

# Hydrolysis of Isopropyl Benzene over Alumina-Zirconia Catalysts Prepared from $\gamma$ -Alumina or Böhmite\*

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## アルミナ-ジルコニア触媒によるイソプロピルベンゼンの加水分解反応

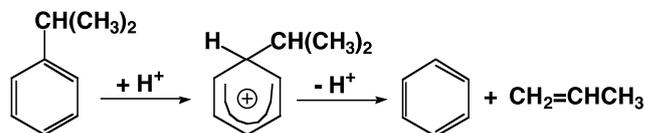
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### 1. Introduction

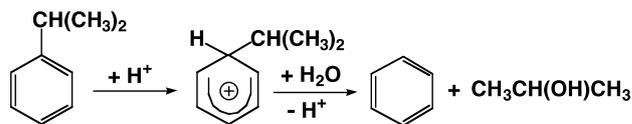
We have previously reported that alumina-zirconia catalysts exhibit significant activity during the hydrolysis of chloropentafluoroethane (CFC-115)<sup>1,2</sup> and that an alumina-zirconia catalyst (alumina-zirconia(A)) prepared from  $\gamma$ -alumina possesses one type of acidity (acidity(I)) while a second catalyst (alumina-zirconia(B)) prepared from böhmite has two types (acidity(I) and acidity(II))<sup>3</sup>. The rate of hydrolysis of CFC-115 over the acidity(I) was found to be faster than that over the acidity(II)<sup>3</sup>, although the acidity(I) was more readily deactivated<sup>4</sup>. Our previous work, however, did not fully determine the natures of these two types of acidities.

It is well known that the catalytic cracking of hydrocarbons is affected by the acidity of the catalyst. As an example, the catalytic cracking of isopropyl benzene takes place over Brønsted acids but not in the presence of Lewis acidity. This is because the cracking reaction of a compound containing an isopropyl moiety occurs through the addition of a proton to the carbon atom attached to the isopropyl group, as shown in Scheme 1. The hydrolysis of isopropyl benzene may therefore proceed through the

same reaction mechanism as the cracking of isopropyl benzene, as shown in Scheme 2. This work investigated the hydrolysis of isopropyl benzene in the presence of alumina-zirconia catalysts prepared from two alumina sources ( $\gamma$ -alumina and böhmite) with the aim of gaining a better understanding of the effects of the two types of acidity on catalytic performance.



Scheme 1 Catalytic cracking of isopropyl benzene.



Scheme 2 Catalytic hydrolysis of isopropyl benzene.

### 2. Experimental

#### 2.1 Catalyst preparation

Alumina-zirconia catalysts were prepared as follows<sup>1,2</sup>. Böhmite and  $\gamma$ -alumina were used as the alumina source and zirconyl nitrate was used as the zirconia source. The alumina source was suspended in an aqueous zirconyl nitrate solution and an aqueous ammonia so-

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lution was added to the suspension until the pH of the mixture was adjusted to a value of 8. The resulting precipitate was filtered, washed with distilled water and dried overnight at 353 K. The dried precipitate was subsequently calcined at 923 K for 3 h, formed into tablets and crushed to produce particles of size 8–12 mesh, which served as the reaction catalyst. The alumina content in these catalysts was varied from 0 to 90 wt%. The alumina–zirconia prepared from böhmite is hereafter denoted as alumina–zirconia(B) while that prepared from  $\gamma$ -alumina is termed alumina–zirconia(A).

## 2.2 Reaction procedure

The catalytic cracking of isopropyl benzene in the presence of water vapor was carried out using a conventional flow reaction apparatus containing 0.01–1.0 g of catalyst in conjunction with gas feed rates of 2.2 mL/min isopropyl benzene, 9.8 mL/min water vapor and 100 mL/min argon. A reaction temperature of 773 K and a total pressure of 0.1 MPa were also applied. The concentrations of both the initial reactants and the hydrolysis products were determined using a gas chromatograph with a flame ionization detector.

## 3. Results

The contribution of the catalyst to the reaction progress can be difficult to determine, since isopropyl benzene undergoes thermal cracking at higher reaction temperatures. For this reason, the thermal cracking of isopropyl benzene was investigated at temperatures ranging from 573 to 973 K. Figure 1 shows the relationship between conversion and reaction temperature and demonstrates that thermal cracking does not occur below 773 K, while the thermal conversion of the isopropyl benzene increases as the reaction temperature is raised above 773 K. Accordingly, the catalytic hydrolysis was investigated at 773 K.

As noted, the cracking of isopropyl benzene over solid acidic catalysts occurs through the addition of a proton to the carbon atom joined to the isopropyl group. This reaction therefore does not proceed over Lewis acids, which do not have a proton to contribute. To determine if the hydrolysis of isopropyl benzene over solid acidic catalysts occurs through the same reaction mechanism, this reaction was examined over both the alumina–zirconia(A) and alumina–zirconia(B) catalysts, each having an alumina content of 90 wt%, at 773 K. The results showed very minimal reaction of isopropyl benzene over the alumina–zirconia(A) catalyst, with a conversion of approximately 4%. Conversely, the use of alumina–zirconia(B) resulted in significant hydrolysis activity, with conversion of about 83%. The hydrolysis of isopropyl benzene over both alumina–zirconia catalysts was confirmed since the hydrolysis reaction products benzene and isopropanol were identified in the post-reaction mixtures in both cases. The surface area of the catalyst evidently plays an important role in the reaction and so the specific surface areas (SSA) of both alumina–zirconia catalysts were measured using the BET method. The SSA of the alumina–zirconia(A) catalyst was about 170 m<sup>2</sup>/g, while that of the alumina–zirconia(B) catalyst was approximately 180 m<sup>2</sup>/g. The alumina–zirconia(B) catalyst thus exhibited a slightly large SSA value, but this greater surface area is insufficient to account for the very large difference in the hydrolysis conversions of the two catalysts. Accordingly, the observed differences between the hydrolysis rates were attributed to the chemical properties of the catalysts.

The hydrolysis of isopropyl benzene was investigated over alumina–zirconia(B) catalysts having various alumina contents, using 0.5 g of catalyst in each trial. Figure 2 shows the relationship between conversion and alumina content, from which it is evident that the conver-

sion increased with increases in the alumina content from 0 to 30 wt%, then plateaued at approximately 83% at alumina contents over 30 wt%. These results may reflect the increasing acidity of the alumina-zirconia(B) catalyst with increases in alumina content. The hydrolysis of isopropyl benzene over alumina-zirconia(B) with alumina contents above 30 wt% therefore appears to reach an equilibrium state under these reaction conditions.

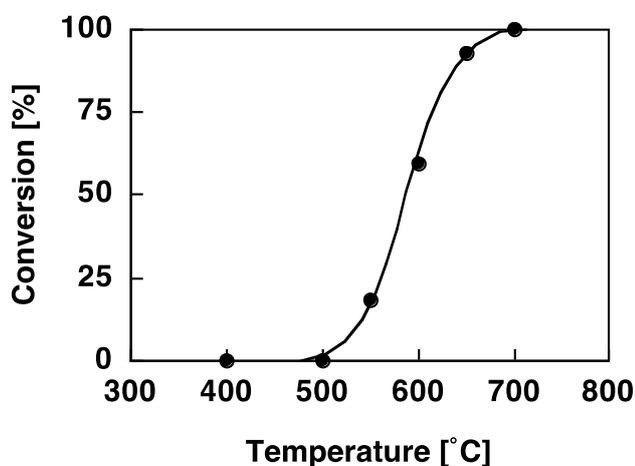


Figure 1. Relationship between conversion and temperature for thermal cracking of isopropyl benzene

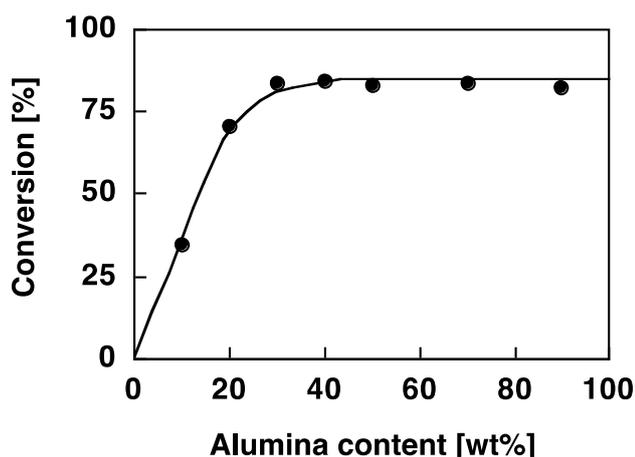


Figure 2. Relationship between conversion and alumina content for hydrolysis of isopropyl benzene

The dependence of isopropyl benzene conversion on catalyst weight was examined during trials using alu-

mina-zirconia(B) catalyst with an alumina content of 90 wt%. Figure 3 shows the relationship between conversion and weight of catalyst, in which the conversion is improved with increased amounts of catalyst over the range of 0 to 0.2 g and then plateaus at catalyst amounts over 0.2 g (at a conversion of about 83%). During the use of a fixed-bed flow reactor, the reaction time (or contact time) typically increases with increases in catalyst weight when the molar flow rate is constant. Thus, since the conversion was constant with catalyst amounts above 0.2 g, the reaction appears to achieve an equilibrium state under these reaction conditions.

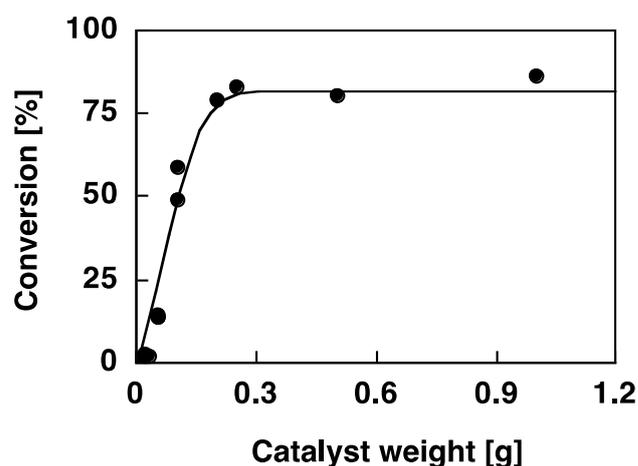


Figure 3. Relationship between conversion and catalyst weight for hydrolysis of isopropyl benzene

The effects of water vapor on the hydrolysis of isopropyl benzene were also studied, using alumina-zirconia(B) catalyst with an alumina content of 90 wt%. Figure 4 shows the relationship between conversion and time on stream, up to a value of 130 min. The conversion in the absence of water vapor is seen to be almost the same as that with water vapor up until the 130 min mark, and the reaction products were benzene and isopropanol both with and without the addition of water vapor. Since the reaction apparatus was not equipped with a drying

column, water vapor present in the argon gas was inadvertently introduced into the reactor. The partial pressure of isopropyl benzene under these reaction conditions was about 2 kPa, while the saturated water vapor pressure at room temperature was approximately 3 kPa. Accordingly, water vapor sufficient to promote the hydrolysis of isopropyl benzene was present in the reactant gas mixture under the applied reaction conditions even before adding additional water vapor, and thus the conversion rate without water vapor addition was almost the same as that with water vapor.

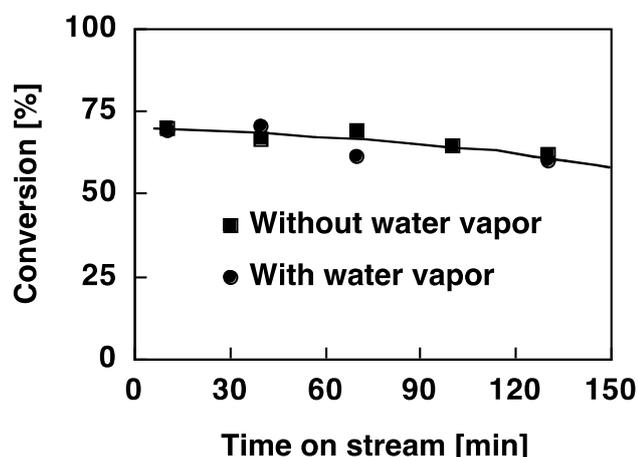


Figure 4. Relationship between conversion and time on stream for cracking of isopropyl benzene with or without water vapor

#### 4. Discussion

As shown in Scheme 2, the hydrolysis reaction of isopropyl benzene by a solid acidic catalyst is believed to occur via protonation of the carbon atom on the benzene ring to which the isopropyl group is bonded. This reaction proceeds in the presence of a Brønsted acid, which has a proton, but not with a Lewis acid, which does not have a proton. In the hydrolysis reaction of isopropyl benzene, in which only a Brønsted acid will be active, the alumina-zirconia(A) catalyst exhibits little activity, while the

alumina-zirconia(B) is highly efficient. Both catalysts have acidic properties, but alumina-zirconia(A) exhibits only acidity(I), whereas aluminum-zirconia(B) exhibits both acidity(I) and acidity(II). In addition, although Lewis and Brønsted acids both show acidic properties, a Lewis acid in the presence of water vapor is believed to form a Brønsted acid<sup>5</sup>. In light of this, and considering the results of these experiments, the following two scenarios are possible:

- (1) Because the reaction is carried out in the presence of water vapor, both acidity(I) and acidity(II) are able to function as Brønsted acids. The difference in the reactivity of the two is therefore related to the relative strengths of the Brønsted acids. In essence, the reaction results indicate that the Brønsted acidity of the acidity(I) is markedly weaker than the Brønsted acidity of the acidity(II).
- (2) The conversion from a Lewis acid to a Brønsted acid in the presence of water vapor results from the adsorption of water vapor onto the acid sites. Since the adsorption of a gas occurs less readily with increasing temperature, at temperatures above 773 K it is not certain that water vapor will have been adsorbed onto all the Lewis acid sites. Therefore, the reaction results indicate that acidity(I) represents Lewis acidity while acidity(II) represents a Brønsted acid.

We have previously reported that the decomposition rate obtained with the acidity(I) is higher than that seen with the acidity(II) during the hydrolysis reaction of chloropentafluoroethane<sup>3</sup>. If scenario (1) were correct, the hydrolysis reactions of the CFC and isopropyl benzene would be occurring over the same Brønsted acid, yet the catalytic activity would be reversed with the two different

reactants (i.e., the CFC hydrolysis is better catalyzed by the acidity(I) but the isopropyl benzene is better catalyzed by the acidity(II)). This scenario seems unlikely. During the present research, the surfaces of the alumina-zirconia catalysts was not directly observed with the infrared absorption measurement of adsorbed pyridine<sup>5,6</sup>, which makes it challenging to reach definitive conclusions. Therefore, although it cannot be proven categorically, it is likely that acidity(I) is associated with the presence of a Lewis acid while acidity(II) involves a Brønsted acid, as in scenario (2).

Experimental trials varying the catalyst alumina content and mass in the isopropyl benzene hydrolysis reaction and using alumina-zirconia(B) consistently resulted in a maximum conversion of approximately 83%. Since the catalyst quantity corresponds to the contact time in a flow-type reactor packed with catalyst, varying the catalyst mass is equivalent to changing the reaction time. Because increasing the catalyst concentration lengthens the reaction time, the fact that the reaction rate remained constant above a certain catalyst concentration clearly shows that the reaction was at equilibrium. In addition, it is known that the total acid quantity increases with an increase in alumina content in the catalyst. In the case of a 0.5 g quantity of catalyst, the alumina content at the equilibrium conversion is 30 wt%, as shown in Fig. 2. In addition, the catalyst quantity necessary for equilibrium conversion at an alumina content of 90 wt% was obtained from Fig. 3. The quantities of acidity(II) (Brønsted acid) on the catalyst surface (alumina content; 30 and 90 wt%) were determined using the temperature-programmed desorption of adsorbed ammonia<sup>3</sup>, and the amount of the acidity(II) (Brønsted acid) required to achieve equilibrium was thus calculated. The required acid quantities determined via these two approaches were comparable at ap-

proximately 0.05 mmol. Accordingly, in this catalyst system, it appears that the isopropyl benzene hydrolysis reaction reaches equilibrium when the quantity of Brønsted acid available is about 0.05 mmol.

In addition, since the hydrolysis reaction was at equilibrium, the pressure equilibrium constant of this reaction at 773 K can be determined using basic thermodynamic principles, including the standard enthalpy of formation and the standard Gibbs free energy of formation. These calculation provide a pressure equilibrium constant of approximately  $6.8 \times 10^{-4}$ . The conversion of the isopropyl benzene at equilibrium under these reaction conditions, as determined from the calculated equilibrium constant, is 2.5%, which is quite different from the experimental results. This suggests that the water/isopropyl benzene molar ratio on the catalyst surface differs substantially from the ratio within the gas phase. Based on the experimentally observed reaction rate, the water/isopropyl benzene molar ratio on the catalyst surface was determined to be approximately 7000, suggesting that the catalyst surface is primarily covered with water.

## 5. Conclusions

The alumina-zirconia(A) catalyst, which was prepared from  $\gamma$ -alumina, had one type of acidity (acidity(I)), while the alumina-zirconia(B) catalyst, which was prepared from böhmite, had two types of acidity (acidity(I) and acidity(II)). The hydrolysis of isopropyl benzene in the presence of both catalysts was investigated as a means of obtaining additional information about these forms of acidity. The following conclusions can be drawn from this study:

- (1) Acidity(I) appears to correspond to Lewis acidity while acidity(II) may represent Brønsted acidity.
- (2) In this catalyst system, the isopropyl benzene hydro-

ysis reaction reaches an equilibrium state in the presence of approximately 0.05 mmol of the Brønsted acid.

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