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XAFS study of iron oxide nanoparticles coated with Ti-containing mesoporous silica

Yuichi KONDO, Kohsuke MORI*, Hiromi YAMASHITA
Divisions of Materials and Manufacturing Science, Graduate School of Engineering,
Osaka University, 2-1 Yamada-oka, Suita, Osaka, Japan.

Introduction

Ti-containing mesoporous silica material has attracted much attention as single-site catalyst, which shows unique activities in selective oxidation reactions. We encapsulated magnetic iron oxide nanoparticles into Ti-containing mesoporous silica. This allows easy recovery from reaction solution by a permanent magnet. Herein, we report the local structures around Fe moieties characterized by X-ray absorption fine structure (XAFS) measurement.[1-3]

Experimental

$FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were dissolved in the deoxygenated water under Ar atmosphere at room temperature, and the resulting solution was added to a 25 % NH_4OH solution after 10 min. After 3 h, 2-propnanol was added to the obtained precipitate solution, and then the solution was heated at 313 K. After 30 min, TEOS was rapidly added and continuously aged at 313 K for 20 h. After calcination at 523 K for 2 h, the obtained reddish-brown materials were well dispersed in ethanol. The solution composed of TEOS, TPOT, dodecylamine, H_2O, ethanol, and 2-propanol was added and stirred at room temperature for 20 h. The as-synthesized sample was calcined at 823 K for 5 h to remove the structure-directing reagent from the materials, giving Ti-HMS/Fe_xO_y as a reddish-brown powder. Fe K-edge XAFS spectra were recorded at room temperature in the fluorescence mode. The EXAFS data were examined by Rigaku EXAFS. The pre-edge peaks in the XANES regions were normalized for atomic absorption, based on the average absorption coefficient of the spectral region.

Results and discussions

Figure 1 shows the Fe K-edge XANES spectra of the Ti-HMS/Fe_xO_y as well as reference iron compounds. The edge position (measured at the half-height of the edge jump) depends on the electronic charge of iron ion, and their energies decreased in the order of Ti-HMS/Fe_xO_y (7122.0 eV) > α-Fe_2O_3 (7119.6 eV) > γ-Fe_2O_3 (7119.2 eV) > Fe_3O_4 (7118.3 eV) > Fe foil (7117.1 eV). The iron oxides encapsulated within silica matrix have higher X-ray absorption edge energy than those of bulk Fe^{2+} and Fe^{3+}. This feature is analogous to that of the Fe_2O_3-intercalated layered compounds, but has not been observed for unsupported Fe_2O_3 nanoparticles. It can be said that, therefore, this effect originates not from the nanosize of iron oxide, but from the environment of iron oxide. Another prominent characteristics of XANES spectra for Ti-HMS/Fe_xO_y is the large white line area due to the main 1s → 4p transition. The white line area represents the extent of an empty orbital. Thus the encapsulated iron oxide nanoparticles appear to be in a highly electron-deficient state. This result is well consistent with the relatively high Fe K-edge energy of the Ti-HMS/Fe_xO_y.

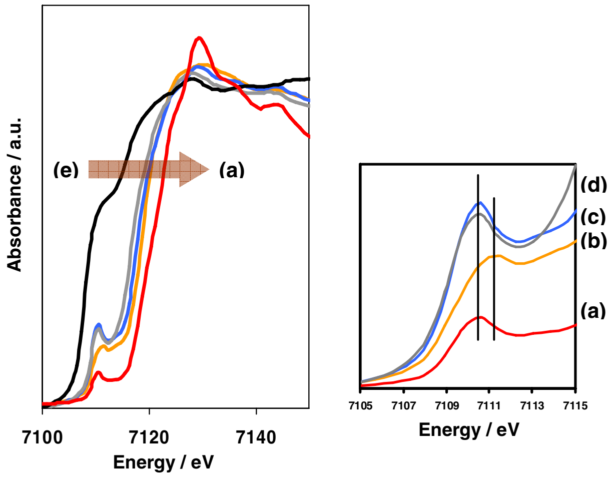

Figure 1. Fe K-edge XANES spectra of (a) Ti-HMS/Fe_xO_y, (b) α-Fe_2O_3, (c) γ-Fe_2O_3, (d) Fe_3O_4, (e) Fe metal. The enlarged figure of pre-edge peaks is shown in the inset.

Moreover, we performed the selective oxidation reaction of 2,6-DTBP using Ti-HMS/Fe_xO_y as catalyst: the corresponding quinine was obtained with 97 % yield. The catalyst could be easily recovered from the reaction liquid with a permanent magnet, and its reactivity was still sustained even 5 th reuse.

Conclusions

A novel multifunctional heterogeneous catalyst, Ti-HMS/Fe_xO_y, has been synthesized *via* the two-step coating method. XAFS study revealed the high electronic state of the encapsulated iron oxide within the silica matrix.

References

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*mori@mat.eng.osaka-u.ac.jp