Solvent-free Synthesis of Clathrasils using Metal–Organic Complexes as Structure-directing Agents

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The two metal–organic complex salts $[Co(C_5H_4Me)_2]PF_6$ and $[Fe(C_6H_6)(C_5H_5)]PF_6$ are tested as structure-directing agents in the synthesis of pure silica zeotype materials and give the clathrasil structure dodecasil-1H only in the solvent-free synthesis system SiO_2–NH_4F–metal complex.

The inclusion of molecular species into the crystallographically defined voids of molecular sieves is a valuable method to generate ordered dispersions of these species, with the molecular sieve controlling their steric confinement and defining their topological arrangement.[1,2] Much effort has been devoted to the introduction of metal complexes to produce immobilized metal-complex catalysts[3,4] or materials with potential applications in linear or nonlinear optics.[4,5] So far, mainly post-synthesis methods have been applied successfully. These methods use the empty pore systems of molecular sieves that were prepared and calcined in a previous step and which are then loaded by diffusional processes (ion-exchange, vapour-phase insertion or ship-in-the-bottle syntheses).[3] These processes tend to give non-stoichiometric and inhomogeneous products and the crystallinity of the host framework may be decreased.

Recently, we have presented our results on the direct incorporation of metal–organic complexes into microporous, crystalline pure silica frameworks (clathrasils).[6,7] The molecules act as structure-directing agents during the synthesis and are occluded in the growing silica framework. These syntheses were carried out under mild hydrothermal conditions in neutral to slightly acidic media using the cobaltocenium cation $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+$ as structure-directing and fluoride[8] as mineralizing agent. With increasing synthesis temperatures ranging from 413 to 463 K, we have obtained three different clathrasil structures from the system SiO_2–NH_4F–$[Co(C_5H_5)_2]PF_6$–H_2O: nonasil (framework topology:[9] NON), octadecasil (AST) and dodecasil-1H (DOH). These compounds showed high crystallinities and well-defined stoichiometries.[6,7] In parallel to our work, Balkus and Shepelev[10] reported the crystallization of cobaltocenium nonasil from basic aqueous solutions.

So far, the application of metal complexes as structure-directing agents has been restricted to the cobaltocenium cation which possesses outstanding stability. Except for alkyl derivatives of this cation, only a few other metal–organic complexes can be expected to withstand the conditions of hydrothermal crystallization because they tend to hydrolyse in aqueous solution or to decompose upon heating.

To extend the applicability of metal complexes in the structure-directed synthesis[11] of zeolite-type (zeotype) materials, milder synthesis conditions are necessary. With regard to the possible hydrolysis, the elimination of water from the synthesis system can be an important step. Dry or nearly dry synthesis methods have first been applied in order to raise the productivity of zeolite syntheses (more efficient use of autoclave volumes), to minimize the amount of valuable amines that act as structure-directing agents, to eliminate the separation step after the synthesis and, consequently, the amount of polluted mother-liquor.[12,13] More recently, Althoff *et al.*[14] have demonstrated that in solvent-free fluoride-based synthesis systems the silica precursor is converted into SiF_4 as a volatile

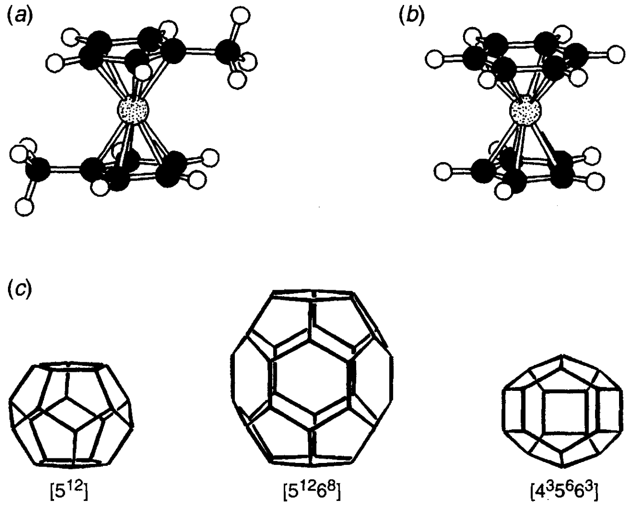

Fig. 1 The metal–organic complex cations 1,1′-dimethylcobaltocenium (*a*) and benzene(cyclopentadienyl)iron (*b*) and the cages (*c*) of the three-dimensional framework structure of dodecasil-1H (DOH). A detailed description of this structure is given in ref. 22.

Table 1 Molar composition of the synthesis mixtures, crystallization conditions and products obtained according to microscopic analysis and powder X-ray diffractometry

Metal complex	SiO_2	NH_4F	H_2O	*T*/K	*t*/d	Product
$[Co(C_5H_5)_2]PF_6$						
0.3	1	1	60	413–433	5–21	NON[6]
0.3	1	1	60	443	7–12	AST[6]
0.08	1	1	10	463	10	AST + DOH[6]
0.25	1	1	0	433	5–11	AST
$[Co(C_5H_4Me)_2]PF_6$						
0.25	1	1	25	413–453	5	clear, yellow solution
0.25	1	1	0	433–453	5	DOH
$[Fe(C_6H_6)(C_5H_5)PF_6$						
0.25	1	1	10–25	423–463	5–10	colourless needles + colourless solution
0.1	1	1	0	433–443	5–10	DOH

and reactive silica precursor ($SiO_2 + NH_4 \rightarrow SiF_4 + 2H_2O$) and that *via* this process the vapour-phase deposition of zeotype materials may be possible. Water is formed as an intermediate during these reactions, but its amount is minimal.

Applying the solvent-free synthesis method, we succeeded in crystallizing DOH-type clathrasils with hexafluorophosphate salts of 1,1′-dimethylcobaltocenium $[Co^{III}(\eta^5\text{-}C_5H_4Me)_2]^+$ or benzene(cyclopentadienyl)iron $[Fe^{II}(\eta^6\text{-}C_6H_6)(\eta^5C_5H_5)]^+$ as structure-directing agents (Fig. 1). In aqueous media no microporous compounds were obtained. Table 1 summarizes the synthesis conditions and the resulting products and Table 2 lists the formulae and the refined lattice constants of the corresponding clathrasils.

The two metal complexes, $[Fe(C_6H_6)(C_5H_5)]^+$ and $[Co(C_5H_4Me)_2]^+$, were synthesized as hexafluorophosphate salts according to published methods.[15,16] Both salts possess intense yellow colours. For the solvent-free synthesis of clathrasils, the starting chemicals were ground and mixed in a mortar in the following order: first, the silica source was mixed with ammonium fluoride and then the metal complex was added. The dry powder was transferred into Teflon-lined steel autoclaves and heated to the crystallization temperature. Surprisingly, on mixing in the order silica–metal complex–NH_4F no crystallization occurs; we assume that only on mixing silica with NH_4F first, are reactive oxofluorosilicate precursors formed, which are necessary for the subsequent crystallization.

With 1,1′-dimethylcobaltocenium $[Co(C_5H_4Me)_2]PF_6$ yellow, hexagonal, plate-like crystals of dodecasil-1H [Fig. 2(*a*)] crystallized from the solvent-free synthesis system whereas no precipitate was found in aqueous systems which were treated hydrothermally for prolonged reaction periods at 413–463 K. Only complete dissolution of the starting materials to give a transparent solution was observed. The yellow colour of this solution indicated that the metal complex was still intact.

$[Fe(C_6H_6)(C_5H_5)]PF_6$ yielded pale yellow DOH crystals of less regular morphology [Fig. 2(*b*)] while from aqueous solution colourless, needle-shaped, bundle-like intergrown crystals grew instead [Fig. 2(*c*)]† and the mother-liquor was colourless, indicating that under hydrothermal conditions the metal–organic iron complex cations were completely decomposed.

The fact that the new DOH clathrasils also possess the typical yellow colours of the metal complexes was a first indication that these were incorporated as intact molecules. Further evidence comes from infrared spectra exhibiting similar absorptions in the region of the C–H and C–C stretching modes as the corresponding metal complex salts.[17,18] No indications of the inclusion of other species, *e.g.* possible decomposition products, were found.

The solvent-free synthesis also works with the cobaltocenium ion $[Co(C_5H_5)_2]^+$, but only AST was formed as yellow, octahedral crystals.

The concept of using metal–organic complexes as structure-directing agents in the synthesis of zeotype materials appears to be a more general approach than might have been anticipated. Balkus *et al.* have recently shown that the cobaltocenium cation can also be used as a structure-directing agent for the formation of $AlPO_4$ molecular sieves, yielding $AlPO_4$-5 (AFI) and $AlPO_4$-16 (AST).[19] As reported in this communication, $[Fe(C_6H_6)(C_5H_5)]^+$ is the first metal complex which is not a cobaltocenium cation and which acts as a structure-director in the synthesis of zeotypes. Other metal complexes are currently being tested and synthesis conditions adapted to their specific reactivities.

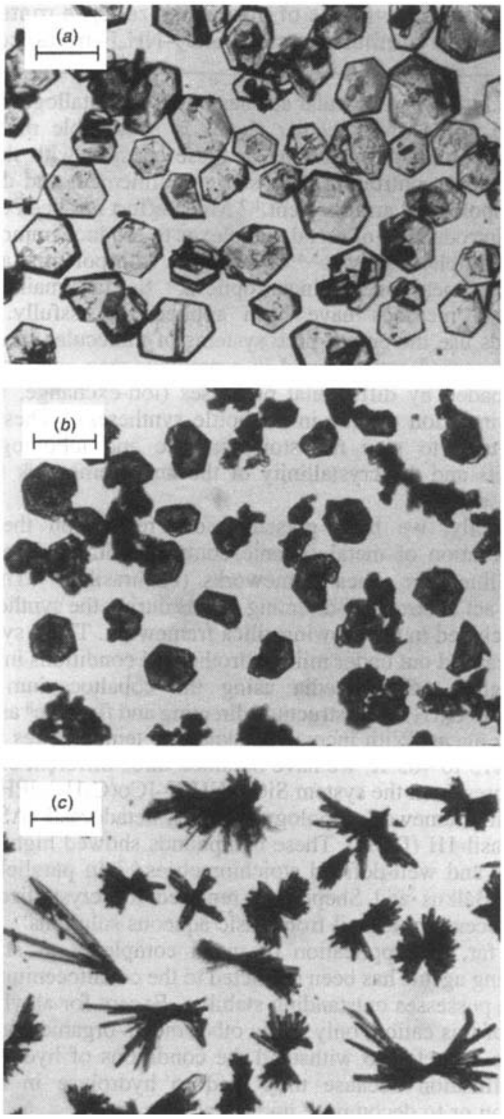

Fig. 2 Optical microscopy of the synthesis products (scale bars correspond to 0.1 mm): (*a*) yellow hexagonal DOH crystals from the solvent-free synthesis with $[Co(C_5H_4Me)_2]PF_6$; (*b*) less regular shaped, yellow DOH crystals from the solvent-free synthesis with $[Fe(C_6H_6)(C_5H_5)]PF_6$; (*c*) colourless needles of an unidentified phase from the aqueous synthesis with $[Fe(C_6H_6)(C_5H_5)]PF_6$

Table 2 Composition and hexagonal lattice constants of DOH-type clathrasils prepared using metal–organic complexes as structure directors. N_1 = number of X-ray reflections used in the final refinement of lattice constants; N_2 = number of X-ray reflections observed in the range 2θ = 10–80° (Cu-Kα_1 radiation)

Compound chemical composition	Lattice constants/Å	U/Å^3	N_1	N_2
Cobaltocenium fluoride–DOH[6]	a = 13.780 (2)	1836	—	—
$[SiO_2]_{34}[Co(C_5H_5)_2]F$	c = 11.167 (4)			
1,1′-Dimethylcobaltocenium fluoride–DOH	a = 13.798 (1)	1846	52	54
$[SiO_2]_{34}[Co(C_5H_4Me)_2]F^-$	c = 11.200 (1)			
Benzene(cyclopentadienyl)iron fluoride–DOH	a = 13.823 (1)	1854	48	51
$[SiO_2]_{34}[Fe(C_6H_6)(C_5H_5)]F^-$	c = 11.204 (1)			

The solvent-free synthesis route[12–14] represents a further outstanding development in zeolite synthesis.[11] Our results demonstrate that this route represents a valuable synthesis technique making possible the use of molecular species in the synthesis of zeolites which are sensitive to hydrolysis. The elimination of solvation effects is another important feature in solvent-free synthesis systems. These effects influence the availability of molecules during the crystallization and the gel chemistry of the synthesis systems. In the case of the 1,1′-dimethylcobaltocenium cation, they may be responsible for the different results obtained in aqueous and solvent-free synthesis systems. The elimination of solvation effects may be exploited to obtain porous framework structures from solvent-free systems that are different from those formed in aqueous media. Even new framework topologies might become available.

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† The powder pattern of this colourless material has been indexed in the monoclinic system [refined lattice constants: a = 11.991(1), b = 6.486(1), c = 9.876(1) Å, β = 107.71(1)°] but we have not been able to identify it using the ICDD Powder Diffraction File.[21]

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