<table>
<thead>
<tr>
<th>Title</th>
<th>ACIDIC PROPERTIES OF ZnO・As₂O₃, ZnO・Sb₂O₃, ZnO・Bi₂O₃, ZnO・ZrO₂ AND ZrO₂・ThO₂ AND CATALYTIC ACTIVITY OF ZnO・Bi₂O₃ FOR ALKYLATION OF PHENOL WITH METHANOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>TANABE, Kozo; ICHIKAWA, Ichiro; IKEDA, Hiroko; HATTORI, Hideshi</td>
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<tr>
<td>Citation</td>
<td>JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 19(3): 185-192</td>
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ACIDIC PROPERTIES OF ZnO·As₂O₃, ZnO·Sb₂O₃, ZnO·Bi₂O₃, ZnO·ZrO₂ AND ZrO₂·ThO₂ AND CATALYTIC ACTIVITY OF ZnO·Bi₂O₃ FOR ALKYLATION OF PHENOL WITH METHANOL

By

Kozo Tanabe, Ichiro Ichikawa, Hiroko Ikeda and Hideshi Hattori

(Received November 4, 1971)

Some limited mixed metal oxides such as SiO₂·Al₂O₃, SiO₂·MgO, SiO₂·ZrO₂, Al₂O₃·B₂O₃, Al₂O₃·MgO have been known to have acid sites on the surfaces which are catalytically active for many acid-catalyzed reactions. Recently, many other mixed metal oxides were found to show significant surface acidity. 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·Bi₂O₃ 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, As₂O₃ and ZnO·As₂O₃: ZnO was prepared by calcining Zn(OH)₂ at various temperatures for 3 hrs which was precipitated by adding 28% ammonia water to ZnCl₂ solution, final pH of the solution being 7 (see ref. 5 for the detailed procedure). As₂O₃ was prepared by filtering the precipitate formed by adding 1 l of water to 500 g of AsCl₃, 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·As₂O₃ was prepared by kneading the mixture of As₂O₃ dried at 120°
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$_2$O$_3$, Bi$_2$O$_3$, ZnO·Sb$_2$O$_3$ and ZnO·Bi$_2$O$_3$: ZnO·Bi$_2$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 pH = 3). The solution was mixed with 200 ml of water in which 67 g of ZnCl$_2$ and 70 g of (NH$_4$)$_2$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 ZnO·Bi$_2$O$_3$ of different compositions and Bi$_2$O$_3$ 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·Bi$_2$O$_3$

<table>
<thead>
<tr>
<th>Mixed oxides (wt. ratio)</th>
<th>ZnO·Bi$_2$O$_3$ (19 : 1)</th>
<th>ZnO·Bi$_2$O$_3$ (1 : 19)</th>
<th>Bi$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>BiCl$_3$</td>
<td>5.4 g</td>
<td>103 g</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>25 ml</td>
<td>100 ml</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>25 ml</td>
<td>27 ml</td>
</tr>
<tr>
<td>Solution</td>
<td>ZnCl$_2$</td>
<td>127 g</td>
<td>6.7 g</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>100 ml</td>
<td>50 ml</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>10 ml</td>
<td>2 ml</td>
</tr>
<tr>
<td></td>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>70 g</td>
<td>70 g</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>100 ml</td>
<td>100 ml</td>
</tr>
<tr>
<td></td>
<td>28% NH$_3$ water</td>
<td>150 ml</td>
<td>60 ml</td>
</tr>
<tr>
<td></td>
<td>Final pH</td>
<td>6.8</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Several mixed oxides of ZnO·Sb$_2$O$_3$ of different compositions and Sb$_2$O$_3$ were prepared similarly as ZnO·Bi$_2$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$_2$, ZnO·ZrO$_2$ and ZrO$_2$·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·Sb₂O₃ (19 : 1) | ZnO·Sb₂O₃ (1 : 1) | ZnO·Sb₂O₃ (1 : 19) | Sb₂O₃  
|-------------------------|------------------|-----------------|-------------------|---------
| I                       | SbCl₃ 9.9 g      | 125 g           | 123 g             | 125 g   |
|                         | H₂O 50 ml        | 100 ml          | 100 ml            | 100 ml  |
|                         | HCl 25 ml        | 30 ml           | 40 ml             | 25 ml   |
| Solution II             | ZnCl₂ 119 g      | 134 g           | 11 g              |         |
|                         | H₂O 100 ml       | 100 ml          | 50 ml             |         |
|                         | HCl 12 ml        | 10 ml           | 10 ml             |         |
| III                     | NH₄Cl 37 g       | 37 g            | 37 g              |         |
|                         | H₂O 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 0.1 N n-butylamine benzene solution, using neutral red (pKa=6.8), methyl red (4.8), 4-phenylazo-1-naphthylamine (4.0), p-dimethylaninobenzene (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 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.
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Results and Discussion

Acidic and Basic Properties

1) ZnO·As$_2$O$_3$: Acidic properties of ZnO·As$_2$O$_3$ calcined at 300°C and 500°C are shown in Table 3. As$_2$O$_3$ did not show any acidic property when calcined at 300°C, but showed weak acidic property when calcined at 500°C. Any of various compositions of As$_2$O$_3$-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·Sb$_2$O$_3$: The acid amounts at various acid strengths of ZnO·Sb$_2$O$_3$ of different compositions calcined at 300°C, 400°C and 500°C are shown Fig. 1. The acid amounts of ZnO sharply decrease when small amounts of Sb$_2$O$_3$ are mixed.

3) ZnO·Bi$_2$O$_3$: The acid amounts at various acid strengths of ZnO·Bi$_2$O$_3$ of different compositions are shown in Fig. 2. Bi$_2$O$_3$ itself showed fairly large acid amounts, the values being about 0.03 mmol/g even at pKa=−3 when it was calcined at 300°C or 400°C. The acid amounts of ZnO·Bi$_2$O$_3$ containing 50% of ZnO

<table>
<thead>
<tr>
<th>Calcination temp. °C</th>
<th>As$_2$O$_3$/ZnO·As$_2$O$_3$ wt. %</th>
<th>Acidity at different pKa values (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4.8</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>− **)</td>
</tr>
<tr>
<td></td>
<td>95*)</td>
<td>&lt;0.07</td>
</tr>
<tr>
<td></td>
<td>50*)</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td></td>
<td>5*)</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td></td>
<td>0*</td>
<td>2.8</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>+***</td>
</tr>
<tr>
<td></td>
<td>95*)</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>50*)</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>5*)</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>0*</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*) Since considerable amount of As$_2$O$_3$ 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.
Acidic Properties of Mixed Metal Oxides and Catalytic Activity of ZnO·Bi₂O₃

Fig. 1. Acidic properties of ZnO·Sb₂O₃ calcined at various temperatures.

○: pKa=6.8, △: 4.8, □: 3.3, ×: 1.5.

Fig. 2. Acidic properties of ZnO·Bi₂O₃ calcined at various temperatures

A: prepared without (NH₄)₂SO₄, B: with (NH₄)₂SO₄.

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 (NH₄)₂SO₄

**Table 4. Acid-Base Properties of ZnO·ZrO₂**

<table>
<thead>
<tr>
<th>Calcination temp. °C</th>
<th>ZrO₂/ZnO·ZrO₂ wt. %</th>
<th>Acid amount at different pKa (mmol/g)</th>
<th>Base amount at different pKa (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>− − − − − ± &lt;0.19 −</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− 0.62</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − − − − ±</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− 0.12</td>
<td>± −</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>− − − − − −</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− 0.12</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − 0.10</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− 0.076</td>
<td>− − − − − −</td>
</tr>
<tr>
<td>550</td>
<td>100</td>
<td>− − − − − −</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− 0.12</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − 0.081</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td>700</td>
<td>100</td>
<td>− − − − − −</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− − − − − − 0.081</td>
<td>0.11 − − − −</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − − − − − 0.070</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− − − ±</td>
<td>− − − − − −</td>
</tr>
</tbody>
</table>

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

**Table 5. Acid-Base Properties of ThO₂·ZrO₂**

<table>
<thead>
<tr>
<th>Calcination temp. °C</th>
<th>ThO₂/ZrO₂·ThO₂ wt. %</th>
<th>Acid amount at various pKa (mmol/g)</th>
<th>Base amount at various pKa (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>− − − − − − ~0.6 −</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− 0.72</td>
<td>+ + + + + +</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− − − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>− ± 0.12</td>
<td>− ~0.8</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− − − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td>550</td>
<td>100</td>
<td>− ± 0.18</td>
<td>− &gt;1.0</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− − − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td>700</td>
<td>100</td>
<td>− − 0.18</td>
<td>− &gt;1.0</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>− − ±</td>
<td>− − − − − −</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>− − − ±</td>
<td>− − − − − −</td>
</tr>
</tbody>
</table>

*) See Table 2 for denotations of +, −, ±.
Acidic Properties of Mixed Metal Oxides and Catalytic Activity of ZnO-Bi₂O₃

(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 \( (p\text{Ka}=1.5) \) 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 \( (0.8\sim1.0 \text{ mmol/g}) \) at \( p\text{Ka}=9.3 \). When ThO₂·ZrO₂ containing 5% of ZrO₂ was calcined at 400°C, it showed not only acid strength of \( p\text{Ka}=4.8 \) 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.

![Graph](image-url)

**Fig. 3.** Alkylation of phenol with methanol over ZnO-Bi₂O₃.

\( \times \): phenol, \( \bigcirc \): o-cresol, \( \bullet \): m- or/and p-cresol,

\( \triangle \): 2, 6-xylenol, \( \blacktriangle \): 2, 4-xylenol, \( \square \): anisol.
Activity of ZnO·Bi_2O_3 for Alkylation of Phenol

Since ZnO·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·TiO_2 which gave only monoalkylated phenols under the same experimental condition. The high selectivity for the alkylation to ortho position found in the case of ZnO·Fe_2O_3 catalyst was not found with the present catalyst.

References