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Hydrothermally Stable Ordered Mesoporous Titanosilicates with Highly Active Catalytic Sites

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Received September 4, 2001

There is currently great interest in titanium-containing zeolitic catalysts for selective oxidation. Since the discovery of microporous TS-1 and TS-2 by Enichem Company,[1] a series of microporous titanosilicates, Ti-ZSM-12,[2] Ti-ZSM-48,[3] and Ti-β,[4] have been reported which have remarkable catalytic properties.[1−7] However, one disadvantage of these titanosilicate catalysts is that their pores are too small for access by bulky reactants in the fine chemical and pharamaceutical industries. Recent progress in solving this has been the incorporation of titanium ions into the framework sites of mesoporous materials (MCM-41, HMS, SBA-15)[8−16] and the grafting of a titanocene complex onto mesoporous silica.[17] These mesoporous titanosilicate materials have pore diameters of 30−60 Å and exhibit catalytic properties for the oxidation of bulky reactants under mild conditions, but unfortunately, when compared with those of TS-1 and Ti-β, the oxidation ability and hydrothermal stability are relatively low, which severely hinders their practical applications. The relatively low oxidiation ability and hydrothermal stability, for example, of Ti-MCM-41, can be attributed to the difference in the titanium coordination environment (amorphous nature of the mesoporous wall).[18] Recently, there had been great progress in the preparation of mesostructured materials assembled from nanoclusters, such as mesostructured metal germanium sulfides[19] and mesoporous aluminosilicate nanoclusters.[20,21] In our preliminary work,[22] we have reported the synthesis of an ordered mesoporous titanosilicate (MTS-9) by the assembly of preformed titanosilicate precursors with triblock copolymers in a strong acidic media. We demonstrate here that MTS-9 shows excellent hydrothermal stability and very high activity for the oxidation of the smaller molecules of phenol and styrene and also of the bulky molecule of trimethylphenol.

MTS-9 was hydrothermally synthesized from an assembly of triblock polymers (P123) with preformed titanosilicate precursors in a strong acidic media (pH < 1) by a two-step procedure. First, precursors containing TS-1 nanoclusters were prepared. Second, the preformed precursors were assembled with triblock copolymers in a strong acidic media (pH < 1).[14,22] The detailed synthesis procedure for MTS-9 has been published previously.[22]

X-ray diffraction (Figure 1) and TEM images (Figure 1S) clearly indicate that MTS-9 has ordered hexagonal arrays of mesopores with uniform size. Notably, the results of XRD and N_2 adsorption isotherms (Figure 1, Table 1) clearly indicate that MTS-9 (with surface area of 980 m^2/g) retains ordered hexagonal structure (with surface area of 720 m^2/g) even after treatments in boiling water for 120 h. In comparison, SBA-15 and Ti-MCM-41 lose most of their mesostructure (with surface area less than 200 m^2/g) (Figure 1, Table 1) by the same treatments. These results indicate that MTS-9 is extremely hydrothermally stable compared to Ti-MCM-41 and SBA-15.

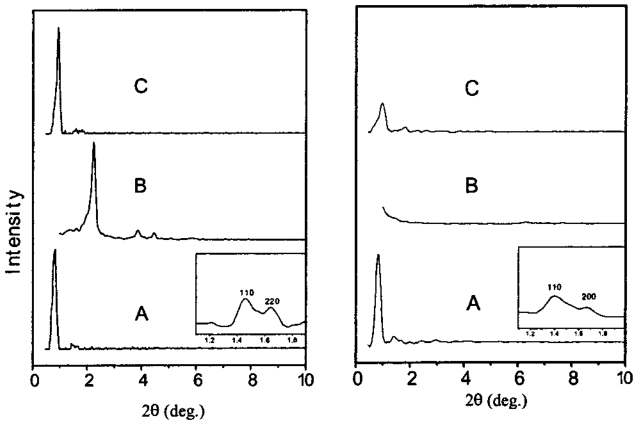

Figure 1. XRD patterns of (A) MTS-9, (B) Ti−MCM-41 and (C) SBA-15 (left) before and (right) after hydrothermal treatment in boiling water for 120 h. (Inset: magnified XRD of MTS-9.)

Table 1. Parameters over MTS-9, Ti-MCM-41, and SBA-15 Samples before and after Treatment in Boiling Water for 120 h[a]

samples	pore size (nm) before	pore size (nm) after	wall thickness (nm) before	wall thickness (nm) after	surf. area (m^2/g) before	surf. area (m^2/g) after
MTS-9	8.0	8.9	4.8	4.3	980	720
Ti-MCM-41	2.7		1.5		1080	55
SBA-15	7.6		3.2		870	187

[a] Ti-MCM-41 and SBA-15 were prepared from published procedures.[12,14] Pore size distributions were determined by BJH method from N_2 adsorption isotherms at 77 K. The wall thicknesses were calculated as: a_0-pore size ($a_0 = 2 \times d(100)/3^{1/2}$).

Catalytic activities for the oxidation of aromatics by H_2O_2 over various catalysts, including MTS-9, Ti-MCM-41, Ti-HMS, and TS-1 are summarized in Table 2. In phenol hydroxylation, Ti-MCM-41 and Ti-HMS shows very low catalytic activity (2.5 and 0.5%, respectively), but MTS-9 exhibits very high catalytic activity, with a phenol conversion of 26% which is comparable with that of TS-1.[1,6] In styrene epoxidation, MTS-9 shows activity and selectivity similar to those of TS-1, which are much different from those of Ti-MCM-41. In 2,3,6-trimethylphenol hydroxylation, Ti-MCM-41 is inactive due to the relatively low oxidation ability of Ti species in the amorphous wall of Ti-MCM-41, and TS-1 is also inactive due to the inaccessibility of the small micropores of TS-1 to the large diameter of a bulky molecule like 2,3,6-trimethylphenol. However, MTS-9 is very active for this reaction with a conversion of 18.8%, indicating that MTS-9 is an effective catalyst for the oxidation of bulky molecules. Additionally, the leaching of Ti during the aforementioned reactions is characterized by element analysis, and the results show no detectable leaching of Ti in our experiments, suggesting the high stability of Ti species in MTS-9.

The Ti species in MTS-9 have been characterized by UV−visible and UV−Raman techniques. The UV−vis spectrum (Figure 2S) for MTS-9 has an adsorption band near 215 nm, indicating that

10.1021/ja0170044 CCC: $22.00 © 2002 American Chemical Society

Table 2. Catalytic Activities in Oxidation Reactions by H_2O_2 over MTS-9, Ti-MCM-41, and TS-1 Samples

samples	reactions	TOF	conv. (%)	product selectivity (%) P1	P2	P3
MTS-9	phenol hydroxylation[c]	6.8	26.3	59.5	39.8	0.7
Ti-MCM-41	phenol hydroxylation[c]	0.5	2.5	60.1	38.0	1.9
Ti-HMS[a]	phenol hydroxylation[c]	0.1	0.5	58.5	41.5	0.5
TS-1^	phenol hydroxylation[c]	5.5	28.0	50.4	48.6	1.0
MTS-9	styrene epoxidation[d]	9.4	56.4	28.0	29.3	42.7
Ti−MCM-41	styrene epoxidation[d]	6.1	48.3			100
TS-1[b]	styrene epoxidation[d]	5.2	54.6	13.3	58.3	29.0
MTS-9	trimethylphenol hydroxylation[e]	7.4	18.8	66.7	21.1	12.2
Ti-MCM-41	trimethylphenol hydroxylation[d]	1.4	4.1	25.5	69.8	4.6
Ti-HMS[a]	trimethylphenol hydroxylation[e]	0.5	2.0	25.0	70.0	5.0
TS-1[b]	trimethylphenol hydroxylation[e]	0.3	1.2	71.1	17.6	11.3

[a] Ti-HMS with Si/Ti ratio of 30 was synthesized according to published procedure.[9] [b] TS-1 with Si/Ti ratio of 30 was synthesized according to published procedure.[1] [c] Reaction conditions: water as a solvent, reaction temperature at 80 °C, phenol/H_2O_2 = 3/1 (molar ratio), reaction time for 4 h, catalyst/phenol = 5% (weight ratio). The products are catechol (P1), hydroquinone (P2), and benzoquinone (P3). The product of tar is not included. [d] Reaction conditions: acetone as a solvent, reaction temperature at 45 °C, styrene/ H_2O_2 = 3/1 (molar ratio), reaction time for 5 h, catalyst/phenol = 5% (weight ratio). The products are styrene epoxide (P1), phenylacetaldehyde (P2), and benzaldehyde (P3). [e] Reaction conditions: acetonitrile as a solvent, reaction temperature at 80 °C, trimethylphenol/H_2O_2 = 3/1 (molar ratio), reaction time for 4 h, catalyst/phenol = 5% (weight ratio). The product are trimethylhydroquinone (P1), trimethylbenzoquinone (P2), others (P3).

the coordination environment of the Ti species in MTS-9 is similar to that in TS-1.[18] In contrast, Ti-MCM-41 shows peak at 230 nm, which had been assigned to titanium with a coordination number between four and six.[12,18] UV−Raman spectroscopy is very sensitive to the coordination environment of Ti species,[23] and its spectrum of MTS-9 shows a band at 1122 cm^{-1} (Figure 3S), which is very close to that of TS-1 (1125 cm^{-1}) and characteristic of isolated four-coordinated Ti species.[23]

We attribute the good hydrothermal stability of MTS-9 in part to the zeolite-like connectivity of TO_4 (T = Si, Ti) in the mesostructure as discussed in previous work[20,21] and in part to its thicker walls.[22] The high catalytic activity of MTS-9 is due to the TS-1-like enviroment of the Ti in MTS-9. The evidence for this is provided by IR spectroscopy of MTS-9. It gives a band at 556 cm^{-1} (Figure 4S) which is characteristic of a five-ring subunit in TS-1 zeolite.[1] In contrast, we cannot detect this band with Ti-MCM-41. Additionally, from the high-magnification TEM image (Figure 5S) we observed some area in the walls of MTS-9 with ordered micropores array. Similar phenomena have never been found in previous work on mesoporous materials. The FFT diffractogram of these areas further confirms the periodical array of these micropores. We notice the size of these areas is about 3 nm, which is well consistent with that of MFI nanoclusters (2.8 nm) reported by de Moor.[24] We think they are a visual indication of preformed TS-1 nanoclusters embedded in the walls of MTS-9.

We proposed that during the preparation of MTS-9 the titanium sites are fixed in the framework of the TS-1 nanoclusters in the first step and are introduced into the mesoporous structure when the nanoclusters self-assemble with the template in the second step. Because of the strong acidic condition in the second step, the nanoclusters prepared in the first step would not grow continuously into large crystals, and thus the appearance of TiO_2 as a separate phase is avoided. Generally, a TiO_2 phase, which is easily formed under the basic conditions used in the preparation of porous titanosilicates such as TS-1 and Ti-MCM-41, often acts as a catalyst poison in oxidation reactions.[25]

Acknowledgment. This work was supported by NSFC (29825108, 29733070, and 20173022), the State Basic Research Project (G2000077507). We thank Prof. Dezeng Wang (Department of Chemical Engineering, Tsinghua University, China) for helpful suggestions and discussions.

Supporting Information Available: Figures S1−S5 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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JA0170044