

XAFS study on the local structure of mesoporous silica supported titanium oxide as water-tolerant Lewis acid catalyst

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1 Introduction

Lewis acid catalysts are one of the most important materials for the synthesis of industrial chemicals. However, the conventional Lewis acids work in strictly anhydrous conditions because of their low tolerance to water. From the viewpoint of the Green Sustainable Chemistry, the organic solvent system should be replaced by water solvent system. For this sake, many efforts were developed to create the solid Lewis acid catalysts. We have recently reported the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ can act as a water-tolerant Lewis acid catalyst [1]. TiO_4 deposited mesoporous silica (TDMS) also showed the high catalytic performance for Lewis acid catalyzed reaction in water [2].

The active site of TDMS seemed to be the isolated TiO_4 tetrahedra, however, it is still unknown whether the local structure is changed or not in the solvent. In this study, the local structure of Ti on TDMS in/out the solvent was characterized by XAFS analysis.

2 Experiment

Mesoporous silica SBA-15 was chosen for the support and synthesized by using a block copolymer P123 as a SDA and tetramethyl orthosilicate as a silica source. Titanium species was immobilized onto SBA-15 by a postgrafting method [2]. Obtained powder was calcined at 823 K to give a TDMS. Ti loading was regulated as 2 atom%. Samples were dehydrated at 573 K under vacuum to remove the physisorbed water. Dehydrated samples were pressed into 20 mm diameter self-supporting discs and sealed in polyethylene bags under nitrogen atmosphere without contacting air and moisture. Solvent exposed samples were prepared by dropping the solvent onto discs at least 10 min before the XAFS measurements.

Ti *K*-edge XAFS data were collected at PF BL-9C with Si(111) double crystal monochromator in a transmission mode. Higher harmonics was reduced by detuning the double crystal at about 60 % intensity of the incident beam. Data analysis was carried out by using the program REX2000 (Rigaku Co.).

3 Results and Discussion

Ti *K*-edge XANES spectra are shown in Fig. 1. As prepared TDMS sample (unexposed to an air) shows a sharp pre-edge peak at around 4968.5 eV (Fig. 1 (c)), which can be attributed to the Ti 1s to 3d mixed with O

2p of tetrahedrally coordinated titanium species. On the other hand, both anatase TiO_2 and rutile TiO_2 show typical weak pre-edge peaks assignable to the transition of octahedrally coordinated titanium species. Ti species on TDMS seem to have the TiO_4 tetrahedra structure.

The TDMS catalyst shows the high activity toward the Mukaiyama-aldol reaction in water comparable as $\text{Sc}(\text{OTf})_3$ catalyst. The high activity seemed to come from this TiO_4 tetrahedra. However, the spectrum was taken in dehydrated state which was far from the reaction condition.

Interestingly, by exposing TDMS sample to the solvent, such as benzaldehyde (Fig. 1 (d)) and water (Fig. 1 (e)), the XANES spectra did not change from original one (Fig. 1 (c)). This suggests the high structural tolerance to water and also benzaldehyde. One of the reasons for showing the high activity is this highly stable Lewis acid site.

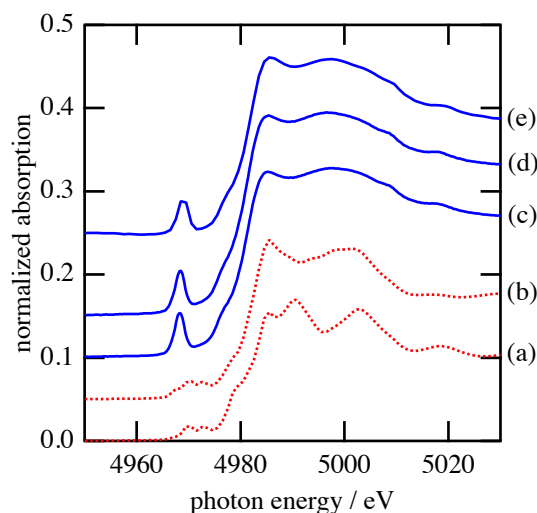


Fig. 1: Ti *K*-edge XANES spectra; (a) TiO_2 (rutile), (b) TiO_2 (anatase), (c) TDMS (as prepared), (d) TDMS with benzaldehyde, (e) TDMS with water.

References

- [1] K. Nakajima *et al.*, *J. Am. Chem. Soc.* **133**, 4224 (2011).
- [2] T. Shintaku *et al.*, *ACS Catal.* **4**, 1198 (2014).

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