XAFS Study on Active Iron Sites in MCM-41 as a Catalyst for Liquid Phase Oxidation

T. Shishido[1,*], Q. Zhang[2], Y. Wang[2], T. Tanaka[3] and K. Takehira[1]

[1]Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-hiroshima, Hiroshima 739-8527, Japan
[2]State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China
[3]Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Abstract

Iron-containing mesoporous molecular sieves (Fe-MCM-41) synthesized by both direct hydrothermal (DHT) and template-ion exchange (TIE) methods have been used as catalysts for the liquid phase oxidation of bulky organic compounds, *i.e.*, anthracene and *trans*-stilbene, with diluted hydrogen peroxide. In the case of Fe-MCM-41-DHT, analysis of Fe K-edge XAFS revealed that isolated and tetrahedrally coordinated Fe species exist in the framework of MCM-41. On the other hand, the Fe-MCM-41-TIE mainly contains small iron oxide clusters, which have octahedrally coordinated Fe species. The tetrahedrally coordinated Fe species in Fe-MCM-41-DHT showed both high activity and efficiency of hydrogen peroxide in the liquid phase oxidations, whereas the iron oxide clusters in the Fe-MCM-41-TIE showed low activity. Moreover, the iron cations incorporated inside the framework of MCM-41 do not leach during the reaction, whereas the small iron oxide clusters leach out into the liquid phase and do not contribute to the catalytic reaction.

1. Introduction

Metal ion-containing mesoporous silicates such as MCM-41 and MCM-48, which possess uniform nano-order mesopores and high concentration of isolated active sites, has attracted much attention as a new type of oxidation catalyst, especially for liquid phase oxidations of bulky organic compounds since a facile diffusion of relatively large molecules can be expected. Many studies have been done for synthesizing and characterizing metal ion-containing MCM-41. Some of these materials, *e.g.*, Ti-MCM-41 and V-MCM-41 showed unique catalytic properties for the reactions of a wide variety of organic substrates such as phenols, alkenes, naphthalenes, alcohols, and thioethers, etc. [1–5].

In order to introduce active metal centers to MCM-41, several kinds of methods have been proposed. The most popular method is the direct hydrothermal (DHT) method. The conventional impregnation, grafting [6] and the template ion exchange (TIE) methods [5] have been also reported. It can be expected that the metal cations with different environments in mesoporous material would result in various catalytic properties. Indeed, Ti-MCM-41 prepared by surface grafting method is more active than that prepared by the DHT method for the epoxidation of cyclohexene with TBHP (*tert*-butyl hydro peroxide) [7]. Vanadium species in V-MCM-41 prepared by the TIE method are dispersed on the surface of channel, preferring the oxidative dehydrogenation of propane, whereas vanadium sites prepared by the DHT method are incorporated in the framework of MCM-41, capable of oxidizing propane to acrolein with moderate selectivity [8]. On the other hand, iron functions as catalytic center in monooxygenase enzymes such as cytochrome P-450 and many selective oxidation systems containing iron, *i.e.*, Gif system and Fenton's reagent have also been developed. Iron is also the active center in many heterogeneous catalysts such as iron-containing microporous amorphous silica synthesized by a sol-gel method, Fe-ZSM-5, Fe-containing Y zeolite with Pd and $FePO_4$, for the selective oxidation of benzene and alkanes.

In the present work, we investigated the structure of iron species in Fe-MCM-41 prepared by two methods, *i.e.*, direct hydrothermal (DHT) and template-ion exchange (TIE) methods by means of Fe K-edge XANES/EXAFS. Iron cations were added into the synthesis gel before hydrothermal synthesis in the former method, while Fe^{3+} ions in the ethanol solution were exchanged with the template cations contained in the as-synthesized MCM-41 in the latter method. The catalytic performances of Fe-MCM-41 thus prepared were tested in the oxidation of both anthracene and stilbenes with H_2O_2, and the effects of the coordination environments of iron species on the catalytic performance are discussed.

2. Experimental

Fe-MCM-41 catalysts were prepared by both hydrothermal synthesis (DHT) and template ion exchanging (TIE) methods according to the previous report [5]. Sodium silicate, iron nitrate and hexadecyltrimethylammonium bromide were used as the sources of Si, Fe and template, respectively. The samples were finally calcined at 823 K for 6 h in a flow of dry air. The mesoporous structure of Fe-MCM-41 was confirmed by XRD and N_2 adsorption. FeO_x/Cab-O-Sil catalyst was also prepared by impregnation method as a reference. Cab-O-Sil is SiO_2, which has no pore structure.

The Fe K-edge XAFS spectra of samples were measured in a fluorescence mode at room temperature at BL7C of KEK-PF with a Si(111) channel cut monochrometer. Normalization of XANES and data reduction on EXAFS were carried out as described elsewhere [9]. Data treatments were carried out with the FACOM M1800 computer system of the DATA Processing Center of Kyoto University.

The liquid phase oxidations were performed using a batch type reactor. Products were identified by GC-MS and quantified by GC.

3. Results and discussion

The XRD patterns showed that all the Fe-MCM-41 with different iron contents had hexagonal regularity of mesopore and their pore diameters determined by N_2 adsorption were around 2.5–3.0 nm.

*e-mail: stetsuya@u-gakugei.ac.jp. Present Address: Department of Chemistry, Tokyo Gakugei University, 4-1-1 Nukui-Kita, Koganei, Tokyo 184-8501, Japan.
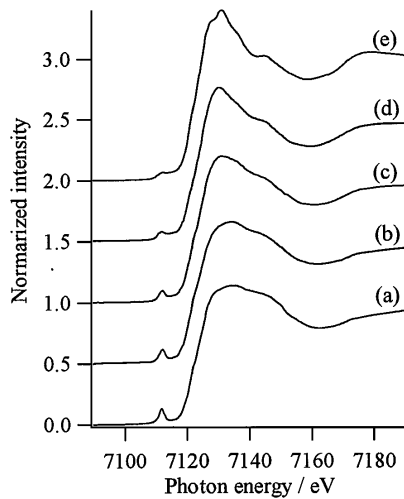
Fig. 1. Fe K-edge XANES spectra of Fe-MCM-41 and reference compounds. (a) Ferrisilicate (Si/Fe = 48), (b) Fe-MCM-41-DHT (Si/Fe = 105), (c) Fe-MCM-41-TIE (Si/Fe = 75), (d) FeOx/Cab-O-Sil (Si/Fe = 96), (e) α-Fe$_2$O$_3$. The numbers in parentheses are the Si/Fe atomic ratios.
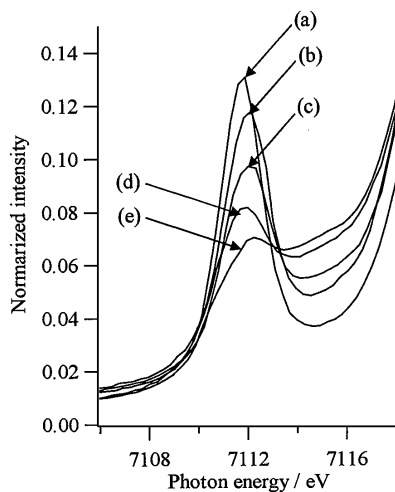

Fig. 2. Pre-edge region of Fe K-edge XANES spectra of Fe-MCM-41 and reference compounds. (a) Ferrisilicate (Si/Fe = 48), (b) Fe-MCM-41-DHT (Si/Fe = 105), (c) Fe-MCM-41-TIE (Si/Fe = 75), (d) FeOx/Cab-O-Sil (Si/Fe = 96), (e) α-Fe$_2$O$_3$. The numbers in parentheses are the Si/Fe atomic ratios.

Figure 1 shows the Fe K-edge XANES spectra of Fe-MCM-41 prepared by both DHT and TIE methods together with the reference compounds, ferrisilicate with MFI structure and α-Fe$_2$O$_3$. Iron atoms in ferrisilicate are mainly in tetrahedral coordination, and those in α-Fe$_2$O$_3$ are in octahedral coordination. A characteristic feature of these XANES spectra can be seen in the pre-edge peak at ca. 7112 eV, attributed to the 1s-3p dipolar forbidden transition. The 1s-3d pre-edge peak of Fe K-edge XANES spectra is sensitive to the electronic and geometric structure of the iron site. Principally, this forbidden transition gains additional intensity when the iron is in a noncentral symmetric environment or through mixing of 3d and 4p orbitals caused by the breakdown of inversion symmetry due to the structure distortion. Since the local symmetry around the iron is lowered from octahedral to tetrahedral coordination, the intensity of this peak tends to increase, *i.e.*, $I_{tetrahedral} > I_{square\ pyramidal} > I_{octahedral}$ [10] (Figure 2). Ferrisilicate which possessed regular tetrahedral coordination structure showed the largest intensity, whereas α-Fe$_2$O$_3$ with distorted octahedral coordination structure
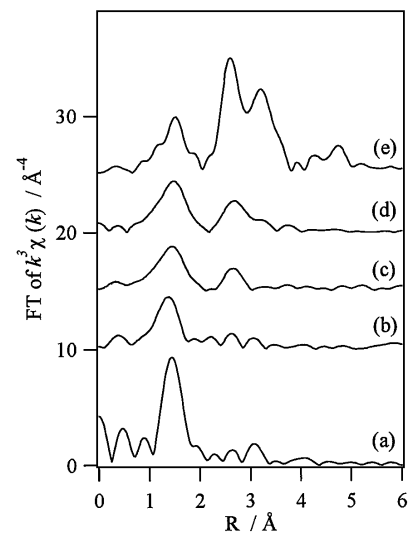

Fig. 3. Fourier transforms of k^3-weighted Fe K-edge EXAFS of Fe-MCM-41 and reference compounds. (a) Ferrisilicate (Si/Fe = 48), (b) Fe-MCM-41-DHT (Si/Fe = 105), (c) Fe-MCM-41-TIE (Si/Fe = 75), (d) FeOx/Cab-O-Sil (Si/Fe = 96), (e) α-Fe$_2$O$_3$. The numbers in parentheses are the Si/Fe atomic ratios.

showed very weak and broad absorption. The pre-peak intensity of the Fe-MCM-41-DHT was slightly lower than that of ferrisilicate. In the case of Fe-MCM-41-DHT, the oscillation by XANES which appears at high energy region (above ca. 15 eV from the absorption edge) is almost similar to that of ferrisilicate. These results indicate that the iron species in Fe-MCM-41-DHT exist in a tetrahedrally coordinated environment. The lower intensity of pre-edge peak may due to the difference in the framework structure of MCM-41 and that of the silicates zeolite. The wall of MCM-41 is essentially amorphous, while silicate zeolite is crystalline. Thus, the Si-O-Fe bonds in the amorphous framework of Fe-MCM-41-DHT may be connected with more relaxing angles than those in ferrisilicate. The pre-edge peak intensity of the Fe-MCM-41-TIE was lower than that of Fe-MCM-41-DHT, whereas higher than that of FeO$_x$/Cab-O-Sil.

Figure 3 shows the Fourier transforms (FTs) of k^3-weighted EXAFS spectra of Fe-MCM-41 FeOx/Cab-O-Sil, ferrisilicate and α-Fe$_2$O$_3$ (Phase shift was not corrected). The peak at 1.5 Å can be assigned to the contribution of the Fe-O shell. It should be noted that no considerable Fe-Fe shell, which is detected in the FTs for Fe-MCM-41-TIE, FeOx/Cab-O-Sil and α-Fe$_2$O$_3$ at around 2.8 Å, was observed for the Fe-MCM-41-DHT and ferrisilicate, suggesting that iron species dispersed as a monomer in the Fe-MCM-41-DHT and ferrisilicate. The curve-fitting analysis

Table I. Results of curve-fitting analysis of Fe K-edge EXAFS[a].

Samples[b]	bond	R	N	$\Delta\sigma^2$
Ferrisilicate (48)	Fe-O	1.85	3.9	−0.00071
Fe-MCM-41-DHT (105)	Fe-O	1.85	4.1	0.00083
Fe-MCM-41-TIE (102)	Fe-O	1.85	3.2	−0.00073
	Fe-O	1.99	3.2	−0.00086
	Fe-O-Fe	3.06	2.1	0.00893
α-Fe$_2$O$_3$	Fe-O	1.91	3.0	0.00070
	Fe-O	2.04	2.9	0.00230

a: R = bond length (Å), N = coordination number; $\Delta\sigma^2$ = Relative Debye-Waller factor (Å^2).

b: The number in the parenthesis is the Si/Fe atomic ratio.

Table II. *Epoxidation of trans-stilbene with hydrogen peroxide.*

Cat.(Si/Fe)[a]	Fe content /wt%	Stilbene conv./%[b]	Sel./%		H_2O_2[c,d] conv./%
			Oxide[b]	Benzald.	
MCM-41	0.0	13.5	84.6	15.4	53.5
Fe-MCM-41-DHT (105)	0.9	36.1	90.1	9.9	88.2
Fe-MCM-41-TIE (102)	0.9	23.8	88.8	11.2	86.1
Fe_2O_3/Cab-O-Sil (96)	1.0	17.5	86.4	13.6	86.5
Ferrisilicate (48)	1.9	6.2	87.4	12.6	78.5

Reaction conditions: catalyst, 0.2 g; reaction temp., 346 K; *trans*-stilbene, 1 mmol; H_2O_2, 9.8 mmol; DMF, 10 ml; reaction time, 2.5 h.
a: The numbers in parentheses are the Si/Fe atomic ratios of the fresh samples.
b: Stilbene, Oxide and Benzald. represent *trans*-stilbene, *trans*-stilbene oxide and benzaldehyde, respectively.
c: H_2O_2 (30 wt% aqueous solution), total 9.8 mmol, 2.45 mmol was added every 30 min in four times.
d: determined by iodometry.

of Fe K-edge EXAFS are summarized in Table I. As for the Fe-MCM-41-DHT, the incorporation of the majority of Fe^{3+} into the framework of MCM-41 with a tetrahedral coordination structure is inferred, since both the Fe-O distance (1.85 Å) and the coordination number (4.2) of Fe-MCM-41 were similar to those of the ferrisilicate with MFI structure. On the other hand, two kinds of Fe-O shells with the lengths of 1.85 and 1.99 Å and the coordination numbers of 3.2 and 3.2, respectively, were obtained in Fe-MCM-41-TIE. The iron in α-Fe_2O_3 possessed two kinds of Fe-O shells with the lengths of 1.91 and 2.04 Å and the coordination numbers of 3.0 and 2.9, respectively. The coordination number of Fe-Fe shell in Fe-MCM-41-TIE (2.1) was much smaller than that in α-Fe_2O_3 (7.9) [11]. These results suggest that small size iron oxide clusters exist in the channel of MCM-41.

The Fe-MCM-41 catalyzed efficiently the liquid phase oxidation of bulky organic compounds such as anthracene and *trans*-stilbene with H_2O_2. The activities of Fe-MCM-41 for the oxidations of anthracene and *trans*-stilbene were higher than those of FeO_x/Cab-O-Sil, which was prepared by a conventional impregnation, and ferrisilicate zeolite with MFI structure. Table II shows the results obtained with several catalysts in the epoxidation of *trans*-stilbene. *trans*-Stilbene oxide and benzaldehyde were formed in the oxidation of *trans*-stilbene. The Fe-MCM-41-DHT showed much higher conversion of *trans*-stilbene and slightly better selectivity to *trans*-stilbene oxide than the Fe-MCM-41-TIE at the same loading amount of iron. FeO_x/Cab-O-Sil

showed not only lower conversion of *trans*-stilbene but also worse selectivity to *trans*-stilbene oxide. The low activity of ferrisilicate can be ascribed to its small pore size (0.51 nm × 0.54 nm) and narrow three-dimensional pore structure. The Fe-MCM-41-TIE showed slightly higher activity than FeO_x/Cab-O-Sil, while the surface area of the Fe-MCM-41-TIE is much higher than that of FeO_x/Cab-O-Sil. This indicates that the surface area of the catalyst is not important factor for the catalytic activity.

From these results mentioned above, we suggest that the isolated and tetrahedrally coordinated iron sites in the framework of MCM-41 over the Fe-MCM-41-DHT are responsible for the oxidations of both anthracene and *trans*-stilbene, whereas the small iron oxide clusters formed over the Fe-MCM-41-TIE are not effective. The Fe-MCM-41-DHT showed no leaching of iron species during the reaction. On the contrary, a large amount of iron cation in Fe-MCM-41-TIE leached out into the liquid phase and do not contribute to the catalytic reaction. Thus, the iron cations tetrahedrally coordinated and incorporated inside the framework of MCM-41 is stable towards leaching, whereas the small iron oxide clusters, which have octahedrally coordinated iron species, leach out.

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