Synthesis and Characterization of Manganese(II)-Phenanthroline Complex Grafted 3-Methacryloyloxypropyl Functional MCM-41

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This paper describes the preparation of manganese(II)-phenanthroline complex functionalized MCM-41 (MCM from Mobil Crystalline Material). The as-synthesized organic group functional MCM-41 and metal-ion-complex functionalized MCM-41 were extensively characterized by powder X-ray diffraction (XRD), TEM, solid-state 29Si and 13C NMR and nitrogen adsorption/desorption isotherms at 77 K, as well as Mn(II) electron spin resonance (ESR) spectroscopy at room temperature. These results indicated that 3-methacryloyloxypropyl group well dispersed in the mesopore of MCM-41, which attached to the silicate walls via Si–O–Si bonds. The mesopore of MCM-41 was tailored by the grafted organic group and the complex, while the coordination state of Mn(II) was unaffected by the process of grafting.

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1. Introduction

The growing interest of the synthesis of organic functional groups modified mesostructures is simulated by potential applications of these materials in adsorption, catalysis, nanotechnology and so on. A range of ferrocenyl groups functionalized MCM-41 and FSM-16 were synthesized from ferrocenyl carbocation. Juan grafted functional 3-chloropropyl and 3-phenylpropyl onto the internal walls of MCM-41 through Si–O–Si bonds. Sulfonic acid functionalized mesoporous silicates performed well in typical strong-acid catalyzed reaction. Many reactive groups such as Cl–Si==, EtO–Si== modified the silica walls in mesoporous materials using suitable organosilane as precursors by self-assembled method.

In the present work, 3-methacryloyloxypropyl functional MCM-41 and the manganese(II) phenanthroline complex functionalized MCM-41 were synthesized. They were characterized by XRD, TEM, 29Si and 13C MAS NMR, nitrogen sorption at 77 K, and ESR spectroscopy.

2. Experimental

2.1 Modification of MCM-41 with 3-methacryloyloxypropyl

A mixture of 1.0 g calcined MCM-41, 5.0 ml (3-methacryloyloxypropyl)trimethoxysilane and 50 ml dry hexane was placed in a 100 ml round-bottom flask. It was stirred and refluxed at 343 K for 12 h under the protection of nitrogen flow. The white 3-methacryloyloxypropyl functional MCM-41 (named MCM-mp) was washed repeatedly with ethanol and then dried at 353 K for more than 12 h. There was about 10.9 mass% 3-methacryloyloxypropyl group in MCM-mp by C, H organic elemental analysis (C: 16.67%, H: 2.75%).

2.2 Mn(II) complex grafted onto functional MCM-mp

Manganese ion complex: [Mn(phen)2Cl]OH·3H2O was synthesized according to the procedure reported previously. 0.02 M solution of manganese(II) complex was prepared by dissolving the appropriate amount of the complex into 50 ml distilled water. 1.0 g MCM-mp was added and the mixture was then stirred at least 10 h at room temperature. Then, the solid product was washed with distilled water and ethanol by filtration. Finally, it was dried in a vacuum oven at 353 K overnight. The as-synthesized manganese functionalized MCM-41 recorded as MCM-mp-Mn(phen)2Cl.

3. Results and Discussion

The synthetic reaction for metal ion complex functionalized MCM-41 occurs in two steps. The first step is the condensation of (EtO)2Si(CH3)2OCOC(CH3)2=CH3 and the peptide OH groups on the pore walls in MCM-41. So, functional group 3-methacryloyloxypropyl modifies the inner surface of MCM-41. Then, in the second step, [Mn(II)(phen)2Cl] + goes into the pores and Mn(II) is coordinated by the grafted vinyl ligands. Thus, Mn(II) complex and MCM-41 are linked with organic functional group, and the complex is attached on the mesopore inner surface of MCM-41. Elemental analysis (AA 6401 Atomic Absorption Spectrometer) indicates that the composite material contains 1.81 mass%Mn (ca. 14.8 mass%Mn(II) complex).

3.1 XRD and TEM

X-ray powder diffraction patterns (Rigaku D/max rb, CuKα, λ = 0.15418 nm) of the samples are illustrated in Fig. 1. All of samples display three or four low-angle reflection (d₁₀₀, d₁₁₀, d₂₀₀, d₂₁₀), which are characteristic of these hexagonal mesostructures. For 3-methacryloyloxypropyl functional MCM-41, a small increase in the d-spacing is obtained (Fig. 1(b)), which could be attributed to the structure expansion analogous to that observed during the postsynthesis restructuring with amines. In contrast, an increase in the XRD (100) intensity is observed for Mn(II) complex func-
3.2 NMR spectroscopy

To investigate how the 3-methacryloyloxypropyl unit bonded to MCM-41, we have studied the material using solid-state $^{29}$Si and $^{13}$C MAS NMR. (Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO$_2$ rotors).

The room temperature solid state $^{29}$Si NMR spectrum of MCM-mp exhibits four resonances (Fig. 3(a)). The two low-frequency resonances at a chemical shift of -111 and -103 ppm, and a very low intensity shoulder at -91 ppm, which are attributed to Q$^1$ [Si(OSi)$_2$], Q$^2$ [Si(OSi)$_3$(OH)] and Q$^3$ [Si(OH)$_2$(OH)$_2$] structure units in the silica framework, respectively. A new signal at δ = -60 ppm is assigned to the silicon nuclei of the organosilyl grafted species. The $^{13}$C MAS NMR spectrum of MCM-mp (Fig. 3(b)) exhibits seven resonances, which the chemical shift are at δ = 168, 137, 125, 68, 23, 18, 10 ppm respectively. The assignment of the signal peaks is marked on Fig. 3(b).

3.3 N$_2$ adsorption/desorption

N$_2$ sorption isotherm is an efficient way for providing information about the pore structure of mesoporous materials. Figure 4 shows the nitrogen adsorption/desorption isotherms (Micromeritics ASAP 2010. The samples were outgassed under 0.4 Pa vacuum at 433 K for 6 h.) at 77 K. Little difference could be observed between the N$_2$ sorption curves of MCM-41 and those of 3-methacryloyloxypropyl functional MCM-41 and Mn(II) complex functionalized MCM-41, revealing that the introduced group and complex don’t affect the mesoporous structure of support MCM-41. Importantly, there is no broad loop indicative of a type H2 hysteresis loop. It confirms that the organic group and complex diffuse through the entire pores rather than agglomerate at the opening of the mesopores associated with “ink bottle” shaped pores, which shows more H2 character. However, in the isotherm a hysteresis loop at relative pressure $>$0.5 is caused by large meso- and macropore. The changes in surface areas, pore volumes and average pore diameter for the samples are illustrated in Table 1. The observation of the decreased surface area and pore volume also indicates the impregnation of functional
Table 1 Pore structure parameters of samples calculated from the desorption branch of N$_2$ sorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface areas (A/m$^2$ g$^{-1}$)</th>
<th>Pore volume (V/cm$^3$ g$^{-1}$)</th>
<th>Average pore diameter (D/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>1048</td>
<td>1.15</td>
<td>3.18</td>
</tr>
<tr>
<td>MCM-mp</td>
<td>748</td>
<td>0.55</td>
<td>2.83</td>
</tr>
<tr>
<td>MCM-mp-Mn(phen)$_2$Cl</td>
<td>713</td>
<td>0.53</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Fig. 4 N$_2$ adsorption/desorption isotherms at 77 K of (a) calcined MCM-41, (b) MCM-mp, (c) MCM-mp-Mn(phen)$_2$Cl.

Fig. 5 ESR spectrum of MCM-mp-Mn(phen)$_2$Cl at 293 K.

...group and Mn(II) complex within the mesopores.

3.4 ESR

The room-temperature ESR spectra of the manganese complex functionalized MCM-41 (Bruker ER-200D ESR spectrometer) is showed in Fig. 5. In addition to the sextet lines a broad siglet at $g_{\perp} = 2.010$ of MCM-mp-Mn(phen)$_2$Cl is observed, which is typical for manganese(II) complex. There is no signal difference between the metal ion complex precursor and metal ion complex functionalized MCM-41. The coordination state of Mn(II) is unaffected by the process of grafting because the coordinative ability of $-\text{C}=$CH$_2$ and $-\text{Cl}$ to center metal ion are relative weak compared to $-\text{phen}.$

4. Conclusion

The functionalization of the pore walls of mesoporous MCM-41 has been achieved by the treatment of 3-methacryloyloxypropyl functional MCM-41 with complex [Mn(phen)$_2$Cl]$^+$. The mesopore structure and the center Mn(II) of the composite material were investigated by XRD patterns, TEM images, MAS NMR spectra, nitrogen sorption isotherms and manganese ion ESR spectroscopy.

REFERENCES