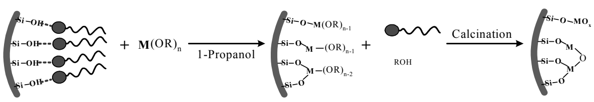
Chemical Coating of Metal Oxides onto As-synthesized Mesoporous Silicas

Yi-Shung Pan (潘易霜) and Hong-Ping Lin (林弘萍)

Department of Chemistry, Cheng Kung University, Tainan, Taiwan

Mesoporous silicas of high surface area, tunable pore size and large pore volume are desirable for catalytic processes involving large molecules. However, the amorphous silica framework of low acidity 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. To increase the catalytic activity, grafting metal oxides onto mesoporous silica is a very promising method. In typical grafting processes, the calcined mesoporous silicas have been widely used. While, there exist three 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 the water sensitive precursor of the metal-oxide. 2. Removal of surfactants is a time- and energy-consuming process. 3. Surface silanol group (Si–OH) density is considerably reduced during high-temperature calcination that leads to a low grafting content of the metal oxide. In this paper, we proposed a new method to coat the metal oxides layer onto the mesoporous silica by directly refluxing the as-synthesized mesoporous silica in a 1-proponal solution of the metal alkoxide and calcination.

Figure 1A shows the TGA curves of the as-synthesized SBA-15 before and after the grafting of Al(*i*-PrO)$_3$ and Ti(BuO)$_4$. One can clearly see a shift in the decomposition temperature from 180 ^oC (i.e. combustion temperature of P123 surfactant in SBA-15) to 280–300 ^oC (i.e. combustion temperature of Al(*i*-PrO)$_{3-x}$ or Ti(BuO)$_{4-x}$ grafted on the SBA-15). This shift indicates the organic component was changed. It is reasonably supposed that the P123 surfactant with weaker hydrogen-bonding interaction was exchanged by the metal alkoxides with stronger chemical-bonding interaction to the silanol groups. As expected, the P123 was recovered from the 1-propanol solution, which can be used to synthesize SBA-15 silica again. The grafting Al(*i*-PrO)$_{3-x}$ or Ti(BuO)$_{4-x}$ can be converted to metal oxides after calcination at 500 ^oC. The reaction mechanism of the metal oxides modification and coating on the silica framework of the as-synthesized mesoporous silicas was shown as followed (eq 1):



(1)

Owing to using the as-synthesized SBA-15 silica, high silanol group density leads to a high grafting content of Al(*i*-PrO)$_3$ or Ti(BuO)$_4$ [7]. The Si/M ratio in the metal oxide-modified SBA-15 is about 6.0. The XRD patterns of the Al_2O_3 or TiO_2-coated SBA-15 silicas demonstrate the representative peaks characteristic of hexagonal structure (Figure 1B). This result indicates that the mesostructural dimension of the SBA-15 was not changed during the mild reflux condition and calcination. In addition to the SBA-15 silica, other mesoporous silicas MCF ($S^0 \cdot\cdot I^0$) and acid-made MCM-41 ($S^+X^- \cdot\cdot I^+$) of hydrogen bonding between silica and surfactants can also be coated with metal oxide via the method we proposed. The mesostructural preservation and steep type-IV N_2 adsorption-desorption isotherms were found in the Al_2O_3-coated SBA-15, MCM-41 and MCF silicas (Figure 1C). The textural properties of all these samples were listed in Table 1. Analyzing the data, the Al_2O_3- and TiO_2-coated mesoporous silicas with different pore sizes have been readily produced. In addition, other metal oxides such as V_2O_5, Fe_3O_4 and ZrO_2-coated mesoporous silica have been prepared by using the proper metal alkoxide precursors.

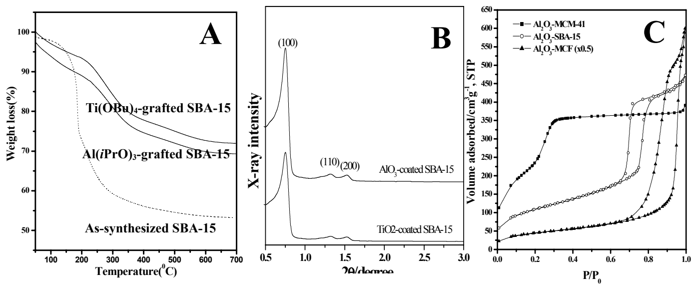


Figure 1. A. The TGA curves of the as-synthesized SBA-15 silicas before and after Al(*i*-PrO)$_3$ and Ti(BuO)$_4$ modification. B. XRD patterns of the Al_2O_3- and TiO_2-coated SBA-15 silicas. C. N_2 adsorption-desorption isotherms of the Al_2O_3-cotaed SBA-15, MCM-41 and MCF silicas.

Table 1 Textural properties and the Si/M ratios of the metal oxide-coated mesoporous silicas.

Sample	Si/M[a]	BET S.A. /m^2g^{-1}	Pore size /nm	Pore volume /cm^3g^{-1}
Al_2O_3-SBA15	5.6	452	7.5	0.61
Al_2O_3-MCF	6.2	360	30.5	1.25
Al_2O_3-MCM-41	5.0	916	1.7	0.45
TiO_2-SBA-15	7.3	438	7.6	0.63
TiO_2-MCF	6.8	335	29.6	1.22
TiO_2-MCM-41	5.2	894	1.6	0.42

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

In brief, we provided a simple method to coat different metal oxides onto the as-synthesized mesoporous silicas and recover the surfactants. Combining with the synthesis of mesoporous silicas in various forms, mesostructures and pore sizes, the high-performance mesoporous catalysts could be obtained to match the applications in catalytic reactions and as solid templates for synthesis of potential materials.