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## SURFACE ACIDITY OF COLORED BINARY METAL OXIDES

By

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### Abstract

Eighteen species of colored binary metal oxides were prepared and the acidities in their oxidized and reduced states were determined by back titration of *n*-butylamine benzene solution with hydrochloric acid. The acidities obtained by the back titration method have been shown to correlate well with those by usual amine titration method. All the colored oxides were found to have fairly large acidity above 0.14 mmol/g and 0.0015 mmol/m<sup>2</sup>, the largest acidity being found for TiO<sub>2</sub>·Fe<sub>2</sub>O<sub>3</sub> in oxidized state. It was also found that most of the oxides decrease their acidities on reduction, whereas reduction increases the acidities of Al<sub>2</sub>O<sub>3</sub>·CdO and Al<sub>2</sub>O<sub>3</sub>·Cr<sub>2</sub>O<sub>3</sub>.

### Introduction

Acidic properties of various binary metal oxide catalysts such as SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>·MgO, Al<sub>2</sub>O<sub>3</sub>·B<sub>2</sub>O<sub>3</sub> etc. have been extensively studied and correlated with their catalytic activities for many acid-catalyzed reactions such as cracking, polymerization, isomerization, alkylation, disproportionation, hydration and dehydration. However, almost all of the catalysts employed for such a study have been limited to colorless solids. The measurement of acidic property of colored mixed oxide has been made only for Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub><sup>1)</sup> and MoO<sub>3</sub>·Fe(MoO<sub>4</sub>)<sub>3</sub>,<sup>2)</sup> the measured acidity of the latter being shown to have a close correlation with its catalytic activity in the oxidation of methyl alcohol to formaldehyde. Since the usual *n*-butylamine titration method<sup>3)</sup> using Hammett indicators cannot be directly applied to colored surfaces, the acidities of the above colored oxides were measured by amine titration of the samples mixed with a known amount of a white solid acid, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>,<sup>1~2)</sup> though the modified method is troublesome and less accurate.

We have attempted to measure the acidities of various colored mixed

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oxides by a back titration of *n*-butylamine benzene solution with hydrochloric acid. The present paper reports the acidities of eighteen colored mixed metal oxides in both oxidized and reduced states together with their specific surface areas and compares the employed method of acidity measurement with usual amine titration method.

### Experimental

**Preparation of oxide samples:** A binary metal oxide sample was prepared by thermal decomposition of a co-precipitated mixture of each hydroxides in air at 500°C for 3 hrs. The co-precipitated mixture was prepared by addition of aqueous ammonia to a mixed equi-molar aqueous solution of water soluble

TABLE 1. Starting materials and colors of binary metal oxides

metal oxides	Starting materials	Colors of oxides	
		Oxidized	Reduced
TiO <sub>2</sub> ·WO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> W <sub>4</sub> O <sub>13</sub> ·8H <sub>2</sub> O, TiCl <sub>4</sub>	yellow	black
TiO <sub>2</sub> ·MoO <sub>3</sub>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O, TiCl <sub>4</sub>	dark green	black
TiO <sub>2</sub> ·Sb <sub>2</sub> O <sub>5</sub>	SbCl <sub>5</sub> , TiCl <sub>4</sub>	yellow	green
TiO <sub>2</sub> ·Fe <sub>2</sub> O <sub>3</sub>	FeCl <sub>3</sub> ·6H <sub>2</sub> O, TiCl <sub>4</sub>	brown	black
TiO <sub>2</sub> ·Cr <sub>2</sub> O <sub>3</sub>	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O, TiCl <sub>4</sub>	dark green	green
TiO <sub>2</sub> ·V <sub>2</sub> O <sub>5</sub>	NH <sub>4</sub> (VO <sub>3</sub> ), TiCl <sub>4</sub>	gray	black
TiO <sub>2</sub> ·Mn <sub>2</sub> O <sub>3</sub>	MnCl <sub>2</sub> ·4H <sub>2</sub> O, TiCl <sub>4</sub>	dark brown	brown
TiO <sub>2</sub> ·Co <sub>3</sub> O <sub>4</sub>	CoCl <sub>2</sub> ·H <sub>2</sub> O, TiCl <sub>4</sub>	black	black
TiO <sub>2</sub> ·NiO	NiCl <sub>2</sub> ·6H <sub>2</sub> O, TiCl <sub>4</sub>	green	black
TiO <sub>2</sub> ·CuO	CuCl <sub>2</sub> ·2H <sub>2</sub> O, TiCl <sub>4</sub>	dark violet	violet
ZnO·Fe <sub>2</sub> O <sub>3</sub>	FeCl <sub>3</sub> ·6H <sub>2</sub> O, ZnCl <sub>2</sub>	brown	black
Al <sub>2</sub> O <sub>3</sub> ·NiO	NiCl <sub>2</sub> ·6H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	dark green	black
Al <sub>2</sub> O <sub>3</sub> ·Co <sub>3</sub> O <sub>4</sub>	CoCl <sub>2</sub> ·6H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	black	dark green
Al <sub>2</sub> O <sub>3</sub> ·MoO <sub>3</sub>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	yellow	black
Al <sub>2</sub> O <sub>3</sub> ·CdO	CdCl <sub>2</sub> ·H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	brown	yellow
Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>	FeCl <sub>3</sub> ·6H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	dark brown	black
Al <sub>2</sub> O <sub>3</sub> ·Cr <sub>2</sub> O <sub>3</sub>	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	black	green
Al <sub>2</sub> O <sub>3</sub> ·MnO <sub>3</sub>	MnCl <sub>2</sub> ·4H <sub>2</sub> O, AlCl <sub>3</sub> ·6H <sub>2</sub> O	brown	brown
TiO <sub>2</sub>	TiCl <sub>4</sub>	white	
CdO	CdCl <sub>2</sub> ·H <sub>2</sub> O	brown	white
Fe <sub>2</sub> O <sub>3</sub>	FeCl <sub>3</sub> ·6H <sub>2</sub> O	brown	black

### *Surface Acidity of Colored Binary Metal Oxides*

salts whose various combinations are given in Table 1. The precipitate was washed thoroughly to remove adhering anions such as chlorine ion. Before calcination, it was dried in air at 110°C for 30 hrs.

Oxidized samples were prepared as follows. The above binary oxide calcined at 500°C in air was ground in an agate mortar and the portion of 100~200 mesh was calcined further in air at 300°C for 1 hr. Reduced samples were prepared as described below. Roughly one gram of powdered sample of binary oxide calcined at 500°C in air was transferred to borosilicate glass tube (12 mm $\phi$ ), and the tube was heated at 400°C for 1 hr in the current of hydrogen. The colors of the oxidized and reduced samples are shown also in Table 1.

**Measurement of acidity:** Acidity of oxide samples were measured by back titration of *n*-butylamine with hydrochloric acid. The powdered sample was calcined in air at 300°C for 1 hr and cooled to room temperature under nitrogen atmosphere and about 1 g of the sample was put in a 20 ml of 0.011 mol/l *n*-butylamine benzene solution. After the suspension was stirred vigorously for 2 hrs at room temperature, the powdered sample was filtered off. Then, the amine benzene solution was titrated with aqueous hydrochloric acid using bromothymol blue as an indicator. An acidity of an oxide sample was calculated readily from the decrease in *n*-butylamine concentration in benzene. In some cases, acidity was measured also by usual amine titration method<sup>3)</sup> using methyl red of  $pK_a=4.8$  as an indicator, for comparison.

**Specific surface area:** The surface areas of oxidized and reduced oxide samples were obtained by applying the BET method to the adsorption isotherm of nitrogen at -196°C.

### **Results and Discussion**

The effect of time taken for *n*-butylamine adsorption on the acidity value measured by the method of the present work was examined by using a well-known colorless solid acid, alumina, whose acidity at  $pK_a=4.8$  is 0.605 mmol/g according to usual amine titration method. The results are shown in Table 2, which indicate that 1~2 hrs of stirring are sufficient for the reaction of *n*-butylamine with the solid. The little larger acidity values found by the present method seems to be partly due to the difference in basic strength between methyl red ( $pK_a=4.8$ ) and *n*-butylamine ( $pK_a=9.1$ ) and partly due to the larger concentration of *n*-butylamine in liquid phase during its adsorption. In a usual amine titration method, no appreciable amount of *n*-butylamine presents in liquid phase.

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TABLE 2. Effect of adsorption time on acidity.

Oxide sample:  $\text{Al}_2\text{O}_3$ , Method: back titration

Time of adsorption (hr)	1	2	3	4	48
Acidity (mmol/g)	0.830	0.794	0.793	0.815	0.815

In order to examine further how the relative acidity values observed by the present method may be correlated with those by usual amine titration method, the acidities of some colorless oxides,  $\text{MgO}$ ,  $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ ,  $\text{SiO}_2 \cdot \text{ZnO}$ ,  $\text{SiO}_2 \cdot \text{TiO}_2$ ,  $\text{Al}_2\text{O}_3 \cdot \text{ZrO}_2$  and  $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$  were measured by both methods. The results are shown in Fig. 1, where the acidity measured by amine titration

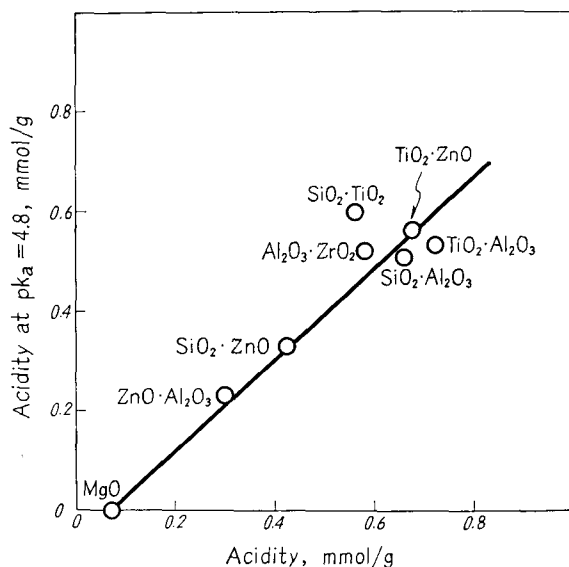


Fig. 1. Acidity by usual amine titration method vs. acidity by back titration method.

method using methyl red ( $\text{pK}_a=4.8$ ) as an indicator was plotted against the acidity by back titration method. A linear relationship is seen between both acidities, indicating that the relative acidities can be measured satisfactorily by the present method.

In Table 3 are now shown the results of acidity measurements of various mixed oxides in their oxidized and reduced states and the specific surface areas. As seen in the Table, all the colored binary oxides show fairly large acidities, the values are above 0.14 mmol/g, and 0.0015 mmol/m<sup>2</sup>. The largest

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TABLE 3. Acidity of binary metal oxides

Metal oxides	Oxidized			Reduced		
	Acidity mmol/g	Surface area m <sup>2</sup> /g	Acidity mmol/m <sup>2</sup>	Acidity mmol/g	Surface area m <sup>2</sup> /g	Acidity mmol/m <sup>2</sup>
TiO <sub>2</sub> · WO <sub>3</sub>	0.167	44.7	0.0037	0.190	50.8	0.0038
TiO <sub>2</sub> · MoO <sub>3</sub>	0.198	28.2	0.0070	0.165	56.0	0.0029
TiO <sub>2</sub> · Sb <sub>2</sub> O <sub>5</sub>	0.477	124	0.0038	0.263	125	0.0021
TiO <sub>2</sub> · Fe <sub>2</sub> O <sub>3</sub>	0.708	109	0.0065	0.353	108	0.0033
TiO <sub>2</sub> · Cr <sub>2</sub> O <sub>3</sub>	0.454	96.6	0.0047	0.343	102	0.0033
TiO <sub>2</sub> · V <sub>2</sub> O <sub>5</sub>	0.199	*)	—	0.140	1.9	0.074
TiO <sub>2</sub> · Mn <sub>2</sub> O <sub>5</sub>	0.502	92.1	0.0055	0.445	95.3	0.0047
TiO <sub>2</sub> · Co <sub>3</sub> O <sub>4</sub>	0.580	77.4	0.0075	0.355	70.8	0.0050
TiO <sub>2</sub> · NiO	0.351	89.8	0.0039	0.403	100	0.0040
TiO <sub>2</sub> · CuO	0.564	27.8	0.020	0.247	23.9	0.0103
ZnO · Fe <sub>2</sub> O <sub>3</sub>	0.243	40.7	0.0059	0.150	38.5	0.0039
Al <sub>2</sub> O <sub>3</sub> · NiO	0.266	85.7	0.0031	0.422	126	0.0033
Al <sub>2</sub> O <sub>3</sub> · Co <sub>3</sub> O <sub>4</sub>	0.349	110	0.0032	0.348	138	0.0025
Al <sub>2</sub> O <sub>3</sub> · MoO <sub>3</sub>	0.621	133	0.0047	0.617	—	—
Al <sub>2</sub> O <sub>3</sub> · CdO	0.351	78	0.0045	0.846	93.8	0.0091
Al <sub>2</sub> O <sub>3</sub> · Fe <sub>2</sub> O <sub>3</sub>	0.691	158	0.0044	0.492	171	0.0029
Al <sub>2</sub> O <sub>3</sub> · Cr <sub>2</sub> O <sub>3</sub>	0.235	154	0.0015	0.518	112	0.0046
Al <sub>2</sub> O <sub>3</sub> · Mn <sub>2</sub> O <sub>3</sub>	0.575	107	0.0054	0.598	—	—
TiO <sub>2</sub>	0.050	38	0.00013	—	—	—
CdO	0.289	2.2	0.131	8.43	**)	—
Fe <sub>2</sub> O <sub>3</sub>	0.279	48	0.0058	0.114	—	—
CuO	0.170	1.5	0.113	***)	—	—

\*) Too small to measure.

\*\*) A part was melted by reduction.

\*\*\*) A part was melted by reduction. Difficult to measure due to evaporation onto wall of vessel.

acidity in oxidized state was found to be 0.708 mmol/g for TiO<sub>2</sub> · Fe<sub>2</sub>O<sub>3</sub> and that in reduced state to be 0.846 mmol/g for Al<sub>2</sub>O<sub>3</sub> · CdO. The acidity of TiO<sub>2</sub> · Fe<sub>2</sub>O<sub>3</sub> is larger than that of TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> alone and that of ZnO · Fe<sub>2</sub>O<sub>3</sub>. Since the latter mixed oxide was reported recently to act as a catalyst for the alkylation of phenol by methyl alcohol and to show extremely high selectivity of more than 90% for the formation of 2,6-xyleneol,<sup>4)</sup> the catalytic activity and selectivity of oxidized TiO<sub>2</sub> · Fe<sub>2</sub>O<sub>3</sub>, whose acidity is much higher

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than that of oxidized  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$  (see Table 3), were examined briefly. The conversion of phenol was found to be about 63 mol% and the selectivity for 2, 6-xylene and *o*-cresol to be 42 and 56 mol% respectively, the formation of other alkylated isomers being negligible. The reaction conditions were as follows: reaction temperature; 330~380°C, LHSV; 0.5 hr<sup>-1</sup>, molar ratio of phenol to alcohol; 1 : 10.

Now we shall see the correlation of acidity with the extent of surface oxidation. As shown in Table 3, the acidities per unit surface area of most of the oxides were decreased by reduction, while reduction increases the acidities of only two species of  $\text{Al}_2\text{O}_3 \cdot \text{CdO}$  and  $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ . The result of  $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$  is not in agreement with Voltz and his coworker's result<sup>1)</sup> that the acidity of the oxide is decreased by reduction. The acidity increase of  $\text{Al}_2\text{O}_3 \cdot \text{CdO}$  by reduction seems partly due to the reaction of reduced cadmium metal with *n*-butylamine. However, the acidities of  $\text{TiO}_2 \cdot \text{CuO}$ ,  $\text{TiO}_2 \cdot \text{NiO}$  and  $\text{Al}_2\text{O}_3 \cdot \text{NiO}$  were decreased or unchanged by reduction, though the metallic copper and nickel are known to react with amines.

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