



A new method for the preparation of peroxyacetic acid using solid superacid catalysts

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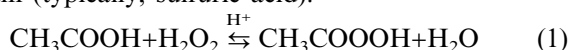
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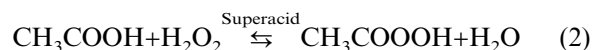
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Abstract—A new method for the preparation of peroxyacetic acid from acetic acid and hydrogen peroxide in the presence of solid superacids as a catalyst under mild conditions has been proposed. The preparation of peroxyacetic acid could be carried out in a batchwise operation as well as in a flow-system operation. Nafion-H was found to be active and very stable catalyst for the preparation of peroxyacetic acid and to be regenerated without the loss of catalytic activity. © 2003 Elsevier Science Ltd. All rights reserved.

Peroxyacetic acid (PAA) is an ideal disinfectant in cleaning-in-place (CIP) systems, for example, in the food and beverages industries because its application does not lead to toxic compounds, i.e. the reaction products are oxygen, water and acetic acid.¹ It therefore replaces other disinfectants such as chlorine-containing substances, quaternary ammonium compounds and expensive ozone. Typical concentrations of PAA are 6.6–13 mM for disinfection purpose.² PAA is technically prepared by the reaction of concentrated hydrogen peroxide with acetic acid in a strongly acidic medium (typically, sulfuric acid):^{3,4}



However, this technique suffers from the drawbacks such as separation of soluble catalyst from the reaction mixture and corrosion of the reactor. Solid superacids have been used effectively in various acid-catalyzed reactions in place of the conventional acid catalysts because of their higher catalytic activity, minimal corrosion problems, ease of separation and reusability.^{5–16} Olah et al. have reported that perfluorinated solid superacid resin Nafion¹⁷ can be used effectively in various acid-catalyzed reactions.^{11–16} In the present paper, we propose for the first time a method for the synthesis of PAA by employing solid superacids as catalysts (Eq. (2)).



The superacid catalysts employed in this study include Nafion-H, Nafion[®] SAC-13, Dowex[®] DR-2030 and Amberlyst[®].

A schematic diagram of experimental set-up is shown in Figure 1. The reactor consisted of a flat-bottomed glass vessel of 200 mL volume and was placed in a constant temperature bath. A typical procedure for the preparation of PAA was as follows: the reactor solution consisting of 15 mL of 1 M CH₃COOH, 15 mL of 0.755 M H₂O₂ and 1.5 g (5 wt%) solid superacid as catalyst was vigorously stirred with a magnetic stirrer at 25°C for several hours. The solid catalyst was then filtered off, and the filtrate was analyzed by HPLC and titration methods.¹⁸ Superacid catalyst Nafion-H (type: NR-50), Nafion SAC-13 (13 wt% Nafion resin/silica composite), Dowex DR-2030 and Amberlyst 36(wet) ion-exchange resin were purchased from Aldrich Chemical Co.

The reaction was also carried out in a flow system in which the glass tube reactor was charged with Nafion-H catalyst. A mixture (1:1 vol. ratio) of 1 M CH₃COOH and 0.755 M H₂O₂ was passed through the catalyst with a constant flow rate of 1.25 mL h^{−1} at 25°C. The PAA concentration was determined by HPLC consisting of the following components: pump TOSOH CCPM, injector valve, column TOSOH ODS Ts (dimension 150×4.6 mm), detector JASCO UV-970, and mobile phase 75% methanol/25% water. The injection volume was 20 µL at a flow rate of 1 mL min^{−1} and the UV detection wavelength was 230 nm.

Keywords: peroxyacetic acid; acetic acid; solid superacid; Nafion-H.

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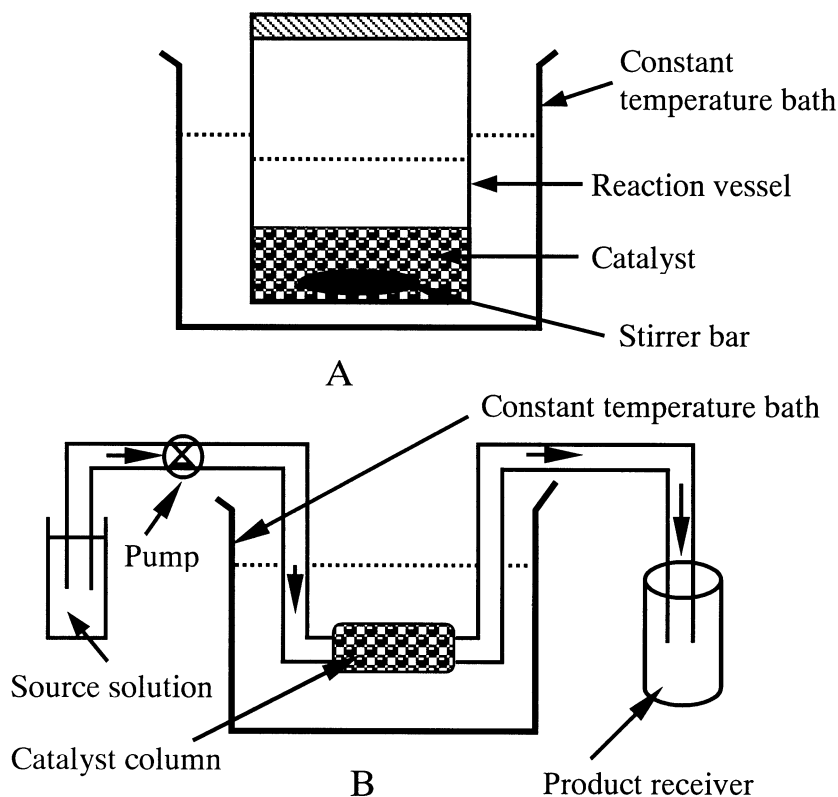


Figure 1. Schematic drawing of the experimental setups used for the preparation of PAA. (A) batchwise operation and (B) flow-system operation.

The PAA solutions could be prepared from the reaction of 0.5 M CH_3COOH and 0.378 M H_2O_2 in the presence of superacid catalysts. The results are summarized in Table 1 for all of the catalysts used in this study. At the same loading of catalysts (5 wt%), Nafion-H was found to be more active than Dowex, Amberlyst and Nafion SAC-13 at a reaction time of 17 h. Moreover, Nafion-H catalyst was observed to be very stable and its catalytic activity remained unchanged for a prolonged period of the operation in the presence of hydrogen peroxide.

Here it should be noted that under the same experimental conditions as above (i.e. 0.5 M CH_3COOH and

0.378 M H_2O_2 were used as reactants), no PAA was produced when 1 M H_2SO_4 was used as catalyst.

When a mixture solution of 1 M CH_3COOH and 0.755 M H_2O_2 in a ratio of 1:1 was allowed to flow through the Nafion-H catalyst at 25°C with a contact time of 4.5 h, a higher concentration of PAA was obtained (run 3), compared with the batchwise operation.

The concentration of PAA was found to increase significantly with increasing the initial concentrations of acetic acid and hydrogen peroxide at a constant amount of catalyst. PAA of 263 mM was produced

Table 1. Preparation of PAA from an aqueous solution containing 0.5 M CH_3COOH and 0.378 M H_2O_2 using various superacid catalysts at 25°C

Run	Catalysts ^a	pH	[PAA] (mM) ^{b,c}	Conversion of acetic acid (%)
1	Nafion-H	2.50	4.07	0.81
2 ^d	—	—	3.95	0.79
3 ^e	—	—	5.25	1.05
4 ^f	—	2.46	263	16.0
5	Nafion SAC-13	2.50	1.71	0.34
6	Dowex	2.45	2.89	0.58
7	Amberlyst	2.52	3.28	0.66

^a Catalyst 5 wt%.

^b Reaction time was 17 h.

^c The concentrations were determined by HPLC.

^d Used Nafion-H.

^e Flow system with contact time of 4.5 h.

^f Initial concentrations of acetic acid and H_2O_2 were 1.65 and 2.85 M, respectively.

when the initial concentrations of acetic acid and hydrogen peroxide were 1.65 and 2.85 M, respectively (run 4). In this case, the conversion of acetic acid into PAA was 16% which is considerably large, compared with that of run 1.

The concentration of PAA solution prepared by the batchwise operation was increased with the reaction time and it was ca. 3.5 mM when the reaction time was 7 h, and at 17 h and longer reaction time it was almost constant (ca. 4.1 mM) (Fig. 2), which is considered as the equilibrium concentration of PAA under the preparation conditions used here.

To examine reusability of the catalyst, the experiment was carried out using the used Nafion-H catalyst. Run 2 is the result for the used catalyst of Nafion-H and is comparable to run 1 for the fresh catalyst. The catalyst used in run 1 was immersed in 20% HNO_3 for 4–5 h at room temperature and then filtered. After that, the catalyst was washed several times with deionized water until a neutral filtrate was obtained and finally was dried under vacuum at 105°C for at least 10 h. The comparison of runs 1 and 2 indicates that the catalytic activity of the regenerated Nafion-H is as good as that of the fresh one.

The dependence of the concentration of PAA upon the loading amount of Nafion-H catalyst is shown in Figure 3. The reaction time was 17 h. The production of PAA was observed to increase with increasing the loading amount of Nafion-H and PAA of ca. 0.3 M was prepared when its loading was 10%.

In conclusion, we have for the first time succeeded in preparing PAA from acetic acid and hydrogen peroxide under mild conditions using solid superacid catalysts. Among the superacid catalysts investigated, Nafion-H was found to be most stable and to possess a high catalytic activity for the preparation of PAA. In addition, the catalyst can be easily separated from the

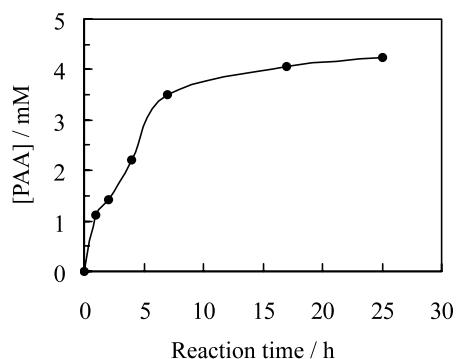


Figure 2. The concentration of PAA produced by the batchwise operation as a function of the reaction time using Nafion-H. Catalyst loading: 5 wt%; initial concentrations: $[\text{CH}_3\text{COOH}] = 0.5$ M and $[\text{H}_2\text{O}_2] = 0.378$ M; temperature: 25°C.

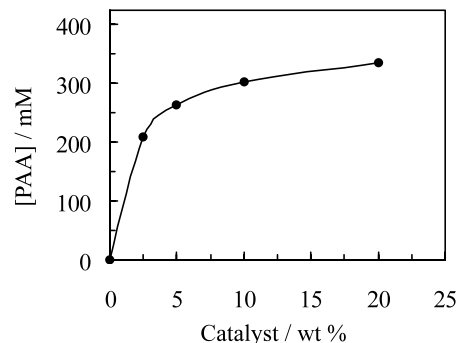


Figure 3. Dependence of the concentration of PAA upon the loading amount of Nafion-H catalyst at 25°C. Initial concentrations: $[\text{CH}_3\text{COOH}] = 1.65$ M and $[\text{H}_2\text{O}_2] = 2.85$ M; reaction time: 17 h.

products and used repeatedly without a decrease in the catalytic activities.

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