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(Note)

ACIDIC PROPERTIES OF $ZnO \cdot As_2O_3$, $ZnO \cdot Sb_2O_3$, $ZnO \cdot Bi_2O_3$, $ZnO \cdot ZrO_2$ AND $ZrO_2 \cdot ThO_2$ AND CATALYTIC ACTIVITY OF $ZnO \cdot Bi_2O_3$ FOR ALKYLATION OF PHENOL WITH METHANOL

By

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Some limited mixed metal oxides such as $SiO_2 \cdot Al_2O_3$, $SiO_2 \cdot MgO$, $SiO_2 \cdot ZrO_2$, $Al_2O_3 \cdot B_2O_3$, $Al_2O_3 \cdot MgO$ have been known to have acid sites on the surfaces which are catalytically active for many acid-catalyzed reactions.[1] Recently, many other mixed metal oxides were found to show significant surface acidity.[2)-5)] Thus, various combinations of oxides of various metals in the periodic table are expected to exhibit acidic property. A systematic study is needed to elucidate the correlation between the combination and the acidic property. For the purpose, several mixed oxides given in the title are prepared and their acidic and basic properties were qualitatively measured and the effects of composition and calcination temperature on acidic and basic properties were also studied. Among five mixed oxides, $ZnO \cdot Bi_2O_3$ which showed highest acidity was tested for its catalytic activity for the alkylation of phenol with methanol.

Experimental

Preparation of metal oxides and mixed oxides

1) ZnO, As_2O_3 and $ZnO \cdot As_2O_3$: ZnO was prepared by calcining $Zn(OH)_2$ at various temperatures for 3 hrs which was precipitated by adding 28% ammonia water to $ZnCl_2$ solution, final pH of the solution being 7 (see ref. 5 for the detailed procedure). As_2O_3 was prepared by filtering the precipitate formed by adding 1 ℓ of water to 500 g of $AsCl_3$, by washing it with water until no chloride ion was detected and by calcining at 300° and 500° for 3 hrs after dried at 120° for 24 hrs. $ZnO \cdot As_2O_3$ was prepared by kneading the mixture of As_2O_3 dried at 120°

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and $Zn(OH)_2$ with a proper amount of water in a kneader for 2 hrs. and by calcining it after dried overnight.

2) Sb_2O_3, Bi_2O_3, $ZnO \cdot Sb_2O_3$ and $ZnO \cdot Bi_2O_3$: $ZnO \cdot Bi_2O_3$ (wt. ratio 1 : 1) was prepared as follows. A 54.1 g of $BiCl_3$ was dissolved in an acidic solution which was made by adding 30 mℓ of conc. HCl into 100 mℓ of water (bismuth hydroxide does not precipitate at less than pH=3). The solution was mixed with 200 mℓ of water in which 67 g of $ZnCl_2$ and 70 g of $(NH_4)_2SO_4$ were dissolved. The mixture was warmed over water bath for 1 hr. and then 28% ammonia water was added until pH of the solution became around 7 and warmed up again to make complete formation of the precipitates. The precipitate was filtered off and washed thoroughly with distilled water until no anions of chloride and sulfate were detected in the washing.

The mixed oxide was obtained by calcining the precipitates at various temperatures for 3 hrs after dried overnight at 110°C. Two other kinds of $ZnO \cdot Bi_2O_3$ of different compositions and Bi_2O_3 were prepared similarly as above, the amounts of used reagents and final pH being given in Table 1.

TABLE 1. Conditions for preparation of $ZnO \cdot Bi_2O_3$

Mixed oxides (wt. ratio)			$ZnO \cdot Bi_2O_3$ (19 : 1)	$ZnO \cdot Bi_2O_3$ (1 : 19)	Bi_2O_3
Solution	I	$BiCl_3$	5.4 g	103 g	31.5 g
		H_2O	25 mℓ	100 mℓ	100 mℓ
		HCl	25 mℓ	27 mℓ	20 mℓ
	II	$ZnCl_2$	127 g	6.7 g	
		H_2O	100 mℓ	50 mℓ	
		HCl	10 mℓ	2 mℓ	
	III	$(NH_4)_2SO_4$	70 g	70 g	
		H_2O	100 mℓ	100 mℓ	
28% NH_3 water			150 mℓ	60 mℓ	33.5 mℓ
Final pH			6.8	7.3	7.6

Several mixed oxides of $ZnO \cdot Sb_2O_3$ of different compositions and Sb_2O_3 were prepared similarly as $ZnO \cdot Bi_2O_3$, except that the solution to which ammonia water was added was not warmed up to prevent the formed precipitates from dissolution. The conditions for preparations are listed in Table 2. Ammonia water was added until pH of the solution became 6.5 in each case.

3) ZrO_2, ThO_2, $ZnO \cdot ZrO_2$ and $ZrO_2 \cdot ThO_2$: ZrO_2 and ThO_2 were prepared

TABLE 2. Conditions for preparation of $ZnO \cdot Sb_2O_3$

Mixed oxides (wt. ratio)			$ZnO \cdot Sb_2O_3$ (19 : 1)	$ZnO \cdot Sb_2O_3$ (1 : 1)	$ZnO \cdot Sb_2O_3$ (1 : 19)	Sb_2O_3
Solution	I	$SbCl_3$	9.9 g	125 g	123 g	125 g
		H_2O	50 mℓ	100 mℓ	100 mℓ	100 mℓ
		HCl	25 mℓ	30 mℓ	40 mℓ	25 mℓ
	II	$ZnCl_2$	119 g	134 g	11 g	
		H_2O	100 mℓ	100 mℓ	50 mℓ	
		HCl	12 mℓ	10 mℓ	10 mℓ	
	III	NH_4Cl	37 g	37 g	37 g	
		H_2O	100 mℓ	100 mℓ	100 mℓ	

by the following manner. Each 50 g of zirconium oxychloride ($ZrOCl_2$) and thorium nitrate ($Th(NO_3)_4 \cdot 4H_2O$) was dissolved in 500 mℓ water and excess of 28% ammonia water (50 mℓ) was added to each solution. The formed precipitates were filtered off and washed with water until pH of the washing decreased to about 8 and then dried at 110°C for 2 days. Their oxides were obtained by calcining their hydroxides respectively at various temperatures for 3 hrs.

The mixed metal oxides of $ZnO \cdot ZrO_2$ and $ZrO_2 \cdot ThO_2$ were prepared similarly as above.

All reagents used were guaranteed reagents of Wako Pure Chemical Co.

Measurement of Acidic and Basic Properties.

The acid amounts and strengths of the oxides and mixed oxides were measured by titrating the 100–200 mesh powder suspended in benzene with 0.1N *n*-butylamine benzene solution, using neutral red (pKa=6.8), methyl red (4.8), 4-phenylazo-1-naphthylamine (4.0), *p*-dimethylaminobenzene (3.3), benzeneazodiphenylamine (1.5), dicinnamalacetone (−3) or benzalacetophenone (−5.6) as an indicator. The basic properties were measured similarly by titrating with 0.1N benzoic acid, using bromothymol blue (pKa=7.1), phenolphthalein (9.3), 2, 4, 6-trinitroaniline (12.2), 2, 4-dinitroaniline (15.0) or 4-chloro-2-nitroaniline (17.2) as an indicaitor.

Alkylation Reaction

The alkylation of phenol by methanol was carried out by using a usual flow method at 400°C. Equimolar amounts of phenol and methanol were passed over about 2 g of catalyst at various contact times (g·sec/mℓ). The products were analyzed by a gaschromatograph using a column of polyethylene glycol on celite.

Results and Discussion

Acidic and Basic Properties

1) $ZnO \cdot As_2O_3$: Acidic properties of $ZnO \cdot As_2O_3$ calcined at 300° and 500°C are shown in Table 3. As_2O_3 did not show any acidic property when calcined at

TABLE 3. Acidic Property of $ZnO \cdot As_2O_3$

Calcination temp. °C	$As_2O_3/ZnO \cdot As_2O_3$ wt. %	Acidity at different pKa values (mmol/g)				
		4.8	4.0	3.3	1.5	−3
300	100	− **)	−	−	−	−
	95*)	<0.07	<0.07	<0.07	<0.07	−
	50*)	0.6±0.2	0.15±0.05	0.15±0.05	<0.11	−
	5*)	0.6±0.2	0.15±0.05	0.15±0.05	<0.10	−
	0	2.8		1.2	0.44	−
500	100	+***)	+	+	±****)	−
	95*)	+	+	+	−	−
	50*)	+	+	+	+	−
	5*)	+	+	+	−	−
	0*)	1.8		1.2	0.67	−

*) Since considerable amount of As_2O_3 sublimed by calcination at 300°C and 500°C, the indicated valus which were calculated from mixing ratios are larger than the true values after calcination.

**) − denotes that acidic color of indicator was not observed.

***) + denotes that acidic color of indicator was observed on the surface.

****) ± denotes that slight acidic color was observed.

300°C, but showed weak acidic property when calcined at 500°C. Any of various compositions of $As_2O_3 \cdot ZnO$ did not change the basic color of the indicator having pKa=−3 to its acidic color and any of the acid amounts observed at pKa=4.8~1.5 were less than the acid amounts of ZnO alone. It would be interesting to note that TiO_2 showed very high acid strength of pKa=−5.6, when it contained 5% of ZnO.[5]

2) $ZnO \cdot Sb_2O_3$: The acid amounts at various acid strengths of $ZnO \cdot Sb_2O_3$ of different compositions calcined at 300°, 400° and 500°C are shown Fig. 1. The acid amounts of ZnO sharply decrease when small amounts of Sb_2O_3 are mixed.

3) $ZnO \cdot Bi_2O_3$: The acid amounts at various acid strengths of $ZnO \cdot Bi_2O_3$ of different compositions are shown in Fig. 2. Bi_2O_3 itself showed fairly large acid amounts, the values being about 0.03 mmol/g even at pKa=−3 when it was calcined at 300° or 400°C. The acid amounts of $ZnO \cdot Bi_2O_3$ containing 50% of ZnO

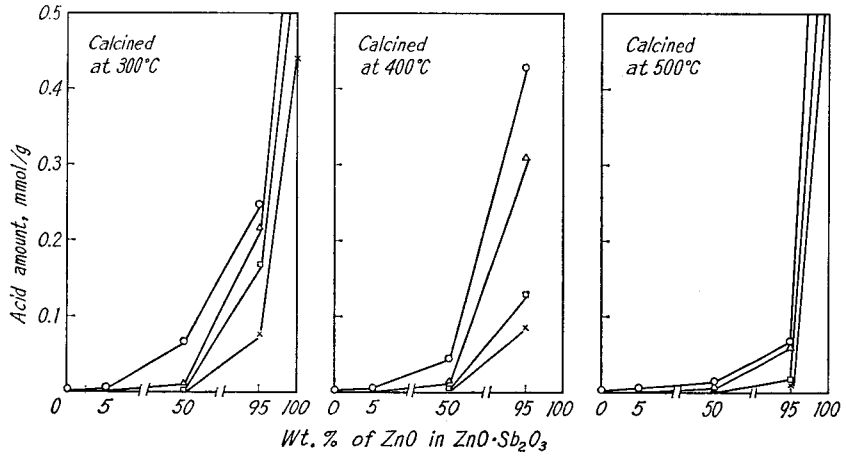

Fig. 1. Acidic properties of $ZnO \cdot Sb_2O_3$ calcined at various temperatures.
○: pKa 6.8, △: 4.8, □: 3.3, ×: 1.5.

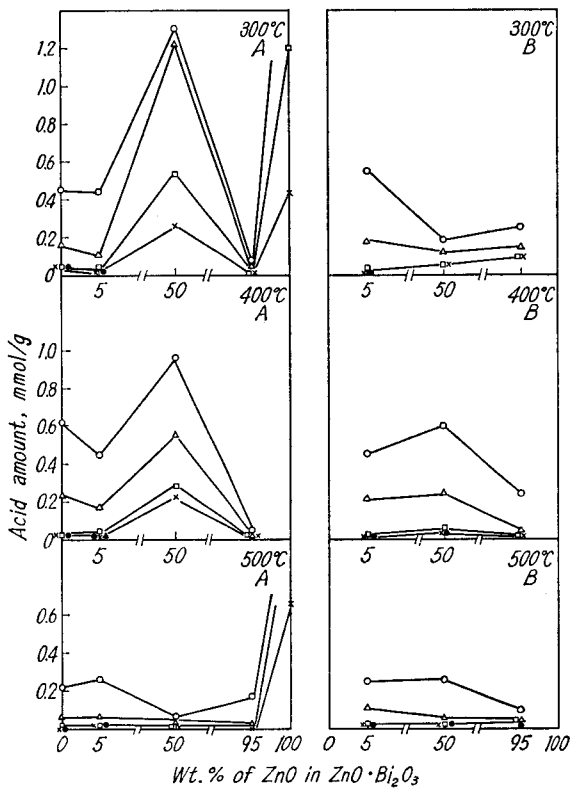

Fig. 2. Acidic properties of $ZnO \cdot Bi_2O_3$ calcined at various temperatures
A: prepared without $(NH_4)_2SO_4$, B: with $(NH_4)_2SO_4$.
○: pKa=6.8, △: 4.8, □: 3.3, ×: 1.5, ●: −3, ▲: −5.6.

were larger than those containing 5% or 95% of ZnO when calcined at 300° or 400°C. The acidity of the mixed oxides prepared by the additon of $(NH_4)_2SO_4$

TABLE 4. Acid-Base Properties of $ZnO \cdot ZrO_2$

Calcination temp. °C	$ZrO_2/ZnO \cdot ZrO_2$ wt. %	Acid amount at different pKa (mmol/g)					Base amount at different pKa (mmol/g)				
		−3	1.5	3.3	4.8	6.8	7.1	9.3	12.2	15.0	17.2
400	100	−	−	−	±	<0.19	−				
	95	−	0.62								0.15
	50	−	−	−	−	±					0.039
	5	−	0.12				±		−		
550	100	−	−	−	−	−	−				
	95	−	0.12								0.12
	50	−	−	0.10							0.16
	5	−	0.076				−	−	−	−	−
700	100	−	−	−	−	−	−				
	95	−	−	−	−	0.081			0.11	−	−
	50	−	−	−	−	0.070					
	5	−	−	±				−	−	−	−

*) See Table 3 for denotations of +, −, ±.

TABLE 5. Acid-Base Properties of $ThO_2 \cdot ZrO_2$

Calcination temp. °C	$ThO_2/ZrO_2 \cdot ThO_2$ wt. %	Acid amount at various pKa (mmol/g)			Base amount at various pKa (mmol/g)				
		3.3	4.8	6.8	7.1	9.3	12.2	15.0	17.2
400	100	−	−	~0.6	−	−			
	95	−	0.72		+	+	+	+	+
	50	−	−	±	−	−	−	−	−
	5	−	−	±	−	−	−	−	−
550	100	−	±	0.12	−	~0.8			
	95	−	−	±	−	−	−	−	−
	50	−	−	±	−	−	−	−	−
	5	−	−	−	−	−	−	−	−
700	100	−	0.18	0.18	−	>1.0			
	95	−	−	±	−	−	−	−	−
	50	−	−	±	−	−	−	−	−
	5	−	−	±	−	−	−	−	−

*) See Table 2 for denotations of +, −, ±.

(see B in Fig. 2) was found to be lower than those prepared without $(NH_4)_2SO_4$.

4) $ZnO \cdot ZrO_2$: The acid and base amounts at various acid and base strengths of $ZnO \cdot ZrO_2$ of different compositions are given in Table 4. Zirconium oxide itself showed slightly weak acidic property only when calcined at 400°C, but did not show any basic property. However, $ZrO_2 \cdot ZnO$ containing 5% of ZnO showed fairly large acid amounts (0.62, 0.12 mmol/g) as well as fairly high acid strength (pKa=1.5) when calcined at 400 or 550°C. The mixed oxides showed also basic property when they contained 5 or 50% of ZnO.

5) $ThO_2 \cdot ZrO_2$: The results of the mixed oxides are given in Table 5. Thorium oxides calcined at 400, 550 or 700°C showed very slightly weak acidic property and the oxides calcined at 550 or 700°C gave considerable amounts of basic sites (0.8~1.0 mmol/g) at pKa=9.3. When $ThO_2 \cdot ZrO_2$ containing 5% of ZrO_2 was calcined at 400°C, it showed not only acid strength of pKa=4.8 higher than that of ThO_2 alone, but also basic property. On the other hand, the mixed oxides calcined at 550 or 700°C showed lower acid strength and gave no basic property.

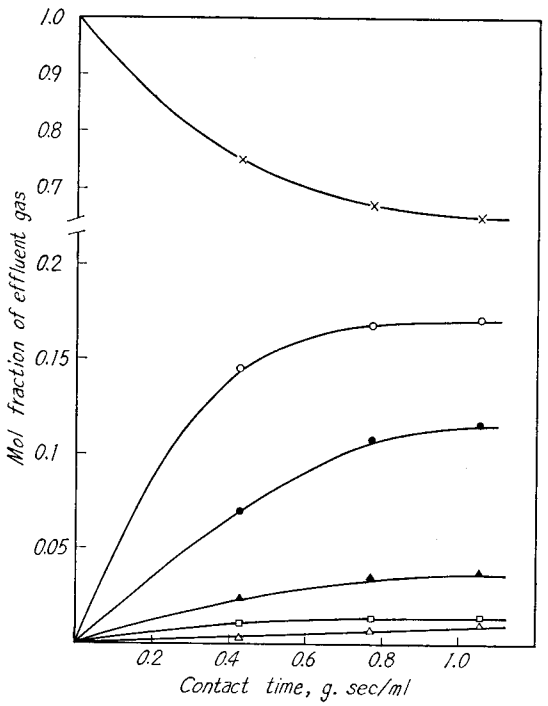

Fig. 3. Alkylation of phenol with methanol over $ZnO \cdot Bi_2O_3$.
×: phenol, ○: *o*-cresol, ●: *m*- or/and *p*-cresol,
△: 2, 6-xylenol, ▲: 2, 4-xylenol, □: anisol.

Activity of $ZnO \cdot Bi_2O_3$ for Alkylation of Phenol

Since $ZnO \cdot Bi_2O_3$ containing 50% of ZnO showed comparatively large acid amounts and high acid strength, the catalytic activity and selectivity of the mixed oxide calcined at 400°C for 3 hrs was tested for the alkylation of phenol with methanol. The mol fraction of effluent gas plotted against contact time is shown in Fig. 3. The catalyst gave both mono- and di-alkylated phenols in contrast with $ZnO \cdot TiO_2$ which gave only monoalkylated phenols under the same experimental condition.[5] The high selectivity for the alkylation to ortho position found in the case of $ZnO \cdot Fe_2O_3$ catalyst[6] was not found with the present catalyst.

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