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Changes of coordination number of Ti in ETS-10 titanosilicate by ion-exchange

Yasuhide GOA[1], Hideaki YOSHITAKE[2], Peng WU[3], Takashi TATSUMI[*3]
[1]Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[2]Graduate School of Environment and Information Sciences, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[3]Graduate School of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Introduction

ETS-10 is one of crystalline microporous titanosilicates with corner-sharing SiO_4 tetrahedra and TiO_6 octahedra linked through bridging oxygen atoms [1], which leads us to a great interest in the ion-exchange, adsorption and catalytic characteristics of the material. Titanosilicates with highly dispersed tetrahedrally coordinated Ti species in the framework, exhibits high oxidation activity of various organic compounds, while Ti atoms in ETS-10 center octahedral environments, which deprives it of oxidation activity. Here we studied on the changes of Ti coordination environment by ion-exchange treatment and the application to oxidation catalyst.

Experimental

ETS-10 was hydrothermally synthesized from the gel with a chemical composition of $5\ SiO_2 \cdot TiO_2 \cdot 3\ NaOH \cdot KF \cdot 75\ H_2O$ at 473 K for 45 h, using Ludox® TM-40 colloidal silica and P25 titania powder as Si and Ti source, respectively. Ion-exchange was conducted using 2.0 mol dm^{-3} NH_4Claq or HClaq at room temperature followed by the calcination at 723 K for 6 h. XRD was performed to confirm the crystallinity of the material. Ti K-edge spectra were collected at BL-7C in a transmission mode and the data were analyzed by REX 2000 (Rigaku). Catalytic tests in the liquid phase were performed using cyclohexene and aqueous hydrogen peroxide as a substrate and an oxidant, respectively.

Results and discussion

XRD proved that all the samples except for the HCl-treated one were almost pure ETS-10. After the HCl-treatment, the crystalline structure of ETS-10 was completely destroyed. Ti K-edge XANES spectra in the pre-edge region of various titanosilicates are shown in Fig. 1. The peak top of the H-exchanged ETS-10 samples slightly red-shifted by 0.6 eV for NH_4Cl-treated sample and 1.6 eV for HCl-treated sample with a slight increase in intensity, which could be caused by the presence of Ti with lower coordination number [2]. Ti species in as-prepared ETS-10 are crystallographically octahedral [1], inactive in the oxidation of organic compounds, while Ti in ion-exchanged ETS-10 are in penta- or tetracoordinated environment. UV-Vis spectroscopic results also agree with the above observations.

Catalytic results are summarized in Table 1. NH_4Cl-treated ETS-10 efficiently catalyzed the epoxidation of cyclohexene. Cyclohexene conversion over NH_4Cl-exchanged ETS-10 was as high as that over [Ti, Al]-Beta, in which Ti occupies framework tetrahedral sites. The selectivity to epoxide was quite low because acid-catalyzed solvolysis of epoxide predominantly proceeded. On the other hand, HCl-treated ETS-10 exhibited low activity owing to the severely low structural order.

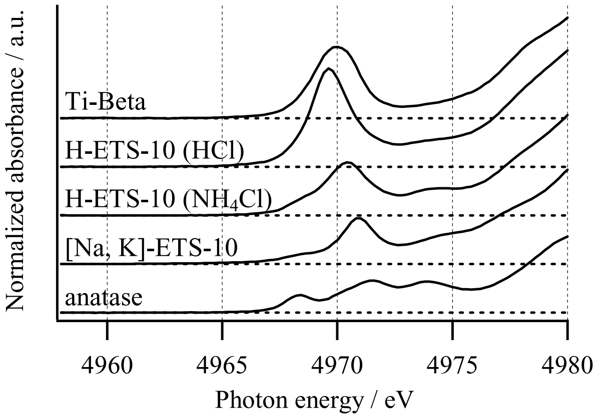

Fig.1 Pre-edge region of Ti K-edge XANES spectra of various titanosilicates.

Table 1 Results of epoxidation of cyclohexene over various titanosilicates.

Catalyst	Conv. / %	Selectivity (b) / %		
		Epox.	Glyc.	Allyl
H-ETS-10 (NH_4Cl)	35.6	5.1	79.1	15.8
H-ETS-10 (HCl)	5.6	11.5	81.9	6.6
[Ti, Al]-Beta (c)	30.4	69.3	14.9	15.8

(a) Reaction conditions: temp., 333 K; time, 3 h; 50 mg of catalyst, 5 cm^3 of acetonitrile as solvent, 8.25 mmol of cyclohexene and 2.5 mmol of H_2O_2aq (31 wt%).
(b) Epox.: cyclohexene oxide, Glyc.: 1,2-cyclohexanediol, Allyl: 2-cyclohexen-1-ol and 2-cyclohexen-1-one.
(c) Si/Ti = 35, Si/Al = 38.

References

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* ttatsumi@ynu.ac.jp