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Catalytic wet air oxidation of carboxylic acids at atmospheric pressure

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Abstract

Catalytic wet air oxidation of carboxylic acids (maleic acid, oxalic acid and formic acid) was carried out in a batch reactor operated at 160 psi or atmospheric pressure. Pt/Al_2O_3 and the sulfonated poly(styrene-co-divinylbenzene) resin were used as catalysts. Maleic acid was proved to be a refractory substance which could not be oxidized on the Pt/Al_2O_3 catalyst at all atmoshperic pressure, and needed high pressure and high temperature operation for its oxidation. On the contrary, oxalic acid and formic acid were readily oxidized into carbon dioxide and water at 353 K and atmospheric pressure. The pathways of maleic acid oxidation were proposed, and the conversion of maleic acid into oxalic acid was the rate-determining step. When the sulfonated resin catalyst was present together with the Pt/Al_2O_3 catalyst, maleic acid could be oxidized at 353 K and atmospheric pressure. The sulfonated resin catalyst was suggested to hydrolyze maleic acid into readily oxidizable compounds. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Wet air oxidation (WAO) process is a very attractive and useful technique for treatment of effluents where the concentrations of organic pollutants are too low for the incineration process and when biological treatments are ineffective, e.g., in the case of toxic effluents [1–3]. WAO was applied to removing total organic carbon (TOC) such as insoluble polymers [4], wastewater [5–8], and certain organic compounds [9,10]. The efficient removal of pollutants via WAO process requires very high temperature and pressure, typically in the range 473–573 K and 7–15 MPa, respectively [11]. However, the severe reaction conditions can lead to high installation costs, and practical applications of this process are limited. Therefore, the development of catalytic wet air oxidation (CWAO) using various catalysts has been attempted in order to reduce the severity of the oxidation conditions. The use of catalysts makes the process more attractive by achieving high conversion at considerably lower temperature and pressure [12–14].

Many organic compounds in WAO gradually degrade to highly refractory lower carboxylic acids. Devlin and Harris [15] investigated non-catalytic WAO of phenol and listed various oxidation products such as maleic acid, acetic acid, oxalic acid and formic acid. These acids were quite stable and difficult to be further oxidized. Therefore, more severe oxidation conditions were required for complete oxidation. The oxidation of these low molecular weight acids was proved to be the rate-controlling step in the CWAO of many organic

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compounds [15,16]. Therefore independent studies of CWAO of low molecular weight acids were carried out by many researchers.

Imamura et al. [17] studied oxidation of oxalic acid at 385–433 K by using Co/Bi[5/1] complex catalyst. They have observed about 30% TOC removal at 413 K. Li et al. [16] reported WAO of oxalic acid at 500–583 K. Shende and Mahajani [18] have studied the kinetics of WAO of glyoxalic acid and oxalic acid in absence and presence of cupric sulfate catalyst at 393–518 K and 0.345–1.38 MPa oxygen partial pressure. Kinetics of the wet oxidation of formic acid were also investigated on various palladium catalyst [19] and on CuO–ZnO catalyst [20]. All these studies, however, have still the problems of the operation at high temperature and high pressure. Till now study of CWAO of carboxylic acids at atmospheric pressure was almost unexplored.

In the present work, CWAO of carboxylic acids at atmospheric pressure and at 373 K was attempted. To do this Pt/Al_2O_3 catalyst was used together with a sulfonated poly(styrene-co-divinylbenzene) resin catalyst. The solid acid resin catalyst will convert the refractory carboxyl acid (in our case maleic acid) to more oxidizable compounds.

2. Experimental

2.1. Materials

High purity maleic acid, oxalic acid and formic acid, supplied from Aldrich, were used without further purification. Platinum(II) acetylacetonate (Aldrich) was used as the precursor of Pt/Al_2O_3 catalyst. γ-Al_2O_3 (Strem Chemicals) was used as the support of Pt/Al_2O_3 catalyst. All other chemicals used were of analytical reagent grade.

2.2. Catalyst preparation

One weight percent of Pt/Al_2O_3 catalyst was prepared by incipient wetness method. In order to locate platinum particles mainly at the exterior surface of γ-Al_2O_3 powder, the pores (pore volume: 0.2 cm^3/g) of γ-Al_2O_3 had been a priori saturated with *n*-hexane. A certain amount of platinum(II) acetylacetonate solution was added to γ-Al_2O_3 drop by drop. The prepared samples were then dried in vacuo at 323 K. The above preparation steps were repeated 10 times to have 1 wt.% Pt loading. The samples were finally calcined at 673 K for 4 h in a programmable furnace. The liner rate of heating up to 673 K was kept to be 0.5°C/min.

Sulfonated poly(styrene-co-divinybenzene) resin catalyst was prepared by the method described in [21]. Through a suspension polymerization with styrene, divinylbenzene and toluene (pore creating agent) at 353 K for 12 h white poly(styrene-co-divinylbenzene) resin particles were formed. The resin particles had a macroreticular structure. As shown in the SEM micrograph of the resin particle (Fig. 1), there existed numerous microgels within the particle. In order to introduce sulfonic acid group at the exterior surface of the gels and therefore to avoid diffusion limitation during CWAO of carboxylic acids, a special method was employed. Twenty-five milliliters of concentrated sulfonic acid was added drop by drop to a beaker containing 32 ml 1, 2-dichloroethane and 92 ml nitrobenzene. Five grams of resin particles were then introduced into the mixture. The slurry solution was stirred mechanically with a glassed blade for 30 min. The sulfonated samples were then washed with sufficient amount of deionized distilled water and were finally dried in vacuo at 393 K for 72 h. The concentration of sulfonic acid group ($-SO_3H$) in the sulfonated resin catalyst was estimated to be 0.9 meq/g.

2.3. Reaction procedures

The oxidation of carboxylic acid solution (3000 mg/l concentration) was performed either in a glass reactor of 1 l capacity equipped with a condenser, stirrer, thermocouple, and air flow meter or in a 1 l SS316 autoclave (Parr Instrument) equipped with a teflon liner and a gas entrainment impeller having a variable-speed arrangement. In the glass reactor, the reactions were conducted at atmospheric pressure in the operation temperature, and air was bubbled into the solution. The flow rate of air was 200 cm^3/min, and 1 g Pt/Al_2O_3 catalyst was generally used. High pressure (160 psig) experiments were carried out in the autoclave with 0.2 g Pt/Al_2O_3 catalyst.

2.4. Characterization and analysis

Dispersion of platinum particles in the Pt/Al_2O_3 catalyst was observed with a transmission electron

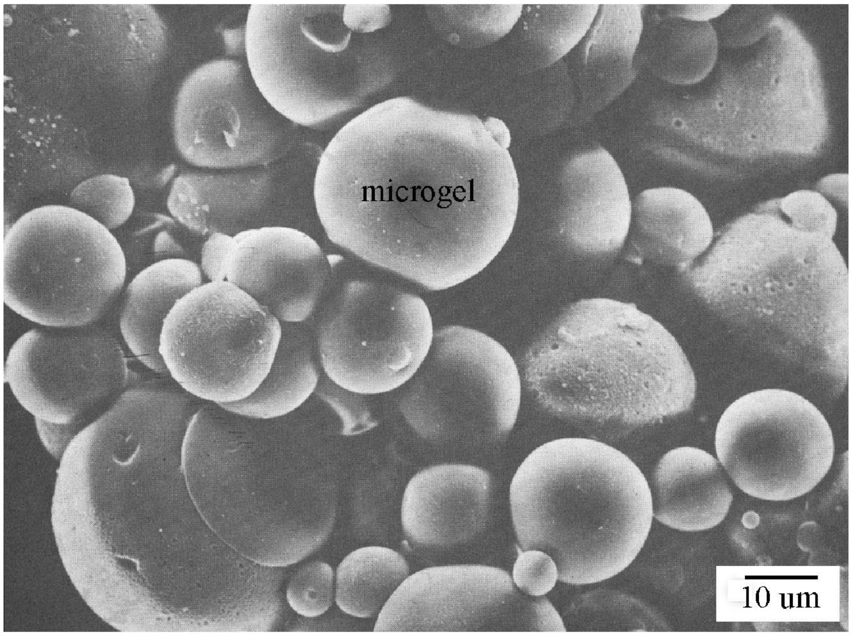

Fig. 1. SEM micrograph of the resin particle.

microscopy (JEOL 200CX) using 160 KeV electrons. Distribution of sulfonic acid group within the sulfonated resin catalyst particle was analyzed with a scanning electron microscopy (SEM, Phillips XL 30). The instrument was fitted with an energy dispersive X-ray (EDX) accessory.

Reaction intermediates and carboxylic acid residuals were identified and quantified with HPLC (Waters) equipped with a tunable absorbance detector. Separation of the components was achieved by Nova-Pak C18 column. Elution was performed at 1 ml/min flow rate of mobile phase ($MeOH:H_2O:H_3PO_4 = 40:60:0.5$ vol.%).

3. Results and discussion

3.1. Characterization of the catalysts

TEM micrograph of the Pt/Al_2O_3 catalyst is shown in Fig. 2. Platinum particles were finely dispersed on the surface of Al_2O_3 support, and the average Pt particle size was estimated to be 20 Å.

The concentration profile of sulfur in the microgel particle in the sulfonated poly(styrene-co-divinylbenzene) resin catalyst was obtained with SEM/EDX analysis. As can be seen in Fig. 3, most sulfonic acid group located selectively at the exterior surface of the microgel particle.

3.2. Maleic acid oxidation

Oxidation of maleic acid solution (3 g/l) was carried out in the high pressure reactor. To assess the extent of the uncatalyzed thermal oxidation of maleic acid and the effect of support, WAO tests were performed without catalyst and with metal-free supports at 453 K. As can be seen in Fig. 4, the uncatalyzed thermal oxidation did occur up to 50% in 40 min, and the use of metal-free Al_2O_3 support resulted in somewhat lower oxidation efficiency than uncatalyzed oxidation. The elevated temperature can lead to the formation of oxygen radicals (O·), which in turn can react with water to form hydroxyl radical (HO·). This radical might have oxidized maleic acid. Metal-free Al_2O_3 support, however, scavenged some of the hydroxyl radical formed.

The use of Pt/Al_2O_3 catalyst enhanced the oxidation appreciably. Almost complete degradation of maleic acid could be obtained in 40 min. Although the results are not shown in this paper, CWAO of maleic acid

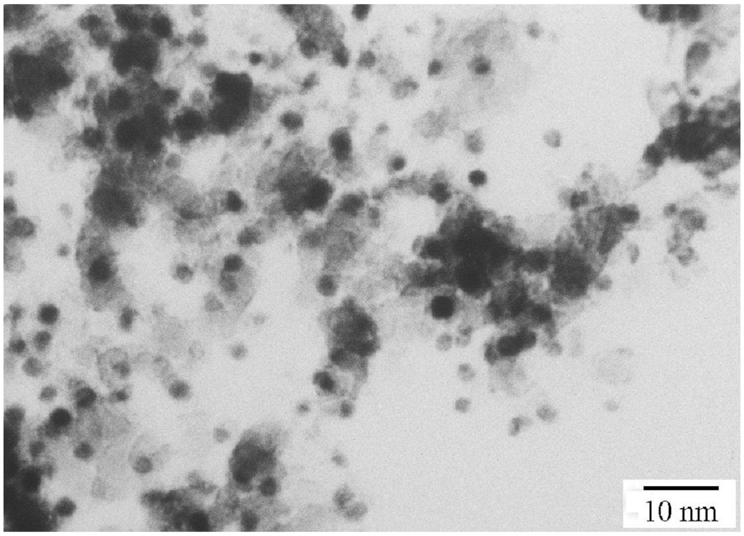

Fig. 2. TEM micrograph of the Pt/Al_2O_3 catalyst.

had also been tested with Pd/Al_2O_3, Rh/Al_2O_3 and Ru/Al_2O_3 catalyst. Among these catalyst Pt/Al_2O_3 catalyst was proved to be the most reactive toward the oxidation of maleic acid solution.

CWAO of maleic acid solution was greatly affected by reaction temperature (Fig. 4). At temperature as low as 393 K the degradation of maleic acid was negligible. When the CWAO of maleic acid solution was carried out at atmospheric pressure and 353 K, maleic acid could not degrade at all.

The reaction pathways of maleic acid oxidation could be confirmed by detecting the reaction intermediates. Fumaric acid, oxalic acid and formic acid were produced as intermediates (Fig. 5). On the basis

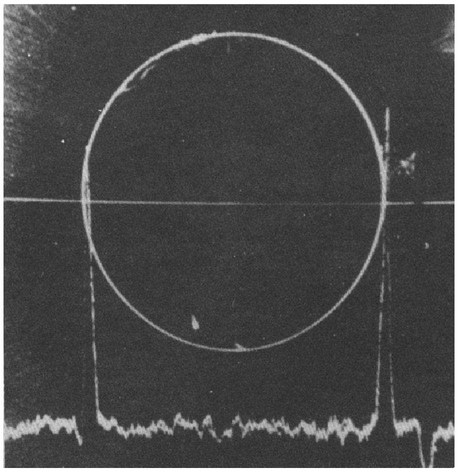

Fig. 3. SEM/EDX analysis for the concentration profile of sulfur within gel particle.

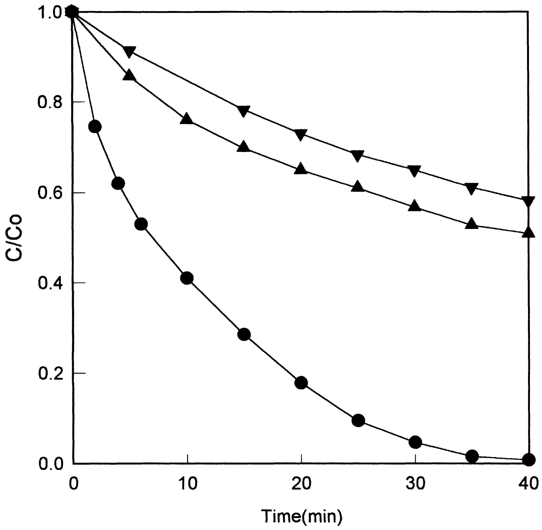

Fig. 4. Catalytic wet oxidation of maleic acid at 453 K and 160 psig: (▲) uncatalyzed reaction; (▼) reaction with metal-free Al_2O_3; (●) reaction with 1 wt.% Pt/Al_2O_3 catalyst.

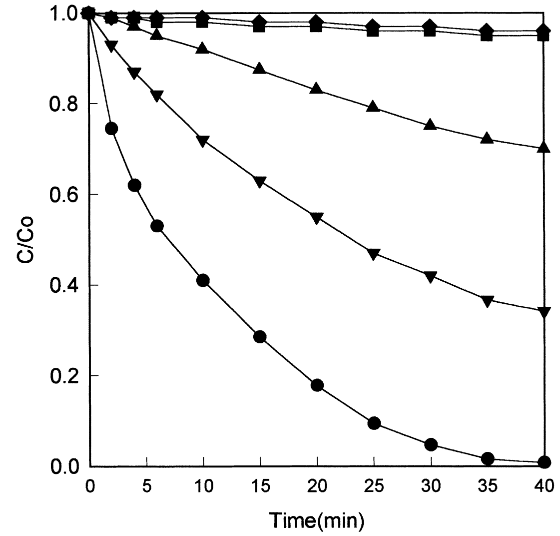

Fig. 5. Effects of temperature on maleic acid oxidation over Pt/Al_2O_3 catalyst: (●) 453; (▼) 433; (▲) 413; (■) 393; (◆) 373 K.

of the sequential production of these intermediates the pathways of maleic acid oxidation were proposed as shown in Fig. 6. Fumaric acid is believed to be formed through the *cis–trans*-isomerization of maleic acid. Maleic acid and fumaric acid are then converted into oxalic acid which subsequently degrades into formic acid. Finally formic acid is totally oxidized into carbon dioxide and water.

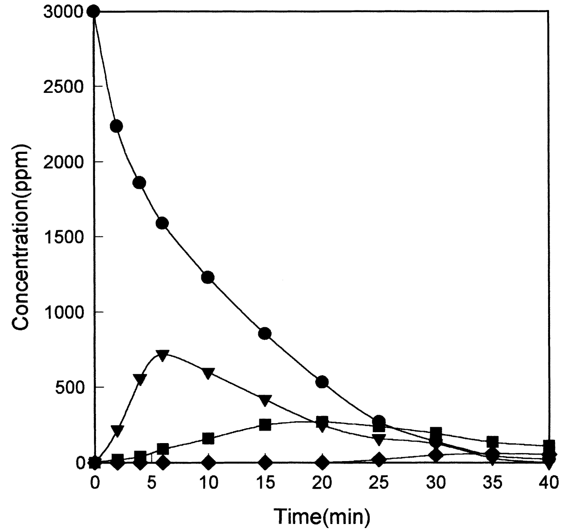

Fig. 6. Concentration profile of intermediates during CWAO of maleic acid solution at 453 K and 160 psig: (●) maleic acid; (▼) fumaric acid; (■) oxalic acid; (◆) formic acid.

3.3. Oxidation of oxalic acid and formic acid

Fig. 7 shows the time dependence of CWAO of oxalic acid and formic acid at 353 K and atmospheric pressure. About 90% destruction of oxalic acid could be achieved in 20 min, and a 100% conversion of formic acid was obtained within 10 min. When compared with maleic acid, the oxidation of oxalic acid and formic acid is known to proceed at extremely fast rates. Under theses operation condition no detectable conversion of maleic acid could have been observed.

Above-mentioned results for the oxidation of maleic acid, oxalic acid and formic acid indicate that the rate-determining step of the CWAO of maleic acid is the conversion of maleic acid into oxalic acid. In order to achieve the total oxidation of maleic acid into

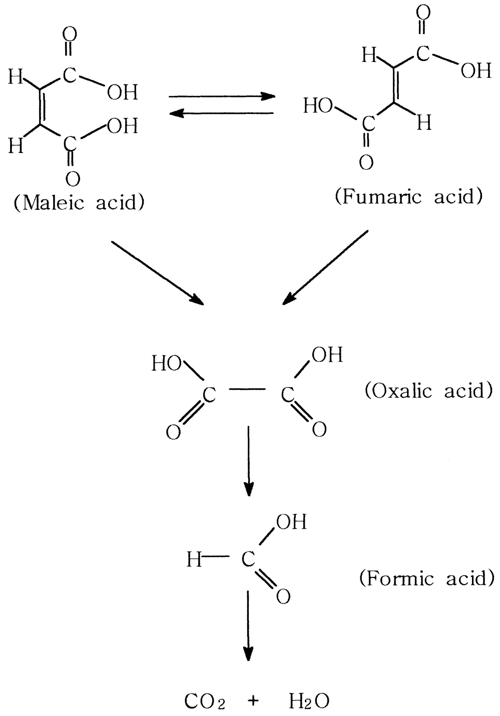

Fig. 7. Proposed reaction pathways of CWAO of maleic acid.

carbon dioxide and water at atmospheric pressure a new catalyst system meeds to be developed.

3.4. Maleic acid oxidation at atmospheric pressure

Figs. 8 and 9 shows the CWAO of maleic acid at 353 K and atmospheric pressure in the presence of the sulfonated resin catalyst and Pt/Al_2O_3 catalyst. Although the oxidation of maleic acid over Pt/Al_2O_3 catalyst alone did not proceed at all, the addition of the sulfonated resin catalyst enhanced the efficiency of maleic acid oxidation remarkably.

The decrease of maleic acid concentration might have resulted in the increase of other reaction intermediates formed. HPLC analysis, however, had not shown any evidence for the formation of other intermediates with appreciable concentration. Just fumaric acid had been observed at very low concentration level. Fumaric acid might be produced through the *cis–trans*-isomerization on the sulfonated resin catalyst. The sulfonated resin catalyst must have played an important role on converting the refractory maleic acid into lower molecular weight compounds which were readily oxidizable on the Pt/Al_2O_3 catalyst. When the catalytic reaction of maleic acid had been performed in the presence of the sulfonated resin catalyst, maleic acid had been converted mainly into formic acid. The formation of formic acid suggests that some acid hydrolysis reaction of maleic acid must have taken place on the sulfonated resin catalyst.

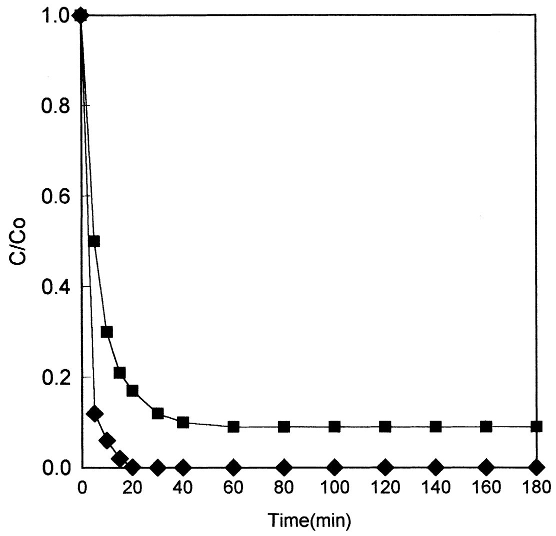

Fig. 8. Catalytic wet oxidation of oxalic acid and formic acid over Pt/Al_2O_3 catalyst at 353 K and atmospheric pressure: (■) oxalic acid; (◆) formic acid.

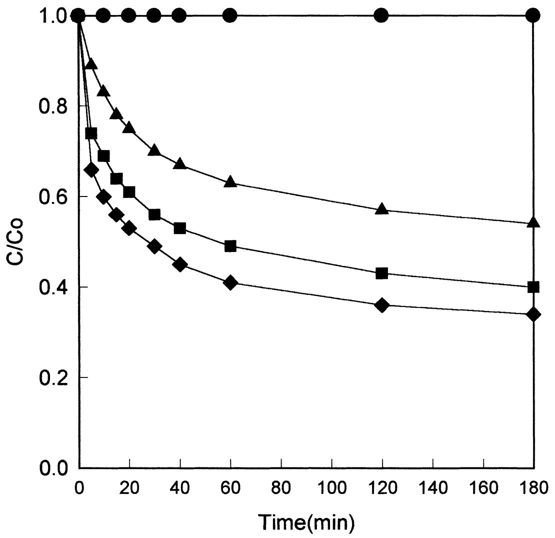

Fig. 9. Conversion of maleic acid solution as a function of reaction time and catalyst mass: (●) 1 g Pt/Al_2O_3; (▲) 1 g Pt/Al_2O_3 and 1 g sulfonated resin Pt/Al_2O_3 and 2 g sulfonated resin; (◆) 1 g Pt/Al_2O_3 and 3 g sulfonated resin.

4. Conclusion

Catalytic wet oxidation of maleic acid was carried out with 1 wt.% Pt/Al_2O_3 catalyst at 453 K and 160 psig. Hundred percent conversion of maleic acid was achieved in 40 min. Fumaric acid, oxalic acid and formic acid were observed as intermediates during maleic acid oxidation. From the sequence of the formation of these intermediates, maleic acid was proposed to be finally oxidized into carbon dioxide and water via oxalic acid and formic acid. Since oxalic acid and formic acid could readily be oxidized even at 353 K and atmospheric pressure, but no detectable conversion of maleic acid could be observed at these conditions, the rate-determining step of maleic acid oxidation is believed to be the degradation of maleic acid into oxalic acid.

The presence of sulfonated poly(styrene-co-divinylbenzene) resin catalyst enhanced the oxidation of maleic acid at 353 K and atmospheric pressure by hydrolyzing maleic acid into more readily oxidizable compounds.

Acknowledgements

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