October, 1986] *Bull. Chem. Soc. Jpn.*, *59*, *2983—2989 (1986)*

Heterogeneous Hydration of Acrylonitrile over the Metal Oxide Catalysts in Liquid Phase

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(Received February 15, 1986)

The liquid-phase hydration of acrylonitrile has been examined over various single metal oxide catalysts at 65 °C. Numerous metal oxides have proved to be active for hydration and have been used to produce three products: acrylamide, ethylene cyanohydrin, and bis(2-cyanoethyl) ether. These oxide catalysts could be divided into two groups with respect to the acrylamide selectivity with 100% or not. A good relationship between the catalytic abilities (activity and selectivity) and the solid acid-base properties of each metal oxide group examined in benzene or in water was observed. Differences in the hydration selectivity to either a C≡N or a C=C bond of acrylonitrile over the catalysts could be explained on the basis of the IR spectra of two adsorbed states of acrylonitrile on the metal oxide surface. It was proved that the liquid-phase hydration of acrylonitrile over the insoluble metal oxide catalysts was an acid-base-catalyzed reaction proceeding on the acidic or basic surface hydroxyl groups.

Acrylonitrile (AN) is a reactive organic molecule owing to two kinds of reactive unsaturated bonds: a C≡N triple bond and a C=C double bond. Many derivatives were produced by an addition reaction to the AN.[1] For example, a water molecule could easily be added to the two functional groups in either acidic or basic media.[2,3] Using sulfuric acid, the acrylamide sulfate was produced during the initial stage of a stoichiometoric reaction as follows:

$$\mathrm{CH_2{=}CH{-}C{\equiv}N + H_2SO_4 + H_2O \longrightarrow CH_2{=}CHCONH_2{-}H_2SO_4} \tag{1}$$

acrylonitrile (AN)

Acrylamide (AA) could be obtained by the neutralization of the sulfate with an alkali solution such as aqueous ammonia.

$$\mathrm{CH_2{=}CHCONH_2{-}H_2SO_4 + 2NH_3 \longrightarrow CH_2{=}CHCONH_2 + (NH_4)_2SO_4} \tag{2}$$

acrylamide (AA)

On the other hand, in a basic medium using an aqueous sodium hydroxide,[4] the hydration of AN catalytically proceeded to produce ethylene cyanohydrin (ECH), bis(2-cyanoethyl) ether (BCE), and AA as follows:

$$\mathrm{CH_2{=}CH{-}C{\equiv}N + H_2O \longrightarrow HOCH_2CH_2C{\equiv}N} \tag{3}$$

ethylene cyanohydrin (ECH)

$$\mathrm{CH_2{=}CH{-}C{\equiv}N + HOCH_2CH_2C{\equiv}N \longrightarrow O(CH_2CH_2C{\equiv}N)_2} \tag{4}$$

bis(2-cyanoethyl) ether (BCE)

$$\mathrm{CH_2{=}CH{-}C{\equiv}N + H_2O \longrightarrow CH_2{=}CHCONH_2} \tag{5}$$

In the case of metal oxides, the heterogeneous catalytic hydration of AN could also be observed,[5–10] and produced the same products as those in the case of the homogeneous hydration. The product distributions on the catalysts were similar to those in homogeneous acid-bese hydration of AN. Consequently, it is considered that the catalytic abilities (hydration activity and selectivity) are correlated with the solid acid-base properties of the metal oxide catalysts.

In this study the relationship between the catalytic behaviors of various metal oxides and their solid acid-base properties was examined in order to confirm whether the mechanism in the liquid-phase hydration of AN could be applied to a heterogeneous acid-base catalytic reaction.

Experimental

Catalyst Preparation: Metal oxides as catalyst were generally prepared by the decomposition of the hydroxides or carbonates of metals-to-metal oxides at 110 °C for 12 h or at >200 °C for 3 h. The surface areas of the catalysts were determined by the B.E.T. method. The catalysts used in this study are listed in Table 1. The detailed preparation methods are as follows;

(1) $\mathrm{MnO_2}$: Commercially available electrolytic manganese dioxide (type FM-H, Toyo Soda Manuf. Co.) was used without further purification.

Samples 2 to 5 were chemically prepared in accordance with a method described by Kanungo[11] as below:

(2) α-$\mathrm{MnO_2}$: $\mathrm{MnSO_4}$ was dissolved in 0.5-M (1 M=1 mol dm^{-3}) hot sulfuric acid at 80 °C, precipitated with ammonium peroxodisulfate until the pink color of the solution disappeared. The precipitate was thoroughly washed with deionized water and then dried.

(3) β-$\mathrm{MnO_2}$: $\mathrm{Mn(NO_3)_2}$ was thermally decomposed in a stream of air.

(4) γ-$\mathrm{MnO_2}$: An aqueous $\mathrm{Mn(NO_3)_2}$ was oxidized with a dilute $\mathrm{KMnO_4}$ solution.

(5) δ-$\mathrm{MnO_2}$: An aqueous (0.38 M) $\mathrm{KMnO_4}$ was reduced with 6-M aqueous HCl at 80 °C.

Other samples were prepared as follows;

(6) $\mathrm{Co_3O_4}$: Cobalt hydroxide was precipitated from an aqueous $\mathrm{Co(NO_3)_2}$ with aqueous NaOH, followed by a thorough washing of the precipitate and drying.

(7) $\mathrm{Co_3O_4}$: Cobalt carbonate was thermally decomposed in a stream of air.

(8) $\mathrm{Co_3O_4}$: Cobalt hydroxide was precipitated from a

$Co(NO_3)_2$ solution with aqueous ammonia.

(9) Co_3O_4: Cobalt hydroxide was precipitated from a $CoCl_2$ solution with aqueous NaOH.

(10) NiO(A): Nickel hydroxide was precipitated from a $Ni(NO_3)_2$ solution with aqueous NaOH, as reported in a previous paper.[10]

(11) CuO(A): Copper hydroxide was precipitated from a $Cu(NO_3)_2$ solution with aqueous NaOH.

(12) Fe_2O_3: Iron hydroxide was precipitated from an $Fe(NO_3)_3$ solution with aqueous ammonia.

(13) PbO_2: Lead nitrate was thermally decomposed in a stream of air.

(14) WO_3: Ammonium parawolframate was thermally decomposed in a stream of air.

(15) SiO_2: Commercially available silica sol (Catalloid H-20, Catalysts & Chemicals Ind. Co.) was dried in air and then calcined.

(16) TiO_2: Titanium hydroxide was precipitated from a $Ti(SO_4)_2$ solution with aqueous ammonia.

(17) Al_2O_3(A): Commercially available alumina (Neobead GB, Mizusawa Chem. Co.) was used.

(18) MnO: Manganese carbonate was thermally decomposed in a stream of nitrogen.

(19) MgO: Basic magnesium carbonate was thermally decomposed in air.

(20) ZnO: Zinc carbonate was thermally decomposed in air.

(21) Cu_2O: Copper(II) oxide was partially reduced in a stream of 2 vol% of propylene diluted by nitrogen, in accordance with the manner described by Mikhal'chenko et al.[12]

(22) NiO(B): Basic nickel carbonate was thermally decomposed in a stream of air, as reported in the previous paper.[10]

(23) CuO(B): Basic copper carbonate was thermally decomposed in a stream of air.

(24) Ag_2O: The precipitate was obtained from an $AgNO_3$ solution with aqueous NaOH.

(25) La_2O_3: Lanthanum hydroxide was precipitated from a $La(NO_3)_3$ solution with aqueous ammonia.

(26) Al_2O_3(B): Aluminum tri-isopropoxide was hydrolyzed, followed by washing of the precipitate and then dried.

(27) PbO: Lead hydroxide was precipitated from a $Pb(NO_3)_2$ solution with aqueous KOH.

Activity Measurement: The hydration of AN was carried out by the use of a four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a screw cap for sampling. Pure water (100 ml) and AN (8.5 ml) purified by distillation were introduced into the reactor and kept at 65 °C. The catalyst (2.5±0.1 g) was transferred from the calcination glass-tube to the reactor, followed by stirring. The rotation speed was 2000 rpm. The reaction products were analyzed by an FID gas chromatograph. Column packing used were both a Porapak QS (4 mmϕ×1 m, 170 °C) for analysis of AN, AA, and ECH and a PS 400 on Chromosorb W (4 mmϕ×2 m, 170 °C) for BCE.

Acid-Base Strength Distribution of Dark-Colored Solid Oxides: As the active catalysts for the hydration of AN to AA were dark-colored metal oxides, the acid-base strength distribution on these colored samples was determined by the modified indicator method that we developed. A characteristics of this method is that a commercially available separate ground-glass Gooch crucible for measuring the acidic or basic properties of the samples can be used, and the dark-colored sample and a white standard probe with a known acidity or basicity is situated in the upper and lower parts separated by a glass filter with a pore size of 20—30 μ. The detailed procedure was described in a previous paper.[13]

Equi-Acid-Base Point (EABP) of Metal Oxides: The value of EABP of metal oxide represents the acid-base properties of the solid catalysts dispersed in water.[14,15] The EABP of metal oxide catalysts was determined by a pH shift method in accordance with the manner described by Tari et al.[16] The metal oxide sample (2.5±0.1 g) and pure water (100 ml) were introduced into an Erlenmeyer flask equipped with a glass stopper in a decarbonated nitrogen atmosphere and then permitted to stand for one week. The pH value of the supernatant solution in the flask was measured with a pH meter.

IR Measurements: Infrared spectroscopic measurements of the AN adsorbed on both SiO_2 and MgO catalysts were made using a JEOL JIR-100 FTIR spectrometer. Sample treatment and adsorption of AN gas were carried out with a glass gas-handling system capable of achieving a 10^{-6} Torr vacuum. The quartz IR cell used was a conventional T-shaped cell with separate zones for heating and for taking spectra. CaF_2 windows were used. Spectra were collected by co-adding 100 scans at a resolution of 4 cm^{-1}. SiO_2 or MgO sample wafers were prepared by pressing 20 mg of a sample under a pressure of 200 kg cm^{-2} to form a disk about 20 mm in diameter. After SiO_2 and MgO wafers were, respectively, heated at 500 °C for 2 h in a cell, AN vapor (45 Torr (1 Torr=133.322 Pa)) was adsorbed to the sample at room temperature for 15 min and then evacuated for 3 min. All spectra were recorded at room temperature.

Amount of AN Adsorbed: Preheated MnO_2 (at 110 °C) or MgO (at 700 °C) sample (2.5 g) was, respectively, put into an Erlenmeyer flask with glass stopper, and then 100 ml of a 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 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 chromatographically.

Results and Discussion

Catalytic Activity and Selectivity: The catalytic activity (conversion of AN) and selectivity of the liquid-phase hydration of AN over various insoluble metal oxides were examined at 65 °C for 6 h in a batch reactor. The reaction results are summarized in Table 1. Many metal oxides had shown the catalytic activity of the AN hydration, and gave three products: AA, ECH, and BCE. The catalysts used in the AN hydration could be classified into two groups with respect to AA selectivity. One group, defined as "Group A," represents the metal oxides with a 100% AA selectivity and another, defined as "Group B," represents other metal oxides with a low AA selectivity.

The order of the catalytic activity of the oxides in Group A resulted as follows:

$$MnO_2 > Co_3O_4 > NiO(A) > CuO(A) > Fe_2O_3 > PbO_2, WO_3 > SiO_2, TiO_2, Al_2O_3(A).$$

Table 1. Catalytic Activity and Selectivity on Various Single Metal Oxides

Catalyst	Raw materials	Calcination temp/°C	Surface area/$m^2 g^{-1}$	Conversion of AN/%	Selectivity/%		
					AA	ECH	BCE
Group A							
1 MnO_2	electrolytic MnO_2	110	33.2	13.3	100	0	0
		200	28.5	10.9	100	0	0
		300	16.3	7.3	100	0	0
2 α-MnO_2	$MnSO_4+(NH_4)_2S_2O_4$	110	20.5	8.2	100	0	0
3 β-MnO_2	$Mn(NO_3)_2$	200	3.9	0.7	100	0	0
4 γ-MnO_2	$Mn(NO_3)_2+KMnO_4$	110	22.4	5.7	100	0	0
5 δ-MnO_2	$KMnO_4+HCl$	110	140	12.7	100	0	0
6 Co_3O_4	$NaOH+Co(NO_3)_2$	250	38.1	7.8	100	0	0
		400	28.2	6.4	100	0	0
		500	25.9	3.7	100	0	0
7 Co_3O_4	$2CoCO_3 \cdot 3Co(OH)_2$	400	47.8	6.9	100	0	0
8 Co_3O_4	$Co(NO_3)_2+NH_3$ aq.	300	17.8	3.4	100	0	0
9 Co_3O_4	$CoCl_2+NaOH$	250	—	2.3	100	0	0
10 NiO(A)	$Ni(NO_3)_2+NaOH$	300	60.9	4.6	100	0	0
11 CuO(A)	$Cu(NO_3)_2+NaOH$	250	32.5	3.6	100	0	0
12 Fe_2O_3	$Fe(NO_3)_3+NH_3$ aq.	400	68.6	1.2	100	0	0
13 PbO_2	$Pb(NO_3)_2$	350	1.4	0.7	100	0	0
14 WO_3	$(NH_4)_{10}W_{12}O_{41}$	500	<1	0.5	100	0	0
15 SiO_2*	colloidal silica	500	482	1.0	100	0	0
16 TiO_2*	$Ti(SO_4)_2+NH_3$ aq.	500	75.5	0.9	100	0	0
17 Al_2O_3(A)*	MIZUSAWA Chem.	500	271	0.9	100	0	0
Group B							
18 MnO	$MnCO_3$ in N_2	500	14.2	64.8	15.4	28.7	55.9
19 MgO	$4MgCO_3 \cdot Mg(OH)_2$	700	65.0	57.2	3.4	12.6	84.0
20 ZnO	$5ZnO \cdot 2ZnCO_3$	500	20.7	35.1	20.8	31.7	47.5
21 Cu_2O	CuO in C_3'	250	—	20.8	24.8	9.1	66.1
22 NiO(B)	$NiCO_3 \cdot 2Ni(OH)_2$	300	16.7	15.6	22.4	34.5	43.1
23 CuO(B)	$CuCO_3 \cdot Cu(OH)_2$	400	20.7	10.6	41.9	27.4	30.7
24 Ag_2O	$AgNO_3+NaOH$	110	1.6	5.0	28.4	27.3	44.3
25 La_2O_3	$La(NO_3)_3+NH_3$ aq.	500	13.8	2.3	37.8	23.0	39.2
26 Al_2O_3(B)	$Al[OCH(CH_3)_2]_3+H_2O$	400	—	0.8	62.6	14.1	23.3
27 PbO	$Pb(NO_3)_2+KOH$	250	<1	0.6	64.9	8.3	26.8

Reaction temperature: 65 °C (*120 °C in autoclave): Reaction time; 6 h: 6.4 wt% AN solution; 108.5 ml: Catalyst weight; 2.5±0.1 g.

Especially, MnO_2, Co_3O_4, NiO(A), and CuO(A) were effective catalysts for AA formation with 100% selectivity. The catalytic activity of both MnO_2 and Co_3O_4 strongly depended on both the catalytic preparation method and the pretreatment temperature.

The order of the catalytic activity of the oxides in Group B was as follows:

$$MnO > MgO > ZnO > Cu_2O > NiO(B) > CuO(B) > Ag_2O > La_2O_3 > Al_2O_3(B), PbO.$$

MnO was the most active catalyst for AN hydration in all the metal oxide catalysts examined. The more active catalysts in Group B showed the lower selectivity to AA.

It should be noted that the NiO, CuO, and Al_2O_3 prepared with two kinds of methods had different AA selectivities, regardless of their same crystal structure, which was determined by an X-ray diffraction method. Also, both carbonates and hydroxides of the manganese, cobalt, nickel and copper were inactive for liquid-phase AN hydration. When their salts were decomposed to the corresponding oxides, a hydration activity just appeared.

From the results of solid acid-base properties summarized by Tanabe[17] it could be proved that almost all the catalysts of Group A possessed a solid acidity, while the catalysts of Group B were rich in basic properties. It seems that the solid acid-base properties of the metal oxide catalysts are closely related to the catalytic activity and selectivity of AN hydration. This correlation is clarified in the next section.

Electronegativity of the Metal Ion and Selectivity to AA: A qualitative acid-base property of metal oxides can be explained by the electronegativity of the metal ion of an oxide.[18] The relationship between the selectivity to AA and the electronegativity of the metal ion of metal oxide catalysts is illustrated in Fig. 1. A good relation was obtained. The value of the electronegativity of Co_3O_4 could be expressed using the value of arithmetic mean of Co^{2+} and Co^{3+} ion. All the metal oxides for which the electronegativity was 11 or greater showed 100% selectivity to AA. The selectivity to AA of the catalysts decreased with decreasing electronegativity of the metal ion. Differences of the selectivity to AA on the NiO, CuO, and Al_2O_3 catalysts could not be

Table 2. The Acidity and Basicity of the Active Catalysts on the Liquid-Phase Hydration of Acrylonitrile

Catalyst	Selectivity to AA/%	Basicity/mmol g^{-1}	Acidity/mmol g^{-1}		
		$H_- \geqq +9.3$	$H_0 \leqq +6.8$	$H_0 \leqq +4.8$	$H_0 \leqq +3.3$
Group A					
1 MnO_2	100	0	0.101	0.078	0.006
6 Co_3O_4	100	0	0.029	0.022	0.003
10 NiO(A)	100	0	0.088	0.037	0
11 CuO(A)	100	0	0.028	0.022	0
12 Fe_2O_3	100	0	0.049	0.018	0.012
Group B					
18 MnO	15.4	0.297	0	—	—
19 MgO	3.4	0.239	0	—	—
20 ZnO	20.8	0.070	0	—	—
22 NiO(B)	22.4	0.023	0.014	0	—
23 CuO(B)	41.9	0.099	0.027	0.013	0

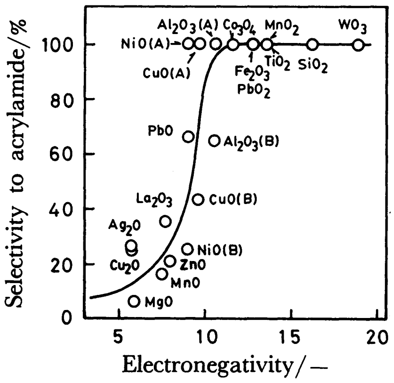

Fig. 1. Relationship between the selectivity to acrylamide and electronegativity of metal cation of metal oxide catalysts.

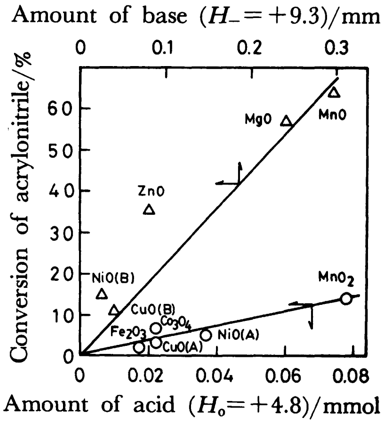

Fig. 2. Relationship between the conversion of acrylonitrile and the amount of acid-base of metal oxide catalysts.

explained from the electronegativity since it is a qualitative measure of the solid acidity or basicity of metal oxide catalysts.

Acid-Base Property on the Metal Oxides: A quantitative measurements of the acidity and basicity on the metal oxide catalysts can be generally made using the indicator titration method. However, the properties of dark-colored solid samples are difficult to measure by this method. Accordingly, our modified titration method[13] was adapted during the course of this. The acid-base properties of some metal oxide catalysts for AN hydration in Group A or B were obtained as shown in Table 2, although not all the catalysts shown in Table 1 were examined.

The Group A catalysts with 100% AA selectivity showed acidic strength between pK_a 3.3 and 6.8; that is, a rather weak acidic site is related to AA formation. On the other hand, Group B catalysts with a low AA selectivity exhibited a pK_a value of 9.3 or greater. The acidic and basic sites on the NiO(B) and CuO(B) catalyst surfaces showed a pK_a of 4.8 or less and a pK_a of 15.0 or greater, respectively. Consequently, the acidic sites on the metal oxide surface participate with the hydration of the C≡N bond in an AN molecule and the basic sites do the same with C=C bond.

As shown in Fig. 2, a good relationship between the catalytic activity of the metal oxides and the amount of acid at p$K_a \leqq +4.8$ or of base at p$K_a \geqq +9.3$ was obtained. Thus, rather weak acid-base properties on metal oxides are closely related to AN hydration. The pK_a value of the oxonium (H_3O^+) or hydroxide (OH^-) ion was -1.7 or $+15.7$, respectively.[19] Consequently, it is considered that the acidic or basic site of metal oxides ranging in a pK_a range between -1.7 and $+15.7$ effectively act for AN hydration. One can conclude that a metal oxide catalysts having moderate acid-base properties is suitable for the liquid-phase hydration of AN.

Equi-Acid-Base Point (EABP) of the Metal Oxides: The acid-base property of an insoluble metal oxide dispersed in water can be represented by the EABP; the pH value is used as a measure of acidity or basicity on the oxides.[15] The EABP values of the metal oxide catalysts used were obtained in the pH range of 3.6—11.2; in this pH range a homogeneous AN hydration in acidic or basic liquid phase did not progress.[20] The EABP value of the metal oxides in Group A was below 7, i.e., rather acidic, while that of the oxides in the Group B was above 7, i.e., rather basic. These results indicate that each of the metal oxides in Group A or B has both acidic or basic properties, even in water. A typical solid acid catalyst, SiO_2–Al_2O_3 showed an EABP value of 7, showing that it is inactive for AN hydration.

Figure 3 illustrates the relationship between the AA selectivity and the EABP value of the catalysts. The metal oxide catalysts which have an acidic property in water showed 100% selectivity to AA. While in the case of the metal oxides which had basic properties in water, the AA selectivity of the catalysts decreased upon increasing their basicity. Figure 4 shows the logarithm of the catalytic activity against the EABP values of the metal oxides, indicating the pattern of a character of "V." The EABP value of the bottom of the "V" was just 7. These results suggested that the hydration activity of the metal oxides are proportional to the amount of acidic or basic sites on the oxide surface.

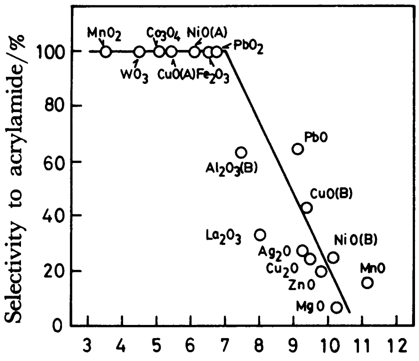

Fig. 3. Relationship between the selectivity to acrylamide and the value of equi-acid-base point of metal oxide catalysts.

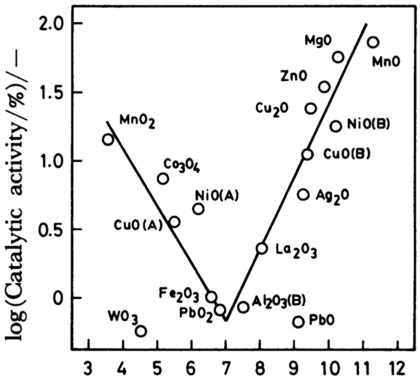

Fig. 4. Relationship between the catalytic activity and the value of equi-acid-base point of metal oxide catalysts.

Effect of Poisoning: As shown in Table 3, the catalytic activity of MnO_2 was depressed by the addition of such basic materials as sodium hydroxide, whereas the activity of an MgO catalyst was inhibited by the addition of such acidic materials as phosphoric acid. Furthermore, by the addition of a buffer solution of pH=7 (such as a tetrachlorozincate anion complex ($ZnCl_4^{2-}$)[20]) the catalytic activity of both MnO_2 and MgO was entirely lost. These results also indicate that the acidic site on MnO_2 and the basic site on MgO act as the active sites of the catalysts for AN hydration.

Effectiveness of the Metal Oxide Surface: The effectiveness of the metal oxide surface on the active sites for the heterogeneous liquid-phase hydration of AN was determined by a comparison of the homogeneous AN hydration in an aqueous acidic or basic solution. As shown in Table 4, heterogeneous AN hydration did not progress in an aqueous H_2SO_4 solution adjusted to pH 3.6, which was the same pH value of EABP of MnO_2 catalyst. AA was not observed until the pH value in the solution became to 2.1. In the case of a basic AN solution, a small amount of products was formed in an aqueous NaOH solution adjusted to pH 10.3. Only when the supernatant solution of MgO catalyst was used, a slight conversion of AN was observed. In conclusion, the AN conversion of homogeneous catalysts was extremely small compared with that of metal oxide catalysts with the same pH value.

In addition, the lower apparent activation energy of MnO_2 and MgO catalysts than that of H_2SO_4 and NaOH could be calculated, and the AN adsorption to

Table 3. Poisoning Effect of the Additives to MnO_2 and MgO Catalyst on the Hydration of Acrylonitrile

Additive	Catalyst	
	MnO_2	MgO
NaOH (0.1 mol)	○	×
H_3PO_4 (0.1 mol)	×	○
Buffer solution of pH=7.0	○	○

○: Detected. ×: Not detected. Reaction conditions are the same as those in Table 1.

Table 4. Hydration of Acrylonitrile in Hetero- and Homogeneous Liquid Phase

Catalyst	Phase	pH[a)]	AN conv.[b)]	AA sel.[b)]	ΔE	Adsorbed AN
			%	%	kcal mol^{-1}	($\times 10^{-4}$ mol/g-cat)
MnO_2	heterogeneous	(3.6)	13.3	100	15	5.3
H_2SO_4	homogeneous	3.6	0	—	36[c)]	—
MgO	heterogeneous	(10.3)	57.2	3.4	16	0.4
$Mg(OH)_2$	homogeneous	10.3	2.9	15.5	—	—
NaOH	homogeneous	10.3	8.8	27.2	19[d)]	—

a) EABP value of the oxide catalyst was shown in parentheses. b) Reaction conditions are the same as those in Table 1. c) Ref. 27. d) The value calculated in the previous paper: Ref. 4.

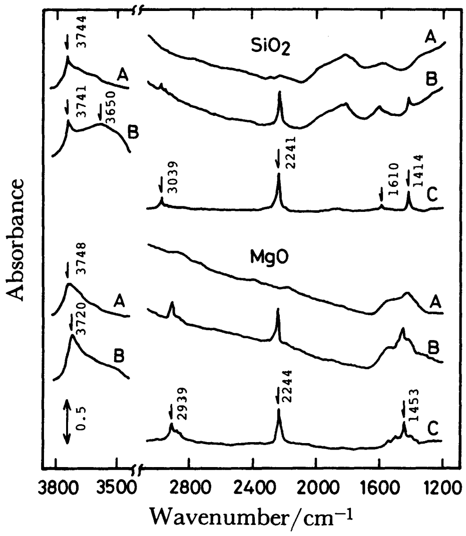

Fig. 5. IR spectra of acrylonitrile adsorbed on SiO_2 and MgO catalysts: (A): Background, (B): after adsorption of acrylonitrile, (C): subtracted spectrum.

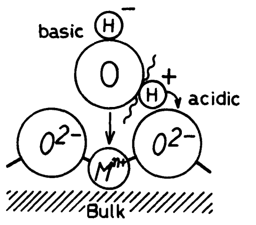

Fig. 6. Hydrated surface model of metal oxide.

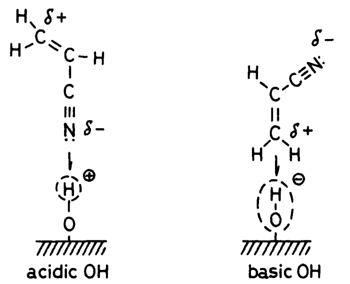

Fig. 7. Adsorbed model of acrylonitrile on surface OH group of metal oxide.

the MnO_2 and MgO surface was actually observed in the liquid phase. Consequently, it can be concluded that the acidic or basic site on metal oxide surface acts as the active site for the liquid-phase hydration of AN.

IR Spectra of Adsorbed AN: The IR spectra of the AN adsorbed on the metal oxides were examined in order to obtain more detailed information with respect to the hydration selectivity to either a C≡N triple bond or a C=C double bond in an AN molecule. The IR spectra of AN adsorbed on SiO_2 and MgO are shown in Fig. 5. The IR spectrum of liquid-state AN shows three characteristic absorption bands; C≡N stretching vibration at 2230 cm^{-1}. C=C stretching vibration at 1609 cm^{-1} and CH_2 deformation vibration at 1415 cm^{-1}, respectively.[21,22] When AN was adsorbed on the SiO_2 C≡N band shifted to higher band (2241 cm^{-1}) and a new broad absorption band of surface OH group at ca. 3650 cm^{-1} appeared. This result suggests that the covalent coordination through an N(2s) lone pair of electrons of the AN[23] takes place on the surface OH group of a SiO_2 catalyst. On the other hand, when AN was adsorbed on the MgO surface, two new bands appeared at 1453 and 2939 cm^{-1} and the C≡N band shifted to a higher frequency. These new absorption bands (1453, 2939 cm^{-1}) instead of indicating the disappearance of the vinyl-group absorption bands could be, respectively, assigned to the C–H bending and stretching vibrations of a chain $-CH_2-$ in the ECH molecule. The broad absorption band of the OH stretching vibration from 3400 to 3700 cm^{-1} appears to indicate the formation of an alcoholic bond between the surface OH group and the terminal carbon atom in the AN molecule. These results suggest that σ- or π-component coordination through the C=C double bond of the AN[24] arises on the surface OH groups of an MgO catalyst.

It is known that an acidic or a basic OH group is formed on a metal oxide surface when a water molecule adsorbs to the surface as shown in Fig. 6.[25,26] The EABP value of the metal oxide mentioned before is the difference of the surface concentration between acidic and basic OH groups.[14] The difference of selectivity to the hydration products of the metal oxide catalysts could be explained according to the EABP values of the catalysts. Therefore, the adsorbed state of AN on the acidic or basic OH groups on the metal oxide surface can be schematically depicted as shown in Fig. 7, based on the IR data. It is considered that the selectivity of AN hydration is controlled by acidic or basic OH groups on the metal oxide surface, and that the catalytic activity is also proportional to the amount of surface OH groups on the catalyst.

Conclusions

On the basis of the results described above, we conclude that the liquid-phase hydration of AN on a metal oxide is an acid-base-catalyzed reaction and that the active sites are probably the acidic or basic OH groups on the metal oxide surface.

1) The metal oxide catalysts on liquid-phase hydration of AN could divided into two groups with respect to AA selectivity. Group A is the oxide which gives the AA selectivity with 100% and Group B is the oxide which forms three kinds of products, ECH, BCE, and AA.

2) A good relationship between the hydration abilities (activity and selectivity) of AN on a metal oxide catalysts and the acid-base properties on metal oxides determined by the indicator titration method was observed. The catalytic activity of catalysts of Group A or B is proportional to the number of acid sites at $pK_a \leqq +4.8$ or basic sites at $pK_a \geqq +9.3$, respectively. A

moderate strength of an acid or base ($3.3<\mathrm{p}K_a\leqq 9.3$) is effective for the liquid-phase hydration of AN.

3) The equi-acid-base point (EABP) values of the metal oxide catalysts of Group A were below 7, and the catalytic conversion increased upon decreasing the EABP value. The EABP value of Group B metal oxides was above 7, and the catalytic activity increased with increasing the EABP value.

4) Two types of the adsorption states assigned to either cyano or vinyl group of AN were observed on the metal oxides.

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