Acid properties and alkali resistance of porous silica-zirconia with controlled local structure

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Abstract: Prous silica-zilconia with different Zr local structure was prepared to be catalyst support by two methods of sol-gel and impregnation. Based on the structural change by exposure to NH_3 and catalytic activity in isomerization of alkene, we clarified the relationship between preparation conditions of silica-zirconia and its properties such as alkali resistance and activity in acid catalysis. Silica-zirconia with low Zr content prepared by sol-gel and calcined at 1000°C was the optimal catalyst support with high alkali resistance and minimized activity in acid catalysis.
Keywords: Prous material, Silica-zirconia, Acid catalyst reaction.

1. Introduction

Porous silica gel has a high specific surface area. Its surface is inactive, and it is often used for a catalyst support. Moreover, various structure control of silica has been reported by using sol-gel method. However, alkali and steam resistances of silica are quite low. Regarding the heat resistance, the pore structure is maintained up to about 800°C, but at higher temperatures the specific surface area decreases. By adding ZrO_2 to silica, alkali and heat resistances are reported to be improved[1]. At the same time, however, acid sites appear on the surface[2], which causes side reactions.

In this study, silica-zirconia with different Zr local structures was prepared by using two preparation methods of sol-gel and impregnation and calcined them at 600°C or 1000°C. These were conducted acid catalysis reaction and alkali resistance experiments.

The purpose of this study is to prepare silica-zirconia with high alkali resistance and minimized activity in acid catalysis by clarifying the relationship between local structure of Zr and variation of properties.

2. Experimental

Tetraethoxysilane (TEOS) and zirconyl nitrate dihydrate were used as silica and zirconia sources, respectively. Poliethylene glycol (PEG, Mw: 20,000) was used as a polymer component to induce phase separation. Nitric acid was used as a catalyst for hydrolysis and polycondensation. Silica-zirconia was prepared by two methods of sol-gel and impregnation. The sol-gel method sample is denoted as SiO_2-ZrO_2, and the impregnation method sample is denoted as ZrO_2/SiO_2. The acid activity of each sample was investigated by 1-octene isomerization reaction. Mesopore structures of samples before and after the exposure to NH_3 gas were compared in order to investigate structural stability under basic conditions.

3. Results and discussion

Figure 1 shows SEM images of samples prepared by the sol-gel method. The ZrO_2 content was varied between 0 - 5 mol%. Regardless of the ZrO_2 content, all the samples could be prepared to have the similar macropore and mesopore diameters.

Figure 2 shows the pore size distribution in mesopore range of the samples before and after NH_3 exposure. In contrast to pure silica, All the samples with Zr maintain mesopores. In detail, SiO_2-ZrO_2 maintains mesopores with narrow distribution even after exposure to NH_3 regardless of the content of ZrO_2, whereas ZrO_2/SiO_2 at low content of ZrO_2 shows broadened pore size distribution. The broadening in pore size distribution by NH_3 exposure suggests that Zr distribution on the surface is not homogeneous in ZrO_2/SiO_2. This results correspond to the structural features observed by XRD, XAFS and IR.

Figure 3 shows the results of isomerization of 1-octene. Samples calcined at 1000ºC had lower activity in acid catalysis than samples calcined at 600ºC. Also, the lower the content of ZrO_2 is, the lower the conversion becomes. At the ZrO_2 content > 2 mol%, SiO_2-ZrO_2 shows higher activity than ZrO_2/SiO_2, whereas activity of SiO_2-ZrO_2 becomes lower than ZrO_2/SiO_2, at low ZrO_2 content. As a result, the silica-zirconia with minimized activity in acid catalysis was that with low Zr content prepared by sol-gel and calcined at 1000ºC.

Details on the relation between Zr local structure and these properties of silica-zirconia will be reported at the conference.

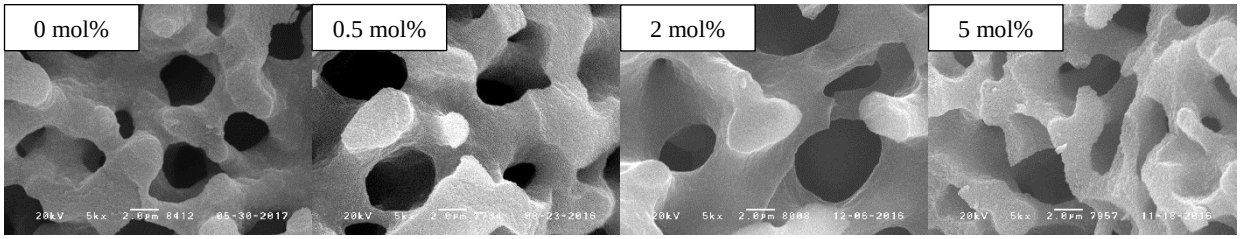

Figure 1. SEM images of SiO_2-ZrO_2. The number in the figure indicates ZrO_2 content.

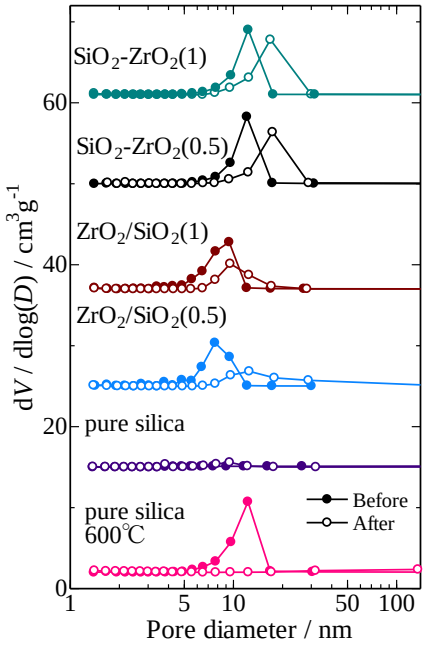

Figure 2. Pore size distribution of samples calcined at 1000ºC before and after NH_3 exposure. The number in parentheses indicates ZrO_2 content.

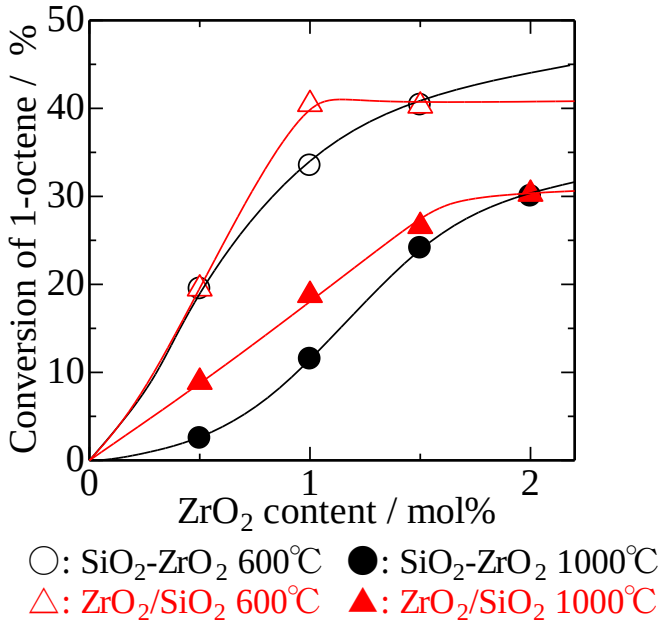

Figure 3. Conversion of 1-octene with each ZrO_2 content.

4. Conclusions

It was found that local structure of Zr was closely related to alkali resistance and acidic property. Because of homogeneous zirconia distribution, sol-gel silica-zirconia shows superior alkali resistance to impregnation one, and lower activity in acid catalysis at low ZrO_2 content.

References

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