

Direct Surface Modification of the Uncalcined Acid-Made Mesoporous Silica Materials in a One-Step Procedure

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We investigate a new approach of surface functionalization of mesoporous silica. A direct template displacement method has been developed to graft silane ligands onto the surface of uncalcined mesoporous silica prepared from acidic condition. The organic surfactants can easily be recovered and re-used as the templates of the mesoporous silicas. The high density of surface silanol group in acid-synthesized silica leads to high loading of silanes. The mild reaction condition and short reaction time lead to the preservation of morphology.

1. INTRODUCTION

In many applications of mesoporous silica materials, the functionalization of surface silanol groups to create designed surface active sites is desired. There exist several ways to graft silyl functional groups onto the wall of nanochannel to obtain the desired surface properties. The conventional methods for surface modification of mesoporous silicas are to reflux the calcined mesoporous silica materials in a solution of silanes [1, 2], or co-condense the trialkylalkoxysilanes with the silicate source in the presence of the surfactant templates [3]. These two well-known procedures have their drawbacks. For calcined mesoporous materials, the surfactants are completely removed, which is rather wasteful especially for the expansive quaternary ammonium halides. Moreover, the surface silanol ($\equiv\text{Si-OH}$) density decreases much after siloxane condensation at high temperature. In the co-condensation process, the amount of grafted silanes is restricted in low silanes coverage to maintain the well-ordered mesostructures, and morphologies of the mesoporous materials can not be easily controlled.

Recently, Jaroniec and coworkers developed the template displacement method for surface modification of uncalcined MCM-41 to overcome these drawbacks [4]. The chemical functionality and surfactant displacement occur simultaneously. They use the modification agent silanes as solvent to create the strong driving force for displacement reaction. Or stronger solvent such as pyridine at a higher temperature and longer time in order to achieve the extraction of surfactant [4]. In either way, excessive amount of silanes has to be used. This is due to the fact that strong electrostatic (S^+I^-) interactions are operative in the alkaline-synthesized MCM-41.

Recently, we developed a direct displacement method to modify the surface of uncalcined

acid-made mesoporous silicas using lesser amount of silanes in ethanol solutions at lower temperature [5]. The density of surface silanol group of acid-made mesoporous silica is higher resulting in higher level of grafting. Due to the milder reaction condition, the silyl-modification reactions leads to the preservation of the morphology.

In our approach, the acid-made mesoporous silicas were used because of the weaker hydrogen bonding interactions between surfactants and silica wall ($S^+X^-I^0$). The weaker interaction makes the template-replacing reaction easier than that of strong electrostatic ones (S^+I^-). Therefore, a mild reaction condition (low temperature) and short reaction time (3 h) were enough for silanes modification. In contrast, the alkaline-made mesoporous MCM-41 needed a high temperature, long reaction time (10-24 h) and high silanes concentration for silane modification.

In this paper, we report on the details of our direct method of surface modification of mesoporous silica using several different amphiphiles as template. It will be shown that the template can be easily recovered and used in synthesizing more materials. It is also shown that we obtain higher density of surface modification than previous methods.

2. EXPERIMENTAL

2.1 *Synthesis of the acid-made mesoporous materials:*

The mesoporous silicas obtained via acid route were synthesized according to previous reports [6, 7]. The amphiphilic templates are quaternary ammonium halides C_nTMAX from Acrôs ($n = 16$ or 18 ; $X = Br$ or Cl) and triblock copolymers P123 [(ethylene oxide)₂₀(propylene oxide)₇₀(ethylene oxide)₂₀; EO₂₀PO₇₀EO₂₀] from Aldrich. The tetraethyl orthosilicate (TEOS, 98%, Acrôs) was used as silica source. HNO_3 or HCl are as acid source. In a typical preparation, a proper amount of amphiphilic templates, TEOS, acid source and water were mixed thoroughly at 25-40 °C for 6-24 hr, where the pH value is < 1 . The solid product was recovered by filtration, washing with deionized water and drying at ambient temperature or 100 °C. The detailed process and chemical composition can be found in elsewhere [7].

2.2 *“Direct silane modification” of the uncalcined acid-made mesoporous silicas:*

1.0 g uncalcined acid-made mesoporous sample and a designed amount of silane sources, such as, Chlorotrimethylsilane ($(CH_3)_3SiCl$; CTS); 3-mercapto-propyltrimethoxysilane ($HS(CH_2)_3Si(OCH_3)_3$; MPTS); 3-aminopropyltrimethoxysilane ($H_2N(CH_2)_3Si(OCH_3)_3$; APTS); 3-trimethoxysilylpropyl chloride ($Cl(CH_2)_3Si(OCH_3)_3$, TSPC); 3-Cyanopropyl trichlorosilane ($CN(CH_2)_3SiCl_3$, CPTS) and Bromomethyldimethyl chlorosilane ($BrCH_2Si(CH_3)_2Cl$, BDCS) were added into 50.0 g ethanol. The mixture was then refluxed at 78 °C for 3 h under stirring or static condition. The moles of silanes relative to 1.0 g uncalcined acid-made mesoporous materials in that solution is in the range of 1-50 mmol. The solid products were recovered by filtration and washed with large amount of ethanol to remove the unreacted silanes, and then dried at 100 °C or ambient temperature. The surfactant templates can be recovered from the ethanol solution by evaporation under reduced pressure.

3. RESULTS AND DISCUSSION

Figure 1A-C show the XRD patterns of the different silanes-grafted mesoporous materials prepared from the C_{18} TMACI-TEOS- HNO_3 - H_2O composition. It can be seen that all of these three samples possess at least 4 distinct peaks, indicating a well-ordered hexagonal structure as before modification. This shows that the mesostructures of the mesoporous silica maintains during the “direct silanes modification procedure”. In a typical silanes-modification process, the silanes-modified sample own high surface area of about $600-800\text{ m}^2/\text{g}$ and narrow pore size distributions (the FWHM is $0.3-0.5\text{ nm}$).

The quaternary ammonium surfactants can be easily recovered from the ethanol solution. Using the regained quaternary surfactant, well-arrayed mesostructural silica also can be synthesized (Fig. 1D). Then, that mesoporous sample can be again modified (Fig.1E). Compared with the initial CTS-grafted mesoporous sample, the recycled modified mesoporous silica nearly has the same sharp XRD patterns and other physical properties. Therefore, the cycle of synthesis and modification reaction has been set up to prepare the silanes-grafted mesoporous materials with continuous reusing of the expansive quaternary surfactants.

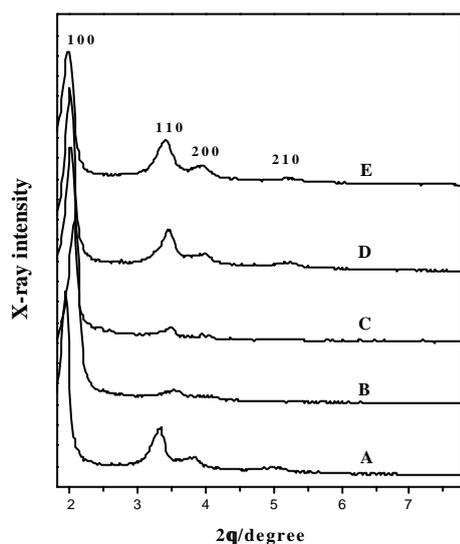


Fig. 1 The XRD patterns of the silanes-modified and unmodified mesoporous materials. A. CTS; B. MPTS; C. APTS; D. mesoporous silica synthesized from recovered surfactants E. CTS-modified sample of D.

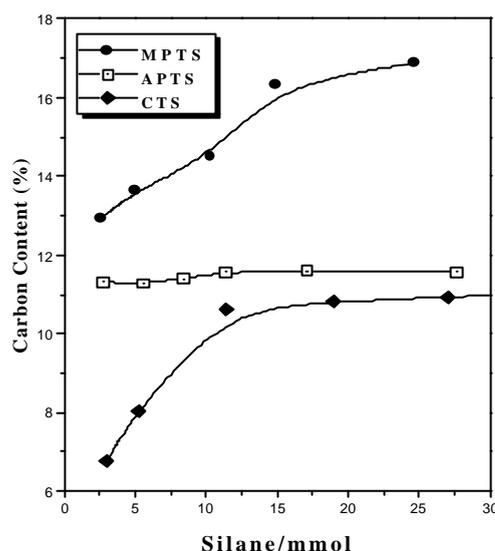


Fig. 2 The carbon elemental content of the silanes-grafted mesoporous samples obtained by varying silanes millimoles in 50 g ethanol solution to 1.0 g acid-made mesoporous silicas.

We used elemental analysis to examine the carbon, nitrogen and sulfur contents of the modified mesoporous silica. It is found that, by nitrogen analysis, there is no residue surfactant left in the modified sample [4]. Also when examining the ^{13}C MAS NMR of the

fully silane-grafted mesoporous samples, the signal of the quaternary surfactant completely disappeared, one see only the silanes peaks. This indicates that the surfactant templates were totally replaced by silanes and extracted out of the nano-channels. Thus the carbon content comes solely from the grafted silanes.

The silane-modification process can be attributed to an interfacial reaction, in which both the surface silanol density and the silane concentration will determine the final ligand coverage. To understand the effect of the silane concentration, we measured the extent of grafting as changing silane solution concentration. In Fig. 2, one can clearly see that the carbon contents of the silanes-grafted samples increase with the silanes concentration and attain a saturation value. The trend for the CTS grafting is similar to a Langmuir monolayer adsorption behavior. The APTS grafting attain its saturation coverage most efficiently; only a very small APTS solution concentration is needed. Apparently, the amine functionality leads to higher affinity with the silica wall. The thiol silane MTPS has the smallest affinity but it shows the highest saturation coverage however.

According to the carbon content, we calculate the saturation amounts of the grafted silanes groups of CTS, MPTS and APTM; they are 3.85, 6.89, 4.03 mmol/g SiO₂, respectively. The direct silanes-modification method is very efficient to prepare the highly silanes-coverage mesoporous silica. To increase the silanes coverage onto the nano-channels surface is particularly important for ions-adsorption and chromatograph applications.

In addition to the silane-modification examples aforementioned, other silane sources have also been used to functionalize the mesoporous materials prepared from C₈TMAB, C₁₆TMAB or triblock copolymer (EO₂₀PO₇₀EO₂₀)-acid-TEOS-H₂O compositions. The physical properties and ligand loading content are listed in Table 1. All of the silane-modified samples possess high surface area (400-900 m²/g), large pore volume (0.30-0.86 cm³/g), tunable pore size (2.1-5.5 nm) and high ligand loading calculated from carbon content (2.54-6.80 mmol/g SiO₂).

Table 1.

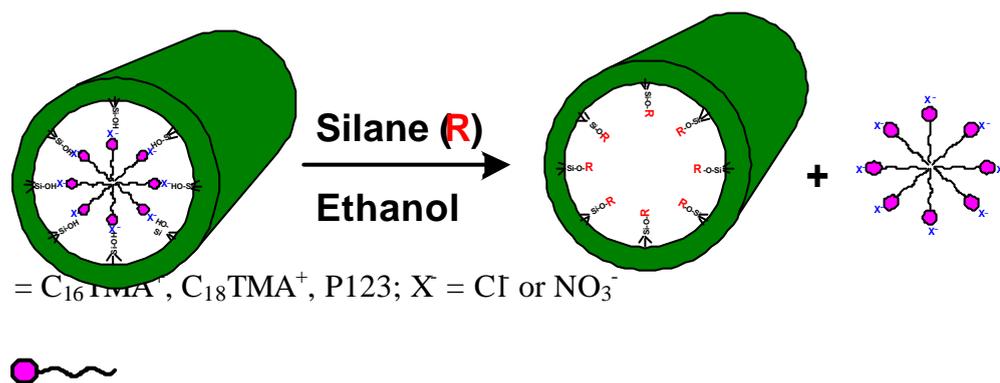
The physical properties, carbon content and ligand loading of the silanes-modified mesoporous silicas via the direct silanes-modification process.

Sample	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Carbon content (C %)	Ligand loading (mmol/g SiO ₂)
C₁₈TMAB-TEOS-HNO₃-H₂O					
CTS	792	2.7	0.851	11.10	3.25
BDCS	922	2.7	0.866	8.41	3.28
MPTS	417	2.1	0.278	16.87	6.89
AMPS	654	2.3	0.461	11.60	4.03
TSPC	798	2.2	0.619	11.89	3.96
CPTS	910	2.6	0.774	10.48	2.54
C₁₆TMAB-TEOS-HNO₃-H₂O					
CTS	922	2.32	0.756	11.40	3.69

MPTS	417	1.83	0.238	13.85	5.41
AMPS	654	1.76	0.414	10.85	3.65
EO₂₀PO₇₀EO₂₀-TEOS-HNO₃-H₂O					
CTS	442	5.5	0.603	10.95	3.52
MPTS	517	5.5	0.557	12.98	4.94
AMPS	243	5.4	0.325	10.87	3.66

One can see that the saturation ligand loading of the mercaptosilane MTPS is always high compared to other ligand. The chlorosilane CPTS binds less to the surface presumably because Si-Cl bond is less efficient to hydrolysis in an ethanol solution. The copolymer templated SBA-15 can also be grafted in the same approach because alcohol can also remove the hydrogen-bonded amphiphile.

From the above results, the “direct silane modification” process can be regarded as surfactant templates-displacement reactions. A proposed mechanism to describe the replacing process between the silanes and surfactants was showed in a schematic diagram as followed



The surface modification and surfactant extraction take place at the same time. Upon removal of the surfactants by the ethanol, the surface silanol groups are exposed and directly react with the silanes. Since no high temperature process is involved, the silanol group density is high that induces the greater ligand loading.

It is known that calcined mesoporous silica is mechanically fragile. Thus, the larger-sized morphologies (especially for the size larger than millimeter-scale) of mesoporous silicas can be easily broken into small fragments by the stirring flow during the modification process. To preserve the millimeter-sized form, we can efficiently functionalize the mesoporous silica surface under static conditions. In Fig.3, one can clearly see that the trimethylsilyl-silica ropes (centimeter-sized length),[7] and macro-sphere (centimeter-sized diameter) possess the same morphology and size as the unmodified ones [8]. Beside of trimethylsilane, other silicas of different functional groups have also been successfully grafted onto the large-sized mesoporous materials. Therefore our method can provide a new way to prepare the desired functionalized mesoporous materials in large scale. The large-sized form of mesoporous silica may be useful in adsorption, catalysis and optoelectronics.

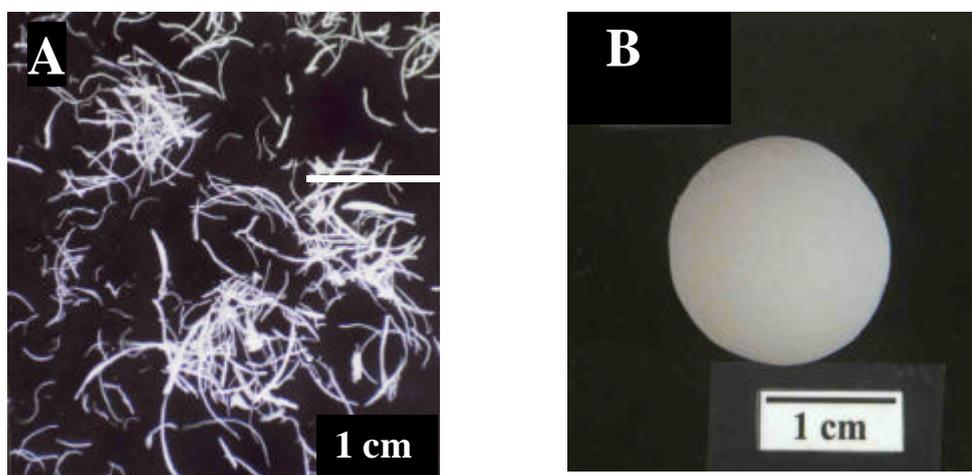


Fig. 3 The photograph of the CTS-modified silica ropes (A), and macro-sphere (B) in centimeter size.

4. CONCLUSIONS

In summary, the uncalcined acid-made mesoporous silicas can be efficiently functionalized via this convenient one-step procedure. This procedure has several advantages: the avoidance of calcination, high silyls coverage, recovery of the expansive surfactants, mild reaction temperature, short reaction time and the preservation of morphology. The “direct silane modification” is a novel and economic process for modifying different silanes onto the mesoporous materials, when the interaction between surfactants and silica frameworks is weak (i.e. hydrogen-bonding). Besides of organic silanes, we believe the inorganic metal alkoxides also can be grafted onto the surface of the mesoporous materials to generate the isolated metal reaction center for catalytic applications by using similar approach. Changing the surface functional groups and tuning the pore size open a new way to make designed adsorbents, catalysts and solid hosts.[8]

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