

## Development and monitoring of mesoporous titania doped with vanadium or anions for selective ethanol oxidation under visible light

**Yasuo Izumi<sup>a,\*</sup>, Kazushi Konishi<sup>b</sup>, Dilshad Masih<sup>c</sup>, Hideaki Yoshitake<sup>d</sup>**

<sup>a</sup>Graduate School of Science, Chiba University, Chiba, 263-8522, Japan

<sup>b</sup>Interdisc. Grad. Sch. of Sci. & Eng. and <sup>c</sup>Global Edge Institute, Tokyo Inst. of Tech., Yokohama, 226-8502, Japan

<sup>d</sup>Graduate School of Engineering, Yokohama National University, Yokohama, 240-8501, Japan

\*Corresponding author: Phone&Fax +81-43-290-3696, E-mail yizumi@faculty.chiba-u.jp

**Abstract:** Mesoporous TiO<sub>2</sub> doped with V or anions (C, N, P, S) were synthesized to exhibit narrow mesopore size distribution and high specific surface area as much as 1000 m<sup>2</sup>g<sup>-1</sup>. Under visible light, mesoporous TiO<sub>2</sub> was inactive for ethanol oxidation and dehydrogenation proceeded over [doped] TiO<sub>2</sub> crystalline (P25). In contrast, selective ethanol dehydration proceeded over mesoporous V-TiO<sub>2</sub> under visible light. Dynamic equilibrium was demonstrated of a few percents of V(III) state reduced by photoelectrons with anionic ethoxyl groups bound to partially-reduced V(IV- $\delta$ ) state by selective XAFS spectroscopy. Tunable, efficient ethanol oxidation proceeded on anion-doped TiO<sub>2</sub> due to lower electron-hole recoupling probability.

**Keywords:** Mesoporous, Visible light responsive, XAFS (X-ray absorption fine structure).

### 1. Introduction

One possibility for solar technology is photocatalysis over TiO<sub>2</sub>-based catalysts. Only 3% of solar energy is used with crystalline TiO<sub>2</sub> at the earth surface. The efficiency can be improved by doping with V,<sup>1</sup> C, N, or S atoms<sup>2,3</sup> and applied to the decomposition of ethanol, methylene blue, and nitric oxide.<sup>4</sup>

In this work, the framework of TiO<sub>2</sub> was ultimately dispersed by mesoporous synthesis technique and doping atom was added in the first synthetic step. Because the specific surface area was as much as 1000 m<sup>2</sup>g<sup>-1</sup>, the doped atoms were effectively dispersed to surface. The surface sites will be coordinatively unsaturated and reactive. The quantum size effect for mesoporous doped TiO<sub>2</sub> and the difference of impurity levels for between doped cation and anions are discussed.

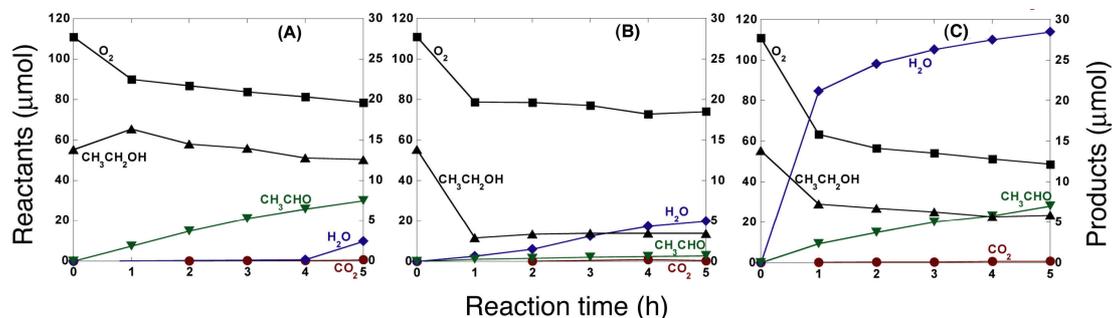
### 2. Experimental section

Mesoporous V-TiO<sub>2</sub> was synthesized from Ti(O-*i*C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, V=O(O-*i*C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, and dodecylamine.<sup>4</sup> The uniform pore size distributed at 3 nm. The doping of C, N, P, or S was performed similarly by adding NH<sub>3</sub>, P=O(OH)<sub>3</sub>, (NH<sub>2</sub>)<sub>2</sub>C=O, or (NH<sub>2</sub>)<sub>2</sub>C=S. 0.1 g of mesoporous doped TiO<sub>2</sub> was homogeneously distributed in quartz reaction cell illuminated with xenon arc lamp operated at 500 W (Ushio). UV-cut filter L42 (Kenko) was inserted to illuminate visible light only (> 420 nm). Ethanol (1.33 kPa) and O<sub>2</sub> (2.67 kPa) were introduced in closed glass system (132 ml) at 290 K. Valence state-sensitive XAFS measurements were performed at beamline 7C of Photon Factory, KEK. V K $\beta_{5,2}$  emission from samples associated with electronic transition from V impurity level (between band gap) to V 1s was analyzed by homemade fluorescence spectrometer and V K-edge XAFS spectra were measured by detecting the V K $\beta_{5,2}$  emission.<sup>5</sup>

### 3. Results and discussion

Results of ethanol oxidation reactions were depicted in Figure 1. In contrast to ethanol dehydrogenation to acetaldehyde over TiO<sub>2</sub> (P25) (A) and poor activity of mesoporous TiO<sub>2</sub> (B), mesoporous V-TiO<sub>2</sub> produced water, especially remarkable in the first 1h in addition to acetaldehyde formation (C). Synthesis

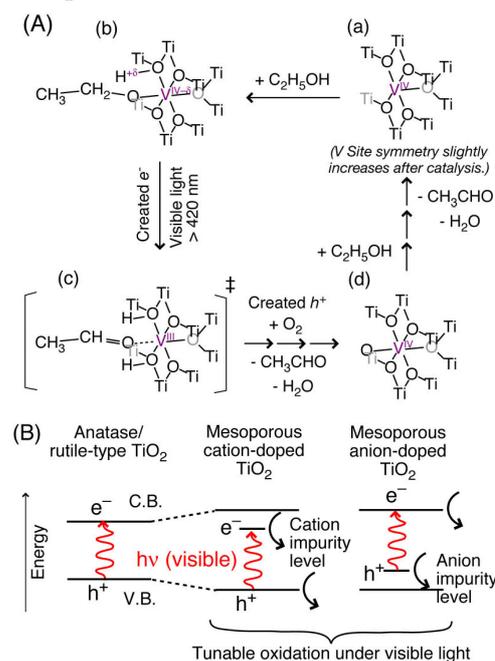
rates for each compound became steady and almost equivalent. The reaction profile (initial remarkable water formation followed by steady ethanol dehydration) was repeated by catalyst reactivation under UV-visible light for 3h between reaction batches. Steady reaction rates to acetaldehyde and water were 79 – 72% and 65 – 44%, respectively, in the repeated batch tests compared to the first batch (Figure 1C).



**Figure 1.** Ethanol oxidation reaction as a function of time under visible light (> 420 nm) over crystalline  $\text{TiO}_2$  (P25) (A), mesoporous  $\text{TiO}_2$  (B), and mesoporous V- $\text{TiO}_2$  (3.0 wt% V; C) at 290 K.

Because mesoporous  $\text{TiO}_2$  was essentially inactive for ethanol oxidation, doped V is the key of photocatalysis. The V site structure transformation was followed step by step according with the specific dehydration. Based on the V  $K\beta_{5,2}$ -selecting XAFS, dissociative adsorption of ethanol was found on V(IV) sites (Figure 2A-b). When visible light was turned on, V(III) sites were discriminated by V(III) state-selective XAFS, but the population of V(III) species was a few percents. Thus, V(III) state reduced by photoelectrons (Figure 2A-c) and anionic ethoxyl groups bound to partially-reduced V(IV- $\delta$ ) species were in dynamic equilibrium. This finding was enabled by V state-selective XAFS to extract and confirm minor V(III) species. The intermediate state was oxidized back (Figure 2A-d, a) by adding  $\text{O}_2$  and/or under visible light.

This paper is especially important because selective O–O bond activation was discovered by creating impurity levels near conduction band for V and near valence band for C, N, P, S (Figure 2B) for mesoporous  $\text{TiO}_2$  and catalytic key role under visible light was clarified by state-selective XAFS.



**Figure 2.** (A) Proposed reaction mechanism of ethanol dehydration over the mesoporous V- $\text{TiO}_2$  under visible light (a – d). (B) Band gap and impurity levels for crystalline and mesoporous doped  $\text{TiO}_2$ .

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