



Hydrogen substitutes for the *in situ* generation of H₂O₂: An application in the Fenton reaction

Mohammad S. Yalfani, Sandra Contreras*, Francesc Medina**, Jesus E. Sueiras

Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain

ARTICLE INFO

Article history:

Received 16 March 2011

Received in revised form 6 May 2011

Accepted 10 May 2011

Available online 17 May 2011

Key words:

Formic acid

Hydrazine

Hydroxylamine

In situ hydrogen peroxide

Fenton reaction

ABSTRACT

This study investigates the ability of formic acid, hydrazine and hydroxylamine to act as H₂ substitutes in conducting phenol degradation by Fenton reaction using *in situ* generated hydrogen peroxide. The processes were performed with semi-heterogeneous (Pd/Al₂O₃ + soluble Fe²⁺) and fully heterogeneous (FePd/Al₂O₃) catalytic systems under ambient conditions. In contrast to bulk H₂O₂ production conditions, hydrazine is able to produce H₂O₂ *in situ* followed by phenol degradation using Pd/Al₂O₃ + Fe²⁺ at pH 3 without the need for halide ions. However, a degree of mineralization exceeding 37% could not be achieved. The significant production of *in situ* H₂O₂ at the inherent acidic pH of hydroxylammonium sulfate in the presence of Pd/Al₂O₃ + Fe²⁺ was also found to differ from the bulk production of H₂O₂, in which no H₂O₂ was detected. A remarkable degree of mineralization (ca. 65%) as well as fast phenol degradation during the reaction started at pH 7 over FePd/Al₂O₃ may be an advantage of using hydroxylamine. On the other hand, using formic acid, H₂O₂ was produced at a moderate rate, thereby achieving higher efficiency in the mineralization of phenol. Most importantly, the catalysts were more stable in the presence of formic acid than hydrazine or hydroxylamine.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The past few decades have seen growing interest in the use of *in situ* generated H₂O₂ for oxidation processes as an alternative to pre-manufactured H₂O₂ [1,2]. In some cases, the application of *in situ* generated H₂O₂ has been found to be potentially safer and more economical than bulk commercial H₂O₂ [3–5]. Few reports have been published on the use of *in situ* generated H₂O₂ for wastewater treatment, specifically for the oxidation of organic pollutants [6,7]. H₂O₂ generation directly from H₂ and O₂ using a metal-supported catalyst has been widely studied [8]. However, this process has several inevitable drawbacks which affect H₂O₂ productivity and selectivity, including (i) the potentially high explosiveness of the O₂/H₂ mixture, requiring researchers to limit their work to less hazardous ratios of the gases; and (ii) the low solubility of O₂ and H₂ in water [9]. The use of alcohols instead of water as a solvent has been suggested by some researchers as a possible method for improving H₂O₂ selectivity [10]. However, if the H₂O₂ generated by means of this process is used *in situ* for the subsequent oxidation reaction, the alcohols themselves may undergo undesired oxidation.

One of the most effective alternatives for overcoming these drawbacks is replacing H₂ with another source. This eradicates the risk of explosion associated with the O₂/H₂ mixture and eliminates one of the low soluble gases. Hydrazine (HZ) and formic acid (FA) have been introduced as H₂ substitutes in the generation of H₂O₂ using alumina-supported Pd catalysts [11,12]. Evans et al. [13] generated H₂O₂ using hydroxylamine (HA) and O₂ catalyzed by Mn complexes. Other authors have shown that alcohols in the presence of homogeneous Pd catalyst and O₂ can produce hydrogen peroxide [14].

HZ and its salts are widely recognized as an H₂ storage material due to their capacity for decomposing to H₂ under mild conditions [15,16]. Choudhary et al. reported that HZ could be used as an H₂ substitute for the production of H₂O₂ over Pd/Al₂O₃ resulting in remarkable H₂O₂ selectivity [11]. In that process, no evidence was found to indicate that H₂ formation occurred through the decomposition of HZ. In other words, H₂O₂ is the product of a direct reaction between HZ and O₂. Pd based catalysts have been found to be inactive for HZ decomposition to H₂ in aqueous solution and under ambient conditions [16]. However, a small amount of H₂ with a short lifetime has been detected in the presence of O₂ [17]. Although HZ is classified as a toxic and possibly carcinogenic compound, no HZ remains at the end of the reaction. The process requires halide ions and mineral acid in order to stabilize the H₂O₂ produced. In the absence of either of these reagents, no H₂O₂ was detected. Recently, the same authors (Choudhary

* Corresponding author. Tel.: +34 977559680.

** Corresponding author. Tel.: +34 977559787; fax: +34 977559621.

E-mail addresses: sandra.contreras@urv.cat (S. Contreras), francesc.medina@urv.cat (F. Medina).

et al.) proposed HA as an H₂ substitute for the *in situ* generation of H₂O₂ using Pd/Al₂O₃ catalyst [18]. The advantage of HA over HZ is its ability to achieve very high H₂O₂ productivity at neutral pH without the need for halide ions. It has been mentioned that without the initial neutralization of the medium, no H₂O₂ was formed. *In situ* generated H₂O₂ from HA and O₂ has been applied in the oxidation of Calmagite dye [7]. We have reported a simple, clean and environmentally friendly method for the generation of H₂O₂ via FA and O₂ [12]. In this method, FA (as an H₂ substitute) and O₂ react over a Pd/Al₂O₃ catalyst under ambient conditions leading to the generation of hydrogen peroxide. Subsequently, this process was applied in the degradation of phenol in the presence of Fe²⁺ (Fenton's catalyst) with significant performance compared to the conventional Fenton process [19]. The process was successfully expanded for different categories of organic pollutants such as chlorophenols and pharmaceutical compounds [20].

In this paper, we study the performance of HZ, HA and FA as H₂ substitutes for the *in situ* generation of H₂O₂ in the presence of O₂. The *in situ* generated H₂O₂ is applied in the degradation of phenol (as representative of organic pollutants) through a Fenton-like reaction. The efficiency of the process is evaluated by means of the phenol conversion, TOC removal results and the evolution of aromatic intermediates (catechol). The effect of the factors enhancing the H₂O₂ formation yield (halide ion and pH) is investigated. The reactions are conducted over a semi-heterogeneous Pd/Al₂O₃ + Fe²⁺ and a fully heterogeneous Pd–Fe/Al₂O₃ catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

Pd/Al₂O₃ (denoted as PdAl) and Fe–Pd/Al₂O₃ (denoted as FePdAl) catalysts were synthesized through conventional impregnation. For PdAl, an acidified solution of PdCl₂ was added to a slurry solution of γ -Al₂O₃ (prepared by sol–gel). The mixture was aged while stirring for 1 h. Water was removed by rotary vapor at 55 °C. The precipitate was dried at 110 °C and was then calcined at 400 °C for 3 h. Finally, the catalyst was reduced under a flow of H₂ (20 ml/min) at 200 °C for 2 h. Pd content on alumina was 5 wt%. To synthesize FePdAl, first γ -alumina was impregnated by an aqueous solution containing a certain amount of Fe(NO₃)₃·9H₂O followed by drying at 110 °C and calcining at 400 °C for 3 h. Afterwards, the calcined solid was impregnated with PdCl₂ followed by drying and calcining through the same procedure as performed for Fe. Finally, the solid was reduced by H₂ at 200 °C for 2 h. The Fe and Pd contents were 1 and 5 wt%, respectively.

The catalysts were characterized by XRD, H₂ chemisorption, H₂-TPR, HRTEM and XPS. The details of the characterization techniques and their results have been explained in previous reports [19,20]. In summary, PdAl showed a metallic Pd phase with an average particle size of 20 nm, whereas smaller Pd particles appeared in the FePdAl sample. H₂-TPR results showed that for PdAl, most of the Pd species were reduced to metallic Pd by H₂ at room temperature due to the negative desorption peak of β -PdH at less than 100 °C. However, in the presence of Fe (the FePdAl sample), a reduction at around 120 °C occurs as well which represents co-reduction of Pd and Fe species. XPS analysis of FePdAl confirmed the partial reduction of Fe species at 100 °C. On the other hand, no Pd–Fe alloy could be detected in this sample by HRTEM, while metallic Pd and Fe₂O₃ were clearly observed. Therefore, it can be concluded that on the FePdAl sample, the major phases are metallic Pd and Fe(III) with a close vicinity. Such vicinity although causes an interaction between Pd and Fe species, does not lead to the formation of the Pd–Fe alloy.

2.2. Catalytic tests

The phenol degradation reactions were performed under ambient conditions (25 °C and atmospheric pressure) in a 100 ml magnetically stirred three-necked glass reactor. The volume of the reaction was 50 ml containing phenol (100 mg/L), Fe²⁺ (if required 10 mg/L), Br[−] (if required 1 mM) and the catalyst (0.1 g). Initial concentrations of FA, hydrazine hydrate (N₂H₄·H₂O) and hydroxylamine sulfate ((NH₂OH)₂·H₂SO₄) were 40 mM, 20 mM and 40 mM respectively. Oxygen was passed through the reaction medium at a flow rate of 20 ml/min. Without exception, all the reactions were performed in darkness to avoid any interfering effect of existing light. The reactions using the FePdAl catalyst were performed under the same conditions as mentioned above, but in the absence of Fe²⁺. It is worth to note that the amount of Fe on FePdAl is theoretically twice the amount of soluble Fe²⁺. However, it should be considered that a significant number of atoms of Fe are not available when they are anchored on the surface of alumina as big clusters. The desired pH of the solution was adjusted using H₂SO₄ or NaOH.

Phenol degradation and FA decomposition were monitored by sampling at regular intervals and analyzing by means of high-performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV–vis detector). A Varian OmniSpher C18 column and a solution containing Milli-Q H₂O and acetonitrile (60:40) at pH 3.80 adjusted by H₃PO₄ as mobile phase were used to analyze phenol and catechol at a wavelength of 254 nm. An Acclaim OA column and a mobile phase containing 100 mM Na₂SO₄ at pH 2.65 adjusted by methanesulfonic acid as mobile phase were used to analyze FA at a wavelength of 210 nm. H₂O₂ evolution during the reaction was monitored semi-quantitatively by *Quantofix* H₂O₂ indicator strips (MACHEREY-NAGEL). HZ was analyzed by titration against KIO₃ in the presence of HCl and chloroform as documented by Penneman et al. [21]. HA was measured by reverse iodometric titration using potassium iodate [22]. Total Organic Carbon (TOC) for each sample was measured using a Shimadzu TOC-5000A analyzer. The reaction solution at the end of each run and after filtration was analyzed by atomic absorption spectroscopy to measure Pd and Fe leaching.

3. Results and discussion

3.1. Formic acid

Phenol conversion profiles (Fig. 1A) using H₂O₂ generated *in situ* from FA and O₂ in the presence of PdAl + Fe²⁺ and over FePdAl show similar performances for both processes. A fast decrease of phenol concentration within 1 h (55–65%) followed by a moderate conversion up to 4 h was observed during the reaction periods. Within 4 h, a degree of mineralization of 55% was obtained by means of the semi-heterogeneous (PdAl + Fe²⁺) system, while better mineralization (66%) was achieved using the fully heterogeneous (FePdAl) catalytic system. Prolonging the reactions up to 6 h resulted in a further decrease of TOC, whereas phenol concentration remained constant. Mineralization occurrence after 4 h can be attributed to the activity of both PdAl and FePdAl catalysts in the degradation of the intermediates in the presence of O₂. The FA decomposition profiles (Fig. 1B) of the above two reactions also demonstrate very similar trends indicating the termination of FA within 4 h. This suggests that Fe does not interfere in FA decomposition over Pd in the reaction over FePdAl.

Halide ions can promote the efficiency of the reaction by poisoning the catalyst, thereby decreasing its hydrogenation activity and the decomposition of H₂O₂ [23]. In the presence of halide ions, H₂O₂ formation using FA and O₂ led to H₂O₂ selectivity enhancement after a long reaction period (1 h), while in a short period (5 min)

H_2O_2 selectivity did not significantly improve, which is an essential component of the *in situ* application of H_2O_2 [12]. This means that the halide ion effect on H_2O_2 generation is more substantial in the bulk production of H_2O_2 . To study the halide ion effect on the *in situ* generation of H_2O_2 , we performed phenol degradation using H_2O_2 generated *in situ* over $\text{PdAl} + \text{Fe}^{2+}$ in the presence of Br^- . The phenol conversion profile of this reaction in Fig. 1A shows a drastically reduced rate in comparison with the same reaction without Br^- . The FA decomposition profile for this process (Fig. 1B) clearly shows a very slow FA disappearance rate. This behavior can be attributed to Br^- , which deactivates the catalyst for the decomposition of FA. It can be concluded that for the *in situ* generation of H_2O_2 , the presence of a poison which deactivates the catalyst leading to the accumulation of H_2O_2 in the medium over a long time is not required; a fast H_2O_2 generation rate for the subsequent oxidation reaction is more important.

In order to test the performance of this catalytic system in a wider pH range, phenol degradation was performed over FePdAl at the initial pH 7 adjusted with NaOH . The phenol concentration profile (Fig. 1A) indicates that no phenol conversion occurred. Other

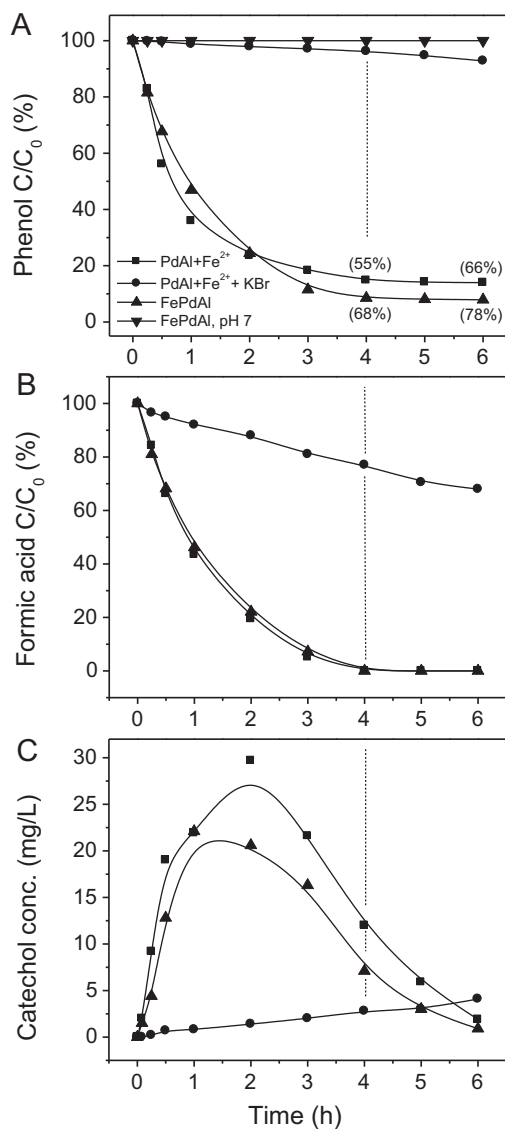


Fig. 1. Phenol degradation using *in situ* generated H_2O_2 from FA and O_2 using $\text{PdAl} + \text{Fe}^{2+}$, $\text{PdAl} + \text{Fe}^{2+} + \text{KBr}$, FePdAl and FePdAl (pH 7). (a) Phenol conversion profiles (b) FA conversion profiles. (c) Evolution of catechol.

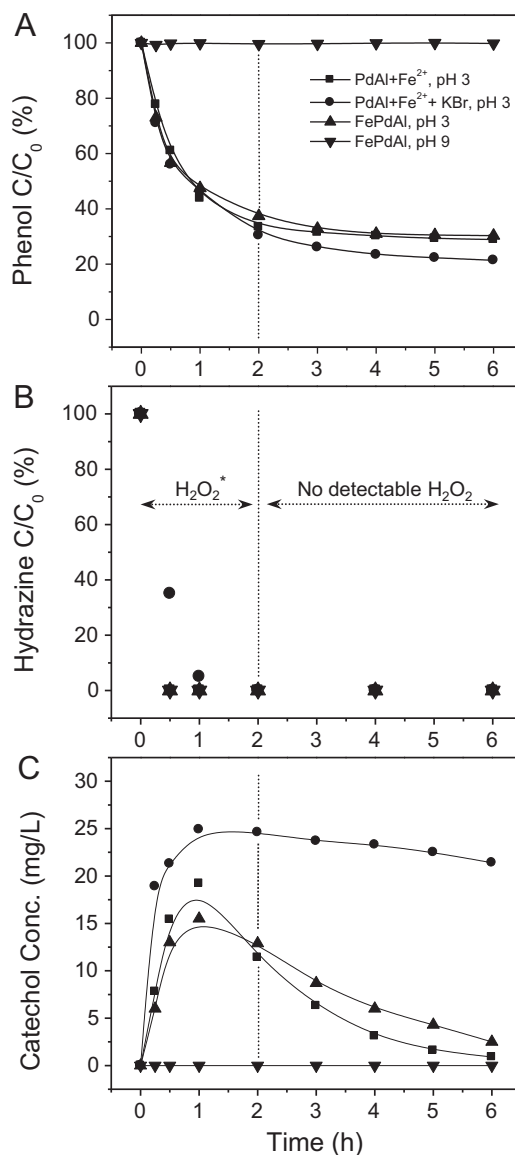


Fig. 2. Phenol degradation using *in situ* generated H_2O_2 from HZ and O_2 using $\text{PdAl} + \text{Fe}^{2+}$ (pH 3), $\text{PdAl} + \text{Fe}^{2+} + \text{KBr}$ (pH 3), FePdAl (pH 3) and FePdAl (pH 9). (a) Phenol conversion profiles (b) HZ conversion profiles. (c) Evolution of catechol. *No H_2O_2 was detected during the reaction performed using FePdAl (pH 9).

studies have found that under ambient conditions and in aqueous solution, the decomposition rate of the formate ion at $\text{pH} \geq 7$ is constant and so much slower than FA itself [17]. Consequently, H_2 cannot be produced at an appropriate rate for the formation of H_2O_2 .

The formation of intermediates during the process of phenol degradation points to the occurrence of oxidation reactions. Consequently, the existence of an *in situ* generated oxidant is proved. We monitored the evolution of catechol as one of the well-known aromatic intermediates of phenol oxidation (Fig. 1C). For the reactions over $\text{PdAl} + \text{Fe}^{2+}$ and FePdAl , catechol appears in similar slopes reaching maxima at 2 h and 1 h, respectively. Over FePdAl , catechol disappears a little faster, suggesting a higher capability of the catalyst in the degradation of intermediates, which had already been demonstrated by the degree of mineralization results. In the presence of Br^- , catechol is formed at a very slow rate representing a weak oxidation process. It is worth noting that during the above reactions apparently no H_2O_2 was detected in the reaction medium, suggesting its rapid consumption by the oxidation reaction.

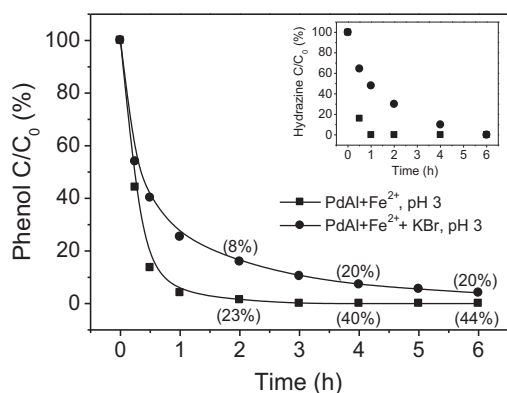


Fig. 3. Phenol (100 mg/L) degradation using *in situ* generated H_2O_2 from hydrazine (40 mM) and O_2 (20 ml/min) using PdAl (0.1 g) + Fe^{2+} (10 mg/L) (pH 3), PdAl (0.1 g) + Fe^{2+} (10 mg/L) + KBr (1 mM) (pH 3) (the numbers in the parentheses are the corresponding TOC removal (%)). Inset: hydrazine conversion during the two above reactions.

For all the above reactions using PdAl and FePdAl, no Pd and Fe leaching was detected in the final solutions. Single Pd shows high stability when it is deposited on alumina [19]. Moreover, the coupling of Fe and Pd promotes the resistance of Fe species against corrosion in a moderately acidic medium [20].

3.2. Hydrazine

The reaction of HZ and O_2 over supported-Pd catalyst is supposed to occur based on the following reactions:



Assuming the optimum circumstance for H_2O_2 formation through the reaction (1), each mol HZ can be oxidized to two mol H_2O_2 . Therefore, in order to have a fair comparison between HZ and FA in this study, HZ was used as half of the initial molar concentration of FA, i.e. 20 mM.

H_2O_2 generated *in situ* from HZ and O_2 using a PdAl + Fe^{2+} system at initial pH 3 (Fig. 2A) quickly converted phenol, within 1 h (>50%). HZ disappeared in less than 30 min (Fig. 2B), as had been previously observed during H_2O_2 generation [11]. H_2O_2 was detected, reaching a maximum (ca. 20 mg/L) at 30 min which vanished after 2 h. The appearance of free H_2O_2 within the solution suggests a higher rate of H_2O_2 formation than H_2O_2 consumption by phenol oxidation. After 2 h, thus, phenol degradation by *in situ* generated H_2O_2 was suppressed. Over FePdAl, similar behavior was also observed for the conversion of phenol and decomposition of HZ (Fig. 2A and B). Most interestingly, while the reaction of HZ and O_2 over Pd/Al₂O₃ in the absence of halide ions and strong mineral acid yielded no H_2O_2 [11], during the oxidation reaction carried out under the same conditions, *in situ* generated H_2O_2 was semi-quantitatively detected.

Phenol degradation using PdAl + Fe^{2+} in the presence of Br^- and started at pH 3 was proceeded at a rate similar to that in the two previous reactions (Fig. 2A), while the conversion of HZ was slightly slower (Fig. 2B). Monitoring of the H_2O_2 produced revealed ca. 40 mg/L H_2O_2 at 30 min, which supports the assumption, mentioned earlier regarding the higher stability of H_2O_2 formed in the presence of halide ions. After 1 h, H_2O_2 concentration was reduced to less than 5 mg/L. The use of a higher initial concentration of HZ (40 mM) better revealed the influence of Br^- on phenol degradation (Fig. 3). HZ conversion clearly decreased in the presence of Br^- , leading to slower conversion of phenol and a weaker degree

of mineralization. This means that the catalyst is poisoned by Br^- and loses its activity for decomposition of hydrazine.

Phenol degradation was conducted without the addition of acid at inherent basic pH (ca. 9) created by the addition of 20 mM hydrazine hydrate over FePdAl. Surprisingly, no phenol conversion was observed (Fig. 2A), whereas HZ disappeared very quickly (shown in Fig. 2B). Furthermore, no H_2O_2 was detected by the indicator strips during the reaction. It seems that the HZ and O_2 reaction under these conditions was directed mostly toward the formation of H_2O (reaction (2)) [11]. By conversion of HZ in less than 1 h, the pH of the solution drops to 4.6 (the pH of a solution containing phenol and the catalyst) remaining constant until the end of the reaction period (6 h). It can be concluded that the H_2O_2 generation by HZ and O_2 for bulk production and *in situ* purposes essentially needs to be carried out in an acidic pH.

Fig. 2C shows the evolution profiles of catechol through the phenol degradation reactions. For the reactions involving FePdAl and PdAl + Fe^{2+} started at pH 3, catechol appears at a high rate, reaching a maximum at 1 h, which confirms the occurrence of phenol oxidation. After 1 h, mild degradation continued until the end of the reaction periods. After 2 h, when no H_2O_2 was generated in the reaction medium, catechol oxidation took place in the presence of O_2 and the catalyst [19]. During a reaction using PdAl + Fe^{2+} in the presence of Br^- at pH 3, catechol was produced along with phenol oxidation within 1 h. The catechol concentration even exceeded the maximum concentration obtained in the absence of Br^- , which is consistent with the higher amount of H_2O_2 apparently detected. Nevertheless, after 1 h, the concentration of catechol remained almost constant. These observations indicate that the activity of the catalyst for the degradation of catechol is drastically reduced by Br^- .

For the reactions conducted using PdAl + Fe^{2+} and FePdAl, TOC removal yielded similar profiles (Fig. 4). In the presence of Br^- , TOC removal was drastically diminished, which is in agreement with the results of catechol evolution, i.e. catalyst deactivation by Br^- . Obviously, no TOC removal was observed for the reaction carried out in the absence of acid (pH 9).

The stability of the catalysts was studied by measuring metal leaching at the end of the reactions. PdAl indicated remarkable stability so that Pd loss was always less than 0.1% compared to the total Pd content of the catalyst. In addition, phenol degradation using the PdAl used (filtered, washed and dried after the first run) + Fe^{2+} yielded results similar to those using fresh catalyst. Pd was also stable on the FePdAl catalyst. However, for this catalyst, Fe indicated marked leaching (5 mg/L, ca. 20% of the total Fe content of the catalyst) for the reaction started at pH 3. This might be due to a decrease

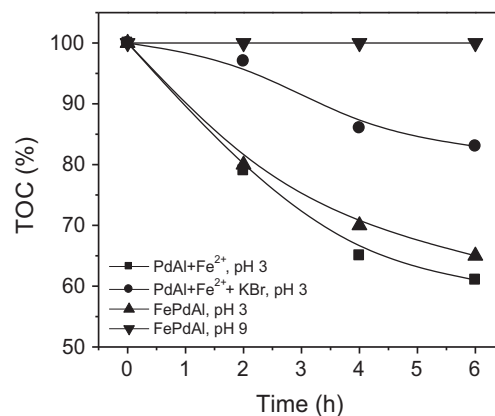
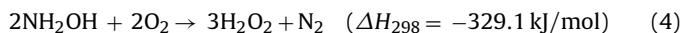
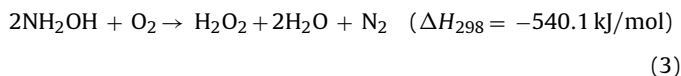


Fig. 4. TOC conversions during phenol degradation using *in situ* generated H_2O_2 from HZ and O_2 .

in pH down to 1.6 during the reaction, which is highly corrosive for Fe.

3.3. Hydroxylamine

In the presence of O_2 , HA conversion can occur as follows:



Assuming the reaction (3) as the predominant route, i.e. formation of 1 mol H_2O_2 by 2 mol HA, 40 mM hydroxylammonium sulfate was used as initial concentration for all the reactions in order to be comparable with FA and HZ. As a hydroxylammonium sulfate salt, HA has an acidic character; therefore, the addition of a 40 mM concentration to a solution containing phenol (100 mg/L) and the catalyst (0.1 g) leads to a pH of 3.8. Phenol degradation using PdAl + Fe^{2+} as shown in Fig. 5A, after a relatively fast

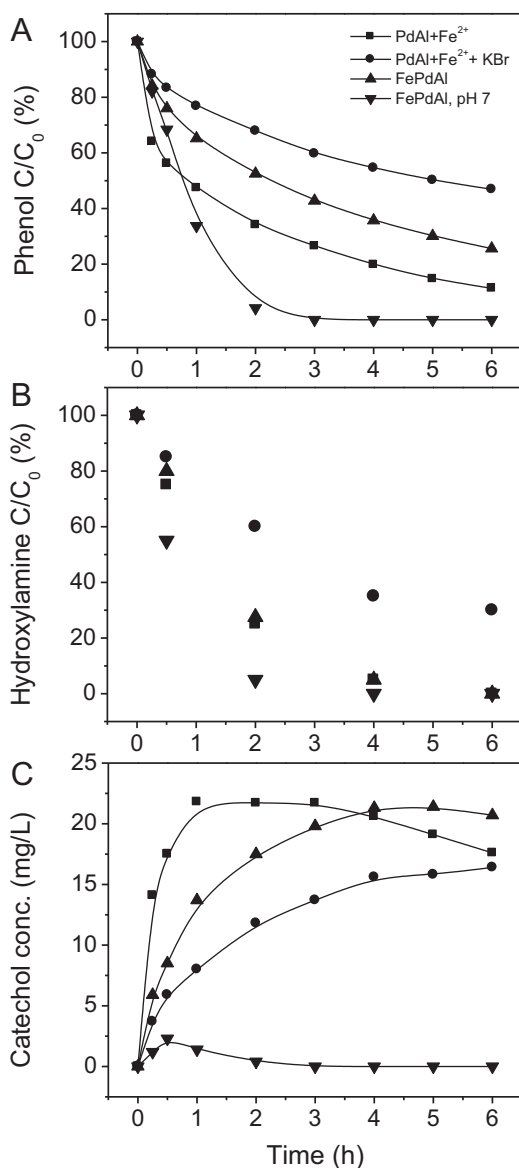


Fig. 5. Phenol degradation using *in situ* generated H_2O_2 from HA and O_2 over PdAl + Fe^{2+} , PdAl + Fe^{2+} + KBr, FePdAl and FePdAl (pH 9). (a) Phenol conversion profiles (b) HA conversion profiles. (c) Evolution of catechol.

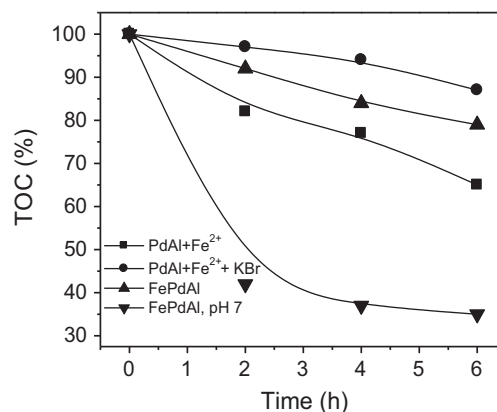


Fig. 6. TOC conversions during phenol degradation using *in situ* generated H_2O_2 from HA and O_2 .

degradation within 1 h, progresses gradually, reaching 88% conversion after 6 h. The conversion of HA (Fig. 5B) reaches ca. 70% within 2 h followed by its complete disappearance at 6 h. Over FePdAl, phenol conversion took place at a lesser rate than over PdAl (Fig. 4A) whereas the conversion of HA was similar to that over PdAl (Fig. 5B). In the presence of Br^- and using PdAl + Fe^{2+} , the phenol conversion rate was drastically decreased (Fig. 5A), leading to a 47% conversion after 6 h. It is clear that Br^- affects HA conversion by poisoning active sites of the catalyst leading to a lower activity. No H_2O_2 was detected during the above reactions, which means that all the H_2O_2 produced was consumed *in situ* by the oxidation reactions. The pH of the medium during the above reactions decreased from 3.8 to 3.2–3.5 at the end of the reaction periods. The oxidation of phenol through the above reactions at such an acidic pH implies H_2O_2 formation. H_2O_2 formation from HA and O_2 had not previously occurred without neutralization [18]. The catalysts showed interesting stability in that no significant metal leaching was detected at the end of each run. Furthermore, a phenol degradation reaction performed using the PdAl used (filtered, washed and dried after the first run) + Fe^{2+} demonstrated results similar to those yielded using fresh catalyst.

Phenol degradation was conducted using HA over FePdAl at the initial pH 7 adjusted by NaOH. Phenol disappeared in less than 3 h as shown in Fig. 5A. Total conversion of HA was achieved in less than 4 h (Fig. 5B) and the formation and the accumulation of a significant amount of H_2O_2 was observed. Within 1 h, a concentration of >150 mg/L H_2O_2 could be detected semi-quantitatively. The H_2O_2 produced showed interesting persistence during the reaction which might be due to the acidic medium created by termination of HA [24]. After 6 h reaction, there still was approximately 15 mg/L H_2O_2 available in the solution. The pH of the solution decreased slowly during the first 30 min from 7.0 to 6.4. Then the pH dropped to 3.0 at 1 h resulting in a final pH of 2.8 after 6 h. Maintaining the medium at this pH for 5 h and releasing of SO_4^{2-} as a result of $(NH_2OH)_2H_2SO_4$ decomposition might be the cause of 2 mg/L Fe leaching (ca. 8% of total iron content of the catalyst) detected at the end of the run. An experiment showed that such a low concentration of Fe^{2+} , although it can slightly proceed the Fenton reaction, is not conclusive for the whole process.

For the reaction performed using PdAl + Fe^{2+} , catechol concentration rapidly reached a maximum at 1 h followed by moderate decomposition up to 6 h (Fig. 5C). Over FePdAl, the catechol evolution profile shows a continuous increase reaching its maximum at 5 h, suggesting a lesser oxidation activity for this reaction. Using PdAl + Fe^{2+} and in the presence of Br^- , the weaker oxidation activ-

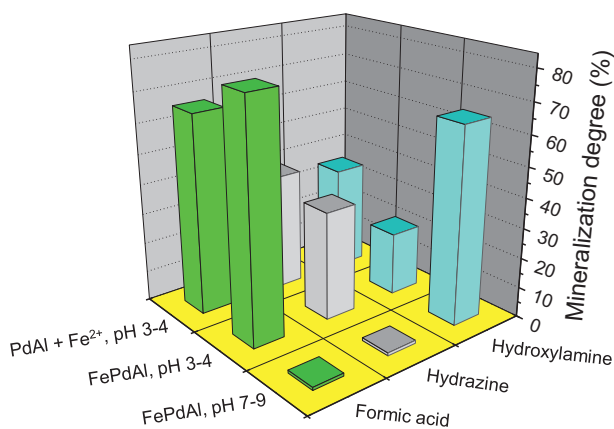


Fig. 7. The comparison of the performances of formic acid, hydrazine and hydroxylamine in phenol degradation using *in situ* generation of H₂O₂ under different conditions.

ity of the system becomes clear, i.e. the formation of catechol is slower. Interestingly, in the case of the reaction performed over FePdAl at initial pH 7, catechol appears in a small quantity (2 mg/L) at 30 min which rapidly degrades in less than 3 h. These results exemplify the remarkable oxidative capability of this system.

The TOC results shown in Fig. 6 indicate a degree of mineralization of 35% achieved using PdAl + Fe²⁺ at acidic pH after 6 h. A lesser degree of mineralization was obtained using FePdAl (21% in 6 h), which is in line with lower phenol conversion and catechol appearance. The lowest capacity for mineralization was observed with PdAl + Fe²⁺ in the presence of Br⁻. Nevertheless, a degree of mineralization of 65% was achieved by the reaction over FePdAl at pH 7 after 6 h. It should be noted that 95% of such achievement was accomplished within 2 h.

4. Conclusions: comparison of H₂ substitutes

Generally speaking, the bulk production of H₂O₂ over Pd-based catalysts requires the presence of a strong acid and halide ions in order to achieve high selectivity. However, the application of H₂O₂ generated *in situ* for phenol degradation in the presence of halide ions, regardless of the H₂ source, is not very efficient. On the other hand, in contrast to the bulk production in which no H₂O₂ was produced in the absence of halide ions, the oxidation of phenol and its intermediates under such conditions confirmed the formation of H₂O₂. Actually, the H₂O₂ produced is consumed by the oxidation reaction before its decomposition to H₂O and O₂. Therefore, it can be concluded that the presence of halide ions is not in favor of *in situ* generation of H₂O₂.

H₂O₂ formation using FA as an H₂ substitute had previously been shown to be less efficient than HZ and HA. However, FA showed better performance during the *in situ* generation of H₂O₂ employed for the oxidation of organic pollutants (Fig. 7). The achievement of higher mineralization and the remarkable stability of the catalyst are advantages of using FA as an H₂ substitute. This behavior of FA suggests a controlled productivity for H₂O₂ which is suitable for the subsequent oxidation process. HZ cannot compete with FA in the *in situ* generation of H₂O₂ applied in phenol degradation. Firstly, its performance is highly dependent on the presence of strong mineral acid, which can reduce catalyst stability due to metal corrosion. Secondly, its fast decomposition over Pd leads to the production of a large quantity of H₂O₂ which is exposed to

dehydration or self-decomposition rather than being consumed as an oxidant. Nevertheless, in the case of HA, the high H₂O₂ productivity obtained at neutral pH may be an advantage when effluents with neutral or nearly basic pH are treated. Phenol degradation by H₂O₂ generated *in situ* from HA was remarkably efficient at neutral pH (Fig. 7). It is worth noting that considering this advantage, the initial concentration of HA and the organic compound to be oxidized should be optimized in order to avoid any loss of the H₂O₂ formed.

Acknowledgements

This work was funded by the Spanish Ministry of Science and Innovation (MICINN) project CTM2008-02453 and the Center for Innovation and Business Development (CIDEM) project VALTEC 08-1-0052. We also thank MICINN for the funding given to S.C. through the Ramón y Cajal program. M.S.Y. acknowledges the URV for the PhD grant awarded. F.M. would like to thank ICREA Academia for its funding support.

References

- M.G. Clerici, P. Ingallina, Oxidation reactions with *in situ* generated oxidants, *Catal. Today* 41 (1998) 351–364.
- S.K. Karmee, L. Greiner, A. Kraynov, T.E. Müller, B. Niemeijer, W. Leitner, Nanoparticle catalyzed oxidation of sulfides to sulfones by *in situ* generated H₂O₂ in supercritical carbon dioxide/water biphasic medium, *Chem. Commun.* 46 (2010) 6705–6707.
- J.E. Remias, T.A. Pavlosky, A. Sen, Catalytic hydroxylation of benzene and cyclohexane using *in situ* generated hydrogen peroxide: new mechanistic insights and comparison with hydrogen peroxide added directly, *J. Mol. Catal. A: Chem.* 203 (2003) 179–192.
- B. Chowdhury, J.J. Bravo-Suárez, M. Daté, M. Haruta, Trimethylamine as a gas-phase promoter: highly efficient epoxidation of propylene over supported gold catalysts, *Angew. Chem. Int. Ed.* 45 (2006) 412–415.
- Q. Chen, E.J. Beckman, One-pot green synthesis of propylene oxide using *in situ* generated hydrogen peroxide in carbon dioxide, *Green Chem.* 10 (2008) 934–938.
- Y.-G. Zhang, L.-L. Ma, J.-L. Li, Y. Yu, *In situ* Fenton reagent generated from TiO₂/Cu₂O composite film: a new way to utilize TiO₂ under visible light irradiation, *Environ. Sci. Technol.* 41 (2007) 6264–6269.
- T.S. Sheriff, S. Cope, M. Ekwegh, Calmagite dye oxidation using *in situ* generated hydrogen peroxide catalyzed by manganese(II) ions, *Dalton Trans.* (2007) 5119–5122.
- J.K. Edwards, G.J. Hutchings, Palladium and gold–palladium catalysts for the direct synthesis of hydrogen peroxide, *Angew. Chem. Int. Ed.* 47 (2008) 9192–9198.
- J.M. Campus-Martín, G. Blanco-Brieva, J.L.G. Fierro, Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process, *Angew. Chem. Int. Ed.* 45 (2006) 6962–6984.
- Q. Liu, J.H. Lunsford, Controlling factors in the direct formation of H₂O₂ from H₂ and O₂ over a Pd/SiO₂ catalyst in ethanol, *Appl. Catal. A: Gen.* 314 (2006) 94–100.
- V.R. Choudhary, C. Samanta, P. Jana, A novel route for *in situ* H₂O₂ generation from selective reduction of O₂ by hydrazine using heterogeneous Pd catalyst in an aqueous medium, *Chem. Commun.* (2005) 5399–5401.
- M.S. Yalfani, S. Contreras, F. Medina, J. Sueiras, Direct generation of hydrogen peroxide from formic acid and O₂ using heterogeneous Pd/γ-Al₂O₃ catalysts, *Chem. Commun.* (2008) 3885–3887.
- D.F. Evans, T.S. Sheriff, The production of hydrogen peroxide from dioxygen and hydroxylamine catalyzed by manganese complexes, *J. Chem. Soc. Chem. Commun.* (1985) 1407–1408.
- R. Bortolo, D. Bianchi, R. D' Aloisio, C. Querci, M. Ricci, Production of hydrogen peroxide from oxygen and alcohols, catalyzed by palladium complexes, *J. Mol. Catal. A: Chem.* 153 (2000) 25–29.
- S.K. Singh, X.-B. Zhang, Q. Xu, Room-temperature hydrogen generation from hydrous hydrazine for chemical hydrogen storage, *J. Am. Chem. Soc.* 131 (2009) 9894–9895.
- M. Zheng, R. Cheng, X. Chen, N. Li, L. Li, X. Wang, T. Zhang, A novel approach for CO-free H₂ production via catalytic decomposition of hydrazine, *Int. J. Hydrogen Energy* 30 (2005) 1081–1089.
- F.-D. Kopinke, K. Mackenzie, R. Koehler, A. Georgi, Alternative sources of hydrogen for hydrodechlorination of chlorinated organic compounds in water on Pd catalysts, *Appl. Catal. A: Gen.* 271 (2004) 119–128.
- V.R. Choudhary, P. Jana, *In situ* generation of hydrogen peroxide from reaction of O₂ with hydroxylamine from hydroxylammonium salt in neutral aqueous or non-aqueous medium using reusable Pd/Al₂O₃ catalyst, *Catal. Commun.* 8 (2007) 1578–1582.

- [19] M.S. Yalfani, S. Contreras, F. Medina, J. Sueiras, Phenol degradation by Fenton's process using catalytic in situ generated hydrogen peroxide, *Appl. Catal. B: Environ.* 89 (2009) 519–526.
- [20] M.S. Yalfani, S. Contreras, J. Llorca, M. Dominguez, J.E. Sueiras, F. Medina, Simultaneous in situ generation of hydrogen peroxide and Fenton reaction over Pd–Fe catalysts, *Phys. Chem. Chem. Phys.* 12 (2010) 14673–14676.
- [21] R.A. Penneman, L.F. Audrieth, Quantitative determination of hydrazine, *Anal. Chem.* 20 (1948) 1058–1061.
- [22] J. Mendham, R.C. Denney, J.D. Barnes, M.J.K. Thomas, *Vogel's Textbook of Quantitative Chemical Analysis*, 6th ed., Pearson Education Limited, Essex, UK, 2000.
- [23] V.R. Choudhary, C. Samanta, Role of chloride or bromide anions and protons for promoting the selective oxidation of H₂ by O₂ to H₂O₂ over supported Pd catalysts in an aqueous medium, *J. Catal.* 238 (2006) 28–38.
- [24] V.R. Choudhary, P. Jana, Factors influencing the in situ generation of hydrogen peroxide from the reduction of oxygen by hydroxylamine from hydroxylammonium sulfate over Pd/alumina, *Appl. Catal. A: Gen.* 335 (2008) 95–102.