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Deactivation mechanism of Pd supported on ordered and non-ordered mesoporous silica in the direct H_2O_2 synthesis using CO_2-expanded methanol

Salvatore Abate*, Siglinda Perathoner, Gabriele Centi

Dipartimento di Chimica Industriale ed Ingegneria dei Materiali and INSTM – CASPE, University of Messina, Italy

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ABSTRACT

The deactivation mechanism of Pd supported on silica and mesoporous silica (SBA-15) using CO_2-expanded methanol as solvent was studied in the direct synthesis of H_2O_2 in batch and semi-continuous batch reactor tests as well as its hydrogenolysis. Fresh and used catalysts were characterized by TPR and CO chemisorption. The results evidence the presence of deactivation, which can be correlated to the loss of accessible active metal surface area due to sintering of Pd, but there is also an effect of the presence of the ordered mesoporous structure and of the reaction conditions. The higher concentration of H_2 in solution in semi-continuous batch reactor tests with respect to batch reactor tests leads to a more relevant deactivation in Pd-SiO_2 with respect to Pd-SBA-15, but a higher initial activity, due to the fact that H_2 accelerates the reduction of the Pd species which are less reducible in Pd-SiO_2 than in Pd-SBA-15. Pd-SBA-15 shows a higher H_2O_2 selectivity and productivity with respect to Pd-SiO_2 in batch reactor tests, related to the presence of easier reducible Pd species. Another difference is related to the different mechanism of sintering. On the SBA-15 support, due to the presence of the ordered mesoporosity, the Pd particles migrate into the SBA-15 channels forming elongated 1D-type particles. In Pd-SiO_2 catalyst, instead, the sintering of the Pd particles leads to large aggregates of Pd particles in the range of 20–25 nm.

1. Introduction

Interest on the direct synthesis of H_2O_2 from H_2/O_2 is rising with the starting of operations of new large scale processes using H_2O_2 as reactant such as synthesis of caprolactame by Sumitomo and propene oxide to Dow-BASF [1,2]. The direct synthesis of phenol from benzene using H_2O_2 is another potential large-scale process, although still not on a commercial scale [3]. With respect to the commercial synthesis of H_2O_2 (anthraquinone route), the direct synthesis is a significantly cleaner and potentially economic process, but shows still a number of issues that have prevented the commercialization.

One major problem in the direct synthesis of H_2O_2 derives from the need to operate with diluted H_2 and O_2 gaseous feeds in order to be outside the explosion range of the O_2/H_2/inert mixture, with the consequence of low productivities, which imply the need of high-pressure operations (ca. 100 bar). This is a critical aspect regarding both security and process costs. A relevant target would be thus to operate with a lower pressure. However, besides to a lower productivity, the pressure is also significantly affecting the selectivity to H_2O_2, another critical issue in the process.

The choice of the solvent for operations is another critical parameter. The most desirable solvent is water, being not toxic, not flammable, and highly miscible with hydrogen peroxide. However, the reactants (H_2 and O_2) have a low solubility in water and therefore the rate of H_2O_2 production and the selectivity are limited. Organic solvents, and in particular methanol, are typically used to increase H_2 and O_2 solubilities [4–6]. Methanol is a good choice, especially if the H_2O_2 solution is then used in propene oxide synthesis, being the preferable solvent for this reaction using Ti-silicalite as the catalyst. However, for phenol production, for example, it is not a good solvent and it is thus necessary to have a step of H_2O_2 separation by distillation [3]. In addition, the use of organic solvents increases the issues related to safety of operations.

An alternative solvent is supercritical CO_2, which is a green solvent, shows high solubilities of H_2 and O_2 and acts as in situ acid promoter [7,8]. Although relatively mild conditions are requested for a single fluid phase ($T_c \geq 31.1\,°C$; $P_c \geq 74$ bar), there are a number of safety and technical problems during the decompression stage after the reaction limiting the technical industrial feasibility of this process. A solution is to operate below the triple point and in the presence of a solvent, i.e. a two fluid phase system, the so-called CO_2-expanded liquid. The use of CO_2-expanded solvents has been indicated as an excellent possibility to improve the performances in various selective oxidation reactions [9]. We reported recently that using CO_2-expanded methanol, it is possible to nearly double

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* Corresponding author at: V.le F. Stagno D'Alcontres 31, 98166 Messina.
E-mail address: sabate@ingegneria.unime.it (S. Abate).

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the selectivity to H_2O_2 and increase the productivity at low pressure (around 10 bar) in comparison with the results of the same experiments made using N_2 as the ballast [10,11].

An issue, however, regards the stability in these conditions, and whether the use of CO_2-expanded methanol may lead to catalyst deactivation. The catalysts used in the direct synthesis of H_2O_2 are almost all based on supported Pd, with the eventual presence of a second element (particularly noble metals such as Au or Pt) [4–6]. Few studies have analyzed the possibility of Pd leaching, with general conclusion that it is not relevant and that the leached Pd is not active in the homogeneous solution, i.e. if the solid catalyst is removed [12–14]. This is thus not a main mechanism of deactivation, but sintering of the supported Pd particles may also occur. We need to remark that in general the question of deactivation in H_2O_2 direct synthesis, and sintering of Pd particles during operations of H_2O_2 synthesis, was not yet investigated in detail. Ma et al. [12] have reported the use of recycled Au/TS-1 catalysts in the direct synthesis of H_2O_2. Hutchings and co-workers [14,15] reported that Pd-Au/TiO_2 catalyst calcined at 400 °C did not deactivate with reuse while the uncalcined samples show a decrease in the H_2O_2 produced in batch conditions after about 30 min of reaction time. Strukul et al. [16] reported that Pd-Au catalysts supported on zirconia can be recycled up to three times without loss of activity and selectivity.

In our previous work [17], analyzing the stability of Pd-γ-Al_2O_3 catalysts, in the direct synthesis, we reported the time-on-stream behavior of the catalyst after three consecutive recycle tests. After few hours of reaction, the same productivity in the fresh and three-times-recycled catalyst was observed in a batch reactor, monitoring the productivity to H_2O_2 only at the end of the tests, as in most of literature data. However, monitoring the productivity as a function of time, a clear deactivation was detected. This indicates the possibility that deactivation could be present, even if apparently not detected, due to the type of tests made.

Morphological changes of Pd entities due to particle growth by different processes including sintering and agglomeration [18] are a major cause for a decrease of activity or even complete deactivation of Pd catalysts. We earlier observed by electron microscopy characterization of the used catalysts [11,17] the presence of sintering of Pd particles during the catalytic reaction. A question, however, is whether this change influences the productivity and selectivity. In fact, the catalytic performances depend on the state of Pd during the catalytic reaction, e.g. metallic Pd or PdO (and all the possible intermediate situations, such as metallic Pd with sub-surface oxygen, a PdO layer on a core of metallic Pd or the contrary, etc.) [19,20]. Thus, it is reasonable that the sintering would affect also these properties, and in turn influence the catalytic behavior in a more complex way with respect to a simple decrease of the active surface area (sintering effect).

The possible sintering during reaction and related effects on the catalytic behavior would certainly considerably depend on the type of support. Usually, acidic supports are reported in patents and fundamental studies, because they promote the selectivity to H_2O_2 [4–6]. Among the supports used for the preparation of Pd-based catalysts active in the direct synthesis of H_2O_2 could be mentioned zirconia [21] and sulphated zirconia [22], fluorinated alumina [23], Keggin-type polyoxometalates [24], silica [19] and sulfonic acid-functionalized silica [25], graphite [26] and active carbon [27], functionalized carbons with sulfonic acid groups or sulfonic acid functionalized polystyrene resins (PS-SO_3H) [28,29], N-doped carbon nanotubes [30], TS-1 [31,32], Ti-MCM-41 [33], etc. It is thus not possible for a systematic analysis of the effect of the support in relation to the stability of Pd particles during the direct synthesis of H_2O_2.

We have thus focused the attention on the use of an acidic support such as silica, for the possibility to prepare it also in the form of an ordered mesoporous material such as SBA-15, in order to have indications on how the presence of an ordered nanostructure could influence the stability during the catalytic reaction. Pd-based catalysts supported on SiO_2 and SBA-15 have been thus analyzed by TPR, TEM and CO chemisorptions before and after use either during the direct synthesis of H_2O_2 or during H_2O_2 hydrogenolysis tests. The latter case corresponds to reaction conditions as those during the synthesis of H_2O_2, but without O_2 and in the presence of added H_2O_2. In both cases, thus the present H_2 dissolved in the reaction medium (CO_2-expanded methanol), but in one case it is present and also dissolved O_2 and in the other case H_2O_2.

2. Experimental

2.1. Catalysts preparation

Palladium supported catalysts were prepared by incipient wetness impregnation method: a solution (ca. 20 mL) of HCl 0.01 M and $PdCl_2$ (Sigma–Aldrich) precursor was added drop-wise to the supports under stirring up to complete filling of the pore volume. The supports investigated are SiO_2 and SBA-15. The samples were dried at 90 °C overnight and then calcined at 500 °C in air for 5 h.

Commercial silica was obtained from PQ Corporation (MS-2050) and has a BET surface area of 515 m^2/g. SBA-15 was synthesized using self-assembling on Pluronic P123 triblock polymer (PEO–PPO–PEO, Aldrich). Twenty grams of PEO–PPO–PEO were dissolved in a mixture of 465 g distilled water and 130 g hydrochloric acid (HCl 37%) and stirred for 30 min at room temperature. Forty grams of tetraethyl orthosilicate (TEOS) were added to this polymer solution under vigorous magnetic stirring. The resulting gel mixture was stirred for 20 h at 35 °C and then heated for 21 h at 90 °C. The solid product was filtered and dried for 6 h at 80 °C in an oven. The product was then slurred in ethanol under reflux condition in order to remove the polymer, filtered and washed with ethanol and dried at 100 °C for 48 h. The white product was calcined at 500 °C for 6 h. The BET surface area was 660 m^2/g.

2.2. Characterization of the catalysts

Surface areas were obtained from N_2-adsorption–desorption isotherms using BET method. The samples were outgassed under vacuum at 100 °C for 5 h. Isotherms were obtained at the temperature of liquid nitrogen using a Micrometrics ASAP 2010 system. The pore size distribution curve was estimated using the BJH formula applied to the adsorption or desorption part of the isotherm for relative (P/P_o) pressures larger than 0.31. TPR and CO chemisorptions were carried out on all samples by Micromeritics Autochem 2920 equipment. TPR has been carried out using heating rate of 5 °C/min from −40 °C to 600 °C (the cryocooler unit with liquid N_2 has been used to reach sub ambient temperature) in a 5%H_2 in Ar mixture at a flow rate of 50 ml/min.

CO chemisorption experiments have been performed by the dynamic pulse method at 30 °C with the following procedure: the sample was loaded inside the U-tube, it was heated in He to 300 °C with a 5 °C/m heating rate, than a mixture containing 5%H_2 in Ar was fed for 2 h. The sample was finally cooled to 30 °C, using the cryocooler unit, and six pulses of 0.5 ml of a mixture containing 10% CO in He were injected into the sample under He flow. The (specific metal surface area) MSA [m^2/g Pd] and active particle diameter were obtained by this analysis using a CO/Pd average stoichiometry of 1.

The wt% of the metal incorporated into the support after the preparation was determined by atomic absorption spectroscopy (AAS) performed with a Perkin-Elmer AAnalyst 200. Samples for analysis were prepared dissolving 20 mg of the dried catalyst in

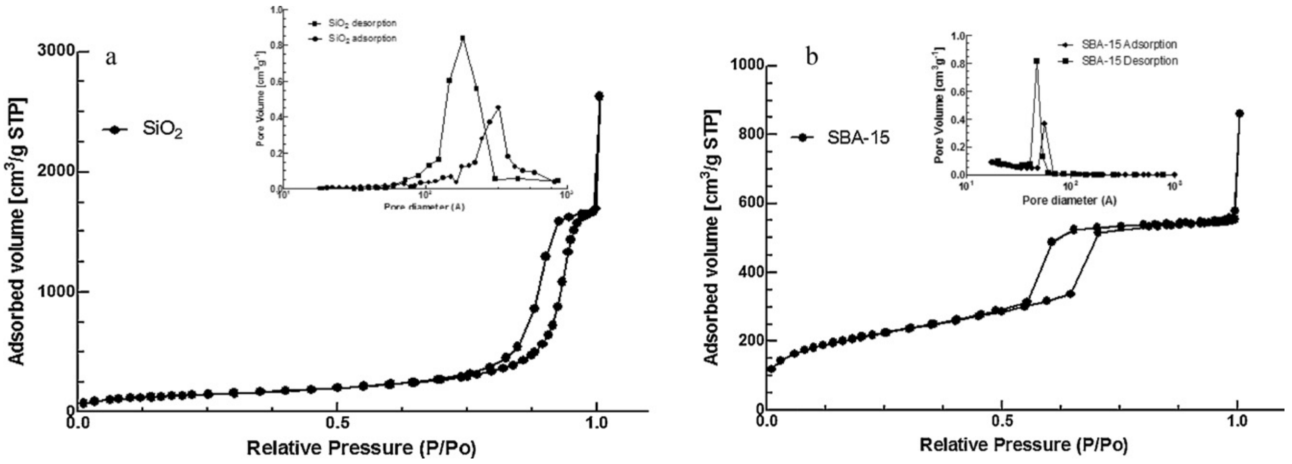


Fig. 1. Nitrogen adsorption isotherm for SiO_2 (a) and SBA-15 (b). In the inset pore size distributions derived from adsorption and desorption branches of the isotherms for both samples.

an aquaregia solution. The amount of Pd (wt%) obtained for the two samples under study was the following: 3.6% (Pd-SiO_2), 4.4% (Pd-SBA-15).

2.3. Catalytic test

The catalysts were tested in the catalytic oxidation of H_2 to H_2O_2 at 20 °C in a stirred steel reactor coated with Teflon (capacity 300 ml), containing 200 mg of catalyst in a fine powder form and 150 ml of anhydrous CH_3OH as a reaction medium with 150 μL of H_2SO_4 as promoter. A gas mixture containing H_2 and O_2 with a H_2/O_2 ratio of 1:2, CO_2 and N_2 was bubbled continuously through the reaction medium at room temperature until the pressure reached the set value of 6.5 bar. After reaching this pressure, the feed was stopped and stirring (1300 rpm) started following the progress of the reaction for 4 h. This procedure for the catalytic tests was indicated as *batch reactor* tests hereinafter. A modification of this procedure is indicated as *semi-batch continuous tests*. In this case, the feed was continuously sent to the autoclave in order to maintain constant the H_2/O_2 ratio. The following feed composition was used (O_2 to H_2 ratio of 2): 7.7% H_2, 15.4% O_2, 61.5% CO_2, 15.4% N_2

The tests, conducted in order to analyze the rate of H_2O_2 hydrogenolysis, were done in batch reactor mode, starting with a solution in which H_2O_2 was already present (2000–3000 ppm) and sending to the reactor the same feeds reported above, except that O_2 was not present and substituted with an equal amount of N_2.

Gas analysis for H_2 and O_2 was made using a gas chromatograph (Agilent 3000A equipped with a Molsieve 5A column using Ar as carrier gas). The reaction products were analyzed by potentiometric titrations of H_2O_2 (Metrohm, 794 Basic Trino) and H_2O (Metrohm, 831 KF Coulometer), respectively. The H_2O_2 selectivity is defined as follows:

$$H_2O_2 \quad \text{selectivity}\,(\%) = \frac{\text{mol}\ H_2O_2}{(\text{mol}\ H_2O_2 + \text{mol}\ H_2O)}$$

3. Results and discussion

3.1. Porosity characterization

The nitrogen sorption isotherm of SiO_2 materials has been used to obtain information about the mesoporosity (Fig. 1). These isotherms are of type IV, according to the IUPAC classification. As shown in Fig. 1a and b, a sharp increase of the adsorbed N_2 volume, characteristic of the capillary condensation within mesopores, occurs for a relative pressure P/P_o larger than 0.5. This jump is irreversible: a hysteresis loop with parallel desorption and adsorption branches is observed. The sharpness of this jump indicates the uniformity of mesopore sizes. Nitrogen condensation occurs at relative similar pressures for SiO_2 (Fig. 1a) and SBA-15 (Fig. 1b) materials, but for the latter one, the adsorption/desorption isotherms are shifted down to lower values of the adsorbed volume. The insert in Fig. 1a displays the pore size distribution determined from adsorption and desorption isotherms for the SiO_2 support. The pore size distribution of the SiO_2 sample is slightly higher than that obtained for SBA-15 sample, which is reported in the inset in Fig. 1b. These analyses confirm the mesoporous character of SiO_2. The choice of the mesoporous SiO_2 was made in order to study the effect of the ordered mesoporous structure on the direct synthesis of H_2O_2.

3.2. TPR profiles

TPR measurements were performed on both catalysts Pd/SiO_2 and Pd/SBA-15 after their preparation (Fig. 2). These profiles were compared with those after reaction in order to investigate the nature of the possible change after the reaction. All TPR profiles show hydrogen desorption peak in the range of 58–62 °C which can be assigned to hydrogen derived from β-PdH decomposition as reported in literature [34–36]. This negative peak is apparently

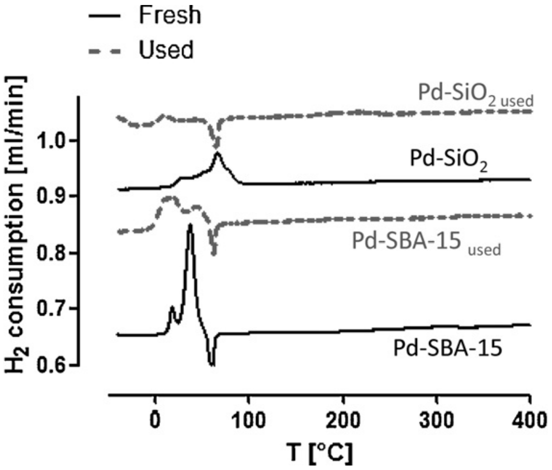


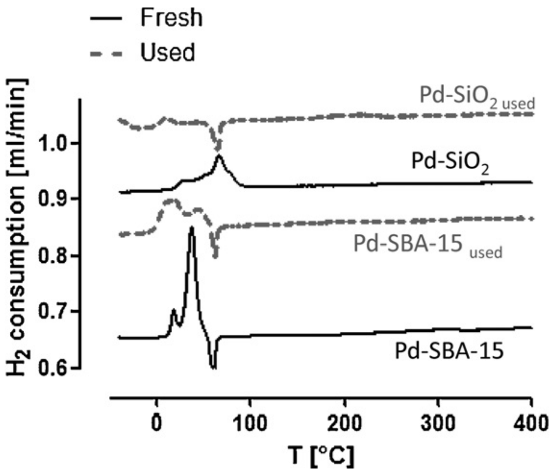
Fig. 2. TPR curves of fresh and used catalysts.

Table 1
Characterization of the fresh and used catalysts by chemisorption of CO.

	$Pd\text{-}SiO_2$			Pd-SBA-15		
	Fresh	Used synthesis	Used hydrogenol.	Fresh	Used synthesis	Used hydrogenol.
MSA ($m^2/g\,Pd$)	90	40	15	88	26	11
Active particle diameter (nm)	4.5	13	25	4	16	28

absent in Pd/SiO_2 catalyst, but it is probably masked, because the formation of the metal phase is not complete in the temperature range of Pd β-hydride stability [35]. Worth to mention that the Pd-hydride forms during the TPR, after reduction of Pd(O) species at lower temperatures. There is no difference (position and intensity) in this negative peak before and after the catalytic tests (see Pd-SBA-15 sample), indicating that the (PdH) has been formed only during the TPR analysis and is not apparently present in the used catalysts.

The TPR profile of Pd/SiO_2 is characterized from a broad adsorption in the 10–100 °C temperature range, with a peak maximum centered at about 65 °C, and the second (broader) centered at about 30 °C. Agostini et al. [35] for Pd on silica–alumina (prepared by decomposition–precipitation) observed only a single TPR peak with maximum around 30 °C, while Karski et al. [37] also observed two TPR reduction peaks similar to our sample in a 5% Pd/SiO_2 catalyst. Moreover Fuentes et al. [38,39] over Pd-alumina catalysts reported the presence of two TPR reduction peaks, although at slightly higher temperatures (in 110–166 °C range).



The interpretation is a two-step reduction process, a first reduction of PdO to Pd_2O followed by reduction of Pd_2O into metallic Pd. The same feature, but with sharper peaks shifted to lower temperatures, is present in the fresh Pd-SBA-15 sample. The TEM characterization of fresh $Pd\text{-}SiO_2$ and Pd-SBA-15 samples [17] indicates for the latter, a slightly higher average diameter of the Pd particles, but a more sharp distribution. Sandoval and Gigola [40] observed for Pd supported on alumina also a main TPR peak at 28 °C that shifted to lower temperatures upon a series of oxidation-reduction cycles which cause a growing of the particles. For Lieske and Volter [41] large Pd-oxide particles reduce at slightly lower temperatures. We could thus conclude that by narrowing the distribution of Pd-supported particles, the TPR peaks become sharper, and shift to slightly lower temperatures on increasing the diameter. This is apparently strange, because one may expect a higher reducibility for smaller particles. However, it could be understood considering the easier presence of defect sites on larger particles which make locally easier the formation of metallic Pd which is then able to produce spillover of hydrogen which accelerates the reduction of the remaining oxidized species Pd(O).

On the basis of this interpretation, it is possible to analyze the TPR curves of the samples after the catalytic tests. In $Pd\text{-}SiO_2$ there is a clear shift to lower temperatures (about 40 °C) of the Pd(O) reduction peaks. After reaction, the reduction peak apparently disappears, but is probably shifted at too low temperatures to be detected. In Pd-SBA-15, the reducibility of Pd(O) species is already higher in the fresh sample with respect to $Pd\text{-}SiO_2$. Two broad peaks, but with the more intense at lower temperature, could be detected. After reaction there is thus a change in the reducibility of Pd(O) species, due to a growing of the particles. Therefore, the presence of an ordered mesoporous structure favors the easier reduction of the Pd particles. Note that the reaction temperature for Pd(O) reduction in TPR curves is very close to the temperature of operation during catalytic tests in direct H_2O_2 synthesis.

3.3. *CO chemisorption*

The results of CO chemisorption experiments are reported in Table 1 in terms of specific metal surface area (MSA) ($m^2/g\,Pd$) and average active particle diameter for the fresh $Pd\text{-}SiO_2$ and Pd-SBA-15 samples and after their use in H_2O_2 synthesis tests and H_2O_2 hydrogenolysis tests. As reported before, in both cases the catalytic tests are made in the presence of H_2 dissolved in the reaction medium (CO_2-expanded methanol). During the H_2O_2 synthesis, O_2 is also present (H_2O_2 as well, because it is formed as a product of reaction), while oxygen is absent during the H_2O_2 hydrogenolysis tests, and the H_2O_2 concentration is higher, being added in an amount of 2000–3000 ppm at the start of the reaction.

The results in Table 1 evidence a significant increase of the average active particle diameter, more enhanced for the Pd-SBA-15 catalyst particularly after the hydrogenolysis tests. Consequently, the MSA decreases from 88 to 40 $m^2/g\,Pd$ after the synthesis reaction and to 15 $m^2/g\,Pd$ after hydrogenolysis reaction for the Pd-SBA-15 catalyst. No change in the MSA was observed when H_2 was absent in the feed mixture during the reaction. The easy reduction of Pd, when H_2 is present in solution leads to a fast mobility of Pd [42], probably enhanced from the presence of the CO_2-expanded methanol, determining a fast sintering of the catalyst. When the catalyst shows an easier reduction (Pd-SBA-15 with respect to $Pd\text{-}SiO_2$), the sintering is enhanced. When O_2 is absent, which partially consumes H_2 for the H_2O_2 synthesis, the sintering effect is larger.

The data on Pd particle size distribution are consistent with HRTEM (high-resolution transmission electron microscopy) data, which have been not reported here and were being discussed in a previous work [17]. However, it is useful to summarize some of these indications obtained by TEM. Information on the particle size distribution was obtained by a systematic TEM analysis on a statistically significant number of particles. Few larger Pd particles aggregates are present in both catalysts, and the distribution of particle size based on statistical elaboration of the TEM images shows a fraction of particles in the range of 3–6 nm for Pd/SiO_2 and 3.5–7.5 for Pd/SBA-15 catalysts. TEM characterization of the samples after H_2O_2 direct synthesis clearly evidences the great mobility of Pd particles, with migration inside the channels and formation of elongated Pd particles in the case of Pd/SBA-15 and formation of particles of 10–20 nm which stick together forming larger

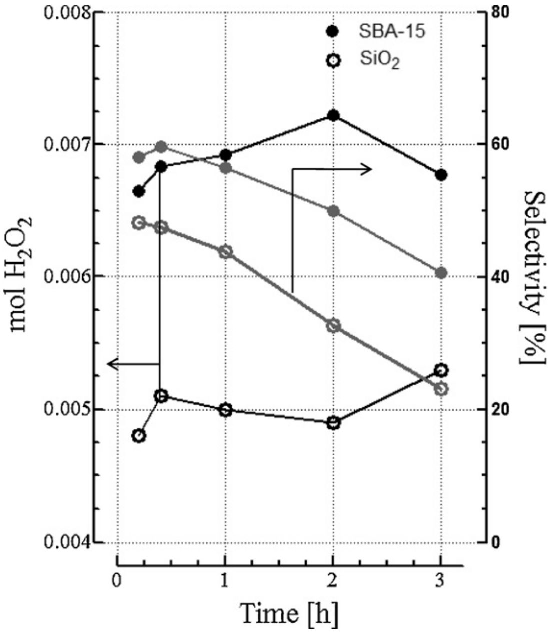


Fig. 3. mol H_2O_2 produced (black line) and selectivity (grey line) in batch reactor conditions as a function of time of reaction using Pd-SiO_2 and Pd-SBA-15 catalysts.

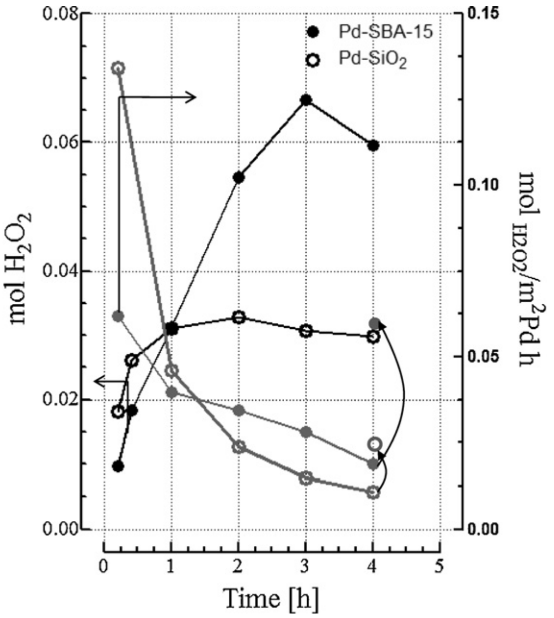


Fig. 4. mol H_2O_2 produced (black line) and specific activity in $mol_{H_2O_2}/m^2$ Pd h (grey line) in semi-batch continuous reactor test as a function of time on stream using Pd-SiO_2 and Pd-SBA-15 catalysts.

aggregates. The Pd/SiO_2 catalyst also evidenced agglomeration of the Pd particles

3.4. Catalytic tests: synthesis of H_2O_2

Reported in Fig. 3 are the catalytic results in H_2O_2 synthesis using CO_2-expanded methanol for both Pd-SiO_2 and Pd-SBA-15 catalysts as a function of time on stream in batch reactor conditions. Fig. 3 reports the amount of hydrogen peroxide (mol H_2O_2) produced and the selectivity to hydrogen peroxide. These data evidence that there is a very fast initial formation of H_2O_2 and after 10 min of time on stream the reaction rate is already significantly slowed down. In fact the rate in the first 10 min is about 15–20 times higher than that for the consecutive 10 min. It may also be noted that after 30 min the reaction rate is very low. It should be noted that the observed rate results are from the difference between rate of synthesis and hydrogenolysis and/or decomposition of H_2O_2. This explains why a maximum in formation of H_2O_2 is observed for the Pd-SBA-15 sample after 2 h of reaction. Due to the progressive lowering of the activity in H_2O_2 synthesis, after this time the rate of further H_2O_2 conversion becomes higher than that of direct synthesis, and the resulting amount of H_2O_2 thus decreases. It is worth to note that notwithstanding the metal surface area of both the fresh catalysts is the same, and the sintering during reaction is even higher in Pd-SBA-15 with respect to Pd-SiO_2 (Table 1), the former shows a better activity. However, considering the higher amount of Pd present in the former catalyst, the difference in the specific activity is limited. The initial specific activity calculated after 0.2 h using the MSA of the fresh catalyst reported in Table 1 is 0.042 $mol_{H_2O_2}/m^2$ Pd h for Pd-SBA-15 and 0.035 $mol_{H_2O_2}/m^2$ Pd h for the Pd-SiO_2 samples. The formal chemical composition of SiO_2 and SBA-15 is the same, but the latter shows an ordered mesoporous structure. However, not only the textural characteristics are different, but also the surface properties, in terms of defects, amount of silanols, etc. It is thus not possible to attribute unambiguously the enhanced activity of Pd-SBA-15 with respect to Pd-SiO_2 to the presence of the ordered mesoporous structure or to other associated aspects.

However, it is possible to note that not only the specific activity but also the selectivity to H_2O_2 is higher for Pd/SBA-15. Also TPR data (Fig. 2) evidence the different characteristics of Pd particles in the two samples. Therefore, SBA-15 stabilizes a slightly different form of Pd particles with higher activity and selectivity. It may be tentatively suggested that the presence of a higher concentration of surface hydroxyl groups in SBA-15 with respect to SiO_2 leads to more active and selective, and easier to reduce, Pd(O) particles.

The selectivity to H_2O_2 decreases with the increase in reaction time in a similar way for the two catalysts. Being the concentration of H_2O_2 in solution nearly constant from about 0.5–3 h of time of reaction, the decrease of selectivity should be attributed to a decrease of the rate of H_2O_2 synthesis with thus an increase in the relative importance of the consecutive reaction of H_2O_2 hydrogenolysis/decomposition to water. Also this result confirms the presence of a significant modification of the catalytic performances during the reaction of H_2O_2 synthesis.

In the batch reactor test the effective partial pressure of H_2 and O_2 changes during the reaction due to the consumption of these reactants. This fact may influence the comparison between the two catalysts. For this reason, we have investigated the behavior of these two catalysts and also in semi-batch continuous tests where the gas phase feed composition and the pressure are maintained constant during the experiments. The results are reported in Fig. 4 in terms of mol of H_2O_2 produced.

Both catalysts show a similar trend during the first hour of time on stream, with a slightly higher activity shown in this case by Pd-SiO_2 catalyst. Both catalysts after one hour show a productivity of 100–200 gH_2O_2/g Pd which is quite good considering the low operation pressure (6.5 bar), while most of the literature data refer to much higher pressure (40–100 bar) for a comparable activity. After 1 h, however, the activity of Pd-SiO_2 nearly stops, while the amount of H_2O_2 continues to increase in Pd-SBA-15 up to around 3 h of time-on-stream, after which it decreases due to the dominance of the reaction of consecutive conversion. The selectivity results for semi-batch tests are quite similar to those reported in batch tests and for this reason these data are not reported in Fig. 4.

It should be observed that the amount of H_2O_2 formed in semi-batch reactor tests is higher with respect to that in batch-reactor

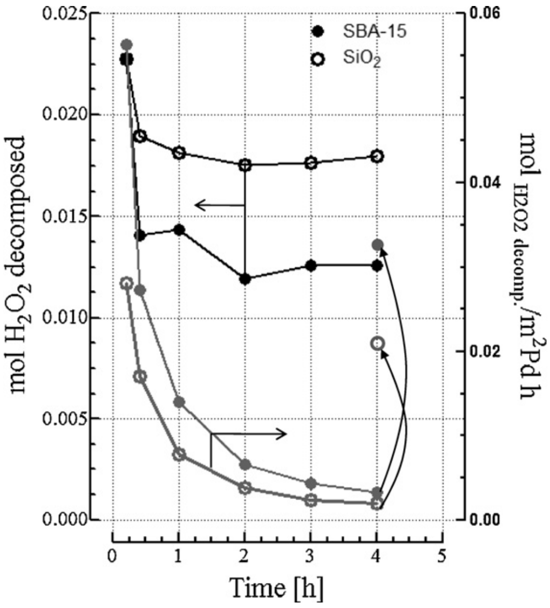


Fig. 5. mol H_2O_2 decomposed (black line) and specific activity in $mol_{H_2O_2}/m^2$ Pd h (grey line) in batch reactor conditions as a function of time of reaction using Pd-SiO_2 and Pd-SBA-15 catalysts.

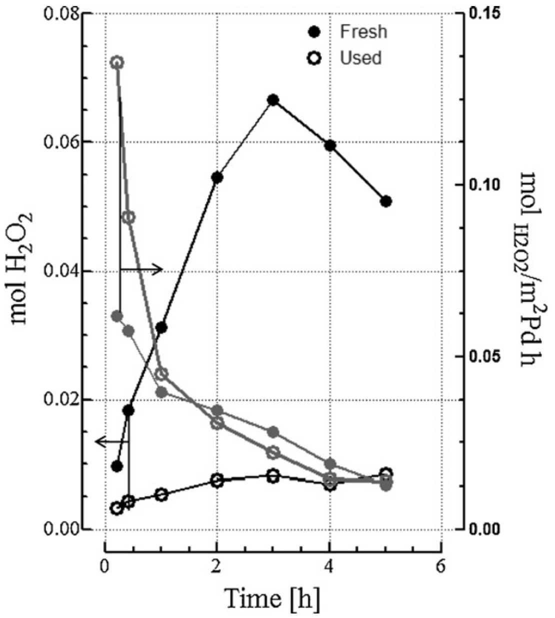


Fig. 6. Comparison of the mol H_2O_2 produced (black line) and specific activity in $mol_{H_2O_2}/m^2$ Pd h (grey line) as a function of the time on stream in semi-batch continuous reactor tests using the fresh and used (recycled) Pd-SBA-15 catalyst.

tests, due to the continuous flow of the reactants. The effective concentration of H_2 and O_2 in solution, and CO_2 as well, during the reaction is thus different, even if the feed concentration was the same. This explains the apparent different results observed in the two cases. In general terms, however, the results of the two types of reactors are consistent, with a fast deactivation observed in both cases, but with a minor effect present in Pd-SBA-15 sample, possibly in relation to the effect of the support in stabilizing slightly different Pd species with respect to silica.

In order to better analyze this question, Fig. 4 reports also the specific activity expressed as square meter of Pd per hour (m^2 Pd h). We used the MSA of the fresh catalyst to calculate the specific activity, but as commented before, we observed sintering of Pd particles during the reaction, so in Fig. 4 we compare the specific activity after 4 h calculated using the MSA values also for the used catalysts. In this way, the specific activity for Pd-SBA-15 (full circle) increases from 0.018 to 0.055 $mol_{H_2O_2}/m^2$ Pd h, which is close to the initial value of activity of 0.062 $mol_{H_2O_2}/m^2$ Pd h. A different behavior has been observed for the Pd/SiO_2 sample (empty circle). In this case the value after 4 h, increase from 0.010 to 0.025 $mol_{H_2O_2}/m^2$ Pd h which is quite different from the initial value of 0.13 $mol_{H_2O_2}/m^2$ Pd h.

Therefore, the higher concentration of H_2 present in solution in semi-continuous batch reactor tests with respect to batch reactor tests leads to a much more relevant deactivation in Pd-SiO_2 with respect to Pd-SBA-15, but a higher initial activity is observed, due to the fact that H_2 accelerates the reduction of Pd(O) which is less reducible in Pd-SiO_2 than in Pd-SBA-15 (Fig. 2).

3.5. Catalytic tests: hydrogenolysis of H_2O_2

These tests are analogous to those for the synthesis of H_2O_2, but O_2 is absent in the feed mixture and an amount of H_2O_2 is initially added. These tests allow analyzing the rate of consecutive hydrogenolysis of H_2O_2, because earlier we observed [43] that this reaction is mainly responsible for the lowering in selectivity in the direct synthesis of hydrogen peroxide.

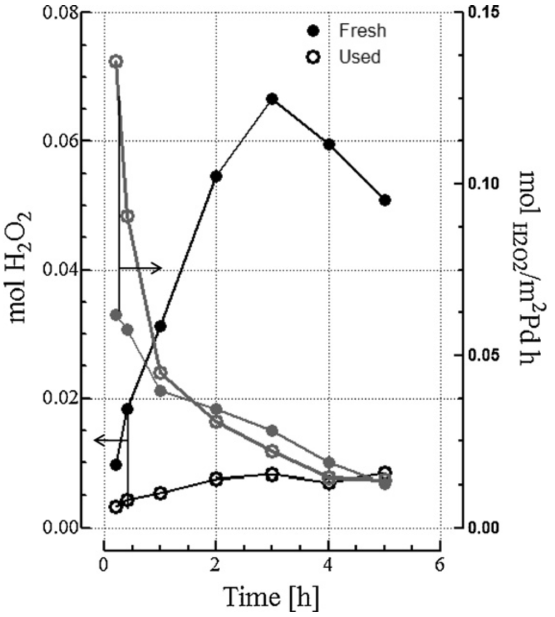
Reported in Fig. 5 are the moles of H_2O_2 decomposed as a function of time of stream for both Pd-SBA-15 and Pd-SiO_2 catalysts. The specific activity expressed in mol H_2O_2 decomposed/m^2 Pd h is also reported. The Pd-SBA-15 sample shows an initial faster hydrogenolysis rate with respect to the Pd/SiO_2 catalyst. In this case, as reported for the synthesis, we calculate the specific activity for the hydrogenolysis reaction using the MSA of the fresh catalyst. For the final value (after 4 h), the specific activity is also calculated considering the MSA of the used catalyst as sake of comparison. For Pd-SBA-15 catalyst the specific activity value increases from 0.0032 to 0.030 $mol_{H_2O_2\,decomp.}/m^2$ Pd h (filled-circle) while the initial value was 0.056 $mol_{H_2O_2\,decomp.}/m^2$ Pd h. In the case of the Pd/SiO_2 catalyst the specific activity value increases from 0.0019 to 0.022 $mol_{H_2O_2\,decomp.}/m^2$ Pd h (empty circle) while the initial value was 0.028 $mol_{H_2O_2\,decomp.}/m^2$ Pd h. The reaction of H_2O_2 hydrogenolysis depends on the concentration of H_2O_2, which varies during the reaction. Assuming a linear dependence, it is possible to normalize the reaction rates with respect to the different H_2O_2 concentrations. Taking into account this aspect, the values of the initial and final reaction rates are almost the same. Therefore, there is a process of sintering, which influences the catalyst activity in H_2O_2 hydrogenolysis, but the specific activity in the initial and final catalysts is similar. This indicates that the specific activity in this reaction is not influenced from the diameter of the Pd particles.

3.6. Leaching of Pd and recyclability of the catalysts

A small amount of Pd was leached during the catalytic tests, less than 5% of the Pd present on the catalyst, in both batch and semi-batch reactor tests. In order to exclude the possible contribution of this leached Pd to the catalytic activity, the catalyst was removed after reaction by careful filtration (at the same temperature of the catalytic tests) and dried at 100 °C overnight. The solution was used again feeding the same gas mixture and no further H_2O_2 was formed. This result excludes that the leached Pd contributes to the reaction in our experimental conditions.

The recyclability of the catalysts after the semi-continuous batch reactor tests, where the sintering was more severe, was analyzed for Pd-SBA-15 catalysts, in order to check whether the deactivation continues in consecutive tests. The catalyst was filtered and dried as indicated above, and then tested again. Reported in Fig. 6 are the moles of H_2O_2 formed as a function of the time on stream using the fresh and used (recycled) Pd-SBA-15 catalysts. In the latter case a marked deactivation was observed. The amount of H_2O_2 produced after 3 h decreases from 0.07 mol for the fresh sample to 0.03 mol for used (recycled) sample. We were not able to characterize by TPR and/or chemisorption the reused catalyst, because after the second filtration the amount of catalyst was not enough to make the analyses. However, the trend of the specific activity, which decreases very fast for both fresh and used catalysts, suggests clearly that a further sintering of the catalyst occurs. It may also be noted that apart from an initial difference, the trend of the specific productivity is very similar, while one could expect a decrease in the rate of sintering on increasing the size of the particles.

TEM characterization of the Pd-SBA-15 catalyst reported in a previous work [11] indicated after use with CO_2-expanded methanol, that Pd migrates into the SBA-15 channels during the reaction forming elongated 1D-type particles with diameter corresponding to that of SBA-15 channels (about 5–6 nm) and length up to over 50 nm. This effect is specific for SBA-15 due to the presence of the ordered mesoporosity, while in Pd-SiO_2 catalyst the sintering of Pd leads to large aggregates of Pd particles.



The formation of the elongated Pd chains inside the SBA-15 mesopores explains the above observation why the trend of the specific productivity as a function of time on stream is the same in fresh and used (recycled) samples, even if the latter has significantly larger average size of the Pd particles (Table 1). In fact, these elongated Pd chains prevent the access to the inner Pd reducing that available for the direct synthesis to that accessible from the H_2 and O_2 reactants at the entrance of the channel. However, due to the confinement in the channels, this accessible part is seen as a particle of average size of 6 nm, i.e. the diameter of the SBA-15 channels. Therefore, initially in the fresh Pd-SBA-15 there is a migration from outside to inside the channels, and then there is a progressive growing and elongation of the Pd chains inside the SBA-15 mesopores. This fact explains the initial difference (first hour) in the trends of the productivity between the fresh and used (recycled) Pd-SBA-15, and the similar trend later.

4. Conclusions

The catalytic behavior of Pd supported on silica and mesoporous silica (SBA-15) in the direct synthesis of H_2O_2 using CO_2-expanded methanol as solvent is significantly dominated from the fast sintering of Pd. The catalytic performances were studied both in the direct synthesis of H_2O_2, following the productivity and selectivity as a function of time in batch reactor and in semi-continuous batch reactor tests, and in the hydrogenolysis of H_2O_2. In both reactions a Pd particles sintering is present, and is accelerated in the case of semi-continuous batch reactor tests. The correlation of the catalytic behavior with the characterization by TPR and CO chemisorption indicates that in general terms the catalyst deactivation depends on the loss of active, accessible metal surface area, but there is also an effect due to the order of the mesoporous structure and of the reactor conditions.

The higher concentration of H_2 in solution in semi-continuous batch reactor tests with respect to batch reactor tests leads to a relevant deactivation in Pd-SiO_2 with respect to Pd-SBA-15, but a higher initial activity is observed, due to the fact that H_2 accelerates the reduction of Pd(O) less reducible in Pd-SiO_2 than in Pd-SBA-15. Pd-SBA-15 shows a higher selectivity with respect to Pd-SiO_2 in batch reactor tests, related to the presence of easier reducible Pd(O) species in the fresh catalysts, tentatively attributed to the higher concentration of surface hydroxyl groups in SBA-15 with respect to SiO_2.

Another difference is related to the different mechanism of sintering. In the presence of CO_2-expanded methanol as solvent, Pd migrates into the SBA-15 channels during the reaction forming elongated 1D-type particles with diameter corresponding to that of SBA-15 channels (about 5–6 nm) and length up to over 50 nm. This effect is specific of SBA-15 due to the presence of the ordered mesoporosity, while in Pd-SiO_2 catalyst the sintering of the Pd particles leads to large aggregates of Pd particles in the range 20–25 nm. As commented above, this different mechanism could be correlated to the observed trends in the productivity to H_2O_2 of the fresh and used (recycled) Pd-SBA-15 catalyst.

In conclusion, there are significant effects of deactivation related to Pd sintering in these catalysts for the direct synthesis of H_2O_2. We will neither extrapolate these results to all catalysts nor mention that these phenomena are more relevant using CO_2-expanded methanol, although methanol is the typical solvent used in the direct synthesis of H_2O_2, and CO_2 was used by other authors as ballast mainly for safety reasons [14,15]. Our results evidence that the sintering is related to the presence of H_2 and is accelerated when the H_2 concentration in solution is higher, either when O_2 is absent (H_2O_2 hydrogenolysis tests) or in semi-continuous reactor tests. Therefore, may exist reaction conditions (for example very high O_2 to H_2 ratios, or lower H_2 concentrations with respect to our experimental conditions) where the effect is minimized. The support also certainly plays a role. However, these results remark the point that more attention to this phenomenon of deactivation by Pd sintering during H_2O_2 synthesis has to be given. As commented in the introduction, often experiments do not allow to analyze properly this problem, while more attention was typically given to the possible leaching of Pd which is a technological problem, also for safety reasons, but a less relevant aspect in terms of catalyst stability.

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