



## Synthesis of peroxypropionic acid from propionic acid and hydrogen peroxide over heterogeneous catalysts

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
### ABSTRACT

This paper proposes a study of different cation exchange resins, used as catalysts for the synthesis of peroxypropionic acid (PPA) from propionic acid and hydrogen peroxide at 40 °C, equimolar concentration of reactants and an apparent Brønsted concentration of 0.2 M. The catalytic activities of the resins are on the same scale as sulfuric acid at comparable concentration level and decrease in the order: Dowex 50Wx2 > Smopex-101 > Dowex 50Wx8 ≈ Amberlite IR-120 > Amberlyst 15. The influence of external and internal mass transfer limitation was evaluated. The experiments also demonstrated that a gelular resin with a degree of cross-linking equal to 8% and a particle size of more than 0.1 mm showed a stronger resistance to deactivation.

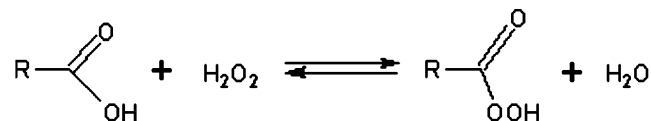
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### 1. Introduction

Peroxy-carboxylic acids are widely used in industrial manufacturing although rarely as pure solutions. These chemicals are employed as disinfecting/antimicrobial agents (destruction of organophosphorus as paraoxon, control legionella bacteria) in alimentary or pharmaceutical industry; as a bleaching agent of wood pulp in paper factory, instead of ecologically non-benign chlorine dioxide; and in fine chemistry for Baeyer–Villiger reaction or olefins epoxidation. All these applications are based on the oxidative prop-

erties of peroxy-carboxylic acid, namely presence of . The main advantage of these chemicals is their harmless impact on the environment because of the non-toxicity of their decomposition products. Indeed, the decomposition of those compounds lead to carbon dioxide, oxygen, water and carboxylic acid.

Two ways of synthesis are possible for the production of peroxy-carboxylic acids: oxidation of the parent carboxylic acid by oxygen or by aqueous hydrogen peroxide. The second way of liquid phase synthesis is more safe, moreover water is an eco-friendly solvent:



Indeed, the main drawback of this reaction is the slow rate and, thus, the necessity to implement an acid catalyst. The process for peroxy-carboxylic acid production is still industrially catalyzed by sulfuric acid [1,2], leading to several drawbacks, such as corrosion, catalyst separation, and threat to environment. Indeed, after the reaction the homogeneous catalyst should be separated (typically by distillation) and recirculated to the process. One way to surmount these problems is to shift from homogeneous to heterogeneous catalysts following the principles of Green Chemistry. The main challenge is to discover a catalyst with a comparable acidic strength as sulfuric acid, which at the same time does not decompose peroxide species and in addition, can be re-used.

In Refs. [3–5], different solid acid catalysts, essentially zeolites and cation exchange resins, have been tested. Among these, cation exchange resins showed the highest catalytic efficiency. It should be noted, however, that no detail information about performance of these solid acid materials is provided, in particular impact of mass transfer, deactivation and even comparison with sulfuric acid.

In this paper we compare the efficiency of some resin catalysts with different cross-linkers and different degree of cross-linking, study the diffusion limitations and determine the deactivation rate

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of various catalysts. It was decided to investigate the perhydrolysis of propionic acid; the choice of peroxypropionic acid is due to its higher stability compared to peroxyacetic acid. In a previous contribution [6], it was demonstrated that the kinetics of propionic acid perhydrolysis, catalyzed by sulfuric acid, is dependent on Brønsted concentration.

In order to facilitate the interpretation of the kinetic data and to make a plausible comparison of these catalysts, an isothermal batch reactor with rigorous stirring was used in the experiments.

## 2. Experimental

### 2.1. 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 to 0 °C) to avoid loss of liquid phase compounds. In case that decomposition of peroxypropionic acid (PPA) or H<sub>2</sub>O<sub>2</sub> appeared, a carrier gas (Helium, AGA, 99.996%) was introduced to the reactor through one of the necks in order to avoid 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 being in contact with the reaction solution were washed with hydrochloric acid followed by another washing, with a phosphate free detergent solution.

At the first stage, propionic acid (Acros, 99 wt.%) and the catalyst were mixed together in the reactor. When the reaction desired temperature was reached, preheated hydrogen peroxide solution (Merck, 30 wt.%) was added through a dropping funnel. At the time “zero” the required amount was introduced into the reactor.

According to a patent [7], during the reaction of hydrogen peroxide and propionic acid in water and in the presence of an acid catalyst, the danger of explosion is suppressed by employing a temperature of maximum 60 °C. Thus, a compromise between rapid kinetics and the safety aspect led us to choose the reaction temperature of 40 °C.

One should keep in mind that the purpose of this paper is to compare the catalytic activity of the different resins. For this reason, all the experiments were carried out under similar conditions regarding the temperature, water amount, initial reactant concentration and apparent Brønsted acid concentration [H<sup>+</sup>]. The estimation of the apparent [H<sup>+</sup>] (the number of Brønsted sites of the solid catalyst present per liter) was carried out on the basis of the cation exchange capacity by dry weight (meq/g) provided by the manufacturer. Fur-

**Table 1**

Experimental parameters for catalysts comparison in the batch reactor.

Reaction temperature	40 °C
Rotation speed	250–600 rpm
[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> /[PA] <sub>0</sub>	0.9–1.0
[H <sub>2</sub> O] <sub>0</sub>	21.8–26.3 mol l <sup>-1</sup>
[PA] <sub>0</sub>	5.5–6.4 mol l <sup>-1</sup>
Apparent [H <sup>+</sup> ]	0.18–0.22 mol l <sup>-1</sup>

thermore, it was assumed that the capacity remains essentially constant, even upon re-use of the catalyst. Table 1 introduces the experimental matrix.

### 2.2. Analytical methods and calculations

Samples were withdrawn from the reaction mixture by a plastic syringe (to avoid contamination of the solution by trace of metals) and were analyzed by the Greenspan and Mackellar method [8]. The concentration of hydrogen peroxide was determined by titration using a standard solution of ammonium cerium sulfate (0.1 N). The concentrations of propionic and peroxypropionic acids were determined by titration with an automatic titrator (Metrohm 751 GPD Titrino) using a standard solution of sodium hydroxide (0.2 N).

The mole fraction of PPA and initial turnover frequency were calculated for comparison of the experimental results.

The initial turnover frequency (T.O.F) was calculated from:

$$\text{T.O.F} = \frac{\text{Initial rate of PPA formation}}{\text{Number of Brønsted acid sites}}$$

The number of Brønsted acid sites was determined on the basis of the cation exchange capacity of the catalyst.

### 2.3. Catalyst properties and characterization

The properties of the tested commercial cation exchange resins are summarized in the Table 2.

Except for Smopex-101, the different cation exchange resins used were composed of similar type of matrix: styrene-divinyl benzene with sulfonic acid functional groups. The shape of the catalysts was the same, i.e. beads.

Smopex-101 (Smoptech) is a fibrous catalyst bearing sulfonic acid functional groups on poly(ethylene-graft-polystyrene). The mean particle diameter is about 0.01 mm and the average length is 4 mm [9].

A comparison was made between native catalysts (used as received) and pretreated ones. The pretreatment consisted of a drying step at 70 °C for 48 h since higher drying temperature could affect the sulfonic acid sites on the catalysts. After the reaction, the catalyst was flushed with water and dried at 70 °C for 48 h.

Scanning electron microscopy (SEM) was used to study the morphology of the resins.

**Table 2**

Properties of the cation exchange resins used.

	Supplier	Polymer type	Cross linking (%)	Moisture content (% mass)	Capacity by dry weight (meq/g)	Native particle size range (mm)	Pores (nm)
Amberlite IR-120	Aldrich	Gel	8	45	4.4	0.3–12	–
Amberlyst 15	Fluka	Macroreticular	20–25	5	4.7	0.45–0.60	40–80
Dowex 50Wx2-100	Acros	Gel	2	78	4.8	0.15–0.3	–
Dowex 50Wx8-400	Sigma–Aldrich	Gel	8	54	4.8	0.04–0.08	–
Dowex 50Wx8-100	Sigma–Aldrich	Gel	8	52	4.8	0.15–0.3	–
Dowex 50Wx8-50	Fluka	Gel	8	55	4.8	0.3–0.84	–
Smopex-101	Smoptech	Fibre	2	6	2.6	–	–

### 3. Results and discussion

#### 3.1. Influence of sulfuric acid at low concentration on the conversion

In order to determine whether there exists a minimum in terms of proton concentration required to observe a significant enhancement of the kinetics; some experiments were carried out without sulfuric acid and with low sulfuric acid concentration. The other goal of these experiments is to establish the amount of solid acid catalyst needed to observe a significant conversion.

Fig. 1 confirms that the perhydrolysis kinetics of propionic acid in the absence of an added catalyst is slow, but propionic acid itself is able to act as a catalyst, therefore some conversion was noticeable [6]. However, one can observe that there is a significant effect of sulfuric acid even at low concentrations (0.001 and 0.004 M), implicating that there is no clear threshold value for the added catalyst concentration.

Nevertheless, to get a significant degree of conversion during a reaction time of 5 h at 40 °C, the concentration of sulfuric acid should be around 0.08 M. As the availability of the proton with sulfuric acid is, *a priori*, higher than in the case of solid acid catalysts, the amounts of solid catalysts were fixed to a level corresponding to an apparent Brønsted acid concentration of 0.2 M on the basis of calculations. During the experiments carried out with the different cation exchange resins, no side reactions such as decomposition of hydrogen peroxide were noticed.

#### 3.2. Scanning electron microscopy

SEM was used to gain a better understanding of the morphology differences between the two cation exchange resins: Amberlite IR-120, which is a gelular or gel-type resin, and Amberlyst 15, which is a macroreticular or macroporous resin.

Prior to analysis of those materials by SEM, they were dried. Figs. 2 and 3 show an overview of the particles of Amberlyst 15 and Amberlite IR-120. At first glance, the surface of Amberlyst 15 is smoother than Amberlite IR-120. Indeed, when a gelular resin is totally dried, the polymer matrix collapses; whereas it does not collapse with macroreticular resin upon loss of water. This implies that the inner structure of the pretreated resins is different than the native one.

However, at higher magnification, one can observe the inhomogeneous surface structure of the macroporous material (Fig. 4), which consists of agglomerates of very small gelular microspheres. Fig. 5 shows a zoom of the surface of Amberlite IR-120, which has a homogeneous distribution of polymeric chains across the bead and, thus, a regular surface structure.

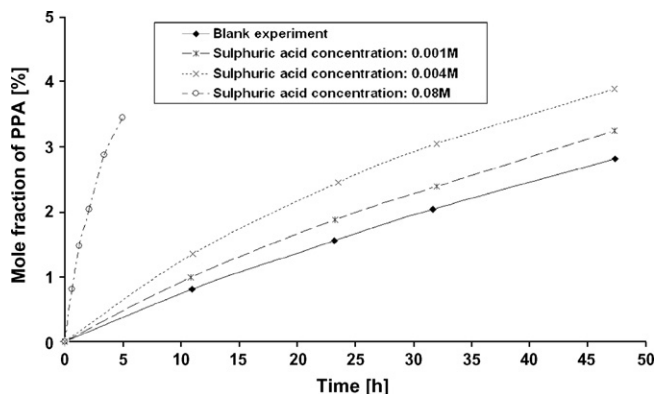


Fig. 1. Mole fraction of PPA versus time at 40 °C with different sulfuric acid concentrations.

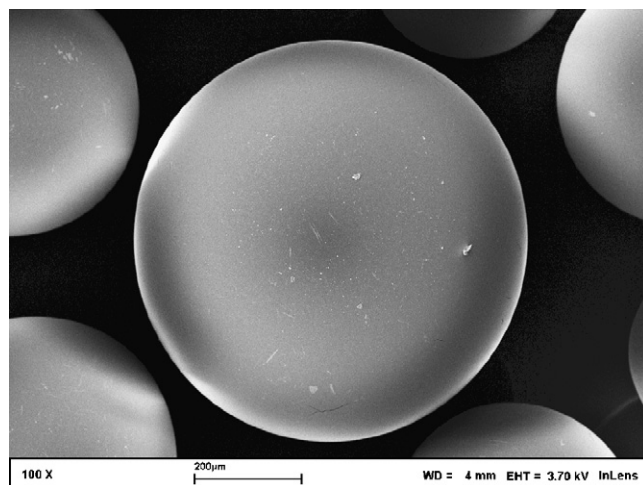


Fig. 2. SEM image of Amberlyst 15.

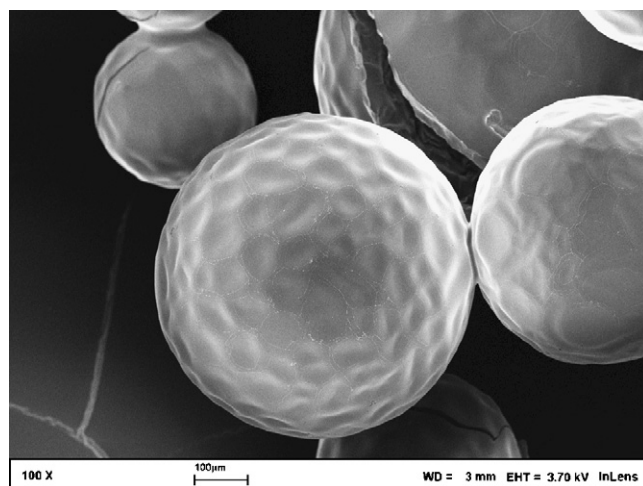


Fig. 3. SEM image of Amberlite IR-120.

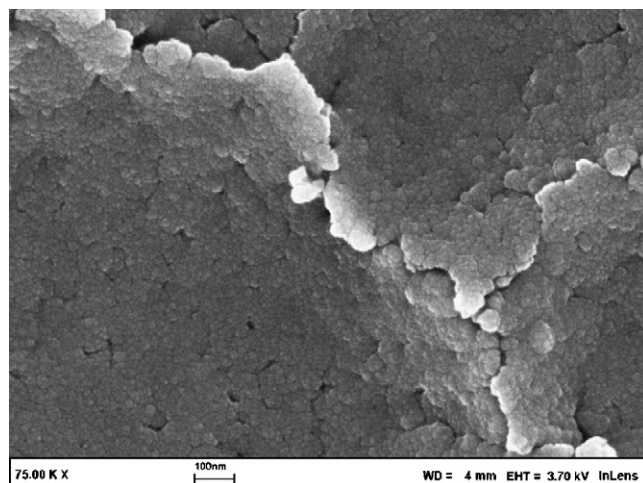


Fig. 4. SEM image of Amberlyst 15.

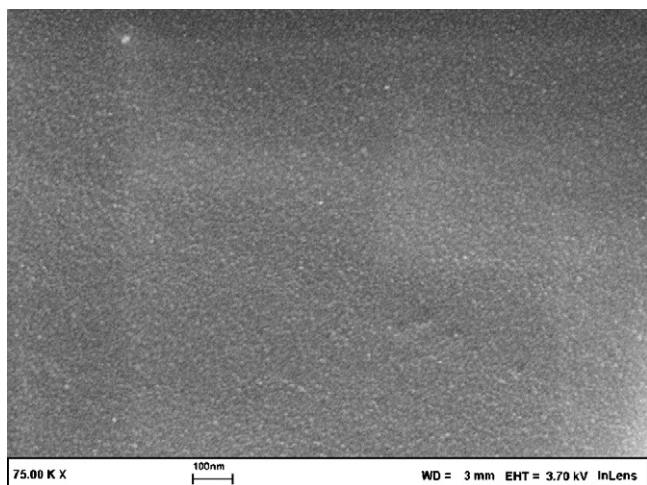


Fig. 5. SEM image of Amberlite IR-120.

### 3.3. Mass transfer effects

#### 3.3.1. Effect of external mass transfer

In order to determine the influence of the external mass transfer around the catalyst particles on the kinetics, identical experiments (see Table 1) were carried out with different rotation velocities (250 and 600 rpm). This phenomenon is characterized by a liquid–solid mass transfer coefficient  $\beta_{LS}$ , which depends mainly on the diameter of the solid particles; consequently, particles with bigger size present stronger external mass transfer resistance. Amberlite IR-120 was selected because of its bigger particle size.

Fig. 6 illustrates the mole fraction of PPA versus time for the experiments carried out with pretreated catalyst at different stirring rates.

It is evident (Fig. 6) that there are no external mass transfer limitations in case of pretreated Amberlite IR-120 at the stirring speed range 250–600 rpm. Experiments carried out in the same conditions, but with native Amberlite IR-120 as well, show absence of external mass transfer. Thus, it can be concluded that no external mass transfer limitations prevailed in the case of other gelular resins with smaller particle size distribution than Amberlite IR-120.

#### 3.3.2. Effect of internal mass transfer

The influence of the mass transfer inside the catalyst particles was studied with Dowex 50Wx8 with different particle size ranges. Fig. 7 illustrates the influence of the particle size distribution on the mole fraction of PPA.

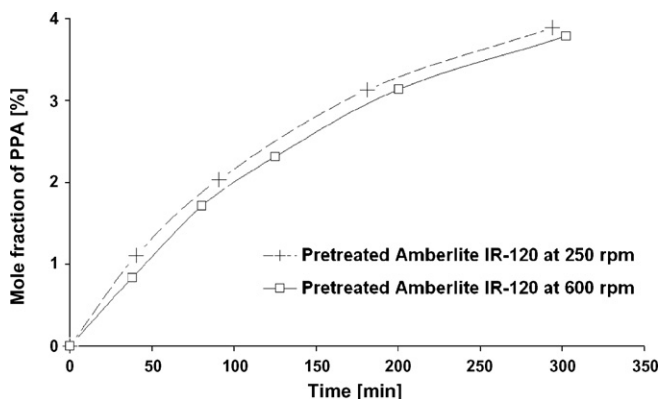


Fig. 6. Effect of the stirring on the mole fraction of PPA with pretreated catalyst at 40 °C.

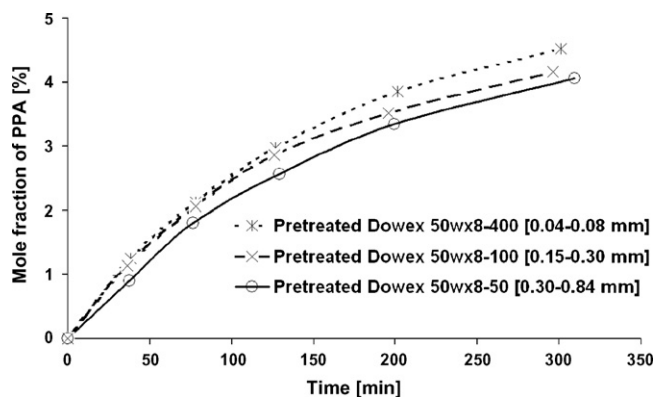


Fig. 7. Influence of internal mass transfer on the mole fraction of PPA at 40 °C and 250 rpm.

Fig. 7 displays that experiments catalyzed by the smallest particles showed rapid kinetics. The influence of the internal diffusion in the experiments carried out with Dowex 50Wx8-400 and 100 might be negligible, although there were slight deviations for the catalysts in the pretreated form. In case of an experiment carried out with native Dowex 50Wx8, the same trend was observed. Diffusion phenomenon can be observed in the case of the experiment carried out with Dowex 50Wx8-50. Assuming that no internal diffusion limitation existed in the case of the smallest particle Dowex 50Wx8-400, the effectiveness factor  $\eta$  can be estimated from:

$$\eta = \frac{\text{Observed rate of PPA formation}}{\text{Rate of PPA without internal diffusion}} \quad (1)$$

From Eq. (1), one can estimate the effectiveness factor for Dowex 50Wx8-100 and Dowex 50Wx8-50. Table 3 summarizes the values obtained at time zero and 90 min after the reaction.

The value of the initial effectiveness factor confirms that the internal diffusion cannot be neglected in the case of particle sizes over 0.3 mm and with a degree of cross-linking at a level of 8%, for pretreated and native resins. However, after 1 h and 30 min, the internal diffusion decreases due to the reverse reaction, which becomes more significant.

Thus, for experiments carried out with Amberlite IR-120, the internal diffusion resistances should be taken into account at the beginning of the reaction.

However, one cannot generalize those conclusions in the case of Amberlyst 15 and Dowex 50Wx2 because the degrees of cross-linking and polymer type are not the same. Indeed, the degree of cross-linkage controls the porosity of the resins, and, therefore, influences the internal diffusion.

### 3.4. Comparison between pretreated and native catalysts

Generally, the pretreatment of solid catalysts has been proven to be important, and have a strong influence on the activity. The main purpose of the pretreatment is to release the water from the catalyst, which represents ca. 50% of the total weight (cf. Table 2).

Table 3  
Effectiveness factor.

	Dowex 50Wx8-100	Dowex 50Wx8-50
0 h		
$\eta$ (with native catalyst)	0.9	0.7
$\eta$ (with pretreated catalyst)	1.0	0.8
1.5 h		
$\eta$ (with native catalyst)	1.00	1.00
$\eta$ (with pretreated catalyst)	1.00	0.95

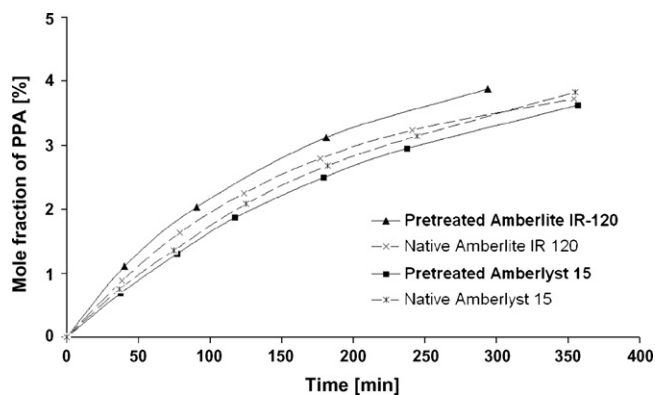


Fig. 8. Effect of the catalyst pretreatment (Amberlite IR-120 and Amberlyst 15) on the mole fraction of PPA versus time at 40 °C and 250 rpm.

One of the characteristic of polymer materials is that in contact with a liquid, they do not only adsorb the liquid, but swell as well. Ion exchange resin absorbs preferably some compounds than the others, and then, a concentration gradient can appear. Consequently, kinetics or thermodynamic parameters can change in case of experiments carried out with a cation exchange resin compared to experiments carried out with a homogeneous catalyst. According to Musante et al. [10], in case of the perhydrolysis of acetic acid by Amberlite IR-120, water is more strongly sorbed than either acetic acid or hydrogen peroxide, and the resin swelling is much higher in water than in acetic acid. However, the difference in kinetics and thermodynamic occurs only between experiments carried out with homogeneous and heterogeneous catalysts, and when the difference of sorption behavior for reactants is significant.

As illustrated by Fig. 8, the difference between pretreated and native Amberlyst 15 is negligible. Because of the macroreticular structure of Amberlyst 15, its polymer matrix is more rigid and, consequently, it does not collapse during the drying procedure. This fact is confirmed by SEM picture (Fig. 2), where one can notice that the matrix of this resin did not collapse, compared to gelular resin.

Nevertheless, the differences in activity were significant for the cation exchange resins in gel form (Figs. 8 and 9), i.e., the velocity of the reaction is higher with pretreated resins. From Fig. 3, one can notice that the structure of the resin has changed during the pretreatment. Consequently, the diffusion properties of these materials are different.

These differences become more significant in the vicinity of the equilibrium. However, according to Table 4, differences in the initial T.O.F ratio between pretreated and native catalyst are not really significant.

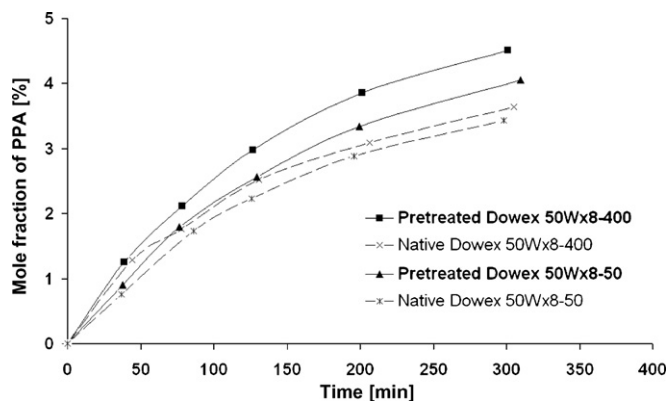


Fig. 9. Effect of the catalyst pretreatment (Dowex 50Wx8-400 and 50Wx8-50) on the mole fraction of PPA versus time at 40 °C and 250 rpm.

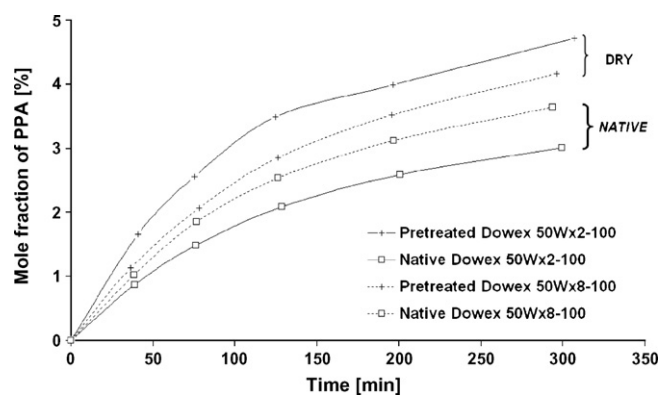


Fig. 10. Effect of the degree of cross-linking on the mole fraction of PPA at 40 °C and 250 rpm.

### 3.5. Effect of the cross-linking

The degree of cross-linking of the resins has a strong influence on their structures, since it controls the porosity of the resin, e.g. X8 (8%) indicates medium porosity and X2 high porosity. To have a better illustration of this effect, experiments were carried out with Dowex 50Wx8-100 and Dowex 50Wx2-100, because of the similarities in their physical and chemical properties, but different cross-linking.

Fig. 10 confirms the fact that there is a difference between pretreated and native catalyst. In the case of pretreated catalyst, the activity of Dowex 50Wx2-100 is higher than the one of Dowex 50Wx8-100. However, this phenomenon is inverted in case of experiments carried out with native catalyst.

Due to the small size of the reactants (propionic acid and hydrogen peroxide) and products (PPA and water), the porosity of these materials does not slow down the diffusion process. The pretreatment modifies the inter-structure of the matrix, and, thus, modify the tortuosity factor. One can notice that the pretreatment improves the activity of the resins, thus, the tortuosity factor decreases. This tendency is confirmed by the fact that the active sites, i.e., sulfonic groups are located inside the particle [10]. The improvement of the tortuosity factor, by the pretreatment, is better for the resin with low percentage of divinylbenzene.

In case of native resin, the tortuosity factor is higher with lower degree of cross-linking.

### 3.6. Comparison of the solid catalysts with sulfuric acid

A comparison of the efficiency of the different solid acid catalysts and sulfuric acid is described in this section. Indeed, the structure of the sulfonic acid group is very close to the sulfuric acid. For the sake of simplicity, only the results obtained with the pretreated catalysts are shown. All the experiments were carried out under similar conditions (see Table 1) and the speed of agitation was fixed at 250 rpm. Fig. 11 illustrates the mole fraction of PPA versus time for the different pretreated catalysts and Fig. 12 represents the T.O.F for them.

As can be seen in Fig. 11, the efficiencies of the resins are lower than for sulfuric acid at the comparable Brønsted acid concentration level, in general. However, the activity of Dowex 50Wx2-100 is similar to that of sulfuric acid, at a concentration level of 0.19 M. Based on the apparent Brønsted concentration, catalyst activity decreases in the order: Dowex 50Wx2 > Smopex-101 > Dowex 50Wx8 ≈ Amberlite IR-120 > Amberlyst 15. Fig. 12 showing the initial T.O.F for the different cation exchange resins displays the same trend.

The highest activity of pretreated Dowex 50Wx2 is because of its lower tortuosity factor. Experiments carried out with Amberlite

**Table 4**  
Turnover frequencies data.

	T.O.F.		Ratio T.O.F (dry catalyst/native catalyst)
	Dry catalyst ( $s^{-1}$ )	Native catalyst ( $s^{-1}$ )	
Amberlite IR-120	6.86E-04	5.92E-04	1.16
Amberlyst 15	4.91E-04	5.12E-04	0.96
Dowex 50Wx2-100	1.01E-03	7.50E-04	1.34
Dowex 50Wx8-400	8.49E-04	7.56E-04	1.12
Dowex 50Wx8-100	8.60E-04	6.62E-04	1.30
Dowex 50Wx8-50	5.94E-04	5.70E-04	1.04

IR-120 and Dowex 50Wx8-50 (the same particle size distribution and degree of cross-linking) gave similar results to that of sulfuric acid, at a concentration level of 0.11 M. The difference of capacity between these resins (Table 2) is not significant to notice a difference in activity.

Thus, the diffusion process for experiments carried out with the gelular resins is essential, and controls the activity toward the perhydrolysis of propionic acid. The catalytic activity of Amberlyst 15 is lower than that of sulfuric acid, at a concentration level of 0.08 M. The macroreticular structure and the high level of cross-linking of this material increase the resistance against the diffusion, and, thus, diminish the activity.

The kinetic curve of Smopex-101 shows that it is possible to use other cross-linkers than divinylbenzene. However, according to our experiments and literature data [9], the swelling effect with this material is important, and strongly influences the diffusion process.

From the experiments data it follows that the pH of the solutions for experiments carried out at 40 °C in the absence of the sulfuric acid and with 0.08 M of sulfuric acid are equal to 1.3 and 0.1, respectively. In case of experiments carried out with cation exchange

resins at 40 °C with an apparent Brønsted concentration of 0.20 M, the pH range is 1.2–1.3, which implies that there is practically no formation of sulfuric acid due to a leaching of the sulfonic group or oxidation of these groups by hydrogen peroxide. Deactivation studies reported in the following section, also confirm, that the activity of cation exchange resins cannot be attributed to the oxidation of sulfonic groups with  $H_2O_2$ , and subsequently release of sulfuric acid into the liquid milieu.

Furthermore, the decrease of the reaction medium acidity by one pH unit compared to sulfuric acid could be beneficial from technological viewpoint.

### 3.7. Catalyst deactivation

Only few articles consider the deactivation of cation exchange resins [11,12]. One of the main difficulties in study this phenomenon is to repeat the experiments under comparable conditions. Our goal was to find the resins which present a strong resistance toward the deactivation process.

For the sake of simplicity, only experiments showing deactivation are displayed in Figs. 13–15.

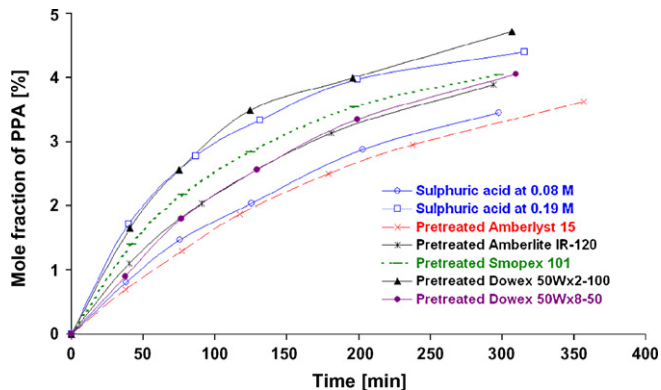


Fig. 11. Synthesis of PPA over different catalysts at 40 °C at 250 rpm.

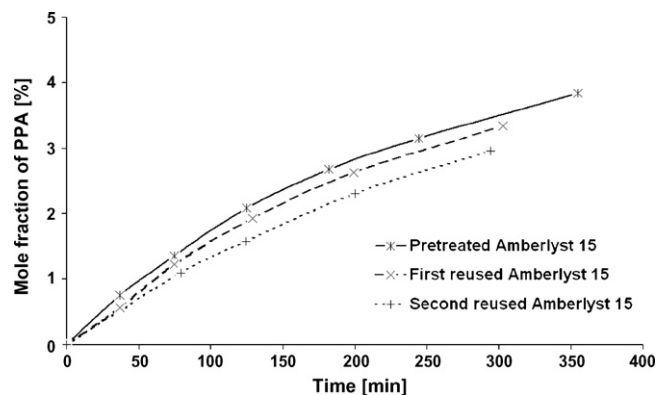


Fig. 13. Deactivation behavior for Amberlyst 15 at 40 °C and 250 rpm.

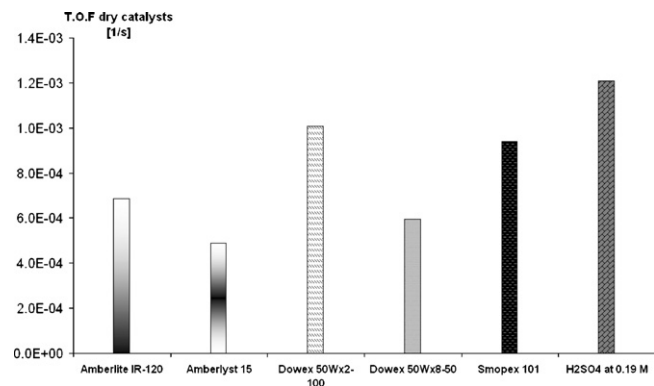


Fig. 12. Turnover frequency for the different pretreated catalysts carried out at 40 °C and 250 rpm.

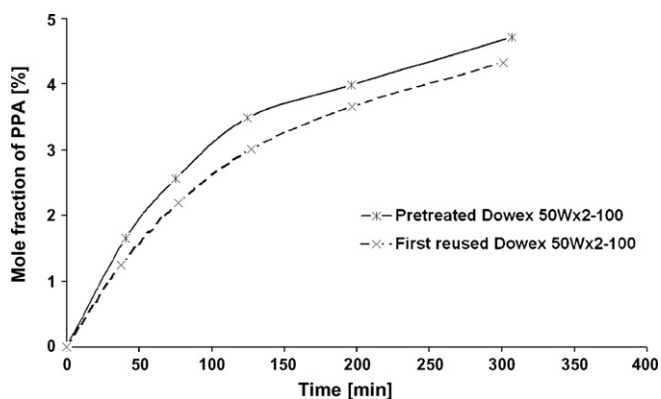


Fig. 14. Deactivation behavior for Dowex 50Wx2-100 at 40 °C and 250 rpm.

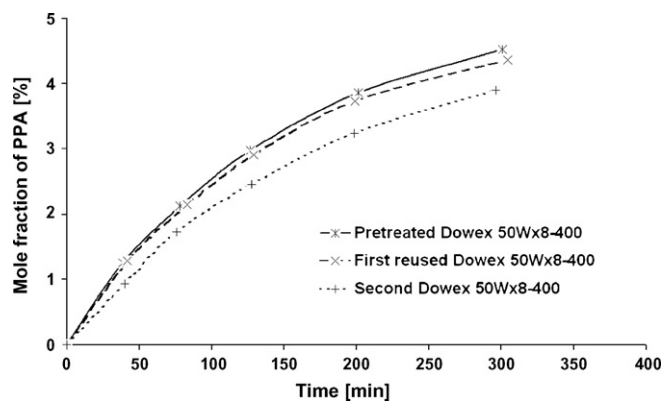


Fig. 15. Deactivation behavior for Dowex 50Wx8-400 at 40 °C and 250 rpm.

The apparent Brønsted concentration  $[H^+]$  was calculated on the basis of the capacity by dry weight (meq/g) of the resins, given by the manufacturer, this capacity was assumed to remain constant from batch-to-batch.

Deactivation rates for Amberlite IR-120, Dowex 50Wx8-100 and Dowex 50Wx8-50 are negligible. The characteristics of these resins are: similar level of cross-linking of 8% and particles with sizes higher than 0.10 mm. Altiokka et al. [12] observed no deactivation for Amberlite IR-120 during the esterification of acetic acid with isobutanol.

Nevertheless, in the case of Dowex 50Wx8-400, Dowex 50Wx2-100 and Amberlyst 15, a significant level of deactivation was visible, as shown in Figs. 13–15.

The deactivation by leaching of sulfonic group is, certainly, not the reason. According to the manufacturer, sulfonic groups volatilize at a temperature of 120 °C, which were not reached during the reaction or pretreatment. Moreover, a deactivation is noticed for experiments carried out with Dowex 50Wx8-400, but not for Dowex 50Wx8-100 or 50Wx8-50 (which have the same properties, except the particle size range). Thus, deactivation by leaching of sulfonic group can be reasonably discarded. However, a more detailed study should be done; to understand deactivation phenomenon in more detail.

#### 4. Conclusion

The goal of this work was to propose a green alternative route for catalyzing the perhydrolysis of carboxylic acid and, thus, avoided corrosive mixture and separation problems. Different cation exchange resins were evaluated. Several experiments were performed in a batch reactor at 40 °C, equimolar concentration of reactants and similar water concentration.

The pretreatment of resins is necessary since it improves the catalytic activity of the gelular resins. The catalytic activity was higher with gelular resins with lower cross-linking, due to a lower value of the tortuosity factor. A comparison with sulfuric acid indicated that the activity is on similar scale, but the resins allow the acidity to be lowered by one unit pH. Furthermore, with the heterogeneous resin catalysts, the catalyst separation problem is avoided.

The external mass transfer can be neglected in case of those experiments that were carried out at the steering speed of

250–600 rpm. However, the initial internal mass transfer was present in the case of gelular resin with a degree of cross-linking equal to 8%, essentially for pretreated catalysts with larger particles (>0.3 mm).

The use of a different cross-linker than divinylbenzene is possible, but the swelling noticed with Smopex-101, which has ethylene cross-linker, affords a stronger resistance against the diffusion.

The deactivation pattern for the resins was dependent on the degree of cross-linking and the particle size. Experiments carried out with a level of cross-linking degree of 8% and particles having sizes over 0.1 mm displayed slow deactivation. However, a better understanding about the deactivation of these materials is needed, by a kinetic modeling which takes into account this phenomenon.

To conclude, the efficiency of the resins is a compromise between their catalytic efficiency and their deactivation. Higher degree of cross-linking resulted in a slower reaction rate. Nevertheless, this relation is opposite regarding deactivation. The environmental and maintenance benefits upon use of cation exchange resins compared to sulfuric acid are important, essentially regarding the possibility to use less corrosive mixture.

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