23 Chemical Coating of the Metal Oxides onto Mesoporous Silicas

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1. INTRODUCTION

Mesoporous silicas have been widely used to support transition metal oxides for catalytic applications because these supports are attractive for their high surface area (1000 m^2/g), tuneable pore size (1.0-30.0 nm) and promotion of well-dispersed active metal sites (Kresge *et al.*, 1992; Zhao *et al.*, 1998). Because the nanochannels of the calcined mesoporous silicas can absorb a huge amount of water from atmosphere, which inhibits metal oxides grafting, a non-polar solvent (such as, toluene) and moisture-free reaction condition were needed to prevent the facile and fast hydrolysis/condensation reactions of the water-sensitive metal alkoxides in many typical metal-oxides grafting cases. Thus, a simple and versatile process for grafting high-content metal oxides onto mesoporous silicas is still desirable.

Basically, one should consider the metal-oxides grafting as simple chemical surface modification mesoporous silica via covalent bonding of metal oxides (Sayari *et al.*, 2001). By using this idea, herein, we designed a convenient strategy for high-coverage grafting metal-oxides onto the as-made mesoporous silica. Due to the avoidance of calcination, whole silanols almost can react with the greatly active metal alkyloxides and form a metal oxides layer on the mesoporous silica wall that makes mesostructure highly hydrothermal stable.

2. EXPERIMENT

The acid-synthesized mesoporous silicas were obtained by typical method reported in the previous literatures (Lin *et al.*, 2000), and the detailed procedures and chemical compositions were demonstrated elsewhere. The metal oxides-coating process is proceeded as follows: 1.0 g uncalcined acid-made mesoporous silica were added into (30-80) g 1-propanol solution containing 1.0-3.0 g proper metal alkyloxides, such as, titanium(IV) n-butoxide ($Ti(OC_4H_9)_4$, Acrôs, 99%), zirconium(IV)propoxide (Aldrich, 70 wt% solution in 1-propanol) or aluminum isopropoxide ($Al(OC_3H_7)_3$, Acrôs, 98%). Then, that solution was refluxed for 24 hr at 80 °C. Filtration, washing, and drying recovered the metal alkyloxides-grafted mesoporous materials. Finally, the metal-coated mesoporous samples were obtained after 560 °C calcination for 6 hr.

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3. RESULTS AND DISCUSSIONS

Figure 1A shows the representative XRD patterns of the calcined ZrO_2, TiO_2 Al_2O_3-grafted mesoporous silicas. One can find that all these samples possess the 3-4 sharp XRD peaks, indicating the well-ordered hexagonal mesostructure. However, the absence of the high-angle diffractions in all these samples indicates that no nano-crystallites of the metal oxides as the byproducts were formed during the grafting procedure (Yang *et al.*, 1998) With the analysis of the N_2 adsorption-desorption isotherms, one can find there existed a sharp capillary adsorption isotherm in each metal-oxides-grafted sample. According to these results, it is reasonably supposed that the metal-oxides could be well dispersed onto the nanochannels of the mesoporous silicas.

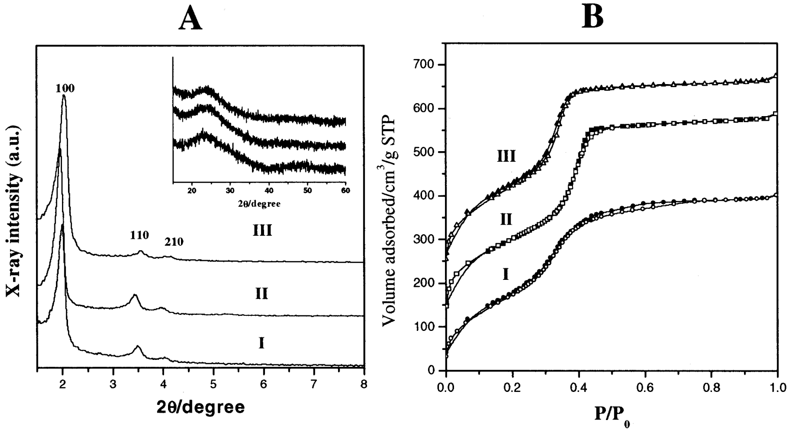

Figure 1. The XRD patterns (A) and N_2 adsorption-desorption isotherms (B) of the calcined metal oxides-coated mesoporous silicas; (I). ZrO_2-mesoporous silicas; (II). TiO_2-mesoporous silicas; (III). Al_2O_3-mesoporous silicas. The inset shows the high-angle XRD patterns.

Table 1 listed the basic physical properties and the metal/silica ratios of the metal-oxides grafted and un-grafted mesoporous silicas. All of the metal oxides-grafted mesoporous silicas posses the advantages of high surface area (~800 m^2/g) and large pore size (~2.6 nm) as those of typical mesoporous materials. It should be mentioned that the metal oxides-grafted mesoporous samples demonstrate the thicker wall thickness than the un-grafted one, and the difference between these values is about 0.4-0.6 nm. Besides, the metal/Si ratios are around 0.5 obtained from the EDS analysis, revealing the extremely high content of metal oxide. Owing to the high content of metal oxides, uniform pore size and, a constant increase of wall thickness, it is reasonable that the grafted metal alkyl oxides species forms a continuous layer on the silica surface; this procedure is therefore referred to as mono-layered metal-oxide coating.

Table 1. The physical properties and metal/silica element ratios of the un-grafted and metal-oxides grafted mesoporous silicas.

Sample	d_{100} /nm	S_{BET} /m^2/g	Pore size /nm	Wall thickness[a] /nm	Metal/Si[b]
Blank	4.24	1140	3.2	1.69	0
TiO_2	4.25	828	2.83	2.08	0.45
ZrO_2	4.26	750	2.61	2.31	0.56
Al_2O_3	4.24	877	2.65	2.24	0.51

a. wall thickness = $2d_{100}/\sqrt{3}$-pore size.

b. The data were obtained by the EDS analysis.

It is known that the improved stability exhibited by metal oxides-coated mesoporous silica with thicker wall-thickness is therefore due to a combination of the strengthened framework in the presence of the metal-oxide protecting layer on the surface of nanochannels. We found the well-ordered XRD patterns of the metal oxides-coated mesoporous silica were still preserved for 60 hr in boiling water. In contrast, the mesostructure of the calcined un-coated mesoporous silicas completely collapsed after 6 hr.

Basically, the direct metal oxides grafting mechanism can be divided into two simultaneous processes as shown in Figure 2. The first step is the surfactant extraction by 1-alkanols. After that, the active reaction sites (silanol groups) expose to the metal-alkyloxides solution, and then react with the metal-alkyloxides. We can reasonably assume that the metal oxides grafting reaction takes place only on the surface Si-OH group without self-bonding between metal alkyloxides. Thus the metal oxides theoretically could be coated to the silica surface in mono-layered form. The extraction of the surfactant and grafting of metal oxides without prior calcination have been achieved by this convenient one-pot process. Because of the recovery of the expensive quaternary ammonium surfactants, this method is economic to prepare the high-dispersed metal oxides catalysts.

This convenient and versatile synthetic procedure also can be extended to prepare the multi metal oxides coated-mesoporous materials could be facilely synthesized by using the solution of the metal alkyloxide mixtures. With a careful adjustment of the metal alkyloxides ratios, one can design the compositions and functionality of the mesoporous catalysts for the desired reactions.

4. CONCLUSION

In general, the metal oxides-coated mesoporous silicas possess the advantages: (1) the high surface area; (2) All metal active sites are surface species; (3) Presenting the maximum access to large reactant molecules. This convenient one-pot synthetic approach afforded the monolayered coating mesoporous silicas that should have the particular electronic, optical and magnetic properties owing to such unique 2-D metal oxide monolayer. Of practical interest, one should mention the combined modification of the mesoporous silica surface by the metal alkyloxides, and the silylating agents, to generate the hydrophobic or multi-composite oxidation catalysts for extending the catalytic application.

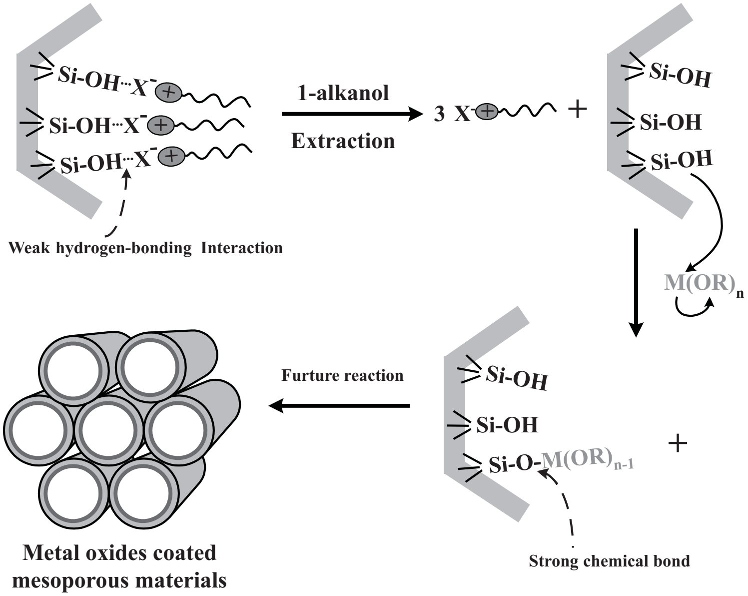

Figure 2. A schematic diagram for descriptions of the metal oxides coating onto mesoporous silicas.

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