Letter

A direct surface silyl modification of acid-synthesized mesoporous silica

Hong-Ping Lin,[a] Lu-Yi Yang,[ab] Chung-Yuan Mou,[c] Shang-Bin Liu[a] and Huang-Kuei Lee[b]

[a] *Institute of Atomic and Molecular Sciences Academia Sinica, P.O. Box 23-166, Taipei, Taiwan 106. E-mail: hplin@gcn.net.tw*
[b] *Institute of Materials Science and Manufacturing, Chinese Culture University, Taipei, Taiwan 111*
[c] *Department of Chemistry, National Taiwan University, Taipei, Taiwan 106*

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A surface silyl modification and surfactant removal of acid-synthesized mesoporous silica process in a single step is investigated; the surfactant–silyl exchange process allows a large amount of surface attachments of silane.

In many applications of mesoporous materials[1] modification of their surface silanol groups is advantageous. Such modifications include heterogenization of molecular catalysts, improvement of structural stability, and modification of the surface adsorption properties. Modified mesoporous materials are usually prepared by grafting silyls to calcined mesoporous materials, co-condensation with the silica/surfactant sources in sol–gel preparation, and reflux of the as-synthesized mesoporous materials in trialkylalkoxysilanes.[2–9] These known methods respectively possess some drawbacks, *i.e.* the waste of the expensive quaternary ammonium surfactants or the sparse grafting of silanol groups during co-condensation.

Mesoporous silica can be synthesized by either the alkaline route[1] or the acidic route.[3] In the alkaline route, surfactant and silicates organize by the strong S^+I^- electrostatic interaction. The tight binding of the surfactant molecule makes its extraction difficult and calcination is the usual method of surfactant removal. Surface modification is then performed on the surface of hollow channels. On the other hand, in the acid route the surfactant/silicate interaction is weaker, the weak hydrogen interactions between the silica wall and the surfactant ($S^+X^-I^0$, S^0I^0) would allow[10,11] facile extraction of surfactant by polar solvents under mild conditions and then the surface silanol groups would be expected to be accessible for direct modification. Furthermore, one expects more surface silanol groups to be available for modification in acid-made silica due to the less complete silica condensation.

In this communication we report a direct procedure to modify efficiently the surface silanols of the acid-synthesized mesoporous silica by using various silane sources in ethanol solution under moderate conditions. The extraction of surfactant and surface modification are accomplished simultaneously in an exchange process with alkylsilanes and alkoxysilanes replacing surfactant. The coupling of silanes to the surface can be accomplished in a single step and the calcination step is avoided.

Also, the acid route is interesting in offering versatile morphologies. Recent advances in copolymer templating and mesoporous silica films, ropes, and fibers are based on the acid synthesis route.[12,13] We show in this paper, that a new mild surface modification process preserves the morphology. This is significant in film applications where in some situations a hydrophobic modification is desired.

The ^{29}Si MAS NMR spectra (recorded with a 400 s pulse delay) of the mesoporous materials obtained from C_{18}TMAB–HNO_3–TEOS–H_2O† mixtures before and after silyl modification are displayed in Fig. 1A. The unmodified (UM) sample possesses a high Q^3 (HO–Si(OSi)$_3$) peak at about δ −100 (Fig. 1A (a)), which indicates a reasonable quantity of surface silanol groups in the acid-made mesoporous material. For the silylated materials, the Q^3 peak intensity apparently decreases (Fig. 1A (b)–(d)) and other high-intensity NMR peaks appear at chemical shifts δ −10, −56 and −65, which can be assigned to $Me_3Si(OSi)$, A–Si(OH)(OSi)$_2$ [T^2]

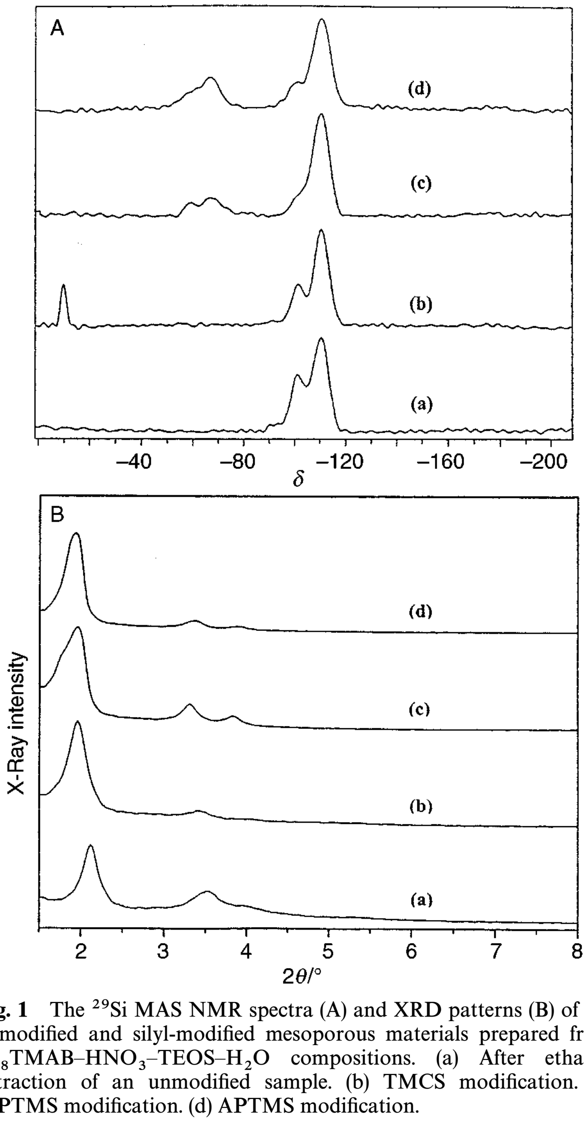

Fig. 1 The ^{29}Si MAS NMR spectra (A) and XRD patterns (B) of the unmodified and silyl-modified mesoporous materials prepared from C_{18}TMAB–HNO_3–TEOS–H_2O compositions. (a) After ethanol extraction of an unmodified sample. (b) TMCS modification. (c) MPTMS modification. (d) APTMS modification.

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and A–Si(OSi)$_3$ [T^3] (A = (CH$_2$)$_3$SH or (CH$_2$)$_3$NH$_2$), respectively.[14] This shows that silanes were successfully grafted onto the mesoporous silica channels.

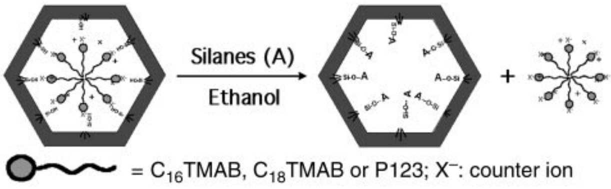
The powder X-ray diffraction patterns for all of the samples in Fig. 1A exhibited 3 XRD peaks and d_{100} values of about 4.50 nm (Fig. 1B). The exhibition of higher order diffraction peaks (110 and 200) suggests well-ordered hexagonal structures remain intact upon silyl modification.

This procedure is also suitable for modification of mesoporous materials prepared from other cationic (C$_{16}$TMAB) and neutral surfactants (P123). The physical properties of all the grafted materials mentioned above are listed in Table 1. They show the large BET surface areas and good capillary condensation characteristics of well-ordered mesoporous materials. The surface area and pore size of the mesoporous materials decrease as a result of silylation on the surface of the nanochannels. The ratio of BET surface area of the modified sample to that of the unmodified sample is roughly equal to the corresponding ratio of the pore sizes. This indicates that the shrinkage of the pore upon surface modification largely accounts for the decrease in surface area. By calculating the difference between the pore size before and after silane modification, the shrinkage of pore size upon attaching TMCS is about 0.5 nm and about 1.0 nm for MPTMS and APTMS respectively. This shows that only a monolayer of silane grafts onto the silica wall of the nanochannels rather than multilayer formation.[15]

After ethanol extraction, the unmodified as-synthesized mesoporous samples still contain some carbon. Their carbon content is about 8% (Table 1). This reveals that the surfactants cannot be completely extracted from the nanochannels of the mesoporous materials. During the silyl grafting, the weak hydrogen bonding interactions between the surfactant and silica wall are replaced by a strong chemical bond formed between the silica wall and the silyl compounds. One could thus suppose that the template surfactants can be completely extracted from the mesoporous channels after the silyl modification procedure. This was confirmed by the near absence of elemental nitrogen content (<0.05 wt%) in TMCS and MPTMS modified samples, and the disappearance of the C–H stretching vibration band at 2933 and 2855 cm^{-1} of the surfactant in all silylated mesoporous silica. The high carbon content of the silylated samples thus comes completely from the grafted organic group. In Table 1, one also finds that the Q^3/Q^4 (Si(OSi)$_4$) ratio of Si-NMR peaks of the modified samples dramatically decreases from 1.2–0.8 in the UM samples to 0.38–0.17. In combination with the high carbon content of the silylated samples (carbon contents >10 wt%, in Table 1), we conclude that the silyl coverage on these mesoporous materials is really high (estimated about 3.50–4.50 mmol silane g^{-1}), comparable to the highest values reported in literature.[5,6,9]

Upon examining the SEM images of the silylated gyroidal sphere and millimeter-sized silica ropes (Fig. 2), it is obvious that these hierarchical morphologies are the same as the corresponding as-synthesized sample. Thus, this efficient silyl-modification process provides moderate conditions for silylation of the mesoporous channel surface without fracturing the brittle hierarchical silica structures. With morphology preservation, the different silyl-modified silica thin films on silicon wafers were successfully made by embedding the silica thin film into various silane/ethanol solutions at 50 °C for 3 h. This is significant for the preparation of hydrophobically modified thin films of mesoporous silica. We note here that Adachi *et al.* recently found that trimethylsilylation treatment helps the elongation of silica nanotubes.[16]

Let us now illustrate the main picture of the proposed silyl-modification process of the mesoporous materials:



There is a simultaneous process of surface silylation and surfactant removal. Upon facile removal of the organic template by ethanol at mild temperatures, the exposed surface silanol

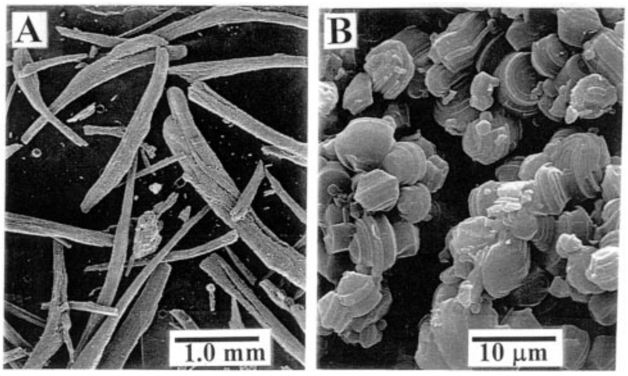


Fig. 2 The SEM micrographs of different hierarchical structure after silyl modification. A Silica ropes. B Gyroidal spheres.

Table 1 The physical properties of the acid-made mesoporous materials synthesized from C$_{18}$TMACl, C$_{16}$TMAB, P123–TEOS–HNO$_3$–H$_2$O compositions with and without silyl modification

Samples[a]	XRD d_{100}/nm	BET surface area/m^2 g^{-1}	Pore size[b]/nm	Q^3/Q^4	Carbon content[c]/wt%
C16-UM	3.63	1102	2.80	0.80	7.60
C16-TMCS	3.89	979	2.32	0.35	11.40
C16-MPTMS	3.92	786	1.83	0.25	12.85
C16-APTMS	3.91	720	1.76	0.20	15.40
C18-UM	4.20	1060	3.26	0.78	7.86
C18-TMCS	4.61	894	2.85	0.32	1185
C18-MPTMS	4.56	798	2.26	0.23	13.01
C18-APTMS	4.55	681	2.15	0.17	14.50
P123-UM	89.5	664	6.02	1.20	6.82
P123-TMCS	90.5	560	5.73	0.38	10.83
P123-MPTMS	91.4	428	5.28	0.30	10.20
P123-APTMS	90.8	383	5.06	0.26	13.62

[a] UM: the as-synthesized sample was embedded in ethanol at 50 °C for 3 h without addition of the silyl sources. [b] The pore size was determined by the BJH method from nitrogen adsorption isotherms. [c] The carbon content data were taken from elemental analysis.

groups were directly modified by silanes. Owing to the high-density of silanol groups on the surface of acid-synthesized mesoporous materials ($^3Q/^4Q \approx 0.8$), the silane modification rate is actually fast (reaction time > 3 h) and efficient (high silanes coverage) under moderate conditions (< 70 °C).[17] In contrast, in the post-calcination modification procedures, the calcination already makes many surface silanol condensations ($^3Q/^4Q \approx 0.3$ in calcined samples) that increase the temperature (> 70 °C) and reaction time (about 12 h) required for silane modification.[2–4] Finally, the easy recovery of the expensive quaternary ammonium surfactant from ethanol solution makes the new method economical in all applications.

In this direct surface modification process, the solvent system is an important factor. When using ethanol, with high surfactant solubility, the silyl functionalization is rapid and effective. In contrast, the process is slow and ineffective in toluene with low surfactant solubility. This direct modification procedure does not work for alkaline-synthesized M41S mesoporous materials due to the strong electrostatic interactions between surfactant cation and silicates (S^+I^-). In Antochshuk and Jaroniec's work[8] of modifying alkaline-made MCM-41, they have to reflux in trialkylsilanes and use a much stronger solvent such as pyridine at a higher temperature and over a longer time in order to achieve the extraction of one surfactant.

We believe that this procedure can also be applied to other mesoporous materials with weak hydrogen-bond interactions between the surfactant and metal oxide wall by using various silane sources. This method, which takes advantage of the acid-route (*i.e.* the easy removal of the surfactant template and flexibly tailored morphologies), would provide a convenient way to manufacture various hierarchical morphologies with different surface properties for potential applications in catalysis, chromatography, and metal-ion extraction.[18]

Experimental

The as-synthesized mesoporous silica *via* acid route, with gyroidal spherical, silica ropes, and thin film morphologies, were prepared according to our previous reports.[11–13] The amphiphiles, silica source and acid used are C_nTMAB ($n = 16$ or 18) or P123 TEOS, and HNO_3 or HCl.[12,13] In a typical preparation, a proper amount of amphiphile templates, TEOS, acid source and water were mixed thoroughly at 32–40 °C for 6–24 h. The solid product was recovered by filtration. The as-synthesized mesoporous samples were obtained from water washing and drying at 100 °C.

Then, the silylation process proceeded as follows: 1.0 g of as-synthesized mesoporous sample and a proper amount of silane sources, such as, TMCS, MPTMS, or APTMS, were added to 20.0 g ethanol. The mixture was then refluxed at 50–70 °C for 1–3 h under stirring or static conditions. The molar composition of silane : EtOH is 1.0 : 51.0. The products were recovered by filtration, washed with large amounts of ethanol and dried at 100 °C or ambient temperature. The unmodified (UM) samples were obtained from the same process as mentioned above, but without the addition of the silane sources.

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Notes and references

† Abbreviations used: C_nTMAB ($n = 16$ or 18) trialkylmethylammonium bromide, UM unmodified, TEOS tetraethyl orthosilicate, P123 $EO_{20}PO_{70}EO_{20}$ (EO = ethylene oxide, PO = propylene oxide), TMCS Me_3SiCl, MPTMS $HS(CH_2)_3Si(OMe)_3$, APTMS $H_2N(CH_2)_3Si(OME)_3$.

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