

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

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### 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 H<sub>2</sub> and O<sub>2</sub> react on gold sites to form H<sub>2</sub>O<sub>2</sub>, which can migrate to Ti tetrahedral sites (Fig. 1, species I) to form Ti-hydroperoxide species (Fig. 1, species II) [1,2]. This peroxy 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.

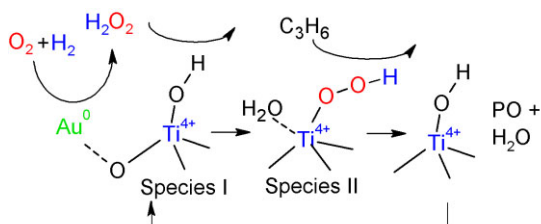


Fig. 1. Possible reaction intermediates during gas-phase epoxidation of propylene on gold/titanosilicates.

### 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 cm<sup>3</sup> min<sup>-1</sup>, 423 K and 0.1 MPa. Under “PO formation” (propylene epoxidation) and “H<sub>2</sub>O<sub>2</sub> formation” conditions gases ratio are C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/O<sub>2</sub>/He = 1/1/1/7 and H<sub>2</sub>/O<sub>2</sub>/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 “H<sub>2</sub>O<sub>2</sub> 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 “H<sub>2</sub>O<sub>2</sub> formation” conditions (Fig. 2B). From Fig. 2B, it is possible to estimate the initial net rate of epoxidation as: slope<sub>H<sub>2</sub>O<sub>2</sub></sub> – slope<sub>PO</sub> = 3.4 × 10<sup>-4</sup> s<sup>-1</sup>. This TOF closely resembles the PO TOF (based on total Ti) after 3 h of reaction measured in the catalyst-testing reactor (3.2 × 10<sup>-4</sup> s<sup>-1</sup>) [3,4]. These results show that species I is a true intermediate during the gas-phase PO synthesis on gold/titanosilicates.

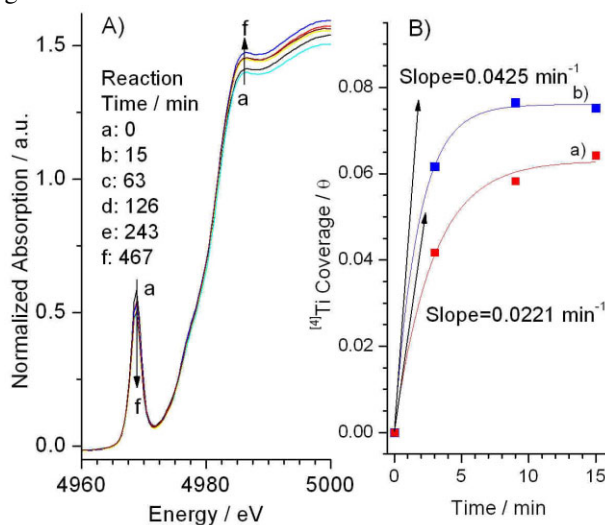


Fig. 2. In situ Ti K-edge XANES spectra for AuBa/TiTUD at A) propylene epoxidation conditions as a function of time; and B) species I coverage during transient conditions at a) propylene epoxidation conditions; and b) “H<sub>2</sub>O<sub>2</sub> formation” conditions.

### References

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