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The Dehydration and Dehydrogenation of Ethanol Catalyzed by TiO_2-ZrO_2

Kazushi ARATA and Hiromitsu SAWAMURA
Hokkaido University of Education, Hachiman-cho, Hakodate 040

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Synopsis. Ethanol was converted into ether, ethylene, and butadiene over TiO_2–ZrO_2 with various contents of ZrO_2 in a flow system. Maximum acidity and activity were obtained at 50% ZrO_2. The butadiene formation was explained by both dehydration and dehydrogenation reactions on acidic and basic sites, implying that TiO_2–ZrO_2 is an acid-base bifunctional catalyst.

Binary metal oxides such as SiO_2–ZrO_2,[1] TiO_2–ZnO,[2] and SiO_2–TiO_2[3] have been found to show remarkable acidic properties and catalytic activity. Shibata and Kiyoura have recently found a new mixed oxide, TiO_2–ZrO_2, which exhibits a quite significant acidic property,[4] and Watanabe *et al.* have showed that its catalytic activity for the amination reaction of phenol to aniline was higher than that of SiO_2–Al_2O_3.[5]

The present study was undertaken to examine the correlation between the acidic property of TiO_2–ZrO_2 and its catalytic activity, as well as the selectivity for the reaction of ethanol.

Experimental

Catalyst. TiO_2–ZrO_2 of various compositions was prepared by two different methods reported by Shibata *et al.*[4] (1): a 1850 ml of 2.16 M ammonia water was added at the rate of 10 ml/min to a mixed aqueous solution (1 l of 1 M) of titanium tetrachloride and zirconium oxychloride with stirring. (2): a mixed aqueous solution (5 l of 0.2 M) of titanium tetrachloride, zirconium oxychloride, and an excess amount of urea (300 g = 5 M) was heated on a boiling water bath for 6—9 h.

The precipitates prepared by both methods were washed thoroughly with distilled water until no chloride ions were detected in the filtrate. They were dryed in air at 110 °C for 30 hr and finally calcined in air at 500 °C for 3 h.

Properties of Catalyst. The acidic properties of the catalysts were determined by the titration method with *n*-butylamine using a series of Hammett indicators. The differential thermal analyses were obtained in the range from room temperature to 720 °C.

Reaction Procedure and Analyses. The reaction was carried out by a conventional flow method using nitrogen as carrier gas at 300—360 °C. Ethanol, purified by distillation over anhydrous calcium oxide, and nitrogen were passed through the catalyst bed (2 g) at the flow rates of 7.5 ml/h and 1.0 l/h, respectively. The reaction products were analyzed by a gas chromatograph with FID using a column of PEG 1000 on Flusin T. The catalytic activity and selectivity were obtained from the product yields, given by the gas chromatograph peak areas (uncorrected), at 25 min after the reaction was initiated.

Results and Discussion

The catalytic activity of TiO_2–ZrO_2 (1:1) precipitated by ammonia was 20% higher than that by urea. Therefore, the TiO_2–ZrO_2 catalysts with various compositions prepared by the former method were mainly studied. The amount of acetaldehyde formed by the dehydrogenation of ethanol was almost negligible over all of the catalysts.

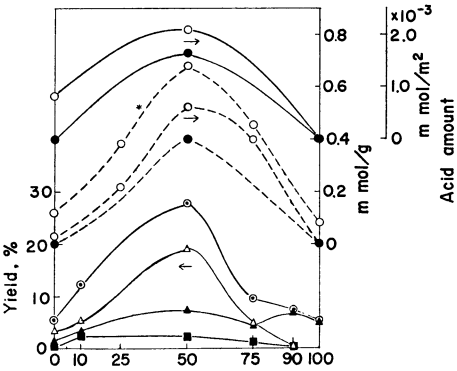

Fig. 1. Catalytic activity and acidity ($pK_a = -3.0$) of TiO_2–ZrO_2.
Reaction temperature: 300 °C, total conversion (—⊙—), yield of ether (—△—), ethylene (—▲—), butadiene (—■—).
Acidity: (○) and (●), for the samples precipitated by urea and ammonia, respectively; solid line, mmol/m^2; broken line, mmol/g.
*$pK_a = 6.8$.

The catalytic activity, that is, the total conversion of ethanol, fairly well correlated with the acitidy*, as is shown in Fig. 1. TiO_2–ZrO_2 (1:1) was most active, and the amount of ether formed was larger than that of ethylene. It is of interest that the total acidity of the sample prepared by urea was higher than that by ammonia, and the shapes of the curves were similar.

The catalytic conversion of ethanol to butadiene has been reported to proceed over solid acids such as Al_2O_3–ZnO,[6,7] though those to ethyl ether and ethylene are usually observed when catalyzed by ordinary solid acids. Therefore, this reaction was tested over the ZnO catalyst, which was prepared by the same procedure as TiO_2–ZrO_2, *i.e.*, the ammonia precipitation of $ZnCl_2$

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* The acid amounts of TiO_2–ZrO_2 (1:1) at various acid strengths were determined. The sample precipitated by ammonia showed 0.563 ($pK_a = 6.8$), 0.440 (3.3), 0.363 (1.5), 0.400 (−3.0), 0.140 (−5.6), and 0.073 (−8.2), while the sample precipitated by urea exhibited 0.684 ($pK_a = 6.8$), 0.460 (2.0), 0.520 (−3.0), 0.414 (−5.6), and 0.250 (−8.2). The acid amount of the sample prepared by urea was higher at each acid strength, in contrast to the observations with TiO_2–ZnO.[2] The amount at $pK_a = 1.5$ or 2.0 was lower than that at $pK_a = -3.0$ in both samples, although the former value should be higher than the latter one. These unusual but interesting results seem to suggest an unusual surface property of TiO_2–ZrO_2.

aqueous solution. The products at 340 °C were 9.6% ethyl ether and 3.8% ethylene (13.4% in the total conversion). The butadiene yield increased at the higher reaction temperature, 330 °C, to 0.7, 2.3, 4.8, 12.4, 7.3, and 2.1% for ZrO_2, TiO_2–ZrO_2 (1: 9, 1: 3, 1: 1, 9: 1), and TiO_2, respectively. TiO_2–ZrO_2 (1: 1) also showed the highest activity for the formation of butadiene as well as that of ethylene and ethyl ether. Niiyama and coworkers have studied the butadiene formation from ethanol over SiO_2–MgO, which is an acid-base bifunctional catalyst, and concluded that the rate-controlling step is the acetaldehyde formation catalyzed by the basic sites.$^{8)}$ Thus, it seems likely that the TiO_2–ZrO_2 catalyst also has basic sites which are effective for producing butadiene, and that the basicity increases by mixing TiO_2 and ZrO_2. In fact, TiO_2–ZrO_2 (1: 1) changed 2,4,6-trinitroaniline ($pK_a=12.2$) to its basic color, though B.T.B. ($pK_a=7.2$) did not change visibly to the basic color over TiO_2 and ZrO_2.

Table 1. Catalytic activity and selectivity of ZrO_2 for dehydration of ethanol at 360 °C

Temperature of calcination (°C)	Acidity$^{a)}$ ($pK_a=6.8$) (mmol/g)	Conversion (%)	Products (%)	
			Ethylene	Butadiene
400	0.142	80.6	72.2	8.4
500	0.077	30.8	29.1	1.7
600	0.047	30.0	29.0	1.0

a) 0.230, 0.237 mmol/g at 200, 300 °C, respectively.

ZrO_2 produced no ether, resulting in a high selectivity for ethylene. A similar selectivity by ZrO_2 was also observed in the dehydration of *sec*-butanol, where 1-butene was formed in more than 90% selectivity.$^{9)}$ The catalytic activity and selectivity of ZrO_2 at 360 °C are shown in Table 1. High selectivity for ethylene and also for butadiene implies that basic sites exist on this catalyst. Yamaguchi *et al.* also pointed out the basic character of ZrO_2 from its catalytic action in the isomerization of 1-butene.$^{9)}$

The strong exothermic peak at around 410 °C observed in DTA with ZrO_2, which is assigned to the crystallization of the amorphous state, moved to 510 to 640 °C as the ratio of TiO_2 mixed increased from 1: 9 to 1: 3. However, no peak was detected up to 720 °C with TiO_2–ZrO_2 (1: 1), probably being observed at above 720 °C. These discrepancies of peak might be related to acidity and catalytic activity.

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