

## Disordered Molecular Sieve with Branched Mesoporous Channel Network

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A disordered mesoporous silica material has been prepared using polymerization of silicate anions surrounding surfactant micelles in the presence of organic salts. The local structure of the material has been investigated using a transmission electron micrograph image of platinum wire grown inside the mesopores. This micrograph imaging technique, developed in the present work, clarifies that the pore structure is a three-dimensional, disordered network of short wormlike channels while the channel widths are uniform. The *fully* disordered channel branching similar to a three-dimensional fractal with *truly* uniform channel widths distinguishes the present material with respect to the recently found ordered mesoporous molecular sieve MCM-41. The branching channel structure has a remarkable advantage for adsorption and catalytic applications, compared with the MCM-41. The structure also exhibits outstanding hydrothermal stability. The recognition of the disordered, branching structure with uniform channel widths is expected to open a new class of noncrystalline molecular sieves, and the unique structures with good stability will provide new opportunities for rational design of heterogeneous catalysts, adsorbents, and other related materials.

In recent years, there have been dramatic advances in the concept of molecular sieves exhibiting uniform pore sizes. The structures of early molecular sieves were typified by crystalline microporous materials such as zeolites and  $\text{AlPO}_4$ 's in which the arrangement of channels (or pores) and the framework atoms are ordered over crystallographically long range. Later, the discovery of ordered mesoporous molecular sieves such as MCM-41 and MCM-48 has opened a new class of molecular sieves in which the channel arrangement is crystallographically ordered while the atomic arrangement is disordered similar to amorphous silica.<sup>1–3</sup> Since then, a few research reports began to show possibilities for finding another class of silicate materials exhibiting disordered arrangement of mesopores with very high specific surface areas and narrow pore-size distribution. One such material was synthesized by Chen et al.<sup>4</sup> using hydrothermal reaction of Na–kanemite (a layered silicate material) and hexadecyltrimethylammonium (HTA) chloride. The structure of the material was suggested to be disordered packing of straight mesoporous channels by the authors. More recently, Bagshaw et al.<sup>5</sup> reported on the synthesis of another mesoporous silica material, designated MSU-1, by a neutral surfactant assembly pathway using tetraethylorthosilicate and non-ionic surfactants. Transmission electron micrograph image of the MSU-1 was interpreted to have disordered, hexagonal-like packing of wormlike channels by the authors, while the pore-size distribution curve had a narrow peak with peak width about 0.9 nm at half height. Guo<sup>6</sup> also reported a disordered mesoporous silicate material and recognized packing of randomly distributed channels.

Accurate information on local structure of the disordered porous materials was difficult to obtain previously, due to lack to long-range structural order. The reported disordered materials showed transmission electron micrograph images which only appeared to be disordered. The materials gave X-ray diffraction (XRD) patterns containing broad diffraction peaks. However, these apparently disordered micrograph images or broad XRD

patterns were difficult to clearly distinguish the materials from MCM-41 samples that were obtained with poor crystallinity. There was no structural information providing evidence whether the reported disordered materials had one-dimensional mesoporous channels entangled similar to spaghetti noodles or the channels were interconnected in a three-dimensional disordered way similar to vegetable fiber *Luffa*.

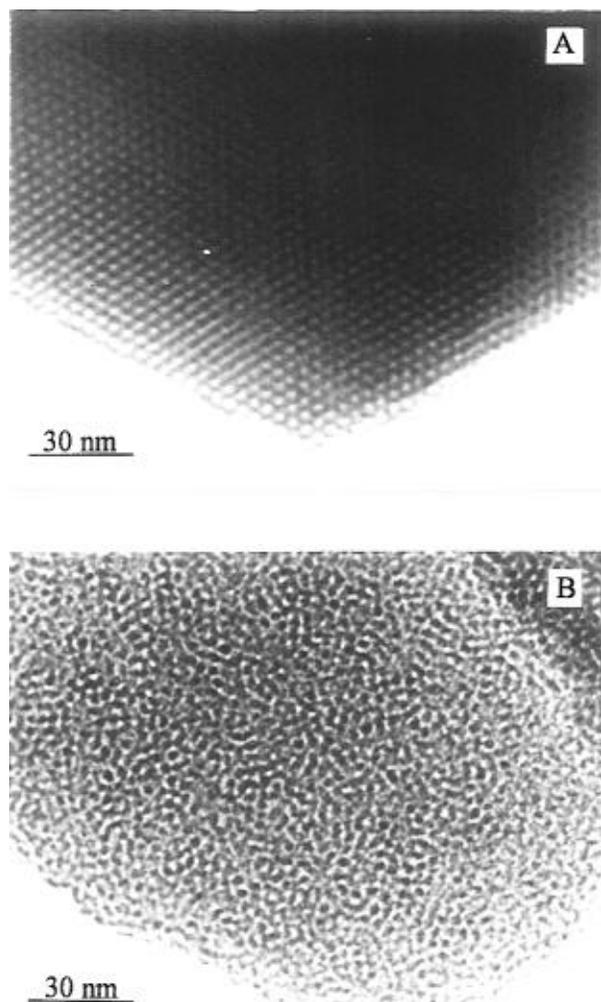
In this paper, we report on the synthesis of a noncrystalline molecular sieve which exhibits short wormlike mesoporous channels interconnected *indeed* in a three-dimensional, disordered way through numerous seams (or branches), while the channel widths are as uniform as the ordered mesoporous molecular sieves, MCM-41. The uniform pore-size distribution with peak width  $\leq 0.3$  nm at half-height has been confirmed using  $\text{N}_2$  adsorption obtained at liquid  $\text{N}_2$  temperature. The three-dimensionally branching local structure of this material has been clarified using transmission micrograph of nanosize platinum wires intergrown through the branches inside the mesoporous channels. The uniform pore widths are very similar to the MCM-41, but the channel arrangement interconnected in a three-dimensional disordered way distinguishes this new molecular sieve most conspicuously from the MCM-41, which exhibits a hexagonal arrangement of straight channels. Besides, the disordered structure has higher thermal stability and hydrothermal stability than the MCM-41 structure. The existence of molecular sieves with such disordered, three-dimensional channel branching motifs having uniform channel widths was not reported previously.

The present material, designated KIT-1 (Korea Advanced Institute of Science and Technology Number 1), was synthesized by an electrostatic templating route using sodium silicate, HTAC1, and ethylenediaminetetraacetic acid tetrasodium salt ( $\text{EDTANa}_4$ ). The silicate was hydrothermally polymerized surrounding HTA micelles in aqueous solution at 370 K, similar to hydrothermal synthesis of MCM-41 using repeated pH adjustment.<sup>7</sup> The surfactant–silicate mesostructure thus obtained is compared with MCM-41 using transmission electron micrographs in Figure 1. While the MCM-41 shows the hexagonal structure in the transmission electron micrograph, no structural orders have been found from the micrograph or the

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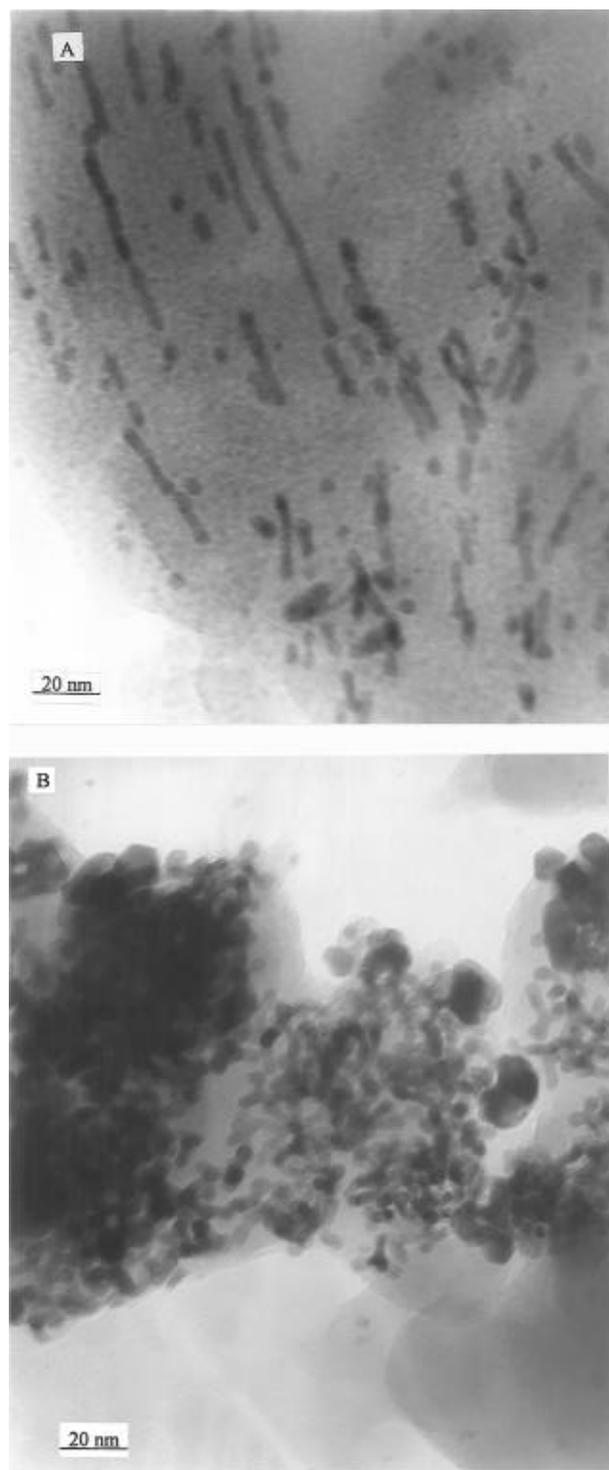


**Figure 1.** Transmission electron micrographs of (A) ordered molecular sieve MCM-41 and (B) disordered molecular sieve KIT-1.<sup>20</sup>

electron diffraction pattern for the KIT-1. Very similar transmission electron micrographs were also obtained when the EDTA salt was substituted by sodium salts of other organic acids such as adipic acid, benzenedisulfonic acid, etc. The surfactant was removed readily from products by calcination in air under static conditions at 823 K. The calcined materials gave essentially the same transmission electron micrograph as the as-synthesized forms.

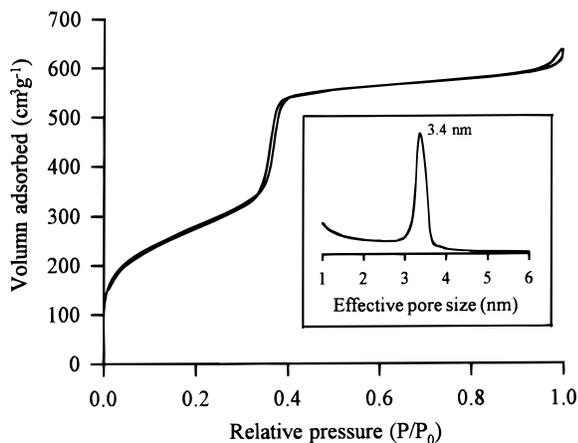
To investigate local structure, we have obtained transmission electron micrograph images presented in Figure 2 for KIT-1 and MCM-41 after supporting platinum wires inside the mesoporous channels. The supported Pt wires were grown inside the channels using a technique that has been developed here by combining the ion exchange and the impregnation methods for supporting metal clusters in zeolite pores.<sup>8</sup> The micrograph images show that the KIT-1 particle contains a large number of short wormlike channels branching and interconnecting to each other in a three-dimensional disordered way, whereas the MCM-41 channels are linear. Thus, the remarkable difference between the two mesoporous materials is clearly shown by the present transmission electron micrograph imaging technique.

Figure 3 shows the pore size distribution curve for the calcined KIT-1 material which has been obtained from N<sub>2</sub> adsorption isotherm at liquid N<sub>2</sub> temperature following the Horvath–Kawazoe analysis.<sup>9</sup> The pore-size distribution curve shows a mesopore with the pore diameter 3.4 nm at maximum of the distribution. It is very remarkable that despite the

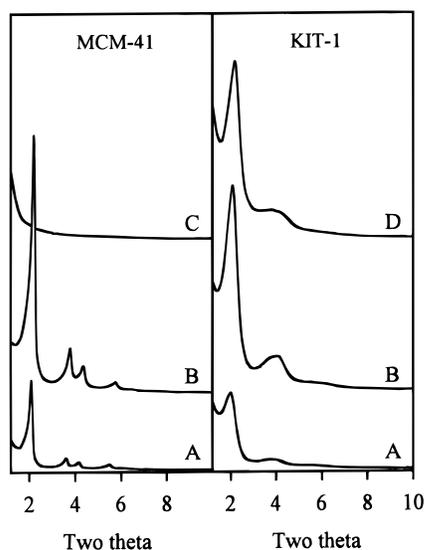


**Figure 2.** Transmission electron micrographs of (A) ordered molecular sieve MCM-41 and (B) disordered molecular sieve KIT-1, after supporting Pt wire inside the mesoporous channels. Note that the KIT-1 contains numerous short wormlike channels interconnected with each other to form a three-dimensional disordered network, while the ordered MCM-41 channels are one-dimensional.

disordered channel arrangement, the mesopore structure of the KIT-1 ( $\sim 0.3$  nm peak width) is as uniform in channel width as the ordered MCM-41 ( $\sim 0.3$  nm peak width) on the basis of the width at half-maximum for the pore-size distribution curve. In this respect, the KIT-1 can be classified as a molecular sieve having *truly* uniform channel widths while the channels are *fully* disordered. The specific surface area of the KIT-1, 1000 m<sup>2</sup> g<sup>-1</sup> obtained by the BET method, is also similar to the ordered MCM-41.



**Figure 3.**  $N_2$  adsorption–desorption isotherms at liquid  $N_2$  temperature for disordered molecular sieve, KIT-1, after calcination. Inset: the corresponding pore-size distribution curve obtained by the Horvath-Kawazoe analysis.



**Figure 4.** Powder X-ray diffraction patterns for ordered mesoporous molecular sieve, MCM-41, and disordered molecular sieve, KIT-1: (A) as-synthesized samples; (B) calcined samples; (C) MCM-41, heated in boiling water for 12 h; (D) KIT-1, heated in boiling water for 2 days.

X-ray diffraction (XRD) patterns obtained for the KIT-1 and the MCM-41 are compared with each other in Figure 4. While the MCM-41 shows well-resolved the same XRD lines characteristic of the hexagonal structure as reported in the literature, the KIT-1 structure has an XRD pattern showing three broad peaks which may arbitrarily be indexed to (100), (200), and (300) diffraction with  $d_{100} = 4.0\text{--}4.2$  nm. Calcination did not affect the XRD pattern, except that the intensity increased 3 times upon calcination and the  $d_{100}$  spacing decreased slightly ( $\leq 0.1$  nm). The presence of the three-line XRD pattern does not indicate that the KIT-1 has a layered structure, but the broad diffraction peaks came from a short-range structural order with very uniform pore sizes.

The formation of the KIT-1 mesostructure during the hydrothermal synthesis using surfactant solution is reminiscent of the disordered phases which are well-known in surfactant solutions<sup>10</sup> and surfactant layers adsorbed on the solid surfaces reported very recently.<sup>11</sup> The role of the salts present in the present electrostatic templating mechanism for the formation of the KIT-1 is similar to the salt effect causing adjacent micelles to coalesce and to give disorder in some surfactant solutions.<sup>12</sup> It is reasonable that the electrostatic interaction of organic salts

such as  $EDTANa_4$  and sodium salicylate with surfactant micelle can moderate the surface potential of the surfactant micelle to cause the micelle to form branches. Then, the channel disorder in the KIT-1 structure can be controlled by the nature and concentration of chemical agents that are used to cause the disorder in the micelle arrangement. Products obtained with the sodium salt of different polyacids gave similar XRD patterns with two or three broad diffraction bands but indicated significant differences in the diffraction line shapes. There seemed to be considerable differences in the density of the seams interconnecting the channels, the distance between adjacent seams, and perhaps the channel-to-channel angle at the seams. Likewise to the MCM-41, it is also possible to tailor the channel widths by use of surfactants with suitable sizes.

The structure of the KIT-1 exhibits outstanding hydrothermal stability and thermal stability, compared with MCM-41. We have obtained pure silica MCM-41 and MCM-48 samples, following hydrothermal synthesis procedures reported in the literature,<sup>1</sup> and compared hydrothermal stability of the samples with that of a pure silica KIT-1 sample. The structure of the KIT-1 was stable in boiling water for 2 days, whereas the structures of the other materials were lost completely due to silicate hydrolysis as shown in Figure 4.<sup>13</sup> The structure of the KIT-1 did not change under 100% steam flow for 2 h at 1020 K. The disordered structure was also stable during heating with air flow containing 2.3 kPa water vapor for 2 h at 1220 K. The high hydrothermal stability of the KIT-1 is very significant, considering that the improvement of hydrothermal stability has been a critical problem for ultimate successful commercialization of the MCM-41 type materials.

Incorporation of aluminum to the KIT-1 framework has been confirmed to be feasible in the range of  $Si/Al = 5\text{--}\infty$  using sodium aluminate during synthesis, without altering the disordered structure. The structure incorporating aluminum (A1KIT-1) also exhibited good stability in boiling water and air with water vapor, similar to the above pure-silica KIT-1. The A1KIT-1 exhibited good cation-exchange capacity into the mesoporous channels from aqueous solutions. In the synthesis of A1MCM-41 with  $Si/Al$  ratios below 15, the structural order can be lost progressively with increasing the Al content.<sup>14</sup> Moreover, calcination of the as-synthesized products with high Al content can lead to the formation of cokes due to the surfactant decomposition, which causes the channel blockage. The cokes formation can be prevented by washing a large fraction of the surfactant using an ethanol–HCl mixture prior to the calcination. However, significant dealumination occurs during the washing. The resulting A1MCM-41 gives very low ion-exchange capacity, and furthermore much of the structural order is lost during the cation exchange due to weak hydrothermal stability of MCM-41.<sup>15</sup> Compared with the A1MCM-41, calcination of the A1KIT-1 can be performed using air under static conditions without the washing with the ethanol–HCl mixture, which is due to facile diffusion of gases through numerous branches in the three-dimensional channel structure during the calcination. Using the ion-exchange capacity increasing with Al content in the channel structure, it is possible to change the charge density over a wide range in the same structure, which may be a remarkable advantage over MCM-41 and ZSM-5 in fundamental researches for advanced electronic materials.

The three-dimensionally branching pore structure with ion-exchange capacity is of great value for the design of supported catalysts. For example, we have ion exchanged metal amine complex cations of Pt, Pd, Rh, Ru, and Ir up to the 1–2 metal wt %, activated the resulting species in  $O_2$  flow or in vacuum,

and subsequently reduced with H<sub>2</sub> flow. The procedures are the same as used for the preparation of small metal clusters inside the supercages (1.3 nm in diameter) of NaY zeolite.<sup>16</sup> The chemical shift in <sup>129</sup>Xe NMR spectra of the adsorbed xenon inside the KIT-1 channels has increased markedly, which indicates the presence of the metal clusters inside the channels.<sup>17</sup> Extended X-ray absorption fine structures of the metals have indicated that the cluster sizes are smaller than those supported on the NaY zeolite. Compared with the 1-nm metal clusters, large Pt clusters about 3–4 nm in diameter have been obtained inside the mesoporous channels when the impregnation technique using H<sub>2</sub>PtCl<sub>6</sub> was used. These Pt clusters are large enough to cause multiple pore blockage in the one-dimensional channel of MCM-41.<sup>17</sup> In the three-dimensional channel structure of the KIT-1, all the Pt clusters can be accessible for ethane hydrogenolysis with H<sub>2</sub>. Thus, we have obtained the catalytic activity for Pt/KIT-1 proportional to the Pt loading within 1–5 wt % Pt. Likewise, it is expected that other large catalytic active centers such as heteropolyacids<sup>18</sup> and metal-locenes<sup>19</sup> can be supported without causing channel blockage in the KIT-1 structure.

Results obtained in the present work clarify the existence of a new class of molecular sieves with *truly* uniform channel widths and *fully* disordered channel arrangement resembling the network of a branched pore fractal, or the vegetable fiber *Luffa*. On the basis of our findings on the disordered molecular sieve, KIT-1, the molecular sieves found hitherto may be classified into three groups according to the degree of the structural order. Members of the first group are crystalline microporous materials such as zeolites and AlPO<sub>4</sub> of which both the atomic arrangement and the channel arrangement are ordered over crystallographically long range. The second group consists of the recently found ordered mesoporous materials such as MCM-41, MCM-48 and SBA-1, -2, -3.<sup>1–3</sup> Channel arrangement in the mesoporous materials is crystallographically ordered, while the atomic arrangement in the channel wall is disordered, similar to amorphous silica. Molecular sieves in the third class are disordered materials exhibiting *truly* uniform pore widths, like the structure of KIT-1. The disordered materials can still be regarded as *true* molecular sieves because the channel width or the diameters are as uniform as the channel sizes for the above second class, even if neither the channels nor the framework atoms are ordered. Thus, our recognition of the disordered structures with uniform channel width is expected to open a new class of noncrystalline molecular sieves.

In summary, the disordered mesoporous material, KIT-1, found in the present work belongs to a new class of molecular sieve in which the short wormlike channels with uniform widths are interconnected in a three-dimensional, *fully* disordered way. The networklike channel structure of the present material gives an advantage for preventing channel blockage over the linear channel in MCM-41. The KIT-1 has also remarkable hydrothermal stability. These findings are expected to provide new opportunities for rational design of heterogeneous catalysts, adsorbents, and other related materials. In addition, the transmission electron micrograph imaging technique developed

here using Pt nanowire will be very useful for the determination of local structure of the forthcoming disordered mesoporous materials.

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