

## Simple Preparation Method of Isolated Iron (III) Species on Silica Surface

Yusuke Yamada,\* Yuichi Ichihashi,† Hisanori Ando,†† Atsushi Ueda, Hiroshi Shioyama, and Tetsuhiko Kobayashi\*  
*Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology (AIST),  
 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577*

†*Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology (AIST),  
 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565*  
 ††*Special Division for Human Life Technology, National Institute of Advanced Industrial Science and Technology (AIST),  
 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577*

(Received December 4, 2002; CL-021034)

The preparation of  $\text{Fe}/\text{SiO}_2$  by impregnation with an acetonitrile solution of  $[\text{Fe}^{\text{III}}(\text{acac})_3]$  promotes the isolation of  $\text{Fe}^{3+}$  ion on a silica surface when the ratio of  $\text{Fe}/\text{Si}$  is smaller than 0.1/100. The tetrahedral coordination of the  $\text{Fe}^{3+}$  was confirmed by X-ray absorption and diffuse reflectance UV-vis spectroscopies. The isolated  $\text{Fe}^{3+}$  promotes the partial methane oxidation catalysis of the  $\text{Fe}/\text{SiO}_2$ .

The direct conversion of methane to formaldehyde or methanol with molecular oxygen is benign process, however, no catalyst was found to be commercially available.<sup>1</sup> At the scientific level, vanadium oxide or molybdenum oxide loaded on silica is known as an effective catalyst for this reaction.<sup>2</sup> The optimal loading is around 5 wt% to form the corresponding metal oxide whose lattice oxygen plays an important role in the catalytic reaction. Our group has reported that silica with a very low loading of iron ( $\text{Fe}/\text{Si} = 0.03/100$ ) also shows partial methane oxidation catalysis.<sup>3</sup> Some spectroscopic results such as reflectance UV-vis indicated that the isolated iron in the silica framework enhances the catalysis of silica. Recently, similar results were observed by other groups.<sup>4,5</sup> Although the increase in the number of isolated irons would enhance the selective oxidation catalysis, the highly cohesive nature of the iron (III) ion disturbs its isolation on a silica surface when a conventional preparation method was used.

Impregnation is a very popular catalyst preparation method. Iron nitrate was often used as a precursor for an iron containing catalyst because of its high solubility in water and the easy removal of nitrate by calcination. The aqueous solution of iron nitrate is not suitable for the isolation of iron because iron nitrate is easily hydrolyzed in water to form a multinuclear species. The multinuclear structure could be maintained after calcination. Here we show the preparation of  $\text{Fe}/\text{SiO}_2$  using an acetonitrile solution of  $[\text{Fe}^{\text{III}}(\text{acac})_3]$  ( $\text{acac} = \text{acetylacetone}$ ). In the solution,  $\text{Fe}(\text{III})$  ion retains its mononuclear form because the solvolysis of the  $\text{Fe}(\text{III})$  complex was suppressed by the lower donation of acetonitrile than water and high formation constant of the acetylacetone ligand to iron(III). The partial methane oxidation catalysis of the  $\text{Fe}/\text{SiO}_2$  prepared with the acetonitrile solution was compared to that of the  $\text{Fe}/\text{SiO}_2$  prepared with the aqueous solution of iron nitrate.

The silica was obtained from Merck GmbH (extra pure, 60–270 mesh,  $400 \text{ m}^2 \text{ g}^{-1}$ ). The appropriate amount of the iron precursors was dissolved into acetonitrile or water. A solution (1 mL) was slowly dropped onto the silica powder (1.00 g) which was manually shaken. The swollen silica was placed on a sonicator

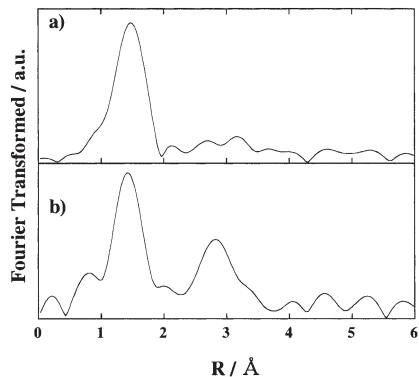
for 30 min and dried at 343 K for 5 h. The dried gel was calcined at 873 K for 5 h at a ramp rate of 10 K/min.

The iron structure on the silica surface was confirmed by X-ray absorption and diffuse reflectance UV-vis spectroscopy. The iron K edge extended X-ray absorption fine structure spectra (EXAFS) were collected at the BL-12C facility of the Photon Factory at the National Laboratory for High Energy Accelerator Research Organization, Tsukuba. The EXAFS data were collected in the fluorescence mode between two polyethylene films. The EXAFS data was treated by the program REX2000 (Rigaku) for Windows 2000. Several data sets were collected for each sample in  $k$  space ( $k = \text{photoelectron wavevector}/\text{\AA}^{-1}$ ). The EXAFS spectra were analyzed according to standard procedures. To perform the Fourier transform, the EXAFS was multiplied by  $k^3$  in the range of  $k = 3\text{--}14 \text{ \AA}^{-1}$ , and a Hanning window was used. A quantitative analysis was performed by fitting the background-subtracted EXAFS signals using a nonlinear least-squares routine and minimization. Bulk  $\alpha\text{-Fe}_2\text{O}_3$  obtained commercially and characterized by XRD was used as standard sample.<sup>6,7</sup> The UV-vis spectra were recorded using a Otsuka Electronics MCPD-2000 spectrometer. The spectra of powdery samples were collected at 220–800 nm referenced to  $\text{BaSO}_4$  with 1.2 nm resolutions.

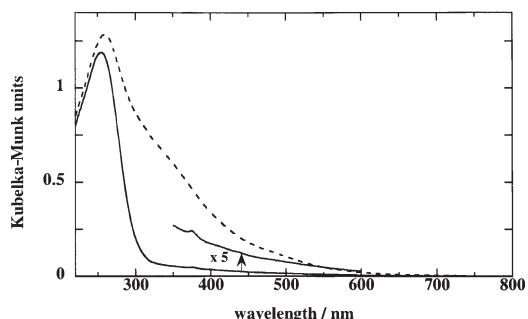
The partial methane oxidation catalysis was tested under the following conditions. A mixture of catalysts and quartz sands (300 mg and 2.7 g, respectively) were loaded into a quartz tube reactor (12 mm inner diameter). A specific amount of quartz sands and wool were placed over and under the mixture to prevent a gas phase reaction. A mixture of methane and oxygen in the ratio of  $\text{CH}_4:\text{O}_2 = 95:5$  at a pressure of 101 kPa was passed through the reactor at a flow rate of  $50 \text{ cm}^3 \cdot \text{min}^{-1}$  at 873 K. The effluent from the reactor was analyzed using an FID-GC with a Porapak Q column and a methanator. The detected products were  $\text{CO}$ ,  $\text{CO}_2$  and formaldehyde.

Figure 1 shows the  $k^3$ -weighted, phase-uncorrected, Fourier transform of the EXAFS function of 0.1%  $\text{Fe}/\text{SiO}_2$  prepared with acetonitrile solution of  $[\text{Fe}(\text{acac})_3]$  (**1**) and the aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  (**2**). The EXAFS peak of **1** shows only one peak originating from the  $\text{Fe}-\text{O}$  interaction, on the other hand, the spectrum of **2** shows two major peaks originating from the  $\text{Fe}-\text{O}$  and  $\text{Fe}-\text{Fe}$  interaction. A quantitative analysis of **1** yielded 3.8 oxygen atoms located at  $1.88 \text{ \AA}$  by the curve fitting. These values are almost the same for the tetrahedrally coordinated iron (III) previously reported.<sup>8–10</sup> This result reveals that the iron ions of **1** were atomically dispersed in the silica matrix.

The tetrahedral coordination of the iron in **1** was confirmed by UV-vis spectroscopy. Figure 2 depicts the UV-vis spectra of **1** and



**Figure 1.**  $k^3$ -weighted, phase-uncorrected, FT of the EXAFS function of Fe/SiO<sub>2</sub> prepared with a) an acetonitrile solution of [Fe(acac)<sub>3</sub>] or b) an aqueous solution of iron nitrate.

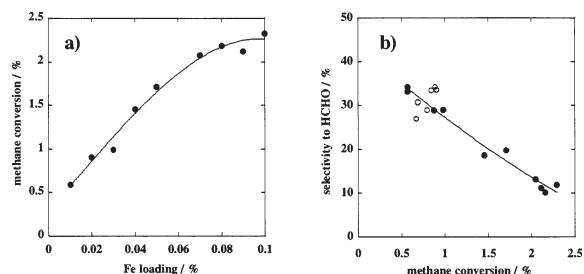


**Figure 2.** Diffused reflectant UV-vis spectra of Fe/SiO<sub>2</sub> (Fe/Si = 0.1/100) prepared with an acetonitrile solution of [Fe(acac)<sub>3</sub>] (solid line) or an aqueous solution of iron nitrate (dashed line).

2. The strong absorption in the 220–300 nm was assigned to ligand to metal Fe<sup>3+</sup> charge transfer band from isolated framework Fe<sup>3+</sup>.<sup>10</sup> 2 shows a broad band in the visible region corresponding to the formation of the bulk iron oxide.<sup>9</sup> 1 shows no visible band but a small peak at 376 nm. The peak was assigned to one of the forbidden d-d transitions of iron with a tetrahedral coordination.<sup>10,11</sup> There should be four peaks in the region between 370 nm and 490 nm, however, the three other peaks were not clearly found because of their weak intensity.

Figure 3 shows the methane conversion on Fe/SiO<sub>2</sub> prepared using the acetonitrile solution of [Fe<sup>III</sup>(acac)<sub>3</sub>] as a function of Fe loadings. The methane conversion increased with increasing Fe loadings, although the selectivity to formaldehyde highly depends on the conversion. When Fe/SiO<sub>2</sub> prepared with the aqueous solution of iron nitrate, the conversion did not increase. These results clearly indicate that isolated iron species accelerates the methane conversion and clustered iron oxide is not effective for the oxidation.

Recently, Arena et al. also reported the preparation of Fe/SiO<sub>2</sub> with an aqueous solution of Fe<sup>2+</sup>.<sup>4</sup> They tested the catalysis of the Fe/SiO<sub>2</sub> under a slightly pressurized condition and found that the catalyst shows a high activity without any loss of selectivity to formaldehyde. The less cohesive property of Fe<sup>2+</sup> than Fe<sup>3+</sup> suppressed the iron oxide formation during the preparation. The catalyst should be prepared under an inert atmosphere to prevent the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. The iron(III)



**Figure 3.** Correlation between methane conversion a) and Fe loading of Fe/SiO<sub>2</sub> or b) and the selectivity to HCHO. (Reaction temperature; 873 K, pressure; 1 atm,  $SV = 10000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) Fe/SiO<sub>2</sub> were prepared with an acetonitrile solution of [Fe(acac)<sub>3</sub>] (closed circles) or an aqueous solution of iron nitrate (open circles).

complex of [Fe<sup>III</sup>(acac)<sub>3</sub>] can be treated much easier than the Fe<sup>2+</sup> containing system.

As a conclusion, the preparation of Fe/SiO<sub>2</sub> using the acetonitrile solution of [Fe(acac)<sub>3</sub>] increases the number of isolated irons on the silica surface owing to the reduction of solvolysis. Fe/SiO<sub>2</sub> prepared by this method shows a higher methane conversion than Fe/SiO<sub>2</sub> prepared by the conventional method, nevertheless, the loading of iron and the support are the same in these two catalysts. This result clearly indicates that the isolated iron on the silica surface plays an important role in the partial methane oxidation and clustered iron oxides are inactive for the reaction.

We are grateful to the staff of the Photon Factory, especially Professor Masaharu Nomura, for the use of the BL-12C facilities. (No. 2001P006) We thank Dr. Masaru Harada for his assistance with the XAFS measurement.

## References

- 1 K. Otsuka and Y. Wang, *Appl. Catal., A*, **222**, 145 (2001).
- 2 R. Pitcher and K. Klier, *Catal. Rev.*, **28**, 13 (1986).
- 3 T. Kobayashi, N. Guilhaume, J. Miki, N. Kitamura, and M. Haruta, *Catal. Today*, **32**, 171 (1996).
- 4 F. Arena, T. Torre, A. Venuto, F. Frusteri, A. Mezzapica, and A. Parmaliana, *Catal. Lett.*, **80**, 69 (2002).
- 5 A. Parmaliana, F. Arena, F. Frusteri, A. Martinez-Arias, M. L. Granados, and J. L. G. Fierro, *Appl. Catal., A*, **226**, 163 (2002).
- 6 S.-T. Wong, J.-F. Lee, S. Cheng, and C.-Y. Mou, *Appl. Catal., A*, **198**, 115 (2000).
- 7 Y. Wang, Q. Zhang, T. Shishido, and K. Takehira, *J. Catal.*, **209**, 186 (2002).
- 8 H. Zhang, J. Z. Niu, Y. Kou, T. Tanaka, and S. Yoshida, *J. Solid State Chem.*, **137**, 325 (1998).
- 9 G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisicaro, A. Zecchina, I. Rossetti, E. Sell, L. Forni, E. Giannello, and C. Lamberti, *J. Catal.*, **208**, 64 (2002).
- 10 S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giannello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, and G. Vlaic, *J. Catal.*, **158**, 486 (1996).
- 11 D. Goldfarb, M. Bernardo, K. G. Strohmaier, D. E. W. Vaughan, and H. Thomann, *J. Am. Chem. Soc.*, **116**, 6344 (1994).