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Communications

Nanosized Zeolites Templated by Metal−Amine Complexes

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Organic molecules containing quaternary ammonium groups are widely used as structure directing agents for stabilization of certain framework type structures possessing variable porosity.[1] Besides, the organic additives alter the degree of super-saturation in the initial precursor solutions and direct the formation of stable nanocrystallites in colloidal form.[2] Templating of molecular sieves is also possible by application of metal complexes in the form of metallocenes,[3] while metal−amine complexes can serve as structure directing agents for the preparation of microporous aluminophosphates ($AlPO_n$) and clathrasil type materials.[4]

This communication reports on the synthesis of nanosized EDI-type zeolites by a dual templating approach, that is, using both metal−amine complexes $[M(NH_3)_4]^{2+}$ (M = Cu, Pd, Pt) and tetramethylammonium hydroxide. The framework structure of EDI-type zeolite consists of an interconnected three-dimensional channel system defined by the apertures of two different types of eight-membered rings (mean diameters of 2.8 × 3.8 Å and 2.0 × 3.1 Å). The EDI-type molecular sieve with nanosized dimensions is essential for preparation of hierarchical porous structures and thin films with high water and ion-exchange capacities.

The microporous nanosized crystals were synthesized from solutions with the following chemical composition: 2.37:0.05:1:4.16:244:0.5:15 $(TMA)_2O/Na_2O/Al_2O_3/SiO_2/H_2O/(TM)O/NH_3$; TM is the transition metal, that is, Cu^{2+}, Pd^{2+}, Pt^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}. The metal nitrate salts, aluminum isopropoxide, Ludox HS-30 Silica, and TMAOH pentahydrate used as reagents for preparation of all samples were obtained from Aldrich. For the synthesis of Cu-containing molecular sieves, several solutions were prepared and abbreviated as follows: without NH_3 (Cu-1), without Cu (N-2), without Cu and NH_3 (Y-0), and with different amounts of Cu (CuN-3 and CuN-4; see Table 1). The precursor solutions were aged at room temperature for 70 h followed by hydrothermal treatment (HT) at 100 °C for 3 days (only the syntheses of Pd-containing samples were carried out at 60 °C for 7 days to avoid the reduction of Pd^{2+} to Pd^0). After purification, the microporous nanocrystals were stabilized in aqueous suspensions with a solid concentration of ∼5 wt % at pH = 10.6 and thoroughly characterized.

The structure of the Cu-containing samples was determined by X-ray diffraction (XRD; Figure 1), and the crystalline products are summarized in Table 1. As can be seen, the precursor solution with no addition of Cu and NH_3 (Y-0) was transformed into pure FAU nanosized crystals (Figure 1a). The same crystallites were obtained from the solutions containing copper (Cu-1) and ammonia (N-2) only (Figure 1b,c). In the case of sample N-2, the formation of nanosized LTA crystals as a side phase was stimulated; the reflections

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Table 1. Amount of CuO and NH_3 in the Precursor Solutions, Type of Crystalline Phase and Chemical Composition of Crystalline Samples Determined by ICP-AES Elemental Analysis (b)

sample	CuO	NH_3	phase[a]	Cu/Al[b]	Na/Al[b]	Si/Al[b]
Y-0			FAU		0.43	1.70
Cu-1	0.5		FAU	0.24	0.43	1.90
N-2		15	FAU		0.39	1.71
CuN-3	0.05	15	FAU + EDI	0.20	0.21	1.76
CuN-4	0.5	15	EDI	0.39	0.08	1.37

[a,b] Based on XRD (a) and chemical composition of crystalline samples determined by ICP-AES elemental analysis (b).

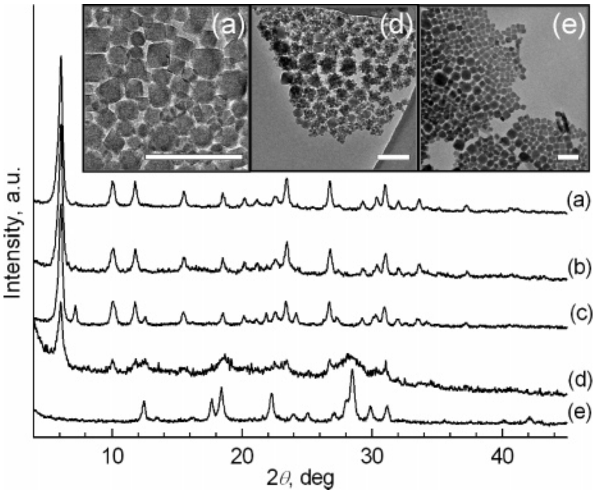

Figure 1. XRD patterns of samples synthesized from solutions Y-0 (a), Cu-1 (b), N-2 (c), CuN-3 (d), and CuN-4 (e); the insets show the TEM pictures of FAU (a), the mixture of FAU and EDI (d), and EDI crystals (e). (M = 200 nm.)

corresponding to the LTA phase at 7.2°, 12.5°, and 21.8° 2θ can be seen in Figure 1c. By combining copper and ammonia in two different ratios (samples CuN-3 and CuN-4, Table 1), a different crystallization pathway was featured in the precursor solutions resulting in the formation of crystalline products with variable framework structures. At low copper concentrations (CuN-3), the crystallization of the FAU-type zeolite was inhibited, and a second set of reflections corresponding to the EDI-type molecular sieve are occurring with low intensity and high broadening (Figure 1d). Furthermore, by increasing the copper concentration in the precursor solutions (CuN-4) and keeping the ammonia constant, discrete EDI nanocrystals were synthesized as a pure phase with a high degree of crystallinity (Figure 1e).

The position of the Bragg reflections match completely with Na-exchanged zeolite K-F (EDI-type); however, a considerable broadening which is a signature of nanocrystallites was observed. The mean sizes of the crystalline domain for pure FAU synthesized from solutions N-2 and Y-0 are very similar, that is, about 80 nm, while in sample Cu-1 a slight increase in the particle size to 90 nm was measured (the results are based on the Scherrer equation). These data are supported by the transmission electron microscopy (TEM) images recorded from purified samples shown as insets in Figure 1. The FAU nanocrystals have orthorhombic morphology (Figure 1, inset a), while the EDI nanocrystals appear as well-built cubes with sharp edges (Figure 1, inset e). In the case of sample CuN-3 (Figure 1, insert d), two separate phases are distinguishable, that is, less orthorhombic FAU crystals and dominant flake-shaped particles assigned as precursors of EDI-type zeolite. The pure Cu-EDI nanocrystals (CuN-4) exhibit perfect cubic shape in contrast to the sample containing both EDI and FAU particles (CuN-3). For sample CuN-3, further growth and complete crystallization of EDI zeolite was not achieved, which is probably due to the low concentration of the copper−amine complex $[Cu(NH_3)_4]^{2+}$ in the precursor solution. This suggests that the copper−amine complex formed in the highly alkaline solutions behaves as a structure directing agent for the formation of colloidal EDI zeolite.

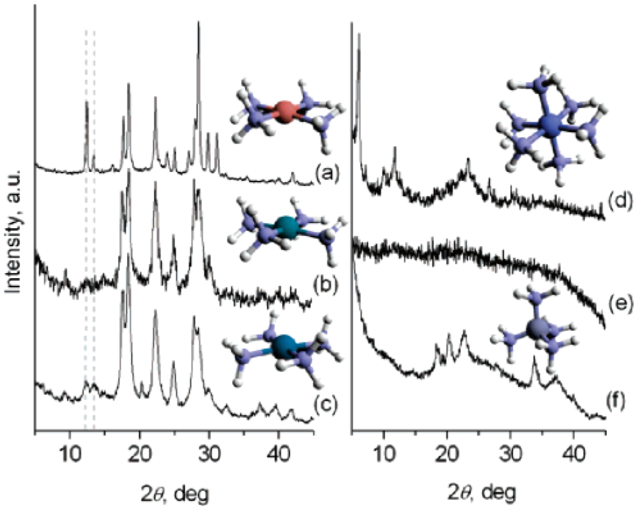

Figure 2. XRD patterns of samples synthesized with Cu (a), Pd (b), Pt (c), Ni (d), Co (e), and Zn (f). The insets show the preferred coordination of the different metals, i.e., square planar $[M(NH_3)_4]^{2+}$ (M = Cu, Pd, Pt) in parts a−c, octahedral $[M(NH_3)_6]^{2+}$ (M = Ni, Co) in part d, and tetrahedral $[Zn(NH_3)_4]^{2+}$ in part f.

The influence of the metal−amine complexes on the templated crystalline products was studied by replacing the copper in the initial precursor solutions with different transition metals (Figure 2). As can be seen, the EDI-type zeolite was only obtained in samples containing Cu^{2+}, Pd^{2+}, and Pt^{2+}, which is probably due to the preferred formation of stable square planar amine complexes $[M(NH_3)_4]^{2+}$ (see the insets in Figure 2). However, no EDI-type crystals were obtained with Ni^{2+} and Co^{2+}, which can be explained with their preferred octahedral coordination. In the case of Zn^{2+}, a tetrahedral amine complex was formed that is resulting in the crystallization of the dense aluminosilicate phase.

To elucidate whether the copper−amine complexes are serving as templating species for EDI zeolite, the samples were subjected to IR study (Figure 3d,e). The first striking difference in the spectra is the appearance of a band at 1275 cm^{-1}, which corresponds to the symmetric deformation of NH_3 coordinated to Cu^{2+}. This band is specific for copper−amine complexes and appears only in the two samples where Cu and NH_3 were used (Figure 3d,e). The TMA cations present in the zeolite structures give rise to the bands at 1490 cm^{-1} (asymmetric deformation mode of the CH_3 groups), 1420 cm^{-1} (N−CH_3 rocking modes), and 950 cm^{-1} (C−N asymmetric stretching vibrations). These bands have the highest intensity in the pure FAU where TMA is the only template (Figure 3a). However, in the dually templated EDI zeolites, the amount of incorporated TMA is less, and therefore the intensity of these bands is lower.

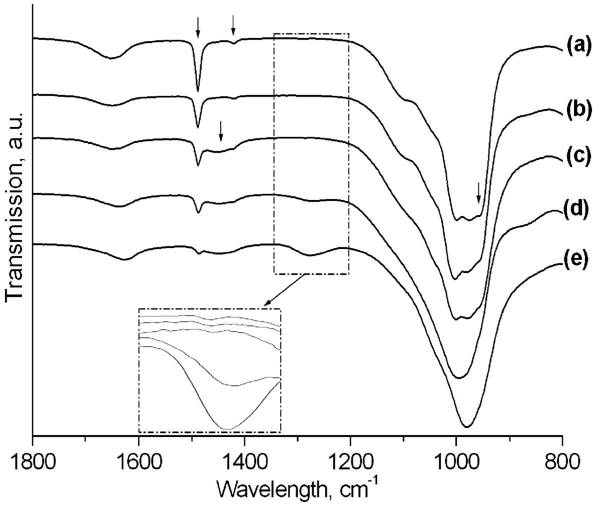

Figure 3. IR spectra of zeolite samples synthesized from solutions Y-0 (a), Cu-1 (b), N-2 (c), CuN-3 (d), and CuN-4 (e).

A significant difference in the optical appearance of the colloidal suspensions containing pure FAU, Cu-EDI, and Cu-FAU is also observed. A white-milky suspension corresponds to pure FAU zeolite templated by TMA only, a green-colored one corresponds to Cu-FAU, while a deeply blue suspension represents Cu-EDI-type zeolite. The deep-blue color of Cu-EDI suspensions is a clear signature for the existence of copper−amine complexes in the crystalline samples.

The chemical composition of the crystalline samples derived from inductively coupled plasma (ICP) elemental analysis shows that the EDI zeolite is an aluminum-rich material with a Si/Al ratio of 1.37 (see Table 1). The amount of Cu in the EDI crystals is increased in comparison with FAU; that is, Cu/Al ratios of 0.24, 0.39, and 0.20 for FAU, EDI, and the FAU/EDI mixture, respectively, were measured. These data coupled with the IR and XRD suggest that $[Cu(NH_3)_4]^{2+}$ complexes are decisive for the growth of EDI-type zeolite.

In conclusion, the crystallization of nanosized EDI-type zeolite is directed by square planar metal−amine complexes $[M(NH_3)_4]^{2+}$ ($M = Cu$, Pd, and Pt) used as co-templating species to the tetramethylammonium cations. Moreover, the single additions of copper cations or ammonia lead to the crystallization of pure nanosized FAU zeolite, whereas the combination of both generated EDI-type microporous material. The application of metal−amine complexes as templates for preparation of colloidal zeolites was achievable because the syntheses were carried out at temperatures lower than 100 °C and, thus, avoided the decomposition of thermally unstable complexes. The current approach opens up the possibility to prepare new or well-known zeolites in colloidal form by using a versatile class of functionalized metal−amine templates. Metal−amine complexes are promising templates for zeolite synthesis as they carry a high positive charge density for interaction with the anionic silicate species and offer new shapes such as square planar or linear, which are not common with classic quaternary ammonium templates.

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