In situ XANES spectroscopy during gas-phase propylene epoxidation on a gold/titanosilicate catalyst

Juan J. BRAVO-SUAREZ¹, Kyoko K. BANDO*¹, Jiqing LU², Masatake HARUTA³, Tadahiro FUJITANI¹, S. Ted OYAMA*¹,4
¹National Institute of Advanced Industrial Science and Technology, Tsukuba, 305-8569, Japan
²Zhejiang Normal University, Jinhua 321004, China
³Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji 192-0397, Tokyo, Japan
⁴Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

Introduction
Gold supported titanosilicates are well-recognized catalysts for gas-phase synthesis of propylene oxide (PO) from propylene, oxygen and hydrogen [1,2]. However, very little is known regarding the mechanism of epoxidation of propylene. It has been assumed that H₂ and O₂ react on gold sites to form H₂O₂, which can migrate to Ti tetrahedral sites (Fig. 1, species I) to form Ti-hydroperoxide species (Fig. 1, species II) [1,2]. This peroxo species then can react with adsorbed propylene to form PO and water, as well as species I [1,3].

In this study, we have carried out transient in situ Ti K-edge XANES at reactions conditions on a AuBa/TiTUD catalyst to follow the coverage of species I.

Experimental
Supports (TiTUD, Ti/Si=3/100; SITUD) and catalysts (AuBa/TiTUD and Au/SITUD [3,4]) were prepared as described in [3,4]. In situ Ti K-edge XANES spectra were collected at BL-9A in the transmission mode using an in situ cell provided with a flow system. Spectra were obtained every 6 min in a step-scanning mode at similar conditions to those used in the catalytic reactor [3]. Typical reaction conditions are a total flow rate of 35 cm³/min, 423 K and 0.1 MPa. Under “PO formation” and “H₂O₂ formation” conditions gases ratio are C₃H₆/H₂/O₂/He = 1/1/1/7 and H₂/O₂/He = 1/1/8, respectively.

Results and discussion
In situ Ti K-edge XANES spectra under “PO formation” conditions are shown in Fig. 2A. Clearly, the intensity of the Ti pre-edge peak (4968.9 eV, Ti tetrahedral, species I) is reduced, while the feature at 4986.2 eV (higher coordinated Ti such as species II) grows as the reaction proceeds. Similar results are observed under “H₂O₂ formation” conditions (not shown). Under transient conditions (first 15 min), species I coverage is measured from the fractional decrease in the Ti pre-edge peak area under both “PO formation” and “H₂O₂ formation” conditions (Fig. 2B). From Fig. 2B, it is possible to estimate the initial net rate of epoxidation as: slope_{PO} – slope_{PO} = 3.4 x 10⁻⁴ s⁻¹. This TOF closely resembles the PO TOF (based on total Ti) after 3 h of reaction measured in the catalyst-testing reactor (3.2 x 10⁻⁴ s⁻¹) [3,4]. These results show that species I is a true intermediate during the gas-phase PO synthesis on gold/titanosilicates.

References
* kk.bando@aist.go.jp; oyama@vt.edu

Fig. 1. Possible reaction intermediates during gas-phase epoxidation of propylene on gold/titanosilicates.

Fig. 2. In situ Ti K-edge XANES spectra for AuBa/TiTUD at A) propylene epoxidation conditions as a function of time; and B) species I coverage during transient conditions at a) propylene epoxidation conditions; and b) “H₂O₂ formation” conditions.