Preparation of aluminosilicate MCM-41 in desirable forms *via* a novel co-assemble route

Wenyong Lin,[a] Qiang Cai,[a] Wenqin Pang*[a] and Yong Yue[b]

[a] *The Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun, 130023, China. E-mail: inorchem@mail.jlu.edu.cn*
[b] *Wuhan Institute of Physics, The Chinese Academy of Science, Wuhan 430071, China.*

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A new alkali-free synthesis system allows us to prepare aluminosilicate MCM-41 directly in a variety of desirable forms: M-AlMCM-41 (M = H, Cu, Zn, Cd, Ni), the solution ion-exchange and subsequent calcination being avoided; the formation is discussed in terms of a co-assemble process.

Aluminosilicate zeolites with desirable cations compensating the framework charge may find wide applications in areas of adsorption, catalysis[1–3] and nanostructure manufacturing.[4–6] To modify the channels/cages of zeolites with suitable cations, various ion-exchange techniques, such as solid-state interaction,[7,8] impregnation,[9] and chemical vapor deposition[10] have been utilized, besides the conventionally used solution ion-exchange method. However, for the recently developed mesoporous molecular sieve MCM-41,[11,12] which has aroused wide interest, successful ion-exchange has only been performed in solution.[6,13–15] This step, however, will cause some structural collapse owing to the weak hydrothermal stability of MCM-41, especially when the exchange level is high.[14] Further, the ion-exchange occurring in solution will inevitably be incomplete because there is always an equilibrium between the ions within the zeolite channels and those in the liquid. In the present report, we describe a novel co-assemble route for the synthesis of MCM-41, which allows for the direct formation of aluminosilicate MCM-41 in a variety of desirable forms, M-AlMCM-41 (M = H, Cu, Zn, Cd, Ni), the solution ion-exchange step thus being avoided. In addition to this, this method offers us a possibility to obtain a deeper understanding into the formation of MCM type materials. We believe, in the present preparation, a co-assemble process occurs, involving surfactant cations, aluminosilicate species and various ammonia coordinated transition metal complex cations: $M(NH_3)_n^{2+}$ (M = Cu, Zn, Cd, Ni, $n = 4, 6$).

This novel method owes much to the synthesis medium, which involves the substitution of organic weak bases for the conventionally used NaOH or TMAOH, allowing us to introduce desirable inorganic cations without competition of Na^+ or TMA^+. A typical synthesis of Cu-AlMCM-41 was as follows: an ethylamine ($EtNH_2$) solution (70 wt%) was added to a stirred solution containing distilled water, cetyltrimethylammonium bromide (CTAB) and $AlCl_3 \cdot 6H_2O$. Then to the mixture was added a solution prepared by addition of ammonia solution (NH_3 25 wt%) to a $CuCl_2$ solution. After this, tetraethylammonium orthosilicate (TEOS) was added dropwise, leading to a composition of $1.0SiO_2 : xAl_2O_3 : 2.5xCu^{2+} : 20xNH_4OH : 0.14CTAB : 2.4EtNH_2 : 100H_2O$ ($0.01 < x < 0.03$). The reaction mixture was further stirred for 4 h at room temperature before being heated at 110 °C for 4 days. The blue product was recovered by filtration and washed with distilled water until no Cu^{2+} could be detected in the filtrate. After being dried at ambient temperature, the product was heated in air at 600 °C for 7 h, with a heating rate of 1 °C min^{-1} from room temperature to 600 °C. The as-calcined sample was blue. ICP (inductively coupled plasma emission spectroscopy) analysis shows that the Si/Al ratio can be as low as 16, and the Si/Cu ratio as low as 25. Using same procedures, AlMCM-41 can be prepared with other transition metals, such as Zn, Cd and Ni which can form NH_3-coordinated complex cations in a basic medium required for the synthesis. If no metal ion was introduced, the resultant AlMCM-41 can be obtained in its H-form after calcination, the NH_4^+ exchange and subsequent calcination being avoided.

For both the as-synthesized and calcined M-AlMCM-41 (M = H, Cu, Cd, Ni, Zn), XRD shows clear lines characteristic of well defined hexagonal structures. Especially for H-AlMCM-41, an intense main peak (100) with low FWHH and three weak peaks (110), (200), (210) can be clearly resolved, suggesting a highly ordered structure.

To confirm the successful introduction of desirable cations into the exchanging sites of zeolite MCM-41, we immersed the as-calcined sample (typically Cu-AlMCM-41, Si/Al = 16, Si/Cu = 25), in distilled water or $NaNO_3$ aqueous solution (0.05 M), corresponding to a liquid to solid ratio of 200 ml g^{-1}. After stirring for 1 h, the samples were filtered and the fitrate was collected in both cases. For the slurry with distilled water, no copper content was detected, while for the slurry with $NaNO_3$ copper ions could clearly detected. ICP analysis indicates that up to 65% of copper ions can be exchanged after slurrying twice. The exchangeable nature of the copper ions within the AlMCM-41 strongly confirms that the most of the metal ions are located as charge compensating cations. The as-calcined Cu-AlMCM-41 shows clear sharp lines ($g_{\parallel} = 2.34$, $g = 2.07$) in its EPR spectra at both room temperature and −197 °C and the spectra are similar to dehydrated Cu-AlMCM-41 prepared by solution ion-exchange,[13] but different from pure silica MCM-41 containing Cu^{II} ions.[16] Thus the Cu^{II} cations are likely to be mainly in a six-coordinate environment, as for Cu^{II} exchanged into AlMCM-41 in solution.

To our knowledge, the ion exchanging sites of zeolites are usually produced by substituting trivalent Al^{3+} for silicon atoms and the pure silica MCM-41 shows no or very low ion-exchange capacity.[13] In the present case, the successful incorporation of Al^{3+} into the framework of MCM-41 is established by NMR measurements (Bruker MSL-400 spectrometer), as shown in Fig. 1 for H-AlMCM-41 and Cu-AlMCM-41 samples before and after calcination. The as-synthesized samples show only one signal at 51 ppm, corresponding to four-coordinate Al in the framework sites. Upon calcination, a small fraction of aluminium becomes extraframework in nature, as shown by a small peak at −3.5 ppm. The four-coordinate Al^{3+} within the silica framework will be compensated by various extraframework cations. From the synthesis procedure above, it is apparent that the involvement of $EtNH_2$ as the base source renders the synthesis mixture alkali-free. However, of $EtNH_2$ is basic enough ($pK_b = 3.25$) not only to form MCM-41 but also to dissolve the Al source material and thus Al^{3+} can be incorporated into the framework readily. Other lyotropic organic amines such as dimethylamine and diethylamine are also suitable for this type of preparation. It is this feature of the synthesis that allows us to introduce various cations into the reaction media, and the cations can be occluded within the bulk product and are subsequently located at the charge-balancing

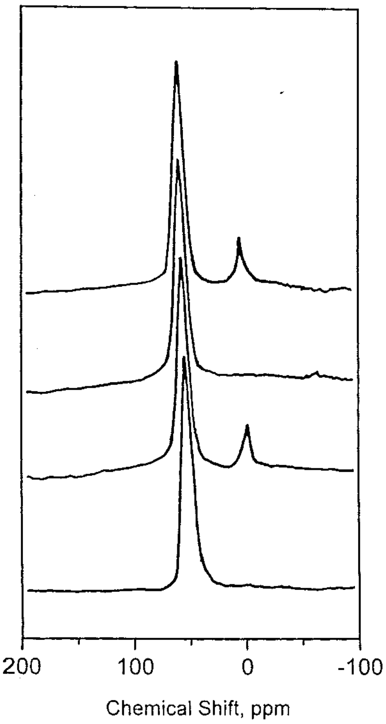

Fig. 1 ^{27}Al MAS NMR spectra of (from bottom to top) as-synthesized H-AlMCM-41, calcined H-AlMCM-41, as-synthesized Cu-AlMCM-41 and calcined Cu-AlMCM-41.

sites upon calcination. On the other hand, ammonia is used to form complex cations with the transition metal ions, preventing them from being precipitated under the basic conditions used.

The occlusion of complex cations within the silicate mesophase may be proposed as a co-assemble process. First, the TEOS molecules are hydrolyzed into oligomeric silicate acids. Then, the surfactant cations (CTA$^+$) displace the protons of these acids to form inorganic–organic composites, which would further assemble into a periodic mesophase. When the basic conditions are taken into account, the metal cations can also associate with the silicate species by exchanging protons of the silicate acids. As a result, when the cross-linking between the silica leads to solidification of the mesophase the complex cations are occluded within the bulk product. The most likely position of these cations is at the interface between inorganic and organic fractions. Upon calcination to remove the surfactant, the metal complex is decomposed and the remaining metal cations are located at the exchange sites of MCM-41, compensating the negative charge of the aluminosilicate framework. Protonic $EtNH_2$ ($EtNH_3^+$), and NH_3 (NH_4^+) could also be occluded within the as-synthesized MCM-41 at the interface between the surfactant and silicate framework. However, both of these cations can be readily removed by calcination.

Thus, the present co-assemble route offers us not only a convenient route for direct preparation of AlMCM-41 in desirable forms, but is also a potential pathway for encapsulating functional cationic inorganic species within the inorganic–organic interface in a highly dispersed state.

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