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Catalytic wet oxidation with H_2O_2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts

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Abstract

The catalytic wet oxidation with hydrogen peroxide (WHPO) of diluted formic, acetic and propionic acid solutions (total organic carbon of 30 mg C/l) in the 25–70°C temperature range using a Fe^{3+}-containing zeolite (Fe/ZSM5) is compared with the behavior of homogeneous Fe^{3+} catalysts at the same experimental conditions. Although the heterogeneous catalysts have a higher reactivity and a reduced dependence on the pH of the solution in comparison to the homogeneous Fe^{3+} catalysts, they also have a higher rate of the side reaction of hydrogen peroxide decomposition to water and oxygen. Leaching tests indicate that the activity of the heterogeneous catalyst is not due to leached iron ions, although a small amount of iron was found in the aqueous solution. It was also observed that catalytic behavior could be reproduced in consecutive catalytic experiments, but an intermediate calcination step is necessary to oxidize the organic species which remain trapped inside the pore of the zeolite. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen peroxide; Wet oxidation; Fe/ZSM5; Propionic acid; Acetic acid

1. Introduction

Wet air oxidation is a common technology for reducing the total organic carbon (TOC) in industrial waste water [1–7], but the high reaction temperature required allows economic operation only when the heat of reaction released during the oxidation allows autothermal operation [8]. For lower TOC values, oxidation agents which are more active than O_2 are necessary in order to work at the lower reaction temperature necessary for autothermal operation. Ozone and H_2O_2 are among the more preferable oxidants, because (i) they are active even at room temperature and (ii) they result in O_2 and H_2O as the only end products. Ozonation is a known technology for water treatment [9–12], but for treating medium range TOC solutions the limited ozone solubility in water at atmospheric pressure and its short lifetime makes the process expensive. H_2O_2 is the prefered oxidant in these case. Furthermore, hydrogen peroxide is a safer reactant than ozone and more suited for 'recalcitrant' (low biodegradability) chemicals such as acetic acid, because homolytic scission yields two hydroxyl radicals from H_2O_2. These hydroxyl radicals are second only to fluorine radicals in terms of oxidizing power.

Hydrogen peroxide is a relatively costly reactant, but operating costs are compensated by the lower fixed capital cost with respect to ozonation and wet air oxidation. It is thus commercially used in several types of treatment plants for industrial water [13–15]. However, for the generation of hydroxyl radicals from H_2O_2 and minimization of the side reaction of decomposition to water, either photochemical or catalytic activation is needed. Photoactivation needs UV

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radiation, but due to the very low extinction coefficient of hydrogen peroxide, the cost of the process is quite high. The operating cost due to energy and consumption of UV lamps is up to 50–60% of the total cost of water purification [13].

Catalytic generation of hydoxyl radicals by iron ions (Fenton mechanism) is well known [16,17] and schematically reported below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \tag{2}$$

The reaction is used commercially to treat industrial water [13–15], but the main drawbacks are the limited range of pH (3–5) in which the reaction proceedes and the need for recovering iron after the treatment.

These drawbacks can be overcome in principle using heterogeneous Fenton-type catalysts, but only a few attempts have been made to evaluate their potential [18–22]. Recently interesting preliminary results on the high catalytic activity of iron-containing zeolites [21] and copper-containing pillared clays [22] for phenol oxidation have been reported. In contrast to the previous findings, these authors reported that it was possible to develop stable catalysts with minimal, if any, leaching of the transition metal, and thus opened up the possibility of the practical application of heterogeneous catalytic wet oxidation with H_2O_2 processes.

In this work the behavior of iron-containing zeolites in carboxylic acid conversion by H_2O_2 wet oxidation will be analyzed and compared with that of homogeneous Fe^{3+} ions in the same reaction conditions, in order to analyze the potentials and limits of the use of these catalysts as well as to have more precise information on the differences in reactivity with respect to the homogeneous Fenton catalyst.

Propionic acid was used as a model reactant, because it gives rise to acetic and formic acids as primary intermediates. These two carboxylic acids are the common products of the oxidation of several organic molecules [23] and acetic acid is one of the most ‘recalcitrant’ molecules [24,25]. As a probe molecule propionic acid can thus give direct information on reactivity in the attack on the carbon chain as well as information on the reactivity of its primary products of oxidation (formic and acetic acids).

Although a Fenton-type reaction is more effective for medium–high TOC solutions (typically higher than 500 mg/l) due to the positive role of organic micropollutants in the radical chemistry in solution, this study was carried out using low TOC solutions (TOC = 30) in order to better highlight differences in the behavior of homogeneous and heterogeneous Fenton-type catalysts and to evidence the possible role of the zeolite in enhancing the rate of reaction by the local change of the concentration of the reactants inside the zeolite microcavities.

2. Experimental

2.1. Preparation of the catalysts

The Fe/ZSM5 sample was prepared by ion exchange starting from the ammonium form of a commercial ZSM5 zeolite (ALSI Penta, $SiO_2/Al_2O_3 = 27$). The ion exchange was carried out at 80°C using an 0.01 M aqueous solution of $(NH_4)_2Fe(SO_4)_2$. The time of the ion exchange was 8 h and the amount of iron introduced into the zeolite was 6.7 wt.% (as Fe_2O_3). After filtration and washing with double distilled water, the sample was dried at 130°C overnight and then calcined at 500°C raising the temperature from room temperature to the final value at a rate of 50°C/h. The surface area of the sample was 380 m^2/g. Prior to the catalytic tests, the sample was washed thoroughly with boiling double distilled water to completely remove any adsorbed organic substances.

2.2. Catalytic tests

Catalytic tests of wet oxidation with hydrogen peroxide were carried out in a glass batch reactor under continuous stirrring in contact with an air atmosphere. 150 ml of freshly prepared aqueous solution of the carboxylic acid with TOC of 30 mg/l was added to the reactor together with 0.1 g of the catalyst, corresponding to a total amount of iron ions of 8.5×10^{-5} moles. The iron ion to propionic acid molar ratio was about 2. After stabilization of the temperature at the selected value and correction of the pH, if necessary, the solution was analyzed to confirm the absence of adsorption by the zeolite. Then a concentred solution of H_2O_2 was added to achieve a H_2O_2/substrate stoichiometric ratio, defined as the amount of hydrogen peroxide required to completely oxidize the substrate to CO_2. For propionic acid this ratio is 7.

The depletion of propionic acid and the formation of acetic and formic acid was followed as a function of time by ion chromatography analysis using an AS14 (2 × 250) column with AG14 (4 × 50) precolumn and UV and conductimetry detectors. The carrier solution was an aqueous $Na_2B_4O_7$ (1.5×10^{-3} moles/l) solution. The same column also allowed the analysis of the residual H_2O_2 using the UV detector at 210 nm. At the end of the tests, the TOC of the solution was measured to confirm the absence of formation of other chemicals not revealed by ion chromatography.

The tests with homogeneous Fenton catalyst were carried out analogously by adding $Fe(NO_3)_3$ salt to the solution. The amount of iron in these tests was 1.06×10^{-4} moles Fe^{3+} and thus nearly equivalent to the total amount of Fe^{3+} ions present in the zeolite in the case of tests with the heterogeneous catalysts.

2.3. Leaching tests

Leaching tests were carried out in two ways. In the first method, the aim was to establish whether small amounts of the dissolved iron were responsible for the observed catalytic activity. After the wet oxidation with hydrogen peroxide the zeolite was filtered at the temperature of the catalytic tests, in order to prevent the possible readsorption of the leached iron during the cooling of the solution. Then, the substrate and H_2O_2 were added to the solution in the same concentrations as before the catalytic tests. Then the conversion of the substrate was measured at the same temperature of the catalytic tests as a function of time, but in the absence of the solid zeolite. If dissolved iron ions were responsible for the catalytic behavior, a reactivity similar to that shown in the presence of the zeolite would be expected.

The second method to check the potential of leaching of the iron from the zeolite involved analysis of the solution by atomic adsorption spectroscopy or ion chromatography. In this case also, the solid was filtered at the temperature of the catalytic reaction, in order to prevent the possible readsorption. This method allowed direct determination of the presence of iron ions in solution.

2.4. Stability tests

In the case of heterogeneous wet oxidation with hydrogen peroxide, the stability of the zeolite was analyzed by two procedures. In the first case, the zeolite recovered by hot filtration from the solution after the catalytic tests, was washed with distilled water, dried at 110°C (overnight) and then tested again at the same reaction conditions. In the second case, the procedure was the same, except that after filtration, the zeolite was also calcined at 500°C for 6 h in order to remove any organic species remaining adsorbed by combustion.

3. Results and discussion

3.1. Propionic acid conversion by Fe^{3+} ions in solution

Reported in Fig. 1 are the results for the catalytic wet hydrogen peroxide oxidation (CWHPO) of propionic acid with a homogeneous iron catalyst at room temperature and 70°C as a function of the time of reaction. The higher temperature of reaction was selected because Fajerwerg and Debellefontaine [21] found this temperature as optimal for the wet hydrogen peroxide oxidation (WHPO) of phenol using Fe/ZSM5 catalysts. At higher temperatures, in fact, the decomposition of hydrogen peroxide becomes dominant. Also the other reaction conditions are close to those reported as optimal by Fajerwerg and Debellefontaine [21]. The H_2O_2/substrate ratio is 1.5 times the stoichiometric value necessary to completely oxidize all the propionic acid present in solution to CO_2.

The propionic acid conversion increases significantly at the heigher reaction temperature. Taking into account the higher H_2O_2 conversion due to higher substrate conversion, decomposition of H_2O_2 does not increase significantly due to higher temperature. In all experiments, a large excess of hydrogen peroxide is still present at the end of the catalytic tests, indicating that the incomplete conversion of the substrate (Fig. 1) is not due to the unavailability of enough hydrogen peroxide, but due to the low rate of propionic acid conversion.

Acetic and formic acid were detected as by-products and their amount continuously increased with the time

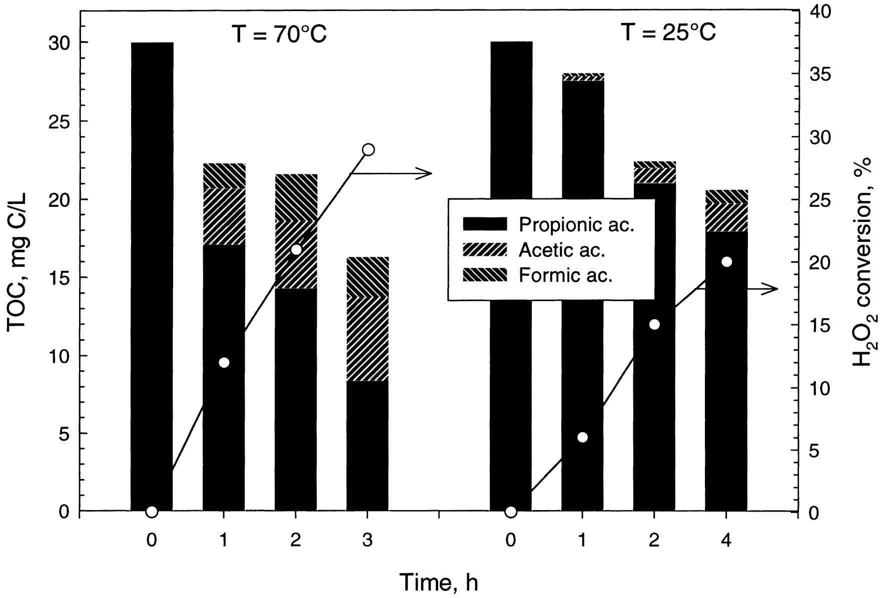

Fig. 1. Total organic carbon (TOC) of solution (the bar indicates the relative contribution of residual propionic acid and acetic and formic acids formed to the total value of TOC) and H_2O_2 conversion after different times of reaction during the wet hydrogen peroxide oxidation of propionic acid (initial TOC = 30, pH = 4.0, H_2O_2/substrate = 1.5) at 25°C and 70°C using Fe^{3+} ions (1.06×10^{-4} moles) in solution as catalysts.

of reaction, indicating that they are more resistant to oxidation than propionic acid. The final TOC value of the solution was in good agreement with that determined from the sum of TOC contributions of propionic, acetic and formic acid, indicating that no other major by-products are formed.

The effect of the initial pH of the solution on the CWHPO activity of Fe^{3+} ions in propionic acid conversion using a homogeneous iron catalyst is shown in Fig. 2. In agreement to literature data for other type of substrates [14–16], a maximum activity around a pH of 4 was observed in propionic acid conversion, upon decreasing or increasing the initial pH of the solution below or above 4, the rate of hydrogen peroxide decomposition increased due to partial transformation of iron to other species catalyzing this reaction. For example, at pH values higher than about 5.5 the precipitation of iron-hydroxide starts to occur and this leads to an enhanced rate of hydrogen peroxide decomposition. Thus only a narrow range of pH values are useful for CWHPO using homogeneous Fe^{3+} salts as Fenton-type catalytsts.

3.2. Propionic acid conversion by Fe/ZSM5

Tests using the solid iron-containing zeolite were carried out using an amount of catalyst equivalent to that necessary to achieve nearly the same amount of total iron in the reactor (0.85×10^{-4} moles of iron in 0.1 g Fe/ZSM5 versus 1.06×10^{-4} moles Fe^{3+} added in the case of homogeneous catalysis). The absorption of the organic by the zeolite was also checked, but found to be negligible for the low amount of catalyst (0.1 g zeolite for 150 ml solution) added.

Summarized in Fig. 3 are the results obtained using the Fe/ZSM5 for various reaction conditions. As for the previous graphs results are reported as residual TOC (bars in which the relative contribution of residual propionic acid, acetic and formic acids is also shown) as a function of the time of reaction for different reaction temperatures and initial H_2O_2/substrate values with respect to the stoichiometric hydrogen peroxide amount necessary to completely oxidize the propionic acid to CO_2. Using open circle, the conversion of hydrogen peroxide for the different times on stream is also reported.

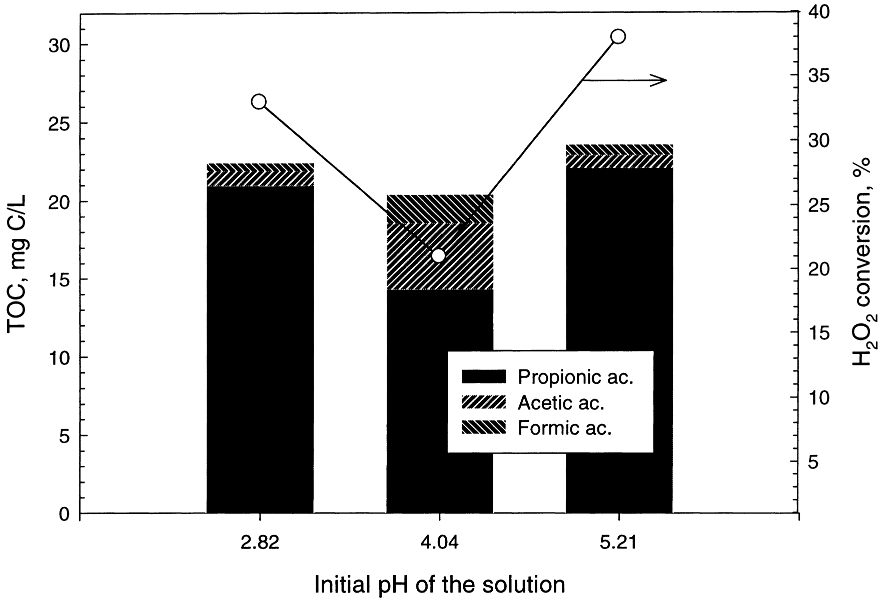

Fig. 2. Effect of the pH of the initial solution on the TOC, distribution of products and H_2O_2 conversion after 2 h at 70°C (pH = 4.0, H_2O_2/substrate = 1.5, Fe^{3+} ions = 1.06×10^{-4} moles) in the case of homogeneous iron catalyst.

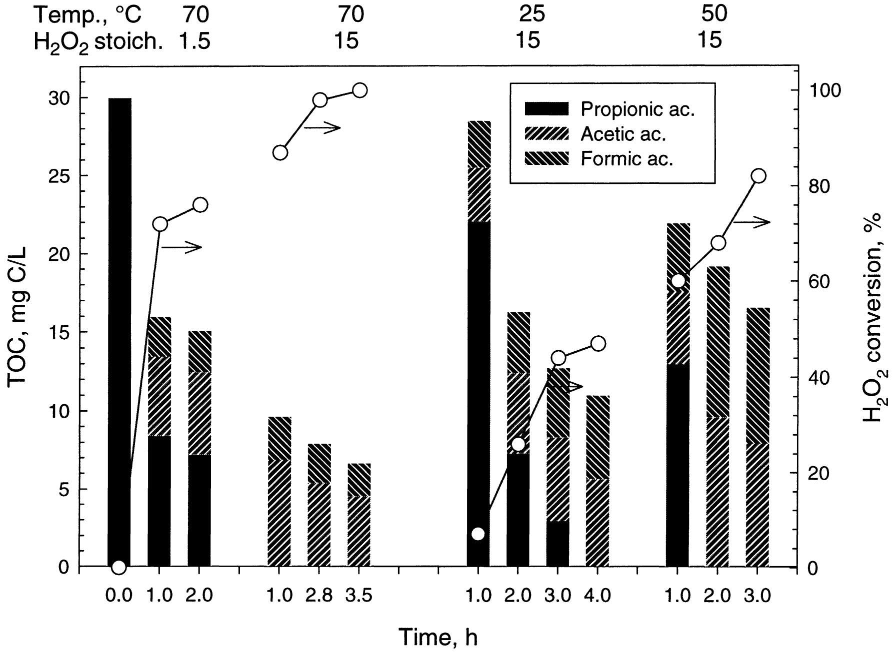

Fig. 3. Effect of the reaction conditions (temperature, H_2O_2/substrate ratio) on the TOC, distribution of products and H_2O_2 conversion as a function of the time of reaction in the case ofthe Fe/ZSM5 catalyst. Experimental conditions: pH = 4.0, 0.1 g Fe/ZSM5.

The first set of data (for a reaction temperature of 70°C and a H_2O_2/substrate ratio of 1.5) is very comparable in terms of experimental conditions to the data for the homogeneous case shown in Fig. 1 (left set of data in Fig. 1). There are two main observations:

- The conversion of propionic acid after 1h is significantly higher for the heterogeneous catalyst than for the homogeneous catalyst (72% with respect to 43% for the homogeneous case). The rate of reaction is higher for the homogeneous catalyst by a factor of about 3–5. Accordingly, about 3 h are necessary for the homogeneous case to reach the same level of conversion obtained in 1 h using the Fe/ZSM5, even though the amount of acetic and formic acid formed for the two cases is roughly the same. This suggests that the rate of propionic acid conversion is different in the two cases, but further conversion of the acetic and formic acid intermediates is not significantly different.
- The conversion of H_2O_2 (at an equivalent level of propionic acid conversion) is roughly twice as high for the heterogeneous catalyst than for the homogeneous catalyst, and even when data are compared at the same time of reaction. This indicates that the zeolite not only promotes the generation of hydroxyl radicals from hydrogen peroxide, but catalyzes the decomposition of the latter to water and oxygen.

Since the conversion of hydrogen peroxide is very high, the effect of having a large excess of H_2O_2 at the same reaction temperature was analyzed. In this case (Fig. 3) the conversion of propionic acid is already 100% after 1 h of reaction, although the intermediates acetic and formic acid are still present in solution. For longer times of reaction, their amount also decreases, but very slowly, confirming the acetic and formic acids lower reactivity with respect to propionic acid. It may be noted that even when using ten times larger amount of hydrogen peroxide, the conversion of hydrogen peroxide is higher using the higher H_2O_2/substrate ratio.

Upon decreasing the reaction temperature to 50°C, while still using a large excess of H_2O_2, complete conversion of the propionic acid is achieved in about 2 h of reaction. About 4 h are necessary for complete conversion of propionic acid at room temperature (Fig. 3). This conversion time for heterogeneous catalyst is only a one fourth that for the homogeneous catalyst. Note that with respect to data in Fig. 1 (homogeneous case) the H_2O_2/substrate ratio is higher using the zeolite (Fig. 3). However, since H_2O_2 conversion is very low in the homogeneous oxidation, an increase in the H_2O_2concentration does not significantly influence the conversion of the substrate and thus comparison of the data in Figs. 1 and 3 (homogeneous and heterogeneous cases) is possible. Thus, even at lower reaction temperatures, the activity of the zeolite remains higher than that of the homogeneous catalyst, although the conversion of hydrogen peroxide is also significantly higher. It may also be noted that the amount of acetic and formic acid is quite large. This is due to the decrease in the rate of their conversion with the low residual hydrogen peroxide available.

The effect of the pH of the initial solution is shown in Fig. 4. Reaction conditions are the same as those used for data reported in Fig. 2 and thus a direct comparison is possible. For the homogeneous case, maximum activity was observed in quite a narrow pH range (around 4). For the heterogeneous catalyst catalytic behavior was not very sensitive to pH (Fig. 4) and furthermore, operation at pH below 2.5 or above 5.5 was also found to be satisfactory, unlike homogeneous case. The use of solid Fenton type catalysts thus makes it possible an extension of the range of pH values for which CWHPO processes are possible.

3.3. Leaching and stability tests

Although the higher reactivity of the heterogeneous catalyst with respect to homogeneous Fe^{3+} ions indicates that the catalytic behavior of Fe/ZSM5 cannot be due to the dissolution of iron on the zeolite, specifc tests were made in order to furnish further proof of this. The results are summarized in Fig. 5 where the behavior of propionic acid conversion over Fe/ZSM5 is compared with that of the same solution at the end of the catalytic run, but from which the solid catalyst was removed by filtration and to which propionic acid and H_2O_2 were then further added to return then to their initial values before the catalytic run. Since it is possible that, after dissolution at high temperature, iron can be readsorbed on the solid catalyst when the slurry is cooled down, filtration to separate the solid was carried out at the same temperature as that of the catalytic run (70°C).

In the absence of the catalyst (filtered solution), conversion of propionic acid was below 5% in 2 h, in con-

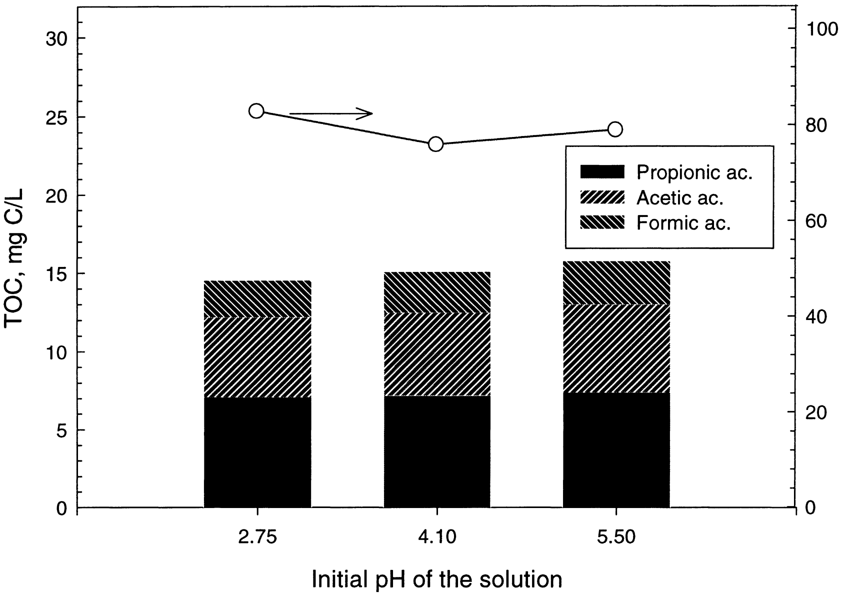

Fig. 4. Effect of the pH of the initial solution on the TOC, distribution of products and H_2O_2 conversion after 2 h at 70°C (pH = 4.0, H_2O_2/substrate = 1.5, 0.1 g Fe/ZSM5) in the case of the Fe/ZSM5 catalyst.

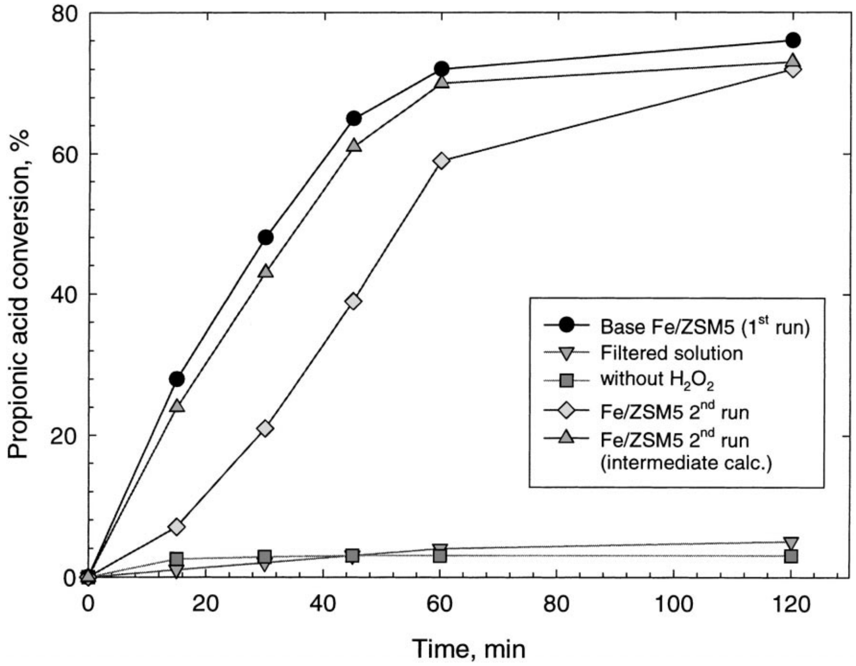

Fig. 5. Conversion of propionic acid as a function of the time of reaction (pH = 4.0, H_2O_2/substrate = 1.5, *T* = 70°C, 0.1 g Fe/ZSM5) in different conditions: (a) Reference Fe/ZSM5 during 1st run; (b) The same solution as catalytic run (a), consecutive filtration at 70°C to remove the solid catalyst and addition of propionic acid up to TOC = 30 and of H_2O_2 up to H_2O_2/substrate = 1.5; (c) Blank test as for case (a), but without adding hydrogen peroxide; (d) As test (a), but reusing the solid catalyst. The catalyst was filtered at 70°C, washed and dried at 110°C; (e) As test (d), but reused solid catalyst was also calcined at 500°C.

Table 1
Percentage of iron leached after 3 h of reaction (with respect to the initial amount of iron in the Fe/ZSM5 catalyst) during WHPO tests at pH = 4.0

	Temp. (°C)			
	25	50	70	70
H_2O_2/substrate	15	15	15	1.5
Fe leached, %	2	4	7	4

trast to a conversion of around 80% in the presence of the solid catalyst. This result demonstrates beyond doubt that the activity of the solid catalyst is not due to iron ions leached from the Fe/ZSM5. Furthermore, since conversion in the absence of a catalyst is negligible, the activity during the catalytic run is not due to other possible agents able to activate the hydrogen peroxide (such as impurities in the reactor, light, etc.).

Also reported in Fig. 5 is the propionic acid conversion in a reference test where the Fe/ZSM5 was added to the solution in the absence of hydrogen peroxide to check for the possible presence of adsorption phenomena which can give rise to a falsely higher conversion of the organic using the heterogeneous catalyst. Data in Fig. 5, however, shows that at the experimental conditions used in this work, the effect of adsorption of the propionic acid is nearly negligible.

Summarized in Table 1 are the results of spectroscopic atomic adsorption measurements after the catalytic runs. Data are reported in terms of the percentage of iron leached with respect to the initial amount present in Fe/ZSM5 for various reaction conditions. Small, but not negligible amounts of iron leached into the solution, although previous tests showed that this quantity of iron does not influence overall reactivity. Under longer term tests, however, deactivation of the sample may occur. The leached fraction increases with the reaction temperature and the amount of H_2O_2 present in solution (Table 1).

Also reported in Fig. 5 are initial data about the stability of the catalytic behavior of Fe/ZSM5 when reused. Two different treatments were carried out on the solid sample recovered from the catalytic run: (i) washing with distilled water followed by drying at 110°C and (ii) washing with distilled water followed by drying at 110°C and calcination at 500°C. When the zeolite was reused after the second treatment, ie. after an intermediate calcination step, its catalytic activity was very close to initial activity, indicating the absence of significant deactivation, either due to the small loss of iron (Table 1) or by in situ transformation of the catalyst. However, with the first treatment, the initial activity is low, but picks up with time. At longer times, propionic acid conversions are quite comparable for the two treatments. Probably, when the catalyst is washed and dried, but not calcined, organic species remain filled inside the pores of the zeolite and delay the start of activity of the catalyst, due to oxidation of the adsorbed organic species.

3.4. Reactivity of Fe/ZSM5 in acetic and formic acid conversion

As discussed before, data for the conversion of propionic acid suggest that acetic and formic acid are the two main intermediates of reaction. These intermediates have a lower oxidizability in comparison to propionic acid. In order to confirm this hypothesis the direct conversion of acetic and formic acids was studied at the same conditions (temperature, amount of H_2O_2) as that for propionic acid. The results are summarized in Fig. 6. Formic acid converts at a slower rate than propionic acid, although difference in reactivity is not

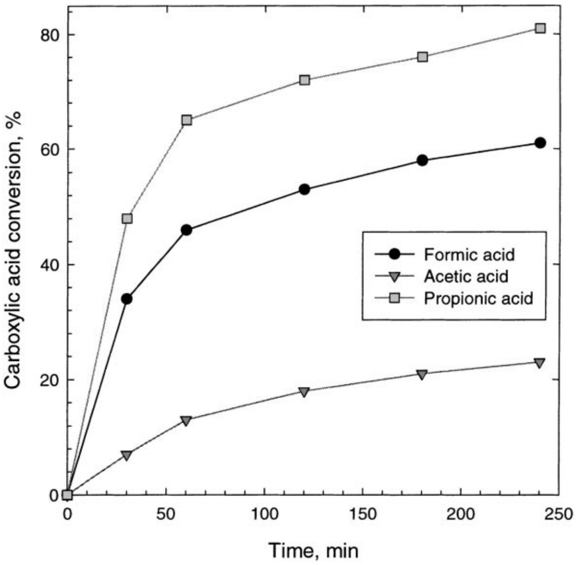

Fig. 6. Conversion of propionic, acetic and formic acids as a function of the time of reaction (pH = 4.0, H_2O_2/substrate = 1.5, 0.1 g Fe/ZSM5).

large. Acetic acid is much less reactive. Compared to wet air oxidation which requires very high temperature, acetic acid does convert slowly at much lower temperature with Fe/ZSM5/H_2O_2 system. Formic acid was formed in small amounts during acetic acid conversion, suggesting that the path of oxidation includes the attack of the carbon chain to form acetic and formic acids first from propionic acid and then two molecules of formic acid are formed from acetic acid. However, more specific studies are necessary to clarify this preliminary suggestion.

4. Conclusions

A comparison of the reactivity of heterogeneous and homogeneous Fenton-type catalysts in wet hydrogen peroxide oxidation of diluted propionic acid solutions shows that the solid catalyst has a higher rate of conversion of the substrate as well as a lower sensitivity with respect to pH than Fe^{3+} ions in solution at the same reaction conditions (temperature, amount of H_2O_2, amount of iron). However, the solid catalyst has a major drawback in its higher rate of hydrogen peroxide decomposition to water and oxygen. Although it was demonstrated that the activity of the solid catalyst is not related to leached iron ions, slight leaching of iron was found to be present, especially at the higher reaction temperatures. This could cause deactivation with prolonged use, although catalyst activity could be reproduced for consecutive runs, if intermediate calcination is carried out. Calcination is probably necessary to burn the organic species which remain trapped in the zeolite which delay the start of the activity of the zeolite during consecutive catalytic experiments.

Wet hydrogen peroxide oxidation using solid Fenton-type catalysts may be a promising technology for treating aqueous solutions containing organics, but the catalyst need to be improved to reduce the side activity for hydrogen peroxide decomposition and the leaching of iron ions.

Acknowledgements

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