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Title	ACIDIC PROPERTIES OF ZnO·As ₂ O ₃ , ZnO·Sb ₂ O ₃ , ZnO·Bi ₂ O ₃ , ZnO·ZrO ₂ AND ZrO ₂ ·ThO ₂ AND CATALYTIC ACTIVITY OF ZnO·Bi ₂ O ₃ FOR ALKYLATION OF PHENOL WITH METHANOL
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(Note)

ACIDIC PROPERTIES OF $\text{ZnO}\cdot\text{As}_2\text{O}_3$, $\text{ZnO}\cdot\text{Sb}_2\text{O}_3$, $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$,
 $\text{ZnO}\cdot\text{ZrO}_2$ AND $\text{ZrO}_2\cdot\text{ThO}_2$ AND CATALYTIC
ACTIVITY OF $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ FOR ALKYLATION OF
PHENOL WITH METHANOL

By

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Some limited mixed metal oxides such as $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$, $\text{SiO}_2\cdot\text{MgO}$, $\text{SiO}_2\cdot\text{ZrO}_2$, $\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$, $\text{Al}_2\text{O}_3\cdot\text{MgO}$ 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, $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ 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 $\text{ZnO}\cdot\text{As}_2\text{O}_3$: ZnO was prepared by calcining $\text{Zn}(\text{OH})_2$ 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. $\text{ZnO}\cdot\text{As}_2\text{O}_3$ was prepared by kneading the mixture of As_2O_3 dried at 120°

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and $\text{Zn}(\text{OH})_2$ 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 , $\text{ZnO}\cdot\text{Sb}_2\text{O}_3$ and $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$: $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ (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 $\text{pH}=3$). The solution was mixed with 200 ml of water in which 67 g of ZnCl_2 and 70 g of $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ 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 $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$

Mixed oxides (wt. ratio)		$\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ (19 : 1)	$\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ (1 : 19)	Bi_2O_3
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
Solution II	ZnCl_2	127 g	6.7 g	
	H_2O	100 ml	50 ml	
	HCl	10 ml	2 ml	
III	$(\text{NH}_4)_2\text{SO}_4$	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 $\text{ZnO}\cdot\text{Sb}_2\text{O}_3$ of different compositions and Sb_2O_3 were prepared similarly as $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$, 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 , $\text{ZnO}\cdot\text{ZrO}_2$ and $\text{ZrO}_2\cdot\text{ThO}_2$: ZrO_2 and ThO_2 were prepared

Acidic Properties of Mixed Metal Oxides and Catalytic Activity of ZnO·Bi₂O₃

TABLE 2. Conditions for preparation of ZnO·Sb₂O₃

Mixed oxides (wt. ratio)		ZnO·Sb ₂ O ₃ (19 : 1)	ZnO·Sb ₂ O ₃ (1 : 1)	ZnO·Sb ₂ O ₃ (1 : 19)	Sb ₂ O ₃
I	SbCl ₃	9.9 g	125 g	123 g	125 g
	H ₂ O	50 ml	100 ml	100 ml	100 ml
	HCl	25 ml	30 ml	40 ml	25 ml
Solution II	ZnCl ₂	119 g	134 g	11 g	
	H ₂ O	100 ml	100 ml	50 ml	
	HCl	12 ml	10 ml	10 ml	
III	NH ₄ Cl	37 g	37 g	37 g	
	H ₂ O	100 ml	100 ml	100 ml	

by the following manner. Each 50 g of zirconium oxychloride (ZrOCl₂) and thorium nitrate (Th(NO₃)₄·4H₂O) 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·ZrO₂ and ZrO₂·ThO₂ 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 (pK_a=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 (pK_a=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 indicator.

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) $\text{ZnO} \cdot \text{As}_2\text{O}_3$: Acidic properties of $\text{ZnO} \cdot \text{As}_2\text{O}_3$ 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 $\text{ZnO} \cdot \text{As}_2\text{O}_3$

Calcination temp. °C	$\text{As}_2\text{O}_3/\text{ZnO} \cdot \text{As}_2\text{O}_3$ 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 values 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 $\text{As}_2\text{O}_3 \cdot \text{ZnO}$ did not change the basic color of the indicator having $\text{pKa} = -3$ to its acidic color and any of the acid amounts observed at $\text{pKa} = 4.8 \sim 1.5$ were less than the acid amounts of ZnO alone. It would be interesting to note that TiO_2 showed very high acid strength of $\text{pKa} = -5.6$, when it contained 5% of ZnO .⁵⁾

2) $\text{ZnO} \cdot \text{Sb}_2\text{O}_3$: The acid amounts at various acid strengths of $\text{ZnO} \cdot \text{Sb}_2\text{O}_3$ 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) $\text{ZnO} \cdot \text{Bi}_2\text{O}_3$: The acid amounts at various acid strengths of $\text{ZnO} \cdot \text{Bi}_2\text{O}_3$ 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 $\text{pKa} = -3$ when it was calcined at 300° or 400°C. The acid amounts of $\text{ZnO} \cdot \text{Bi}_2\text{O}_3$ containing 50% of ZnO

Acidic Properties of Mixed Metal Oxides and Catalytic Activity of $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$

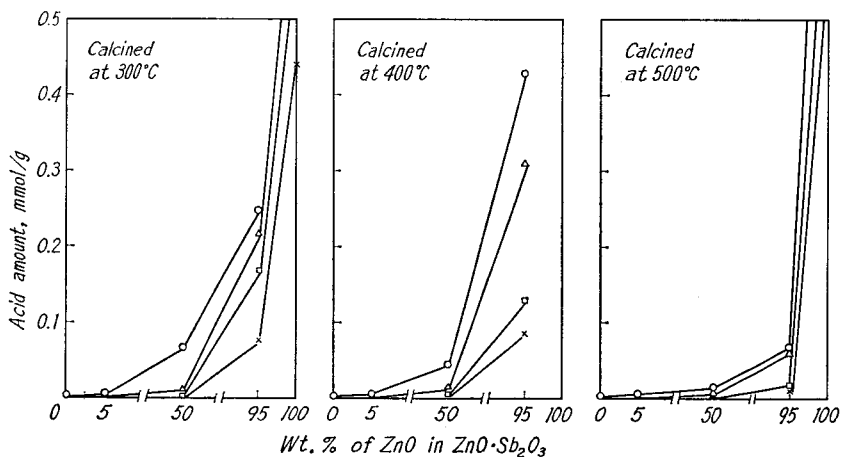


Fig. 1. Acidic properties of $\text{ZnO}\cdot\text{Sb}_2\text{O}_3$ calcined at various temperatures.
 ○: pKa 6.8, △: 4.8, □: 3.3, ×: 1.5.

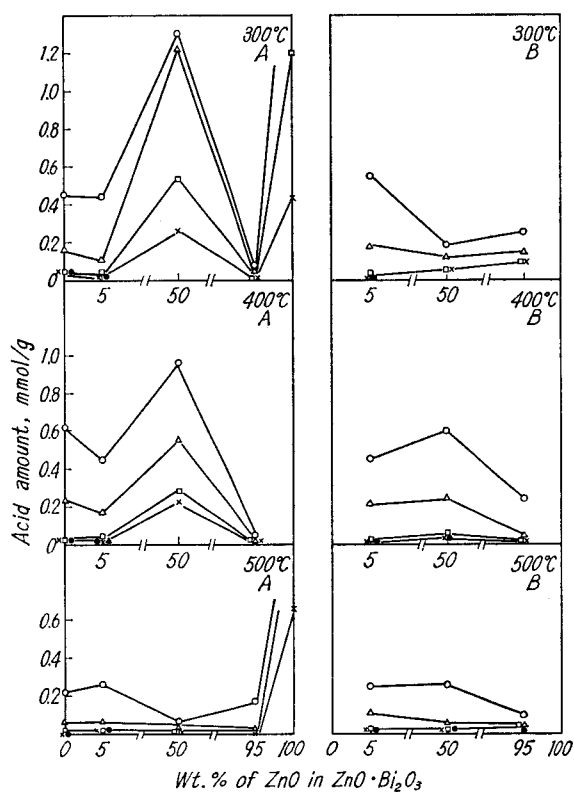


Fig. 2. Acidic properties of $\text{ZnO}\cdot\text{Bi}_2\text{O}_3$ calcined at various temperatures
 A: prepared without $(\text{NH}_4)_2\text{SO}_4$, B: with $(\text{NH}_4)_2\text{SO}_4$.
 ○: pKa=6.8, △: 4.8, □: 3.3, ×: 1.5, ●: -3, ▲: -5.6.

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 addition of $(\text{NH}_4)_2\text{SO}_4$

TABLE 4. Acid-Base Properties of $\text{ZnO}\cdot\text{ZrO}_2$

Calcination temp. °C	$\text{ZrO}_2/\text{ZnO}\cdot\text{ZrO}_2$ 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 $\text{ThO}_2\cdot\text{ZrO}_2$

Calcination temp. °C	$\text{ThO}_2/\text{ZrO}_2\cdot\text{ThO}_2$ 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 +, -, ±.

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(see B in Fig. 2) was found to be lower than those prepared without (NH₄)₂SO₄.

4) ZnO·ZrO₂: The acid and base amounts at various acid and base strengths of ZnO·ZrO₂ 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, ZrO₂·ZnO containing 5% of ZnO showed fairly large acid amounts (0.62, 0.12 mmol/g) as well as fairly high acid strength (pK_a=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) ThO₂·ZrO₂: 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 pK_a=9.3. When ThO₂·ZrO₂ containing 5% of ZrO₂ was calcined at 400°C, it showed not only acid strength of pK_a=4.8 higher than that of ThO₂ 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.

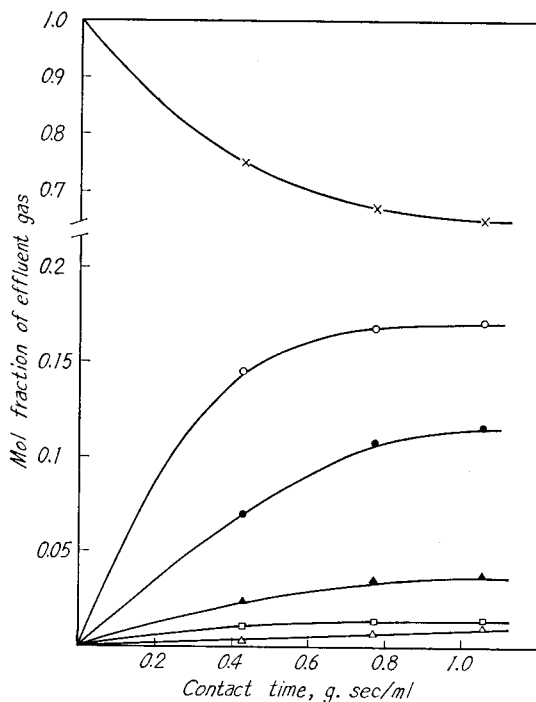


Fig. 3. Alkylation of phenol with methanol over ZnO·Bi₂O₃.
 ×: phenol, ○: *o*-cresol, ●: *m*- or/and *p*-cresol,
 Δ: 2,6-xylene, ▲: 2,4-xylene, □: anisol.

K. TANABE *et al.***Activity of ZnO·Bi₂O₃ for Alkylation of Phenol**

Since ZnO·Bi₂O₃ 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·TiO₂ 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·Fe₂O₃ catalyst⁶⁾ was not found with the present catalyst.

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