Tuning the acidic properties of Ce-Zr mixed oxide catalysts with different Ce/Zr ratio

Jeong Bae Kim, Eunpyo Hong, Ye-Seul Jeong, Chae-Ho Shin*

Department of Chemical Engineering Chungbuk National University, Cheongju, Chungbuk 28644, Korea
* Fax: +82-43-269-2370 / E-mail: chshin@chungbuk.ac.kr

Abstract: The ceria-zirconia mixed oxide catalysts were synthesized via a co-precipitation method, and their physico-chemical properties were analyzed. Acidic properties were largely influenced by atomic composition and calcination temperature. From the results of IPA-TPD measurements, the acid strength of catalysts exhibited a volcano-shaped curve as a function of Ce/Zr in Ce-Zr mixed oxide, and the Ce-Zr catalyst calcined at high temperature showed low BET surface area due to sintering but exhibited relatively high Brönsted acidity and showed good activity in IPA dehydration reaction. Also, better acidic properties could be verified in IPA-TPD and Pyridine IR analysis.

Keywords: Ceria-zirconia, Mixed oxide, Acid property

1. Introduction

The cerium-zirconium (Ce-Zr) mixed oxides have been extensively studied due to its high oxygen storage capacity and excellent thermal stability in various applications, such as reforming of carbon dioxide and methane oxidation. However, the research on acidic properties of Ce-Zr catalysts has not been conducted relatively much. Therefore, we synthesized the Ce-Zr catalysts, and variations in physico-chemical properties including surface acidic properties were carefully investigated depending on molar composition and calcination temperature.

2. Experimental

Ce-Zr hydroxide was prepared by coprecipitating a solution prepared by changing Ce / Zr molar ratio using Ce(NO₃)₃·6H₂O and ZrO(NO₃)₂·2H₂O precursors with 14.7 M NH₄OH solution as a precipitant at pH = 9.5. The resulting solution was aged at 100 °C for 72 h. The obtained precipitate was washed and dried. Finally dried samples were calcined at a desired temperature in the range of 600, 700, 800, and 900 °C for 6 h. The calcined products were labeled as Cex-Zry temp, where x, y and temp indicate each molar compositions and calcination temperature in °C. To characterize the catalysts, N₂-sorption, IPA-TPD, XRD, SEM, TG-DTA and Pyridine IR analysis were used. The catalytic activity was compared in the dehydration of IPA at atmospheric pressure.

3. Results and discussion

From the N₂-sorption measurements, the BET surface area of catalysts calcined at 600 °C for 6 h gradually decreased as Ce content was increased from 266 m²/g for ZrO₂ to 49 m²/g for CeO₂, and this result
was closely related with crystallization temperature obtained from DTA [1]. For the measurement of acidic properties of Ce-Zr catalysts, the IPA-TPD was performed, as shown in Fig. 1. Typically, in IPA-TPD analysis, the peak area indicates the quantity of acid sites which is proportional to BET surface area, and the position of peak temperature reflects the acid strength [2]. Therefore, Fig. 1A shows that quantity of acid sites gradually decreased with increasing Ce content, while the acid strength exhibits a volcano-shaped curve, with the lowest peak temperature for Ce7-Zr3 catalyst which means the best catalytic activity in IPA dehydration. Furthermore, acidic properties were also influenced by calcination temperature (Fig. 1B). Although quantity of acid sites decreased as a function of calcination temperature, the acid strength rather increased.

![Fig. 1. IPA-TPD profiles of (A) Ce-Zr catalysts calcined at 600 °C and (B) Ce7-Zr3 catalyst calcined at different temperatures.](image)

In addition, the Ce-Zr catalysts were applied to IPA-dehydration as a model acid-catalyzed reaction. As a result, its catalytic activity was correlated with the peak temperature of IPA-TPD. The evolution of \( \cdot \text{C}_3\text{H}_5 \) (m/z = 41) fragment, which is the main fragment of propylene as the main product of IPA dehydration, tends to be similar to that of IPA dehydration reaction [3].

3. Conclusions

Though the quantity of acid sites in Ce-Zr catalyst was well correlated with BET surface area, acid quantity of Ce-Zr catalysts gradually decreased with increasing Ce content. However, acid strength of catalysts showed a volcano-shaped curve as a function of atomic composition, which is maximized with Ce7-3Zr catalyst, and the increase of calcination temperature resulted in enhancement of acid strength. Consequently, the 7Ce-3Zr catalyst showed the highest catalytic activity with 99% propylene selectivity in the IPA dehydration reaction.

References