

## One-Step Grafting of Al<sub>2</sub>O<sub>3</sub> onto Acid-Made Mesoporous Silica

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We report a one-step convenient chemical coating method of high alumina content onto mesoporous silicas. Alumina-coated mesoporous silica with high surface area (~900 m<sup>2</sup>/g), tuneable pore size (2.0-3.0 nm) and high hydrothermal stability (> 60 h) is obtained. The method may also be generalized for grafting other metal oxides onto mesoporous silica in future work.

**Keywords:** Mesoporous silica; One-step; Alumination; Hydrothermal stability.

### INTRODUCTION

Mesoporous aluminosilicate is an important solid acid catalyst with a wide range of applications.<sup>1</sup> However, in a standard synthesis of framework Al-substituted mesoporous aluminosilicate, the incorporation of Al in the synthetic gel often leads to low Al content, low acidity and low hydrothermal stability. Recently, post-synthesis surface alumination of mesoporous silica has been shown to lead to materials with much improved stability and high Al content.<sup>2-7</sup> Grafting of Al onto the wall surface protects the weak silica from degradation. The extra-high hydrothermal stability of Al-grafted mesoporous silica is due to the Al<sub>2</sub>O<sub>3</sub> layer on the surface. In addition to improving stability of the mesoporous materials, the introduction of more surface acidity in Al-grafting is also useful as a catalyst support.<sup>8</sup> Moreover, in thin film form, Al<sub>2</sub>O<sub>3</sub> stabilized mesoporous aluminosilicate may be used as dielectric materials.<sup>9,10</sup>

In the alumination process, an often encountered problem is either the leaching of Al ions from the ion-exchange method of Al salts or the competing self-condensation of the Al(*i*-OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> under minor moisture which will lead to bigger clusters and hence pore blocking of the mesopores. Thus Mokaya et al. have employed supercritical CO<sub>2</sub> as solvent for the grafting of aluminum alkoxide onto the channel wall.<sup>4</sup> However, this would require special equipment and a tedious procedure; a simpler post-synthesis method for well-dispersed Al grafting is still much desired. Previously, we have developed a direct method of surface functionalization, without calcinations, of mesoporous silica which was demon-

strated to give high and uniform surface loading.<sup>11,12</sup> This method may be adapted to graft metal alkoxide and lead to a uniform surface coating of mesoporous silica. In this paper, we report a method for grafting a layer of alumina onto the pore surface of mesoporous silica.

Aluminum-grafting mesoporous silica materials have been prepared by a one-step surface-modification, in which dried HNO<sub>3</sub>-made mesoporous silica was directly combined with Al(*i*-OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> in 1-PrOH solution. The modified materials possess a better thermal stability. Besides, this method allows for more aluminum loading (Si/Al < 3) without disintegration of the mesoporous structure compared to common hydrothermal-made Al-MCM-41.

### EXPERIMENTAL

The micelle-templated mesoporous silicas (MMS) prepared via acid route were synthesized according to our previous report.<sup>13</sup> The one-step modification process of aluminum oxide coating is described as follows: 1.0 g uncalcined mesoporous silica (MMS, pre-heated in a 100 °C oven for 6 hr) was added into 40~100 g 1-propanol (C<sub>3</sub>H<sub>7</sub>OH, Acrôs, pa. 99.5%) solution containing the aluminum *iso*-propoxide (Al(*i*-OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, Acrôs, 204.25, 98+%). Then, the solution was refluxed for 10~95 hr. After filtration, washing with warm 1-PrOH twice, and drying, the Al-alkoxide grafted mesoporous materials were obtained. Finally, the Al-alkoxide coated mesoporous samples were calcinated at 560 °C to remove the unreacted alkoxides groups. Some NMR tech-

Dedicated to Professor Ching-Erh Lin on the Occasion of his 66<sup>th</sup> Birthday and his Retirement from National Taiwan University

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niques were investigated to determine the environment of proton, Al- and Si-sites, including MAS-NMR (Bruker MLS-500) of  $^1\text{H}$ ,  $^{27}\text{Al}$  and  $^{29}\text{Si}$ . Hexagonal array and porous properties are examined by small-angle XRD (Scintag X1,  $\lambda = 0.154$  nm) and  $\text{N}_2$  adsorption-desorption isotherms (Micrometric ASAP 2010) before and after hydrothermal stability tests.

## RESULTS AND DISCUSSION

Here we report on the physicochemical properties of Al-grafted mesoporous silica. Extraordinarily high loading of alumina is achievable by this one-step grafting ( $\text{Si}/\text{Al} = 1.97\text{--}2.85$ ). As we found in Table 1, Al-MMS-III ( $\text{Si}/\text{Al} = 2.07$ ) has a high surface area of  $877\text{ m}^2\text{ g}^{-1}$  and pore volume of  $0.670\text{ cm}^3\text{ g}^{-1}$ . Moreover, the calcined sample shows a very narrow pore-size distribution (curve II in Fig. 2B) with higher pore volume and larger pore size ( $R$ ). It indicates the thickness of coated alumina is well-controlled and adjustable by varying the concentrations of Al precursors.

All Al-grafted materials maintain their mesostructure well. In addition, the aluminated mesoporous silica has been proved to have durable hydrothermal and  $900\text{ }^\circ\text{C}$  steam stabilities.<sup>14</sup> The fresh as-grafted Al-MMS ( $\text{Si}/\text{Al} = 2.29$ ) sample exhibited well-resolved higher order (110) (200) XRD peaks after being in boiling water for 60 h (curve II in Fig. 1). As a result of calcination, alumina coated materials still have their hydrothermal stabilities. For siliceous mesoporous sil-

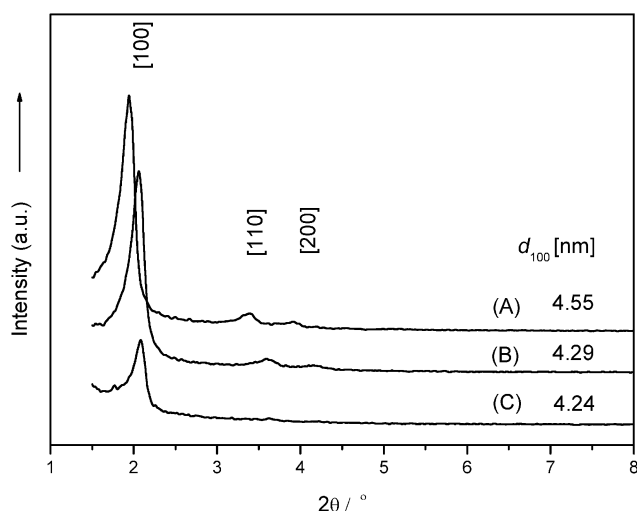


Fig. 1. Powder XRD patterns of (A) as-grafted  $\text{Al}(i\text{OPr})_3$  mesoporous silica (Al-MMS), (B) after 60 h hydrothermal test (Al-MMSH), (C) after calcination and then hydrothermal test (Al-MMSCH).

Table 1. Physicochemical properties of Al-MMS

Sample Entries	Si/Al	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$d_{100}$ ( $\text{Å}$ )	R ( $\text{Å}$ )	$W_{\text{pore}}$ ( $\text{Å}$ )	Pore vol. ( $\text{cm}^3/\text{g}$ )
Si-MMSc	$\infty$	1083	44.2	32	19	1.190
Al-MMS-I	8.85	915	43.3	26	24	0.729
Al-MMS-II	2.38	898	42.4	24	25	0.641
Al-MMS-III	2.07	877	42.8	24	25	0.670
Al-MMSc-III	2.27	795	41.6	25	22	0.728
Al-MMScH-III	2.46	830	39.4	26	20	0.757
Al-MMS-IV	1.97	854	42.9	26	24	0.655

ica, the mesostructure usually collapses within 24 h in boiling water. The improved hydrothermal stability may be attributed to a thin layer coating of alumina and reduced silanols in the calcined Al-MMS sample. After hydrothermal tests in autoclaves, the typical characteristics of type-IV  $\text{N}_2$  sorption isotherms still persist but wall thickness ( $W_{\text{pore}}$ ) of Al-MMScH-III decreases as shown in Table 1. Although Al-MMScH exhibits a little hysteresis loop (curve III in Fig. 2A) after the hydrothermal process, which may suggest some defects in the mesostructure, the materials with more interconnected channels help the free diffusion of reagents and products when used in catalytic applications.

In this work we chose  $\text{Al}(i\text{-OC}_3\text{H}_7)_3$  as the raw material for alumina grafting. From  $^{27}\text{Al}$  MAS NMR spectra, there are several contributions to chemical shifts, and the peak position is a function of (i) the coordination number,<sup>15</sup> (ii) the Al-O-Si angle,<sup>16</sup> (iii) the mean Al-O distance, and (iv) the presence of quadrupolar interaction. In Fig. 3A, the chemical shifts show  $^{27}\text{Al}$  nuclei with two different kinds of structural coordinations: such as tetrahedral ( $T_d$ ), pentahedral ( $P_d$ ) and octahedral ( $O_h$ ) sites in our samples. Moreover, evidence of the presence of zeolite-like connectivities in Al-NMMS was provided by the observation of a single  $T_d$  aluminum peak at about 60.5 ppm with almost the same intensity to  $O_h$  at about 4.3 ppm (Fig. 3A). Population of  $T_d$  Al species increased a little after calcination and hydrothermal treatment of these samples<sup>18</sup> (Curve II in Fig. 3A). Interestingly, there are a few penta-coordinated ( $P_d$ ) aluminum sites found in Fig. 3A. They were quantitatively resolved by  $^{27}\text{Al}$  FAM(II)-MQMAS NMR and regarded as the electron-deficient Lewis sites.<sup>17</sup>  $^{29}\text{Si}$  MAS NMR also supports that alumina are attached onto the surface. In Fig. 3B, three primary peaks of curve II at -109 ppm ( $Q^4$ ), -103 ppm ( $Q^3$ ) and -94 ppm ( $Q^2$ ) are characteristic of the as-grafted Al-MMS. The intensity of  $Q^3$  signal decreases after alumination. It infers that  $\text{Al}_2\text{O}_3$  are formed by the consumption of the surface silanols and the formation of Si-O-Al bonding with higher  $Q^4/Q^3$  values.

Acidity is essential for the application of the mesoporous materials in catalysis. Several techniques can be employed to characterize the proton environment on the surface.  $^1\text{H}$  MAS NMR spectrum is a powerful tool to distinguish the isolated  $\text{SiOH}$  (*i*-OH at about 1.9 ppm) and the weakly hydrogen bonded  $\text{SiOH}$  (*b*-OH at about 3.0) of the parent siliceous mesoporous materials after calcinations (curve I in Fig. 4). Compared to Al-grafted MMSc (curve II), the much-reduced peak at 1.77 ppm can be regarded as the residual isolated silanols.<sup>19</sup> It infers that the reduced intensities are due to the formation of Al-O-Si bonding upon the surface, rather than by the self-condensation of the surface silanols.

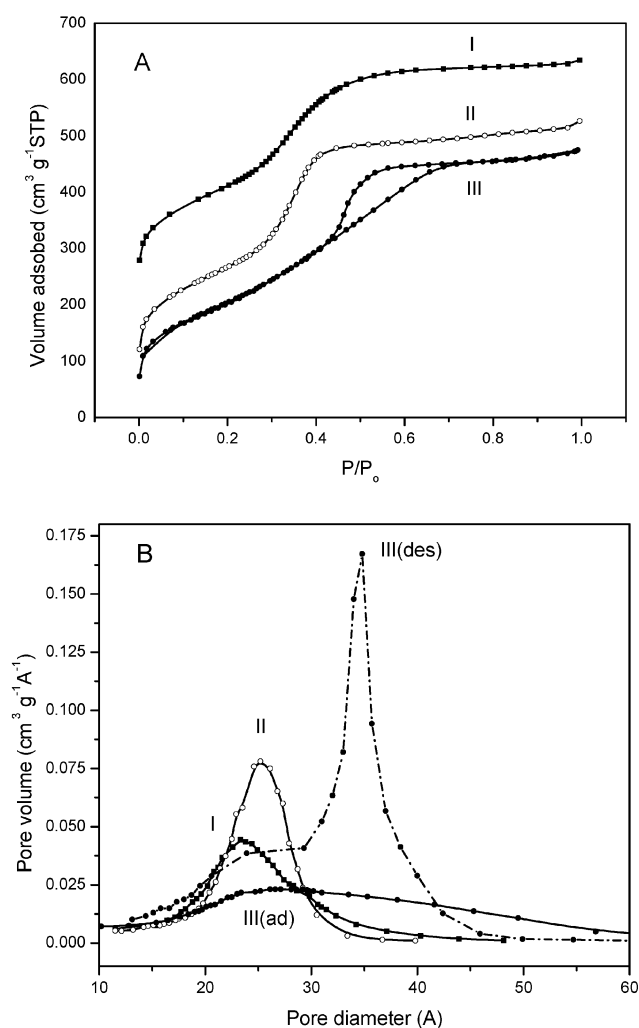


Fig. 2. (A) Nitrogen sorption isotherms and (B) pore size distributions (PSDs) of as-grafted  $\text{Al}(\text{iOPr})_3$ -mesoporous silica (sample I: Al-MMS), after calcination (sample II: Al-MMSc) and after calcination and then 60 h hydrothermal test (sample III: Al-MMScH) of adsorption III(ad) and desorption III(des).

In summary, the thickness of alumina coated on the mesoporous silica is about 5-6 Å before calcinations and 3 Å after calcinations in Table 1. The surface areas ( $S_{\text{BET}}$ ) of variously Al-grafted mesoporous silicas are modestly reduced after removal of organic templates and incorporation of aluminum precursors. Interestingly, the  $S_{\text{BET}}$  will keep decreasing after calcinations due to removal of organic alkoxides, but will inversely increase after hydrothermal test by formation of hydroxyl groups on the surface. All this evidence reveals that the highly dispersed aluminas were coated on the surface of nanochannels of mesoporous silica by formation of strongly bonded Al-oxo species.

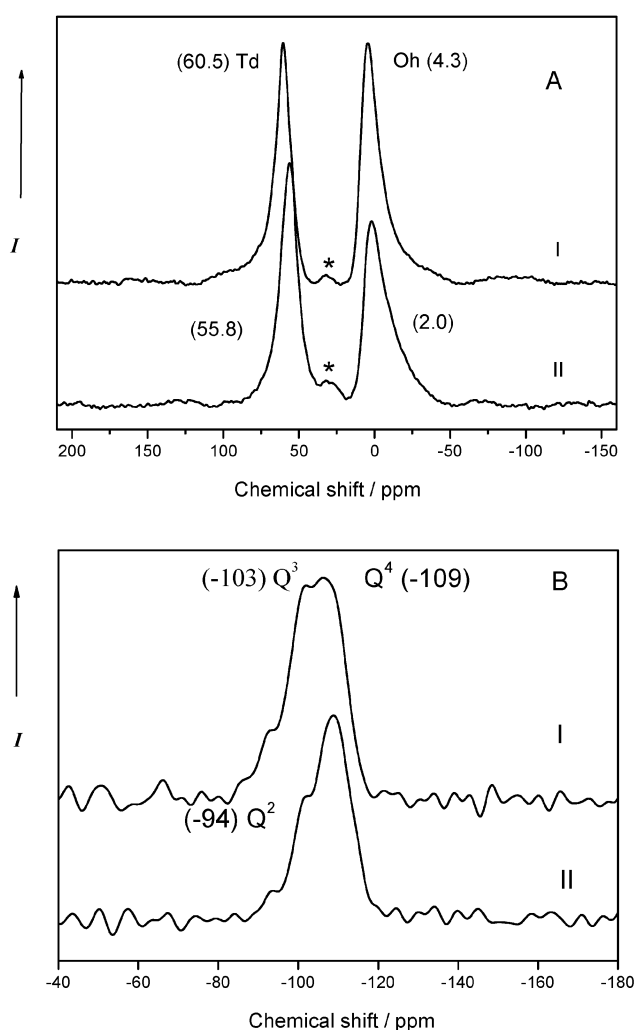


Fig. 3. (A)  $^{27}\text{Al}$  and (B)  $^{29}\text{Si}$  NMR of as-grafted  $\text{Al}(\text{iOPr})_3$  mesoporous silica (sample I: Al-MMS;  $\text{Si}/\text{Al} = 2.07$  from ICP-AES), after calcinations at 560 °C and then 100 °C hydrothermal (sample II: Al-MMScH;  $\text{Si}/\text{Al} = 2.46$ ). Asterisk denoted five-coordinated ( $P_d$ ) aluminum sites.

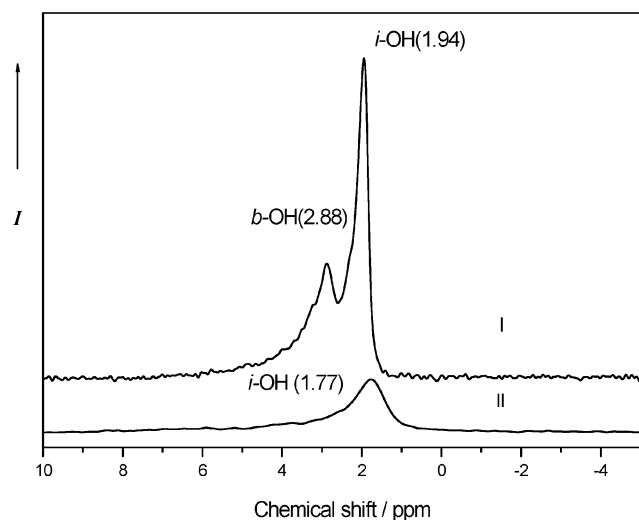


Fig. 4.  $^1\text{H}$  MAS solid NMR of purely siliceous MMS after 560 °C calcination (sample I: MMSc) and  $\text{Al}_2\text{O}_3$ -grafted mesoporous silica after 560 °C calcination (sample II: Al-MMSc).

The success of this direct grafting method relies on the exclusion of water inside the nanochannels during grafting. It is known that excess water will cause self-condensation of metal alkoxides among themselves, instead of grafting. The adsorbed water in calcined MMS usually leads to a non-uniform grafting and pore constrictions upon surface modification. The as-synthesized MMS, without calcinations, would keep most of the water out of the nanochannels. At the same time, the surfactants inside the channels would favor only thin coating along the wall. The mesoporous silica coated with alumina has been assessed with acid catalytic activity toward alkylation and cracking in our previous tests.<sup>20</sup> Moreover, it has great potential to replace the commercial alumina material as catalyst support due to its high hydrothermal and thermal stabilities.<sup>8</sup> This one-step method would introduce a general strategy for the convenient post-grafting of other metal oxides also.

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