

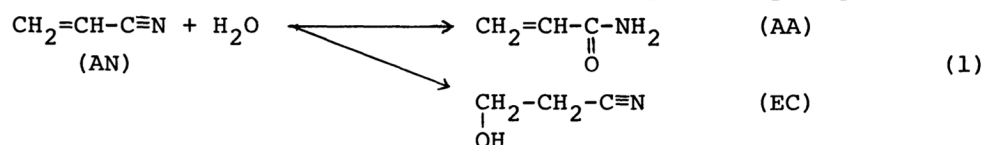
## SELECTIVE HYDRATION OF ACRYLONITRILE ON METAL OXIDE CATALYSTS

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The selective hydration of acrylonitrile to form acrylamide has been studied on several metal oxide catalysts.  $\text{MnO}_2$ ,  $\text{CuO}$  and  $\text{Co}_3\text{O}_4$  catalysts were found to be active and selective. Catalytic activities were strongly affected by the method of preparation. Hydration activity of  $\text{MnO}_2$  was related to the amount of phenol adsorption.

Numerous studies on hydration of aromatic nitriles<sup>1-3)</sup> or of saturated aliphatic nitriles<sup>4,5)</sup> have been made, but the reaction of an unsaturated aliphatic nitrile, e.g., acrylonitrile (AN), is dealt only in a few papers.<sup>6-9)</sup> Especially basic studies on the hydration of AN on metal oxide catalysts are very few. The hydration of AN yields both acrylamide (AA) and ethylenecyano-hydrine (EC) by adding to the  $\text{C}\equiv\text{N}$  and  $\text{C}=\text{C}$  bond in AN, respectively (Eq.1).



The selective hydration of the  $\text{C}\equiv\text{N}$  bond to form AA has an industrial importance and was the subject of our previous paper,<sup>10)</sup> in which the supported copper catalysts were reported to be active and selective for this reaction. In addition we observed that some of the metal oxides which were used as supports were also catalytically active, although not selective to AA formation. This observation led us to study this reaction on several metal oxide catalysts.

The reaction was carried out in a flask equipped with a stirrer similar to that used in the previous study.<sup>10)</sup> The reaction conditions used were as follows; AN/ $\text{H}_2\text{O}$  = 16.5 ml/198 ml, catalyst weight 5.0 g, reaction temperature 70°C, reaction time 8 h.

A summary of catalyst preparations and reaction results are shown in Table 1. With the exception of electrolytic  $\text{MnO}_2$  (No.3), supplied by Toyo Soda Co., the catalysts were prepared from the reagents shown in Table 1. Catalysts made from metal carbonates (No.1,8 and 11) were prepared by direct calcination of the carbonates in air at 400°C for 5 h. The other catalysts were prepared by admixing aqueous solutions of the materials shown in Table 1 to form precipitates. The resulting precipitates were filtered, washed with water, and calcined in air at the temperatures indicated in Table 1. The catalysts were submitted for X-ray diffraction analysis, and the formation of the respective compounds was

Table 1. Selective hydration of acrylonitrile on metal oxide catalysts

catalyst	raw materials	calcination temp. (°C)	conversion of AN (%)	selectivity to AA (%)
1. Mn <sub>3</sub> O <sub>4</sub>	MnCO <sub>3</sub>	400	trace	(100)
2. γ-MnO <sub>2</sub>	MnSO <sub>4</sub> +KNO <sub>3</sub> +KMnO <sub>4</sub>	110	8.0	100
3. MnO <sub>2</sub>	electrolytic MnO <sub>2</sub>	-	13.4	100
4. α-Fe <sub>2</sub> O <sub>3</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub> +NH <sub>3</sub> aq.	400	1.3	100
5. Fe <sub>2</sub> O <sub>3</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub> +NH <sub>3</sub> aq.	110	1.7	96
6. Co <sub>3</sub> O <sub>4</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> +NH <sub>3</sub> aq.	400	7.8	100
7. Co <sub>3</sub> O <sub>4</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> +NH <sub>3</sub> aq.	110	3.7	100
8. NiO	NiCO <sub>3</sub> ·Ni(OH) <sub>2</sub>	400	2.5	36
9. NiO	Ni(NO <sub>3</sub> ) <sub>2</sub> +NH <sub>3</sub> aq.	400	2.2	100
10. NiO	Ni(NO <sub>3</sub> ) <sub>2</sub> +KOH	400	1.6	100
11. CuO	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	400	5.2	69
12. CuO	Cu(NO <sub>3</sub> ) <sub>2</sub> +NaOH	110	10.7	100
13. Ag <sub>2</sub> O	AgNO <sub>3</sub> +NaOH	110	5.2	28

confirmed with the exception of No.3, 5 and 7, which were found to be amorphous. The catalysts No.5 and 7, which were calcined only at 110°C, might be hydroxides, even though they are listed as oxides in Table 1. In addition to the catalysts shown in Table 1, V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> were also tested, however they had no activity for both AA and EC formation.

In comparison to our previous studies on supported copper catalysts the oxide catalysts were less active, but the formation of EC was negligible except for No.5, 8, 11 and 13 catalysts.

Among the catalysts tested, MnO<sub>2</sub> (No.2 and 3), Co<sub>3</sub>O<sub>4</sub> (No.6) and CuO (No. 12) were active for AA formation, with 100% of selectivity. From

Table 1 it is apparent that the method of preparation has a marked effect on the activity and selectivity of oxide catalysts. For example, catalysts No.8 and 11 formed considerable amounts of EC, while the selectivities of catalysts No.9, 10 and 12 were 100% for AA formation. In case of Mn oxides, No.1 was almost inactive while No.3 had the highest activity among all the catalysts studied. Catalysts prepared from hydroxides are generally more active in AA formation than those prepared from

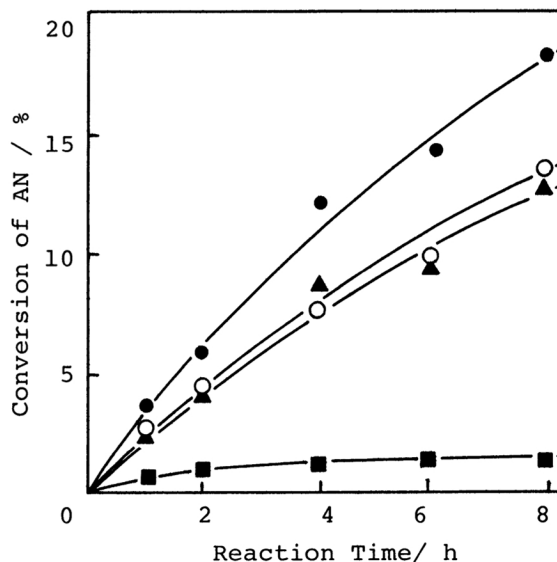


Fig.1. Poisoning effect of pyridine, thiophene and phenol on the hydration activity of electrolytic MnO<sub>2</sub> catalyst. —○—run without additives; —●—pyridine; —▲—thiophene; —■—phenol.

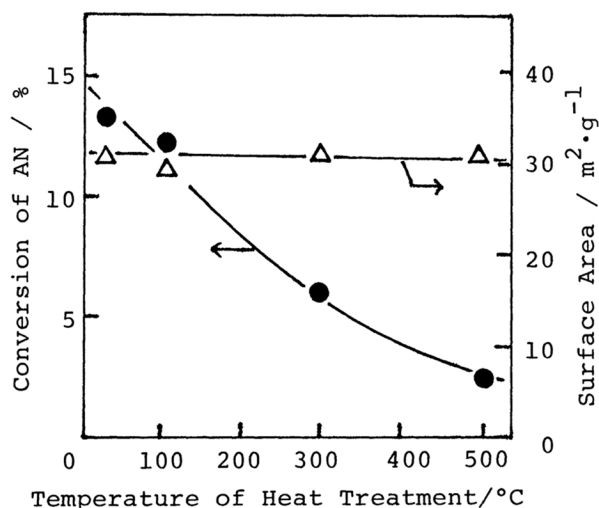


Fig. 2. Effect of heat treatment of electrolytic  $\text{MnO}_2$  catalyst on surface area ( $\Delta$ ) and hydration activity ( $\bullet$ ).

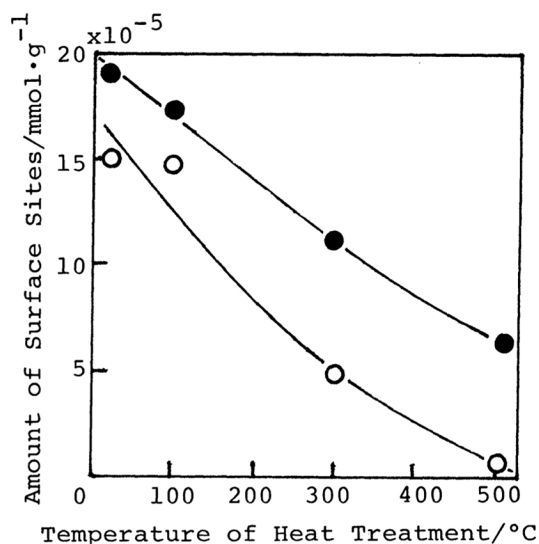


Fig. 3. Effect of heat treatment of  $\text{MnO}_2$  on amount of surface OH ( $\bullet$ ) and amount of phenol adsorption ( $\circ$ ).

carbonates. Because metal carbonates require higher temperature of decomposition than hydroxides of the same metal, small amount of carbonate ions seems to remain on the surface of the oxides prepared by calcination of carbonates, which poisons the active sites and results in lower activity for AA formation.

From Table 1 it is apparent that catalyst No. 3, electrolytic  $\text{MnO}_2$ , is the most effective catalyst for this reaction. In order to probe the origin of the active centers, we performed the following experiments. First, 1 g of pyridine, thiophene or phenol was added respectively to the reactor and the poisoning effect on  $\text{MnO}_2$  catalyst was followed. The results are shown in Fig. 1. Addition of thiophene had virtually no effect on the reaction. Addition of pyridine increased the activity, but the formation of EC was also increased and the amount of AA formation was nearly equal to that observed in the absence of additives. On the other hand, the addition of phenol resulted in a sharp decrease in the catalytic activity of AN hydration.

In a second experiment, electrolytic  $\text{MnO}_2$  was calcined in air at 100°C, 300°C and 500°C, respectively, for 1 h. The relationship between the surface area or the hydration activity and the temperature of heat treatment was shown in Fig. 2. While the specific surface area showed little change with heat treatment, activity for hydration decreased sharply. A sample of  $\text{MnO}_2$  was heated *in vacuo* from 100°C to 500°C at a rate of 5°C/min, and the desorbed gas was analyzed mass-spectrometrically. It was found that the gas consisted primarily of  $\text{H}_2\text{O}$  (50-150°C, 200-400°C) with a smaller amounts of  $\text{O}_2$  (400-500°C). The first TPD peak of  $\text{H}_2\text{O}$  is due to the desorption of physically adsorbed water, whereas the second peak seems to be due to the dehydroxylation of the surface. Since catalyst deactivation occurs on samples treated at 300-500°C, the dehydroxylation appears

to be most responsible for this effect.

In a third experiment, amount of surface OH groups was measured by means of KI titration method.<sup>11)</sup> In addition, amount of phenol adsorption was measured on the same heat-treated MnO<sub>2</sub> catalysts. Figure 3 shows changes in the amount of surface OH and of adsorbed phenol against the temperature of heat treatment. These two factors change in parallel in the same manner as the conversion of AN in Fig.2. Indeed, conversion of AN is almost proportional to the amount of phenol adsorption.

These results show that hydration activity of MnO<sub>2</sub> is related to the amount of surface OH groups and of phenol adsorption. Hydration of AN probably proceeds by adsorption of AN on surface Mn ions, followed by reaction of the adsorbed AN with nearby OH groups to form AA. In the presence of phenol, basic sites seem to be poisoned since phenol is acidic. It is well established<sup>12)</sup> that the basic sites on well dehydrated oxides such as calcined MgO or CaO consist of O<sup>2-</sup> (strong site; formed by dehydration at high temperatures) and OH<sup>-</sup> (weak site). In the present study, however, measurements were made in aqueous media, and only OH<sup>-</sup> sites seem to be present on the surface. Figure 3 also supports the idea that surface OH groups participate in the adsorption of phenol. Perhaps phenol is adsorbed dissociatively on surface OH and Mn ions as H<sup>+</sup> and C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>, respectively. It is well understood that the adsorption of AN on Mn ions is hindered and hydration activity of OH is poisoned in the presence of phenol.

In conclusion oxides of Mn, Co and Cu were found to be active and selective catalysts for AA formation, and the nature of active sites on MnO<sub>2</sub> was characterized by adsorption of phenol.

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