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Acid–Base and Catalytic Properties of Al_2O_3–ZnO

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Alumina–zinc oxide catalysts of various compositions were prepared from their nitrates by coprecipitation and the acidic and basic properties were measured by titrations with *n*-butylamine and benzoic acid using various indicators. The acidities (the numbers of acid sites) at $H_0 = -3.0$ and $H_0 = -5.6$ of Al_2O_3–ZnO catalysts prepared from their nitrates, were found to be lower than those of Al_2O_3–ZnO catalysts prepared from their chlorides by the same method. With the increase in ZnO content, the acidities per unit surface area decreased monotonously, whereas a maximum basicity was observed on Al_2O_3–ZnO (1:1), the highest base strength (pK_a) being 12.2. The activity change for alkylation of phenol with methanol was correlated well with the acidity change and the highest selectivity (almost 100%) for formations of *ortho* products, *o*-cresol and 2,6-xylenol, was observed on Al_2O_3–ZnO (1:9). Isomerization of 1-butene was suggested to proceed on basic sites on Al_2O_3–ZnO catalysts. In isomerization of 3-carene (I), the selectivity for formation of 2-carene (II) was more than 90% over Al_2O_3–ZnO (1:9). From poisoning experiments with CO_2 and pyridine, the active sites for formation of 2-carene were concluded to be both acidic and basic sites.

INTRODUCTION

Alumina–zinc oxide is known to catalyze the formation of isoparaffin from water gas (*1*) and the formation of butadiene from crotonaldehyde and ethanol (*2*). As for the surface property, Al_2O_3–ZnO prepared from aluminum chloride and zinc chloride by coprecipitation has recently been reported to show high acid strength as well as high acidity (*3*). However, no study has been made on the relations between preparation methods of Al_2O_3–ZnO and the acidic property and between the acid–base property and catalytic property. In the present work, acid–base properties of Al_2O_3–ZnO prepared from their nitrates by coprecipitation were measured and the catalytic activity as well as the selectivity for the alkylation of phenol with methanol and the isomerizations of 1-butene and 3-carene were examined. The catalytic action of Al_2O_3–ZnO is discussed in terms of the surface acid–base property.

EXPERIMENTAL

Preparation of catalysts. Alumina–zinc oxide catalysts were prepared by thermal decomposition of the hydroxides of aluminum and zinc at 500°C for 2 hr in air. The hydroxides were coprecipitated by adding an aqueous solution of aluminum nitrate and zinc nitrate to a buffer solution (pH 9.8) of ammonia water–ammonium nitrate, followed by drying at 110 to 120°C for 24 hr. Molar ratios of Al_2O_3 to ZnO were 9:1, 1:1, and 1:9. Alumina and ZnO were prepared similarly as above.

Measurements of surface area and acid–base property. Specific surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at −196°C. Surface acidity at various acid

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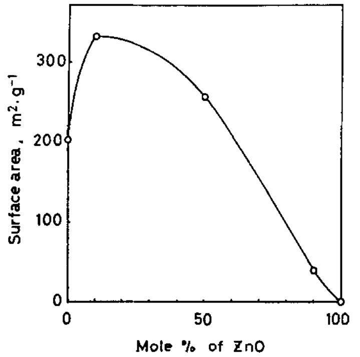


FIG. 1. Change in specific surface area of Al_2O_3–ZnO catalysts calcined at 500°C with change in ZnO content.

strengths was determined by Benesi's method (*4*) using the following indicators: methyl red (pK_a = +4.8), phenylazonaphthylamine (+4.0), *p*-dimethylaminoazobenzene (+3.3), dicinnamalacetone (−3.0), benzalacetophenone (−5.6), and anthraquinone (−8.2). Surface basicity was determined by titrating with a benzene solution of benzoic acid using phenolphthalein (pK_a = +9.3) as an indicator (*5*). Base strength was qualitatively measured by observing the color changes of the following indicators on the surface (*5*): bromothymol blue (pK_a = 7.1), phenolphthalein (9.3), 2,4,6-trinitroaniline (12.2), and 2,4-dinitroaniline (15.0).

Reaction procedures. Alkylation of phenol with methanol was carried out at 395°C by a conventional flow method. The reaction mixture (molar ratio of phenol/methanol = 1) was passed through about 1 g of catalyst bed at an appropriate flow rate. The catalysts (16–24 mesh) were recalcined under a nitrogen stream at the reaction temperature before the reaction. The reaction products were trapped with ice and analyzed by gas chromatography on a column containing 25% DC-550 on Shimalite. The catalytic activity and *ortho* selectivity were expressed by [(mole percentage of all alkylated products per mole percentage of supplied phenol) × 100] and [(mole percentage of *o*-cresol and 2,6-xylenol per mole percentage of all alkylated products) × 100], respectively.

Isomerization of 1-butene was carried out in a closed circulation system at 100°C. Catalysts which had been calcined were evacuated at 100 or 500°C before the reaction. For the analysis of butenes, a 5-m column packed with 30% dimethyl fluoride on alumina and thermostated at 0°C was used.

For isomerization of 3-carene, a microcatalytic pulse reactor which was directly combined with a gas chromatographic column was employed (*6*). The catalyst was pretreated under a helium stream at 500°C for 2 hr. The reaction temperature was 100°C. The reaction products were trapped at −196°C and then flash evaporated into a gas chromatographic column. The same column as used in our previous work (*6*) was employed. Effects of poisoning with carbon dioxide and pyridine were tested as follows. A pulse of the poison, amounts of which were just sufficient to cover a monolayer of the catalyst, was introduced after the third pulse of 3-carene. Then, the catalytic activities of the successive two pulses of 3-carene were measured.

RESULTS AND DISCUSSION

Surface Area and Acid–Base Property

The specific surface areas of Al_2O_3–ZnO of various compositions, calcined at 500°C for 2 hr, changed with the change in ZnO content, a maximum value being observed when about 10 mole% of ZnO was contained in the binary oxide, as shown in Fig. 1.

The acidities at various acid strengths of Al_2O_3–ZnO of various compositions calcined at 500°C for 2 hr are shown in Fig. 2. The acidities at $H_0 \leq -3$ decreased monotonously with the increase in ZnO, while the acidities at $H_0 > -3$ of Al_2O_3–ZnO (1:1) and (1:9) were almost comparable. The acidities, at $H_0 = -5.6$, -3.0, and $+3.3$, of Al_2O_3–ZnO catalysts contain-

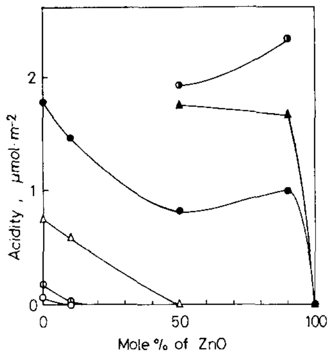


FIG. 2. Change in acidic property of Al_2O_3-ZnO catalysts calcined at 500°C with change in ZnO content: (○) $H_0 \leq -8.2$; (⦶) $H_0 \leq -5.6$; (△) $H_0 \leq -3$; (●) $H_0 \leq +3.3$; (▲) $H_0 \leq +4.0$; (◑) $H_0 \leq +4.8$.

ing 10 mole% ZnO which were prepared from the nitrates were 0.091, 0.61, and 1.5 mole/m², respectively; these values were lower than those (1.1, 1.7 and 3.9 µmole/m²) of Al_2O_3-ZnO catalysts containing the same amount of ZnO prepared from the chlorides by the same method (*3*). It was reported previously that the acidity of TiO_2-ZnO catalysts prepared from sulfates was much higher than that of TiO_2-ZnO catalysts prepared from chlorides (*7*). In the case of Al_2O_3-ZnO, the acidity of the binary oxide from the nitrates was found to be lower than that from the chlorides. These results indicate that the effect of anions on the acidic property of binary oxides is interesting and important.

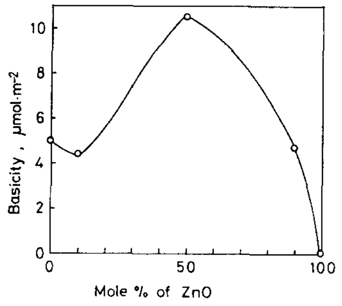


FIG. 3. Change in basicity at $pK_a = 12.2$ of Al_2O_3-ZnO catalysts calcined at 500°C with change in ZnO content.

Basic Property

The basicities of Al_2O_3-ZnO calcined at 500°C for 2 hr, measured by using phenolphthalein as an indicator, are shown in Fig. 3. The basicity of Al_2O_3 increased upon mixing with ZnO; a maximum basicity was observed when 50 mole% ZnO was mixed. Only three examples of an increase in basicity caused by mixture of two metal oxides have been reported in the cases of Al_2O_3-MgO (*8*, *9*), MgO-TiO_2 (*10*), and TiO_2-ZrO_2 (*11*), though there are many known examples of an increase in acidity of binary oxides (*3*, *12*). The increase in basicity in the case of Al_2O_3-ZnO is a fourth example.

The base strengths of Al_2O_3, Al_2O_3-ZnO, and ZnO are given in Table 1. The base strength of Al_2O_3-ZnO of any composition was higher than that of Al_2O_3 or ZnO. The highest base strength of Al_2O_3-ZnO was $pK_a = 12.2$.

Alkylation of Phenol with Methanol

Figure 4 shows the changes in activity and selectivity of Al_2O_3-ZnO for the alkylation reaction at 395°C with the change in ZnO content. The curve for the change in activity is similar to the curves for the acidities at $H_0 = +3.3$ in Fig. 2. Therefore, the main active sites on Al_2O_3-ZnO for the reaction are considered to be acid sites which cover relatively weak acid strength.

TABLE 1

Base Strengths of Al_2O_3, Al_2O_3-ZnO, and ZnO

pK_a	Al_2O_3	Al_2O_3-ZnO			ZnO
		9:1[a]	1:1	1:9	
7.1	+[b]	+	+	+	+
9.2	+	+	+	+	−
12.2	−	+	+	+	−
15.0	−	−	−	−	−

[a] Molar ratio.

[b] (+) Indicators showed the basic colors on the surface; (−) no color change of indicators.

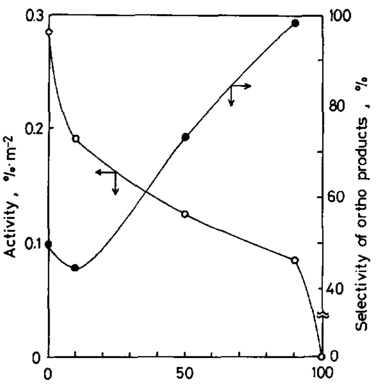


FIG. 4. Activity (○) and selectivity (●) of Al_2O_3–ZnO catalysts for alkylation of phenol with methanol at 400°C.

The reaction products in the alkylation were anisol; *o*-, *m*-, and *p*-cresols; 2,3-, 2,4-, and 2,6-xylenols; and 2,4,6-trimethyl phenol. The *ortho* selectivity for the formation of *o*-cresol and 2,6-xylenol increased as the ZnO content increased. An Al_2O_3–ZnO containing 90 mole% ZnO showed almost 100% *ortho* selectivity. This extremely high selectivity can be understood by our previous argument on the basis of an infrared study, that is, catalysts are so weakly acidic that they do not interact with the π-electrons of the benzene ring of phenolate formed on the catalyst surface give high *ortho* selectivity (*13*).

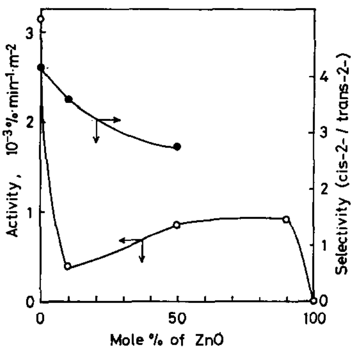


FIG. 5. Activity (○) and selectivity (●) for isomerization of 1-butene at 100°C of Al_2O_3–ZnO catalysts calcined at 500°C followed by evacuation at 100°C.

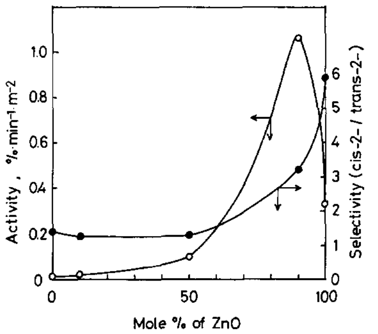


FIG. 6. Activity (○) and selectivity (●) for isomerization of 1-butene at 100°C of Al_2O_3–ZnO catalysts calcined at 500°C followed by evacuation at 500°C.

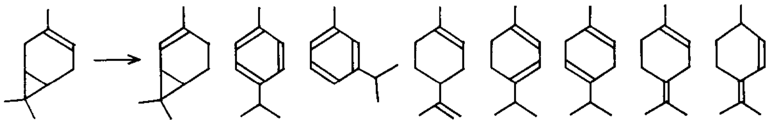
Isomerization of 1-Butene

The activities and selectivities for the isomerization reaction of Al_2O_3–ZnO calcined at 500°C for 2 hr followed by evacuation at 100 and 500°C are shown in Figs. 5 and 6. The change in activity of Al_2O_3–ZnO evacuated at 100°C after calcination at 500°C with the change in ZnO content is similar to the change in basicity shown in Fig. 4, except that the activity of pure Al_2O_3 is higher than those of Al_2O_3–ZnO of various compositions. The selectivity (the ratio of *cis*-2-butene to *trans*-2-butene) of Al_2O_3–ZnO is about 3, which is a value observed frequently over basic catalysts (*14–17*). Thus, these results suggest that the isomerization proceeds through π-allyl carbanion intermediates over the Al_2O_3–ZnO catalyst.

The activity of Al_2O_3–ZnO evacuated at 500°C after calcination at 500°C became much higher than that of Al_2O_3–ZnO evacuated at 100°C after calcination at 500°C (cf. Figs. 5 and 6) and the change in activity was different from that in Fig. 5, the maximum activity being observed for Al_2O_3–ZnO containing 90 mole% ZnO. Based on the selectivity value (3.2), the active sites of Al_2O_3–ZnO (molar ratio = 1:9) are also thought to be basic. If measurement of the basicity of the catalysts evacuated at 500°C were possible, the change in activity in Fig. 6 would have correlated with the change in basicity. The activity of Al_2O_3 evacuated at 100°C was almost the same as that of Al_2O_3 evacuated at 500°C, whereas the activities of Al_2O_3–ZnO were markedly increased by raising the evacuation temperature from 100 to 500°C. In the case of Al_2O_3–ZnO (1:9), the activity became about 1000 times higher (cf. Figs. 5 and 6). These results suggest that the nature of the active sites on Al_2O_3–ZnO is different from that on Al_2O_3.

Isomerization of 3-Carene

The reaction products of the isomerization were 2-carene (**II**), cymenes (**III, IV**), limonene (**V**) and other menthadienes (**VI–IX**). In Fig. 7 the mole percentages of each product are plotted against the mole percentage of ZnO in Al_2O_3–ZnO calcined at 500°C for 5 hr in air and at 500°C for 2 hr in a helium stream. Large amounts of 2-carene formed by double bond isomerization of 3-carene were found when Al_2O_3–ZnO (1:1) and (1:9) were used as catalysts. In the case of Al_2O_3–ZnO (1:9), the selectivity for 2-carene formation was 92% at 46% conversion. The deterioration in activity was least compared with those of the 13 metal oxide catalysts tested previously (*18*). The amounts of cymenes formed by dehydrogenation were large over Al_2O_3–ZnO (9:1) and (1:1). On the other hand, the amounts of menthadienes such as limonenes formed by opening of the three-membered ring of 3-carene were largest over pure Al_2O_3 and decreased with the increase in ZnO content.



I II III IV V VI VII VIII IX

The formation of 2-carene over Al_2O_3 and Al_2O_3–ZnO (1:1) and (1:9) was retarded by the addition of both CO_2, an acidic molecule, and pyridine, a basic molecule, as shown in Table 2. Therefore, the active sites for the formation of 2-carene are suggested to be both basic and acidic sites. By the same argument, the active sites for the formation of cymenes over Al_2O_3–ZnO (1:1) are considered to be both acidic and basic sites.

The formation of menthadienes from 3-carene is known to be catalyzed by liquid (*19, 20*) and solid acids (*21, 22*). In the present work, the change in activity

TABLE 2

Poisoning with CO_2 and Pyridine[a]

Catalyst	Al_2O_3		Al_2O_3–ZnO (1:1)		Al_2O_3–ZnO (1:9)	
poison	CO_2	Pyridine	CO_2	Pyridine	CO_2	Pyridine
2-Carene	0	0.17	0.42	0.66	0.25	0
Cymenes	—	—	0.78	0	—	—
Menthadienes	2	0	—	—	—	—

[a] Values are the ratios of the activity for the formation of each product over poisoned catalysts to that over unpoisoned catalysts.

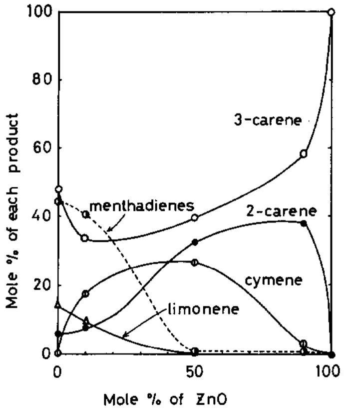


FIG. 7. Activity and selectivity for isomerization of 3-carene at 100°C of Al_2O_3–ZnO catalysts calcined at 500°C for 5 hr in air and at 500°C for 2 hr in a helium stream.

of Al_2O_3–ZnO with the change in ZnO content was found to correlate with the change in acidity (cf. Figs. 2 and 7) and there was a loss in activity upon addition of pyridine, but not upon addition of carbon dioxide. Therefore, the active sites on Al_2O_3–ZnO and Al_2O_3 for the formation of menthadienes are considered to be acidic.

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