

The Local Structure of Titanium Oxide Loaded on the Bimodal Silica Particles

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Introduction

Recently, we have found that zeolite particles the external surface of which was partially modified with alkylsilyl groups could be located at a liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic compounds and act as an efficient catalyst for epoxidation of alkene without agitation [1-3]. In the present study, we have focused on the clarification of the effect of local structure of active sites on the activity and selectivity in the alkene epoxidation.

Experimental section

Silica (AEROSIL 200) loaded with titanium oxide species (44-528 $\mu\text{mol/g}$) was prepared as follows: titanium(IV) tetraethoxide ($\text{Ti}(\text{OEt})_4$) was added to 2-propanol under a dry Ar atmosphere and silica was added to the mixture. After stirring the suspension at room temperature for 3 h, the solid were collected by a centrifugation, dried at 383 K for 2 h, and calcined at 773 K for 6 h. The as-prepared hydrophilic catalysts are called w-Ti/SiO₂. Bimodal catalyst powders (w/o-Ti/SiO₂) whose external surface was partially covered with alkylsilyl groups were prepared according to the previously reported procedure [2].

Epoxidation of 1-octene with aqueous H₂O₂ (30 %) at room temperature was performed as a test reaction. Details of reaction procedures and product analysis were described previously [2].

XAFS spectra were measured at the BL-9A facility of PF-KEK with Si(111) double-crystal monochromator. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 298 K.

Results and Discussion

Contents of 4-coordinated and 6-coordinated titanium oxide species in the Ti/SiO₂ samples were determined by deconvolution of XANES spectra with the those of their reference samples. Figure 1 shows the XANES spectra of w-Ti/SiO₂ and their best linear-combination fitting curves (dotted lines). For the catalysts containing Ti species < 158 $\mu\text{mol/g}$, the %-proportion of 4-coordinated titanium oxide was > 80 % and increased with increase in the Ti content. For the catalysts with > 158 $\mu\text{mol/g}$ Ti species, the 6-coordinated titanium species was predominant.

For the epoxidation of 1-octene with H₂O₂, the catalysts having relatively higher proportion of 4-coordinated titanium oxide species exhibited the higher epoxide selectivity, and the yield of epoxide seemed almost proportional to the amount of 4-coordinated

titanium oxide species. On the other hand, the catalysts with higher ratio of 6-coordinated titanium oxide species showed much lower yield of epoxide. These results suggests that the active sites on the phase boundary catalysts is 4-coordinated titanium oxide species, but not 6-coordinated ones.

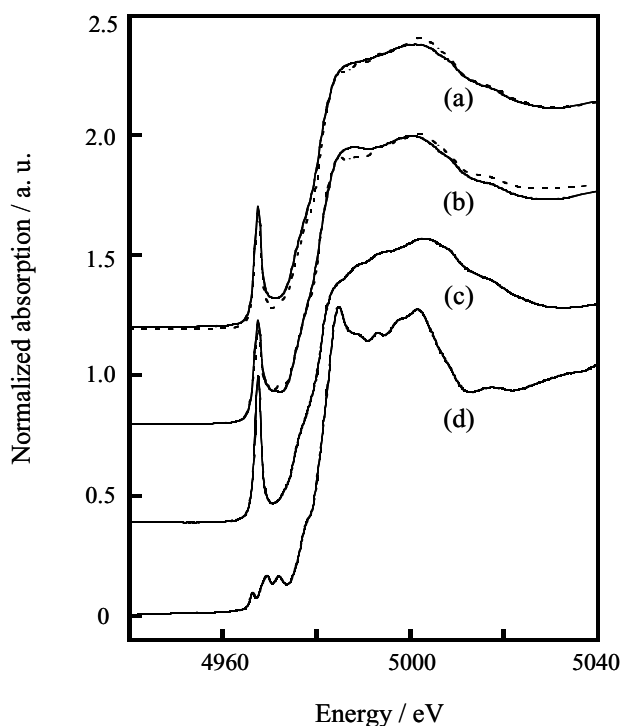


Figure 1 Ti K-edge XANES spectra of w-Ti/SiO₂ catalysts. (a) w-Ti/SiO₂-1 (158 $\mu\text{mol/g}$ as Ti), (b) w-Ti/SiO₂-2 (528 $\mu\text{mol/g}$ as Ti), (c) TS-1 as a reference of 4-coordinated titanium oxide, (d) P-25 as a reference of 6-coordinated one. Dash lines show the leaner combination fitting spectra from (c) and (d).

References

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