Mg K-Edge XAFS Study of Silica-Magnesia Systems

H. Yoshida, T. Yoshida*, T. Tanaka*, T. Funabiki*, S. Yoshida*, T. Abe, K. Kimura and T. Hattori

Department of Applied Chemistry, School of Engineering, Nagoya University, Nagoya 464-01, Japan

**Department of Molecular Engineering, School of Engineering, Kyoto University, Kyoto 606-01, Japan*

Abstract. Mg K-edge XAFS study was carried out to clarify the local structure of silica-magnesia systems prepared in four ways; by impregnation of silica with an aqueous solution of magnesium nitrate or with a methanol solution of magnesium methoxide, and by sol-gel method with tetraethyl orthosilicate and magnesium solutions mentioned above. It is clarified that the preparation method decides the structure of Mg species respectively; (i) MgO particle on silica, (ii) dispersed Mg species on silica surface, (iii) dispersed Mg tetrahedral species in silica bulk.

1. INTRODUCTION

Silica-magnesia system is known as an acid-base bifunctional catalyst which promotes dehydration and dehydrogenation of alcohols and so on [1-3]. However, the function of the catalysts was not controlled completely, since the acid-base properties are affected by various factors, *e.g.* preparation method, composition and treatment [4-6]. In order to control the function sophisticatedly, it is important to know the status of component ion, especially the local structure of Mg ion; *e.g.* Mg ion in magnesium oxides is octahedrally coordinated, while it is believed that Mg ion located in silica matrix is tetrahedral coordinated [4, 5, 7, 8]. In this study Mg K-edge XAFS was employed to obtain information of the local structure of the Mg ions in silica-magnesia samples.

2. EXPERIMENTAL

Silica-magnesia samples were prepared in following four ways. MgO content of each sample was 15 mass% as standard. (I) Supported sample MgO/SiO₂(W) was prepared by impregnation of silica with an aqueous solution of Mg(NO₃)₂ followed by evaporation to dryness and calcination in air at 773 K. Silica support was prepared from Si(OC₂H₅)₄, ethanol and water by sol-gel method [9]. (II) Another supported sample MgO/SiO₂(M) was prepared in the same manner with a methanol solution of Mg(OCH₃)₂ instead of the aqueous solution. The solution was prepared by reaction of magnesium metal with refluxed methanol [10]. (III) Binary oxide sample MgO-SiO₂(W) was synthesized from Si(OC₂H₅)₄, ethanol and an aqueous solution of Mg(NO₃)₂ by sol-gel method followed by drying and calcination. (IV) Another binary oxide sample MgO-SiO₂(M) was synthesized in the same way with a methanol solution of Mg(OCH₃)₂ instead of the aqueous solution. In addition to these four samples, a reference catalyst [11] JRC-SM-1 (MgO contents was 29 mass%, the Catalysis Society of Japan) was also employed, which was synthesized hydrothermally from MgO and SiO₂. X-ray absorption experiments were carried out on the BL-7A at UVSOR, Institute for Molecular Science, Okazaki, Japan [12], with a ring energy 750 MeV and stored current of 80-200 mA. Spectra were recorded at room temperature, using a beryl two-crystal monochromator in a total electron yield mode. The sample was mixed with active carbon in dry hexane and was put on the first photocathode made of Cu-Be of the electron multiplier.

3. RESULTS AND DISCUSSION

Figure 1 shows XANES spectra of the silica-magnesia samples a) - e) and reference compounds f) - k). Reference spectra f) - k) seem to be dominantly composed of three peaks, though the energy position, intensity and sharpness are different from each other. The spectra of the prepared silica-magnesia samples a) - d) are classified into three types, indicating that the local structures around Mg atom are obviously distinguishable.

The XANES of MgO/SiO₂(M) b) is obviously identical with that of MgO f) of typical rock salt structure, indicating Mg ion exists as MgO particle, *i.e.* the Mg ion is octahedrally surrounded by 6-oxygen atoms. It has been also reported that MgO small particles on silica [13] and zeolite [14] were produced in this method. Mg(OCH₃)₂ easily reacts with water. In methanol solution, Mg(OCH₃)₂ reacts with surface hydroxyl groups on silica and/or reacts with H₂O and Mg(OCH₃)₂ molecules in methanol. Each reactions leads to dispersed Mg species and MgO particle, respectively. Since MgO particle was produced in this sample, the latter reaction would be dominant;

The XANES of MgO-SiO₂(M) d) is essentially identical to that of JRC-SM-1 e) and a magnesium silicate, Mg₂Si₃O₈ i). Sol-gel method and hydrothermal synthesis are known to be suitable for preparing binary oxide whose components are well mixed at an atomic level, i.e., Mg ions would be completely in the silica tetrahedral matrix. Therefore this spectra would be assigned to the tetrahedrally coordinated Mg ion. Through hydrolysis and condensation between Mg(OCH₃)₂ and Si(OC₂H₅)₄, Mg-O-Si network would be constructed, and high dispersion of Mg ion in silica matrix would be achieved;

MgO/SiO₂(W) a) shows another type of XANES which has twin broad peaks at 1310 and 1315 eV. There are no identical spectrum of the references. Generally in the supported catalysts, metal oxide loaded is classified into alternative structures; particle or dispersed species on the surface. The XANES of MgO/SiO₂(W) is clearly different from that of the former, therefore this is assigned to the latter species. Since the species on the silica surface would be affected by silica matrix structurally or electronically, we tentatively propose that it is surface tetrahedral species. The difference between the spectra a) and d) would be explained by the location of Mg species; on the surface or in the bulk. This sample MgO/SiO₂(W) a) was prepared by using aqueous solution of Mg(NO₃)₂. A similar spectrum has reported for Mg/zeolite prepared in the same manner [14]. Under the preparation, it is suggested that Mg ion in aqueous solution adsorbed on the negative charge points of silica surface so that Mg oxide species produced are dispersed and strongly affected by silica surface.

The sample MgO-SiO₂(W) were also prepared by using aqueous solution of Mg(NO₃)₂. The spectrum c) is identical to that of MgO/SiO₂(W) a), suggesting that the magnesium species are mainly located on the surface of silica. While Mg ion exists as a hydrate cation in aqueous solution, silica-gel network was constructed through the hydrolysis and condensation,

Mg ion would not react with Si(OC₂H₅)₄ but only adsorb on silica gel, resulting in the dispersed Mg oxide species like that of MgO/SiO₂(W).

In conclusion, it is clarified that three types of magnesium oxide species in silica-magnesia systems are respectively prepared by each suitable method; (i) MgO particle on silica, where Mg ion is located octahedral site, (ii) dispersed magnesium oxide species on the silica surface, which is interacted with surface silica matrix, (iii) dispersed Mg species in the silica matrix, which is tetrahedral.

Acknowledgements

X-ray absorption experiments were approved by the Joint Studies Program (1991-1995) of UVSOR of the Institute for Molecular Science. HY was supported by a grant in aid from the JSPS for Japanese Junior Scientists.

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Figure 1 XANES spectra of the silica-magnesia samples and reference compounds. a) MgO/SiO₂(W), b) MgO/SiO₂(M), c) MgO-SiO₂(W), d) MgO-SiO₂(M), e) JRC-SM-1, f) MgO, g) Mg₂SiO₄ [13], h) MgSiO₃ [13], i) Mg₂Si₃O₈, j) MgAl₂O₄, k) Mg(OH)₂.