February, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***60,*** *453—456 (1987)* 453

Liquid-Phase Hydration of Acrylonitrile to Acrylamide over the Manganese Dioxide Catalyst

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(Received June 9, 1986)

The liquid-phase hydration of acrylonitrile to acrylamide was examined over a manganese dioxide catalyst at 65 °C. When the catalysts were treated at 110—500 °C, both the acidity and the reaction activity of the catalysts decreased at temperatures above 110 °C. The reduction of the solid acidity of heat-treated samples decreased the catalytic activity of the catalysts. It was confirmed that the solid acidity of manganese dioxide was derived from acidic hydroxyl groups on the catalyst surface through their dispersion in water. A good relationship between the number of surface hydroxyl groups and the catalytic activity of the manganese dioxide was observed; its hydration ability was depressed by the addition of an aqueous base as a NaOH solution. These results show that the acidic surface hydroxyl group of a manganese dioxide catalyst is the active site of acrylonitrile hydration. The kinetic behavior of both acrylonitrile and water was examined and the reaction rate showed both first and zero orders with respect to the acrylonitrile and water concentration, respectively. The hydration mechanism of acrylonitrile on the manganese dioxide catalyst is discussed.

In our previous papers,[1,2] it was reported that the heterogeneous hydration of acrylonitrile (AN) proceeded on various metal oxide catalysts in the liquid-phase. The hydration selectivity to the reaction products (acrylamide (AA), ethylene cyanohydrin and bis-(2-cyanoethyl) ether) was governed by the solid acid-base properties in the liquid phase. The acidic metal oxide catalysts selectively hydrated the C≡N triple bond of an AN molecule and only AA formed, while the basic metal oxide catalysts hydrated the C=C double bond rather than C≡N. AA is an especially useful material among those three products owing to such industrial uses as paper-strengthening agents, flocculants and crude-oil recovery agents. For AA production, manganese dioxide (MnO_2) was the most effective catalyst among the metal oxides since it exhibits a selectivity to AA.

The high catalytic ability of MnO_2 is well-known. A few examples include the oxidation of CO,[3,4] hydrocarbons[5,6] and the decomposition of H_2O_2.[7,8] Furthermore, since MnO_2 prepared by an electrolytic oxidation method has been used as a depolarizer of drycells, the surface properties of MnO_2 also have been studied by many investigators.[9–12] Regarding the catalytic abilities of MnO_2 on the liquid-phase hydration of AN to AA, they have been scarcely clarified. This study, therefore, aims to clarify the properties at the active sites of a MnO_2 catalyst as well as the hydration mechanism.

Experimental

Catalyst Preparation. A MnO_2 catalyst produced from the electrolytic oxidation of manganeous sulfate was supplied by Toyo Soda Manuf. Co. It was preheated at 110—500 °C for 1 h in air and then used for the hydration. MnO_2 catalysts having a differential surface coverage of Zn^{2+} ions were also prepared by an ion exchange of Zn^{2+} and the hydroxyl group on the MnO_2 samples preheated at 110 °C. The surface area was determined by the BET method. The crystal structure was identified by using the X-ray diffraction method.

Activity Measurement. The liquid-phase hydration of AN was carried out in a batch reactor system. Ordinary experimental conditions were as follows: reaction temperature of 65 °C, 6-h reaction time, 2.5-g catalyst, purified AN 8.5 and 100 ml of H_2O. A detailed description of the procedure was described in a previous paper.[2] The inhibition effects of the additives were examined by the addition of HNO_3, NaOH, AA, or acrylic acid in the reaction system suspended with a MnO_2 sample. After the reaction temperature reached 65 °C, AA was added.

Surface Hydroxyl Group. The amount of hydroxyl groups on the MnO_2 surface was determined in accordance with the manner described by Kozawa;[9,13,14] this method can be described as follows: a preheated MnO_2 sample (1.0 g) was placed into an Erlenmeyer flask with glass stopper, into which 25 ml of the zinc solution was poured. The zinc solution was prepared as follows: two moles of NH_4Cl and 0.1 mol of ZnO were dissolved in one liter of water and then adjusted to a pH of 7.0 by the addition of aqueous ammonia. The resulting suspension was shaken with the use of a vibrator for 12 h; it was then allowed to stand for 1 h. A portion of the supernatant solution was titrated by the EDTA method. The difference between the amount of Zn^{2+} adsorbed in this procedure and that consumed by the original solution corresponds to the number of Zn^{2+} ions. Another portion of the supernatant solution was titrated with a standard solution of HCl (0.01 mol dm^{-3}) using Methyl Orange as an indicator for determining the amount of released H^+. The difference between the amount of HCl consumed in this titration and that consumed by the original solution corresponds to the number of hydrogen ions released by the ion-exchange reaction.

Amount of AN Adsorbed. A preheated MnO_2 sample (2.5 g) was placed into an Erlenmeyer flask with a glass stopper; then, 100 ml of 2.5 wt% AN aqueous solution was poured into the flask. After stirring for 6 h, the sample was allowed to stand for 40 h at room temperature and was then kept at 40 °C for 4 h. The amount of adsorbed AN was determined from the difference of the concentration of AN before and after adsorption. The concentration of AN was measured by gas chromatography.

Acidic Properties. The surface acidity of MnO_2 samples was determined by an indicator titration method using

Table 1. Properties of the Manganese Dioxide Catalysts after Heat Treatment at Various Temperatures

Sample No.	Calcination temp(°C)	Surface area ($m^2 g^{-1}$)	Nitrile conv (%)[a]	Acid amount at $pK_a=+4.8$ ($mmol\ g^{-1}$)	Equi-acid-base point/pH	X-ray diffraction analysis
1	110	33.2	13.3	0.078	3.6	γ-MnO_2 (amorphous)
2	200	28.5	10.9	0.051	4.1	γ-MnO_2
3	300	16.3	7.3	0.019	4.4	γ-MnO_2
4	400	13.3	5.4	0.029	5.2	γ-MnO_2
5	500	12.9	1.7	0.015	5.9	γ-MnO_2 (+ trace Mn_2O_3)

a) Reaction conditions: Reaction temperature; 65 °C: Reaction time; 6 h: Acrylonitrile 8.5 ml, pure water 100 ml: Catalyst weight; 2.5±0.1 g.

Table 2. Amount of Adsorbed Zn^{2+} and Released H^+ Ion by the Ion-Exchange Reaction on the Manganese Dioxide Samples

Sample No.	Calcination temp(°C)	Amount of adsorbed Zn^{2+} ($mmol\ g^{-1}$)	Amount of released H^+ ($mmol\ g^{-1}$)	H^+/Zn^{2+} ratio	Amount of Surface OH groups ($mmol\ g^{-1}$)[a]
1	110	0.26	0.54	2.1	0.52
2	200	0.23	0.44	1.9	0.46
3	300	0.19	0.40	2.1	0.38
4	400	0.07	0.14	2.0	0.14
5	500	0.05	0.11	2.2	0.10

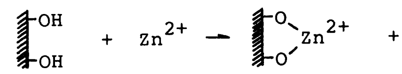
a) Double molar quantity of the adsorbed Zn^{2+} was defined as the amount of surface OH groups on the MnO_2 samples on the basis of Kozawa's results.[9]

Methyl Red ($pK_a=+4.8$) as the indicator. The equi-acid-base point of MnO_2 samples, representing the solid acid-base properties of a metal oxide dispersed in water, was determined by a pH-shift method.[15] A detailed description of the procedure for both acidic property measurements was given in previous papers.[2,17]

Results and Discussion

Acidic Properties and Catalytic Activity. In one previous paper,[16] we reported that a large number of moderate-strength acid sites was present on the MnO_2 surface. The relationship between the acidic properties and the catalytic abilities of MnO_2 on the liquid-phase hydration of AN was investigated. As shown in Table 1, the catalytic activity (conversion of AN after a 6-h reaction) of MnO_2 catalysts decreased upon increasing the calcination temperature. A heat treatment of the catalysts simultaneously led to a reduction of both the specific surface area and the solid acidities, indicated by acid amounts at $pK_a=4.8$ and values of their equi-acid-base point. However, transformations of the crystal structure by heat treatments could not be observed, although the crystal growth was observed. The stability of the structure was also supported from the fact that neither the endothermic nor the exothermic peak was observed by a DTA analysis until 500 °C. Therefore, it was concluded that the reduction of the catalytic activity by the heat-treatment was caused by a decrease in the acidic property of the catalysis accompanying a specific surface-area loss.

Surface Hydroxyl Groups. On the MnO_2 surface cation-exchangeable hydroxyl groups are present.[9,10] It was confirmed in a previous study[17] that the surface hydroxyl group had remained on the sample, even under a heat-treatment at 500 °C. The number of surface hydroxyl groups on the MnO_2 dispersed in water was determined by the cation-exchange method. The obtained results are shown in Table 2. The number of adsorbed Zn^{2+} and released H^+ ions decreased upon increasing the heat-treatment temperature. The amount of released H^+ was twice that of adsorbed Zn^{2+}. This simple integral ratio indicates that a single Zn^{2+} ion exchanges with two H^+ ions of the surface hydroxyl groups as follows:



(1)

Therefore, a double molar quantity of the adsorbed Zn^{2+} was defined as the amount of surface hydroxyl groups on the MnO_2 samples.

The relation between the catalytic activity and the amount of surface hydroxyl groups of MnO_2 treated at 110—500 °C was examined. The catalytic activity was directly proportional to the amount of surface hydroxyl groups (Fig. 1); the relationship between them can be described by

$$\text{ANconv.} = a[\text{-OH}]_s, \tag{2}$$

where a and $[\text{-OH}]_s$ are the constant of proportionality and the number of surface hydroxyl groups, respectively. The value of the correlation coefficient of a was determined to be 0.997. This result suggests that the acidic hydroxyl groups on the surface are the active sites for AN hydration.

The poisoning effects were examined. As shown in Fig. 2, the conversion of AN on the MnO_2 catalysts

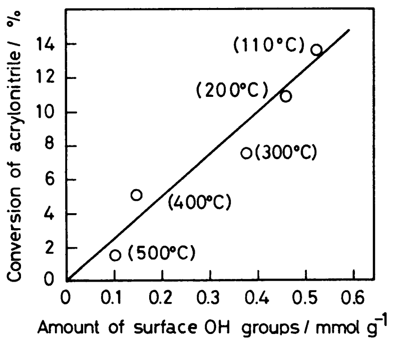


Fig. 1. Relationship between the conversion of acrylonitrile and amount of surface hydroxyl groups of the MnO_2 catalysts heat-treated at various temperature. The values in parentheses is that of calcination temperature. Reaction conditions are the same as those in Table 1.

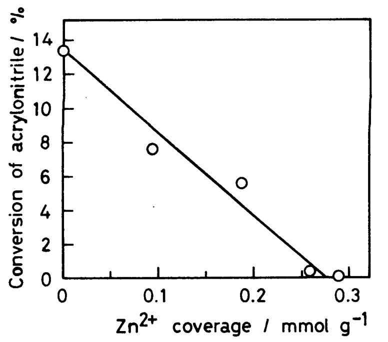


Fig. 2. Relationship between the conversion of acrylonitrile and surface covarage of Zn^{2+} ion on the MnO_2 catalysts treated at 110°C.

Table 3. Poisoning Effect of the Additives to MnO_2 Catalyst on the Hydration of Acrylonitrile[a)]

Additive	Nitrile conv(%)	Amide sel(%)
Blank	13.3	100
HNO_3 0.2 mmol	13.0	100
0.4 mmol	13.8	100
0.6 mmol	13.5	100
NaOH 0.2 mmol	12.2	100
0.4 mmol	10.1	90.6
0.6 mmol	7.1	73.1

a) Reaction conditions are the same as those in Table 1.

coated with various amounts of Zn^{2+} linearly decreased upon increasing the surface coverage of adsorbed Zn^{2+}. When acid or alkali was added to an AN solution the catalytic activity changed as shown in Table 3. The addition of HNO_3 had little effect on the catalytic activity and selectivity to AA; in the case of the addition of NaOH the catalytic abilities of MnO_2 decreased.

Consequently, we could conclude that the active site of a MnO_2 catalyst on the liquid-phase hydration of AN to AA is the acidic surface hydroxyl group.

Hydration Mechanism. The number of AN molecules adsorbed on the preheated MnO_2 samples was shown in Fig. 3. A good relationship between the number of adsorbed AN molecules and surface hydroxyl groups was observed with a slope of unity. Therefore, we concluded that an AN molecule adsorbs on a surface hydroxyl group.

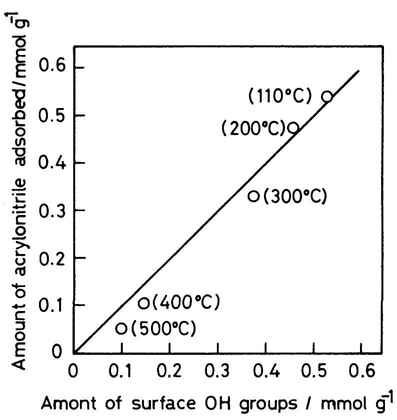


Fig. 3. Relationship between the amount of both adsorbed acrylonitrile and surface hydroxyl group of the MnO_2 catalysts treated at various temperature. Adsorption temperature: 40°C

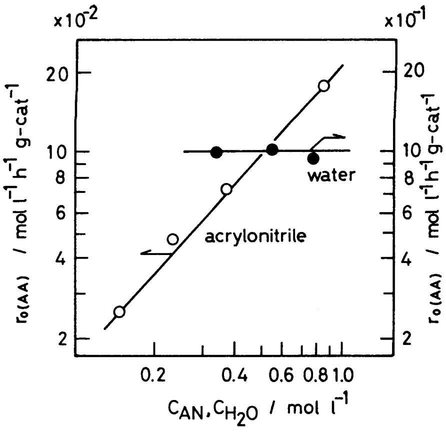


Fig. 4. Dependence on the concentration of acrylonitrile or water.
Reaction temperature: 65°C

The dependence of AN and the water concentration on the hydration rate of AN was examined and the results are given in Fig. 4. From this figure, the dependence on the concentration of each reactant was first order to the AN concentration and zero order to water. Consequently, the rate equation can be given as

$$r=k[\mathrm{AN}]^{1.0}[\mathrm{H_2O}]^{0}, \qquad (3)$$

where k, [AN] and [H_2O] show a rate constant, concentration of AN and water, respectively. The rate equation shows that excess water is adsorbed on the catalyst surface and that its concentration on the surface is constant during hydration. The reaction between the adsorbed AN and adsorbed water is rate-determining. In addition, since the conversion of AN is proportional to the number of hydroxyl groups on the cata-

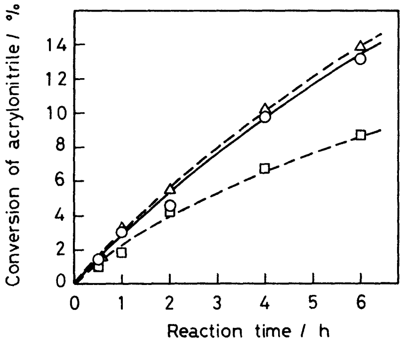


Fig. 5. Effect of additives.
(□): Acrylamide, (△): acrylic acid, (○): no addition
Reaction temperature: 65°C.

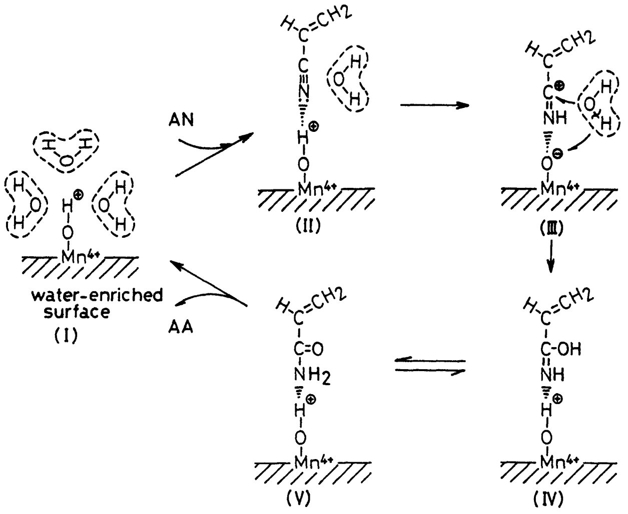


Fig. 6. Hydration scheme of acrylonitrile to acrylamide.

lyst surface, the equation can be rewritten as

$$r'=k'[\mathrm{AN}]^{1.0}[\mathrm{H_2O}]^{0}[\mathrm{-OH}]_{\mathrm{S}}^{1.0}. \tag{4}$$

The catalytic abilities of MnO_2 were retarded by the addition of AA (Fig. 5). Thus, these results suggest that an accumulation of AA takes place on the MnO_2 surface during hydration in a batch reactor, retarding the reaction.

On the basis of the results described above, the hydration mechanism of AN to AA on the MnO_2 catalyst was postulated (Fig. 6). An acidic hydroxyl group exists on a Mn^{4+} ion of the MnO_2 surface and is surrounded by a large number of water molecules (see Fig. 6 (I)). An AN molecule first adsorbs on an acidic hydroxyl group (Fig. 6 (II)); then, a covalent coordination through N (2s) lone-pair electrons of a C≡N bond by the electrostatic force of attraction will take place on the surface hydroxyl group of MnO_2. Then, a hydroxide anion supplied from the surrounding water attacks the carbonium ion of the C≡N bond, whereas the residual proton adsorbs on Mn-$O^{\ominus}$ to regenerate hydroxyl group (III→IV). An amide group is formed by a 2,4-shift reaction of the precusor in the tautomerism system; then AA desorbs from the site (V). In this manner the liquid-phase hydration of AN to AA on the acidic hydroxyl group of MnO_2 will catalytically proceed as a Langmuir-Hinshelwood-type reaction mechanism.

Conclusion

The results of the liquid-phase hydration of AN to AA on a MnO_2 catalyst can be summarized as follows:

(1) The catalytic activity is proportional to the amount of the acidic surface hydroxyl group.

(2) An AN molecule adsorbs on a surface hydroxyl group.

(3) The reaction order is first-order with respect to AN and zero-order with respect to the water concentration, respectively.

(4) AA inhibits AN hydration.

It is concluded that active site of a MnO_2 catalyst is the acidic surface hydroxyl group and that hydration proceeds through a Langmuir-Hinshelwood-type mechanism between adsorbed AN and adsorbed water.

The authors greatly thanks the Toyo Soda Manuf. Co., Ltd. for supplying the MnO_2 sample.

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