Oxoanions-induced Rapid Synthesis of Highly Ordered Mesoporous Silica

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(Received September 16, 2005; CL-051191)

Highly ordered mesoporous silica have been rapidly synthesized by using oxoanions as promoter and nonionic triblock copolymer P123 as template, and the reaction products has been characterized by N_2 adsorption–desorption, XRD, FE-SEM, and TEM.

It is well known that mesoporous silica materials are synthesized by synergistic self-assembly between surfactant and silica species to form mesoscopically ordered composites.[1] Generally, ionic surfactants such as alkyltrimethylammonium bromide[1,2] and nonionic surfactants such as poly(alkylene oxide)-type copolymers[3–11] are used for the formation of mesoporous silica materials. Compared with ionic surfactant, nonionic surfactants are easily removable, nontoxic, biodegradable, and relatively inexpensive.[6a,9,11] In 1998, Stucky[3] and co-workers firstly reported that well-ordered mesoporous SBA-15 has formed in acid media by using a large number of liquid acids such as HCl, HBr, HNO_3, and so on, as pH adjustor. Science then, many efforts have been made to lower HCl utilization, including adjusting the mol ratio of SiO_2 to P123,[11] addition of fluorocarbon-surfactant[12] or small amounts of fluoride.[13] Most zeolites are synthesized by hydrothermal methods, which generally suffer from the drawback of long crystallization times.[14] Stucky and co-workers' experimental results exhibit that if only reduce molar ratio of HCl to Si, in order to obtain ordered hexagonal mesoporous silica, the crystallization time will become very long.[13] Approach to shorten crystallization time of zeolites and related molecular sieves using inorganic anions such as $ClO_4{}^-$, $PO_4{}^{3-}$, $NO_3{}^-$, and so on as promoters has been reported.[15] To the best of our knowledge, this is the first report of synthesis of ordered hexagonal SBA-15-type mesoporous silica with very small amounts of HCl and oxoanions promoter, without compromising the crystallization time.

In this paper, we report a facile and rapid approach for the synthesis of highly ordered mesoporous silica by addition of small amount of oxoanions. Nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$ (designated Pluronic P123; Aldrich) was used as a structure-directing agent. The addition of a small of oxoanions such $MoO_4{}^{2-}$, $WO_4{}^{2-}$, $W_7O_{24}{}^{6-}$ significantly lowers HCl utilization during the mesoporous silica formation without compromising the short crystallization time and highly ordered mesostructure. In a typical synthesis batch, 4.0 g of P123 was dissolved in 105 g of distilled water with vigorously stirring at room temperature for 3 h, then 0.82 g $Na_2MoO_4{\cdot}2H_2O$ was added into the solution. After P123 was dissolved completely, 8.55 g of TEOS and 0.95 mL of c-HCl were added dropwise to the above mixture solution. The chemical composition of the reaction mixture was 4 g copolymer:0.041 mol TEOS:0.0034 mol $MoO_4{}^{2-}$:0.011 mol HCl:5.83 mol H_2O. Subsequently, the mixture was stirred at 40 °C for 20 h and crystallized at 96 °C for 6 h. The products were filtered, washed and dried at 45 °C for 2 days. Finally, the samples were calcined at 550 °C in air for 8 h (heating rate of 1 °C/min).

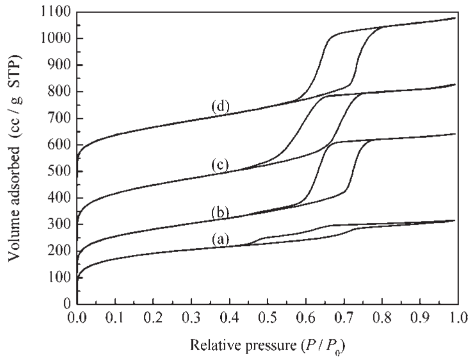

Figure 1. (A) N_2 adsorption–desorption isotherms for calcined mesoporous silica: (a) without oxoanion promoter, (b) with $Na_2MoO_4{\cdot}2H_2O$, (c) with $(NH_4)_6W_7O_{24}{\cdot}6H_2O$, and (d) reference. The adsorption–desorption isotherms of (b), (c), and (d) are shifted by 120, 240, and 480 mL (STP) g^{-1}, respectively, for clarity.

Representative N_2 adsorption–desorption isotherms for mesoporous silica synthesized with oxoanions are provided in Figure 1. For comparison, it is helpful to refer to the N_2 adsorption–desorption isotherms of sample prepared without oxoanions. According to the IUPAC classification, the N_2 adsorption–desorption isotherms of the mesoporous silica synthesized with (b) $Na_2MoO_4{\cdot}2H_2O$, (c) $(NH_4)_6W_7O_{24}{\cdot}6H_2O$, and (d) reference are found to be of type IV, and a clear H_1 hysteresis loop[16] is observed for three of them. The P/P_0 of the inflection points is related to a diameter in the mesopore range and the sharpness of the step indicates the uniformity of mesopore size distribution. The pore size distribution of the mesoporous silica synthesized with $Na_2MoO_4{\cdot}2H_2O$ and $(NH_4)_6W_7O_{24}{\cdot}6H_2O$ assuming cylindrical pores presented as BJH plot in Figure S1 (see ESI) was calculated from the desorption branch of the isotherms. Both of them show quite narrow pore size distributions with peak pore radius centered around 27.5 and 24.4 Å, respectively, and the former exhibits more narrower distribution.

The pore structure parameters for various mesoporous silica calculated from the X-ray diffraction data and N_2 adsorption–desorption and the corresponding reaction yields are given in Table 1. With the same synthesis conditons, the yield of samples prepared with oxoanions is above 93%, while the yield of sample synthesized without oxoanions is about 85%, based on silica. One the other hand, the former samples are well ordered hexagonal structure but the latter is amorphous. In order to obtain well ordered mesoporous structure, the reaction (crystallization) time would obviously increase if the molar ratio of HCl to Si is lower

Table 1. Physicochemical properties of hexagonal SBA-15 prepared under various synthetic conditions

Promoter	HCl /mol	Si/Me[a]	CT[b] /h	d_{100} /Å[c]	S_{BET} /$m^2 g^{-1}$	PV /mL g^{-1}[d]	APD /Å[e]	Wall thickness /Å[f]	Product Yield /%	Crystal Structure[g]
$Na_2MoO_4 \cdot 2H_2O$	0.011	12.2	24	111(96.1)	691	0.96	55.6	55.4	95.3	Hexagonal
$Na_2MoO_4 \cdot 2H_2O$	0.011	12.2	6	106(92.5)	594	0.82	55.2	51.6	94.5	Hexagonal
$Na_2WO_4 \cdot 2H_2O$	0.011	12.2	6	101(90.4)	771	0.95	49.3	55.1	94.2	Hexagonal
$(NH_4)_6W_7O_{24} \cdot 6H_2O$	0.011	12.2	6	100(85.3)	746	0.91	48.8	49.7	93.7	Hexagonal
None	0.011	—	6	—	662	0.49	29.6	—	84.8	Amorphous
None(reference)[h]	0.24	—	24	105(97.9)	795	0.97	48.8	64.2	96.7	Hexagonal

[a]Molar ratio, Me = W or Mo. [b]CT = Crystallization time. [c]The value inside and outside brackets for d_{100} is the SBA-15 samples calcined at 550 °C in air for 8 h and as-made, respectively. [d]PV = Pore volume. [e]APD = Average pore diameter = 4 × pore volume/BET surface area. [f]The wall thickness = a_0-average pore diameter, and $a_0 = 2 \times d_{100}/\sqrt{3}$. [g]Crystal structure was characterized by XRD. [h]Sample was prepared by following the reported conventional synthesis route (ref 3a).

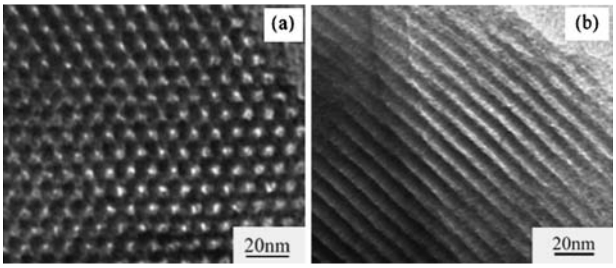

Figure 2. Representative TEM images of mesoporous SBA-15 prepared with $Na_2MoO_4 \cdot 2H_2O$ obtained on a JEM-2010EX microscope at different view plane.

than 0.59 and without any promoter's addition,[13] and the molar ratio is about 0.27 in our experiment. The results confirm the oxoanion's promotable roles, which are distinct for ordered mesoporous silica formation. In addition, the apparent energies of nucleation and crystallization using Mo oxoanions are lower than those of the corresponding W oxoanions, and similar result was observed for P and As oxoanions.[15] The apparent energies are closely related to crystallization process and time, which might be associated with the textural property difference.[10]

The morphology of the product was examined using FE-SEM and TEM. The curved and bent macroscopic structures are observed in Figure S2 (see ESI). TEM images (Figure 2) show well ordered hexagonal arrays of 1D mesoporous channels and confirm that the samples have a 2D hexagonal structure (*P6mm*) as do previous reports for mesoporous silica materials.[2] From high-dark contrast in the TEM image of the SBA-15 sample, the distance between two consecutive mesopores is estimated to be ca. 10.8 nm, and pore diameter is around 5.5 nm. The average wall thickness is about 5.3 nm, which is much larger than that of MCM-41.[2] The results are consistent with the results from N_2 adsorption–desorption and XRD experiments.

In conclusion, we have developed a novel route for rapid synthesis of ordered mesoporous silica by using oxoanions as promoter. Small amounts of oxoanions were added into the synthesis media, which resulted in substantially reducing HCl: Si molar ratio and shortening crystallization time. The oxoanions would cause the apparent energies of nucleation and of crystallization to reduce, which might be responsible for rapid synthesis of ordered mesoporous silica at low HCl concentration.

This work is supported by Key Project of National Natural Science Foundation of China (Grant No. 20433030), National High Technology Research and Development Program of China (Grant No. 2003AA302220), and Natural Science Foundation of Zhejiang Province (Grant No. M203078).

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Published on the web (Advance View) November 29, 2005; DOI 10.1246/cl.2006.12