A New Nonsurfactant Pathway to Mesoporous Silica Materials Based on Tartaric Acid in Conjunction with Metallic Chloride

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Mesoporous silica materials have been prepared via the sol−gel reactions of tetraethyl orthosilicate through a new nonsurfactant pathway based on organic compound tartaric acid in conjunction with metallic chloride such as magnesium chloride or aluminum chloride as templates or pore-forming agents. The mesoporous silica materials were obtained upon the removal of the pore-forming agents by extraction with ethanol from the sol−gel composites. The effect of the metallic chloride amount in the synthesis on the physicochemical properties of the porous silica materials is investigated. The results from nitrogen sorption isotherms, transmission electron microscopy, and powder X-ray diffraction indicate that the pore volumes and pore diameters of the extracted samples generally rise with the increase of the amount of the metallic chloride. The results also show that magnesium chloride and aluminum chloride are more effective than sodium chloride in the pore-forming for the preparation of mesoporous materials. The analyses from X-ray fluorescence and infrared spectrometry indicate that the magnesium and aluminum atoms coordinate with the carboxylate anions of tartaric acid and consequently the coordination complexes act as the pore-forming agents.

Introduction

Since the discovery of novel mesoporous molecular sieve M41S was reported in 1992,[1,2] the synthesis of mesoporous materials continues to draw a great deal of attention due to the potential application of these materials in catalysis,[3−5] separation technology,[6−8] polymerization,[9] and nanoelectronics.[10] Many synthetic strategies[11−13] have been developed to synthesize diverse mesoporous materials, which include mesoporous hybrid materials.[14,15] In most of the studies, ionic[14−24] and neutral[25−28] surfactants have been employed as templates, which direct the mesophase formation on the basis of the electrostatic and hydrogen bonding interactions, respectively. In the surfactant templating route to mesoporous materials, pore diameter could be controlled by changing the alkyl chain length of the surfactant[2,20,25] by adding auxiliary hydrocarbons,[2,27] or by adjusting the initial pH of the synthesis mixture.[23] It is noteworthy that the pore size of hexagonal mesoporous materials could be expanded to ~30 nm by adding 1,3,5-trimethylbenzene as an organic swelling agent.[27] A versatile, low-cost, and nontoxic nonsurfactant route to mesoporous materials via the sol−gel

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Corma, A.; Navarro, M. T.; Perez Pariente, J. *Chem. Commun.* **1994**, 147.

(4) Maschmeyer, T.; Rey, F.; Sankar, G.; Thomas, J. M. *Nature* **1995**, *378*, 159.

(5) Rao, Y. V. S.; De Vos, D. E.; Bein, T.; Jacobs, P. A.*Chem. Commun.* **1997**, 355.

(6) Raimondo, M.; Perez, G.; Sinibaldi, M.; De Stefanis, A.; Tomlinson, A. A. G.*Chem. Commun.* **1997**, 1343.

(7) Dai, S.; Burleigh, M. C.; Shin, Y.; Morrow, C. C.; Barnes, C. E.; Xue, Z. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1235.

(8) Hata, H.; Saeki, S.; Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Mater.* **1999**, *11*, 1110.

(9) Kageyama, K.; Ogino, S.; Aida, T.; Tatsumi, T. *Macromolecules* **1998**, *31*, 4069.

(10) Peng, Z. Y.; Shi, Z.; Liu, M. L. *Chem. Commun.* **2000**, 2125.

(11) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.

(12) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 56.

(13) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403.

(14) Hall, S. R.; Fowler, C. E.; Lebeau, B.; Mann, S. *Chem. Commun.* **1999**, 201.

(15) Lim, M. H.; Blanford, C. F.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090.

(16) Huo, Q.; Margolese, D. I.; Clesia, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(17) Luan, Z.; Cheng, C. F.; Zhou, W.; Klinowski, J.*J. Phys. Chem.* **1995**, *99*, 1018.

(18) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.

(19) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692.

(20) Namba, S.; Mochizuki, A.; Kito, M. *Chem. Lett.* **1998**, 569.

(21) Mokaya, R.; Zhou, W.; Jones, W. *Chem. Commun.* **1999**, 51.

(22) Das, D.; Tsai, C. M.; Cheng, S. *Chem. Commun.* **1999**, 473.

(23) Wang, A.; Kabe, T. *Chem. Commun.* **1999**, 2067.

(24) Mokaya, R. *J. Phys. Chem. B* **2000**, *104*, 8279.

(25) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(26) Attard, G. S.; Glyde, J. C.; Goltner, C. G. *Nature* **1995**, *378*, 366.

(27) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(28) Boissiere, C.; Larbot, A.; Van der Lee, A.; Kooyman, P. J.; Prouzet, E. *Chem. Mater.* **2000**, *12*, 2902.

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process has recently been developped,[29−33] wherein nonsurfactant organic compounds were employed as templates (or pore-forming agent). Mesoporous materials with large specific surface area and pore volume could be obtained upon removal of the template by solvent extraction. The pore volume and pore diameter could be well tuned by varying the template content in the sol−gel silica composites. However, the control ability of pore parameters by template content is limited, in that the template molecules will crystallize from the gel at high template content.[29,33] This nonsurfactant sol−gel pathway is advantageous to synthesize polymer-modified mesoporous hybrid silicas.[34−36] The pore design mechanism is similar to that of Vycor glass,[37,38] which is generally produced by spinodal decomposition of a borosilicate glass followed by leaching of the boron-rich phase to leave a SiO_2 skeleton.[37] However, for Vycor, a fused porous glass, no organic phases are formed.

In 1999, Pinnavaia et al.[39] reported a new nonionic surfactant pathway to mesoporous molecular sieve silicas with long-range framework order, wherein nonionic surfactant such as poly(oxyethylene), $R(EO)_nH$, and chloride salts of Co^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} were used as structure-directing agents. Tartaric acid (TA) has been used as pore-forming agent to prepare monolithic mesoporous silicas[31] in our laboratary. Carboxylate anions were reported to have the tendency to coordinate with aluminum atoms[40] through two possible coordination modes as monodentate or bridging bidentate modes. Inspired by all the above, herein, we report the preparation of mesoporous silica materials using TA in conjunction with magnesium chloride ($MgCl_2$) or aluminum chloride ($AlCl_3$) as pore-forming agents. It was found that the pore volumes and pore diameters of the samples increased with increasing metallic chloride.

Experimental Section

Synthesis of Mesoporous Materials. The synthetic procedure was similar to that of our previous literatures;[29,31] tetraethyl orthosilicate (TEOS, Acros Organics, 98%) was prehydrolyzed with deionized H_2O in ethanol using HCl as catalyst (at TEOS:HCl:H_2O:EtOH molar ratios of 1:0.01:4:3) at about 343 K for 5−6 h. Upon cooling of the sample to room temperature, the prehydrolyzed solution (e.g., 10.5 mL for TA25−Mg-2 or TA25−Al-2; the same below) was added to a designed amount of aqueous solution (e.g., 1.0 mL of 0.45 g mL^{-1}) of TA compound under stirring for 5 min, followed by adding a designed amount of aqueous solution (e.g., 6.0 mL of 1.0 mol L^{-1}) of $MgCl_2$ or $AlCl_3$. Then the beakers were sealed with a cellophane film containing several pinholes to allow the slow evaporation of the solvent and reaction byproducts. The transparent and monolithic template-containing silica disks were obtained after the gel formed and dried within about 2 months at room temperature. Then the silica disks were ground into fine powders, followed by Soxhlet extraction with 95 wt % ethanol for 3 days and vacuum-drying at 353K to afford the porous silica materials.

Characterization and Instrumentation. The surface area, pore volume, and pore diameter of the silica samples after solvent extraction were measured on a Micromeritics ASAP2010 analyzer. Before measurement, the samples were degassed at 473 K and below 1.33 Pa for more than 4 h. The data were processed using the software from Micromeritcs Corp. The powder X-ray diffraction (XRD) pattern was recorded on a Rigaku DMAX2400 instrument using Cu Kα radiation ($\lambda = 0.15418$ nm, 40 kV, 100 mA) at scanning rates of 1° min^{-1} in the 2θ range of 0.6−10° and of 8° min^{-1} in the ranges of 10−40 and 5−70°. Morphologies of the porous samples were examined on a JEOL JEM-200CX transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV. The samples for TEM were prepared by dipping an ethanol suspension of finely ground sample powders onto a Cu grid coated with a holey C film. The magnesium and aluminum contents of the samples before and after extraction with ethanol were acquired by X-ray fluorescence (XRF) analysis on a Shimadzu XRF-1700 sequential XRF spectrometer, operating at 40 kV and 80 mA. The FT-IR spectra of the samples were measured in the form of KBr powder-pressed pellets on a Bruker Vector 22 FT-IR spectrometer.

Results and Discussion

Mesoporous silica materials have been prepared via the sol−gel reactions of TEOS in the presence of TA in conjunction with different amount of $MgCl_2$ or $AlCl_3$. The pore parameters of the porous silica materials upon the removal of pore-forming agents are summarized in Table 1. As shown from Table 1, the pore volumes and the average pore diameters of the silicas after extraction with solvent rise continuously with the increase of the metallic chloride amount in the as-synthesized gels, under the fixed amount of TA compound. It provides an effective way to increase the pore diameter of the porous silica instead of increasing the content of the organic compounds.[29−33] The control sample (TA25−Mg-0) prepared with 0.45 g of TA alone exhibits a small pore volume of 0.382 cm^3 g^{-1}. The t-plot analysis indicates the dominant microporosity. However, the contribution from micropores becomes more and more negligible with the metallic chloride amount increased. The mesoporous samples with large Brunauer−Emmett−Teller (BET) specific surface areas (e.g., 1000 m^2 g^{-1}) and pore volumes (e.g., 1.7 cm^3 g^{-1}) have been prepared using TA in conjunction with high amounts of $MgCl_2$ and $AlCl_3$, respectively. From the results, it can be seen that the surface areas decrease for the samples prepared with high metallic chloride amount (e.g., from TA25−Mg-1 to TA25−Mg-2). This is expected because there are two competing factors that affect the total surface area in opposite directions. At a fixed pore size, higher pore volume leads to greater surface area. On the other hand, at a fixed pore volume, an increase in pore size results in a decrease in the surface area. Therefore when the effect from the pore size increase is comparable or greater to that from the pore volume increase, the total surface area levels off or decreases. When the same amount of metallic chloride is used (e.g.,

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(29) Wei, Y.; Jin, D.; Ding, T.; Shih, W. H.; Liu, X.; Cheng, S. Z. D.; Fu, Q. *Adv. Mater.* **1998**, *3*, 313.

(30) Wei, Y.; Xu, J.; Dong, H.; Dong, J. H.; Qiu, K. Y.; Jansen-Varnum, S. A. *Chem. Mater.* **1999**, *11*, 2023.

(31) Pang, J. B.; Qiu, K. Y.; Wei, Y.; Lei, X. J.; Liu, Z. F. *Chem. Commun.* **2000**, 477.

(32) Pang, J. B.; Qiu, K. Y.; Wei, Y. *Chinese J. Chem.* **2000**, *18*, 693.

(33) Pang, J. B.; Qiu, K. Y.; Xu, J.; Wei, Y.; Chen, J. *J. Inorg. Organomet. Polym.* **2000**, *10*, 39.

(34) Wei, Y.; Feng, Q. W.; Xu, J. G.; Dong, H.; Qiu, K. Y.; Jansen, S. A.; Yin, R.; Ong, K. K. *Adv. Mater.* **2000**, *12*, 1448.

(35) Pang, J. B.; Qiu, K. Y.; Wei, Y. *Chin. J. Polym. Sci.* **2000**, *18*, 469.

(36) Feng, Q. W.; Xu, J. G.; Dong, H.; Li, S. X.; Wei, Y. *J. Mater. Chem.* **2000**, *10*, 2490.

(37) Levitz, P.; Ehret, G.; Sinha, S. K.; Drake, J. M. *J. Chem. Phys.* **1991**, *95*, 6151.

(38) Nakanishi, K.; Soga, N. *J. Am. Ceram. Soc.* **1991**, *74*, 2518.

(39) Zhang, W.; Glomski, B.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Commun.* **1999**, 1803.

(40) Landry, C. C.; Pappe, N.; Mason, M. R.; Apblett, A. W.; Tyler, A. N.; MacInnes, A. N.; Barron, A. R. *J. Mater. Chem.* **1995**, *5*, 331.

Table 1. Feed Composition of the Sol−Gel Silica Composites and the Physicochemical Properties of the Porous Sol−Gel Silicas Prepared Based on Tartaric Acid (TA) in Conjunction with $MgCl_2$ or $AlCl_3$ after Extraction with Ethanol

sample code	SiO_2 weight[a] (g)	TA weight (g)	metal/TA (mol/mol)	specific surf area (m^2/g)	tot. pore vol[b] (cm^3/g)	av pore diameter by BET[c] (nm)	av pore diameter by BJH[d] (nm)	micropore[e] surf area (m^2/g)	micropore[e] pore vol (cm^3/g)
TA25−Mg-0	1.35	0.45	0	786	0.382	1.9	2.7	527	0.241
TA25−Mg-0.1	1.35	0.45	0.1	910	0.455	2.0	2.7	456	0.207
TA25−Mg-0.25	1.35	0.45	0.25	1052	0.543	2.1	2.6	327	0.139
TA25−Mg-0.5	1.35	0.45	0.5	1139	0.661	2.3	2.8	138	0.049
TA25−Mg-1	1.35	0.45	1	1305	0.919	2.8	3.1		
TA25−Mg-2	1.35	0.45	2	1069	1.719	6.4	5.7		
TA40−Mg-0	1.35	0.9	0	1243	0.749	2.4	2.8	91	0.024
TA40−Mg-0.25	1.35	0.9	0.25	1304	0.942	2.9	3.1		
TA40−Mg-0.5	1.35	0.9	0.5	1059	1.040	3.9	3.9		
TA40−Mg-1	1.35	0.9	1	1057	1.953	7.4	6.7	17	
TA25−Al-0	1.35	0.45	0	786	0.382	1.9	2.7	527	0.241
TA25−Al-0.25	1.35	0.45	0.25	1161	0.620	2.1	2.7	228	0.089
TA25−Al-1	1.35	0.45	1	1290	1.034	3.2	3.5		
TA25−Al-2	1.35	0.45	2	962	1.680	7.0	6.1		
TA50−Al-0	1.35	1.35	0	910	1.087	4.8	4.6	37	0.006
TA50−Al-0.06	1.35	1.35	0.06	685	1.014	5.9	5.4	31	0.006
TA50−Al-0.25	1.35	1.35	0.25	664	1.284	7.7	6.8	25	0.003

[a] As calculated from the feed composition under the assumption that TEOS is completely transformed into SiO_2. [b] Single point total pore volume at the relative pressure of ca. 0.995. [c] Average pore diameter calculated from $4V/A$, where V is the total pore volume and A is the BET surface area, under the assumption that the materials contain regularly cylindrical channel or pores, using the software from Micromeritics Corp. [d] Average pore diameter calculated by BJH analysis from the adsorption branches of the isotherms, using the software from Micromeritics Corp. [e] The surface area and pore volume of micropores were obtained by t-plot analysis using the Harkins−Jura equation.

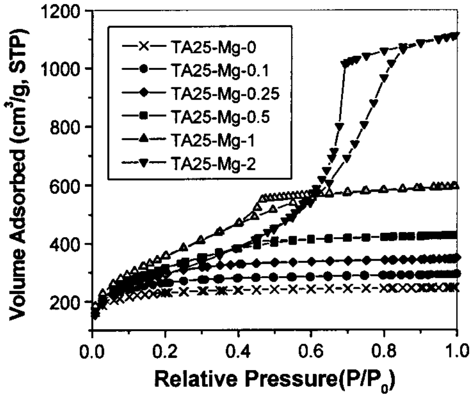

Figure 1. N_2 adsorption−desorption isotherms for the extracted silicas prepared with 0.45 g of TA in conjunction with different amounts of $MgCl_2$ under the Mg/TA molar ratios of 0−2.

TA25−Mg-0.5 vs TA40−Mg-0.25), with more TA, the larger pore volume and pore diameter of the extracted silicas are reached. It is consistent with the reported results,[29−33] where only organic compounds were used as pore-forming agents. It should be noted that the control sample prepared with $MgCl_2$ alone, corresponding to the sample TA25−Mg-0.5, exhibits a small pore volume of 0.330 cm^3 g^{-1} and an average pore diameter of 1.9 nm (from BET analysis), which are smaller than that of TA25−Mg-0.5. It indicates that TA molecules in conjunction with $MgCl_2$ act as the pore-forming agents.

The N_2 adsorption−desorption isotherms were determined at various relative pressures (P/P_0) on the extracted silica samples. Figure 1 shows the sorption isotherms for the silicas prepared with fixed 0.45 g of TA and different amounts of $MgCl_2$. The samples prepared with Mg/TA molar ratios less than 0.25 exhibit reversible type I isotherms, indicating the microporosity.[41] When the Mg/TA molar ratios are higher than 0.5, the samples exhibit type IV isothermes with type H2 hysteresis loops according to IUPAC,[41] which are always given by many mesoporous industrial adsorbents.[41] It is obvious that the final volumes adsorbed generally increase along with the increase of $MgCl_2$ amount, as well as the hysteresis loops moving to higher P/P_0. Similar results were observed for the samples prepared with $AlCl_3$.

Other evidence was obtained by TEM and XRD analyses. The TEM images for the samples prepared with high metallic chloride amounts generally show numerous mesopores as the previously reported materials.[32,33] Figure 2 shows the TEM images of the samples TA25−Mg-2 (Figure 2a), TA25−Mg-1 (Figure 2b), and TA25−Mg-0 (Figure 2c), respectively. It can be obviously seen that the pore diameters rise with increase of the $MgCl_2$ amount. From the image analysis, the pore diameters for sample TA25−Mg-2 and TA25−Mg-1 are about 6 and 3 nm, respectively, which is comparable to the values by N_2 sorption analysis. Numerous wormlike channels or pores with disordered arrangements are clearly revealed in the images (Figure 2a,b). However, the mesoporosity is not clearly shown in the TEM image for the sample TA25−Mg-0 (Figure 2c) with the same magnification times. The samples prepared with $AlCl_3$ also show similar results. Since the pore design of silica could be based on phase separation,[30,33,38] the comparison of the TEM images for the samples indicates that the metallic salts promote the phase separation between silica and tartaric acid in the composites.

Figure 3 exemplifies the powder XRD patterns for the samples prepared with 0.45 g of TA and different amounts of $MgCl_2$. It can be seen that the intensity of the diffraction peaks in the small-angle range rise with the increase of $MgCl_2$ amount, indicating the improved mesoporosity by adding $MgCl_2$. The XRD pattern for the control sample sol−gel silica prepared with neither TA

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(41) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.

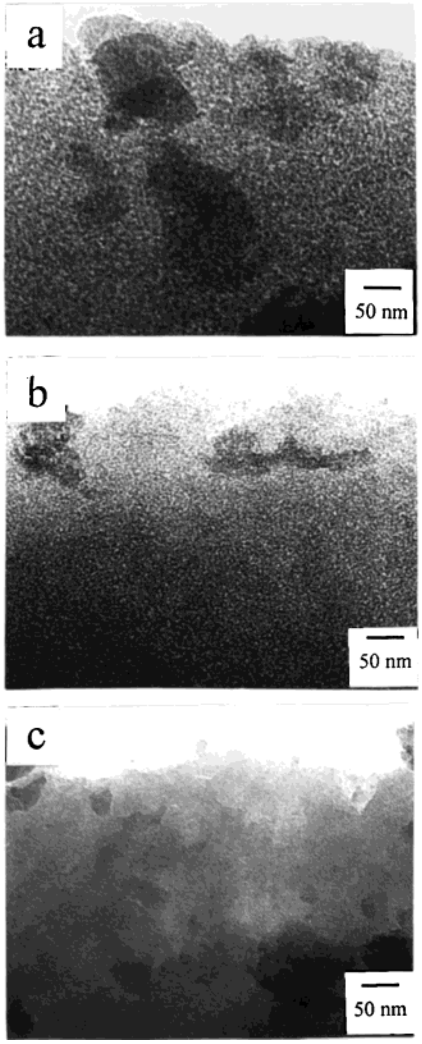

Figure 2. TEM images for the samples TA25−Mg-2(a), TA25−Mg-1(b), and TA25−Mg-0 (c), respectively.

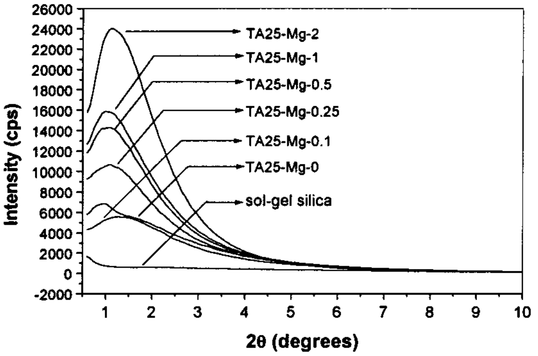

Figure 3. Powder XRD patterns for the extracted silicas prepared with 0.45 g of TA in conjunction with different amounts of $MgCl_2$ under the Mg/TA molar ratios of 0−2 and the XRD pattern for the control sample sol−gel silica.

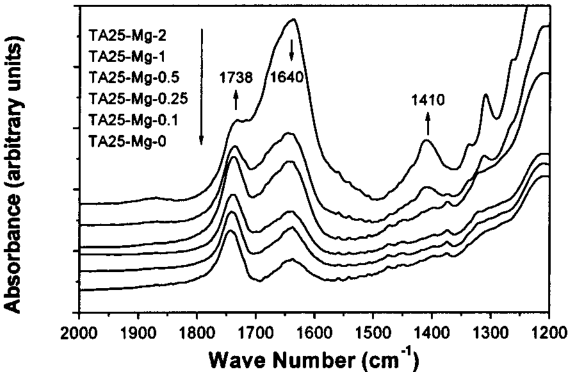

Figure 4. FT-IR spectra for the sol−gel silica composites prepared with 0.45 g of TA in conjunction with different amounts of $MgCl_2$ under the Mg/TA molar ratios of 0−2 before extraction with solvent.

nor $MgCl_2$ exhibits no diffraction peak in the small-angle range, while the sample TA25−Mg-0 prepared with 0.45 g of TA alone only shows a weak and very broad diffraction peak at the 2θ value of ca. 1−2°, indicating the poor porosity. As the $MgCl_2$ content increases, the intensity of the diffraction peaks increases. Some reported mesoporous materials[25] by a nonionic surfactant templating route had analogous XRD patterns.

To clarify the reason why the pore parameters change along with the metallic chloride amount, the metal magnesium and aluminum contents of the silica samples before and after extraction with ethanol were determined by XRF analysis. From the XRF measurement results listed in Table 2, we can see that the measured metal contents in the as-synthesized samples before extraction with ethanol were similar to the designed contents. However, only small amounts or even traces of metals were retained in the extracted materials. We believe that the magnesium and aluminum atoms in the sol must have coordinated with the carboxylate anion of TA molecules, which promotes the aggregation of TA molecules and increases the size of aggregates. So the pore volume and pore diameter rise with the increase of the metallic chloride amount used in the synthetic procedure. This indicates that TA molecules in conjunction with the metallic chloride actually act as the pore-forming agents.

The FT-IR spectra of the silica composites prepared with fixed 0.45 g of TA and different amounts of $MgCl_2$ before extraction with ethanol are given in Figure 4. The band at 1738 cm^{-1} is assigned to the C=O stretching vibration absorption for the carboxylate group of TA molecules in the TA-containing silica composites. It is noted that the absorption band at 1640 cm^{-1} for TA25−Mg-0 is attributable to the O−H vibration of H_2O molecules[42] adsorbed into the samples and KBr substrate. When $MgCl_2$ is introduced, the bands at 1640

Table 2. Magnesium and Aluminum Composition (g) in the Sol−Gel Silica Materials before and after Extraction with Ethanol[a]

	sample code				
	TA25−Mg-0.5	TA25−Mg-1	TA25−Mg-2	TA25−Al-1	TA25−Al-2
as-synthesized[b]	0.0555 (0.0604)	0.1047 (0.1208)	0.2038 (0.2416)	0.1368 (0.1529)	0.2562 (0.3058)
after extractn	0.0005	0.0013	0.0011	0.0103	0.0128

[a] The XRF-determined magnesium and aluminum contents are given in terms of oxide. [b] The data in the parentheses are the designed values calculated from the feed composition.

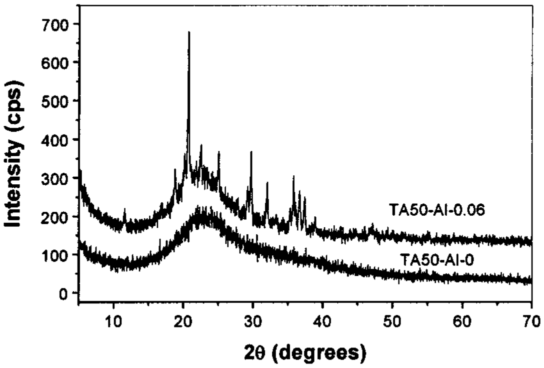

Figure 5. Powder XRD patterns for the composite TA50−Al-0 and TA50−Al-0.06 after standing for 8 months more at room temperature.

and 1410 cm^{-1} increasing in intensity with the $MgCl_2$ content are generally taken as a proof of the coordination of the carboxylate group with magnesium atoms.[40,42] As known, 1640 and 1410 cm^{-1} are assigned to the asymmetric and symmetric stretching frequency of the carboxylate anions of carboxylic acid salts.[42] Similar results were obtained for the sol−gel silica composites prepared by TA in conjunction with $AlCl_3$. So we confirm that the magnesium and aluminum atoms coordinate with the carboxylate group of TA molecules, even form metal carboxylate compounds, and act as the pore-forming agents together. Further studies are in progress in our laboratary to examine the framework cross-linking and some other properties of these materials in comparison to those prepared without metallic chloride. The primary results show that the materials prepared with aluminum chloride are more hydrothermally stable than that prepared without metallic salts.

The structural change of the sol−gel composite without extraction has been investigated by XRD. The results show that no characteristic diffraction peaks were recorded for the composites prepared either with or without metallic salts just before solvent extraction. However, after the samples were standing for more time (e.g., 8 months) at room temperature, the difference of the XRD patterns between the presence and absence of metallic salts were observed as shown in Figure 5. It can be seen that no distinct diffraction peaks were recorded for sample TA50−Al-0, except for the amorphous halo at about 23°.[29,32,33] However, the diffraction peaks corresponding to tartaric acid crystals were shown for the sample TA50−Al-0.06. It supports that the metallic salts could promote the phase separation between silica and tartaric acid in the composites.

The incorporation of sodium chloride (NaCl) into the sol−gel reactions of TEOS in the presence of TA has also been investigated. The results show that the pore volume and pore diameter for the silicas are less than that for those prepared by TA in conjunction with $MgCl_2$ or $AlCl_3$ under the same molar ratios of metallic chloride to TA. For example, the extracted silica from the composite prepared with 1.35 g of SiO_2, 0.45 g of TA, and a NaCl/TA molar ratio of 1 exhibits a pore volume of 0.544 cm^3 g^{-1} and a pore diameter of 2.7 nm (from BJH analysis), which are less than those for the samples prepared by TA in conjunction with $MgCl_2$ or $AlCl_3$ under the corresponding molar ratio of $MgCl_2$ or $AlCl_3$ to TA (see Table 1). Figure 6 shows the N_2 sorption isotherms for the samples prepared by TA in conjunction with $AlCl_3$, $MgCl_2$, or NaCl under the metallic chloride/TA molar ratios of 1. It can be found that the sample TA25−Na-1 exhibits a nearly reversible type I isotherm; however, the isotherms for TA25−Al-1 and TA25−Mg-1 are of type IV. The final volume adsorbed indicates the much lower pore volume of TA25−Na-1 than TA25−Mg-1 and TA25−Al-1. The results from XRF and FT-IR analyses show that sodium atom also coordinates with the carboxylate group of TA molecules to form a sodium carboxylate salt. However, the univalence nature of the sodium might be attributable to the results, since a larger number of tartaric acid molecules can interact with Mg^{2+} or Al^{3+} than that with Na^+.

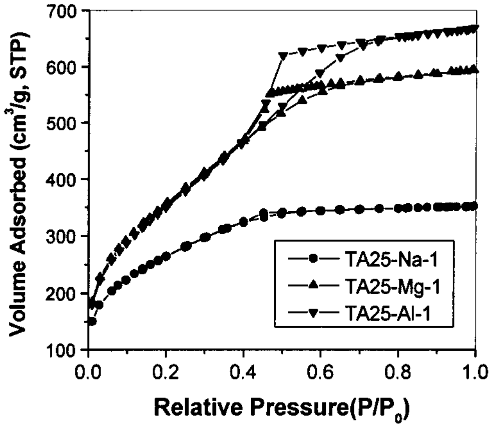

Figure 6. N_2 adsorption−desorption isotherms for the extracted silicas TA25−Na-1, TA25−Mg-1, and TA25−Al-1, respectively.

Conclusions

A new nonsurfactant pathway based on TA in conjunction with metallic chloride $MgCl_2$, $AlCl_3$ has been employed to prepare mesoporous silicas. The monolithic and transparent silica composites were first prepared through the sol−gel reactions of TEOS in the presence of different amounts of TA in conjunction with $MgCl_2$ or $AlCl_3$. After the composites were extracted with ethanol, porous silicas were obtained. The analyses results from N_2 sorption isotherms, TEM, and XRD show that the pore volumes and pore diameters of the extracted samples increase with an increase of the amount of $MgCl_2$ or $AlCl_3$ used in the synthesis. From the analyses of XRF and FT-IR, it can be shown that the magnesium and aluminum atoms coordinate with the carboxylate anions of TA in the silica composite; therefore, the coordination complexes act as the pore-forming agents.

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(42) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: New York, 1980; p 65.