Acidic properties of Binary Metal Oxides

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Eighteen binary metal oxides consisting of TiO_2–M_mO_n, ZnO–M_mO_n and Al_2O_3–M_mO_n (M_mO_n: metal oxide) were prepared by the usual co-precipitation method, their acid amounts and strengths being determined by *n*-butylamine titration using various acid-base indicators. The acid strengths of fourteen of the tested binary oxides of molar ratio 1 : 1 were found to be remarkably higher than those of the component single oxides. High acid strengths were as follows: $H_0 \leqq -8.2$ for TiO_2–SiO_2, $H_0 \leqq -5.6$ for TiO_2–Al_2O_3 and Al_2O_3–ZrO_2 and $H_0 \leqq -3$ for TiO_2–CdO, TiO_2–SnO_2 and ZnO–SiO_2. The acid amounts of sixteen binary oxides were larger than those of the component oxides. The effect of the composition of binary oxides on acidity was examined for TiO_2–Al_2O_3, ZnO–Al_2O_3 and Al_2O_3–ZrO_2. The acidity maxima appearing for TiO_2–Al_2O_3 and ZnO–Al_2O_3 were found to be of molar ratio$\simeq$9 : 1 and for Al_2O_3–$ZrO_2 \simeq 3$: 2. A fairly good correlation has been demonstrated between the observed highest acid strengths and the average electronegativities of metal ions of binary oxides.

Some binary metal oxides such as SiO_2–Al_2O_3, SiO_2–ZrO_2, SiO_2–MgO and Al_2O_3–Bi_2O_3 are known to show acidic property and have long been used as solid acid catalysts.[1] These combinations of oxides contain either SiO_2 or Al_2O_3, both essential constituents of clay minerals. However, combinations such as TiO_2–ZnO, TiO_2–ZrO_2 and ZnO–Bi_2O_3 containing no clay mineral component were recently found to exhibit remarkable acidic property[2–6] and catalytic activity.[2,4] Since many other combinations are also expected to exhibit acidic property and it is considered important for theoretical development and practical use of mixed oxides to find combinations of oxides giving acidic property and to correlate it with the physico-chemical properties of metal oxides, we prepared various binary oxides and examined their acid amounts and sterngths. The binary oxides are restricted to colorless materials to which an acidity measurement by the amine titration method using indicators can be applied. The observed acid strengths are correlated with the electronegativities of metal ions of binary oxides. The effect of the composition of some binary oxides on acidic property was also examined.

Experimental

Preparation of Metal Oxides. Binary metal oxides were prepared by the thermal decomposition of their hydroxides at 500 °C for 3 hr. in air. The hydroxides were co-precipitated by adding 28% of ammonia water to the mixed aqueous solution of water soluble metal salts (Table 1). The precipitates were washed thoroughly to remove adhering anions such as chloride ion. Each single oxide was prepared similarly as above. Binary oxides containing silica were prepared by kneading the wetted hydroxides of silicon and other metal and calcining at 500 °C for 3 hr after drying at 70—80 °C. The silicon hydroxide was prepared from aqueous sodium silicate by adding aqueous hydrochloric acid and drying at 70—80 °C for 3 hr. The amount of oxide in the binary oxides containing silica was determined by gravimetric analysis of the oxide obtained by calcining the hydroxide.

Table 1. Starting materials of oxides

Oxides	Starting materials	Oxides	Starting materials
TiO_2	$TiCl_4$	Bi_2O_3	$BiCl_3$
ZnO	$ZnCl_2$	SiO_2	Na_2SiO_3
Sb_2O_5	$SbCl_5$	PbO	$Pb(NO_3)_2$
ZrO_2	$ZrOCl_2$	CdO	$CdCl_2$
Al_2O_3	$AlCl_3$	SnO_2	$SnCl_2$
MgO	$MgCl_2$		

Measurement of Specific Surface Area and Acidity. Specific surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at −196 °C. Surface acidity was measured by *n*-butylamine titration using the following indicators: methyl red ($pK_a = +4.8$), phenylazonaphthylamine (+4.0), *p*-dimethylaminoazobenzene (+3.3), benzeneazodiphenylamine (+1.5), dicinnamalacetone (−3.0), benzalacetophenone (−5.6) and anthraquinone (−8.2).

X-Ray Diffraction. X-Ray powder diffraction diagrams were recorded with an X-ray diffractometer (Rigakudenki, Geigerflex SG-7). Nickel filtered CuK_α was used as X-ray radiation source.

Results and Discussion

Single Oxides and Binary Oxides Containing Titanium Oxide. The acidity distribution of single oxides which are component oxides of binary oxides are shown in Table 2, together with the surface areas. SiO_2 gave no X-ray diffraction lines indicating its amorphous form. Al_2O_3 gave only weak diffraction lines indicating its partial crystal and TiO_2, ZrO_2, CdO, SnO_2, ZnO, Sb_2O_5 and PbO gave strong diffraction lines indicating each crystal. We see that the acid strengths of the single oxides are generally weak ($H_0 > +1.5$), TiO_2 and ZnO weaker than those observed previously.[2] This is considered to be due to the difference in the mode of preparation.

1) K. Tanabe, "Solid Acids and Bases," Kodansha, Tokyo, Academic Press, New York, London (1971).
2) K. Tanabe, C. Ishiya, I. Matsuzaki, I. Ichikawa, and H. Hattori, This Bulletin, **45**, 47 (1972).
3) K. Shibata and T. Kiyoura, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **19**, 35 (1971).
4) K. Tanabe, I. Ichikawa, H. Ikeda and H. Hattori, *ibid.*, **19**, 185 (1971).
5) K. Shibata, T. Kiyoura and K. Tanabe, *ibid.*, **18**, 189 (1970).
6) "Cracking activity and acidity of hydrous oxide composites," Honors Thesis of Mariel Meents (1961) with Professor J. D. Danforth, Grinnell College, Grinnell, Iowa.

TABLE 2. ACIDITY DISTRIBUTION OF SINGLE OXIDES

Oxides	Surface area m^2/g	Acid amount (mmol/g) at different pK_a's						
		+4.8	+4.0	+3.3	+1.5	−3.0	−5.6	−8.2
TiO_2	38.5	0.057	0.057	0				
ZnO	7.4	0.006	0					
Al_2O_3	190	—	0.285	0.075	0			
SiO_2	289	0.264	0.109	0.066	0			
ZrO_2	72.0	—	0.280	0.060	0.060	0		
MgO	49.1	0						
Bi_2O_3	6.5	0.250	0.250	0				
Sb_2O_5	77.0	—	0.055	0.055	0			
PbO	0.7	0.065						
CdO	2.2	0.289						
SnO_2	27.7	0.133						

TABLE 3. ACIDITY DISTRIBUTION OF BINARY OXIDES

Binary oxides	Surface area m^2/g	Acid amount (mmol/g) at different pK_a's						
		+4.8	+4.0	+3.3	+1.5	−3.0	−5.6	−8.2
TiO_2-Al_2O_3	204	0.422	0.422	0.337	0.252	0.220	0.060	0
TiO_2-SiO_2	222	0.565	0.565	0.565	0.565	0.565	0.248	0.053
TiO_2-ZrO_2	230	—	0.475	0.380	0.350	0.375	0.125	0.050
TiO_2-MgO	13.6	0.089	0.089	0.022	0			
TiO_2-Bi_2O_3	35.6	0.099	0.049	0.025	0.025	0		
TiO_2-CdO	35.0	0.193	0.136	0.136	0.090	0.064	0	
TiO_2-SnO_2	12.1	0.154	0.108	0.046	0.031	0.018	0	
ZnO-Al_2O_3	117	0.332	0.332	0.270	0.166	0		
ZnO-SiO_2	77.0	0.216	0.175	0.175	0.175	0.042	0	
ZnO-ZrO_2	29.4	0.144	0.144	0.144	0.144	0		
ZnO-MgO	6.0	0.025	0					
ZnO-Sb_2O_5	68.3	0.011	0.011	0				
ZnO-Bi_2O_3	11.0	0.175	0.015	0.015	0			
ZnO-PbO[a]	5.5	0						
Al_2O_3-ZrO_2	320	—	0.590	0.205	0.205	0.045	0.045	0
Al_2O_3-Sb_2O_5	38.1	0.079	0.079	0.079	0			
Al_2O_3-Bi_2O_3	21.2	0.087	0.083	0.088	0.070	0		
ZrO_2-CdO	102	—	0.399	0.391	0.343	0.106	0	

a) Color of the indicator ($pK_a = +6.8$) changed.

The acid amounts and strengths of the binary oxides containing TiO_2 (molar ratio=1) are shown in Table 3. The X-ray diffraction diagrams of TiO_2–SiO_2 and TiO_2–ZrO_2 showed only diffused or weak diffraction lines and were assumed to be amorphous. TiO_2–Al_2O_3 gave only the diffraction lines of TiO_2. Thedif-fraction lines of TiO_2–MgO, TiO_2–Bi_2O_3, TiO_2–CdO and TiO_2–SnO_2 were those of the component oxides. The results indicate the binary oxides are not mechanically mixed oxides. The acid strengths of TiO_2–SiO_2 and TiO_2–ZrO_2, found to be surprisingly high, were $H_0 \leqq -8.2$ and those of TiO_2–Al_2O_3 and TiO_2–CdO, also high, −5.6 and −3, respectively. Since SiO_2–ZrO_2 is known to have very high acid strength ($H_0 \leqq -8.2$),[7] it can be said that the combinations of oxides of metals (Si, Ti and Zr) which belong to the same fourth group in the periodic table show the highest acid strength. All the binary oxides containing TiO_2 showed higher acid strength than each component oxide. The acid amount at a certain acid strength per unit surface area of any binary oxide was larger than the sum of the acid amounts divided by the sum of the surface areas of the component oxides. The results indicate that the new acidic sites which differ from those of single oxides are created on the surface of binary oxides.

The acidity change with variation of composition was examined in the case of TiO_2–Al_2O_3. As shown in Fig. 1, the acidity maximum was observed when the molar ratio of TiO_2–Al_2O_3 is about 1 : 9. It is interesting to note that the acidity maximum of SiO_2–Al_2O_3 appears when the molar ratio is about 8 : 2,[8] despite the fact that both TiO_2 and SiO_2 are oxides

7) V. A. Dzisko, Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, I, No. 19 (1964).

8) see ref. 1), p. 126.

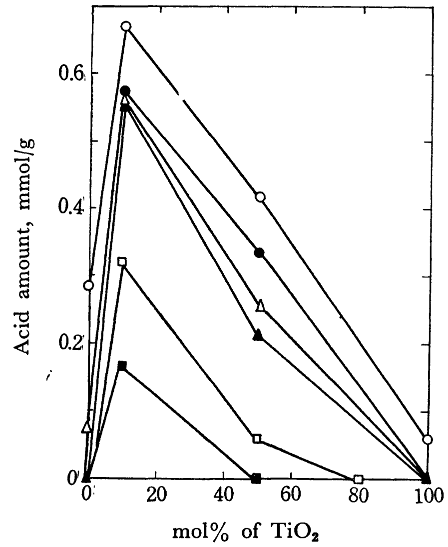

Fig. 1. Acid amounts at various acid strengths of TiO_2–Al_2O_3 *vs.* mol% of TiO_2.
(-○-): $H_0 \leqq 4.8$, (-●-): $H_0 \leqq 3.3$, (-△-): $H_0 \leqq 1.5$, (-▲-): $H_0 \leqq -3.0$, (-□-): $H_0 \leqq -5.6$, (-■-): $H_0 \leqq -8.2$

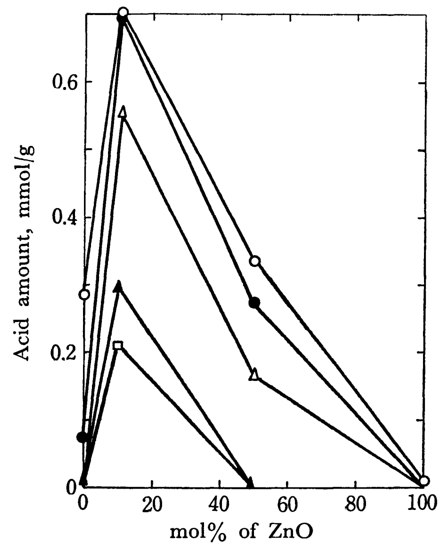

Fig. 2. Acid amounts at various acid strengths of ZnO-Al_2O_3 *vs.* mol% of ZnO.
(-○): $H_0 \leqq 4.8$, (-●-): $H_0 \leqq 3.3$, (-△-): $H_0 \leqq 1.5$, (-▲-): $H_0 \leqq -3.0$, (-□-): $H_0 \leqq -5.6$

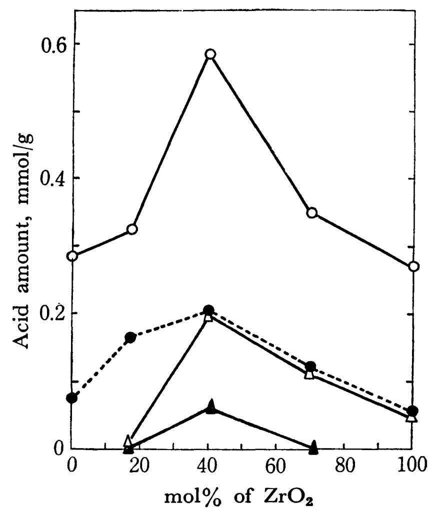

Fig. 3. Acid amounts at various acid strengths of ZrO_2–Al_2O_3 *vs.* mol% of ZrO_2.
(-○-): $H_0 \leqq 4.0$, (-●-): $H_0 \leqq 3.3$, (-△-): $H_0 \leqq 1.5$, (-▲-): $H_0 \leqq -3.0$

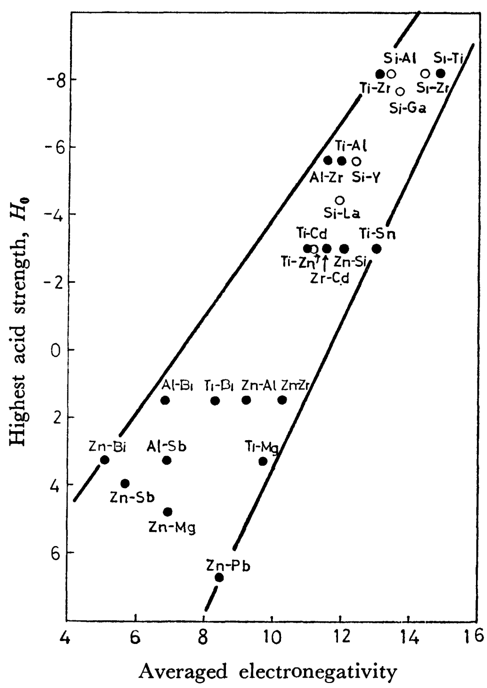

Fig. 4. Highest acid stength *vs.* averaged electronegativity of metal ions of binary oxides (molar ratio=1).

of metals of the same fourth group in the periodic table and that the acidity maximum of TiO_2–ZnO[2] appears when the molar ratio is 1 : 9 as in the case of TiO_2–Al_2O_3. Recently, TiO_2–Al_2O_3 was reported to show high catalytic activity for the synthesis of aniline from phenol and ammonia.[9] The high activity can be now understood to be due to its high acid strength. SiO_2–TiO_2 shows higher activity than SiO_2–Al_2O_3 for the aniline synthesis.[10]

Binary Oxides Containing Zinc Oxide or Alumina and Other Binary Oxides. The acidity distribution of the binary oxides containing ZnO or Al_2O_3 and other binary oxides (molar ratio=1) is shown in Table 3. According to X-ray diffraction, ZnO–SiO_2 and Al_2O_3–ZrO_2 were amorphous and ZnO–MgO gave only the diffraction lines of ZnO. ZnO–Al_2O_3, ZnO–ZrO_2, ZnO–Sb_2O_5 and ZnO–PbO gave diffraction lines differing from those of the component oxides. The results indicate that these binary oxides are not mechanically mixed oxides. The binary oxides which showed high acid strength were ZnO–SiO_2, Al_2O_3–ZrO_2 and ZrO_2–CdO. The acid strengths of binary oxides containing ZnO are relatively weak. The acidity changes of ZnO–Al_2O_3 and Al_2O_3–ZrO_2 with composition are shown in Figs. 2 and 3, where the acidity maxima are found when the molar ratios are

9) R. S. Parker, Japanese Pat. Sho 42-23571.
10) K. Tanabe, M. Ito, and M. Sato, *Chem. Commun.*, in press.

approximately 1 : 9 and 3 : 2, respectively. Many binary oxides show higher acid amount and strength than each component oxide (Table 3). The acid strengths of ZnO–MgO and Al_2O_3–Sb_2O_5 were the same as those of one of the component oxides, whereas their acid amounts per unit surface area were smaller. In the case of ZnO–Sb_2O_5 and ZnO–PbO, both acid strength and amount were lower than those of the component oxides. It was reported that both SiO_2 and ZnO are almost inactive for the isomerization of butenes, although the combination of both oxides is active.[11] The activity is considered to be due to the action of strong acid sites generated on the surface of SiO_2–ZnO.

Correlation between Acid Strengths of Binary Oxides and Electronegativities of Metal Ions of Metal Oxides. The observed highest acid strengths of binary oxides (molar ratio=1) are plotted against the algebraically averaged electronegativities of metal ions in Fig. 4, where the data indicated by open circles were cited from the literature (Ref. 2 for TiO_2–ZnO; Ref. 7 for SiO_2–ZrO_2; Ref. 12 for SiO_2–Al_2O_3, SiO_2–Y_2O_3, SiO_2–La_2O_3). The electronegativity values of various metal ions were cited from the work of Tanaka and Ozaki.[13] The highest acid strengths were found to increase with the increase of the algebraically averaged electronegativities. The correlation between the acid strengths and the geometrically averaged values of electronegativities was slightly worse than but almost the same as that shown in Fig. 4. Since the electronegativity of metal ion (Me^{+n}) is related to its acid strength (pK_a) as shown in $Me^{+n}+H_2O \rightleftarrows [Me(OH)]^{+(n-1)}+H^+$, the relation given in Fig. 4 seems to be reasonable. However, the reason why the algebraically or geometrically *averaged* values of electronegativities are correlated with the acid strengths is not yet clear. Nevertheless, the correlation in Fig. 4 is useful for predicting the acid strengths of unknown binary oxides.

11) K. Tanabe, T. Sumiyoshi, and H. Hattori, *Chem. Lett.*, **1972**, 723.

12) N. S. Kotsarenko, L. G. Karakchiev, and V. A. Dzisko, *Kinet. Katal.*, **9**, 158 (1968).

13) K. Tanaka and A. Ozaki, *J. Catal.*, **8**, 1 (1967); K. Tanaka, "Shokubai Kogaku Koza," Vol. 10, ed. by A. Ozaki, K. Tamaru, K. Tanabe, and S. Nishimura, Chijinshokan & Co. Ltd., Tokyo, (1967), p. 752.