

# XAFS Analysis of Iron Species Supported on Alumina

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## 1. Introduction

Some noble metals can act as the active catalyst for a lot of conversion reactions with high activity, and the present human society is highly depended on the use of such catalysts. The exhaust gas of automobile is detoxified by the three-way catalyst, which is composed of Pd, Rh, and Pt supported on alumina. The key material, molecular hydrogen, for future society can be generated from convenient substrates by catalytic reforming reactions with the noble metal catalyst, and is converted to atomic hydrogen on an anodic electrode of fuel cell by the Pt catalyst. However, the creation of corresponding functions with alternative metal elements becomes more and more important without using such noble metals because of the limited utilization. Recently, the iron compound is attempted to use as the supporting material of the three-way catalyst, and the comparable performance has been reported for the Pd catalyst without Rh and Pt. The supporting iron species must contribute to the catalysis reactions, and the reduction/oxidation behavior of the iron species is essential to understand the catalysis mechanisms. In this study, the chemical states of the iron species have been analyzed by means of the XAFS spectroscopy to know the reduction/oxidation characteristics on the most convenient support, alumina.

## 2. Experimental

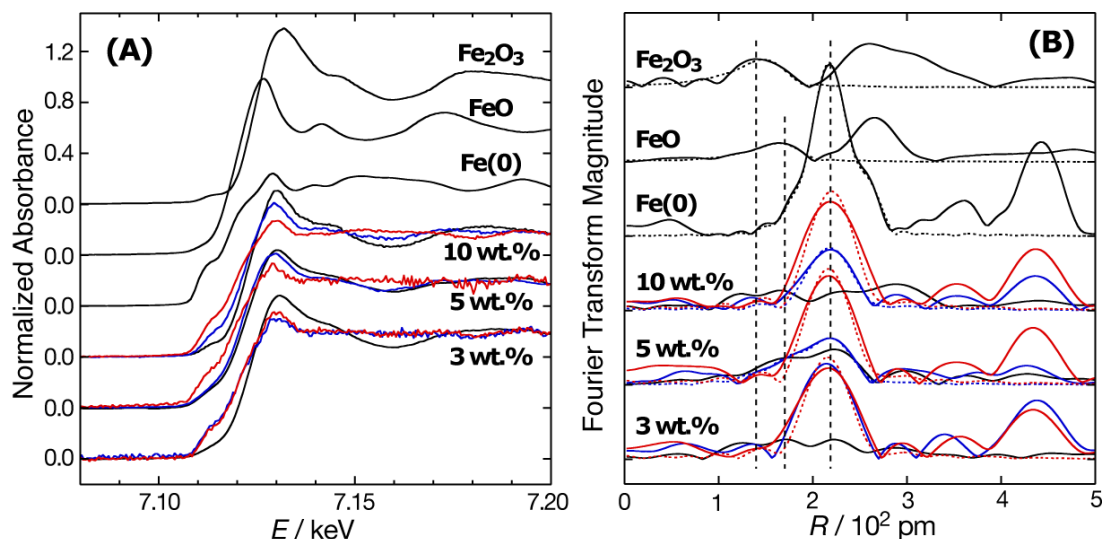
Supported iron on alumina was prepared by the incipient wetness impregnation method of  $\alpha$ -alumina with the acidified aqueous solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  by changing the content of iron from 3 to 10 % by weight. The resulting solids were calcined at 773 K in air for 24 h. The samples were reduced under the  $\text{H}_2$  flow at different temperatures from 673 to 873 K. The reduced irons were oxidized in air at 773 K to check the reversibility of the reduction/oxidation processes. The XAFS measurements were carried out at BL-3 of SR Center, Ritsumeikan University at the vicinity of the Fe K edge. The XRD patterns were recorded using the laboratory X-ray diffractometer (RINT-2200, Rigaku).

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### 3. Results and Discussion

The XANES spectra (Fig. 1(A)) indicate that the metallic iron forms in the samples reduced at 876 K. The XRD patterns consistently demonstrate the reduction of iron, and the average diameter of the metallic particle is estimated to be *ca.* 30 nm by the analysis of the line width by means of the Scherrer equation. The coordination number of the Fe–Fe interaction is calculated to be  $7.9 \pm 0.2$  for all samples with different loading by the curve fitting of a main peak of the Fourier transforms (Fig. 1(B)), and is comparable to the bulk iron. The fitted Fe–Fe distance,  $250 \pm 1$  pm, is also in accordance with that (248 pm) of bulk. The iron species is thus reduced quantitatively under the reductive atmosphere at 876 K and is independent on the loading of iron. On the other hand, the XAFS spectra show that the oxidized iron(III) species is predominant for the sample of 10 wt.% treated at 673 K, and that the degree of reduction is found to be dependent on the loading of iron at lower temperature. The high loading of iron shows the resistance against the reduction. The XRD pattern indicates that the particle size of oxidized form is enlarged from 11 nm (3 wt.%) to 22 nm (10 wt.%), and the coordination number of Fe–O is also increased from 5.5 (3 wt.%) to 5.8 (10 wt.%). The present XAFS analyses clearly demonstrate that the larger oxide particle formed under the high loading of iron resists to the reduction at lower temperatures, but the reduction/oxidation processes become reversible at the elevated temperature.



**Fig. 1:** XANES spectra at Fe K edge (A) and Fourier transform magnitude (B) of Fe species supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The reduction temperature was 673 K (black), 773 K (blue), and 876 K (red). The dotted lines in (B) represent the fitted function. The spectra of Fe foil, FeO, and Fe<sub>2</sub>O<sub>3</sub> are included for comparison.