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Preparation and characterization of titanium-substituted MCM-41

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Abstract

Combination of X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) demonstrated that Ti replaced Si in the MCM-41 framework and that its coordination environment was similar to that of TS-1 except that TS-1 had a much better-defined structural regularity of Ti–O–Si units.

Keywords: MCM-41, Ti-substituted; Characterization; XANES; EXAFS; XRD

1. Introduction

MCM-41 is the collective name for a family of crystalline mesoporous molecular sieve materials with hexagonal structure recently invented by Mobil [1,2]. The materials possess a hexagonal array of uniform pores with the diameter ranging from 1.5 to 10 nm. Their silicate framework could also be modified by partial isomorphous substitution with such elements as Al, Ti, V, Sb, Fe or Pd [3–5]. Substitution with Ti is particularly interesting because of the success of Ti-substituted zeolites in the oxidation of various organic substrates [6,7]. Due to their larger pores compared to zeolite-based materials, Ti-substituted MCM-41 (TiMCM-41) could be applied to the oxidation of bulky substrates usually employed in the synthesis of fine chemicals. This paper presents structural characterization of TiMCM-41 prepared with a wide range of pore sizes and framework Si/Ti ratios. Small angle X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) are main techniques employed, with the former probing the MCM-41 structure and the latter the coordination environment of titanium sites. The reactivity and stability of TiMCM-41 has been reported elsewhere [8].

2. Experimental

TiMCM-41 samples were synthesized following a procedure similar to ones described by Beck et al. [1,2] and Corma et al. [5]. Template solutions $C_nH_{2n+1}(CH_3)_3NBr/OH$ were prepared by a partial ion exchange of $C_nH_{2n+1}(CH_3)_3NBr$ (Sigma) with Amberlite IRA-400 (OH) (Aldrich, 3 meq g^{-1} of template). Tetraethylorthosilicate and tetrabutylorthotitanate were dissolved into the solution and the mixture was stirred for 0.5 h. Zeosil (an amorphous silica, Hanbul Chemicals) was added to give a template/Si mole ratio of 0.5 and varying Si/Ti ratios and the mixture was stirred for another 0.5 h. The resulting solution was heated without mixing at 393 K for three days. Solid products were recovered by filtration,

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washed with water, and then dried in an oven at 333 K for a day. Finally, the synthesized samples were calcined at 813 K in helium for 2 h and then in oxygen for 6 h to remove the organic template from the pores of TiMCM-41. A sample of TS-1 (Ti-substituted MFI-type zeolite) with Si/Ti mole ratio of 33 was employed for comparison.

The small angle XRD (2θ=1–10°) was performed on a Mac Science X-ray diffractometer M18XHF with Cu K_{α} radiation. In order to reduce the total reflectance in scanning such small angles, the small divergence and scattering slits of 0.5° were employed. X-ray absorption spectra were taken in a transmission mode for K-edge of titanium at beamline 7C of the Photon Factory in Tsukuba, Japan. The data were analyzed by the UWXAFS 2.0 package. The physisorption of nitrogen at 77 K was used to determine BET surface areas and pore size distributions. For transmission electron microscopy (TEM), a suspension of the sample powder was dropped onto a microporous carbon grid and allowed to dry. The micrographs of thin edges of the sample were taken with a JEM 2000-EX instrument of Jeol operating at 200 keV. All infrared (IR) absorption data were obtained on 1800 FT–IR spectrometer of Perkin-Elmer using the KBr wafer technique. Powders containing 1 wt% TiMCM-41 in KBr was pressed at 1000 kg cm^{-2} into a thin wafer with an effective thickness of 90 mg cm^{-2}. A spectrum is an average of 30 consecutive scans recorded between 600 and 2200 cm^{-1} with a spectral resolution of 0.5 cm^{-1}.

3. Results and discussion

3.1. TEM and nitrogen adsorption

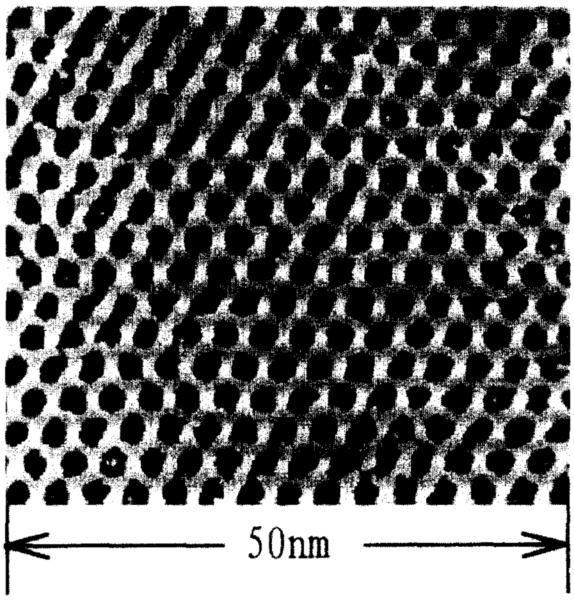

Fig. 1. TEM image of TiMCM-41 prepared with the C_{12} template and Si/Ti mole raio of 69.

Fig. 1 shows a representative transmission electron micrograph of TiMCM-41 prepared from the C_{12} template and with Si/Ti mole ratio of 69. The regular hexagonal array of uniform channels is clearly seen. The shape of the pore opening is also hexagonal as emphasized in a recent high resolution TEM study [9]. The isotherms of N_2 adsorption were obtained for TiMCM-41 prepared with different templates and analyzed by BET and Kelvin equations. The resulting average pore diameters, specific surface areas, and pore volumes are listed in Table 1. As expected, pore size shows a progressive increase with increasing template sizes. However, the BET area and pore volume shows a maximum between C_{10} and C_{16}.

3.2. X-ray diffraction

The small angle XRD is a useful technique to characterize the structure of crystalline mesoporous

Table 1
Analysis of N_2 adsorption for calcined TiMCM-41 (Si/Ti mole ratio of 69)

Template	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
Pore diameter (nm)	1.09	1.73	2.12	2.38	2.69	3.12	3.76
Pore volume[a] (cm^3 g^{-1})	0.175	0.479	0.618	0.695	0.965	1.019	0.865
Surface area (m^2 g^{-1})	281	861	1268	1426	1208	1210	869

[a] Amount of N_2 adsorbed at the relative pressure (P/P_0) of 0.8.

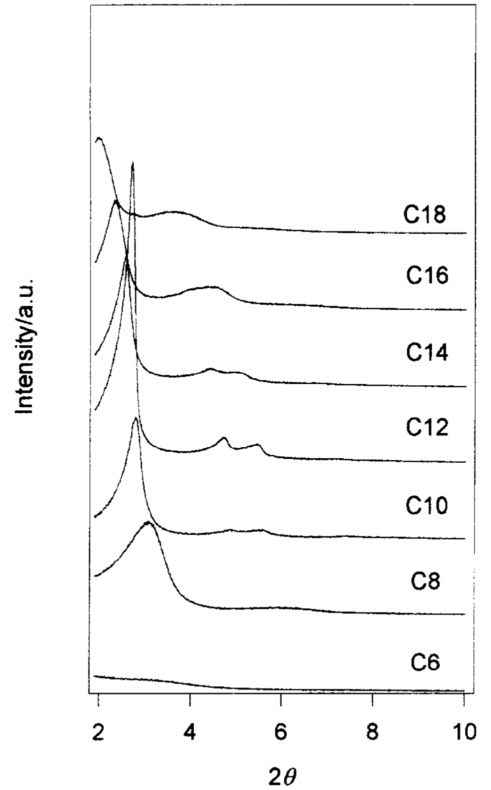

Fig. 2. XRD pattern of TiMCM-41 (Si/Ti=69) after calcination prepared with different templates.

materials. Fig. 2 shows XRD patterns of TiMCM-41 prepared with different templates. The peaks could be indexed as *hko* reflections of a hexagonal lattice. This diffraction pattern is originated from the regular hexagonal array of uniform channels, characteristic of MCM-41. The number of well-defined peaks and their relative intensity represent relative regularity of the MCM-41 structure. It should be noted, however, that the structural regularity probed by the quality of XRD patterns represents how regularly the pores are arranged, yet provides no information on the structure of the framework although they may be correlated (vide infra). The position of the first (1 0 0) peak gives the repetition distance of the pores d_{100} by the Bragg law or the lattice parameter a of the hexagonal unit cell by $a = 2d_{100}/\sqrt{3}$.

As expected, the position of (1 0 0) peak moves towards smaller 2θ values or larger d_{100} values as the size of template increases. The intensity of peaks also changes systematically. The sample prepared from C_6 shows no XRD peaks, an indication of a completely amorphous material. The intensity of the XRD peaks increases as the template size increases, shows a maximum, and then decreases again. The best-defined XRD pattern is observed for C_{12} template. The regularity of MCM-41 structure should follow the same trend. The difference between d_{100} measured by XRD and pore diameter by N_2 adsorption will give the wall thickness of MCM-41 structure. As seen in Fig. 3, the wall thickness estimated this way remains almost invariant at approx. 1 nm. The distance corresponds to about three layers of Si–O–Si units and indicates that a large fraction of involved atoms are exposed to the surface.

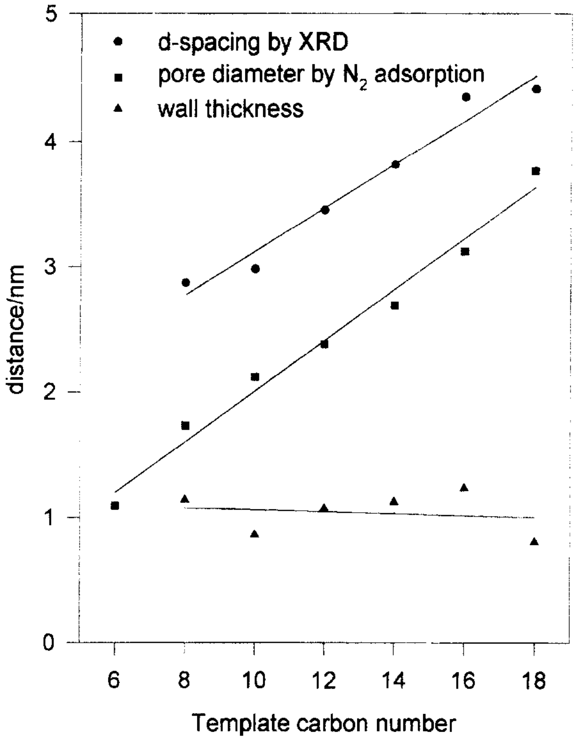

Fig. 3. Thickness of the pore wall by the difference between d_{100} of XRD and pore diameter by N_2 adsorption.

Fig. 4 shows the effect of Si/Ti mole ratios introduced into the preparation solution. As more Ti is introduced into the system, there is a gradual shift of (1 0 0) peak to lower 2θ positions. This may reflect the fact that the preferred Ti–O–Si distance (0.36 nm) is longer than that of Si–O–Si (0.34 nm). Introduction of

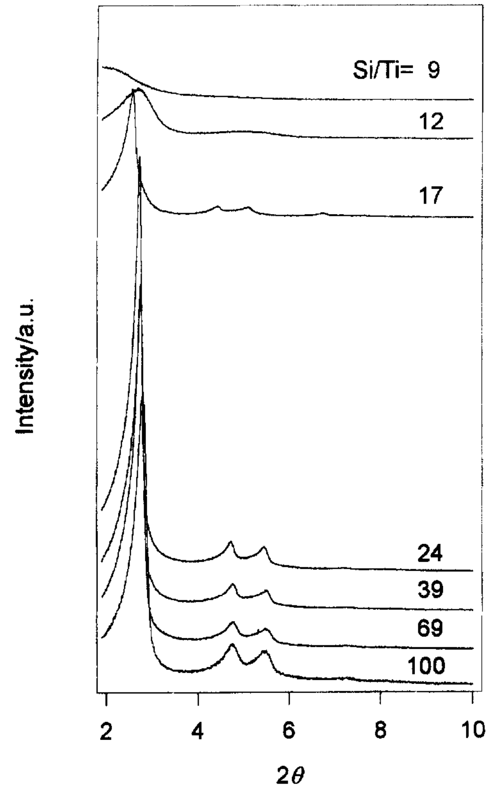

Fig. 4. XRD pattern of TiMCM-41 (C_{12} template) after calcination with different Si/Ti mole ratios.

more Ti also impairs the regularity of pore structure. This again appears to be due to the different preferred distances between Ti–O and Si–O. Thus, introduction of Ti into the Si framework would disturb the regularity of silicate framework, which in turn affects the pore structure. In any case, this is the trend generally observed for zeolites in which introduction of aluminum disturbs the regularity of the silicate framework [10]. Under extreme conditions (Si/Ti<12), the MCM-41 structure is not formed at all.

3.3. X-ray absorption fine structure

In order for the titanium-substituted materials to be active catalysts for oxidation reactions, isolated titanium species should be isomorphously substituted into the silicate framework. The systematic change in d_{100} positions and peak intensities of XRD pattern may be taken as evidence that Ti has indeed substituted Si in the MCM-41 framework. The evidence, however, is at best indirect. The X-ray absorption fine structure (XAFS) is an ideal technique to probe the chemical and structural environment surrounding titanium. Particularly useful is the X-ray absorption near edge structure (XANES) of titanium K-edge. Tetrahedrally coordinated titanium gives rise to a strong pre-edge peak at 4668 eV. In contrast, titanium in a highly symmetric octahedral environment such as in titanium oxides (rutile, anatase or brookite) shows three weak pre-edge peaks.

When Ti was loaded into a siliceous MCM-41 (Si/Ti=∞) by impregnation in amounts that would give Si/Ti=9–100, and calcined under the same conditions used for the preparation of TiMCM-41, all the pre-edge peaks were triple. As-synthesized TiMCM-41 before calcination in Fig. 5(a) also show triple pre-edge peaks. After calcination, the single-peak pre-edge feature appears as shown in Fig. 5(b). Only the sample with Si/Ti of 9 shows a sign of shoulders and a much broader post-edge peak, indicating the presence of a significant amount of octahedral species. It should also be noted that this sample does not form MCM-41 structure as shown in Fig. 4. Thus, titanium could substitute silicon in the framework of MCM-41. This substitution takes place mainly during the calcination step of the preparation. Yet, the substitution is not achieved by impregnation of preformed (calcined) siliceous MCM-41 with a titanium species. There is no clear indication of how much Ti could be substituted into the framework without forming a significant amount of an octahedral species. Detailed examination of the shape (symmetry and width) of the pre-edge peak suggests the limit is somewhere between 4 mol% (Si/Ti=24) and 8 mol% (Si/Ti=12). These values are higher than that usually observed for TS-1 (approx. 3 mol%), and may reflect the more flexible framework of MCM-41 compared to that of zeolites (vide infra).

The information on the coordination environment surrounding titanium sites could be further obtained from the extended X-ray absorption fine structure (EXAFS). Fig. 6 compares the radial structure function (RSF) of several titanium compounds with TiMCM-41 with Si/Ti mole ratio of 9 and 39. The position of the first largest peak corresponds to Ti–O distance if corrected by a phase shift. The Ti–O distance in TiMCM-41 is the same as that in TS-1

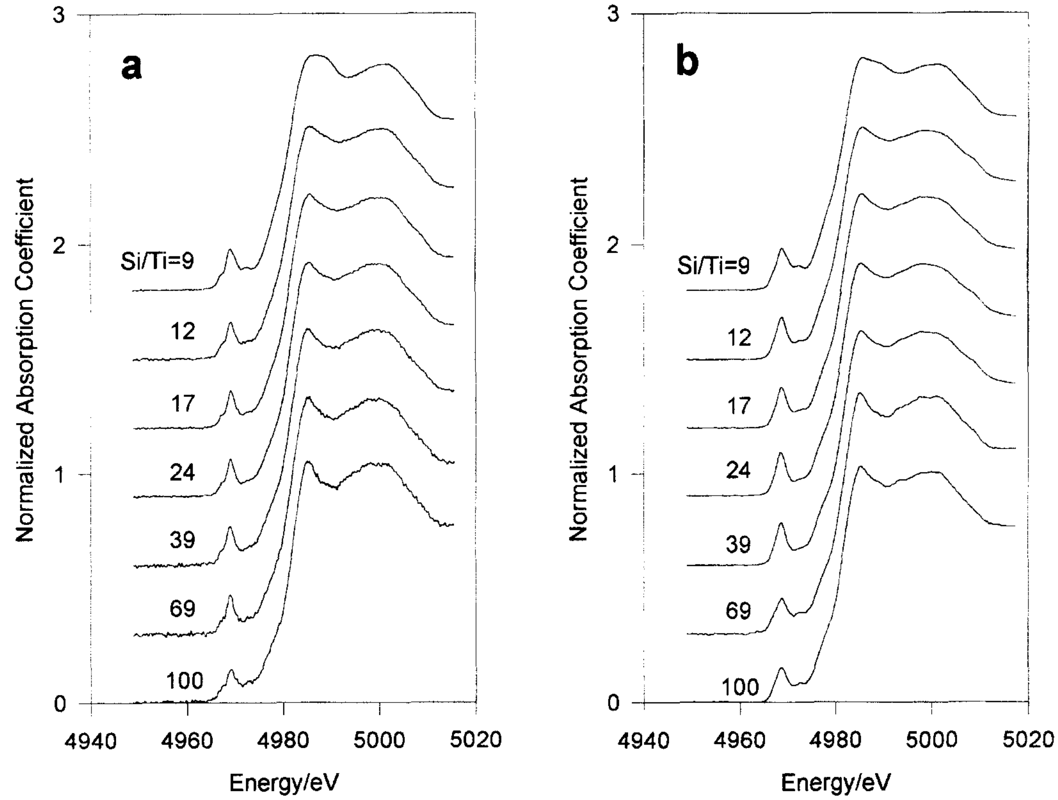

Fig. 5. XANES spectra of TiMCM-41 (C_{12} template) prepared with different Si/Ti mole ratios: (a) as synthesized, (b) calcined.

and significantly longer than those in TiO_2 (rutile or anatase). This is in agreement with the report that octahedral Ti–O distances (0.194–0.196 nm) are longer than tetrahedral distances (0.180–0.186 nm). The most obvious difference between the RSF of TS-1 and that of TiMCM-41 is the intensity of higher-shell peaks corresponding to Ti–Si distances. Two peaks are clearly observed for TS-1, while TiMCM-41 does not show any higher-shell peaks with significant intensity. This indicates absence of any long-range order in TiMCM-41 framework unlike in TS-1 whose MFI zeolite framework gives rise to the well-defined higher-shell peaks. The RSF of two TiMCM-41 samples with different Ti contents are indistinguishable except for the slightly higher intensity for the sample with Si/Ti of 9. It should be remembered that the sample with Si/Ti of 9 does not form MCM-41 structure and contains some octahedral titanium species. Thus, MCM-41 seems to be made of a framework that lacks precise repeat of Si position at the second nearest neighbor (Si–Si) scale as also indicated by the results of ^{29}Si NMR and IR [11]. It is interesting to note that the Ti–Si distance in TS-1 is slightly longer than Ti–Ti distance in TiO_2. As mentioned, Ti–O distance is longer than Si–O distance. Hence, the result suggests a greater bond angle of Ti–O–Si compared to that of Ti–O–Ti.

3.4. *Fourier-transform infrared*

The presence of an infrared band near 960 cm^{-1} has been taken as evidence of the isomorphous substitution of Si by Ti [5,12] because the band is absent in pure silicates. All TiMCM-41 samples showed a peak at 962 cm^{-1} as shown in Fig. 7. More recent interpretation of this band is the stretching mode of SiO_4 units bonded to a transition metal cation (rather than due to unique feature of Ti=O bond) [13], or Si–O stretching vibration of Si–O$\cdots$H [14]. No reliable

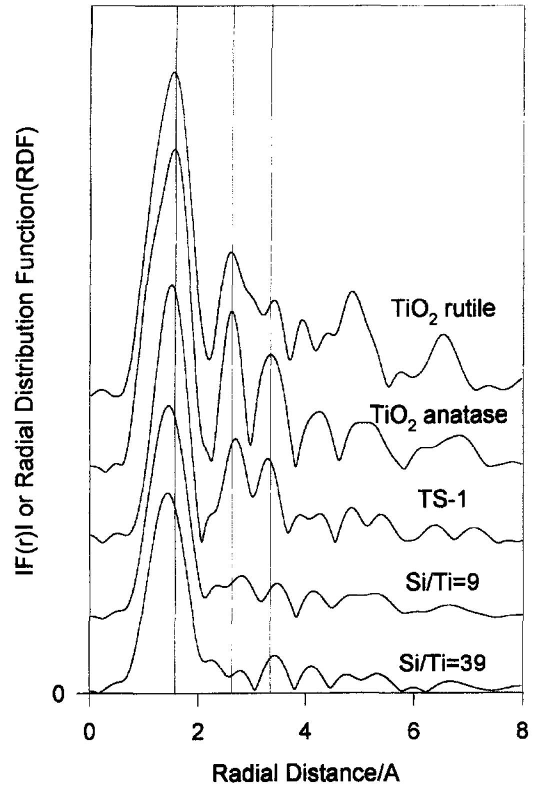

Fig. 6. Radial structure functions of some reference Ti compounds and TiMCM-41 (C_{12} template).

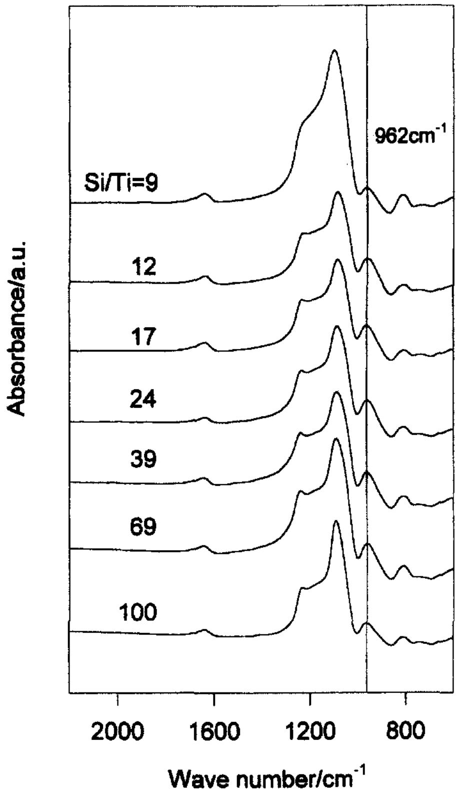

Fig. 7. FT–IR spectra of calcined TiMCM-41 (C_{12} template) with different Ti contents.

information regarding titanium incorporation could be drawn from FT–IR data.

4. Conclusions

The combination of XRD and XAFS is a highly effective means for characterizing Ti-substituted MCM-41 to determine both the frame structure of MCM-41 (XRD) and the coordination environment of Ti (XAFS). Titanium replaces Si in the MCM-41 framework up to at least 4 mol% which is higher than in TS-1. XAFS has demonstrated that Ti in TiMCM-41 is in the same coordination and structural environment as Ti in TS-1. However, TS-1 has a better-defined structural regularity of Ti–O–Si units. In the synthesis of TiMCM-41, there exist optimum template sizes (C_{12}–C_{14}) that give the best-defined MCM-41 structure. The thickness of the wall of MCM-41 remains constant near 1 nm irrespective of the size of the templates and the formed pores.

Acknowledgements

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