Promoted and Controllable Self-Assembly of Hydrolyzed Siloxane and Triblock Copolymer under Organic Polyhydroxy Acids

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Large-molecule polyhydroxy organic acids such as tartaric acid and citric acid were found to significantly promote the cooperative formation of mesoporous silica SBA-15 with homogeneous well-defined hexagonal mesostructure under much weaker acidities without addition of volatile inorganic acids; therefore a novel environmental benign route for SBA-15 synthesis was developed. It is suggested that the polar groups of polyhydroxy acid molecules can greatly strengthen the assembly interactions between the silica species and the triblock copolymer by providing hydrogen bonding. More interestingly, by controlling the strength of hydrogen-bonding interaction that is dependent on the concentration of carboxylic acids, the particle size of the product can be tailored. The silica with small particle size synthesized with a small amount of polyhydroxy acids was favorable support of palladium catalyst for the complete oxidation of volatile organic compounds in atmosphere, probably due to the facilitated diffusion of reactant molecules.

1. Introduction

By using pluronic triblock copolymer as template agent, mesoporous silica SBA-15 with large pore diameter, thick pore wall, and good thermal and hydrothermal stability was first synthesized by Zhao et al.,^{1,2} which has aroused particular interest in the synthesis of mesoporous materials because of their potential versatile applications in the fields of catalysis, adsorption separation, microelectronics, chromatography, sensors, and so on.^{3–8} SBA-15 was generally synthesized in the presence of hydrochloric acid with a high a concentration of more than 1.6 M.^{1,2,9} The concentrated inorganic acids appeared to facilitate the rapid synthesis of periodic mesoporous materials by accelerating the hydrolysis of siloxane, promoting the condensation of silica species, as well as improving the hexagonal packing of the silica–surfactant hybrid micelles.^{9–13}

However, the synthesis of SBA-15 under strong acidities has some shortcomings. For example, the corrosive solutions containing a high concentration of volatile inorganic acids are disadvantageous for large-scale production. Furthermore, strong acidities suppress the direct incorporation of heterogeneous atoms into the framework of the silica to obtain functionalized catalysts.^{14–16} Therefore, some attempts have been made to synthesize SBA-15 under moderate conditions.^{17–22} However, weak acidities seem difficult to afford quick phase separation of mesostructured composites,^{1,12} and some inorganic salts are often needed to promote the formation of ordered mesostructure.^{13,17,22–27} For example, Chen et al.¹⁷ synthesized mesoporous silica materials under acid-free conditions with the aid of salt and alcohol, and it was revealed that the formation of mesostructures depended on the concentrations of the additives and the copolymer. Nonetheless, it was noticed that the obtained mesoporous silica were still less ordered in comparison to the conventional SBA-15 synthesized under strong acidities, as most samples featured only one or two weak Bragg peaks in the X-ray diffraction (XRD) patterns. Some other

researchers also demonstrated that the use of inorganic salts under acidic conditions could dramatically widen the domains of synthesis conditions to produce ordered structure.^{22–24} But there would be some potential problems in disposal of the wastewater containing a high concentration of inorganic salts after the synthesis. Some other efforts have been made to accelerate the hydrolysis of siloxane and the condensation of the resultant silica precursors.^{18–20} TMOS was sometimes used as a silica source instead of the extensively used TEOS because the former hydrolyzed more quickly.^{18,20} Fluoride ions were also often used to accelerate the hydrolysis of siloxane and promote the condensation of silica species.^{19,20,24} Fluoride could induce ordered hexagonal mesostructures in a wide acidity range of pH 0–9 with tetramethyl orthosilicate (TMOS) as silica source²⁰ and also enhance mesostructural ordering at values of up to pH 2.7 with Tetraethyl orthosilicate (TEOS) as silica source.¹⁹ But fluoride ions are one of the major concerns for environmental pollutants. Alternatively, sometimes prehydrolysis of TEOS under lower pH values was adopted to form silica oligomers or monomers before they were mixed with the template solution to start the assembly reactions.^{21,28–30}

Recently, combined use of hydrochloric acid and other inorganic acids were employed for synthesis of SBA-15 under relatively moderate acidities. Luo et al.³¹ found that the addition of a small amount of heteropoly acids could afford a rapid synthesis of SBA-15 with a low concentration of hydrochloric acid, and the authors suggested that the heteropoly acids strengthened the assembly forces. In another work, it was found that the amount of hydrochloric acids could be greatly reduced when phosphoric acid was also present in the synthesis solution,³² and the obtained SBA-15 has significantly enlarged surface areas and pore volumes. It seemed that the phosphoric acid modified the ionic strength and pH of the environment around the template phase.³²

An interesting work was done recently by Hsu et al.,⁹ in which they used carboxylate-terminated triblock copolymer P123 as template agent to synthesize SBA-15 with additional intraparticle porosity. During the synthesis the terminal hydroxyl group of the Pluronic P123 needs to be first oxidized to the

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carboxyl group by potassium dichromate or potassium permanganate, and the synthesis could be carried out with a low hydrochloric acid concentration of 0.3 M. It was revealed that the carboxyl group could catalyze the hydrolysis of siloxane.⁹ In another work about synthesis of SBA-15,³³ carboxylic acids were used to prehydrolyze TEOS, but the assembly still occurred in hydrochloric acid solution with high concentration of 2 M.

Herein, we will show the synthesis of SBA-15 using weak organic acids as a single component of the acid source. A single component of weak organic acids has rarely been used to adjust the acidities in the synthesis of SBA-15 because it is difficult for them to achieve strongly acidic conditions in the absence of additional inorganic acids. Nonetheless, we found that under moderate acidities at $\text{pH} > 1$ some large-molecule carboxylic acids with polyhydroxy can promote the formation of high-quality mesoporous silica that is comparable to the conventional SBA-15 synthesized under strong acidities, although it was previously suggested that no ordered mesostructure could be formed under such acidities with the use of strong mineral acids.^{1,2} In this present work, various organic carboxylic acids were used as acid source, TEOS was used as silica source without prehydrolysis, and the addition of fluoride or other salts was also avoided. Interestingly, it was found that the size of the primary particle in the product could be controlled by varying the concentration of polyhydroxy carboxylic acids, and therefore the lengths of mesochannels could be tailored for special catalysis applications.^{34–36} Furthermore, the polyhydroxy carboxylic acids are in solid state and nonvolatile; thus, they can be more safely handled during the synthesis in comparison to the generally used hydrochloric acid. The synthesis processes are environmentally friendly with use of biodegradable carboxylic acids instead of fluoride or other salts as promoter. In addition, some products with controlled particle size showed an advantage in catalytic elimination of volatile organic compounds, probably due to facile mass transfer.

2. Experimental Section

2.1. Chemicals. The nonionic Pluronic triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_n = 5800$) was purchased from Sigma-Aldrich. Tetraethyl orthosilicate (TEOS, containing 28% of SiO_2) was purchased from Tianjin Fuchen Chemical Reagent Factory. Citric acid (99.9%), acetic acid (99.9%), oxalic acid (99.5%), and palladium chloride (containing 58% of palladium) were purchased from Beijing Chemical Reagents Co. Tartaric acid (99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used as received without any further purification.

2.2. Material Preparation. The typical synthesis of mesoporous silica was similar to the general synthesis procedure of SBA-15 under strong acidities except for the moderately acidic conditions.^{1,2} A 4 g amount of P123 was dissolved in 150 g of water, followed by adjusting the pH value of the solution in the range from 1 to 7 through adding a certain type of organic acid; then 8.5 g of TEOS was added to the acidic P123 solution under stirring. After continuous stirring for a half-hour, the mixture underwent the first aging at a low temperature of 35 °C for 1 day and the second aging in an autoclave at a high temperature of 100 °C for a subsequent 2 days. The resultant solid was filtered, dried at 100 °C, and then calcined in air at 550 °C for 3 h, thus forming the silica powder product. The acids used in this work included acetic acid, oxalic acid, tartaric acid, and citric acid. Correspondingly, the products were denoted as MS_{a-y} , MS_{ox-y} , MS_{t-y} , and MS_{ci-y} , respectively, where y denotes the pH value of the synthesis solution.

Mesoporous silica supported palladium catalysts with a loading of 0.3 wt % were prepared by incipient aqueous wetness impregnation method using palladium chloride as precursors of the catalytic phase. The impregnated solids were dried at 100 °C overnight, calcined in air at 500 °C for 3 h, and then reduced in hydrogen flow at 480 °C for 1 h before activity evaluation.

2.3. Material Characterizations. Small-angle XRD patterns were recorded on a Siemens D5005 diffractometer at 40 kV and 30 mA using $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) images were taken on a Hitachi H-7500 electron microscope operating at an acceleration voltage of 80 kV. Prior to observation, all samples were crushed, dispersed in ethanol, sonicated for 10 min, and deposited on a microgrid to evaporate the solvent. Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were obtained on NOVA1200 gas sorption analyzer. The samples were degassed at 300 °C in a vacuum for more than 5 h before measurements. The Brumauer–Emmet–Teller (BET) surface areas were calculated on the basis of the linear part of the BET plot ($P/P_0 = 0.05–0.25$). The total pore volumes were estimated according to nitrogen uptake at a relative pressure (P/P_0) of ca. 0.99. The pore size distributions (PSD) were derived from the desorption branch of the N_2 isotherms using the Barrett–Joyner–Halenda (BJH) method. Infrared spectra were recorded on a Bruker Tensor 27 using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) techniques.

2.4. Catalytic Activity Evaluation. Catalytic activities toward the complete oxidation of benzene were evaluated in a continuous-flow fixed-bed reactor. An online gas chromatograph equipped with flame ionization detector (FID) was used to analyze the concentration of benzene in the feed and effluent gas. In each test run, 50 mg of catalyst (40–60 mesh) was used, and the total flow rate was kept at 320 mL/min with a benzene concentration of 1050 ppm.

3. Results and Discussion

3.1. Effect of Acidity and Acid Source on Mesostructure. To obtain high-quality SBA-15 with the use of strong inorganic acids, previous work has revealed that it is important that the synthesis is carried out at $\text{pH} < 1$; otherwise, no precipitation or formation of silica gel occurs.^{1,2} Organic acids are rarely used because they are hardly capable of achieving strongly acidic conditions. Unexpectedly, it was found in this work that some organic polyhydroxy acids such as tartaric acid and citric acid can actually induce very good mesostructural ordering under moderately acidic conditions. The XRD patterns of MS_t silica synthesized at various pH values adjusted by tartaric acid are shown in Figure 1a. At $\text{pH} \leq 2.8$, the MS_t samples possess more than three Bragg peaks in their XRD profiles, which can be indexed as (100), (110), and (200) diffractions and reflect a two-dimensional hexagonal mesostructure with a space group of $P6mm$.^{1,2} Especially, for the samples synthesized at pH 1.4–1.8, the additional (210) diffraction peak can be clearly resolved, indicating these materials have a high quality of mesostructural ordering (the long-range regularity of wall mesostructure) that is comparable to those synthesized under strongly acidic conditions induced by strong mineral acids.^{1,2} Figure 1b shows the XRD patterns of MS_{ci} silicas synthesized at various pH values adjusted by citric acid. Citric acid has similar effects on the mesostructural ordering of the product as tartaric acid does, namely, the obtained MS_{ci} silicas synthesized at $\text{pH} \leq 2.8$ possess fine mesostructural ordering with more than three diffraction peaks

Figure 1. XRD patterns of silicas synthesized at various pH values adjusted by large-molecule polyhydroxy carboxylic acids: (a) MS_i and (b) MS_{ci} .

Figure 2. XRD patterns of silicas synthesized at various pH values adjusted by small-molecule carboxylic acids: (a) MS_a and (b) MS_{ox} .

in the XRD patterns, and the additional (210) diffraction peak appears at pH 1.6–1.8.

However, small-molecule organic acids, including acetic acid and oxalic acid, seemed to induce less ordering to the product. Figure 2 shows the XRD patterns of MS_a and MS_{ox} silicas that were synthesized at various pH values adjusted by acetic acid and oxalic acid, respectively. Although somewhat ordered structure can be formed within a narrow acidity range at pH > 2, the diffraction intensity is much weaker than the cases when tartaric acid or citric acid were used. It seems that the optimal pH value is ca. 2.2, because three diffraction peaks can be resolved in both MS_a -2.2 and MS_{ox} -2.2, whereas, not more than two peaks can be found in other samples.

Figure 3 shows some TEM images of MS_i and MS_{ci} silicas synthesized at different pH values adjusted by using large-molecule polyhydroxy acids, which further corroborates the fine periodicity of mesopores in these samples. It can be seen from high-magnification images (Figure 3a,c,e,g) that the number of the packed channels in each silica particle synthesized at pH < 2 is substantially larger than that synthesized at pH 2.8 for both MS_i and MS_{ci} . It reveals that relatively higher concentration of organic acid favors the formation of an enlarged ordered domain. In addition, the low-magnification images (Figure 3b,d,f,h) show that the primary particles are fine rods or curved rods for all samples synthesized at pH $\leq$ 2.8, and the sizes of the rods (diameter and length) increase with decreasing pH values. For example, the rods of sample MS_i -2.8 are, on average, ca. 260 nm in diameter and ca. 1.3 μ m in length, whereas the diameter

Figure 3. High-magnification TEM images of (a) MS_a -1.6, (c) MS_i -2.8, (e) MS_{ci} -1.8, and (g) MS_{ci} -2.8 and low-magnification TEM images of (b) MS_i -1.6, (d) MS_i -2.8, (f) MS_{ci} -1.8, and (h) MS_{ci} -2.8.

and length of the rods for sample MS_i -1.6 increase to ca. 650 nm and ca. 3.4 μ m, respectively.

Strong acidities used to be considered as a prerequisite for the formation of highly ordered mesoporous silica when mineral acids were used as acid sources.⁹ A high concentration of hydronium ions in the strongly acidic solution can catalyze hydrolysis of siloxane.^{10–13,28} Moreover, strong acidities can induce intensive protonation of the PEO corona of triblock copolymer micelle,^{13,37} which offers strong electrostatic and hydrogen bonding interactions with silica species, facilitating the assembly of silica precursors around the micelle template.^{38–43} Under weak acidities actually only a very small amount of silica precipitated if hydrochloric acid or nitric acid was used as the acid source due to limited silica condensation reactions. However, it has been shown in this work that some large-molecule polyhydroxy carboxylic acids can also lead to highly ordered mesostructure even under moderately weak acidic conditions (pH 1.5–2.0). We tentatively propose that the

Figure 4. Example for polyhydroxy carboxylic acid molecules bridging silica species and template phases by hydrogen bond.

Figure 5. (a) Nitrogen sorption isotherms and (b) mesopore size distribution profiles of MS_i silicas synthesized at various pH values adjusted by tartaric acid.

promoting effect of polyhydroxy carboxylic acids on the formation of ordered mesostructure arises primarily from their mediating effect on the interactions between the silica precursors and the triblock copolymers, as is exemplified in Figure 4. This assumption might be supported by the FT-IR spectra of the as-synthesized materials before calcinations (Figure S1 in Supporting Information). The FT-IR spectra indicate that both as-synthesized MS_{ci} and MS_t samples contain carboxyl groups, which could indicate that some organic acid molecules were incorporated into the silica-polymer hybrids. The molecules of both tartaric acid and citric acid bear several carboxyl and hydroxyl groups, and these polar groups can hydrogen-bond with both the copolymers and the silica species because their electropositive hydrogen atoms can have high affinity to the electronegative oxygen atoms in both the copolymer chains and the silica species. Therefore, the assembly forces between the silica species and the template phase can be strengthened due to the bridging capability of polyhydroxy carboxylic acid molecules, which can accelerate the accumulation of silica species around the charged PEO corona, kinetically prompt their condensation around the templates, and finally pack them into hexagonal structure.⁴⁴ In addition, carboxylic acids are effective catalysts for the hydrolysis of siloxane,^{9,45} which is also quite favorable for the assembly reactions. But the small-molecule organic acids, such as acetic acid and oxalic acid, have much less polar groups in their molecules; thus their mediating effect on the assembly forces is too weak to promote the formation of ordered mesoporous materials.

3.2. Effect of Acidity and Acid Source on Textural Property. Figure 5 displays the nitrogen sorption isotherms and pore size distribution profiles of MS_i silicas synthesized at various pH values. All the materials synthesized at $\text{pH} \leq 2.5$ feature type IV isotherms with typical H1-type hysteresis loop, indicating their typical characteristic of mesoporous materials.⁴⁶ The remarkably sharp capillary condensation steps of isotherms at relative pressure of $P/P_0 = 0.75\text{--}0.85$ and narrow sharp pore

Figure 6. (a) Nitrogen sorption isotherms and (b) mesopore size distribution profiles of MS_a silica synthesized at various pH values adjusted by acetic acid.

Table 1. Textural Properties of Various Mesoporous Silicas

sample	A_{BET} (m^2/g)	V_{total} (cm^3/g)	d_{BJH} (nm)	fwhm ^a (nm)
$\text{MS}_t\text{-1.6}$	756	1.3	7.3	1.1
$\text{MS}_t\text{-2.8}$	835	1.3	7.5	1.4
$\text{MS}_{ci}\text{-1.8}$	802	1.4	8.1	1.0
$\text{MS}_{ci}\text{-2.8}$	864	1.3	7.5	1.4
$\text{MS}_a\text{-2.7}$	784	1.8	8.8	3.5
$\text{MS}_{ox}\text{-2.8}$	925	1.6	9.6	2.9

^a Full width at half-maximum of the BJH peak.

size distribution peaks reveal that the materials have uniform cylindrical mesopore channels. Increase of the synthesis values from pH 2.8 to 3.5 leads to the formation of H3-type hysteresis loop in the nitrogen isotherm,⁴⁶ and the low and broad pore distribution peak of $\text{MS}_t\text{-3.5}$ indicates it features decreased mesopore uniformity. A similar evolution trend with acidity can be observed for MS_{ci} silica (Figure S2 in Supporting Information).

Figure 6 shows the nitrogen sorption isotherms and pore size distribution profiles of MS_a silicas. Typical H1-type hysteresis loop can be obtained only at $\text{pH} \sim 2.7$ with the use of acetic acid. Furthermore, the mesopore uniformity of the materials synthesized using small-molecule organic acid seems inferior to that of those synthesized using large-molecule organic acids. It can clearly be seen from pore size distribution peaks and their full-width at half-maximum height (fwhm) listed in Table 1 that the former has broader peaks. Similar results can also be obtained with the use of oxalic acid (Figure S3 in Supporting Information).

The physical properties of some samples synthesized under organic acid are listed in Table 1. Apparently, the pore sizes and pore volumes of the materials synthesized with the use of citric acid or tartaric acid are relatively smaller than those synthesized with the use of acetic acid or oxalic acid, which might suggest that the micelle conformation of triblock copolymer is influenced by the acid molecules. It is well-established that the hydrophobic PPO core of the copolymer micelle contributes primarily to the formation of mesoporosity.^{1,2,42} And the hydrophilic PEO corona region contributes to the formation of part of the framework wall.^{42,47} However, some researchers demonstrated that a fraction of the PEO segments also contributed to the formation of the mesoporosity,⁴⁷ some EO units adjacent to the PPO core were not solvated by water depending on the acidities, and they are incorporated into the hydrophobic part. As discussed previously, the polar hydroxyl groups and carboxyl groups of these large-molecule organic acids can

Figure 7. Illustration for the influence of the acid sources on the hydrophobicity of the copolymer micelle template: (a) in the presence of small-molecule carboxylic acids; (b) in the presence of polyhydroxy carboxylic acids. ‡, Molecules of polyhydroxy carboxylic acid; ○, molecules of small-molecule carboxylic acid; ●, molecules of solvent water.

Figure 8. XRD patterns of MS_i-1.6 synthesized with low-temperature aging at 35 °C for different time.

interact strongly with the PEO chains by hydrogen bonding, which favors them to penetrate into the inner part of the PEO shell of the copolymer micelles, being accompanied by the intrusion of solvent water,⁴⁸ thus producing a larger hydrated corona and a concurrently reduced hydrophobic volume, as illustrated in Figure 7. In contrast, the small-molecule carboxylic acids cause a lesser degree of hydration in the PEO shell and a larger hydrophobic volume; consequently the products have relatively larger pore diameters. The decrease of the hydrophobic volume of triblock copolymer micelle in the presence of polar molecules was indirectly revealed in previous work,⁴⁹ where the researchers found that the addition of urea that borne polar amido groups into the aqueous solution of copolymer resulted in the decrease of the aggregation number of copolymer micelle. It could be expected that the copolymer molecules would become loosely aggregated in the micelles with the decrease of the aggregation number,²⁷ which might also facilitate the intrusion of water into the inner part of the PEO block and concomitantly decrease the hydrophobic volume.

3.3. Effect of Low-Temperature Aging on Material Structure. In this work, the synthesis solutions were first aged at a low temperature of 35 °C prior to high-temperature hydrothermal treatment at 100 °C. The influence of the low-temperature aging on the structure of the final products was studied. Figure 8 presents the XRD patterns of the MS_i silicas synthesized at pH 1.6 with low-temperature aging at 35 °C for different time. The material synthesized without low-temperature

Figure 9. (a) Nitrogen sorption isotherms and (b) mesopore size distribution profiles of the MS_i-1.6 synthesized with low-temperature aging at 35 °C for different time.

aging does not show any long-range order. In contrast, the material synthesized with a low-temperature aging for 2 days exhibits the most intensive diffraction peaks, indicating it has the best mesostructural ordering. But excess low-temperature aging time of more than 3 days seems to decrease the ordering as evidenced by the gradual reduction in diffraction intensity.

Figure 9 presents the nitrogen sorption isotherms and pore size distribution profiles of the MS_i silica synthesized at pH 1.6 with low-temperature aging at 35 °C for different time. The isotherm of product synthesized without aging at low temperature features a H2-type hysteresis loop, which is indicative of a broad pore size distribution.^{50,51} In contrast, the other materials synthesized with enough low-temperature aging time have uniform cylindrical mesopores as reflected by the H1-type hysteresis loop on their sorption isotherms and narrow pore size distributions.^{50,51}

This indicates that the induction period at a relatively lower temperature (35 °C) is necessary to form highly ordered mesostructure. If the initial limpid synthesis solutions were directly subjected to high-temperature aging at 100 °C, the intensified thermal motions of both silica species and copolymer molecules would break seriously the weak hydrogen bonding as well as electrostatic assembly interactions,^{28,50,51} resulting in the formation of disordered mesoporous materials. On the other hand, it should be mentioned that well-ordered mesostructure was not always fully acquired during the induction period of the synthesis.⁵² The development of periodic mesostructure is fulfilled by continued reorganization of the aggregates in further hydrothermal aging.^{40–43,53,54} Because the condensation reaction is relatively slower at low temperature,⁵² the initial precipitates formed during the induction period are expected to be flexible complexes with low condensation degree.^{52,55} It is known that the high temperature could drive the surfactant aggregates to form more ordered superstructures.^{56,57} As a result, during the subsequent aging at elevated temperature of 100 °C, the flexible silica solids are capable of undergoing continuous reorganization along with the phase transformation of the copolymer micelles, and further polymerize to concrete solids with hexagonal structure.^{55,58,59} In this work, 2 days of low-temperature aging is optimal for the formation of the best ordered structure, but more than 3 days of low-temperature aging time causes a negative effect on the quality of the product. Excess aging at 35 °C possibly results in a somewhat densified rigid structure due to excessive cross-linking, which inhibits the further structural transformation at the high-temperature aging period.

Figure 10. Ignition curves of benzene over palladium catalysts supported on mesoporous silicas.

3.4. Effect of Material Morphology on Catalytic Activity. Because of the high surface areas and large pore sizes, SBA-15 is expected to be a desirable catalyst support. In this work, the ordered silica with variable particle sizes controlled by the added amount of tartaric acid were used as support of palladium catalysts, and their catalytic performances were evaluated in the catalytic oxidation of benzene, one of the volatile organic pollutants of most concern from industrial emissions. The ignition curves of benzene over the catalysts are shown in Figure 10. The catalysts are capable of catalyzing the complete oxidation of benzene at a temperature of less than 250 °C, but it was ever revealed that the conversion of benzene was negligible even when the temperature was raised to 500 °C without catalysts.⁶⁰ Furthermore, MSI-2.8 composed of small particles seems superior to MSI-1.6 with large particle size in the catalytic oxidation of benzene.

The catalytic removal of benzene is a complicated heterogeneous reaction, and comprehensive investigations are required to reveal the exact factors that govern the catalysis activity. Here we just tentatively explain the difference in the activity of the mesoporous catalysts in terms of the morphological properties of silica supports. For mesoporous molecular sieves based catalysts, their particle sizes might significantly affect the catalytic behaviors.^{34–36} For the preparation of supported catalyst by an impregnation method, a small particle size of the mesoporous silica support can afford good dispersion of active metals into the inner porosity, leading to high surface areas of active phases.⁶¹ Furthermore, a small particle favors the easy diffusion of reactants to the inner active sites. Thus, the palladium catalyst supported on MSI-2.8 composed of the smallest particles exhibits better efficiency in the oxidation of benzene. However, studies on confinement effect are still required for clearly understanding the acting mechanism of the catalyst.⁶² It is very interesting that the morphology and pore structure can be tailored for specific applications by simply varying the synthesis acidities and acid sources.

4. Conclusions

Polyhydroxy carboxylic acids such as tartaric acid and citric acid have profound promoting effect on the synthesis of homogeneous ordered SBA-15 under moderate acidities at pH ≤ 2.8 , but small-molecule organic acids such as acetic acid and oxalic acid do not. The ordered domains grow with increasing concentration of the polyhydroxy carboxylic acids. The several polar groups on the molecules of the polyhydroxy acids might promote the assembly forces by bridging the silica species and copolymer micelles via hydrogen bonding. The synthesis of SBA-15 with the use of polyhydroxy acids to adjust acidity can

afford a safe, environment-friendly, and large-scale preparation method under the mild conditions. Furthermore, it is interesting that particle sizes of the mesoporous silicas can be easily tailored by adjusting the concentration of polyhydroxy carboxylic acids, which is desirable for catalysis or other applications due to the controllable mass transfer.

Acknowledgment

Financial support from the National Basic Research Program of China (Grant 2004CB719500), the National High Technology Research and Development Program of China (Grant 2006AA06A310), and the National Science Fund of China (Grants 20807050 and 20725723) is gratefully acknowledged. J.J.L. appreciates the scientific research start fund from the Chinese Academy of Sciences.

Supporting Information Available: Nitrogen sorption isotherms of MSI and MS_{ox} silica synthesized under various acidities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review January 20, 2009
 Revised manuscript received May 21, 2009
 Accepted May 24, 2009