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# Local Structure around Zr Species in $SiO_2$ Doped with Zr

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## 1 Introduction

Acidic catalysts are widely used for petroleum refinery and organic synthesis of bulk and fine chemicals [1,2]. This study was made to find out correlation between the state of dispersing or aggregating and acidity on complex oxide ($SiO_2$-$XO_a$) doped other metal oxide ($XO_a$) in $SiO_2$. We have found out that $SiO_2$-$ZrO_2$ have good acidity, which changed by preparation methods and amount of doped zirconium. In the present report, zirconia supported on $SiO_2$ will be examined using XAFS in order to understand the local structure around zirconium.

## 2 Experiment

$SiO_2$-$ZrO_2$ were prepared via an impregnation method using aqueous zirconium nitrate and $SiO_2$. In the present study, two atomic ratios of Zr/Si (0.004 and 0.007) in $SiO_2$-$ZrO_2$ are employed for XAFS analysis. As reference samples, monoclinic $ZrO_2$ and perovskite-type $SiZrO_3$ were used.

Analysis of XAFS near Zr-K edge was carried out at the High Energy Accelerator Research Organization With a storage ruing current of 400 mA (6.5 GeV). The X-rays were nonochromatized with Si(311) at an NW10A station. The absorption spectra were observed using ionization chambers in the transmission mode. The photon energy was scanned in the range of 17,498.90-19,098.90 for the Zr-K edge.

The average coordination number was estimated from the comparison of XANES spectra of these two samples and pattern-fitting analysis of EXAFS of both samples referring the data for $ZrO_2$ and $SiZrO_3$.

## 3 Results and Discussion

Monoclinic $ZrO_2$ and perovskite-type $SrZrO_3$ used as reference samples possess 7-coordinated and 6-coordinated structures with lattice oxygen. XAFS spectra of $SiO_2$-$ZrO_2$ (Zr/Si = 0.004 or 0.007) were similar to that of $SrZrO_3$. Therefore, the local structure around Zr in these $SiO_2$-$ZrO_2$ is dissimilar to that in monoclinic $ZrO_2$ while seems to be similar to that perovskite-type $SiZrO_3$ that is 6-coordinated structures with lattice oxygen, that is, oxygen octahedron structure.

It should be noted that the increase of Zr/Si ratios in $SiO_2$-$ZrO_2$ resulted in the enhancement of peak intensity due to monoclinic $ZrO_2$. These results indicate that the local structure around Zr of $SiO_2$-$ZrO_2$ (Zr/Si = 0.004 or 0.007) may be present between 6- and 7-corordinated structure with lattice oxygen.

Table 1 showed the average coordination number estimated from the pattern-fitting analysis using XANES of both $SiO_2$-$ZrO_2$ and those of the reference samples ($ZrO_2$ and $SrZrO_3$). In Table 1, catalytic activity ratio and the corresponding selectivity of aldol condensation were also described. As shown in Table 1, it was further supported that the increase of Zr/Si ratio resulted in the enhancement of the average coordination number. In using Zr-$SiO_2$ (0.004 and 0.007), the catalytic activity for the production of a chemical that proceeded on acidic catalyst was examined. Although the enhancement of Zr/Si ratio in $SiO_2$-$ZrO_2$ resulted in the same activity of the reaction, under the same conversion level, the selectivity on $SiO_2$-$ZrO_2$ (0.004) was evidently greater than that on $SiO_2$-$ZrO_2$ (0.007).

Therefore it can be estimated in the present study that the enhancement of Zr/Si ratio in $SiO_2$-$ZrO_2$ did not contributed to the enhancement of the catalytic reactivity in the present system, while the presence of 6-coordinated structure such as perovskite-type $SiZrO_3$ may be needed for the catalytic reaction.

The enhancement of the 6-coordinated structure in $SiO_2$-$ZrO_2$ may be next target to obtain the great activity on the present catalyst system.

Table 1: Average coordination number and the corresponding catalytic activity

| Zr/Si In Zr-$SiO_2$ | Average coordination number | Catalytic activity ratio | Selectivity ratio |
|---|---|---|---|
| 0.004 | 6.29 | 1.00 | 1.00 |
| 0.007 | 6.38 | 0.99 | 0.96 |

## References

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