Chemical Coating of Aluminum Oxide onto As-synthesized Mesoporous Silicas

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The Al_2O_3-coated mesoporous silicas with high surface area, different pore sizes, and high acidity can be efficiently obtained from a fast surface modification on the as-synthesized mesoporous silicas with the aluminum isopropoxide in 1-propanol and calcination at 560 °C.

Mesoporous silicas of high surface area, tunable pore size, and large pore volume are desirable for catalytic processes involving large molecules.[1] However, the amorphous silica framework hinders the applications in acidic–catalytic reactions. The attractiveness of mesoporous silicas as potential catalysts can be enhanced by a modification of their surface with other metal oxides.[2] To increase the acidity, grafting Al_2O_3 onto mesoporous silica is a very promising method.[3–6] In typical grafting processes, the calcined mesoporous silicas have been widely used. However, there are two main disadvantages in using calcined mesoporous silica: 1. The calcined mesoporous silica has high absorption capability for water, which can lead to a serious self-clustering of metal oxide.[7] Thus, dry solvent and vacuum system were required to graft the metal oxide to the calcined mesoporous silica.[2–9] 2. Removal of surfactants is a time- and energy-consuming process, and the surface silanol-group density is considerably reduced during high-temperature calcination. In this communication, we propose a new method to coat the Al_2O_3 layer onto the mesoporous silica by directly refluxing the as-synthesized mesoporous silica in a 1-propanol solution of the aluminum isopropoxide.

The typical process for the Al_2O_3-coating onto mesoporous silica is as follows: 1.0 g of the as-synthesized mesoporous silicas such as SBA-15, acid-made MCM-41, and mesoporous cellar foams (MCF) are added into a mixture of 0.85 g of aluminum isopropoxide ($Al(i\text{-}PrO)_3$) and 30.0 g of 1-propanol, and then that solution is refluxed for 1.0–3.0 h. Filtration, washing with 1-propanol, and drying yielded aluminum–alkoxide-coated mesoporous silica. After calcination at 560 °C in air, the aluminum–alkoxide-coated mesoporous silica is converted to the Al_2O_3-coated mesoporous silicas. The detailed synthetic procedures and chemical compositions of the mesoporous silicas have been reported elsewhere.[10–12]

Figure 1a shows the TGA curves of the as-synthesized SBA-15 before and after $Al(i\text{-}PrO)_3$ grafting. A shift can be clearly seen in the decomposition temperature from 180 °C (i.e. decomposition temperature of P123 surfactant) to 280 °C (i.e. decomposition temperature of $Al(i\text{-}PrO)_3$). This shift indicates that the organic component was changed. It is reasonably supposed that the $Al(i\text{-}PrO)_3$ with chemical bonds to the silanol groups is attached to the silica surface and displaces the surfactant P123 into 1-proponal solution (eq 1).

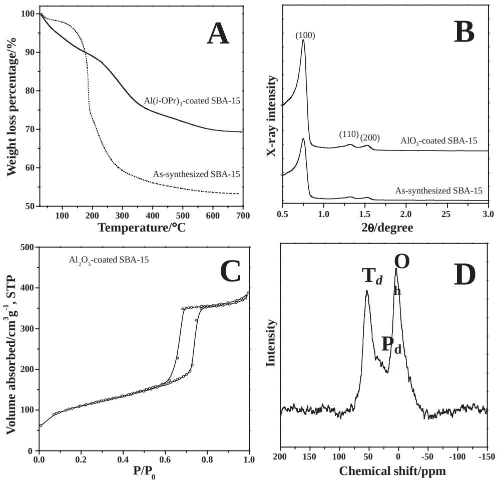
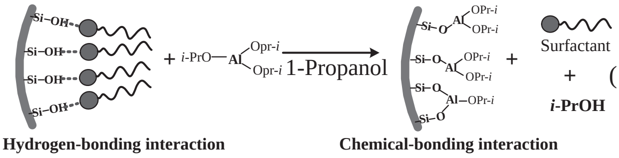


Figure 1. (A) TGA curves of the SBA-15 mesoporous silicas before and after modification of the aluminum isopropoxide. (B) XRD patterns of the SBA-15 mesoporous silicas before and after Al_2O_3 coating. (C) N_2 adsorption–desorption isotherm of the Al_2O_3-coated SBA-15 mesoporous silica. (D) ^{27}Al MAS NMR spectrum of the Al_2O_3-coated SBA-15 mesoporous silica.



(1)

Accordingly, the P123 surfactant recovered from the 1-propanol solution can be used to synthesize SBA-15 silica again. It should be noted that selecting 1-propanol as solvent is critical for the fast grafting of the aluminum alkoxides. The 1-propanol with high solubility for the surfactant can help the leaching of the surfactant from mesopores, and the relatively low water content reduces the possibility of self-condensation of the water-sensitive aluminum alkoxides. In contrast, using ethanol with high water content would induce a serious self-aggregation of the Al_2O_3 particles, while using toluene with low solubility for the surfactant can not achieve the modification of aluminum alkoxides.

Using the as-synthesized SBA-15 silica, high silanol group (–Si–OH) density leads to a high grafting content of $Al(i\text{-}PrO)_3$.[13] The Si/Al ratio in the $Al(i\text{-}PrO)_3$-modified SBA-15 is about 5.6. The SBA-15 silica modified with $Al(i\text{-}PrO)_3$ after calcination at 560 °C forms the corresponding Al_2O_3-coated SBA-15. Comparing the XRD patterns of the SBA-15 silicas before and after Al_2O_3 coating, we found that they have similar peak positions and intensities (Figure 1b). This result indicates that the mesostructural dimension of the SBA-15 was not changed during the mild reflux condition and calcination. The Al_2O_3-coated SBA-15 exhibits a steep N_2 adsorption–desorption isotherm as does the SBA-15 silica (Figure 1c). The narrow pore size distribution reveals that the Al_2O_3 was homogeneously coated onto the silica wall. Distinct from the mesoporous aluminosilicate (i.e. Al is only in tetrahedral site),[12] the Al_2O_3-coated SBA-15 demonstrates three peaks in the ^{27}Al MAS NMR spectrum, which are regarded to three kinds of structural coordination such as tetrahedral (T_d: ca. 56 ppm), pentahedral (P_d: ca. 30 ppm) and octahedral (O_h: ca. 0 ppm) sites (Figure 1d).[14]

In addition to the SBA-15 silica, other mesoporous silicas MCF (S^0I^0) and acid-made MCM-41 ($S^+X^-I^+$) of hydrogen-bonding interaction between silica and surfactants can also be coated with Al_2O_3 via the method we propose. The mesostructural preservation and steep N_2 adsorption–desorption isotherms were also found in the Al_2O_3-coated MCM-41 and MCF silicas (see the Supporting Information). The textural properties of all these samples are listed in Table 1. Analyzing the data, the Al_2O_3-coated mesoporous silicas possess the high surface area, large pore size and pore volume are close to the mesoporous silica without Al_2O_3 coating. Therefore, Al_2O_3-coating mesoporous silicas with different pore sizes have been readily produced by using different mesoporous silicas. The pore size can be tuned in a wide range from 1.7 to 30.5 nm.

To examine the acidity of the Al_2O_3-coated mesoporous silicas, cumene cracking was performed as the test reaction. Figure 2a shows that all Al_2O_3-coated mesoporous silicas have catalytic activity to convert cumene.[15] As the pore size decreases, the cumene conversion increases. In particular, the Al_2O_3-coated MCM-41 shows a 100% conversion at 400 °C. The high conversion of the Al_2O_3-coated MCM-41 is ascribed to the high Al_2O_3 content and that the pore size is relatively close to the molecular size of cumene.

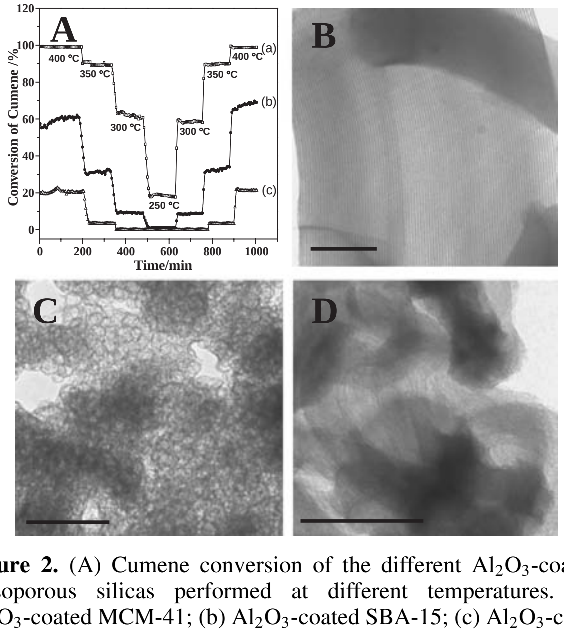


Figure 2. (A) Cumene conversion of the different Al_2O_3-coated mesoporous silicas performed at different temperatures. (a) Al_2O_3-coated MCM-41; (b) Al_2O_3-coated SBA-15; (c) Al_2O_3-coated MCF. (B) TEM image of the mesoporous carbon templated with the Al_2O_3-coated SBA-15. (C) TEM image of the mesoporous carbon templated with the Al_2O_3-coated MCF. (D) TEM image of the mesoporous carbon templated with the Al_2O_3-coated MCM-41. All scale bars: 200 nm.

Table 1. Physical properties and the Si/Al ratios of the Al_2O_3-coated mesoporous silicas

Sample	Si/Al[a]	BET S.A. /$m^2\,g^{-1}$	Pore size /nm	Pore volume /$cm^3\,g^{-1}$
Al_2O_3-SBA15	5.6	452	1.7	0.61
Al_2O_3-MCF	6.2	420	7.5	1.25
Al_2O_3-MCM-41	5.0	916	30.5	0.45

[a] The Si/Al ratios were determined by EDX or ICP-AES.

In addition, the Al_2O_3-coated mesoporous silicas can act as nanotemplate to synthesize the mesoporous carbons. Because of the acidic sites in the Al_2O_3-coated mesoporous silicas, the furfuryl alcohols adsorbed within the mesopores via an incipient-wetness process were polymerized within the mesopores at 80 °C.[16] After pyrolysis at 1000 °C and aluminum oxide–silica removal by HF-etching, mesoporous carbons with different mesostructures were obtained. Figures 2b–2d clearly show the well-ordered CMK-3, carbon hollow spheres and disordered carbons synthesized form Al_2O_3-coated SBA-15, MCF, and MCM-41, respectively. These mesoporous carbons have high surface area ($>1000\,m^2\,g^{-1}$), large pore size and pore volume as well as those previously reported.

In conclusion, we demonstrate that the Al_2O_3-mesoporous silicas of different pore sizes and high acidity have been conveniently prepared with the as-synthesized mesoporous silicas via a simple refluxing reaction and calcination. With the 1-propanol solution that has high solubility of the surfactant, the modification rate of aluminum alkoxides is rapid and the surfactant can be regained. This chemical coating is very flexible and could be applied as coating other metal oxides (such as, TiO_2, ZrO_2, Fe_2O_3, V_2O_5,...) by using the proper metal alkoxides.[2] Combined with the synthesis of the mesoporous silicas in different morphologies, mesostructures, and pore sizes, the high-performance mesoporous catalysts could be prepared for applications in catalytic reactions of the large molecules and solid nanotemplates.

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