanied by several side reactions, as clearly described in Scheme 2.1.

The presence of subsequent side-reactions mainly affects negatively the selectivity toward  $\text{H}_2\text{O}_2$ : in particular the competing reaction of water formation is thermodynamically more favourable (with a  $\Delta H = -241.6$  kJ/mol compared to a  $\Delta H = -135.8$  kJ/mol), leading to the formation of important amounts of water. In addition, since all four reactions (two of synthesis and two of decomposition) are highly exothermic and therefore favoured by similar operative conditions, the  $\text{H}_2\text{O}_2$  formed is not that stable, but can easily be converted into water via hydrogenation or disproportionation, again decreasing both selectivity and productivity.

Hence the choice of the catalyst appears to be crucial: in fact there is the need for a compound able to enhance the interesting reaction in spite of the water formation one, and, at the same time, not catalytically active for the decomposition reactions, mainly the hydrogenation one. As one can immediately understand the requests are difficultly satisfiable: that is the reason why a great effort has been made in the last decades in searching a performant catalyst for the direct synthesis, without avoiding even exoteric solutions. Thus a great variety of catalysts can be found in literature, among which common elements can still be found, such as the active metal, almost always Pd



**Scheme 2.1:** Reactions involved in the  $\text{H}_2\text{O}_2$  direct synthesis. Adapted from Zancanella [2010].

or Pd alloys, and the solvent (methanol or methanolic (CH<sub>3</sub>OH-H<sub>2</sub>O) solutions).

Apart from the needs to increase the H<sub>2</sub>O<sub>2</sub> selectivity, another main concern is safety: mixtures of hydrogen and oxygen (or air) are explosive over a wide range, namely 4 – 94% mol of H<sub>2</sub> in O<sub>2</sub> (or 4 – 75% mol in air) [Centi, Perathoner, and Abate, 2009]. In the past few years a lot of patents have been issued with the direct synthesis carried out inside the explosive range (e.g. DuPont, BASF [ivi]), but after the explosion of a pilot-scale reactor at DuPont, higher attention has been given to safety aspects. Nowadays, in fact, nearly all the research is conducted outside the explosive range, in particular below, i.e. with hydrogen as the starving reactant, in order to limit the rate of the undesired hydrogenation reaction. In particular an elegant solution can be the use of an inert, such as N<sub>2</sub> or CO<sub>2</sub>, to reduce the explosive range, as employed also by Eni [ivi].

In the following of the chapter an overall view of the state of the art of direct synthesis is presented, focusing on catalysts employed, reactors design and operative conditions.

## 2.1 STATE OF THE ART AND RECENT ADVANCEMENTS

Direct synthesis of hydrogen peroxide from its elements, although being well-known since the beginning of the 20th century, only from the '80s has been intensively studied in companies and universities, with a focus mainly on catalysts and reactors design.

As already stated above, a great variety of catalysts has been studied and tested, nearly all of them based on Pd as the active species: few

**Table 2.1:** Selection of catalysts used in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Also the reaction medium and operative conditions are reported. Adapted from [ivi].

Company	Catalyst	P bar	T °C	Solvent
CSIR	5%Pd/Al <sub>2</sub> O <sub>3</sub>	1	30	H <sub>2</sub> O + Br/H <sub>3</sub> PO <sub>4</sub>
Degussa	0.25%wt Pd-Au (95:5)/α-Al <sub>2</sub> O <sub>3</sub>	50	25	CH <sub>3</sub> OH + Br/H <sub>3</sub> PO <sub>4</sub>
Repsol	1.5%Pd on Lewatit K2641	100	40	CH <sub>3</sub> OH-H <sub>2</sub> O (96:4) + HBr
Eni	Pd (1%)-Pt(0.1%) on carbon	100	6	CH <sub>3</sub> OH-H <sub>2</sub> O (95:5) + HBr + H <sub>2</sub> SO <sub>4</sub>

examples are given in [Table 2.1](#).

The reaction medium is usually methanol or a methanol-water solution (typical ratio 95 : 5, according to [Centi, Perathoner, and Abate \[ivi\]](#)), mainly because the solubility of both gaseous reagents is higher in organic solvents compared to that in pure water: [Zhou \*et al.\* \[2003\]](#), in fact, stated that the productivity of  $\text{H}_2\text{O}_2$  depends linearly from a parameter called Solvent Selection Parameter ( $\text{SSP}^1$ ), which is of one order of magnitude higher for methanol compared to water.

However care must be taken when dealing with organic solvent, since they further limit the range of operative concentrations that avoid explosive mixture, being larger the explosion limit for the mixture  $\text{CH}_3\text{OH} - \text{H}_2 - \text{O}_2$  (in particular it is risky to operate with high concentration of oxygen).

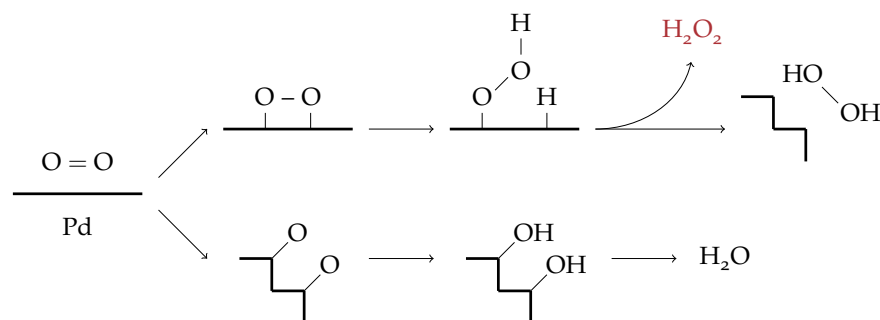
Apart from these observations, the choice of the solvent has to be connected to the final use of  $\text{H}_2\text{O}_2$ : if methanol is the perfect solvent for a hydrogen peroxide to be used in the oxidation of propene, avoiding the separation and purification steps and thus positively affecting the cost effectiveness of the whole process, on the other hand water remains necessary for application in wastewater or bleaching treatments.

Finally  $\text{scCO}_2$  appears to be an interesting and potentially clean solvent, even if a  $\text{CO}_2$ -soluble catalyst must be used and the results are still unsatisfactory for industrial applications. Rather than using (supercritical) carbon dioxide as the reaction medium, it could be used as an inert to reduce explosion risks in hydrogen and oxygen mixtures: in fact, when compared to other inert such as nitrogen,  $\text{CO}_2$  has the advantage to expand organic solvents (like methanol), enhancing their properties, in particular  $\text{H}_2$  and  $\text{O}_2$  diffusivity. This could lead to higher productivity and selectivity, as preliminary studies using  $\text{CO}_2$ -expanded methanol seems to prove [[Centi, Perathoner, and Abate, 2009](#)].

Another typical feature in the direct synthesis of  $\text{H}_2\text{O}_2$  is the presence of promoters such as  $\text{NaBr}$  or  $\text{HBr}$ , preferred compared to chlorine ions (mainly because of corrosion problems and possibility of gaseous  $\text{Cl}_2$  production), typically in small amounts (few ppms): they are responsible for increasing both productivity and selectivity, even if [Centi, Perathoner, and Abate \[ivi\]](#) state that their effect is of secondary order, remaining thus surprised by the large number of publications that deal with their effects. [Ford \*et al.\* \[2010\]](#) suggest that the enhancement in  $\text{H}_2\text{O}_2$  production and selectivity connected to these halogen compounds is obtained by a combination of geometric and electronic effects on avoiding or reducing the cleavage of the O—O bond.

Nevertheless the use of such compounds give rise to problems of pu-

<sup>1</sup>  $\text{SSP} = \sum_i w_i S_i$ , with  $w_i$  is the weight fraction of solvent component 'i' and S the solubility of hydrogen in the pure component at standard conditions.



**Figure 2.1:** Role of defects of the Pd surface in lowering the selectivity toward H<sub>2</sub>O<sub>2</sub>. Adapted from [Centi, Perathoner, and Abate, 2009]

rifications and production of wastes, so to maintain the greenness of this process they should be avoided.

In patents and in literature a common observation is that the addition of acid or the use of an acidic support for the catalyst promotes the selectivity, since it is well known that H<sub>2</sub>O<sub>2</sub> is more stable in an acid medium; the presence of a strong acid, however, could lead to corrosion and purification problems, whereas the employ of an acidic support appears to be a less problematic solution, minimizing the need for acid in solution and, at the same time, avoid re-adsorption of H<sub>2</sub>O<sub>2</sub>, thus reducing the rate of the two decomposition reactions. Therefore zirconia, sulphatated zirconia or fluorinated alumina has extensively been used as support for Pd [Melada *et al.*, 2006; Zancanella, 2010].

One of the most interesting innovation in the last year has been presented by Headwater Nanokinetix Inc. (former HTI) in their project 'Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology' [Centi, Perathoner, and Abate, 2009] and in subsequent patents [Cavani and Gaffney, 2009], in which an innovative nanocatalyst called NxCat™ is presented, claiming its ability of achieving higher selectivities than the usually reported (around 70 – 80%). The key feature of this catalyst is that the preparation method allows to obtain a top layer of metal atoms with a controlled nearest-neighbor coordination number of 2 and to stabilize medium-small supported Pd particles (dimensions < 5 nm) doped with Pt, with a preferential exposition of the 110 crystal face, to which the high selectivity is associated [ivi]. In fact it is claimed that this particular superficial structure hinders the four electron reduction of oxygen, that would lead to water formation, allowing only a two electron reduction, that is the desired one. Even though no solid proof are still available to prove that explanation, it is, however, a pretty common idea that a more irregular and defective structure of Pd-crystallites leads to a lower rate of H<sub>2</sub>O<sub>2</sub> synthesis, even if the metal surface area is higher compared to a more reg-

ular crystal [Centi, Perathoner, and Abate, 2009]. A simplified model of this idea is shown in Figure 2.1.

As a matter of fact these considerations are some of the reasons behind the catalysts' choice made in this work, i. e. a polycrystalline Pd disk and a model catalyst: the peculiar superficial structure of the latter, which will be discussed and clarified in Section 3.2, allows to expose to the reactants an ordered and well characterized surface (to which a certain Miller index is associated), leading to obtain experimental proofs to the theoretical beliefs by comparing its results to those of the polycrystalline Pd, that, on the other hand, exposes to the gases a non ordered superficial distribution of atoms.

Apart from monometallic catalysts, bimetallic catalysts are another area of great interest for researchers, both from a theoretical [Ham *et al.*, 2009; Joshi, Delgass, and Thomson, 2007; Li, Ishihara, and Yoshizawa, 2011] and an experimental [Bernadotto *et al.*, 2009; Biasi *et al.*, 2011a; Zancanella, 2010] point of view. In particular gold is, usually, the chosen metal in the Pd alloy: in fact, as clearly stated in the work made by Ford *et al.* [2010], Au is the only transition metal that shows a prevalence for the formation of  $\text{H}_2\text{O}_2$ , while Pd leads preferentially to a complete reduction to water via an associative mechanism. The reasons why gold acts in such a way are:

- $\text{H}_2\text{O}_2$  formation is barely activated and substantially less activated than OOH dissociation, that is it should take place more easily;
- hydrogen peroxide formation is also less activated than its decomposition paths, either via O–O bond scission or via dehydrogenation;
- O–O bond scission in  $\text{H}_2\text{O}_2$  is least exothermic on Au, compared to other transition metals (like Pd, Pt, Ag).

However Au shows a very low thermochemical activity: that is why, even if the  $\text{H}_2\text{O}_2$  route is the prevalent, the metal is not able to catalyze it, mainly because of the poor  $\text{O}_2$  coverage. So Ford *et al.* [ivi] suggest that a good compromise could be the combination of Au with a more active metal, namely Pd, to form a bimetallic alloy able to preferentially catalyze the desired pathway; however, a good compromise should be achieved in the catalyst composition, since it is true that higher is the Au concentration and higher is the selectivity, but lower the  $\text{H}_2$  conversion.

In that sense Nomura *et al.* [2008] experimentally proved that the highest  $\text{H}_2\text{O}_2$  formation rate and selectivity is achieved with a molar concentration of Au over Pd of 15%.

Other recent studies compared the performance of a Pd catalyst with those of a AuPd, both in the formation of  $\text{H}_2\text{O}_2$  [Li, Ishihara, and Yoshizawa, 2011] and the decomposition and hydrogenation of

the formed H<sub>2</sub>O<sub>2</sub> [Li *et al.*, 2011].

From Density Function Theory calculation the authors have been able to prove that:

1. the concentration of H atoms over Au is very low, whereas hydrogen easily adsorbs and dissociates at the Pd sites, making the Au atoms like islands in a sea of H;
2. O<sub>2</sub> atoms will be adsorbed at the top-bridge-top site on one Pd atom and one Au atom;
3. competition between the main reaction (formation of H<sub>2</sub>O<sub>2</sub>) and the side reactions is actually a competition between the two O–O and M–O bonds, with M being Pd (when the catalyst is pure palladium) and Au (with the alloy AuPd): in the first case the Pd–O bond is stronger than the O–O in OOH intermediates and in H<sub>2</sub>O<sub>2</sub>, thus the side reactions exceed the main one, whereas Au–O cannot compete with O–O bond, leading to an easy release of produced H<sub>2</sub>O<sub>2</sub> from the AuPd surface and a strong reduction of the side reactions involving O–O cleavage;
4. all the side reactions, namely decomposition and hydrogenation of H<sub>2</sub>O<sub>2</sub>, are O–O bond dissociation processes.

Therefore even these theoretical studies advise to employ the AuPd alloy as catalyst for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, being able to suppress all side reactions and, at the same time, favour the formation of hydrogen peroxide.

Finally, with regard to the reactor design, the most attractive solution, in the last decades, seems to be the use of a microreactor, employed both for theoretical [Voloshin and Lawal, 2010] and industrial purposes, as proposed by Degussa and FMC [Centi, Perathoner, and Abate, 2009].

Microchannel reactors allow to operate safely with hydrogen concentrations higher than 5%, since the characteristic dimension of void spaces is smaller than the quenching distance of hydrogen and oxygen radicals. Past works available in literature [Janicke *et al.*, 2000; Veser, 2001] showed that hydrogen-oxygen explosions, caused by radical-propagated chain reaction, is practically impossible in microreactors.

However such a reactor system is suited only for small-scale application, being too high the costs on a larger scale, and still there are problems in long-term operations.

Despite that, two of the main H<sub>2</sub>O<sub>2</sub> producers, FMC and Degussa, are trying to develop a microchannel system to be used in the direct synthesis, mainly coupled with the propene epoxidation, since it seems not so far to meet the requirement of a 5%wt of H<sub>2</sub>O<sub>2</sub> needed in the PO production.

In fact FMC has been able to achieve, in collaboration with Stevens



Institute of Technology, a production of more than 2%wt of  $\text{H}_2\text{O}_2$  with a single channel reactor and is now undergoing optimization processes, whereas Degussa has performed a pilot demonstration of microreactor technology on the scale of 8 t/y for the production of PO using  $\text{H}_2\text{O}_2$  as the oxidizing agent, showing very stable and safe reactor operations, even if the reactants are well within the explosive range of concentrations [Centi, Perathoner, and Abate, 2009].

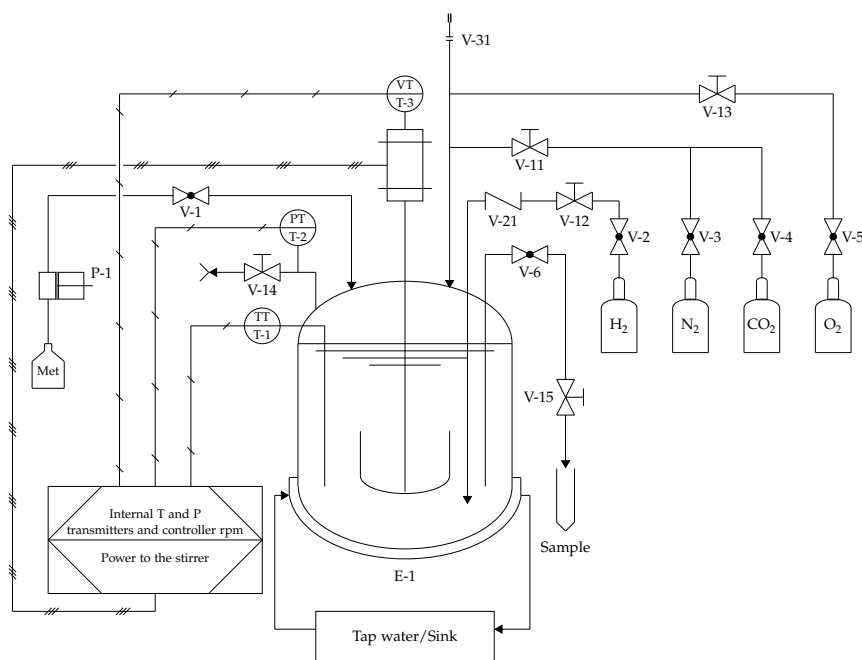


## EXPERIMENTAL INSTRUMENTATIONS AND PROCEDURES

The experimental instrumentations used in the thesis work will be described in the following chapter, starting with the reactor autoclave in [Section 3.1](#), followed in [Section 3.2](#) by the types of catalyst tested, focusing mainly on the monocrystalline Pd and its properties. Finally, in [Section 3.3](#) the analytical part is pointed out, underlying peculiarities and problems in the methodic utilized, while in [Section 3.4](#) the procedure followed during each experiment is showed, with, in conclusion, some considerations about the explosion limits.

### 3.1 THE AUTOCLAVE REACTOR

The complete plant employed in all the experiments presented in this work can be appreciated in [Figure 3.1](#): the reactor (visible also in [Figure 3.2](#)) is an autoclave of the american Autoclave Engineers and has a nominal volume of 120 ml that, taking into account all the objects inside (i. e. stirrer, catalyst and its support, thermocouple, hydrogen feed line and the sampling line, all visible in [Figure 3.3](#)), is reduced to a free volume of around 100 ml. The material is stainless steel AISI136



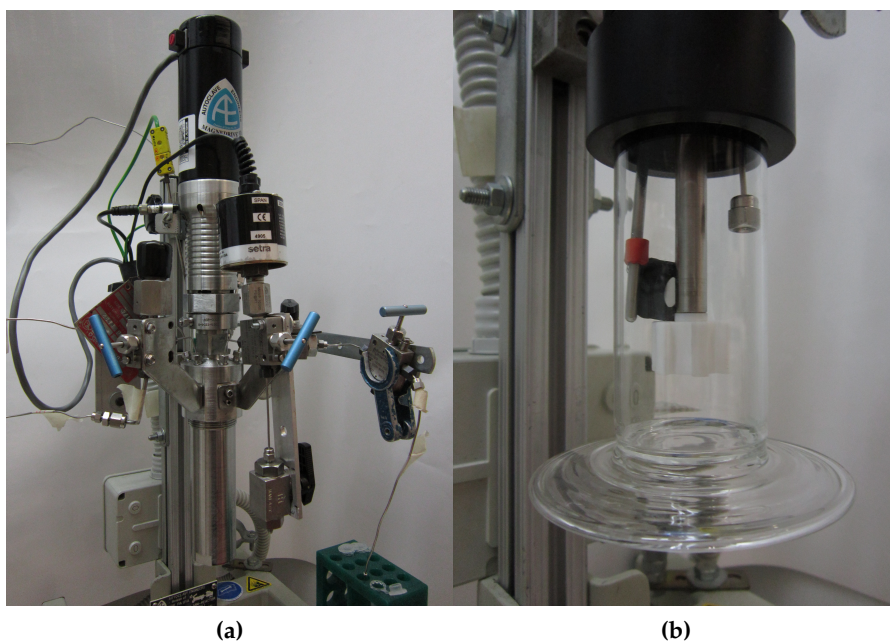
**Figure 3.1:** Scheme of the experimental apparatus used in the experiments. Adapted from [Zancanella \[2010\]](#).

**Table 3.1:** Description of the equipments of the experimental apparatus schemed in [Figure 3.1](#).

Name	Description
E-1	Reactor
V-1	Ball valve
V-2	Ball valve
V-3	Ball valve
V-4	Ball valve
V-5	Ball valve
V-6	Ball valve
V-11	Needle valve
V-12	Needle valve
V-13	Needle valve
V-14	Needle valve
V-15	Needle valve
V-21	Check valve
V-31	Rupture disc
T-1	Termocouple
T-2	Pressure transmitter
T-3	Magnetic rpm gauge
P-1	HPLC pump

with a micrometrical film of chromium oxide as protective barrier for the stainless steel, that helps, at the same time, to maintain the stability of  $\text{H}_2\text{O}_2$ , highly reactive with Fe. The stirring is provided by an Autoclave Engineers MagneDrive, in which agitation is obtained with the rotation of external magnets that actuates the internal magnets attached to the shaft, that ends with a radial impeller in PTFE (see [Figure 3.3](#)): the choice of such an impeller has been made mainly for its inertia to the reaction, while the type (radial vs axial) derives from dedicated tests carried out with a glass reactor (visible in [Figure 3.2](#)), from which has been also observed that a velocity of 1500 rpm is enough to thoroughly mix the solution and to renew the gas-liquid contact surface.

Internal temperature is analyzed with a thermocouple, while a transducer measures the pressure: all these devices are connected with a tablet pc, in which a dedicated program allows to register all data (i. e. temperature, pressure, impeller's rpm, power to the shaft) and control the velocity of the stirrer.



**Figure 3.2:** Reactors employed in this work: **(a)** front view of the autoclave; **(b)** glass reactor.

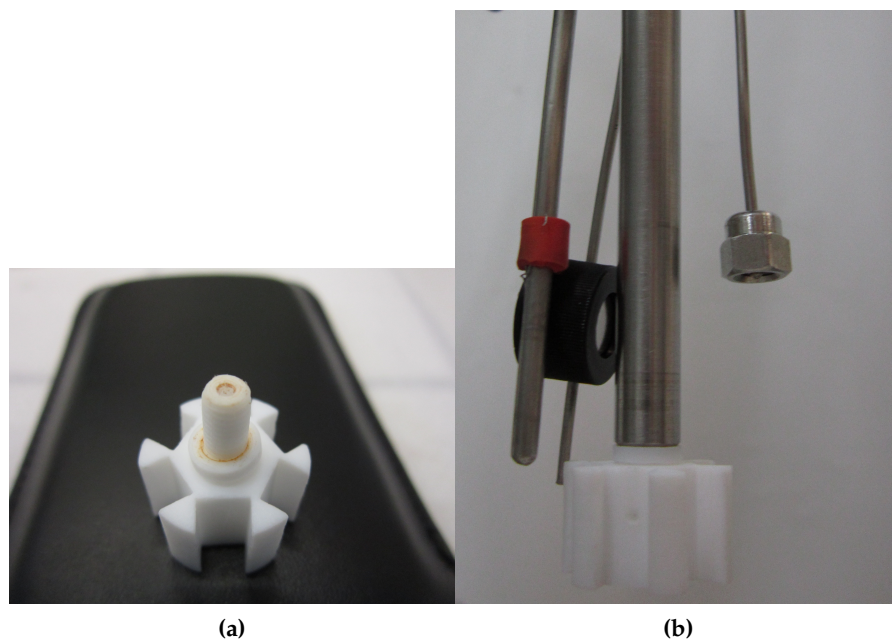
Between the gas tanks and the reactor several ball valves allows to intercept the gases, whereas needle valves are employed to carefully measure out the amount of each compound introduced in the autoclave. All connections are made in stainless steel and have a diameter of  $1/16''$ , except the sample line that have a HPLC pipe of  $1/16''$ , but with a smaller internal diameter.

Hydrogen, due to its intrinsic dangerousness, is fed via a dedicated connection that has, after the needle valve, a check valve in order to avoid back mixing and assure security while carrying the reaction. Nitrogen and carbon dioxide are fed using the same pipe, alternatively connected with the respective tank, so that the number of total valves needed is reduced.

Since operative pressure is usually higher than 20 bar, in case of uncontrolled increase of pressure the reactor is equipped with a rupture disk, again as a security feature.

Temperature is controlled with a jacket that uses tap water, since operative temperature never exceed  $20\text{ }^{\circ}\text{C}$ , so such a solution is enough to carry out the reaction at constant ambient temperature.

Finally, a HPLC Shimadzu pump is employed to feed methanol, with a ball valve to reduce the risk of back mixing of gases; methanol, that goes to form the liquid reaction medium, is introduced in the quantity of 50 ml, i.e. 39.5 g, using a balance with a conical flask over it, topped to reduce losses of methanol (that is a VOC) while not in use.



**Figure 3.3:** Particulars of the autoclave reactor: **(a)** radial impeller; **(b)** internal parts: from the left, thermocouple, catalyst in its support, hydrogen pipe, stirrer and sampling line.

### 3.2 TYPES OF CATALYSTS EMPLOYED

A catalyst is a key component of a reaction, due to its ability in reducing the energetic demand to transform reagents in products, by conducting the reaction through a different reaction pathway, significantly less energy consuming compared to the non catalyzed one.

Obviously each reaction needs a proper catalyst and suitable operative conditions to let the latter operating at the best: that is why a huge effort is still made in first discover new catalysts and, afterward, engineer them. To engineer a catalyst means that once the active metal or metals blend is found, its catalytic ability must be maximized by selecting the proper support, the proper oxidation or reduction state, the right operative conditions.

Commercial catalysts are made of an active (usually noble) metal, like Au, Pt, Pd, etc., finely dispersed on a solid porous support, among which alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ) are the most common: this component has several functions, like being inert to the reaction and assuring thermal resistance and conductivity, even if the most important is surely to increase the metal exposition to the reactants, thus increasing the overall catalyst activity.

Another degree of freedom is given by the preparation method, since the technique employed to prepare the catalyst can affect its performance; the most used are:

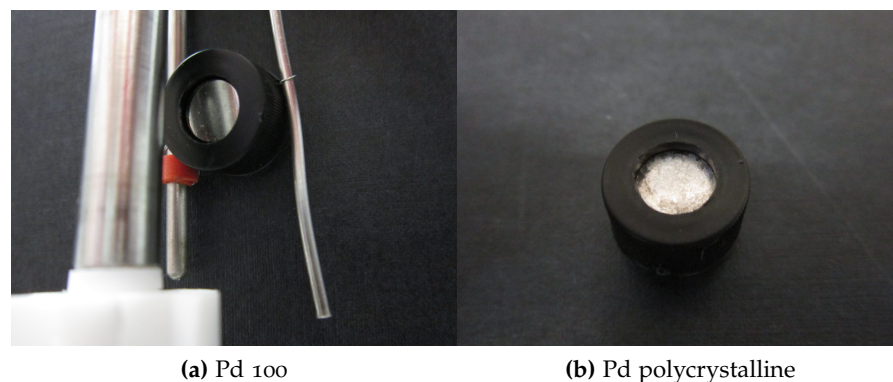
**PRECIPITATION:** a solution of a metal salt, called precursor, is initially treated with an alkaline solution (usually ammonium hydroxide or ammonium carbonate) with the aim of precipitate the hydroxides (or carbonates) of the metal, that are insoluble. At this point the dimension of the precipitated's crystals can be partially controlled by acting on solution's pH, temperature and agitation: too thin crystals, although being more active, may not be suitable for the following treatments, mainly the filtration. Afterward to the solid mass of metal hydroxides a particular form is given (grains, spheres, etc.), a step in which lubricants or ligands may be added; then the obtained particles are dried and calcinated, in order to both exclude the extraneous materials and convert hydroxides to oxides, and, in addition, to give an incipient sintering due to the high operative temperature. Finally the last step is the reduction of the oxides, that is usually carried out at the highest temperature possible in order to guarantee a fine dispersion of the metal on the support's surface;

**IMPREGNATION:** in this case two possibilities are available, namely a wet impregnation and an incipient wetness impregnation. If in the first case the porous support is simply soaked in a solution with excess of the precursor for a certain time, and after filtrated, dried, calcinated and reduced, in the second case the support is treated, usually by nebulization, with a volume of the precursor's solution precisely equal or slightly in defect to that of its pores. The concentration of the solution must be strictly controlled in order to guarantee that inside the solid there is the desired amount of precursor.

With wettable solid, like alumina, the solution's distribution in the solid particles is evenly and uniform, since capillary forces help the liquid to penetrate the pores, whereas with non easily wettable supports care must be taken, and different ways, like ultra vacuum operation or employing organic solvent instead of water, should be tried.

These preparation methods, although allowing to somehow control the metal particle growth, are characterized by the randomness of the metal deposition on the support, allowing to state that each pellet produced using these techniques is not the perfect replica of the others. The superficial distribution of the metal, in fact, is first of all different from one catalyst to another but also difficult to be described, requiring techniques like BET, chemisorption, TPD, making difficult the comparison between different catalysts (this problematic will be analyzed in details in § 4.1.1). This is actually the fundamental difference with the model catalyst, with which is possible to carefully and quantitatively characterize the number of atoms in the surface, as well as their displacement, two crucial informations in both the mechanism





**Figure 3.4:** Comparison between the two catalyst disks once inserted in their support: it can be appreciated that the exposed superficial area is the same.

of adsorption/desorption and in the reaction (as well as leading to easier comparison between catalysts).

In this work three different types of catalyst have been tested and compared with respect to their activity toward  $\text{H}_2\text{O}_2$  production, all of them having in common their active metal, i. e. palladium:

1. Sigma Aldrich® pellet 0.5%wt Pd over  $\text{Al}_2\text{O}_3$ , specific geometrical volume of  $564.86 \text{ mm}^3/\text{g}$  and specific geometric area equals to  $10.29 \text{ cm}^2/\text{g}$ , specific superficial area<sup>1</sup> of  $199.52 \text{ m}^2/\text{g}$ ;
2. polycrystalline disk of pure palladium, superficial area of approx.  $1.57 \text{ cm}^2$ , exposed area of  $50.25 \text{ mm}^2$ ;
3. monocrystalline disk of pure Pd(100) with an exposed area of  $50.25 \text{ mm}^2$ .

The reason why the exposed superficial area of the two disk catalysts is equal to  $50.25 \text{ mm}^2$  resides in the catalyst support used to place it inside the reactor (as one can appreciate in [Figure 3.4](#)).

Since not only three different catalysts, but also their conditions and/or superficial characteristics have differed during the various experiments carried out in this work, and, moreover, to make easier the comparison between their results, in the following list all the different catalysts' configurations are summarized and labeled:

P: Sigma Aldrich® pellet, employed as it is;

PC0: pure Pd polycrystalline disk, left in a shelf for years and previously employed in other synthesis, dirty on both surfaces, total exposed area of  $1.57 \text{ cm}^2$ ;

PC1: PC0 cleaned with aqua regia, a sputtering and an annealing treatment; exposed surface of  $50.24 \text{ mm}^2$ ;

<sup>1</sup> From B.E.T. calculations.



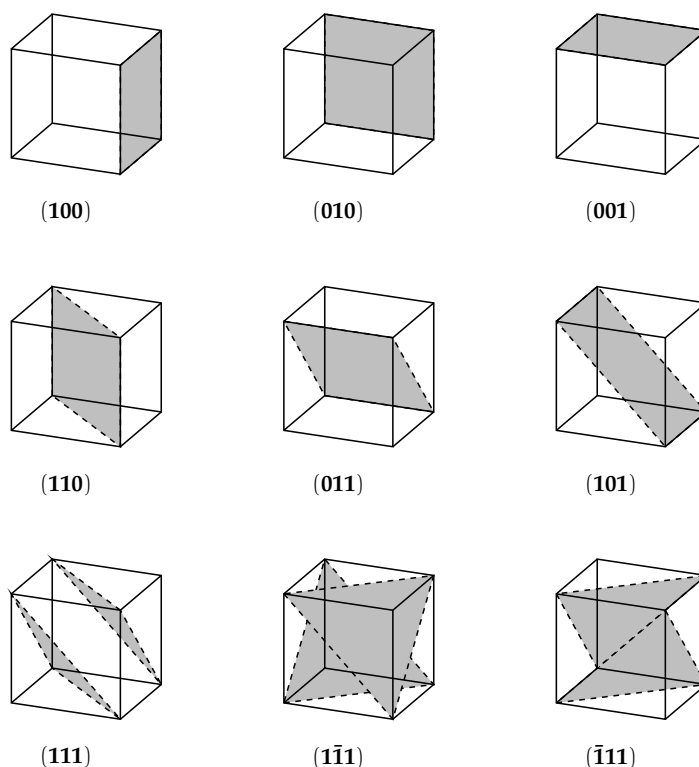
- PC2: PC1 preoxidized for ca. 20 h at 10 bar;
- MC1: pure Pd monocrystalline disk, cleaned with sputtering and annealing;
- MC2: MC1 after two synthesis, then cleaned with sputtering and annealing;
- MC3: MC2 after the prereduction test (see § 4.2.1), then cleaned with sputtering and annealing ;
- MC4: MC3 prerduced for 1 h at 10 bar;
- MC5: MC4 after 30 min at 10 bar of O<sub>2</sub> plus 10 bar of N<sub>2</sub>;
- MC6: MC5 prerduced for 1 h at 10 bar and preoxidized for 1 h at 10 bar;
- MC7: MC6 after 1 h at 10 bar of pure H<sub>2</sub>;
- MC8: MC7 after 1 h at 10 bar of pure H<sub>2</sub> and another hour at 10 bar of pure O<sub>2</sub>;
- MC9: MC8 after 30 min at 10 bar of pure H<sub>2</sub> and 2 h at 20 bar of pure O<sub>2</sub>;
- MC10: MC9 after two synthesis with preoxidation, a synthesis with prereduction and, finally, another preoxidation.

As one can easily note the disk catalysts has often undergone two treatments at the DISC, namely:

**SPUTTERING** with Ar<sup>+</sup> plasma for 30 min at an energy in the range 1.5 – 2 kV, a treatment that, although not modifying the superficial structure, allows to clean the crystal from contaminants, such as oxides (with which an high efficiency is obtained), by producing a sort of scraping of the surface on a nanometric scale;

**ANNEALING** at 650 °C in ultra high vacuum, that aims to somehow flatten the surface after the sputtering, by giving energy to the atoms to diffuse. In fact the flat configuration is the most stable and, therefore, the spontaneous one, even though only terraces, broken by defects, can be obtained.

In the following, on the other hand, it is clarified what a model catalyst is and why it is possible to state that its peculiar characteristic is to exhibit an ordered arrangement of superficial atoms.



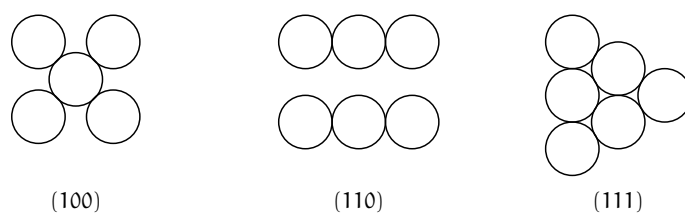
**Figure 3.5:** Miller indices for a fcc lattice. Adapted from [Wikipedia \[2012\]](#).

### 3.2.1 Model catalyst and Miller indices

Miller indices represent a conventional way in crystallography to identify directions and planes in crystal, or Bravais, lattices; usually a index consists of a tern numbers  $h, k, l$ , with each of these denoting a family of planes orthogonal to a direction in the basis of the lattice vectors. For example, the index  $(100)$  denotes a plane (and those parallel) orthogonal to the  $h$  direction, whereas the  $(110)$  planes orthogonal to both  $h$  and  $k$  directions (in [Figure 3.5](#) some more examples are given).

An interesting aspect is that to different crystallographic plane is (sometimes) possible to associate a different superficial atomic density (see [Figure 3.6](#)), a parameter that influences the adsorption/desorption mechanism and, as a consequence, the reactivity of the metal toward the chemisorbed molecules. In particular if one compares the most thermodynamically stable and, thus, common planes, the so-called low index surfaces (i. e.  $(100)$ ,  $(110)$  and  $(111)$ ), of a face centered cubic crystal, it can be noted that a different superficial atomic disposition is associated to each of the different index:

$(100)$ : all superficial atoms are equivalent and the surface is smooth and shows three different type of adsorption sites, that is:



**Figure 3.6:** Schematic description of different atomic arrangement of the top-most layer of the low index surfaces for a fcc structure: clearly the (111) surface shows the highest superficial atomic density.

- on-top sites, i. e. above each single metal atom;
- bridging sites, between two metal atoms;
- hollow sites, with a bond between four atoms.

Therefore over this surface a species can adsorb either to one, two or four metal atoms.

(110): this superficial arrangement shows the less packed topmost layer of atoms among the three, with atoms in contact along the horizontal direction, whereas a gap can be noted in the perpendicular direction. Therefore atoms of the second atomic level are somehow exposed at the surface, leading to an atomically rough surface, highly anisotropic, and to a wide variety of adsorption sites:

- on-top sites;
- short bridging between two in contact atoms;
- long bridging between two not in contact atoms;
- higher coordination sites.

This great availability of adsorption sites makes the (110) surface the most reactive.

(111): this structure represents the most efficient way of packing atoms within a single layer, hence called the close-packed one, and shows similar adsorption sites to those of the (100).

Even if the adsorption sites available on a metal surface strongly depends on the adsorbate molecule (i. e. its dimensions, physical and chemical properties, structure, etc.), the simplified description pointed out above still demonstrate how to each low index surface a different superficial atomic arrangement and, therefore, behaviour toward the reagent molecules is associated.

Therefore if the superficial atomic disposition influences the atomic density, the latter is connected to the stability of the surface by the surface energy, in a way that the most stable surface is the one with

the highest number of atom or, in other words, the best packed structure: therefore, on the other hand, the less packed structure will also be the one that easier adsorb atoms, thus the more reactive. So, finally, one can state that the reactivity of the low index surfaces is:

$$\text{fcc}(110) > \text{fcc}(100) > \text{fcc}(111) \quad (3.1)$$

Keeping in mind this concept, now it is necessary to define what is meant for model catalyst. The concept of model catalyst is strongly bounded to that of surface science, in a way that this peculiar type of catalyst has been developed to overcome many of the experimental issues in applying surface science studies to catalysis or, in other words, to mime real catalysts' behaviour by employing single crystals. In fact when, in late 1960s, Ultra High Vacuum (UHV) equipments made their first appearance, model catalysts were obtained by creating well ordered extended surface of a catalytic metal, so that their electronic behaviour and, moreover, their chemical properties could successfully investigated using common surface science technique. Hence a catalyst can be called model when showing three peculiar characteristics of the metal surface:

- long range order in the crystalline structure of metal surface;
- repetition of the interatomic distances;
- when radiated with X rays, it shows diffraction.

However to obtain a perfectly homogeneous surface with a fixed Miller index is only an ideal belief, since in reality what is observed is that defects are present in the ordered structure, mainly due to the growth of surfaces (having the same index) along different directions; these 'pieces' of well long-range ordered surface are usually called terraces, whereas the points in which different terraces become in contact are called stair-step defects, since arising from differences between the levels (of height) of these terraces.

Thermal desorption spectroscopy's analysis [Le Moal *et al.*, 2010] proved that the catalytic activity is somehow connected with the atom density in the surface, in a way that to higher atomic density (i. e. higher number of neighboring atoms) an higher energy request to form a new bond is associated, with the latter being, at the same time, characterized by a lower the strength. In this configuration the defects, to which a lower atomic density is associated, appear, therefore, as favourable adsorption sites for the molecules, resulting in being the effective reaction sites.

Therefore the superficial density of atoms and the amount of superficial defects appear to be two crucial factors in controlling the reactivity of a model (and disk) catalyst. So the comparison between

model catalysts with different Miller index could lead to prove theoretical conclusions [Ford *et al.*, 2010; Li, Ishihara, and Yoshizawa, 2011], according to which a more packed, and less reactive, structure of superficial atoms should be the most efficient one for a catalyst to be employed in the direct synthesis.

Moreover, this idea that a less reactive catalyst would be the most suitable one could be somehow proved also by comparing a highly defective structure with a more ordered one: this is actually what is done in this work in the comparison between the results of a Pd(100) monocrystalline disk with those of a polycrystalline disk, and presented in Chapter 4.

A similar concept is nowadays a proved characteristic of the direct synthesis of  $\text{H}_2\text{O}_2$ : as demonstrated by Biasi *et al.* [2011b], the ratio  $\text{H}_2/\text{Pd}$  appears as a crucial parameter, showing that it is not straightforward that a higher amount of catalyst leads to higher productivities of  $\text{H}_2\text{O}_2$ , whereas it is rather the other way round. The reason can be somehow connected with the idea underlying this thesis work: an higher activity of the catalyst, that means higher amount of defects in the case of disk (monocrystalline or polycrystalline) catalysts while with the supported means higher amount of Pd in the catalyst, does not lead to better performances in the synthesis of  $\text{H}_2\text{O}_2$ . The reason is probably inside the reaction network: a more active catalyst enhance the undesired reaction as well as the desired one, but the net result is a lower final concentration of  $\text{H}_2\text{O}_2$ .

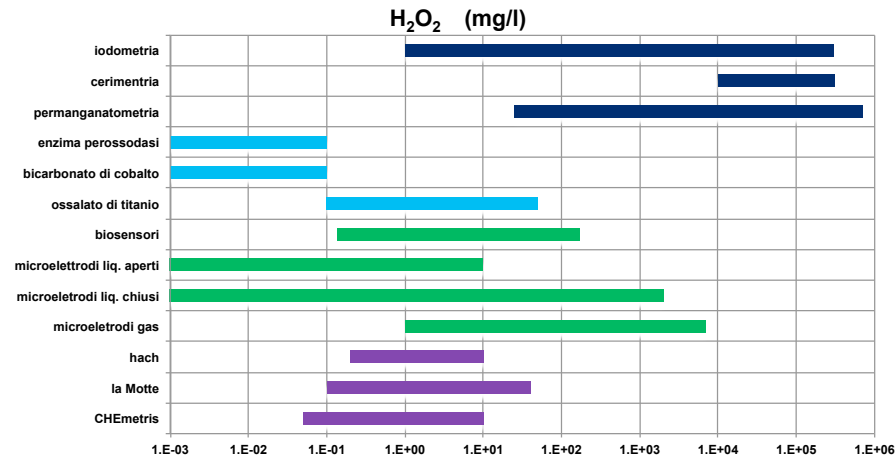
The polycrystalline disk catalyst, in fact, is characterized, as all polycrystals are, by monocrystalline faces, called grains, randomly distributed and rotated, delimited by what is called a grain boundary: thus it does not show any long range order in the superficial structure.

Since the low index surfaces are the most thermodynamically stable, then it is more likely that even in a polycrystalline metal these are the most present surfaces, that is actually why the most suitable comparison is with model catalysts showing these surfaces.

Besides being an unordered structure, the exposed surface of a polycrystalline metal is rough and dominated by defects, being therefore much more reactive that the model catalyst and, possibly, less selective toward  $\text{H}_2\text{O}_2$ .

### 3.3 SAMPLES' ANALYSIS

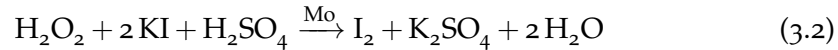
To determine the amount of hydrogen peroxide produced the analytical method chosen has been the iodometric titration, as previous works have shown to be the preferable one for present operative conditions (see Figure 3.7). In fact the typical amount of  $\text{H}_2\text{O}_2$  produced is in the order of 50 – 100 mg/l, suitable to be titrated with a iodometric method, that may be less precise compared to other techniques,



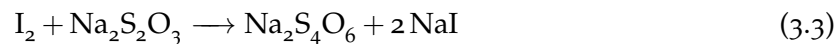
**Figure 3.7:** Comparison between H<sub>2</sub>O<sub>2</sub> measurement methods [Zancanella, 2010].

like the permanganate titration, but is also less susceptible to interferences by organic substances.

The iodometric titration consists in the measure of the iodine produced by the oxidation reaction between hydrogen peroxide and iodide (usually introduced under the form of KI), in an acidic environment and in the presence of a Mo catalyst to speed up the reaction, that is:



The iodine is then titrated with sodium thiosulfate and starch ( $\beta$ -amilose) as indicator, that gives to the solution a violet-blue colour:



Therefore the concentration of H<sub>2</sub>O<sub>2</sub> is indirectly calculated from the knowledge of the amount of thiosulfate needed to titrate all the iodine; sodium thiosulfate, one of the few reducing agents stable when in contact with air, is employed because it shows a unique reaction with iodine, that is:



The formation of the tetrathionate ion is specific for the iodine, whereas with other compounds the thiosulfate ion forms the most common sulfate ion (SO<sub>4</sub><sup>2-</sup>).

Moreover, to avoid iodine losses by volatilization, a common operative feature is to work with an excess of KI, allowing to form the triiodide ion



a compound soluble in water and that takes part in the previous Equation 3.4.

Although being a common and widely used method for the titration of  $\text{H}_2\text{O}_2$ , several advices should be kept in mind while operating:

- an excess of  $\text{I}_2$  decomposes the starch, so the indicator should be added just before reaching the turning point;
- atmospheric oxygen can oxidate iodide to iodine, leading to an overestimation of  $\text{H}_2\text{O}_2$ : thus the contact with air has to be minimize while titrating, meaning, in particular, that the agitation should not being excessive;
- the environment (i. e. the solution to be titrated) has to be acid: a basic one would lead to disproportion of iodine. Moreover the reaction of  $\text{S}_2\text{O}_3^{2-}$  to  $\text{S}_4\text{O}_5^{2-}$  can take place only with a neutral or weakly acid pH.

The analytical procedure starts by filling an eppendorf with ca. 0.25 mg of solution (i. e. the sample), that is injected in a vials (that contains a small magnet) placed on a technical balance using a 1 ml syringe: after weighting the sample, the reactants<sup>2</sup> are added to it, starting with KI and  $\text{Mo-H}_2\text{SO}_4$ ; afterward it is titrated by carefully adding  $\text{Na}_2\text{S}_2\text{O}_3$  through a graduated burette, with the sample, now showing a yellow coloration, placed on a magnetic stirrer to guarantee an adequate agitation.

Just before the turning point, the starch is added to the sample and the titration continues until the violet-blue color disappears. A good titration is obtained if the sample gets back a violet-blue color after ca. 30 min, otherwise the thiosulfate added has been excessive.

### 3.3.1 *Experimental error on samples' analysis*

The experimental error can be calculated from data of repeated analysis, with small changes between them in operative conditions, sampling methodology and measured concentrations. Therefore the estimation of this quantity has not been that easy in this thesis work, since usually an experiment is not repeated twice, for, mainly, two reasons:

- the aim of this work is to enhance the  $\text{H}_2\text{O}_2$  production, so from one experiment to another some new feature (e. g. pretreatment of the catalysts, type of the catalysts, etc.) is usually tested;
- each experiment, from its preparation until the shut down, lasts for more than six hours, making difficult to perform two experiments per day.

<sup>2</sup> In Section A.2 the preparation methods are described.

Hence only few experiments has been repeated without changing the conditions, and from their data the experimental error affecting the  $\text{H}_2\text{O}_2$  analysis has been calculated in the following way:

1. the relative errors is first calculated at each time for each couple of experiments, that is:

$$e_j^{\text{rel}} = \sqrt{\frac{1}{\bar{y}} \frac{\sum_{i=1}^N (y_i - \bar{y})^2}{N-1}} \quad (3.6)$$

Since  $N$  always equals to 2, then [Equation 3.6](#) becomes:

$$e_j^{\text{rel}} = \sqrt{\frac{(y_1 - y_2)^2}{y_1 + y_2}} \quad (3.7)$$

2. the average relative error is the obtained by summing up all the  $e_j^{\text{rel}}$  and dividing by the total number of sampling time:

$$\bar{e}_{\text{syn}}^{\text{rel}} = \frac{1}{N_t} \cdot \sum_{j=1}^{N_t} e_j^{\text{rel}} = 0.046 \simeq 5\% \quad (3.8)$$

The data series analyzed have been those labeled with MC1, MC3, MC6, MC7 and the result has been, hence, extended to all the data collected. This result does not take into account also the experiment MC2, since it has been a really noisy one: in fact, by including also the errors associated to it, the final value of  $\bar{e}_{\text{syn}}^{\text{rel}}$  would have been equal to ca. 10%.

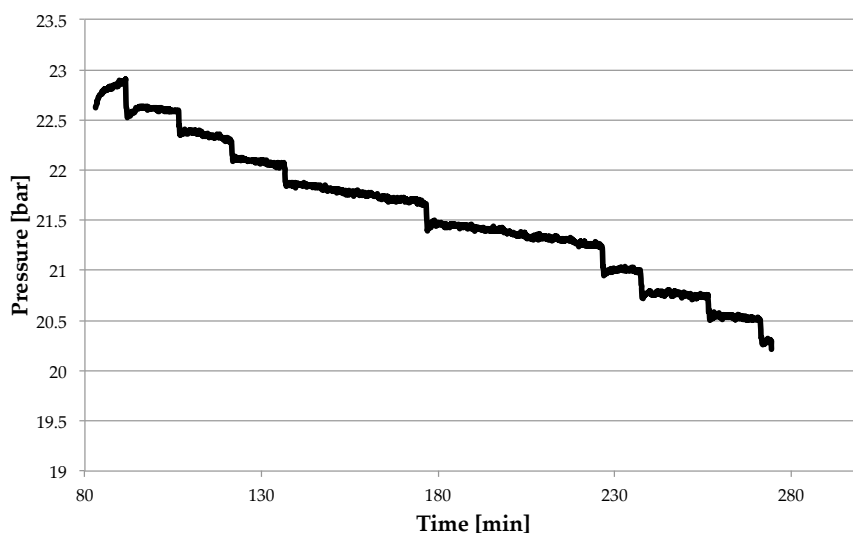
A similar calculation has also been carried out for the decomposition experiments, in which the fractions of  $\text{H}_2\text{O}_2$  analyzed were higher (usually around 1 mg/g): the obtained average relative error is  $\bar{e}_{\text{dec}}^{\text{rel}} = 0.019 \simeq 2\%$ . This result, however, is calculated over a lower number of experimental points compared to that of the synthesis reaction.

### 3.4 EXPERIMENTS' PROCEDURE

The detailed procedure followed during each experiment can be found in [Section A.3](#), from which is possible to understand (applying the IG law) that the final fractions of the gases (i.e.  $\text{CO}_2/\text{O}_2/\text{H}_2$ ) are 64%/32%/4%. The most important aspect of this procedure is that it allows to carefully control the amount of hydrogen introduced in the autoclave, usually equal to 1 bar (that, using again the IG law, equals to 0.0033 mol): since  $\text{H}_2$  is the limiting reactant, in order to be reproducible between different experiments its amount has to be strictly controlled.

The reproducibility is one of the most important advantages of this procedure and, moreover, a fundamental aspect of a work aiming to





**Figure 3.8:** Typical pressure profile during an experiment.

compare different catalysts: the only differences, therefore, might be in the operative temperature (mainly due to seasonal fluctuations) and the pressure of  $O_2$  and  $CO_2$ , but always on the order of 0.2 bar. During an experiment the pressure should not change too much, in order to keep the experimental conditions as much even as possible: in [Figure 3.8](#) a typical experimental pressure trend is shown, in which it is possible to see that the pressure is, at the beginning (after charging the methanol), around 23 bar, and that decreases, due to sampling and reactant consumption, until 19 bar. Therefore it can be stated that the final conditions do not differ too much from the initial, thus assuring that the influence of the change in the operative conditions on the results is minimized, i. e. assuring the repeatability of the  $H_2O_2$  measurements.

#### 3.4.1 Explosion limits analysis

Since the direct synthesis reaction involves the mixture of highly explosive gases as reactants, the problem concerning the explosion limits arose during the thesis work, mainly as a double check of the procedure.

Unfortunately few information are available for a three component system working at high pressure, but still some clarifications has been found in the paper by [Schroeder and Holtappels \[2005\]](#): in this article the explosion limits for  $H_2$  in air are measured with four different standard test methods in order to compare them. Further this comparison is also carried out (at atmospheric pressure and room temperature) with the mixture  $H_2$ - 40% $N_2$  - air, that is somehow assimilable to the mixture used in this work, except for the fact that the inert employed is not nitrogen but carbon dioxide (a difference that actu-

**Table 3.2:** Influence of the initial pressure on the explosion limits of hydrogen-oxygen mixtures, measured at room temperature [Schroeder and Holtappels, 2005].

Initial pressure [bar]	LEL [%mol H <sub>2</sub> ]	UEL [%mol H <sub>2</sub> ]
1	4.0	95.2
5	4.6	94.6
10	5.0	94.2
20	5.4	94.2
50	5.5	94.6
100	5.7	94.9
150	5.7	95.1
200	5.9	95.1

ally cannot be neglected): by comparing the result in this case with those of the previous, one can appreciate the effect of increasing the amount of inert on the explosive limits, understanding that the lower explosion limit is not affected by the addition of nitrogen, while the higher explosion limit is almost halved.

This result is in agreement with what reported by Piqueras, García-Serna, and Cocero [2011], that stated that, with a prediction of LFL based on the calculation of the adiabatic flame temperature, the use of nitrogen as inert in a H<sub>2</sub>-O<sub>2</sub> mixture does not modify the gas-like behaviour, with only a small increases of the lower limit.

In the same article, however, it is also shown that the same calculations employing CO<sub>2</sub> instead of N<sub>2</sub> as diluent give different results: the LFL, in fact, is increased from 4.5 % mol H<sub>2</sub> at 1 bar up to ca. 7.0 – 9.0 % mol H<sub>2</sub> at 200 bar, due, as suggested by authors, to the increase in the heat capacity of the mixture. This reason is, actually, able to explain also why with nitrogen, a gas with cryogenic characteristics, the increase in LFL is not that important.

The increase in LFL obtained with CO<sub>2</sub> at 200 bar, however, may not only be connected with the properties of the inert gas, but also with the increase in pressure: Schroeder and Holtappels [2005], in fact, investigated also the pressure effect on the explosion limits of hydrogen-oxygen mixtures, showing that increasing the pressure does not reduce the lower explosive limit, but rather the other way round; as one can appreciate in Table 3.2, in fact, the LFL increase while increasing the pressure, whereas the upper explosion limit exhibit an anomaly, since after decreasing until a pressure around 20 bar, it increases again.

**Table 3.3:** Total pressure and molar fractions of gases during the experiments.

$P_{\text{tot}}$ [bar]	$y_{\text{H}_2}$ [% mol]	$y_{\text{CO}_2}$ [% mol]	$y_{\text{O}_2}$ [% mol]
1	100.00	0.00	0.00
2	50.00	50.00	0.00
3	33.30	66.67	0.00
4	25.00	75.00	0.00
5	20.00	80.00	0.00
6	16.67	83.33	0.00
7	14.29	85.71	0.00
8	12.50	87.50	0.00
9	11.11	88.89	0.00
10	10.00	90.00	0.00
11	9.09	90.91	0.00
12	8.33	91.67	0.00
13	7.69	92.31	0.00
14	7.14	92.86	0.00
15	6.67	93.33	0.00
16	6.25	93.75	0.00
17	5.88	94.12	0.00
18	5.56	94.44	0.00
19	5.26	94.74	0.00
20	5.00	90.00	5.00
21	4.76	85.71	9.52
22	4.55	81.82	13.64
23	4.35	78.26	17.39
24	4.17	75.00	20.83
25	4.00	72.00	24.00
26	3.85	69.23	26.92
27	3.70	66.67	29.63
28	3.57	64.29	32.14

Therefore, since safety of operations is assured by keeping the hydrogen concentration below the LEL particularly when introducing the oxygen, a safe configuration would be assured by keeping the hydrogen fraction below 5.9 % mol  $\text{H}_2$  at 20 bar. In the experiments done in this work this fraction depends on the amount of inert gas fed to

the reactor, as one can see in [Table 3.3](#), in which is also possible to understand how the different gases are fed into the reactor: first of all 1 bar of hydrogen, followed by 18 bar of carbon dioxide and, at last, 9 bar of oxygen. So the critical point is when oxygen is introduced in the reactor, namely when the total pressure is raised from 19 bar to 20 bar: at that time the  $H_2$  fraction is (applying the IG law) equal to  $1/19 = 5.26\% \text{ mol } H_2$ , thus the safety request is fulfilled.

Nevertheless Juan García-Serna, one of the authors of the previously cited article<sup>3</sup>, with which there has been a discussion on the safety of the experimental operations carried out in this thesis work, advises to operate below  $4\% \text{ mol } H_2$ , since the risks connected to mix of  $H_2$  and  $O_2$  in the direct synthesis are too high compared to the benefits achievable by increasing the hydrogen fraction in the reaction, at least for research purposes.

Therefore a safer configuration would be assured by increasing the content of carbon dioxide in the system, namely from 18 bar to 25 bar. Hence this analysis helped to prove that the experiments conducted so far were carried out in a safe configuration, although a safer procedure can guarantee a higher degree of safety of the operator.

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<sup>3</sup> Piqueras, García-Serna, and Cocero, 2011.

## EXPERIMENTS AND RESULTS

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The main results obtained in this work are presented in the following, by starting with a preliminary comparison (because only based on the  $\text{H}_2\text{O}_2$  produced) between the performances of the polycrystalline disk (PC0) and the commercial pellet (P) (see [Section 3.2](#) for the details on catalysts' labels): it is this evidence that actually started the research presented in this thesis, proving that even a bulk disk catalysts can be effective in the direct synthesis, as much as a commercial one.

Further the results obtained with the model catalyst are exposed and compared to that of the other catalysts, in particular with the polycrystalline disk of Pd, as well as the influence of different pretreatments on the catalysts, with a focus on the effects of a prereduction made with pure hydrogen.

### 4.1 PRELIMINARY RESULTS

In [Figure 4.1](#) the different performances of the PC0 catalyst and those of the P are shown: it appears immediately clear that they are comparable in term of  $\text{H}_2\text{O}_2$  formation, evidence that encouraged to deeply investigate the disk catalysts. In fact the Sigma Aldrich® pellet was expected to show better performances since it is an industrial catalyst and, moreover, there is, in the scientific community, the belief that model (or disk) catalyst cannot be suitable for industrial applications even at a laboratory scale, but rather for ultra high vacuum operations, that is in a perfectly controlled atmosphere.

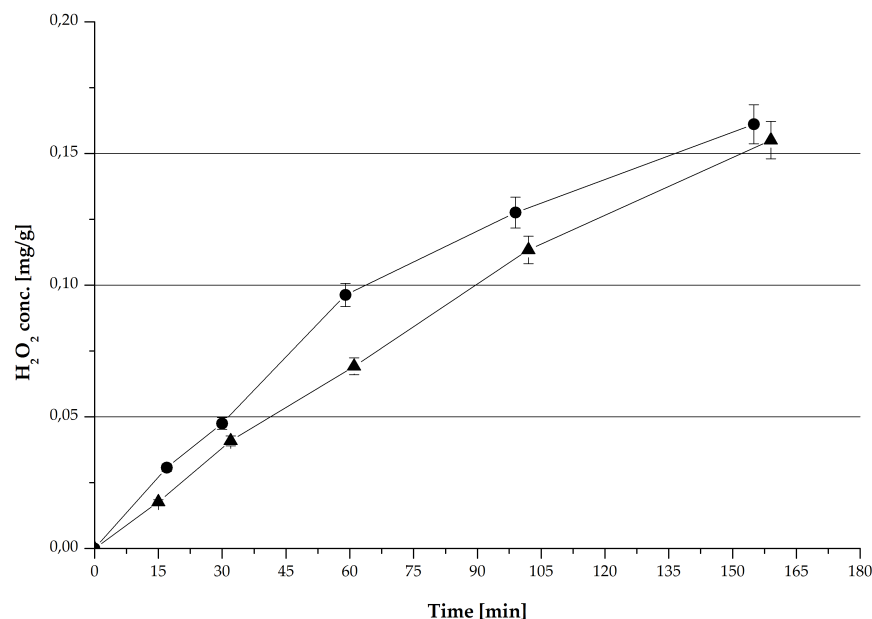
After the first surprising results the Pd(100) disk catalyst has been tested in order to understand which were its performances: as [Figure 4.2](#) shows, the concentrations of  $\text{H}_2\text{O}_2$  obtained are nearly doubled compared to those previously obtained with the other two catalysts, with an overall yield, assuming complete conversion of hydrogen, given by

$$Y_{\text{H}_2\text{O}_2} = \frac{w_{\text{H}_2\text{O}_2} \cdot m_{\text{sol}}}{1000 \cdot MW_{\text{H}_2\text{O}_2}} \cdot \frac{\mathcal{R}T}{P_{\text{H}_2} V_{\text{R}}} \quad (4.1)$$

that equals to ca. 7.5 % for the Pd(100) (MC1) and 4.39 % for the polycrystalline (PC0).

This difference is maximized in the beginning of the experiment, as can be underlined by the calculation of the superficial productivity (per  $\text{cm}^2$  of palladium) of  $\text{H}_2\text{O}_2$ , that is:

$$P_{\text{H}_2\text{O}_2} = \frac{w_{\text{H}_2\text{O}_2} \cdot m_{\text{sol}}}{MW_{\text{H}_2\text{O}_2} \cdot A_{\text{Pd}} \cdot \Delta t} \quad (4.2)$$



**Figure 4.1:** Comparison between P (●) and PC0 (▲).

with the solution being composed of pure methanol, since water produced in the reactor can be neglected.

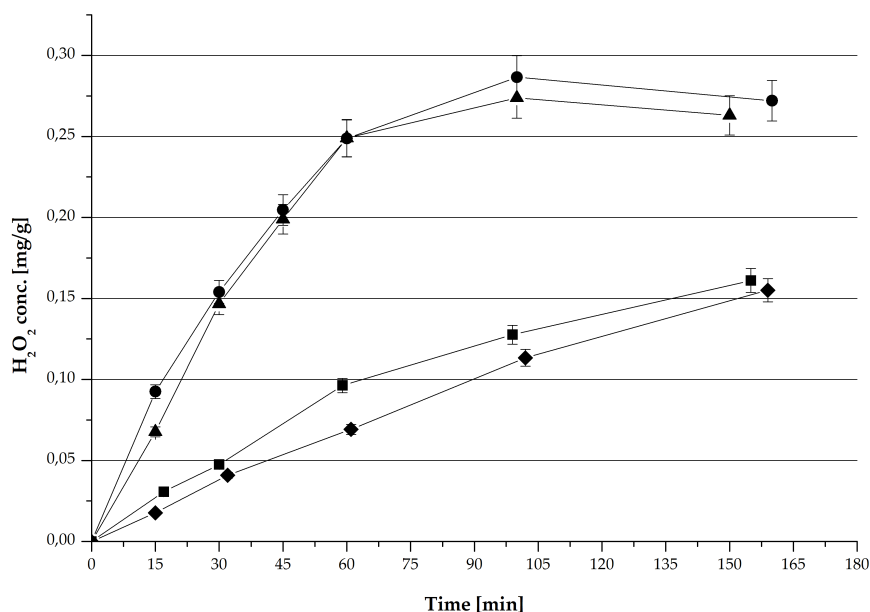
The calculation gives an hydrogen peroxide productivity after 30 min for the Pd(100) (MC1) of around  $0.7 \text{ mmol/cm}^2/\text{h}$ , whereas that for the polycrystalline (PC0), always after 30 min, is  $0.057 \text{ mmol/cm}^2/\text{h}$ .

The results appeared to be really promising, characterized by a high initial slope in the plots and by a good reproducibility, a feature confirmed also by subsequent tests.

At that point, in order to see how a synthesis at more than 20 bar had modified the superficial structure of the Pd atoms, the model catalyst (MC1) has undergone an X-ray diffraction analysis, that showed an increased faceting: this may also be the reason why the following experiments have not confirmed the initial results, giving only concentrations comparable with those of the pellets (as one can see in [Figure 4.7](#), MC2 results).

However these unsatisfactory outcomes pushed the research to investigate possible superficial modifications able to improve the catalytic performances of the disk catalyst, under the idea exposed also by [Melada \*et al.\* \[2006\]](#) that the catalytic activity was connected not to the pure metal, but rather to a thin layer of palladium oxides formed on the metal surface. Actually this is a common feature of Pd: in fact the metal forms oxides just after being exposed to the atmosphere.

Therefore in the next section the results obtained with experiments in which the synthesis has been preceded by a treatment of the catalyst, either with  $\text{H}_2$  or  $\text{O}_2$ , are presented.



**Figure 4.2:** Comparison between MC1 (▲ and ●), P (■) and PC0 (◆).

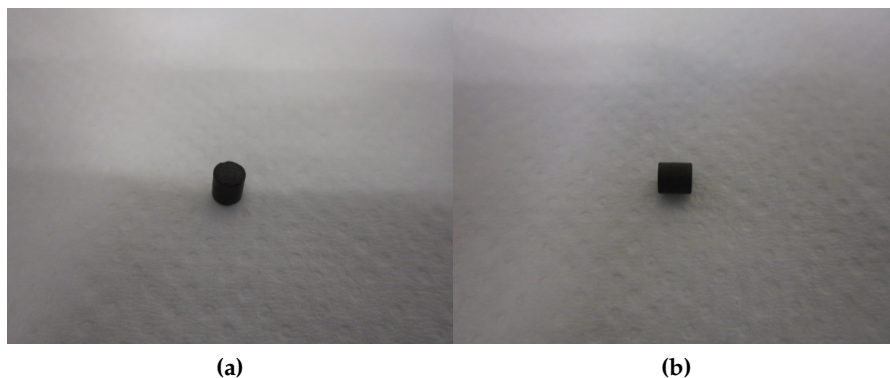
In the next subsection, on the other hand, the issue of comparing results obtained with different catalyst is exposed in details, by presenting the various possibilities of comparison.

#### 4.1.1 Comparison of different catalysts' results

From a general point of view there are several physical quantities to which refer to in the calculation of the productivity (e.g. in Equation 4.2 the geometrical area has been employed): the pros and cons of each quantity with each of the three catalysts employed in this work are analyzed in the following.

**GEOMETRICAL AREA:** the use of this quantity is straightforward for the disk catalysts, since they only expose a well defined surface to the reactants. On the other hand with the pellet it is not that easy to estimate the effective catalyst's area exposed, since it is not flat as the disks, but shows an important porosity, as the B.E.T. calculation enlighten: the specific geometrical area of the pellet (visible in Figure 4.3) is just  $10.29 \text{ cm}^2/\text{g}$ , whereas the specific superficial area, that takes into account also the porosity, is more than five orders of magnitude higher ( $199.52 \text{ m}^2$ ).

Moreover the surface of a disk catalyst is made of pure palladium, whereas that of an impregnated pellet (superficial plus internal) is more like a leopard's skin, with the Pd atoms as small spots in the alumina matrix. Therefore even being able to carefully determine the catalyst's surface exposed to the atmosphere, then one should be able to estimate the fraction of this



**Figure 4.3:** Sigma Aldrich® pellet employed in this work.

occupied by palladium; finally the availability of the pores to the gases cannot be the same of a flat surface, introducing another degree of uncertainty in the comparison.

Therefore a comparison based on  $\text{cm}^2$  of palladium exposed is suitable for disk catalysts, but absolutely inappropriate with commercial catalysts.

**MASS OF ACTIVE METAL:** this is a commonly employed tool in literature to perform comparison between different commercial catalysts having not the same percentage of active metal, being therefore suitable with the Sigma Aldrich® pellet. However it is not easily practicable with the disks made of pure Pd, since only the superficial atoms take effectively part in the reaction and thus one should be able to calculate the mass of superficial palladium. By taking the number of atoms per surface for an fcc crystal, that equals  $N_{\text{at}} = 1.3 \times 10^{15}$  atoms/ $\text{cm}^2$ , then the superficial mass (i. e. the mass of active metal taking part in the reaction) is given by

$$\begin{aligned} m_{\text{sup}} &= \frac{N_{\text{at}} MW_{\text{Pd}}}{N_{\text{av}}} \\ &= \frac{106.42 \cdot 1.3 \times 10^{15}}{6.022 \times 10^{23}} = 22.97 \times 10^{-8} \left[ \text{g}/\text{cm}^2 \right] \end{aligned} \quad (4.3)$$

which leads to a massive productivity (using the data from the MC1 results presented in Figure 4.2) of  $\bar{P}_{\text{H}_2\text{O}_2} = P_{\text{H}_2\text{O}_2}/m_{\text{sup}} = 3 \times 10^6$  mmol/g/h.

Comparing this result with productivities found in literature [Melada *et al.*, 2006], that are in the order of 100 mmol/g/h, or those found for the pellet (P), visible in Table 4.1, it appears clear that even this is not a practicable way: the difference is probably connected with the fact that in the case of a slurry catalyst not all the active metal introduced in the reactor is actually taking part in the reaction, a situation that is more likely to take place with disk catalysts.



**NUMBER OF ATOM EXPOSED:** in this case the problem is somehow similar to that discussed in the conclusion of the first point of this list, since it is almost impossible to know how many atoms are present on the surface of a commercial pellet. A rough calculation could be done by applying even to the total superficial area the fraction of active metal in the catalyst, in a way that a catalyst with 0.5 %wt of Pd over  $\text{Al}_2\text{O}_3$  would have also the 0.5 % of the total surface covered by Pd atoms.

However it is not possible to act in such a way, being too high the uncertain degree associated to a comparison carried out in this manner.

**NUMBER OF ACTIVE SITES:** chemiadsorption analysis allow to determine the number of adsorption sites available on a catalyst's surface, either this is a disk, a pellet or a powder. Therefore it appears, at least in theory, suitable for the purpose of comparing the results of different catalysts.

However there are several limitations as well:

- the sample (i. e. the catalyst) must suit in the analyzer, an important aspect when dealing with catalyst of so different shapes: in fact, if the instrument is designed to operate with powders, then one may think that crushing the pellet could be an elegant solution, but in such a way the catalyst's structure would be change and, in particular, its porosity partially eliminated;
- usually the catalyst must undergo some pretreatments before being analyzed, such as a reduction cycle at high temperature. Such a treatment, although necessary, can in practice change the catalyst characteristics, making useless the sites determination, since this information cannot be used in the comparison. This is an important aspect mainly with the disk catalyst, since a desired information is how (and which) pretreatments of the catalyst can actually affect its catalytic performance by modifying its adsorption/desorption characteristics;
- finally one can argue than not all the adsorption sites are in reality also catalytic active sites, i. e. reaction sites, since not all the adsorbed molecules take part in the reaction. On the other hand it can also be underline that the ability to let all the adsorbed molecules to take part in the reaction may be, after all, a peculiar characteristic of a certain catalyst.

Therefore from the previous analysis it can be stated that to employ the geometrical area is a reasonable decision when comparing among them disk catalysts' results, whereas the determination of the number of active sites, although being affected by some problematics, appears

necessary when comparing different catalysts, such as pellets and disks.

## 4.2 DISK CATALYSTS' RESULTS

### 4.2.1 *Pretreatments influence on disk catalysts' activity*

To understand the effects of prereducing the model catalyst, besides comparing the results in term of  $\text{H}_2\text{O}_2$  produced, a series of XPS analysis have also been done, in order to confirm that the surface of a prerduced palladium shows much less oxides compared to a non reduced one. These analysis has been done at DISC by professor Granozzi's group.

The first problem arose in setting up this comparative analysis has been due to the fact that, as already stated above, palladium is likely to adsorb atmospheric oxygen, meaning that a reduced sample easily became oxidized when exposed to the atmosphere. Since usually the reaction medium in the experiments is methanol, it has been decided to keep, just after the reduction cycle, the sample completely dipped into the solvent until introduced in the XPS analyzer: although appearing an easy solution, this has meant to keep a droplet of solvent on the catalyst surface while placing it into the analyzer. Clearly this procedure did not assured that the metal surface has seen no atmospheric oxygen at all, but there was no simpler way to operate, reflecting the difficulty to bridge chemical engineering and surface science, that is connecting an industrial way of operate with the quasi ideal environment guaranteed by the UHV operations. However this is also the novelty of this work, since it is unknown to chemical engineering the ability of surface science to characterize catalysts, although being of crucial importance for their performances in industrial applications.

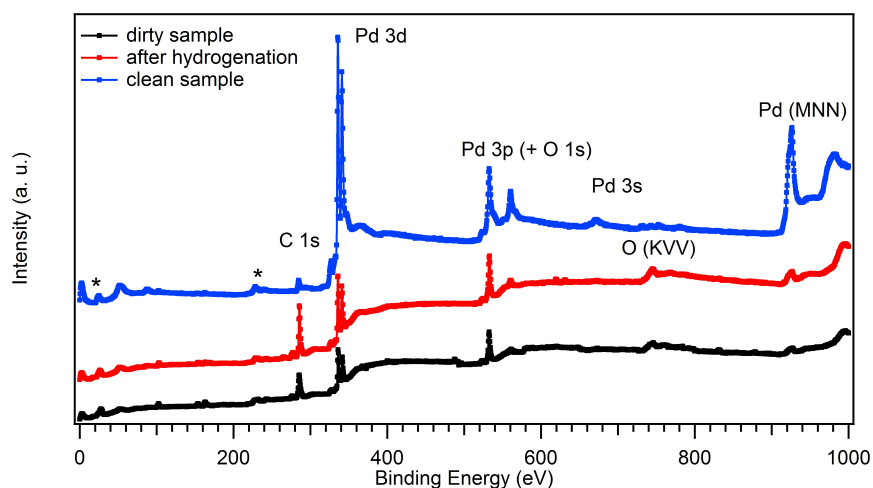
The results showed in the following compare the model catalyst in three different situations:

**CLEAN SAMPLE:** a Pd disk (i. e. MC1) that has undergone a cycle of sputtering with  $\text{Ar}^+$  plasma, followed by annealing at  $650^\circ\text{C}$  in ultra high vacuum, then analyzed in situ;

**DIRTY SAMPLE:** a former clean sample exposed to the atmosphere and employed for synthesis of  $\text{H}_2\text{O}_2$  (i. e. MC1 after two synthesis), introduced in the vacuum and analyzed;

**AFTER HYDROGENATION:** a clean sample (MC2) left inside the autoclave for 1 h at 10 bar of  $\text{H}_2$  and then protected with methanol until introduced in the vacuum for the XPS analysis.

The three wide range XPS spectra (called surveys) are visible in [Figure 4.4](#), in which the stars denotes photoemission peaks due to the

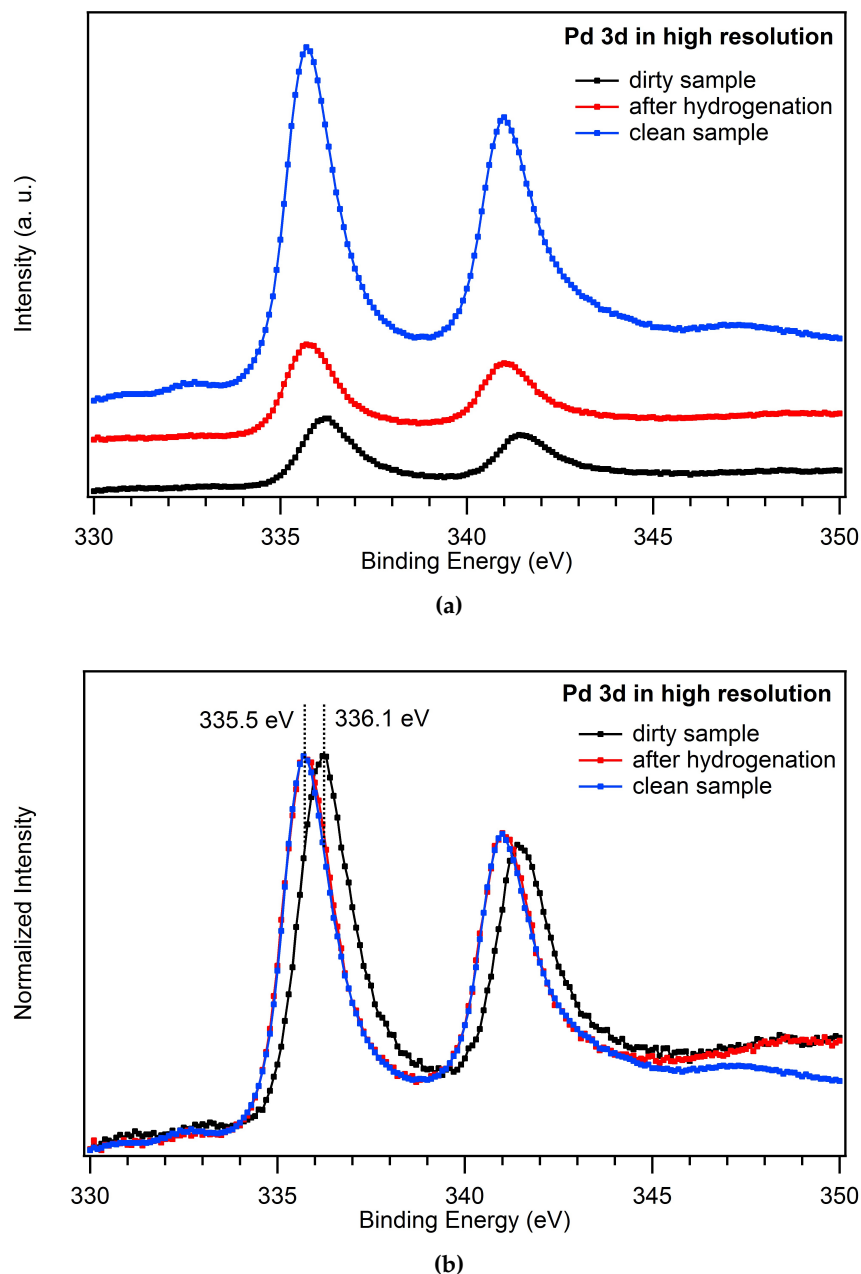


**Figure 4.4:** XPS spectra for the three different samples. From the top: clean sample, after hydrogenation, dirty sample. The differences in intensity are probably due to dirty on samples exposed to the atmosphere that soften the signal.

sample support (respectively Ta and Mo).

The topmost spectrum in [Figure 4.4](#) is a typical one for a clean Pd sample, as one can observe the series of photoemission and the Auger (MNN) peaks of Pd, whereas the C 1s signal is probably due to chemisorbed CO or to carbon present on the sample support. The presence of O is in traces, as the weak signal of the Auger (KVV) peak at 740 eV suggests, and is probably carried by the sample support. The oxygen, in fact, cannot be directly identified from the core peak 1s, since its binding energy ( $B_e \approx 530$  eV) is within the range of the Pd 3p, therefore it is distinctive the presence of the Auger (KVV) peak. The other two spectra denote higher peaks for the C 1s, probably due to dirty, and the presence of oxygen, since this time the signal of the Auger (KVV) peak is high. In particular the reason why the hydrogenated sample results to be the dirtiest is associated to the fact that the sample has been carried and continuously covered with methanol ( $\text{CH}_3\text{OH}$ ), so the higher intensity of these signals are associated to residual alcohol contaminations; further, this is also the reason why it appears oxidized.

For the dirty sample a zoomed analysis of the Pd 3d peaks (shown in [Figure 4.5](#)), namely  $3d_{5/2}$  and  $3d_{3/2}$ , allows to state that there is the presence of a superficial oxide, by associating to oxygen the  $B_e$  of the Pd 3d. In fact the binding energy is distinctive of the oxidation state of an element, since the chemical neighborhood influence the kinetic energy of the emitted photoelectrons, thus the  $B_e$ ; in particular an higher oxidation state is reflected by a positive shift of the binding energy. By analyzing the spectra in [Figure 4.5](#) it is visible that the dirty sample shows a  $3d_{5/2}$  peak 0.6 eV higher than the clean



**Figure 4.5:** XPS spectra zoomed in the Pd 3d zone. **(a)** From the top: clean sample, after hydrogenation, dirty sample; **(b)** normalization of the intensity to clearer show the shift between clean sample (as well as hydrogenated) and dirty sample.

sample (335.5 eV), i. e. at 336.1 eV, a value in agreement with those reported for PdO. On the other hand, instead, the hydrogenated sample overlaps perfectly the clean one, demonstrating that prereducing the model catalyst remove the superficial oxide.

Once the effect of prereducing the model catalyst on the surface of the latter is clearly demonstrated, one may argue whether a reduced or an oxidized surface shows a different catalytic performance in the

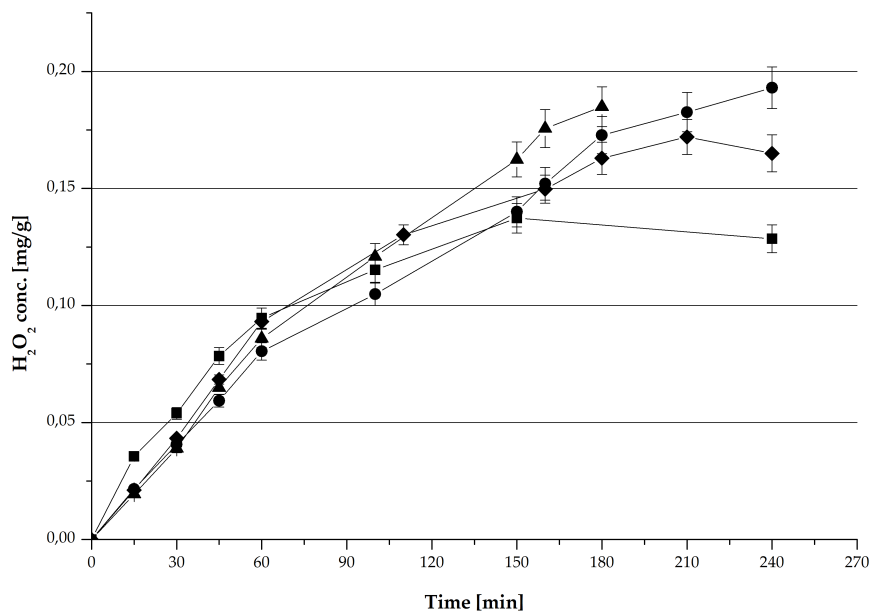


Figure 4.6: MC3 (● and ▲) compared to MC4 (◆) and MC5 (■).

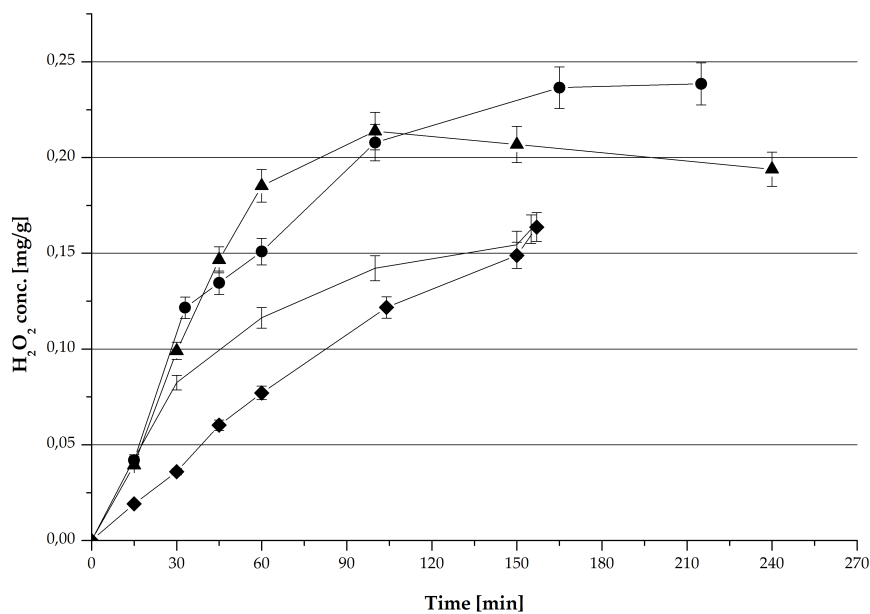
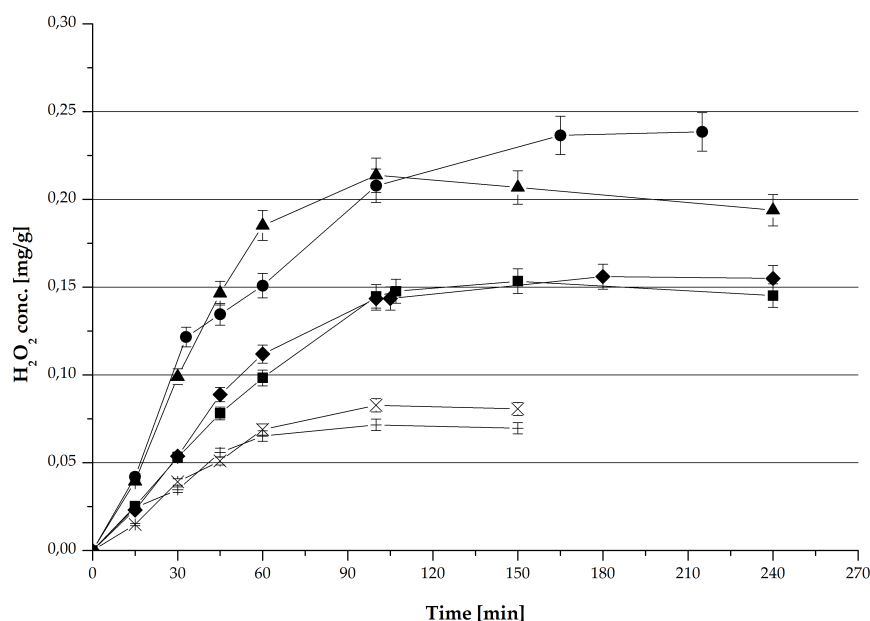


Figure 4.7: MC6 (▲ and ●) compared to MC2 (■ and ◆).

direct synthesis of  $H_2O_2$  or not.

Experiments with a prereduction of the catalyst has been done on Pd(100) disk, showing no remarkable effect toward the  $H_2O_2$  production, as visible in Figure 4.6. However the disk catalyst performance in this case was not as good as those presented in Figure 4.2, an aspect that urged the research to investigate whether a pretreatment



**Figure 4.8:** Prehydrogenation effects on the model catalyst: MC6 (▲ and ●) compared with MC 7 (■ and ◆), MC8 (×) and MC9 (+). The repeated tests (● and ◆) have been carried out with the catalyst as it was, without repeating the pretreatments.

with oxygen could increase the  $\text{H}_2\text{O}_2$  concentration obtained. Even in this case no relevant results, presented in Figure 4.6 as well, were obtained, if not the fact that the hydrogen peroxide concentration trend tends to bend at slower concentration, a difference that may underlie a change in the chemistry of the catalyst. Therefore the idea to combine the two pretreatments arose, that is to put in series the prereduction with a preoxidation of the disk catalyst: that combination ended up to be a right choice, as Figure 4.7 clearly shows.

Now that good performances of the model catalyst has been restored, one can test again the effect of a prereduction, and indeed the results were as expected: Figure 4.8 shows a strong reduction of hydrogen peroxide produced at each subsequent prereduction cycle, proving that reducing the superficial oxides leads to decrease both the final concentration obtained and the initial productivity. All tests has been repeated twice in order to confirm the results, and again high reproducibility is shown by the model catalyst, appearing to be one of its key features.

However last results enlighten also one of the limits found in this work so far, that is the difficulty to restore high performance of the model catalyst: in fact the lowest curves in Figure 4.8, namely the MC8 and MC9, were expected to show a completely different behaviour, that is to increase the  $\text{H}_2\text{O}_2$  concentration rather than decrease it, since undergone to both the pretreatments in series. Unfor-

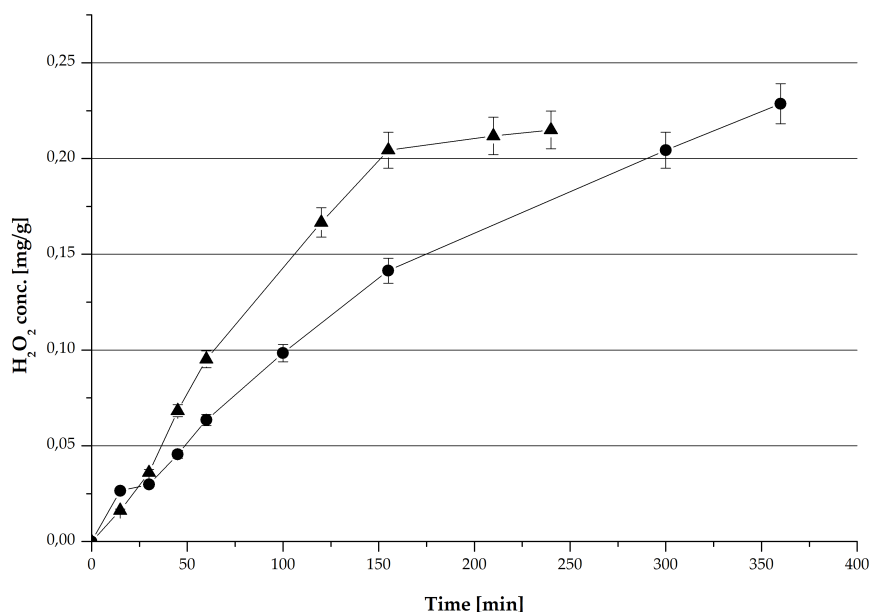


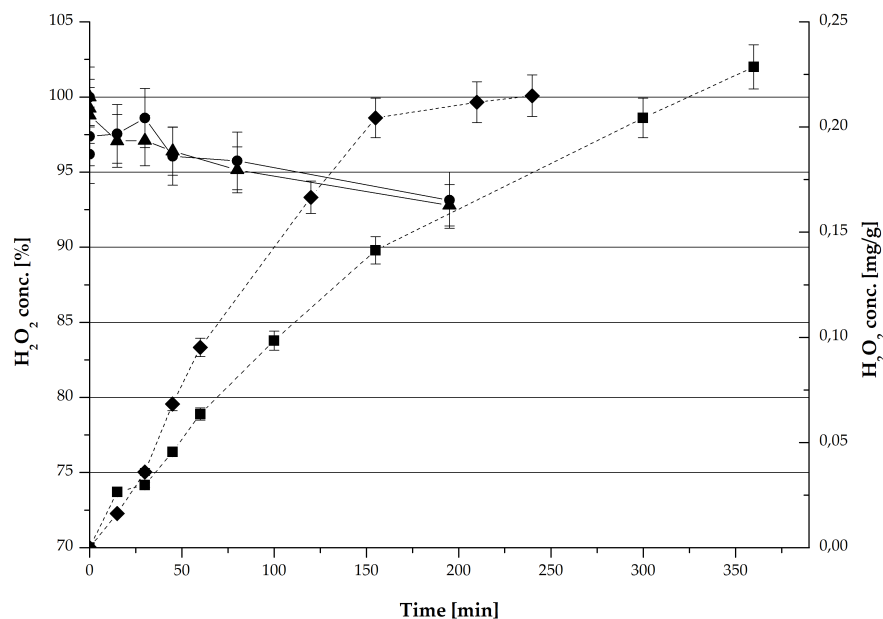
Figure 4.9: Comparison between PC1 (▲) and PC2 (●).

tunately even massive preoxidations (the longest lasted ca. 24 h) were not able to increase the productivity. Further investigation are needed to clarify this aspect.

Finally the effect of pretreatments has been investigated on the cleaned polycrystalline (PC1), starting with a preoxidation treatment, that gives the results shown in Figure 4.9: there is not such relevant change, even if letting the reaction to continue up to 5 h it is possible to see that the preoxidized catalyst gives the same H<sub>2</sub>O<sub>2</sub> concentration of the non preoxidized one, but in double time. Moreover the trend of the latter tends to bend after 150 min, whereas the slope of that of the preoxidized polycrystalline is nearly linear from 150 min up to 360 min.

Moreover it has been investigated whether the different behaviour in H<sub>2</sub>O<sub>2</sub> synthesis reflects also on the disproportionation reaction (which results are presented in § 4.2.2), in a similar way done also in the following comparison between PC1 and PC2.

The results are shown in Figure 4.10 and make it clear that the preoxidizing treatment does not affect the disproportionation reaction; this concept was already guessable from Figure 4.9, since no high H<sub>2</sub>O<sub>2</sub> concentrations would be achieved after 360 min if the decomposition reaction was strongly active. Besides this the latter idea could lead to further speculation on the hydrogenation reaction, whether its behaviour has been modified or not by the pretreatment, a concept that future tests may investigate.



**Figure 4.10:** Comparison between PC1 (▲ and ◆) and PC2 (● and ■): the solid lines refer to the disproportionation reaction, whereas the dashed lines indicate the corresponding performances in the H<sub>2</sub>O<sub>2</sub> synthesis.

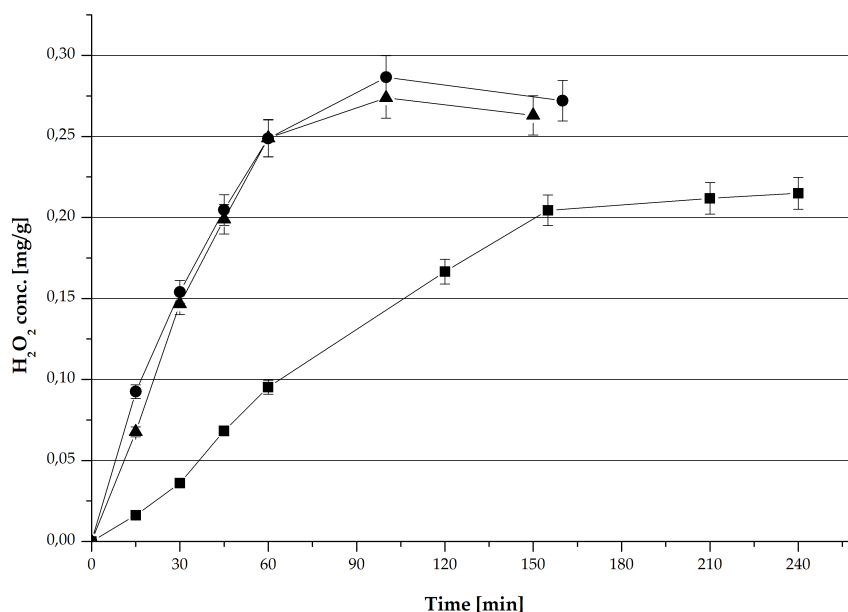
#### 4.2.2 Comparison between polycrystalline and monocrystalline Pd.

Besides the effect of different oxidation states of superficial atoms of Pd on the synthesis of H<sub>2</sub>O<sub>2</sub>, the main aim of the present work was to understand whether there is a different behaviour of a catalyst with an ordered superficial structure compared to an unordered one.

Initial results obtained by comparing the Pd(100) (MC1) with the dirty polycrystalline disk (PC0) have been later confirmed also by similar tests with the clean polycrystalline Pd (PC1), as visible in [Figure 4.11](#): although showing comparable final concentration (i. e. around 150 min), the monocrystalline disk catalyst is characterized by a higher productivity in the first hour, where the concentrations achieved are double compared to that of the polycrystalline. The bending of the Pd(100) curve, probably due to the competition of the decomposition reactions, is also the reason why the final concentrations in the two cases came close.

Therefore it is possible to state that an ordered superficial structure appears more performant than a random one, even if from water analysis (via Karl-Fischer titration) further insight might be possible, thus investigating if the better performances are connected to a higher selectivity toward the H<sub>2</sub>O<sub>2</sub> route instead of the H<sub>2</sub>O one, with the polycrystalline Pd being evenly catalytic active toward both reactions. Further, investigations on the two decomposition reactions may help to understand if the idea, presented in [Figure 2.1](#), that a defective





**Figure 4.11:** Comparison between MC1 (▲ and ●) and PC1 (■)

structure preferentially decomposes the hydrogen peroxide produced is actually taking place in reality. In the following initial results in that direction are presented and discussed, even though further analysis are needed to confirm them.

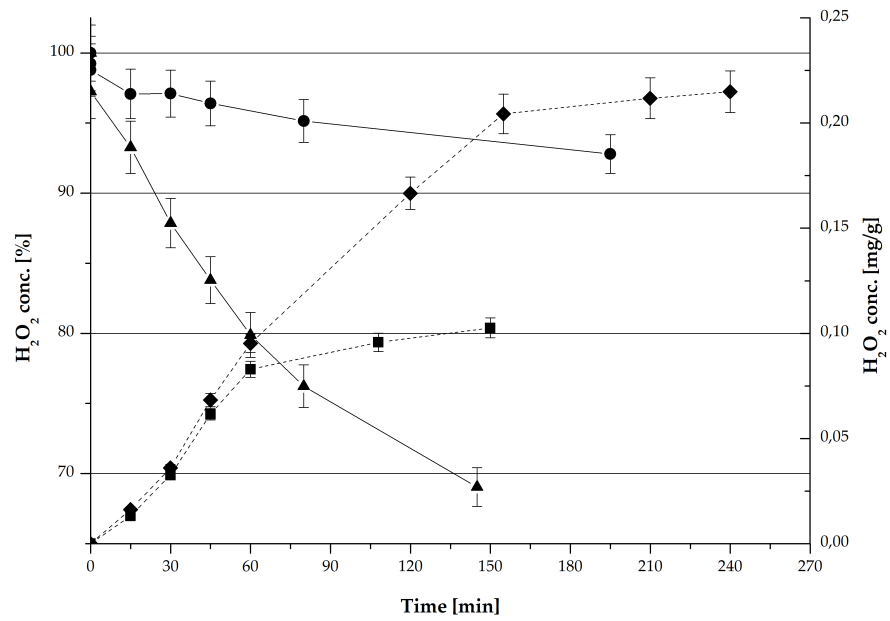
One of the reason that can explain different performances between one catalyst and another, as well as between different tests carried out with the same catalyst, may be a different catalytic activity toward the two decomposition reactions of the four reactions network of the direct synthesis, namely the disproportionation and the hydrogenation of  $H_2O_2$ .

Previous works demonstrated how the hydrogenation ( $H_2O_2 + H_2 \rightarrow 2H_2O$ ) leads in the decomposition mechanism of  $H_2O_2$ , with the disproportionation contributing only marginally [Choudhary, Chanchal, and Prabhas, 2007; Zancanella, 2010].

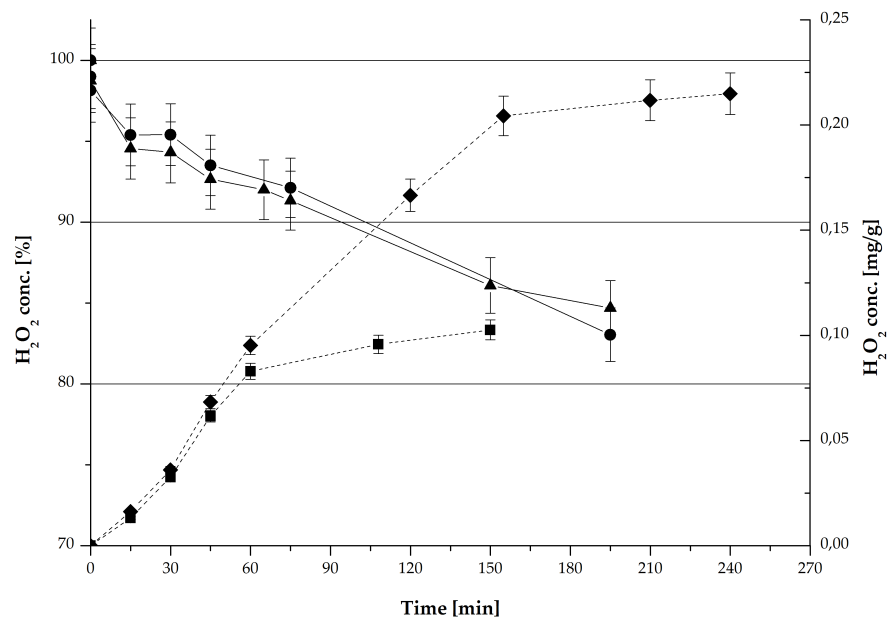
To be coherent with the synthesis' experiments, the procedure followed in these tests has been substantially the same, with two main differences:

- in disproportionation tests the hydrogen has been substituted with nitrogen, still in the amount of 1 bar;
- similarly in hydrogenation experiments 9 bar of nitrogen has been fed instead of oxygen.

The initial concentration of  $H_2O_2$  in the mixture with methanol introduced in the autoclave has been maintained around 1 mg/g, in order to emphasize the reactions; the presented results has been normalized, in a way that makes the comparison easier and clearer.



(a)



(b)

**Figure 4.12:** Comparison between MC10 (▲ and ■) and PC1 (● and ◆). The solid lines refer to: (a) the disproportionation of  $H_2O_2$ ; (b) the hydrogenation reaction. The dashed lines, instead, indicate the corresponding performances in the  $H_2O_2$  synthesis.

In [Figure 4.12](#) the results for the disproportionation are shown: as one can clearly see the results for the model catalyst (MC10) are surprising, with the polycrystalline palladium (PC1) showing a much lower activity in the  $\text{H}_2\text{O}_2$  destruction. Although being somehow unexpected, these results for the model catalyst appear coherent with those shown in the hydrogen peroxide synthesis: in fact in [Figure 4.12](#) the performances of both catalysts in terms of  $\text{H}_2\text{O}_2$  produced are also compared, showing that the Pd(100) (MC10) reaches lower concentrations, with a bent in the trend after just 60 min, whereas the polycrystalline (PC1) shows the bent at 150 min.

For what concerns the hydrogenation reaction the results, presented in [Figure 4.12](#) as well, shown comparable performances between the two different disk catalysts, leading to state that the difference in the  $\text{H}_2\text{O}_2$  concentrations achieved is not connected to differences in the activity toward the hydrogenation reaction, but rather to differences in that toward the disproportionation reaction.

For the polycrystalline disk (PC1), as expected, the hydrogenation reaction makes a more pronounced contribution to  $\text{H}_2\text{O}_2$  destruction compared to the disproportionation, since it is likely to happen that when hydrogen is added to the system the two decomposition reaction sum up, in a way that a certain percentage of  $\text{H}_2\text{O}_2$  reduction ascribed to the hydrogenation reaction is actually due to the disproportionation one.

Therefore the results obtained for the Pd(100) (MC10) appear, besides in contrast to those reported in literature, poorly coherent with the previously stated concept: in this case the hydrogen seems to deactivate the active sites toward the disproportionation reaction instead of increasing the destruction of  $\text{H}_2\text{O}_2$ . However these surprising results urge to deeply investigate this behaviour with further tests.

In the following, finally, a summary of all mentioned experiments is presented in [Table 4.1](#).

**Table 4.1:** Results of the different experiments presented in this chapter. For the catalysts' label see [Section 3.2](#), whereas the productivity and the yield are calculated, respectively, using [Equation 4.2](#) and [Equation 4.1](#). Finally the productivity of the pellet (P) is calculated over the grams of Pd instead that over the  $\text{cm}^2$ .

Catalyst	Productivity		Yield
	at 15 min	at 30 min	
P	505.16	443.38	4.57
PC0	0.0523	0.0568	4.39
PC1	0.150	0.166	5.66
PC2	0.245	0.138	3.92
MC1	0.626	0.678	7.41
MC1	0.800	0.700	7.66
MC2	0.200	0.188	3.90
MC2	0.195	0.180	4.52
MC3	0.364	0.458	5.75
MC3	0.388	0.496	6.57
MC4	0.214	0.248	4.32
MC4	0.234	0.245	4.25
MC5	0.137	0.181	2.23
MC6	0.226	0.160	1.93
MC7	0.121	0.151	2.84

CONCLUSIONS AND FUTURE DEVELOPMENTS

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The presented work demonstrates that model catalysts can be effective as much as commercial ones in the direct synthesis of hydrogen peroxide, despite their 2-D configuration that allows to expose to the reactants only few grams of active metal: the concentration achieved with a commercial Sigma Aldrich®, in fact, has been doubled by a single Pd(100) disk, notwithstanding a specific surface much lower, by orders of magnitude.

This results can be interpreted in different ways:

- higher concentrations are due to the well ordered superficial arrangement of atoms guaranteed by the model catalyst;
- the pellet is evenly active toward all the four exothermic reactions in the DS network, therefore the selectivity toward  $\text{H}_2\text{O}_2$  is low and the productivity is limited by the decomposition reactions;
- the model catalyst's flat configuration allows to achieve a better usage of the exposed Pd atoms since it does not require mass transport in the pores, thus enhancing the reaction even if the number of active metal atoms is lower.

Moreover, by comparing the results of a random structure of a polycrystalline disk to those of the model catalyst (i. e. monocrystalline disk), it is clear that a different chemistry is followed by the reaction: higher concentrations are rapidly achieved with an ordered structure of the superficial atoms, with a productivity nearly six times higher with respect to the polycrystalline. Therefore the idea often suggested in the literature that a less defective structure has to be preferred when carrying out the direct synthesis is here confirmed, even if a deeper investigation has to be conducted to clarify the reasons why there is such a difference. Whether the model catalyst is more selective toward  $\text{H}_2\text{O}_2$  or less active toward the decomposition reactions is one of the most important future issue to be investigated. In the first case water analysis using the Karl-Fischer titration method should be enough to clarify the point, whereas in the second case further investigations are needed, even if in this work preliminary observations has been presented.

From these, although it cannot be stated whether a more defective structure is also more active toward the decomposition reactions or not, two main conclusions can still be pointed out:

1. a catalyst showing worse performances in the direct synthesis shows also better performances in the disproportionation, suggesting that differences in the concentrations achieved in the synthesis are related to a different activity of the catalyst to this decomposition's reaction;
2. the hydrogenation reaction shows the same trend with both catalysts, no matter their performances in the synthesis.

Therefore the hydrogenation seems to be insensible to the superficial order of the atoms, even if it has to be noted that the model catalyst employed in the cited experiment (i. e. MC10) may present an elevated degree of faceting, since it has previously been employed in several synthesis.

Another important result of this thesis has been achieved by clarifying the central role of superficial Pd oxides in catalyzing the direct synthesis: a catalyst treated with pure hydrogen has shown a strong reduction in the concentrations of  $H_2O_2$  achieved, proving that the catalytic activity has to be related with the presence of Pd-O<sub>2</sub> complexes (destroyed by the reductive cycle done on the catalyst, as XPS analysis have demonstrated) on the catalyst's surface.

Moreover it has been investigated a way, by combining different pretreatments of the catalyst, to build these oxides to achieve higher concentrations, even if no solid conclusions can still be stated: this should also be one of the focus of future investigations, taking advantages for chemisorption analysis that may underline which structure the oxides should have and/or which combination of pretreatment allows to form a structure that enhances the adsorption, thus the reaction of reactants' molecules.

Further the problematic of comparing results coming from different catalysts has been investigated in order to clarify which of the available figures of merit could be used to perform the more accurate comparison as possible: in that sense again chemisorption analysis should be employed to estimate the number of active sites in a given catalysts appears to be the most suitable solution, since it allows to calculate the turn over frequency using its original definition, almost avoiding possible misuses or misunderstanding. In fact employing quantities such as gram or  $cm^2$  of Pd often leads to errors or difficulties when comparing different catalyst, since their configurations are rarely similar.

Finally this work has the aim to enlighten a new possible way to study industrial reactions, that is employing model catalysts and surface science techniques: even if suitable only for laboratory scale, the possibility to get rid of all complexities connected with the use of commercial catalysts can allow to perform fundamental studies on the characteristics that an active metal should have to be really effective in the synthesis. From this studies a lot of crucial informations

on poorly known reactions can be obtained, as well as beliefs only suggested in literature be proved, knowing that the structure of the catalyst is completely described.

Moreover this structure is also tunable or designable: in that sense one of the most attractive future perspective of the presented work is to design and test a bimetallic catalyst obtained by alloying Pd and Au, again giving experimental proofs to theoretical conclusions presented in literature.

Another fundamental step is to test the other two low index structure of Pd, i. e. the (110 and (111), showing which (and why) is the most suitable. The answer to these questions could lead to a real breakthrough in the direct synthesis, demonstrating which peculiarities a catalyst needs to have to be really effective in the  $\text{H}_2\text{O}_2$  production: the possibility of conducting such a study is the crucial feature connected with the use of a model catalyst.





TECHNICAL MATERIAL

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A.1 R AND S PHRASES FOR H<sub>2</sub>O<sub>2</sub>

The list of R phrases are:

- R 5: Heating may cause an explosion.
- R 8: Contact with combustible material may cause fire.
- R 20/22: Harmful by inhalation and if swallowed.
- R 35: Causes severe burns.

whereas the S-phrases are:

- S 1: Keep locked up.
- S 2: Keep out of the reach of children.
- S 17: Keep away from combustible material.
- S 26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S 28: After contact with skin, wash immediately with plenty of water.
- S 36/37/39: Wear suitable protective clothing, gloves and eye / face protection.
- S 45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

## A.2 REACTANTS PREPARATION FOR SAMPLES' ANALYSIS

POTASSIUM IODIDE: weight 1 mg of KI in a flask and then fill it with 100 ml of demineralized water;

MO CATALYST: weight 0.124 mg of NH<sub>4</sub>MoO<sub>4</sub> in a flask, then add 100 ml of demineralized water and, afterward, 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub>;

STARCH INDICATOR: fill a small (25 ml) flask with demineralized H<sub>2</sub>O, then heat it up to the boiling point, then quickly add a spatula (the precision is not that important in this case) of starch. Keep the solution obtained well mixed for half an hour;

SODIUM THIOSULFATE: from a vial of known concentration (available on the market), prepare a mother solution in a flask, that needs to be protected from sunlight. From that one prepare the diluted solution that best fit the amount of  $\text{H}_2\text{O}_2$  to titrate.

### A.3 METHODOLOGY FOR THE EXPERIMENTS

During each experiment a rigorous methodology has been followed, in order to guarantee the reproducibility; here it is schematically given in its main steps:

1. check the titration solutions, namely starch, KI and  $\text{Mo-H}_2\text{SO}_4$  solution;
2. close the autoclave after positioning the catalyst;
3. open tap water for the cooling jacket;
4. feed twice 10 bar of  $\text{N}_2$ , in order to minimize the amount of atmospheric oxygen in the autoclave's volume, with careful cleaning of the sample line during the depressurization; moreover during the second feed, a check of the sealing of the autoclave should be made, by keeping it under pressure for several minutes (after temperature stabilization);
5. now feed for three times 10 bar of hydrogen to be able to precisely predict the amount fed, that should be 1 bar (absolute, 0 bar relative) after temperature stabilization;
6. rise the pressure up to 19 bar with  $\text{CO}_2$  as an inert to avoid dangerous contact between hydrogen and oxygen;
7. feed 9 bar of  $\text{O}_2$ , then wait until the  $T_{\text{exp}}$  is achieved. A relative pressure of 27 bar should be reached;
8. finally feed 39.5 g of methanol (i.e. 50 ml) with the HPLC pump; then turn on the stirring up to 1500 rpm.

## NOTATION

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$P_{H_2}$	hydrogen pressure
$V_R$	free volume of the reactor
$\mathcal{R}$	universal constant of gases
$T$	reaction's temperature
$P_{H_2O_2}$	superficial productivity of $H_2O_2$
$w_{H_2O_2}$	fraction of $H_2O_2$
$m_{sol}$	total mass of the solution
$MW_{H_2O_2}$	molecular weight of $H_2O_2$
$A_{Pd}$	catalyst's geometrical area exposed
$\Delta t$	time lapse
$m_{sup}$	mass of superficial atoms of Pd
$N_{at}$	number of atoms of Pd per area
$MW_{Pd}$	molecular weight of Pd
$N_{av}$	Avogadro's number
$\bar{P}_{H_2O_2}$	massive productivity of $H_2O_2$
$e_j^{rel}$	relative error at a fixed sampling time
$\bar{e}_{syn}^{rel}$	average relative error for the synthesis' reactions
$\bar{e}_{dec}^{rel}$	av. relative error for the decomposition's reactions
$y_i$	'i'-th concentration at a fixed time
$\bar{y}$	average of concentrations at a fixed time
$N$	number of concentrations at a fixed time
$N_t$	total number of sampling times



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