Selective Hydration of Acrylonitrile to Acrylamide over a Manganese Dioxide Catalyst

Since acrylonitrile (AN) has two unsaturated bonds, C≡N and C=C, the hydration of AN yields both acrylamide (AA) and ethylenecyanohydrine (EC) by addition of H_2O to the respective bond. Several reports concerning catalyst selectivity in the hydration have been currently made. However, a general aspect of the catalyst selectivity is still uncertain.

The selective hydration to form AA is particularly interesting because of a practical value of AA in use for flocculants and paper strengthening agents, etc. For the hydration to AA, metallic Cu catalyst became recently known to be highly active and selective (1–3). However, it has also been described that a drastic decrease in activity and selectivity is unavoidable when the catalyst or the reaction mixture is exposed to air in the case of metallic Cu catalyst (2, 3). A few papers (4, 5) have already mentioned that MnO_2 catalyst promotes selectively the hydration to AA. However, little is known about details of the catalytic behaviors and the reaction rates. Our preliminary experiment has revealed that air has no influence upon the activity and selectivity of the MnO_2 catalyst. In this report, we will describe an experimental study on the characteristics of MnO_2 catalyst and the reaction rates in the selective hydration to AA.

Manganese(IV) dioxide (γ-MnO_2) supplied from Daiichi Carbon Company Ltd. was used as a catalyst in a large part of this work. This material prepared by electrolysis (to be subsequently referred as the electrolytic MnO_2 catalyst) was of high purity and of finely powdered about 100–150 mesh. Unless otherwise noted, the material was used as a catalyst without further heat treatment. For comparison, MnO_2 on carrier activated granular for elementary analysis supplied from Merck Company Ltd. was used. In order to characterize the activity and selectivity of the MnO_2 catalyst, ion-exchange resin, K_2O–MgO, CoO, NiO, and CuO were also used as a catalyst.

The catalytic hydration in an aqueous phase over solid catalyst was conducted with the ordinary batch reaction apparatus equipped with a stirrer and a reflux condenser. The reaction mixture was vigorously stirred so that mass transfer of reactants from bulk fluid to outer surface of the catalyst particles had no effect on the reaction rate. Products of the catalytic reaction were quantitatively analyzed by gas chromatographic unit at regular time intervals.

The activities and selectivities of various catalysts are summarized in Table 1, where AN conversion and selectivity to each product are represented in mole percent. Table 1 shows that MnO_2 catalysts are excellent in both the activity and the selectivity to AA. The activity of the electrolytic MnO_2 catalyst was slightly higher than that of the MnO_2-carrier catalyst supplied from Merck Company. Equally with MnO_2 catalyst, such a high selectivity to AA as 100% has been achieved by CoO catalyst. However, CoO was far less active than MnO_2. Both NiO and CuO catalyst led the simultaneous formation of EC and/or the other byproducts, besides the hydration to AA. In contrast to the catalysts mentioned above, a strong-basic ion-exchange resin (Amberlite IRA-400) preferentially promoted the formation of EC and the resulting selectivity to EC was close to 100%. K_2O–MgO was highly active for the hydration, how-

TABLE 1

Activity and Selectivity of Various Catalysts

Catalyst	Weight (g)	Time (h)	AN conversion (%)	Selectivity (%)		
				AA	EC	By product[e]
MnO_2[a]	9	4	31	100	0	0
MnO_2-carrier[b]	9	4	28	100	0	0
CoO	9	4	12	100	0	0
NiO	9	4	8	89	11	0
CuO	9	4	29	42	38	20
IRA-400[c]	9	4	23	0	100	Trace
K_2O–MgO[d]	3	2	52	17	67	16

[a] Electrolytic manganese(IV) dioxide (Daiichi Carbon Co.).

[b] Manganese(IV) dioxide on carrier for elementary analysis (Merck Co.).

[c] The moist, basic (regenerated) form of Amberlite IRA-400 resin.

[d] Prepared by the impregnation method using KOH solution and MgO-carrier, and calcined at 700°C (K_2O content was about 20 wt%).

[e] Polymers of the unidentified structure and acrylates were included.

FIG. 2. Log $(1/(1 - x))$ vs t plots. Reaction temperature (°C): (1) 50, (2) 60, (3) 70, (4) 80, C_0: 0.8 mol/liter, W (catalyst weight): 9.0 g, V (volume of the reaction mixture): 102 ml.

ever, the selectivity to AA was very low owing to the formation of a large amount of EC.

Such acidic catalysts as hetero-poly-acid ($H_3[PMo_{12}O_{40}]$ or $H_3[PW_{12}O_{40}]$), strong-acidic ion-exchange resin (Amberlite CG-120), H^+-Zeolon, and SiO_2–Al_2O_3 were entirely inactive for the reaction.

All the subsequent experiments were carried out by using the electrolytic MnO_2 catalyst. Measurements of the reaction rates were made on aqueous solutions ranging in AN concentration from 0.25 to 0.70 mol/liter. The initial reaction rates (r_0) evaluated
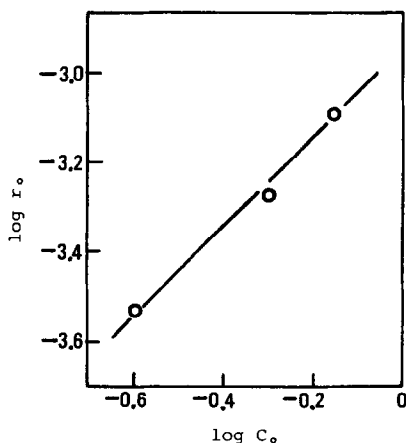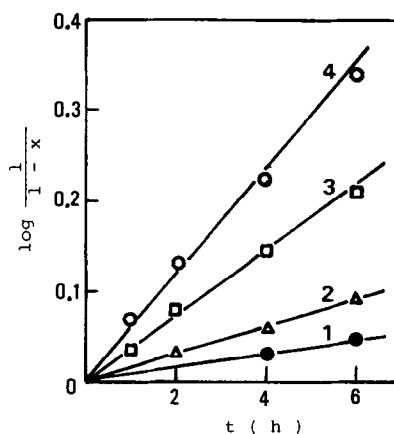
from the slopes of time-conversion curves are shown as a function of the initial AN concentration (C_0) in Fig. 1. A plot on logarithmic coordinates of r_0 vs C_0 shows a straight line with a slope close to unity, as required by the first-order rate in AN concentration. With regard to H_2O dependence of the reaction rate, zero-order has been tacitly assumed because of the large excess in aqueous phase.

The variation of AN conversion (x) with reaction time (t) at temperatures of 50 to 80°C was shown by a conventional plot of $\log[1/(1 - x)]$ vs t in Fig. 2. Figure 2 indicated that the data gave the straight lines with different slopes depending on the reaction temperatures. Thus, it can be concluded that even at higher conversions there is no serious deviation from the integral form of the first-order rate equation. Arrhenius plot of the rate constants evaluated by slopes of the straight lines gave an apparent activation energy of about 15.0 kcal/mol, and hence the reaction rate (r in mol/g-cat·h) has been expressed in the following equation:

$$r = k'[AN]$$

FIG. 1. Log r_0 vs log C_0 plots (70°C).

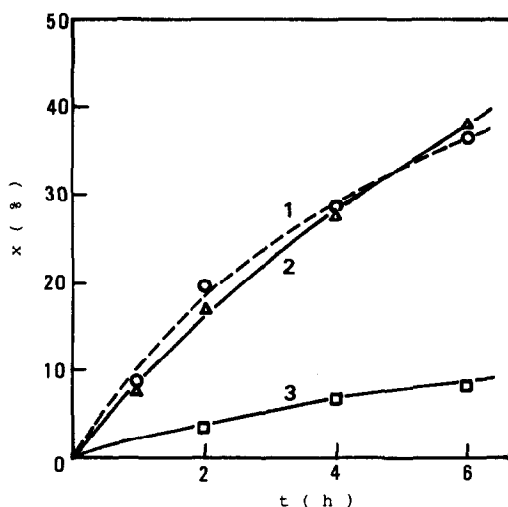$$= 3.6 \times 10^6 \exp\left\{\frac{-15,000}{RT}\right\} [AN]$$

FIG. 3. Effect of the additives upon the reaction. Curve 1: (dotted line) without additive, curve 2: 0.01 mol of pyridine added, curve 3: 0.01 mol of phenol added. Reaction temperature: 70°C, W: 9.0 g, V: 102 ml, C_0: 0.8 mol/liter.

where k' is apparent rate constant (1/g-cat·h) and [AN] is concentration of AN (mol/liter). The reaction rates calculated from this equation agreed very closely with the reaction rates observed for a wide range of the reaction condition.

The influence of addition of small amounts of pyridine or phenol into the aqueous phase of reaction mixture is shown in Fig. 3. It is obvious that AN converison is little affected by the addition of pyridine, whereas the conversion is vigorously depressed by the addition of phenol. At that time, the selectivity was entirely unaffected by the additions. This behavior of the catalytic activity suggests that basic sites of the MnO_2 surface play an important role in the catalytic action. At the present stage, OH^- groups of the catalyst surface are supposed to serve as the basic sites.

As an additional experimental result, the following fact should be noted: the catalytic activity of the electrolytic MnO_2 drastically decreases with an elevation in temperature of the catalyst pretreatment. For example, by the preheating at 400°C the catalyst activity is reduced to about one-twentieth of that of nontreated catalyst. The drastic decrease in the activity by that treatment is believed to be caused by both the dehydroxylation of MnO_2 surface and the phase transition to β-MnO_2 which is less active as a catalyst. In addition, the reduction pretreatment of the catalyst with a hydrogen stream at 130°C for 2 h converted MnO_2 to $MnO(OH)$ and resulted in a drastic decrease in the selectivity to AA. These behaviors strongly suggest that coexistence of Mn^{4+} and OH^- on the catalyst surface is required for the selective hydration to AA. Details of the more definitive reaction mechanism will be reported in a separate paper.

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