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One-step H_2O_2 and phenol syntheses: Examples of challenges for new sustainable selective oxidation processes[☆]

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A R T I C L E I N F O

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Dedicated to Jose L.G. Fierro on occasion of his 60th birthday to celebrate his continuous innovative effort in the development of both fundamental and applied aspects of heterogeneous catalysts for the conversion of small molecules.

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A B S T R A C T

Selected results which outline issues and perspectives on the direct synthesis of H_2O_2 from H_2/O_2 and of phenol by benzene hydroxylation with H_2O_2, as examples of the challenges for new sustainable selective oxidation processes, are presented after an introduction on the industrial context underlying the motivations to develop these reactions. It is shown how they combine a lower impact on the environment and meet together demand and process economics opportunities giving a chance for innovation not only limited to a chemical production context, e.g. they are an interesting example of trends for a sustainable chemical production.

1. Introduction

Chemistry, sustainability and innovation are three key components for the future of our society [1,2]. The chemical and associated industries will remain competitive based on technology leadership and innovation. The CEFIC's (European Federation of Chemical Industries) survey on the most important innovation for the future of chemical industry [3] indicated process technologies and catalysis at the 2nd place after biotechnology, but before than IT, environmental technologies, alternative energy/fuel cells, nanotechnology, combinatorial chemistry, and simulation/modeling (in the order). Therefore, advances in an integrated approach of catalysis and process technology is seen from the companies as one of the major elements towards innovation and sustainability of the chemical production.

Often sustainable chemistry is considered as a synonymous of "green chemistry", but there are many concepts which go beyond those at the basis of the latter. Between these, two relevant concepts are those of (i) down-size and integrate (chemical) production to minimize transport and storage, avoid large plants and concentration in one single location, and (ii) integrate processes (multi-step reactions—catalysis, reaction and separation) [4,5].

Down-size chemical production, e.g. break-down scale economy though a modular design, is a new challenge for production of chemicals. In order to reach this objective, the development of many tools is necessary, ranging from micro-reactors and process intensification, integration of reaction-separations, to new ways to supply energy (from heat to photons, electrons, microwaves, etc.), new catalysts and nanotechnology, smart products (on-line microsensors), etc. The advantages are to make production compatible with environmental sustainability (self-cleaning capacity), reduce investment (accelerate the introduction of new processes) and facilitate the introduction of cleaner production to non-chemical areas.

Realizing new processes for small-scale modular productions requires also the development of new solutions for direct syntheses which avoid multi-step reactions even in cascade mode. One interesting example in this direction is the direct catalytic synthesis of H_2O_2 from H_2/O_2 and of phenol by direct hydroxyla-

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tion of benzene with the H_2O_2 produced in the first step. This was the objective of an European Project (NEOPS), some of obtained results will be discussed here, even though new recent advances in particular for the direct synthesis of H_2O_2 will be presented. A growing research interest is also focalized on the latter reaction. Recent results in particular on the reaction mechanism and nature of the active species were summarized by Fierro and coworkers [6] in an excellent review, while aspects more related to patents and reactor technology were discussed by Centi et al. [7].

Literature information on the direct benzene hydroxylation are instead more limited. Advances on catalysts design for phenol synthesis via catalytic hydroxylation of benzene in China were reviewed by Zheng [8], but further progresses have been made later. Different routes were explored for the direct benzene hydroxylation to phenol, for example the use of (i) N_2O over Fe-containing microporous materials [9–11], (ii) H_2O_2 with Fe-doped carbon [12], (iii) H_2O_2 in aqueous biphasic ionic liquids [13], (iv) H_2O_2 with VO_x/SiO_2 in acetonitrile [14], (v) O_2 in the presence of ascorbic acid and a VO_x/CuSBA-15 catalyst [15], and (vi) H_2O_2 with modified titanium silicalite [16,17]. It must be remarked, however, that often published results are far from the possibility of industrial exploitation. For example, results in solution using Fenton-type catalysts (Fe and Cu) are quite interesting in terms of selectivity, but productivity per volume of reactor is too low for industrial exploitation. Other catalysts show a too low selectivity with respect to H_2O_2, the critical factor for cost. The only feasible approach developed up to small pilot unit level was the use of H_2O_2 in combination with modified TS-1, the well-known catalyst developed by Eni/Polimeri Europa for the epoxidation of alkenes, hydroxylation of phenol to diphenol and caprolactame synthesis [18]. An analysis of the different alternatives for direct phenol production starting from benzene has been reported by Ricci et al. [19].

It should be also remembered that for both the direct synthesis of H_2O_2 and of phenol some of the most recent interesting advances are based on new micro-reactor technologies [20,21], further demonstrating the concept reported above of modular small-scale design. However, due to space constrains, these aspects will be not discussed here.

The aim of this contribution is not to provide a state-of-the-art review on these reactions, but to present selected results which outline issues and perspectives on the direct synthesis of H_2O_2 from H_2/O_2 and of phenol by benzene hydroxylation with H_2O_2, as examples of the challenges for new sustainable selective oxidation processes. For this reason, initially the industrial context underlying the motivations for the development of these reactions will be briefly presented in order to evidence how they combine a lower impact on the environment and meet together demand and process economics opportunities giving a chance for innovation not only limited to a chemical production context, e.g. an example of trends for a sustainable chemical production.

2. Motivations and industrial context for direct synthesis of H_2O_2 and phenol

Hydrogen peroxide is commercially almost exclusively produced by catalytic hydrogenation followed by auto-oxidation of a suitable organic molecule, predominantly alkylated anthraquinone. The alkylated anthraquinone process accounts for more than 95% of the world production of H_2O_2, mainly because the process operates in mild conditions and direct contact of O_2 and H_2 is avoided. The alkylated anthraquinone is solubilized in a mixture of non-polar and polar solvents. The non-polar solvent is needed to dissolve the alkylated anthraquinone. Alkyl-aromatics (C9–C11) are typically used. The polar solvent is needed to dissolve the product of reaction (alkylated anthrahydroquinone). Hydroterpineol, trioctyl phosphate or urea derivates are typically used. This mixture is hydrogenated using typical hydrogenation catalysts (Pd or Ni) in trickle bed or slurry three-phase reactors. The reaction occurs under mild conditions (pressures lower than 5 bars and reaction temperatures lower than 80 °C). The hydrogenation product (alkylated anthrahydroquinone) is then auto-oxidized with air in packed or bubble columns with the production of H_2O_2 and regeneration of the starting alkylated anthraquinone. The main drawbacks of this process are the following [22]:

- significant impact on the environment and generation of wastes (mainly associated to lower then 100% selectivity in the reduction and oxidation steps—formation of hydroxyanthrones, anthrones, anthracenes, and epoxides, some solvent stripping by air used in the oxidation step, and in the crude H_2O_2 stream);
- limited solubility of the reactant (alkylated anthraquinone) and of H_2O_2 in the reaction mixture (usually, below 15% and 1.5% wt., respectively) and low maximum conversion possible to limit side reactions ($<$70%) which determines a low efficiency of the process;
- intense energy use of the process, due to a high rate of recirculation and the need of purification of crude H_2O_2; in addition, the purification of crude H_2O_2 is very energy intensive;
- process complexity and risks of explosion;
- presence of mass-transport limitations in the hydrogenation and oxidation reactors.

Due to the high degree of complexity, this process is suited especially for large-scale productions, but now increasing demand of new processes (from chemical to environmental applications) needs a small onsite production in order to avoid the transport risks of concentrated H_2O_2 and the presence of stabilizers in H_2O_2 solutions which are necessary for its transport. Small-size uses of H_2O_2 as clean oxidant are fast expanding worldwide. Furthermore, the cost of H_2 and O_2 reactants with respect to the total cost of hydrogen peroxide is about 30–35% (depending mainly on the H_2 cost). There are thus several incentives to consider a process of direct reaction of H_2 and O_2 to form H_2O_2. This process could significantly reduce the impact on the environment, the energy consumption and the process cost with respect to the alkylanthraquinone route. In addition, it is suited for small-medium scale dedicated productions of H_2O_2.

In terms of market size, actual H_2O_2 production is about 2,2 million metric tons per year, but demand in new applications, particularly propene oxide (PO) is rising and it is expected to reach 150,000 m.tons in 2009 [23]. Demand of H_2O_2 for wastewater treatment and soil remediation is also rising above 5% per year.

Phenol is one of the most important intermediates of the chemical industry. Its current global capacity is about 8 million tons per year and the forecast for the growth is near 4.5%/year through to 2009. Fast phenol demand growth is due to a robust polycarbonate industry and rapid growth of Asian economies, especially China. Over 95% of commercial phenol synthesis in made by the cumene route. The process is based on three different reactions: (i) Friedel-Crafts alkylation of benzene with propene to afford cumene (isopropylbenzene); (ii) cumene oxidation with oxygen to cumyl hydroperoxide; and (iii) cleavage of cumyl hydroperoxide in acidic medium to get phenol and acetone (usually about 0.62 tons acetone are formed per ton of phenol). The critical step is the second, due to explosivity of cumyl hydroperoxide which requires to operate at low conversion per pass (typically 20%), limiting overall phenol yield per pass (typically in the 7–8% range).

In addition, propene supply from steam crackers and refineries cannot keep up with demand and therefore a growing supply of propylene from on-purpose routes (propane dehydrogenation and butene metathesis) is required. Phenol producers find thus more difficult or more costly to secure propene for cumene synthesis. In addition, one of the advantages of the cumene route was the co-production of acetone which had up to year 2000 a good market. However, from that year the demand for phenol was outpacing the demand for acetone. Phenol demand will grow 5.4% per year in the next years, while global acetone demand is projected to grow only 2–3% per year. Furthermore, one of the main uses (over 30%) of acetone [methyl methacrylate (MMA) via the acetone cyanohydrin route] will be progressively stopped due to environmental problems and thus even more market surplus of acetone will be present in the near future. For 2010 acetone surplus is projected to be about 150,000–200,000 tons. A clear demand to find a phenol production route which avoids the co-production of acetone is expected. The many drawbacks in phenol production via the cumene route can be summarized as follows:

- Complexity and use of energy (three steps);
- low global yield (<10%);
- economic only for large productions;
- formation of co-products and in particular acetone (propanone);
- differences in the market for acetone and phenol;
- treatment of water and organic waste: about 0.5 tons of wastewater and 0.06 tons of heavy organic products are produced per ton of phenol;
- risk: use of a potentially explosive intermediate.

3. Direct oxidation of benzene to phenol with hydrogen peroxide

We will limit here discussion on some key concepts for this reaction, focused in particular on the use of titanium–silicalite (TS-1) as the catalyst. A further more extended analysis has been reported by Ricci et al. [19]. Some of the key aspects of the proposed process are also described in the patent of Bianchi et al. [24].

Both homogeneous and heterogeneous catalysts have been investigated in the direct oxidation of benzene to phenol by hydrogen peroxide. In the first case, soluble iron complexes were used under biphase conditions, while titanium-containing zeolites were selected as heterogeneous catalysts. The general problem is that the direct oxidation of benzene to phenol has a poor selectivity, because phenol is significantly more reactive towards oxidation than benzene itself and consecutive reactions occur, with substantial formation of over-oxidized products like catechol, hydroquinone, benzoquinones, and tars.

In order to increase the selectivity to phenol it is necessary to separate catalyst and products into different environments. The use of an aqueous/organic biphasic reaction medium, in particular water and acetonitrile in a volume ratio of 1:1, dramatically affects the selectivity. The concentration of benzene in the aqueous phase raises from 0.18% (the solubility of benzene in water) to 0.76%, and the produced phenol is extracted for the most part (85%) in the organic phase. As a consequence, the benzene/phenol molar ratio is only 0.25 in the aqueous phase of a water/benzene mixture, whereas it raises up to 3.7 in the water/acetonitrile/benzene one. In this way, the biphasic operation minimizes the over-oxidation reactions by reducing the contact between phenol and the catalyst, segregated in the aqueous phase.

Using $FeSO_4$ as catalyst, an equimolar amount of methylpyrazine-5-carboxylic acid *N*-oxide and trifluoroacetic acid, and as reaction medium a water/acetonitrile/benzene (5/5/1, v/v/v) biphasic system, with benzene/H_2O_2/$FeSO_4$ = 620/60/1 ratio, a benzene conversion of 8.6% is achieved (35 °C, 4 h). Hydrogen peroxide conversion is almost complete (95%) and selectivities to phenol are 97% (based on benzene) and 88% (based on H_2O_2) [17,25].

Even if the selectivity is excellent, the limit of this homogeneous biphasic Fenton-type process is the low volume productivity, e.g. the amount of produced phenol in a given time per liter of reactor volume. This aspect, together with the cost of separation, makes the homogeneous process too costly. It is thus interesting to analyze the possible use of solid catalysts which selectively activate H_2O_2 molecules allowing to reduce the costs of separation and improve volume productivity. TS-1 (titanium–silicalite) shows excellent properties in the selective oxidation with H_2O_2 in a large variety of reactions, including alkanes oxidation, olefins epoxidation, alcohol oxidation, phenol hydroxylation, and cyclohexanone ammoximation [18]. However, the activity of TS-1 in the oxidation of benzene is very poor. In addition, TS-1 does not perform very well in two-phase systems, so that only solvents able to homogenize the hydrophobic substrate and the aqueous hydrogen peroxide can be used. Even in this case, using solvents such as acetone, acetonitrile or *tert*-butanol, the selectivity to phenol rapidly drops at very low benzene conversion, mainly due to the formation of dioxygenated products and tars: typically, selectivity was already less than 50% at benzene conversion as low as 5%. Even worse results were obtained using methanol, which was oxidized in competition with benzene to give formaldehyde dimehyl acetal.

However, it could be possible to use a similar trick of a biphasic system, e.g. the use of a solvent which reacts with phenol to form a complex whose further reactivity is strongly inhibited. In this way, the further conversion of phenol is drastically reduced and selectivity improved. Using sulfolane as solvent (sulfolane forms a complex with phenol via hydrogen bond) it is possible to obtain a conversion of benzene close to 8% maintaining the selectivity to phenol higher than 80%. Detected byproducts are catechol (7%), hydroquinone (4%), 1,4-benzoquinone (1%), and tars (5%) [16]. Other micro- and meso-porous Ti–silicalites, however, show worse performances. A post-synthesis treatment of TS-1 with both H_2O_2 and NH_4HF_2 (H_2O_2/F/Ti = 10/2.5/1; 60 °C; 4 h) allows to further improve the performances. Upon such treatment, a substantial amount of titanium is extracted from the framework, even if the crystalline structure of the zeolite is preserved. The turn-over frequency of residual titanium atoms rises from 31 to 80 h^{-1} and selectivities, both based on benzene and on hydrogen peroxide, increase from 83 to 94% with formation of catechol (4%), and hydroquinone (2%) as the only byproducts [16].

To further increase the overall yield of the process, a second step can be added in which dihydroxylated by-products (DHB), hydroquinone and catechol, are treated with hydrogen and partially deoxygenated to phenol, which is recycled back to the process [26]. The hydrodeoxygenation reaction (HDO) is carried out in gas phase in a fixed bed reactor (400 °C, 25 bar of hydrogen), using commercial nickel and molibdenum oxides supported on alumina as catalysts. The HDO allows a quantitative transformation of dioxygenated compounds to phenol with a selectivity of 96%.

The block diagram for the process is reported in Fig. 1. The oxidation reaction is carried out in a biphasic mixture of benzene, sulfolane and water (30/50/20, w/w/w). Hydrogen peroxide is used as an aqueous solution (35 wt.%), with a total molar ratio H_2O_2/benzene = 0.21. The oxidation is carried out in fixed bed reactors, operating at 6 atm in adiabatic conditions with inlet temperature of 95 °C and outlet temperature of 110 °C. The overall oxidation section performances per pass are reported in Table 1 together with those for the overall process, including oxidation and HDO sections.

The process economy strongly depends on the acetone to propylene sale prices ratio and on the cost of H_2O_2. The possibility of coupling with direct H_2O_2 synthesis is interesting in this respect,

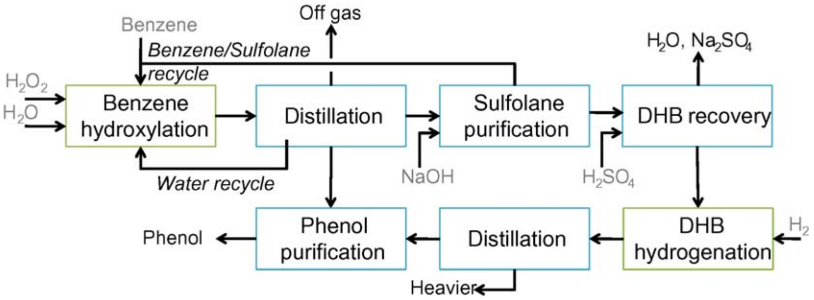

Fig. 1. Block scheme for the Polimeri Europa TS-1/H_2O_2 process for benzene direct hydroxylation to phenol. Adapted from Ricci et al. [19].

Table 1
Per pass oxidation section results and overall process performances, including oxidation and HDO sections, of the Polimeri Europa TS-1/H_2O_2 process for benzene direct hydroxylation to phenol. Adapted from Ricci et al. [19].

	Oxidation section (per pass) (%)	Overall process (%)
Benzene conversion	15.4	100
H_2O_2 conversion	100	100
Selectivity on benzene[a]	84.6	97.7
Selectivity on H_2O_2[b]	61.4	71.0

[a] Moles of produced phenol/moles of converted benzene × 100.
[b] Moles of produced phenol/moles of converted H_2O_2 × 100.

but a current limit regards the still poor performances in direct H_2O_2 synthesis using sulfolane as the solvent.

4. Direct synthesis of hydrogen peroxide

A comparison of selected examples from patents [27–31] on the performances in direct H_2O_2 synthesis is reported in Table 2. A further more detailed analysis of recent patents on direct synthesis of H_2O_2 has been reported elsewhere [7].

Palladium is the active element for the reaction, but the performances could be improved by doping with either Pt or Au. Selectivities in H_2O_2 ranges in the 80–99% and critical factors to achieve higher selectivities are the overall pressure (typically 100 bars or above), the O_2 to H_2 ratio and the use of solvents which promote oxygen solubility. While more recent patents focused attention on the use of an H_2 and O_2 concentration in the feed outside the explosion range, several results were presented inside the explosivity region which are not feasible to be industrially exploited, if not by using special reactor configurations having a very high wall to volume ratio (in micro-reactors, for example). Therefore, often results in terms of performances and productivity are not comparable.

Degussa (now Evonik) has created a joint venture with Headwaters Nanokinetix Inc. (former Hydrocarbon Techn. Inc. – HTI) in 2004 in order to develop and commercialize a direct synthesis process for hydrogen peroxide (DSHP) [32]. The initial phase of activity by Degussa-Headwaters was the construction and operation of a DSHP pilot plant. The pilot plant has successfully operated since the beginning of 2005 leading to the next step in commercial development, construction of a DSHP demonstration plant. The key of the process is a new "nanocatalyst technology" (called NxCat^{TM}), where it is claimed, but not scientifically proven, that it is possible to obtain a preferential exposition of the (1 1 0) crystal face to which the high selectivity and productivity is attributed. Table 2 shows, in fact, that the patented performances of this catalyst [30] are superior both in terms of productivity and especially selectivity, even if in terms of composition and metal particle size the catalyst features are not different from those reported in patents by other companies or in open literature.

The solvent plays a critical role. The use of organic solvents instead of water increases the productivity/selectivity and in some cases also the catalyst lifetime. H_2 conversion was typically lower than total, ranging from 30 to 70%. A H_2 recycle is thus necessary. Staged (sequential) addition of H_2 to maintain more uniform the O_2:H_2 ratio in the reactor and avoid excess O_2 has shown to improve the performances. Batch-type autoclave or continuous fixed bed (trickle-bed) or stirred reactors have been used. Operations were typically under pressure in the 50–100 bar range, while reaction temperature was ranging from 4 to 65 °C. Decreasing the temperature, H_2 solubility increases, but the catalysts specific activity decreases.

A critical issue is the use of non-corrosive solutions. Although bromide ions are typically present to improve selectivity, their concentration is kept low at about 4–6 ppm, except in few cases. NaBr or HBr are used as additives. The use of acids (H_2SO_4, H_3PO_4 principally) is also typically promoting the performances. In some cases, relative high acid concentrations are used, but this could create problems of corrosion on one side and purification of produced H_2O_2 on the other side. Relatively low acid concentrations (100–200 ppm) have been demonstrated to be enough for good selectivities, especially using an acidic support. For example, functionalization of carbon with sulfonic groups promotes the

Table 2
Comparison of selected examples from patents on the performances in direct H_2O_2 synthesis.

Company	Catalyst	H_2O_2 (wt.%)	Selectivity (%)	Reaction conditions
Dupont [27]	Pd–Pt (Pt/Pd + Pt = 0.08) colloidal on alumina	19.6	69	136 bar, 5–8 °C, 18% H_2 in O_2, aqueous acid solution (0.1N HCl)
ENI [28]	1% Pd–0.1%Pt on carbon	7.3	74	100 bar, 8 °C, (autoclave, after 600 h), 3.6% H_2, 11% O_2 in inert 95:5 methanol:H_2O solution (+additives)
BASF [29]	Pd on monolith	7.0	84	144 bar, 10% H_2 in O_2, methanol (+additives)
HTI [30]	Pd(–Pt) on carbon black (140 m^2/g)[a]	9.1 (276 g/g Pd.h)	99	~120 bar, ~35 °C, (autoclave, after 600 h), 3% H_2 in air solvent and additives not indicated
Degussa [31]	2.5% Pd–Au (95:5) on a-Al_2O_3	5.1 (13.8 g/g Pd.h)	72	50 bar, 25 °C (trickle bed), 3% H_2, 20% O_2 methanol (+additives)

[a] It is claimed that using a precursor solution containing an ionic polymer (Na acrylate) it is possible to deposit Pd nanocrystals exposing preferentially the 110 and 220 faces which contain the active sites.

performances. The presence of sulfur in the carbon also promotes dispersion of the noble metal.

In this respect, the very interesting results of Fierro and coworkers [33–35], particularly in terms of high productivity using Pd supported on acid resins [sulfonic acid functionalized polystyrene resins, PS-SO_3H], should be cited. H_2O_2 is more stable in acid medium, but a strong acid could create problems of corrosion and further treatments of the solution. One of the motivations for the use of acidic supports was thus the reduction of the required concentration of inorganic acids in solution and hence minimization of its impact on corrosion. On the other hand, re-adsorption of H_2O_2 (a weak acid) should be avoided on a strong acidic support, and thus the rate of consecutive reactions of H_2O_2 minimized. Fierro and coworkers [6,35], however, suggested on the basis of XPS studies that the high performances of Pd/PS-SO_3H systems result also from the ability of the sulfonic acid groups of the resin to interact and stabilize the Pd^{II} ions without further reduction to metallic palladium. This interaction creates a positive charge on the Pd particles which enhances the selectivity for hydrogen peroxide. Many parameters thus influence the selectivity and catalyst productivity to H_2O_2:

- The relative surface coverage of chemisorbed bimolecular oxygen vs. chemisorbed hydrogen which depends on the surface crystalline structure and the O_2/H_2 concentration in the liquid/solid boundary layer.
- The relative rates of undissociative O_2 chemisorptions vs. dissociative O_2 chemisorptions which depends in general terms from the presence of defective Pd sites on the surface.
- The effect of H_2 in the modification of Pd properties. This aspect was never studied in relation to direct H_2O_2 synthesis, but could be important, particularly to explain the role of Pd particle size and some of the effects on modification of catalytic behavior with time on stream. In fact, it is known that H_2 may fast dissociate on Pd and diffuse in the bulk as H atoms. The formation of interstitial H atoms leads to an expansion of the Pd lattice even before the formation of regular structures such as Pd-hydrate. In small Pd crystallites, H cannot diffuse in the bulk and thus remains mainly on the surface. In medium size Pd crystallites the diffusion of H in the bulk reduces the surface concentration and at the same time induces an expansion of the lattice, leading to an increase of the Pd–Pd distance. Both these effects contribute in limiting the $4e^-$ vs. $2e^-$ reaction with O_2, and thus allow an increase of the selectivity. This effect do not exclude the possibility of stabilization of specific, more effective crystal planes, due to an interaction with the support. For larger particles, the more irregular structure and the lowering of the surface to bulk ratio, leads to a further lowering of the performances.

Safety of operations is a very critical issue, in particular for industrial development. The general issue is that operations outside the explosion region do not correspond to those which maximize the productivity to H_2O_2. Furthermore, in the mixing region or when a dead zone forms in the reactor, local explosion conditions may be present. The use of catalytic membranes offer the potential of intrinsically safe operations, due to a physical separation between H_2 and O_2 in the gas phase [36–38]. This approach offers advantages over a conventional suspended catalyst: (i) intrinsically safe operations are possible due to the separated supply of both gaseous reactants as well as reduced mass transfer limitations by maintaining a thin catalytic zone, (ii) efficient contact of the gaseous reactants on the surface of the wetted solid catalyst and (iii) easy scaling up, particularly for small-scale on-site production of H_2O_2. However, volume productivity is low.

The role of solvent and additives are also critical aspects. The use of organic solvents promotes of one order of magnitude the productivity, essentially due to the higher solubility of H_2 and O_2. However, organic solvents further limit the possible range of operations to avoid explosive mixtures. Operations with very high O_2 concentrations, which increase the selectivity, are possible only using water as the solvent. However, both productivity and selectivity using water are significantly lower than using methanol as the solvent. Increasing the chain length in alcohols increases the H_2 and O_2 solubility, and thus ethanol or isopropanol allow better performances than methanol. However, these solvents are not suited in most of the cases, when the produced H_2O_2-solvent solution should be used for consecutive steps, for example, for propene oxide synthesis using TS-1 as catalyst. Similarly, several of the promoters often used in literature, for example acetate ions, are not compatible with the consecutive step and their removal by distillation is too costly.

The use of organic solvents further limits the range of possible O_2 concentrations (due to a larger explosivity region) and this would require higher reaction pressures to reach enough volume productivities. However, higher reaction pressures lead not only to higher fixed and running costs, but also to an exponentially increase in the risks of operations. It is thus a priority for research to find novel solutions which allow operations at lower reaction pressures.

One of the opportunities to go in these directions is the use of CO_2 to expand organic solvents [39], in order to increase their solubility towards H_2 and particularly O_2, due to the change of solvent polarity. Although studies on this topic are limited, particularly with reference to catalysis, probably CO_2 may also reacts with O_2 to form a reversible peroxocarbonate species ($CO_4^{=}$) which increases the effective solubility of O_2 (a critical factor for selectivity and productivity to H_2O_2) and possibly plays also additional roles [40].

CO_2 can be the ballast to dilute the H_2–O_2 feed in substitution of N_2. Preliminary results using CO_2-expanded methanol are very promising, with a nearly twice selectivity and a large increase of productivity compared with the same experiments performed using N_2 as the diluent [41]. The effect could be further enhanced by using CO_2-expanded methanol in combination with the confinement in mesoporous materials. Due to wall effect (confinement) in mesoporous materials an enthalpic excesses during adsorption processes is expected [42]. Confinement effect was shown to influence the catalytic behavior and positions of IR vibrations of supercritical CO_2 indicate formally higher pressures than the applied one, once confined inside a periodically organized mesoporous material [42,43].

Fig. 2 reports an example of this effect with the comparison of the behavior of Pt supported on silica or deposited inside the channels of a mesoporous silica (SBA-15), using methanol of CO_2-expanded methanol. The amount of Pd in both samples was about 4 wt.% and the size or Pd particles similar. These tests were made at low pressure (6.5 bar) to better evidence the effect. Reaction temperature was 25 °C and the amount of catalyst corresponding to 8 mg Pd for a total reaction volume of 150 ml anhydrous methanol containing 240 μmoles H_2SO_4. No bromine ions or other promoters were present. Tests were carried out in a batch autoclave and the atmosphere in equilibrium with the solvent was the following: (A) CO_2 expanded CH_3OH: 4 bar CO_2, 1 bar N_2, 1 bar O_2, 0.5 bar H_2. (B) CO_2-free CH_3OH: 5 bar N_2, 1 bar O_2, 0.5 bar H_2.

Results in Fig. 2 evidence that the use of CO_2-expanded methanol increases largely the productivity and the selectivity to H_2O_2 for both catalysts, but the effect is particularly enhanced in the case of the mesoporous material. Therefore, reactions in confined environments could further enhance the performances of

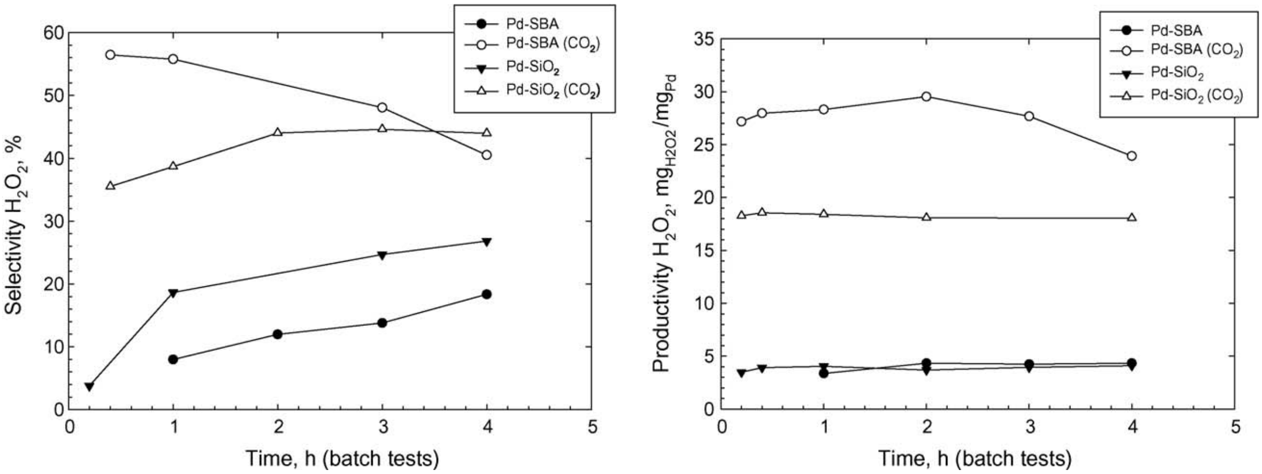

Fig. 2. Selectivity and productivity in H_2O_2 direct synthesis at room temperature using Pd–SiO$_2$ and Pd–SBA-15 catalysts and CO_2-free or CO_2-expanded methanol. See text for reaction conditions.

CO_2-expanded solvents allowing to realize the direct synthesis of H_2O_2 in milder and safer conditions.

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