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Stability of hydrogen peroxide during perhydrolysis of carboxylic acids on acidic heterogeneous catalysts

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Abstract This paper describes a study of the stability of hydrogen peroxide in the presence of different aluminosilicate materials, in connection with an investigation of carboxylic acid perhydrolysis. During the reaction, aluminosilicate materials such as H-β zeolites, mesoporous material H-MCM-41 and alumina initiate the decomposition of hydrogen peroxide. The reason of the spontaneous decomposition of H_2O_2 is related to the partial dealumination of these zeolites. However, in the case of experiments carried out with H-ZSM-5 zeolite catalysts, a slight catalytic effect on the perhydrolysis and no spontaneous decomposition of hydrogen peroxide were noticed. The use of cation exchange resins as catalysts is more kinetically beneficial than H-ZSM-5 zeolite catalysts.

Keywords Perhydrolysis · Aluminosilicate materials · Decomposition · Hydrogen peroxide

Introduction

Interest in hydrogen peroxide has increased in the last decade. For instance, the world production of hydrogen peroxide was around 1.9 million tonnes in 1994, and grew to 2.2 million tonnes in 2006 [1]. The applications of this compound are versatile: it is used as an oxidizing agent for inorganic and organic compounds, a

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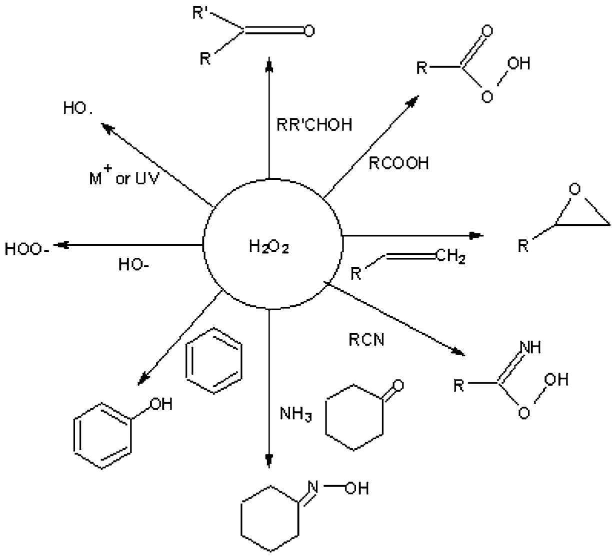
bleaching agent for textiles and wood, as an antiseptic for therapeutic use, as a disinfectant for wastewater and as a sterilizing agent.

The use of H_2O_2 as an oxidizing agent [2] in chemistry avoids the use of conventional heavy-metal oxidants which form toxic waste; application of nitric acid which forms the greenhouse gas N_2O; and utilization of molecular oxygen, which requires safety precautions. Scheme 1 illustrates the application of hydrogen peroxide in some fine chemical synthesis reactions [3].

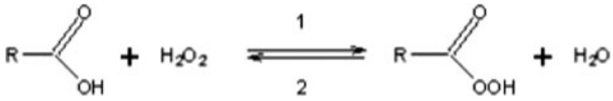
From an environmental and economical point of view, these reactions should be carried out with heterogeneous catalysts, which should not decompose hydrogen peroxide.

The aim of this paper is to treat the stability issues of H_2O_2 in an acidic environment over different heterogeneous catalysts, and especially aluminosilicate materials. Traditionally, synthetic aluminosilicate materials, and more particularly synthetic zeolites, are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. The use of zeolites for fine chemicals production is widespread: acylation, alkylation, hydroxyalkylation of aromatic and heterocyclic compounds, and rearrangement reactions [4]. Selectivity (including shape selectivity), catalytic effects and environmental regulations explain the application of such materials in industry. In particular, oxidation reactions such as epoxidation of olefins, hydroxylation of arenes, and oxidation of O-, S- and N-functionalities with hydrogen peroxide are conducted using Ti-zeolites. The originality of this paper is the investigation of an oxidation reaction with H_2O_2 in the presence of titanium-free aluminosilicate materials.

To illustrate the stability of H_2O_2, the peroxycarboxylic acids synthesis was selected as a model reaction (Scheme 2).



Scheme 1 Applications of H_2O_2 in fine chemical reactions



Scheme 2 Synthesis of PCA from the parent carboxylic acid and hydrogen peroxide

This reaction occurs at acidic pH [5–7], and is traditionally catalyzed by sulfuric acid. This reaction was selected because spontaneous decomposition of hydrogen peroxide or peroxycarboxylic acids is negligible [8–10] in traditional experimental conditions (pH: 1–3; and temperature: 20–50 °C); and configurational diffusion can be neglected because the size of the reactant molecules is smaller compared to the pore size of the materials used (Table 1). Thus, by using heterogeneous catalysts for this reaction, only decomposition due to the solid acid catalyst can occur.

In a previous paper, we have demonstrated that cation-exchange resins [11] are suitable heterogeneous catalysts for the carboxylic acids perhydrolysis. Our objective in the present study is to elucidate hydrogen peroxide stability towards aluminosilicate type materials, and to compare the catalytic efficiency of these aluminosilicate materials versus cation-exchange resins in such reactions.

Except for the communication of Palani et al. [12], in which the efficacy of different zeolites and mesoporous materials was investigated, there are no other scientific papers dealing with perhydrolysis of carboxylic acids over these materials.

Experimental section

Apparatus and experimental procedures

All experiments were performed in a 250-mL jacketed glass reactor vessel. The reactor was equipped with a mechanical agitator and a temperature probe. Water was pumped through the outer jacket of the vessel to control the temperature of the reaction mixture. A pitched blade impeller (PTFE coated) was used to ensure a vigorous mixing during the reaction.

A reflux condenser was attached to the top of the reactor (adjusted at 0 °C) to avoid loss of volatile liquid-phase compounds. In case decomposition of peroxypropionic acid (PPA) or H_2O_2 appeared, an inert carrier gas (Helium, AGA,

Table 1 Channel structure of the tested aluminosilicate materials

Aluminosilicate materials	Channel structure
β	3-Dimensional pore system; 12-ring channel in c direction with pores 7.6 × 6.4 Å plus two 12-ring channels in a direction perpendicular to c-direction with pores 7.6 × 6.4 Å and 5.5 × 5.5 Å
ZSM-5	3-Dimensional pore system; straight 10 member-ring 5.2 × 5.7 Å channels connected by sinusoidal 5.3 × 5.6 Å channels. Intersection cavity: 9 Å
MCM-41	1-Dimensional hexagonal arrangement of uniformly open channels from 15 to 100 Å

99.996%) was introduced to the reactor through one of the necks to avoid the accumulation of oxygen in the gas phase.

To prevent contamination induced by alkaline and metal components, which initiate the catalytic decomposition of peroxypropionic acid and hydrogen peroxide, all parts of the reactor system in contact with the reaction solution were washed with hydrochloric acid, followed by another washing with a phosphate-free detergent solution.

In the experiments carried out for testing the stability of hydrogen peroxide towards zeolite, at the first stage, deionized water and zeolites were mixed together in the reactor. As the desired reaction temperature was reached, the preheated hydrogen peroxide solution (Merck, 30 wt.%) was added through a dropping funnel. In fact, hydrogen peroxide was preheated at the same temperature as the reaction temperature. At the time "zero", the required amount was introduced into the reactor.

In the experiments carried out for checking the catalytic effect of zeolites on the propionic acid perhydrolysis reaction, at the first stage, propionic acid (Acros, 99 wt.%) and the catalyst were mixed together in the reactor. Thereafter, the same protocol as described above was followed.

According to a patent [13], during the reaction of hydrogen peroxide and propionic acid in water in the presence of an acid catalyst, the danger of explosion is suppressed by employing a temperature of maximum 60 °C.

From our previous study [9, 11], the kinetics of propionic acid perhydrolysis is demonstrated to be dependant on the Brønsted acid sites in the cases of homogeneous and heterogeneous catalysis. One should keep in mind that the goal is to check the stability of hydrogen peroxide towards aluminosilicate materials in an acidic environment by studying the reaction of perhydrolysis. Due to the low Brønsted acid site amount of these catalysts and the difficulty of measuring them in the temperature range 40–50 °C, the kinetic comparisons were based on catalyst loading. Table 2 introduces the experimental matrix.

Analytical methods

Samples were withdrawn from the reaction mixture by a plastic syringe (to avoid contamination of the solution by trace of metals) and they were analyzed by the Greenspan and Mackellar method [14]. The concentration of hydrogen peroxide was determined by titration by using a standard solution of ammonium cerium sulphate

Table 2 Experimental parameters for the catalyst comparison in the batch reactor

Reaction temperature (°C)	40–50
Rotating speed (rpm)	250–350
H_2O_2 (mol L^{-1})	5.75–6.10
PA (mol L^{-1})	5.70–580
H_2O (mol L^{-1})	23.85–24.10
Catalysts loading (g L^{-1})	8.26–43.40

(0.1 N). The concentrations of propionic and peroxypropionic acids were determined by titration with an automatic titrator (Metrohm 751 GPD Titrino) by using a standard solution of sodium hydroxide (0.2 N).

Catalyst properties

The acidic properties of the different aluminosilicate materials are summarized in Table 3. The Brønsted and Lewis acid sites were determined by FTIR using pyridine as probe molecule [15–18]. The specific surface area was determined by N_2 adsorption, calculated by the Dubinin method for the microporous materials and by the BET method for the mesoporous H-MCM-41 [15–18].

A comparison between a cation exchange resin, i.e., Amberlite IR-120 and zeolites, was carried out. The characteristics of this commercial resin are summarized in Table 4.

The pretreatment of Amberlite IR-120 consisted of a drying step at 70 °C for 48 h, since a higher drying temperature might affect the sulfonic acid sites on the catalyst. The parameter capacity by dry weight represents the number of Brønsted groups bearing (i.e., sulfonic group) by the resins, which is equivalent to the Brønsted acid sites of zeolites displayed in Table 3.

To dealuminate zeolite, the protocol of Marques et al. [19] was applied to H-β-25 zeolite, i.e., an acid treatment at 30 °C by HCl (1 N) for 10 min was performed.

The Al concentration in the reaction mixture was measured by ICP-OES (PerkinElmer Optima 5300DV).

Table 3 Properties of the aluminosilicate materials

	SiO_2/Al_2O_3 mol/mol	Brønsted acid sites at 523 k µmol/g	Lewis acid sites at 523 k µmol/g	Specific surface area m^2/g
H-β-25	25	269	162	807
H-β-75	75	147	39	664
H-β-300	300	82	30	805
H-ZSM5-23	23	416	36	443
H-ZSM5-31	31	–	–	–
Al_2O_3	–	7	156	299
H-MCM-41	40	26	40	1242

Table 4 Properties of Amberlite IR-120

Supplier	Aldrich
Polymer type	Gel
Cross-linking (%)	8
Moisture content (% mass)	45
Capacity by dry weight (meq/g)	4.4
Native particle size range (mm)	0.3–1.2

Results and discussion

Experiments of the perhydrolysis of propionic acid over different aluminosilicate materials gave two antagonist observations: either the catalyst was active in perhydrolysis, or no formation of peroxypropionic acid was observed due to the decomposition of hydrogen peroxide over these acidic materials.

Aluminosilicate materials initiating the decomposition of hydrogen peroxide

During the reaction of perhydrolysis, decomposition of hydrogen peroxide was observed with the following materials: H-β zeolites, H-MCM-41 and alumina. For the sake of simplicity, the ratio $\frac{[H_2O_2]}{[H_2O_2]_0}$, where $[H_2O_2]_0$ is the initial concentration, was plotted versus the reaction time. An experiment with only hydrogen peroxide without any catalyst was carried out at 50 °C; no spontaneous decomposition of this reactant was observed.

According to Sengupta et al. [20], the decomposition of hydrogen peroxide on un-impregnated silica-alumina material is dependent of the strength of acid sites. In our previous studies [9, 11] no decomposition of hydrogen peroxide was noticed due to Brønsted acidity in either sulfuric acid or sulfonic groups bearing by the resins. For that reason Lewis acid sites in such materials can be considered to be responsible for the decomposition of hydrogen peroxide.

However, Rocha et al. [21] have studied the kinetics of peroxyacetic acid formation from acetic acid and hydrogen peroxide in the presence of scandium (III) triflate. They have demonstrated that the use of this strong Lewis acid enhanced the reaction rate sixfold compared to the catalyst absence; and no decomposition of hydrogen peroxide was reported.

Several articles treat the dealumination of H-β zeolites [22, 23], or type A and Y zeolites [24] by acidic leaching. Marques et al. [19] have shown that treatment of HBEA zeolite (Si/Al = 12.5) with an HCl solution at 30 °C causes a rapid dissolution of the extraframework Al species, especially the monomeric ones and a slow dissolution of the framework Al atoms bridging OH groups and structure defects. These Al species released in the reaction mixture could catalyze the H_2O_2 decomposition.

In this section, the reason of hydrogen peroxide decomposition will be discussed regarding the Lewis acid, partial dealumination and SiO_2/Al_2O_3 ratio.

Figure 1 displays three different experiments carried out with H-β-25 zeolites.

The difference of pH is due to the presence of PA, which acidifies the mixture. In experiments carried out with a mixture PA and H_2O_2, the concentration of PA remains constant. Even if the decomposition of H_2O_2 is strongly dependent on the pH, one can conclude that the production of PPA or the presence of PA does not influence the kinetic of decomposition. From Fig. 1, the kinetics of hydrogen peroxide decomposition for experiments carried out with PA and H_2O_2 mixture in the presence of H-β-25 and dealuminated H-β-25 by acidic treatment is similar. This observation implies that the decomposition of hydrogen peroxide is due to Al species, in particular dissolution of Al atoms from the framework of the zeolite. The difference of aluminium concentration between the end and the beginning of the

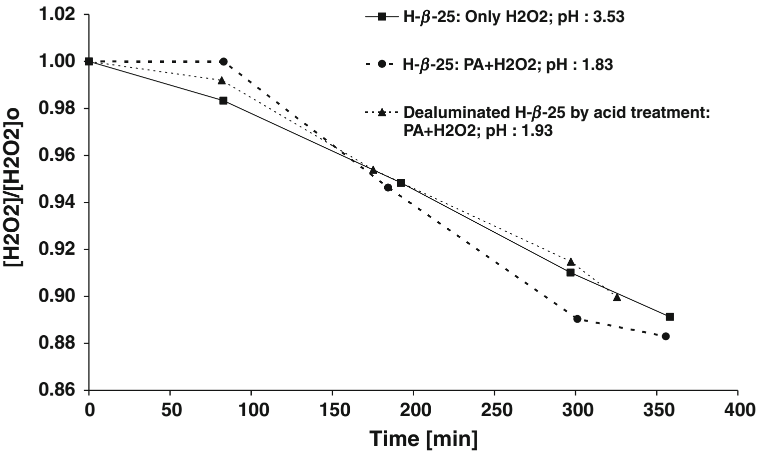


Fig. 1 Experiments carried out in the presence of H-*β*-25 zeolite at 50 °C, at 350*g*, and loading of 18.25 g/L

experiment carried out with H-*β*-25 and PA and H_2O_2 mixture was measured to be equal to 181 mg L^{-1}, which can explain the decomposition of hydrogen peroxide.

From Fig. 1, one can notice the presence of an initial retarding period, which is more significant in the case of the experiment carried out with H-*β*-25 and PA and H_2O_2 mixture. The presence of the initial retarding effect, occurring for a long time period, during the decomposition of hydrogen peroxide is not the first observation in the literature. For instance, this phenomenon of retarding phase was noticed in the case of H_2O_2 decomposition by Fe(III). De Laat et al. [25] explained it by the formation of $^{\cdot}OH$ radicals via Fenton's reaction, with the duration of this phase depending on various parameters, such as the initial concentration of Fe(III). In the present case, this retarding period could be explained by the dissolution of Al. Indeed, in the case of experiments carried out over dealuminated H- *β*-25, this retarding period seems to be shorter, because Al atoms from the extra-framework have already been removed by acidic treatment.

To check if the decomposition of hydrogen peroxide in such conditions is due to the partial dissolution of Al species in the liquid phase, an experiment with aluminium oxide was carried out (Fig. 2). Alumina was chosen instead of an aluminium salt because its structure is closer to Al species present in the zeolites.

Figure 2 shows that hydrogen peroxide decomposes over Al_2O_3, which implies that the assumption of H_2O_2 decomposition is related to the partial dissolution of Al species is plausible. The ratio $[PA]/[PA]_0$ remained constant during this experiment.

To check if the decomposition of hydrogen peroxide is related to the ratio SiO_2/Al_2O_3, H-*β* zeolites with three different SiO_2/Al_2O_3 ratios were used as shown in Fig. 3. No production of PPA was noticed, but instead, decomposition of hydrogen peroxide was observed.

During these experiments, the concentration of PA remained constant (Fig. 3). The kinetic curves are similar, but there is an initial retarding effect during the experiments carried out with H-*β*-75 and H-*β*-25. No decomposition of hydrogen

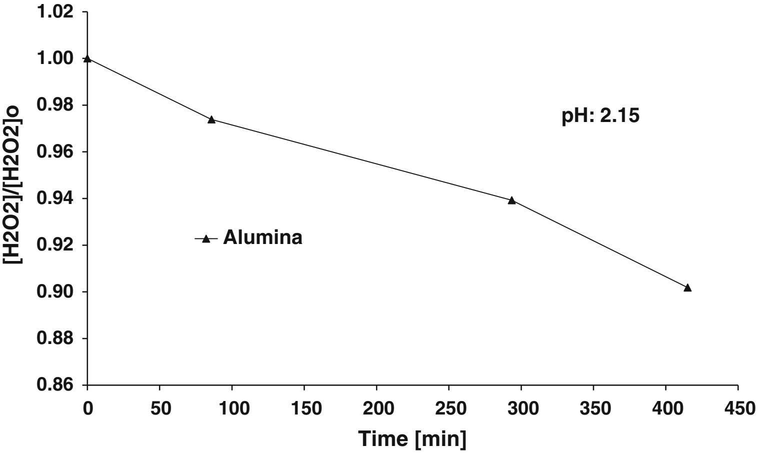


Fig. 2 Experiment carried out with a mixture of PA and H_2O_2 over alumina at 50 °C, at 350*g*, and loading of 18.25 g/L

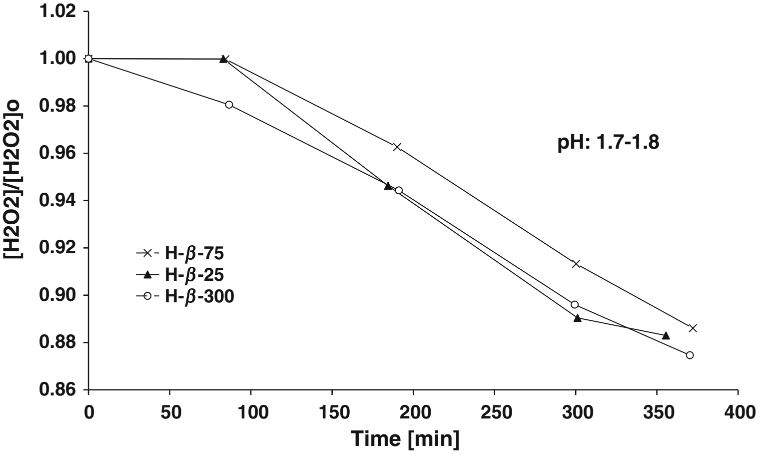


Fig. 3 Experiments carried out with a mixture of PA and H_2O_2 over H-*β* zeolites at 50 °C, at 350*g*, and loading of 18.25 g/L

peroxide was reported in the paper of Palani et al. [12] during the synthesis of peroxyacetic acid using H-*β* with a ratio Si/Al equal to 12, catalyst loading lower than 1 g/l and at 25 °C. From Fig. 3, it can be concluded that the decomposition is not directly related to the SiO_2/Al_2O_3 ratio.

Although the amount of Lewis acid sites is 5 times higher in the case of H-*β*-25 than H-*β*-75 or H-*β*-300 (Table 3), the kinetics of decomposition is similar. Thus, the Lewis acid sites bearing on these materials are not responsible for the H_2O_2

decomposition. Furthermore, the amount of Lewis acid sites in H-ZSM-5-23, which does not induce the decomposition of H_2O_2, is of the same order of magnitude as in H-β-75, H-β-300 or H-MCM-41 (Table 3). Thus, the assumption that the decomposition of hydrogen peroxide is due to the presence of Lewis acid sites in aluminosilicate materials can be rejected.

During the experiments, the decomposition of H_2O_2 appeared only at zeolite loadings exceeding 8.26 g/L, which explains the absence of decomposition in the study of Palani et al. [12]. Below this catalyst loading, the perhydrolysis of propionic acid due to the protolysis of the carboxylic acids occurs [7]. The change of the catalyst loading in the range 10.24–18.25 g/L does not influence the kinetics of H_2O_2 decomposition at 50 °C (Fig. 4). In both cases, there is a retarding effect; however, this induction period is longer for the experiment carried out with a loading of 18.25 g/L.

A mesoporous material, H-MCM-41, was used to study its behavior in the mixture of PA and H_2O_2. Figure 5 displays the kinetics of H_2O_2 decomposition versus time for this mixture over H-MCM-41 and H-β-75 at 40 °C. During these reactions, the concentration of PA remains constant. From Fig. 5, one can notice the same trend as with alumina or H-β materials, i.e., a decomposition phase of hydrogen peroxide. The retarding period is more pronounced at the beginning of the reaction (until 300 min) for H-MCM-41 than for H-β-75, which can be explained by the higher stability of the mesoporous material towards an acidic environment. After the induction period, the kinetics of H_2O_2 decomposition is similar in both cases.

The decomposition of hydrogen peroxide is due to the presence of Al species dissolved from the framework structure of the H-β zeolites and mesoporous material H-MCM-41. The slow kinetics of H_2O_2 is related to the fact that the dissolution of Al species from the framework is a slow phenomenon [19]. Furthermore, the Al

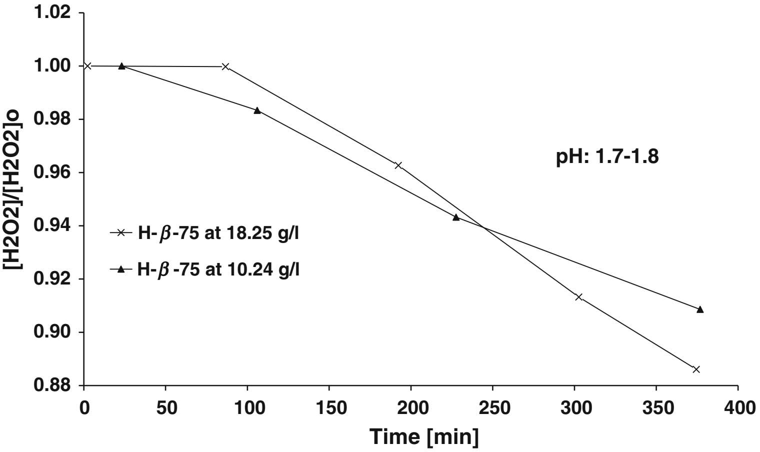


Fig. 4 Experiments carried out with a mixture of PA and H_2O_2 over H-β-75 zeolites at 50 °C and at 350*g*

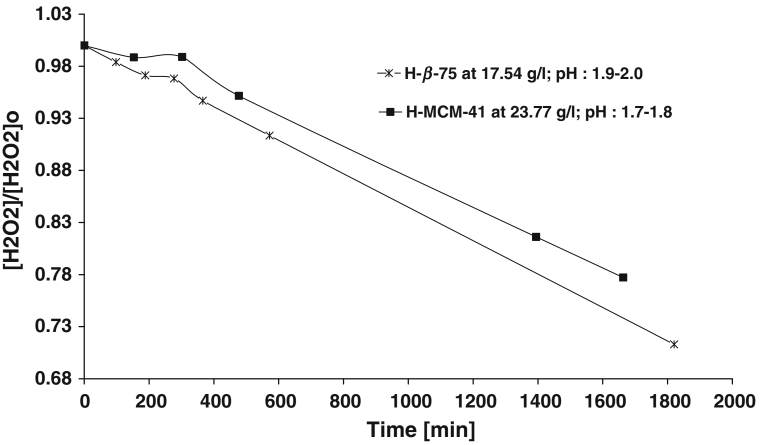


Fig. 5 Experiments carried out with a mixture of PA and H2O2 over H-MCM-41 and H-*β*-75 at 40 °C and at 350*g*

species released are in oxide or hydroxide form, and according to Mani et al. [26], their catalytic activity towards hydrogen peroxide decomposition is minor.

Materials which catalyze the perhydrolysis reaction

In the case of experiments carried out with H-ZSM-5 or Amberlite IR-120, no decomposition of hydrogen peroxide was noticed, while the catalytic effect on the perhydrolysis of propionic acid was visible. The purpose of this section is to propose an explanation for the selectivity of the aluminosilicate materials towards the reaction between H_2O_2 and PA, and to perform a comparative study of these materials. This comparison was based on equal catalyst loadings, and the experiments were carried out under similar conditions.

Figure 6 shows that H-ZSM-5 zeolite catalyzes the perhydrolysis of propionic acid. Moreover, the activity of H-ZSM-5-23 is higher than H-ZSM-5-31, due to a higher amount of Brønsted acid sites. In the case that no external catalyst is added, some perhydrolysis takes place (Fig. 6). This is due to the fact that propionic acid itself is a weak Brønsted acid having some catalytic effect.

Figure 6 demonstrates that cation exchange resins are more beneficial than zeolites for the synthesis of peroxypropionic acid from hydrogen peroxide and propionic acid. An estimation of the apparent second-order rate constants based on the product $[PA]*[H_2O_2]$ is provided in Table 5. The apparent Brønsted acid concentration $[H^+]$ is also displayed for each catalyst (except for H-ZM5-31), which is the sum of the amount of Brønsted acid sites of the solid catalyst and the number of hydroxonium ions released due to the protolysis of PA present per litre of reaction mixture.

Figure 7 displays the rate constants versus the apparent Brønsted acid concentration $[H^+]$ for each catalyst. As can be seen, the apparent rate constants are linearly proportional to $[H^+]$, which confirms the fact that the reaction of perhydrolysis is catalyzed by the Brønsted acid sites. Amberlite IR-120 catalyzes 4

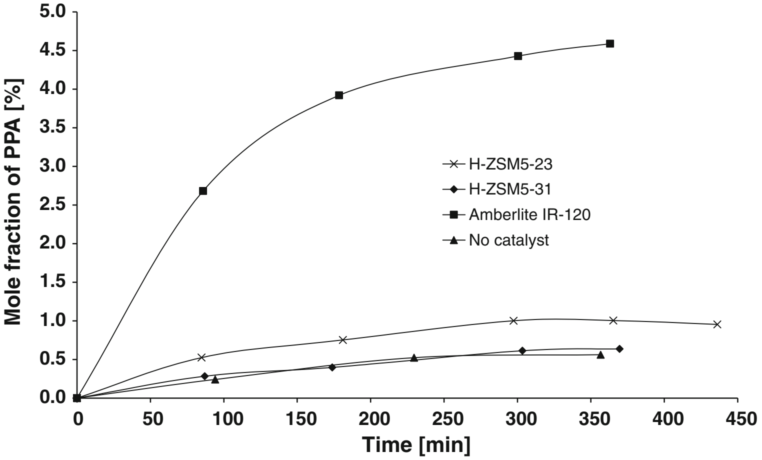


Fig. 6 Formation of PPA over different catalysts at 50 °C at 43.38 g/L of loading and 350*g*

Table 5 Apparent rate constants and [H$^+$]

	k(L mol^{-1} s^{-1})	Apparent [H$^+$] (mol L^{-1})
H-ZSM-5-23	5.51×10^{-6}	1.80×10^{-2}
H-ZSM-5-31	2.95×10^{-6}	–
Amberlite IR-120	2.18×10^{-6}	1.91×10^{-1}
Without catalyst	1.15×10^{-6}	5.64×10^{-3}

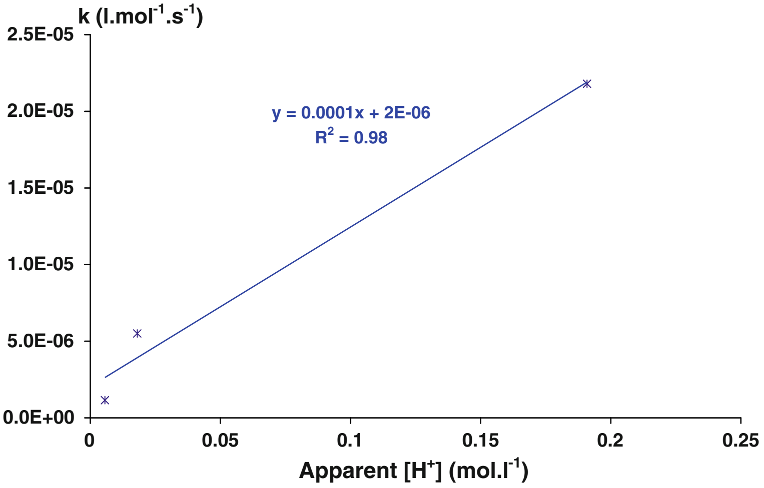


Fig. 7 Rate constants versus apparent [H$^+$]

times faster the perhydrolysis of PA than H-ZSM-5-23, and for this reason cation exchange resins are preferred in practice.

According to Lutz et al. [27], the dense-structured zeolites of types ZSM-5 (MFI) are relatively stable under treatment by liquid water for 72 h up to 513 K, whereas the open-structured zeolites of type beta (BEA) undergo strong decomposition in the same range. This statement shows that H-β zeolites are more fragile than H-ZSM-5 zeolites regarding the dealumination. In other words, the dissolution of Al species is easier in the case of H-β zeolites than H-ZSM-5 zeolites.

More generally, material with an MFI structure seems to be used preferentially in the case of oxidation by hydrogen peroxide. For instance, titanium silicate zeolite TS-1, which has an MFI structure, is a material specifically designed for industrial oxidation reaction with hydrogen peroxide [28].

Conclusions

This paper describes a study of hydrogen peroxide stability over different aluminosilicate materials in the perhydrolysis of propionic acid. Several experiments were carried out in an isothermal batch reactor at temperatures of 40–50 °C, equimolar concentrations of the reactants, and with hydrogen peroxide alone.

It was observed that some aluminosilicate materials (such as H-β, H-MCM-41 or alumina oxide) decompose hydrogen peroxide, but others (such as H-ZSM-5) catalyze the perhydrolysis reaction in a moderate way.

Experiments carried out with H-β zeolites showed that the decomposition of hydrogen peroxide is not directly proportional to the ratio SiO_2/Al_2O_3 or to the Lewis acid site bearing by these materials. But it appears that the decomposition of hydrogen peroxide over these catalysts is related to the partial dealumination of the zeolites framework, releasing Al species in the midst which induce the decomposition mechanism. This assumption was supported by the literature, and by the observation that alumina oxide material decomposes hydrogen peroxide during the propionic acid perhydrolysis reaction. A certain minimal amount of material (ca. 8.26 g/L) is needed to initiate the decomposition. The change of catalyst loading in the range 10.24–18.25 g/L does not change the kinetics of H_2O_2 decomposition.

The retarding period preceding the H_2O_2 decomposition is connected to the partial dealumination period of the zeolites. The duration of this period depends on several parameters, such as pH of the solution, catalyst loading, and the nature of the zeolite structure.

H-ZSM-5 does not decompose hydrogen peroxide, and in the case of a high number of Brønsted acid sites, a catalytic effect on the perhydrolysis of propionic acid is observed. Amberlite IR-120 was, however, even more beneficial by 4 times compared to H-ZSM-5-23.

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References

1. R. Hage, A. Lienke, Angew. Chem. Int. Ed. **45**, 206 (2006)
2. R. Noyori, Chem. Commun. **14**, 1807 (2005)
3. C.W. Jones, *Application of Hydrogen Peroxide and Derivatives*, 1st edn. (Royal Society of Chemistry, Cambridge, 1999), pp. 49–53
4. M.G. Clerici, Top. Catal. **13**, 373 (2000)
5. L.V. Dul'neva, A.V. Moskvin, Russ. J. Gen. Chem. **75**, 1125 (2005)
6. X. Zhao, T. Zhang, Y. Zhou, D. Liu, J. Mol, A. Catal, Chemical **271**, 246 (2007)
7. S. Leveneur, T. Salmi, D.Yu. Murzin, L. Estel, J. Wärnå, N. Musakka, Ind. Eng. Chem. Res. **47**, 656 (2008)
8. N. Musakka, T. Salmi, J. Wärnå, J. Ahlkvist, M. Piironen, Chem. Eng. Sci. **61**, 6918 (2006)
9. S. Leveneur, T. Salmi, N. Musakka, J. Wärnå, Chem. Eng. Sci. **62**, 5007 (2007)
10. X. Zhao, K. Cheng, J. Hao, D. Liu, J. Mol, A. Catal, Chemical **284**, 58 (2008)
11. S. Leveneur, D. Yu. Murzin, T. Salmi, J.-P. Mikkola, N. Kumar, K. Eränen, L. Estel, Chem. Eng. J. **147**, 323 (2009)
12. A. Palani, A. Pandurangan, Catal. Commun. **7**, 875 (2006)
13. G. Prescher, O. Weiberg, H. Waldmann, H. Seifert, International Patent US4088679 (1978)
14. F.P. Greenspan, D.G. MacKellar, Anal. Chem. **20**, 1061 (1948)
15. D. Kubička, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, T. Salmi, D.Yu. Murzin, J. Catal. **222**, 65 (2004)
16. P. Mäki-Arvela, N. Kumar, V. Nieminen, R. Sjöholm, T. Salmi, D. Yu Murzin, J. Catal. **225**, 155 (2004)
17. E.M. Sulman, V.V. Alferov, Yu.Yu. Kosivtsov, A.I. Sidorov, O.S. Misnikov, A.E. Afanasiev, N. Kumar, D. Kubicka, J. Agullo, T. Salmi, D.Yu. Murzin, Chem. Eng. J. **134**, 162 (2007)
18. A. Aho, N. Kumar, K. Eränen, T. Salmi, M. Hupa, D.Yu. Murzin, Fuel **87**, 2493 (2008)
19. J.P. Marques, I. Gener, P. Ayrault, J.C. Bordado, J.M. Lopes, F.R. Ribeiro, M. Guisnet, C. R. Chimie **8**, 399 (2005)
20. P.K. Sengupta, R.N. Tiwari, S. Bhagat, Chem. Eng. World **32**, 89 (1997)
21. G.O. Rocha, R.A.W. Johnstone, B.F. Hemming, P.J.C. Pires, J.P. Sankey, J. Mol, A. Catal, Chemical **186**, 127 (2002)
22. A.E.W. Beers, J.A. van Bokhoven, K.M. de Lathouder, F. Kapteijn, J.A. Moulijn, J. Catal. **218**, 239 (2003)
23. D.M. Roberge, H. Hausmann, W.F. Hölderich, Phys. Chem. Chem. Phys. **4**, 3128 (2002)
24. R.L. Hartman, H.S. Fogler, Ind. Eng. Chem. Res. **44**, 7738 (2005)
25. J. De Laat, G.T. Le, B. Legube, Chemosphere **55**, 715 (2004)
26. B. Mani, Ch. Ravi Mohan, V. Sitakara Rao, React. Kinet. Catal. Lett. **13**, 277 (1980)
27. W. Lutz, H. Toufar, R. Kurzhals, M. Suckow, Adsorption **11**, 405 (2005)
28. M. Guisnet, F.R. Ribeiro, Les zéolithes, un nanomonde au service de la catalyse; EDP sciences (2006)