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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^2, the largest acidity being found for $TiO_2 \cdot Fe_2O_3$ in oxidized state. It was also found that most of the oxides decrease their acidities on reduction, whereas reduction increases the acidities of $Al_2O_3 \cdot CdO$ and $Al_2O_3 \cdot Cr_2O_3$.

Introduction

Acidic properties of various binary metal oxide catalysts such as $SiO_2 \cdot Al_2O_3$, $SiO_2 \cdot MgO$, $Al_2O_3 \cdot B_2O_3$ 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 $Cr_2O_3 \cdot Al_2O_3$[1]) and $MoO_3 \cdot Fe(MoO_4)_3$,[2]) 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[3]) 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_2O_3 or $SiO_2 \cdot Al_2O_3$,[1~2]) 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
$TiO_2 \cdot WO_3$	$(NH_4)_2W_4O_{13} \cdot 8H_2O$, $TiCl_4$	yellow	black
$TiO_2 \cdot MoO_3$	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $TiCl_4$	dark green	black
$TiO_2 \cdot Sb_2O_5$	$SbCl_5$, $TiCl_4$	yellow	green
$TiO_2 \cdot Fe_2O_3$	$FeCl_3 \cdot 6H_2O$, $TiCl_4$	brown	black
$TiO_2 \cdot Cr_2O_3$	$Cr(NO_3)_3 \cdot 9H_2O$, $TiCl_4$	dark green	green
$TiO_2 \cdot V_2O_5$	$NH_4(VO_3)$, $TiCl_4$	gray	black
$TiO_2 \cdot Mn_2O_3$	$MnCl_2 \cdot 4H_2O$, $TiCl_4$	dark brown	brown
$TiO_2 \cdot Co_3O_4$	$CoCl_2 \cdot H_2O$, $TiCl_4$	black	black
$TiO_2 \cdot NiO$	$NiCl_2 \cdot 6H_2O$, $TiCl_4$	green	black
$TiO_2 \cdot CuO$	$CuCl_2 \cdot 2H_2O$, $TiCl_4$	dark violet	violet
$ZnO \cdot Fe_2O_3$	$FeCl_3 \cdot 6H_2O$, $ZnCl_2$	brown	black
$Al_2O_3 \cdot NiO$	$NiCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$	dark green	black
$Al_2O_3 \cdot Co_3O_4$	$CoCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$	black	dark green
$Al_2O_3 \cdot MoO_3$	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $AlCl_3 \cdot 6H_2O$	yellow	black
$Al_2O_3 \cdot CdO$	$CdCl_2 \cdot H_2O$, $AlCl_3 \cdot 6H_2O$	brown	yellow
$Al_2O_3 \cdot Fe_2O_3$	$FeCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$	dark brown	black
$Al_2O_2 \cdot Cr_2O_3$	$Cr(NO_3)_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$	black	green
$Al_2O_3 \cdot MnO_3$	$MnCl_2 \cdot 4H_2O$, $AlCl_3 \cdot 6H_2O$	brown	brown
TiO_2	$TiCl_4$	white	
CdO	$CdCl_2 \cdot H_2O$	brown	white
Fe_2O_3	$FeCl_3 \cdot 6H_2O$	brown	black

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 mmϕ), 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(3) using methyl red of pKa = 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 pKa = 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 (pKa = 4.8) and *n*-butylamine (pKa = 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.

TABLE 2. Effect of adsorption time on acidity.
Oxide sample: Al_2O_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, MgO, $ZnO \cdot Al_2O_3$, $SiO_2 \cdot ZnO$, $SiO_2 \cdot TiO_2$, $Al_2O_3 \cdot ZrO_2$ and $Al_2O_3 \cdot TiO_2$ were measured by both methods. The results are shown in Fig. 1, where the acidity measured by amine titration method using methyl red (pKa=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.

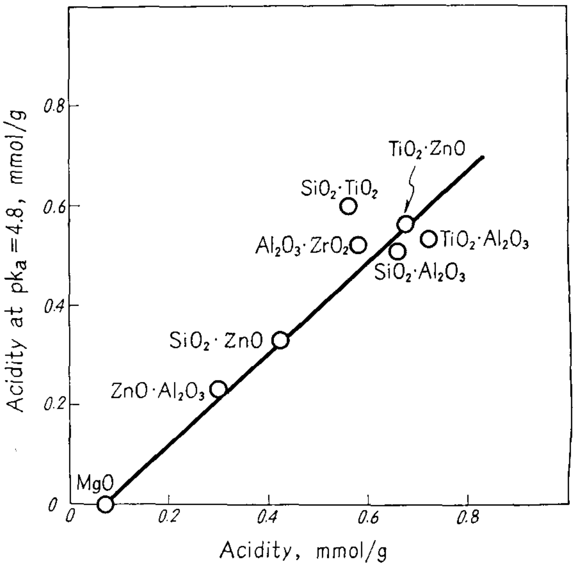

Fig. 1. Acidity by usual amine titration method *vs.* acidity by back titration method.

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^2. The largest

TABLE 3. Acidity of binary metal oxides

Metal oxides	Oxidized			Reduced		
	Acidity mmol/g	Surface area m^2/g	Acidity $mmol/m^2$	Acidity mmol/g	Surface area m^2/g	Acidity $mmol/m^2$
$TiO_2 \cdot WO_3$	0.167	44.7	0.0037	0.190	50.8	0.0038
$TiO_2 \cdot MoO_3$	0.198	28.2	0.0070	0.165	56.0	0.0029
$TiO_2 \cdot Sb_2O_5$	0.477	124	0.0038	0.263	125	0.0021
$TiO_2 \cdot Fe_2O_3$	0.708	109	0.0065	0.353	108	0.0033
$TiO_2 \cdot Cr_2O_3$	0.454	96.6	0.0047	0.343	102	0.0033
$TiO_2 \cdot V_2O_5$	0.199	*)	—	0.140	1.9	0.074
$TiO_2 \cdot Mn_2O_5$	0.502	92.1	0.0055	0.445	95.3	0.0047
$TiO_2 \cdot Co_3O_4$	0.580	77.4	0.0075	0.355	70.8	0.0050
$TiO_2 \cdot NiO$	0.351	89.8	0.0039	0.403	100	0.0040
$TiO_2 \cdot CuO$	0.564	27.8	0.020	0.247	23.9	0.0103
$ZnO \cdot Fe_2O_3$	0.243	40.7	0.0059	0.150	38.5	0.0039
$Al_2O_3 \cdot NiO$	0.266	85.7	0.0031	0.422	126	0.0033
$Al_2O_3 \cdot Co_3O_4$	0.349	110	0.0032	0.348	138	0.0025
$Al_2O_3 \cdot MoO_3$	0.621	133	0.0047	0.617	—	—
$Al_2O_3 \cdot CdO$	0.351	78	0.0045	0.846	93.8	0.0091
$Al_2O_3 \cdot Fe_2O_3$	0.691	158	0.0044	0.492	171	0.0029
$Al_2O_3 \cdot Cr_2O_3$	0.235	154	0.0015	0.518	112	0.0046
$Al_2O_3 \cdot Mn_2O_3$	0.575	107	0.0054	0.598	—	—
TiO_2	0.050	38	0.00013	—	—	—
CdO	0.289	2.2	0.131	8.43	**)	—
Fe_2O_3	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 $TiO_2 \cdot Fe_2O_3$ and that in reduced state to be 0.846 mmol/g for $Al_2O_3 \cdot CdO$. The acidity of $TiO_2 \cdot Fe_2O_3$ is larger than that of TiO_2 or Fe_2O_3 alone and that of $ZnO \cdot Fe_2O_3$. 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-xylenol,[4] the catalytic activity and selectivity of oxidized $TiO_2 \cdot Fe_2O_3$, whose acidity is much higher than that of oxidized $ZnO \cdot Fe_2O_3$ (see Table 3), were examined briefly. The conversion of phenol was found to be about 63 mol% and the selectivity for 2, 6-xylenol 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^{-1}, 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 $Al_2O_3 \cdot CdO$ and $Al_2O_3 \cdot Cr_2O_3$. The result of $Al_2O_3 \cdot Cr_2O_3$ is not in agreement with Voltz and his coworker's result[1] that the acidity of the oxide is decreased by reduction. The acidity increase of $Al_2O_3 \cdot CdO$ by reduction seems partly due to the reaction of reduced cadmium metal with *n*-butylamine. However, the acidities of $TiO_2 \cdot CuO$, $TiO_2 \cdot NiO$ and $Al_2O_3 \cdot NiO$ were decreased or unchanged by reduction, though the metallic copper and nickel are known to react with amines.

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