

# Local structure of mesoporous silica FSM-16 studied by X-ray absorption spectroscopy

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## Abstract

The local structure around Si species in mesoporous silica FSM-16 was investigated by Si K-edge XAFS. As expected by the previous studies, local symmetry of Si species in FSM-16 is almost identical to that of amorphous silica. The Si-O bond length was longer than those of  $\alpha$ -quartz, ZSM-5 and amorphous silica. Relations between the prolonged bond length and acidic property of FSM-16 were discussed.

## 1. Introduction

The pore wall structure of hexagonally ordered mesoporous silica such as FSM-16<sup>1</sup> and MCM-41<sup>2</sup> has been much attention in order to understand the physicochemical properties and utilize them as functional materials. Since Chen et al.<sup>3</sup> carried out the pioneering <sup>29</sup>Si NMR and Raman study for MCM-41 in 1993, the hexagonally ordered pore structure of which is almost identical to that of FSM-16, wall structure of mesoporous silicas has been recognized as amorphous. The first molecular dynamics study by Feuston et al. demonstrated that the pore wall of MCM-41 mainly consists of four and five membered rings, whereas bulk silica mainly consists of six membered ring.<sup>4</sup> The wide range X-ray scattering characterization of MCM-41 has been carried out by several research groups.<sup>5-7</sup> As for the first coordination sphere around silicon atom, Pauly et al. reported that a Si-O bond length in MCM-41 is longer than that of amorphous silica,<sup>7</sup> but results by Ookawa et al. were opposite.<sup>6</sup> As Popahl et al. pointed out,<sup>5</sup> structure of the coordination sphere around silicon in mesoporous silicas have been in debate.

It is well known that acid strength of amorphous silica is very weak to promote typical acid catalyzed reactions.<sup>8</sup> Nevertheless, catalyses by siliceous FSM-16 and MCM-41 have been reported since 1995 such as isomerization of butenes and/or pinenes,<sup>9-11</sup> dehydration of alcohols,<sup>12,13</sup> Beckmann rearrangement,<sup>14</sup> methylamine synthesis,<sup>11</sup> acetalization,<sup>15</sup> and aldol reaction.<sup>16</sup> In 1998-9, we have examined acid property of FSM-16, and reported that both the textural structure and the hydration state closely relates to the surface property.<sup>10,11</sup> The summary is as follows: (1) The hexagonally ordered structure is indispensable for generation

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of the acidic property; (2) The maximum acid strength is  $H_0 = -3.0$ ; (3) Weakly perturbed silanol groups act as Brønsted acid site; (4) Strained siloxane bridge formed by dehydration of isolated silanol groups acts as Lewis acid site; (5) More than 70% of acid sites are Lewis acid on FSM-16 calcined at 823 K; (6) The amount of Lewis acid site increases by thermal treatment above 873 K. The subjects (1) and (2) were confirmed in cases for siliceous MCM-41 by Iwamoto et al. in 2003.<sup>15b</sup> They also proposed that an assembly of weakly acidic OH may act as an effective/strong acid site. Recently, Fukuoka et al. found that the lattice oxygen of mesoporous silica is incorporated into CO<sub>2</sub> during preferential oxidation of CO over Pt/FSM-16.<sup>17</sup> Although catalyses by siliceous mesoporous silicas have been reported by several research groups, there have been no direct evidences about reasons why the mesoporous silicas exhibit acidic property.

Because Lewis acid site has been confirmed on the surface of fresh FSM-16,<sup>10</sup> we assume that strained siloxane bridge exists inside the pore wall intrinsically. Existence of the strained siloxane bridge has been proposed by characteristic two IR bands at 892 and 912 cm<sup>-1</sup>, which appear on samples by evacuation above 873 K.<sup>10,11,18</sup> However, there has been no direct evidence whether the analogue structure exists on the fresh FSM-16. The elongated Si-O bonding has not been confirmed yet. In the present study, we recorded Si-K edge X-ray absorption spectra of various silica materials to investigate the origin of the acid property of siliceous FSM-16 by the coordination environment. To our knowledge, no EXAFS analysis of mesoporous silicas at Si K-edge has been reported.

## 2. Experimental

FSM-16 was synthesized according to the literature,<sup>19</sup> and the procedure has been previously reported in detail.<sup>10</sup> As a silica source and a template, water glass (Fuji Silysia Chem. Co. LTD; SiO<sub>2</sub> = 15.3 wt%, Na<sub>2</sub>O = 6.1 wt%, Al = 0.6 ppm, Fe = 0.4 ppm) and hexadecyltrimethylammonium bromide were used, respectively. FSM-16s with different pore sizes (FSM16-MES, FSM16-C12) were also prepared. As the surfactant, hexadecyltrimethylammonium bromide + mesitylene at the molar ratio of 0.5 or dodecyltrimethylammonium bromide was utilized for FSM16-MES or FSM16-C12 synthesis, respectively. The amorphous silica precursor was prepared by ion exchange of layered sodium silicate kanemite, which is the same starting material for FSM-16 synthesis, with octyltrimethylammonium bromide. As-synthesized samples were calcined in the air at 823 K for 6 h. As a reference for silica materials, quartz (Wako) and Na-ZSM-5 (JRC-Z5-1000NA; SiO<sub>2</sub>: 97.9 wt%, Al<sub>2</sub>O<sub>3</sub>: 1240 ppm, Na: 0.12 wt%) were utilized.

The Si K-edge X-ray absorption experiments were carried out on the BL-10 at Ritsumeikan University SR Center (Shiga, Japan). X-ray absorption spectra were recorded in a total electron yield mode with an InSb(111) two-crystal monochromator at room temperature. The incident X-ray and electron emitted from a sample were simultaneously monitored by a

Ni mesh and MCP, respectively. The EXAFS analysis was performed by the Rigaku REX2000 Ver. 2.5.7 program.<sup>20</sup> For a curve fitting analysis, the backscattering amplitude and the phase shift functions of Si-O pair were obtained from a  $k^3$ -weighted EXAFS spectrum of  $\alpha$ -quartz.

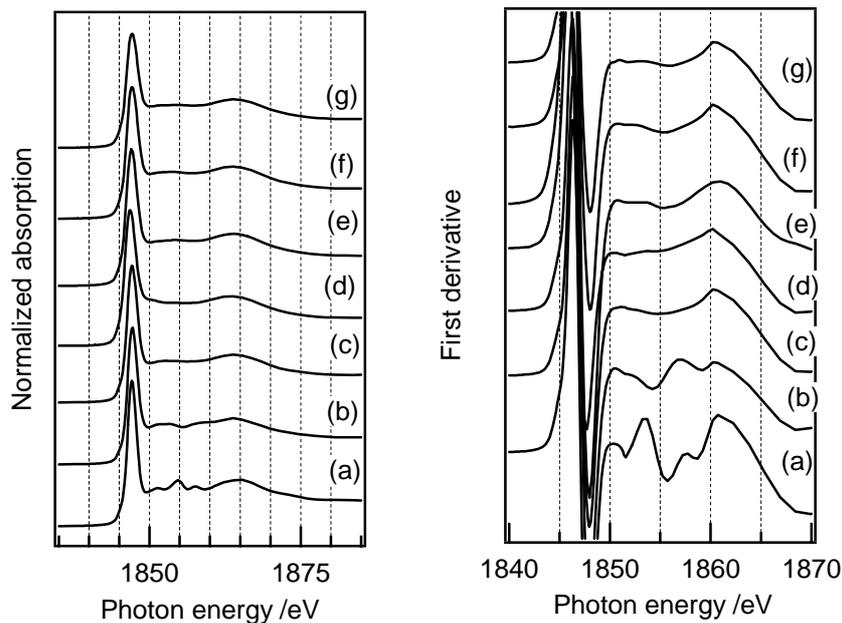
### 3. Results and discussion

The textural parameters of samples are listed in Table 1 accompanied with results of EXAFS analyses discussed below. The tentative pore wall thickness of hexagonally ordered mesoporous material is possible to estimate by subtraction of a pore diameter of from the lattice constant. It is clear that pore wall thickness of the present FSM-16 is less than 2 nm, although Kanda et al. pointed out that pore size obtained by analysis of a N<sub>2</sub> adsorption isotherms using conventional Kelvin model is underestimated by ca. 1 nm against Kelvin-model diameter of 2-4 nm.<sup>21</sup> Therefore present EXAFS spectra corrected in a total electron yield mode reflect on the whole wall structure. Fig. 1 shows Si K-edge XANES spectra of silica materials and the first derivatives. All XANES spectra exhibited a strong white line around 1847 eV due to transition of 1s electron to 3p orbital in SiO<sub>4</sub> tetrahedral species.<sup>22,23</sup> The peak energy and spectral configuration of each FSM-16s resembled to that of amorphous silica. Fine peaks around 1850-60 eV appeared on XANES spectra of quartz and microporous crystal ZSM-5. Single broad peak was confirmed in the energy region on those of amorphous silica and FSM-16s, but not on as-synthesized FSM-16. Wu et al. carried out full multiple scattering calculations for Si Kedge XANES of quartz with the different cluster size.<sup>23</sup> They reported that the fine peaks observed in the experimental spectrum are reproduced by the 109-atom cluster calculation, but are absent using 5-atom-cluster.

**Table 1.** Results of curve fitting analysis of silica samples for the first coordination sphere.

Sample	$a_0$ Å	$d_{\text{BJH}}^a$ Å	$S_{\text{BET}}^b$ m <sup>2</sup> /g	$k^1$			$k^3$		
				$r/\text{Å}$	$\sigma^2/\text{Å}^2 \times 1000$	R/% <sup>c</sup>	$r/\text{Å}$	$\sigma^2/\text{Å}^2 \times 1000$	R/% <sup>c</sup>
quartz				1.610±0.009	3.0±0.8	5.1	1.609±0.008	3.5±0.8	0.6
ZSM-5		(5.3x5.6; 5.1x5.5) <sup>d</sup>		1.598±0.009	2.9±0.8	4.9	1.594±0.008	3.5±0.4	0.7
amorphous silica		-	200	1.595±0.009	2.2±1.1	2.9	1.594±0.007	2.4±0.6	1.1
				1.601±0.010	4.9±0.6	7.6	1.599±0.008	5.3±0.3	0.9
FSM-16	41.4	28	990	1.619±0.009	3.4±0.7	4	1.619±0.008	4.2±0.3	0.6
FSM-16 as-syn.	43.2			1.609±0.009	0.7±3.0	3.4	1.608±0.007	1.2±1.0	0.6
FSM16-MES	59.3	36	875	1.625±0.009	2.1±1.0	0.7	1.632±0.007	1.6±0.7	1.3
FSM16-C12	41.4	21	780	1.611±0.009	3.2±0.7	2.3	1.617±0.007	3.7±0.4	1.4

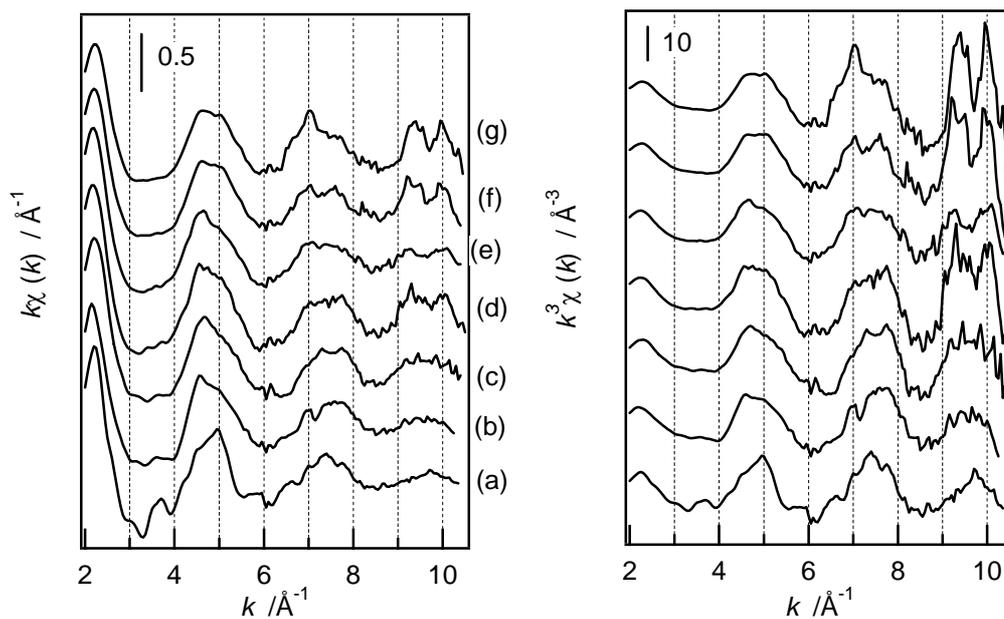
<sup>a</sup>BJH pore diameter, <sup>b</sup>BET specific surface area, <sup>c</sup>R =  $\Sigma(k^n\chi_{\text{obs}} - k^n\chi_{\text{calc}})^2 / \Sigma(k^n\chi_{\text{obs}})^2 \times 100$ , <sup>d</sup> Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth-Heinemann: London, 1992.



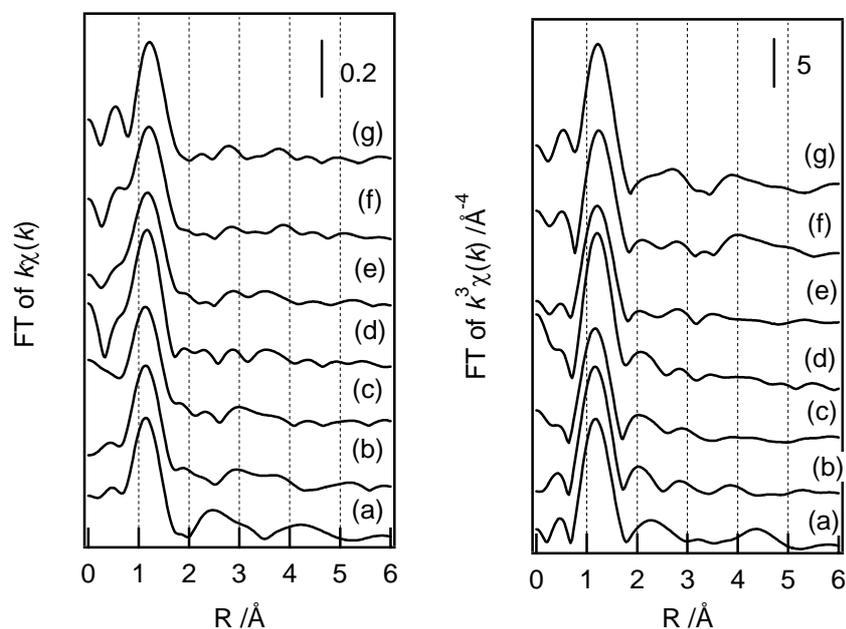
**Figure 1:** Si K-edge XANES spectra of (a) quartz, (b) ZSM-5, (c) amorphous silica, (d) FSM-16-C16-as syn, (e) FSM16-C16, (f) FSM-16-C12, and (g) FSM-16-Mes.

It shows that silicon species in FSM-16s exist as  $\text{SiO}_4$  species which do not possess long-ranged ordering, especially in as-synthesized FSM-16. The less amount of Si-O-Si network, which increases by condensation of Si-OH groups upon calcination, in as-synthesized FSM-16 is consistent with  $^{29}\text{Si}$  NMR characterizations by Inagaki et al.<sup>19</sup>

To investigate the local structure around silicon atom in more detail, EXAFS analyses were performed. Fig. 2 shows  $k^1$ - and  $k^3$ -weighted EXAFS spectra of silica samples. An EXAFS spectrum of quartz consists of at least two curves with different frequencies. The other spectra of all mesoporous samples, ZSM-5 and silica gel were almost similar to each other, but a tiny shoulder around  $7 \text{ \AA}^{-1}$  was confirmed on mesoporous samples. It suggests that the coordination environment around silicon slightly differs. Fig. 3 shows radial structure functions (RSFs) of silica materials obtained by Fourier transformation of each EXAFS spectrum in the  $k$ -range of ca.  $2.8\text{--}9.1 \text{ \AA}^{-1}$ . The distinct second coordination sphere was confirmed in a RSF of quartz around  $2.4 \text{ \AA}$ . The original purpose was to analyze the second coordination sphere of mesoporous samples based on the two assumptions: (1) a Si-Si inter-atomic distance in FSM-16 is shorter than that of amorphous silica; (2) the distance varies with the pore diameter. However, no distinct peaks were confirmed in their RSFs as well as that of ZSM-5. The most reliable reason for a lack of the second coordination sphere is larger static disorder for Si-Si, i.e. Si-Si bond length is not uniform. ZSM-5 contains 5-, 6- and 10-fold siloxane rings, T-O-T bond angle of which varies in the range of  $144\text{--}178^\circ$ .<sup>24</sup>



**Figure 2:** The  $k^1$ - and  $k^3$ -weighted Si K-edge EXAFS spectra of (a) quartz, (b) ZSM-5, (c) amorphous silica, (d) FSM-16-C16-as syn, (e) FSM16-C16, (f) FSM-16-C12, and (g) FSM-16-Mes.

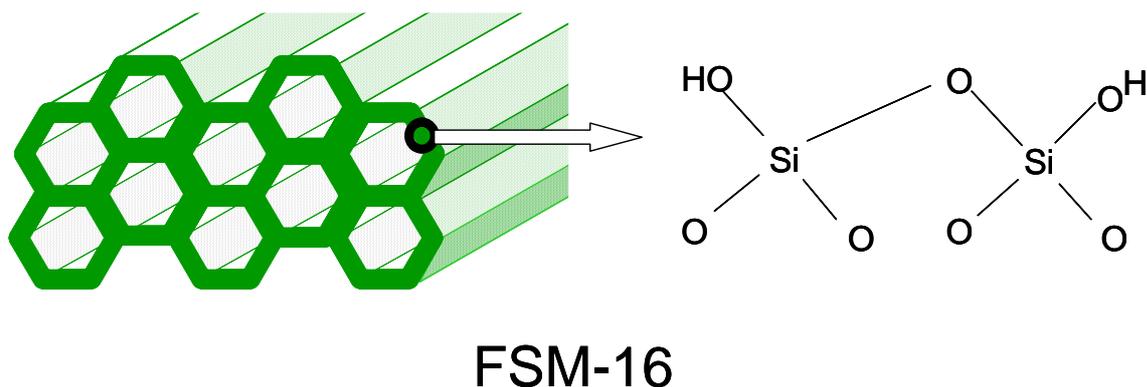


**Figure 3:** Fourier transforms of  $k^1$ - and  $k^3$ -weighted Si K-edge EXAFS in the  $k$ -range of ca.  $2.8 - 9.1 \text{ \AA}^{-1}$ : (a) quartz, (b) ZSM-5, (c) amorphous silica, (d) FSM-16-C16-as syn, (e) FSM16-C16, (f) FSM-16-C12, and (g) FSM-16-Mes.

It is well known that the size of siloxane ring in amorphous silica is distributed. Then contributions of the second coordination sphere to EXAFS were scarce, especially in narrow  $k$  ranges.

Finally, a curve fitting analysis for the first coordination sphere was performed. Each coordination number and the edge energy were fixed at 4 and the initial values. The  $k^1$ - and  $k^3$ -weighted EXAFS analyses gave identical results, which are summarized in Table 1. The estimated Si-O bond length for ZSM-5 was well in consistent with the crystallographic data (averaged as 1.589 Å<sup>24</sup>). No systematic changes in the bond length against a pore diameter were confirmed. It should be noted that Si-O bond lengths for mesoporous silicas were slightly longer than that of amorphous silica by ca. 0.02 Å. This discrepancy for the Si-O bond length among them and the estimated absolute values were consistent with results of synchrotron X-ray scattering analysis for MCM-41 by Pauly et al.<sup>7</sup> Based on Monte Carlo and molecular dynamics simulation study, Oumi et al. proposed that Si-O bond distance in the MCM-41 is longer than that of MFI-type zeolite.<sup>25</sup> On the other hand, Ookawa et al. concluded Si-O bond length in MCM-41 is shorter than that of amorphous silica by 0.02 Å.<sup>6</sup> Because the utilized X-ray source was an X-ray tube with Mo target, the experimental uncertainties might be large against such the minute differences. Campbell et al. investigated bulk structure of porous amorphous silica, and predicted Si-O distance increases with the mass density decreasing by increment of nano-scale-void.<sup>26</sup> However, they discussed about the second through fourth coordination sphere, but not about the nearest Si-O bonding. One possible reason for longer Si-O inter-atomic bond is the presence of six-fold coordinated silicon species such as R<sub>2</sub>O-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glasses (R = Li, Na and K), the EXAFS analysis of which has been reported by Ide et al.<sup>27</sup> Because the present samples do not contain P, we assume that SiO<sub>6</sub> species does not exist in the present siliceous materials. The population of surface silicon species increases as function of the surface area, resulting that the population of Si-OH species also increases. Wada et al. measured neutron diffraction of silica glass and gels, and reported that the first nearest Si-O distances are almost identical (within 0.006 Å).<sup>28</sup> The silica gels prepared by the same authors contain 43-56% Q<sup>3</sup> and 7% Q<sup>2</sup> species,<sup>29</sup> whereas most of silicon species in silica glass is generally Q<sup>4</sup>. It suggests that populations of surface Si-OH groups little affects on the averaged inter atomic distance.

Here, we propose this slightly longer Si-O inter-atomic distance for FSM than that of amorphous silica is not an experimental artifact, but is an evidence of the strained pore wall structure. The strained siloxane bridge would result in partial enlargement of a Si-O bridge, and the possible structure is shown in Fig. 4. We presume that the pseudo coordinative unsaturated silicon species acts as Lewis acid site. Kawakami et al. proposed that a special structure consisting of a surface 3-coordinated Si and an adjacent four-coordinated Al under the surface is capable of generating particularly strong acidity.<sup>30</sup> They also predicted that the analogue structure consisting of silica species exhibits strong acidity. Bunker et al.<sup>31</sup> and



**Figure 4:** Possible structure of strained silicon species in the mesoporous silica

Morrow et al.<sup>32</sup> proposed that silicon atom in a edge-shared strained siloxane bridge exhibits Lewis acidic character. The evidence for strained siloxane species has been confirmed on FSM-16<sup>10,11,18</sup> or amorphous silica<sup>32,33</sup> treated above 1073 K by FTIR spectroscopic characterizations. The present EXAFS analysis does not compete with our proposal that strained SiO<sub>4</sub> species, which responsible for the acid site of the ordered mesoporous silica, exist inside pore wall intrinsically. However, estimated Si-O bond length is an averaged one. Further experimental work about amount of strained species and the true bond length is needed.

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