

## XAFS study of supported ruthenium oxide photocatalyst

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### 1. Introduction

Hydrogen is a very important clean source and can be produced by the decomposition of water with an aid of photocatalysts under light illumination. We have found that the combination of ruthenium oxide and BaTi<sub>4</sub>O<sub>9</sub> makes good photocatalyst to decompose water to oxygen and hydrogen in a stoichiometric ratio. The photocatalytic activity strongly depended on the conditions of ruthenium oxides dispersed on BaTi<sub>4</sub>O<sub>9</sub>, and it is essential to characterize their chemical states and local structures for the design of efficient photocatalysts.

Ruthenium oxides on BaTi<sub>4</sub>O<sub>9</sub> were obtained by the oxidation of ruthenium species deposited on the surface by an impregnation method. The catalytic activity was a function of oxidation temperature, and in the present study, the ruthenium oxides prepared by various oxidation temperatures were investigated.

### 2. Experimental

BaTi<sub>4</sub>O<sub>9</sub> samples were prepared according to the method in the literature [1]: BaTi<sub>4</sub>O<sub>9</sub> was impregnated with Ru<sub>3</sub>(CO)<sub>12</sub> in THF solution at 333K, dried at 353K and oxidized in the temperature range 473-873K in air. Water decomposition was carried out in a closed circulating reaction system under UV irradiation. The Ru K-edge X-ray absorption spectra were recorded at room temperature in a fluorescence mode at BL38B1 station with an attached Si(311) monochromator.

### 3. Results

For all the catalyst samples, the XANES spectra showed the ruthenium peaks similar to those for tetravalent valent ruthenium, that is, Ru(IV), indicating that the Ru species on BaTi<sub>4</sub>O<sub>9</sub> was present as RuO<sub>2</sub>. Fig.1 shows the Fourier transforms(FTs) of k<sup>3</sup>-weighted EXAFS of a sample oxidized at 473-873K. The FT magnitudes of Ru-O and Ru-Ru bonds increased with increasing oxidation temperature, reached a maximum at 673K, and then decreased. Although an oxidation temperature suitable for high photocatalytic activity was slightly different from that for the maximum intensity of FT, the results indicated that fine crystallized RuO<sub>2</sub> particles were responsible for efficient photocatalytic performance. To confirm this view, the detailed analysis for the relationship between RuO<sub>2</sub> structure and catalytic activity is in progress.

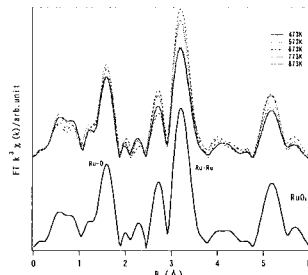


Fig.1 Fourier transforms of k<sup>3</sup>-weighted EXAFS of Ru K-edge of Ru combination

[1] Y.Inoue, Y.Asai, K. Sato, J. Chem. Soc., Faraday Trans., 1994,90,797

## Developing of *In-situ* XAFS for Understanding the Formation Mechanism of Microstructures at Ultra Fine Grained Steel

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Nano Metal Project has started since 2001 as a Japanese national project in order to clarify the mechanism of nano-sized phenomena like nano-cluster and nucleation of precipitation in metals.

The performance in micro- alloyed steel strongly depends on the nano-sized morphology of alloying elements. The morphology depends on heat treatments. *In-situ* XAFS at high temperature was firstly tried and succeeded in micro-alloyed steel.

The high-temperature (~1273K, ~1.6Pa) furnace of experimental use of in-heating XAFS was installed in BL38B1 station of SPring-8. Both copper *K*-edge spectra and titanium *K*-edge spectra were measured by x-ray fluorescence detection method, and 19-elements SSD was installed in BL38B1. The x-ray beam was monochromatized by using Si(111) double crystal monochromators, which focused by using an Rh-

coated cylindrical SiO<sub>2</sub> mirror. The steel (Fe-0.3%C-2.0%Cu-0.5%Mo-0.5%V-0.5%Ti-0.5%Nb) of 1mm in thickness was placed in Al<sub>2</sub>O<sub>3</sub> furnace. Heat-treating which exceeded 1573K was added to the sample used for the measurement beforehand.

The *K*-edge XAFS spectra for Cu and Ti are shown in Figs.1 and 2, respectively. From the results of FEFF8.2 calculations, it is suggested that Cu atom forms like the structure of Cu in Fe(fcc), in 300K. On the other hand, Ti atom forms TiC structure, in 300K. It is suggested that the spectra of Cu in 1023K likes fcc and Ti in 1223K shows characteristic shape possibly thought to be formed the composite carbide. It is necessary to wait for a more detailed analysis about the precipitation phenomenon of Cu and Ti carbides.

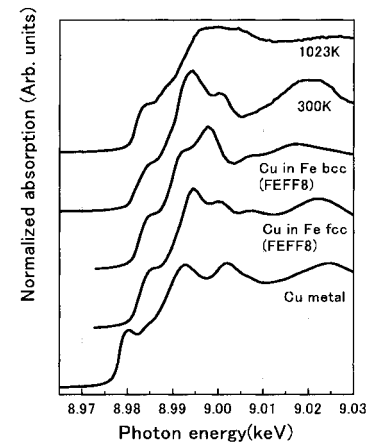


Fig. 1 Copper *K*<sub>edge</sub> XAFS of ultra fine grained steel in 300K, and in-heating at 1023K.

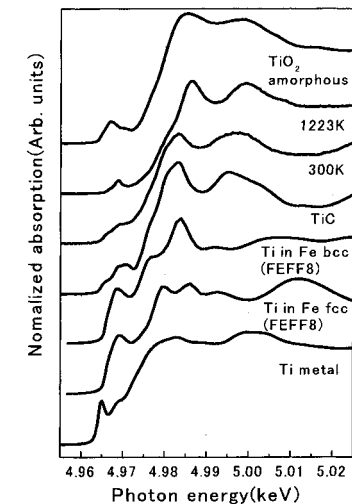


Fig. 2 Titanium *K*<sub>edge</sub> XAFS of ultra fine grained steel in 300K, and in-heating at 1223K.