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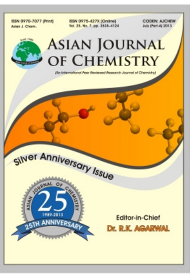

Direct Room-Temperature Synthesis of Organic-Inorganic Hybrid MCM-48 Nanoparticles

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A series of organic-inorganic hybrid MCM-48 materials were directly synthesized by a rapid and facile way at room temperature without employing hydrothermal synthesis for the first time. The resultant samples were characterized through XRD, N_2 adsorption/desorption, FT-IR, FESEM and HRTEM. The characterization results revealed that all the samples with typical mesoporous structure were successfully modified by the introduced organic groups.

Key Words: Facile synthesis, Direct functionalization, Characterization, Organic-inorganic hybrid material, MCM-48.

INTRODUCTION

In the last decade, organic-inorganic hybrid mesoporous molecular sieves have received many attentions for the use in adsorption, separation, catalysis, biotechnology and chromatography owing to the modified and functionalized surface. Compared with pure silica mesoporous molecular sieves, they not only maintain the highly ordered structure, high surface area, uniform pore size distributions and the open-framework pore structure, but also exhibit high hydrothermal and mechanical stability because of their hydrophobicity as a consequence of the organic groups in the surface or framework[1,2]. In principle, the organic functionalization can be achieved either by a grafting method due to the presence of a large number of silanol (Si-OH) groups on the surface of pure silica mesoporous molecular sieves or by a co-condensation of silane and organosilane during the synthesis of mesoporous molecular sieves under surfactant control. In a comparison with grafting method, which would lead organic groups to be anchored preferentially at the external surface and near the pore opening, co-condensation process can achieve higher loadings and more homogeneous distributions of organic functional groups.

As a member of M41s family discovered in 1992 by the Mobil group[3,4], MCM-48 has attracted a great deal of interests. And a few literatures about easy synthesis of MCM-48 have been reported. Schumacher *et al.*[5] reported a novel and fast method, which is a modified Stöber synthesis, to synthesize metal-incorporating MCM-48 spheres. Boote *et al.*[6] prepared cubic MCM-48 by a rapid and facile way without employing hydrothermal process in 0.5 h at room temperature. Moreover, great efforts have been made in the fields of modificating the surface of MCM-48 with different organic groups[7]. In this work, a series of organic groups modified MCM-48 have been synthesized facilely and rapidly without employing hydrothermal synthesis process at room temperature by co-condensation process in one step for the first time.

EXPERIMENTAL

The organic-inorganic hybrid MCM-48 mesoporous molecular sieves were synthesized by a rapid and facile way as previously reported[6]. Samples were prepared from tetraethylorthosilicate (TEOS, Sinopharm Chemical Reagent Shanghai Co. Ltd., China), cetyltrimethylammonium bromide (CTAB, Sinopharm Chemical Reagent Beijing Co. Ltd., China), ethanol (Tianjin Chemical Reagent Co. Ltd., China), aqueous ammonia (Baiyin Chemical Reagent Factory, China) and silane coupling agent including triethoxyvinylsilane [CH_2=$CHSi(OC_2H_5)_3$], 2-cyanoethyl triethoxysilane [$CN(CH_2)_2Si(OC_2H_5)_3$] and 3-methacryloylpropyltrimetho xysilane [CH_2=$C(CH_3)COO(CH_2)_3Si(OCH_3)_3$]. The composition of the reaction medium was 0.41 CTAB: 52 CH_3CH_2OH: 12 aq. NH_3: 1.0 TEOS: 343 H_2O: 0.1 silane coupling agent. In 50 mL of deionized water, 1.2 g of CTABr was diluted and the mixture was kept under stirring at 30 ºC until a clear solution was achieved. Then 25 mL of ethanol and 6 mL of aqueous ammonia were added. Finally, 1.8 mL of TEOS and various silane coupling agent

TABLE-1
TEXTUAL PROPERTIES OF ALL THE SAMPLES WITH DIFFERENT ADDED SILANE COUPLING AGENT: (A) TRIETHOXYVINYLSILANE, (B) 2-CYANOETHYL TRIETHOXYSILANE, (C) 3-METHACRYLOYLPROPYLTRIMETHOXYSILANE

Samples	d_{211}[a] (Å)	a_0[b] (Å)	S_{BET}[c] (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore diameter (nm)
A	33.08	81.03	783	0.42	2.16
B	32.57	79.78	691	0.43	2.97
C	31.69	77.62	557	0.26	1.85

[a]*d* value of peaks (211) in low-angle XRD patterns; [b]The cell parameter a_0 is calculated from the formula $a_0=d_{211}6^{0.5}$; [c]BET surface area

was added and the mixture was stirred mildly for another 4 h. The resulting white precipitate was filtered by Büchner funnel and the white product was dried at room temperature overnight. The resulting powder was extracted by ethanol using Soxhlet extractor for 24 h to remove the templates. Finally, solid products were dried in vacuum for 24 h at 85 °C. Functionalized MCM-48 materials have been named herein as sample A (triethoxyvinylsilane), B(2-cyanoethyl triethoxysilane) and C (3-methacryloylpropyltri-methoxysilane) according to the added various silane coupling agent.

The properties of all the samples were confirmed by XRD (Shimadzu XD-3A), N_2 adsorption/desorption (ASAP 2020), FT-IR (Bruker, IFS120HRFTIR), FE-SEM (JEOL, JSM-6701F) and HRTEM (JEOL, JEM-2010).

RESULTS AND DISCUSSION

The crystallinity of the obtained molecular sieves was characterized by X-ray diffraction in Fig. 1. The patterns for all samples with different organic groups show characteristic peak (211) at 2.7º and sample A exhibits a weak shoulder peak (220) at about 3.1º, which can be indexed in the space group Ia3d. It can also be observed that the intensities of (211) reflection are in the trend of A > B > C and there is no obvious peak (220) in sample B and C, indicating the negative impact of organic groups on the structure of MCM-48 solids. Larger organic group introduced by sliane coupling agent results in a decrease in the structural order of the cubic network.

N_2 adsorption/desorption isotherms of hybrid samples all give typical type-IV isotherms with a sharp inflection at $p/p_0 > 0.3$ in Fig. 2. This is characteristic of capillary condensation, which points to the uniformity of the mesopore size distribution. The textural properties of these samples are listed in Table- 1. It can be seen that these samples exhibit a pore size ranging from 1.85 to 2.97 nm and a BET specific surface area in the range of 557 to 783 m^2/g. The BET surface area of these samples decreases with the increasing of carbon chain due to a partial collapse of the mesoporous structure. It should be noticed sample B gives the largest pore volume (0.43 cm^{-3}/g) and pore size (2.97 nm), which could be attributed to the moderate size of anchored organic group in the internal pore surface making the size of pore volume and average pore diameter increased.

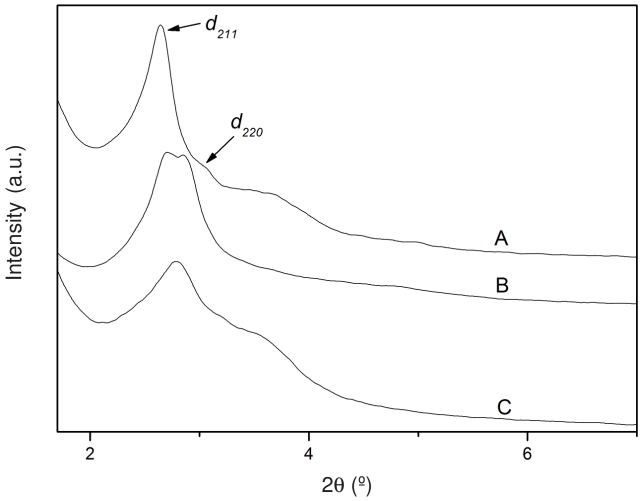


Fig. 1. Low-angle XRD patterns of all the samples with different added silane coupling agent: (A) triethoxyvinylsilane, (B) 2-cyanoethyl triethoxysilane, (C) 3-methacryloylpropyltrimethoxysilane

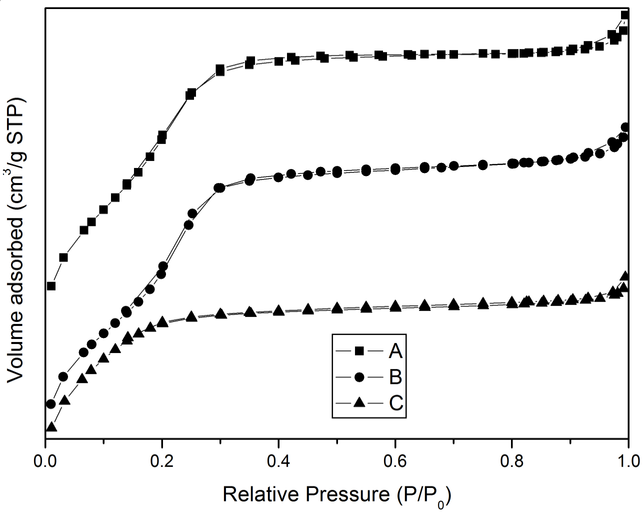
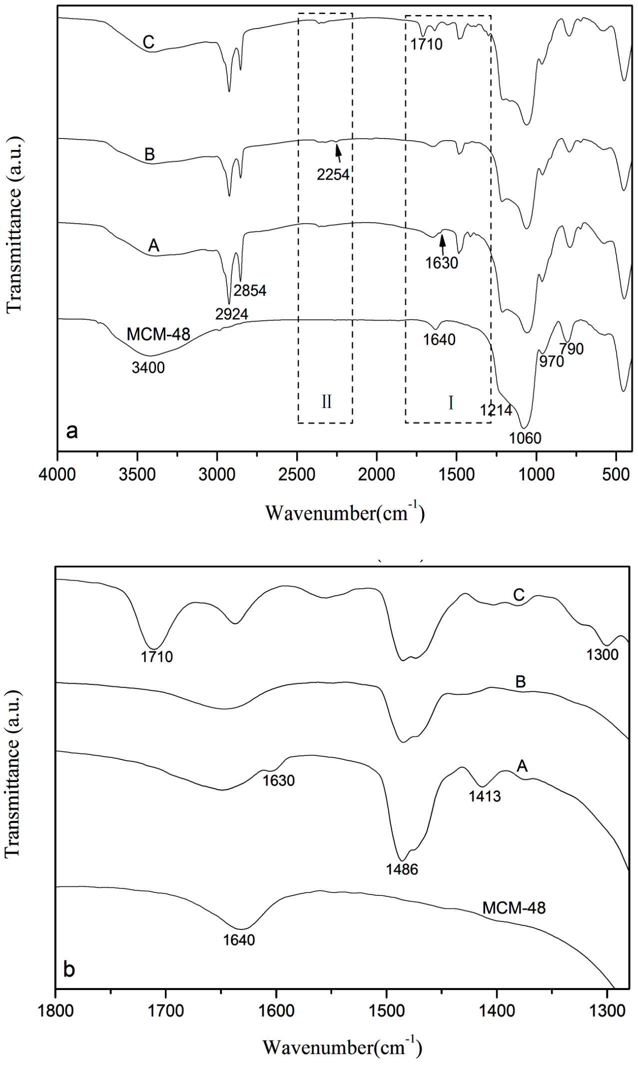


Fig. 2. N_2 adsorption/desorption isotherms of all the samples with different added silane coupling agent: (A) triethoxyvinylsilane, (B) 2-cyanoethyl triethoxysilane, (C) 3-methacryloylpropyltrimethoxysilane

Fig. 3 showed the Fourier transform infrared spectra (FT-IR) for the functionalized samples, which display distinctive characteristics because of the bonding of functional groups and unmodified MCM-48 for comparison. In Fig. 3a, the spectra of all the samples exhibits bands assigned to silica and adsorbed water at 3400 cm^{-1} (the O-H stretching of adsorbed water and the hydrogen bonded silanol groups), 1640 cm^{-1} (the O-H bending of adsorbed water), 1214-1060 cm^{-1} (the Si-O asymmetrical stretching of siloxane), 970 cm^{-1} (the Si-O-(Si, H...H_2O) bending) and 790 cm^{-1} (in-plane bending of geminal silanol) [8,9]. Obviously, the absorbance of the absorption bands at 3400 and 1640 cm^{-1} (Fig. 3b) due to the O-H vibrations of silanol and adsorbed water decreases compared with pure siliceous MCM-48, suggesting the hydrophobicity of the surface of the functionalized MCM-48. Moreover. The IR spectra of all the modified MCM-48 exhibit strong bands assigned to the C-H stretching vibration of methyl, methylene and vinyl groups at 2924, 2854, 1486 and 1413 cm^{-1} (Fig. 3b)[10], indicating that the organic molecules are bonded on the surface of these ordered mesoporous materials successfully. It is known that the modified samples exhibit characteristic features corresponding to the attached functional groups. For the further research, the I and II region of Fig. 3a are enlarged in Fig. 3b and Fig. 3c, respectively. The sample A synthesized with triethoxyvinylsilane shows the feature peaks at 1630 cm^{-1} (alkenyl C=C stretching) and 1413 cm^{-1} (C-H bending mode of the vinyl group) in Fig. 3b. It also can be found that sample C shows the feature peaks at 1710 cm^{-1} (ester C=O stretching) and 1300 cm^{-1} (ester C-O stretching). In Fig. 3c, sample B gives an obvious absorption band at 2254 cm^{-1}, which could be assigned to the C=N stretching of nitrile group. Generally, the band at 2360 cm^{-1} should be assigned to the adsorbed CO_2 of the functionalized samples.

FESEM, HRTEM image and particle size distribution of sample A are shown in Fig. 4. The FESEM image (Fig. 4a) reveals that the vinyl-modified MCM-48 material are nearly spherical with particle diameters ranging from 80 to 120 nm (Fig. 4c). HRTEM image (Fig. 4b) shows worm-like pore channels which run throughout the spherical particles.



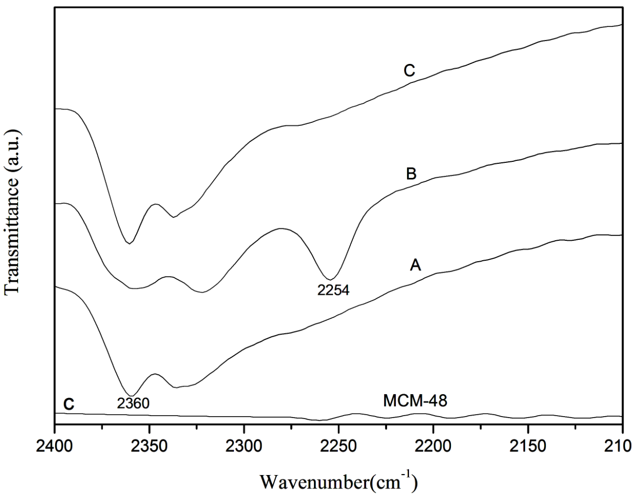


Fig. 3. a) FT-IR spectra of all the samples with different added silane coupling agent: (A) triethoxyvinylsilane, (B) 2-cyanoethyl triethoxysilane, (C) 3-methacryloylpropyltrimethoxysilane. b) Enlarged I region of Fig. 2a. c) Enlarged II region of Fig. 2a

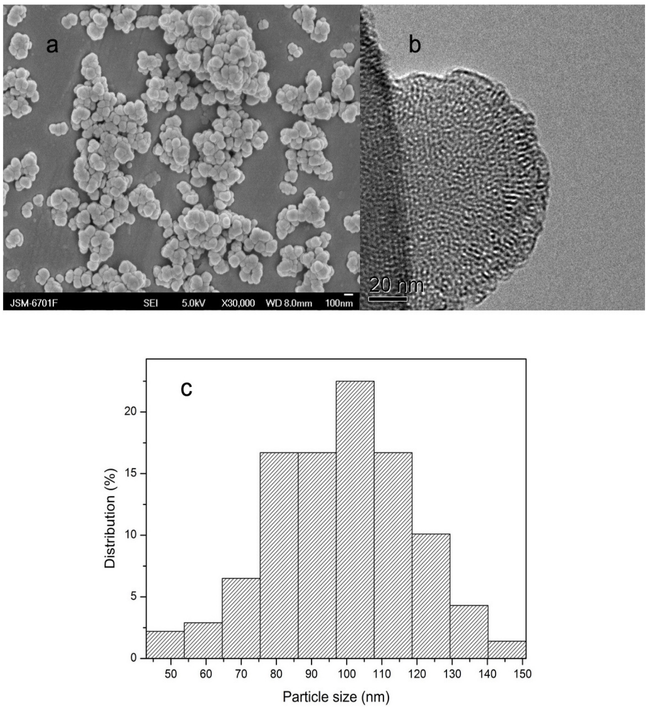


Fig. 4. FESEM, HRTEM images and particle size distribution of sample A with the added triethoxyvinylsilane

Conclusion

This work illustrates that it is possible to prepare organic-inorganic hybrid MCM-48 by co-condensation using various silane coupling agent at room temperature in one-step. The process is facile and rapid without employing hydrothermal synthesis. Characterizations of samples by XRD, N_2 adsorption/desorption, FESEM and HRTEM revealed the high crystallinity, the nano-sized particles morphology and the uniformity of the mesopore structure. FT-IR indicated that added organic groups were anchored on the surface of MCM-48 successfully. Moreover, both the level of ordering and porosity of solids obtained by co-condensation were found to decrease when increasing the length of carbon chain.

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