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*Franco Laeri, Ferdi Schüth, Ulrich Simon, Michael Wark (Eds.)*



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**Part 1**  
**Synthesis Routes for Functional Composites**  
**Based on Nanoporous Materials**

## Synthesis Routes for Functional Composites Based on Nanoporous Materials

*Michael Wark*

Molecular engineering is reaching highly elaborate levels of sophistication. The analysis of the cooperative behavior of single molecules or clusters of molecules within controlled spatial assemblies is a field undergoing continuous progress. The most common inorganic matrices for the construction of inorganic/inorganic or inorganic/organic host–guest composites are zeolites, aluminum phosphates, and mesoporous silicates or aluminum silicates. An overview of their synthesis procedures was recently published by van Bekkum, Flanigan, Jacobs, and Jansen [1]. Over the past 20 years, there has been a dramatic increase in the literature of design, synthesis, characterization, and property evaluation of zeolites and molecular-sieve based composites for catalysis and optical applications. In addition to metal and metal oxide clusters embedded in the regular pore systems of the host materials, the encapsulation of organic dye molecules and metal organic compounds has gained particular attention. A summary of novel composite materials based on zeolites and related structures, including pigments, phosphors, optical hole burning materials, nonlinear optical materials, quantum size effect materials, molecular wires, membranes, and sensors, is given by Behrens and Stucky [2].

Reviews summarizing the synthesis procedures leading to the formation of metal clusters or metal nanoparticles in the pore systems have been written by Kawi and Gates [3] and by Schulz-Ekloff [4]. Principles important for the introduction of metal oxide or metal sulfide clusters were reviewed by Weitkamp et al. [5].

Bioinorganic chemistry is profiting from a more and more developed design of molecular systems and nanoscale mechanisms. For example, bio-inorganic structural motifs can potentially model metalloenzyme structures and functions in terms of steric effects imposed by the inorganic edifice. One aim of such model systems is the mimicking of enzymatic systems. Overviews regarding synthesis routes and properties of zeolite-based supramolecular assemblies of metal organic compounds, such as salens or phthalocyanines, are given by De Vos and Jacobs [6], or very recently by Wark [7]. The preparation and the optical properties of all kinds of chromophores in zeolites, porous silica, and are described by Schulz-Ekloff et al. [8].

The chapters in this section highlight some recent and detailed developments in the synthesis and construction of host–guest composites with novel optical properties and high potential for applications such as miniaturized optical switches, optical gas sensors, or highly effective light emitters.

The first four chapters concentrate on organic dye molecules as guests, mainly on microporous zeolites or aluminophosphates as matrices providing pores with diameters less than 2 nm. In the subsequent chapters mesoporous materials with channel diameters between 2 and 10 nm are mainly used. The synthesis of these hosts is based on long-chain alkyl amine surfactants [9], block copolymers [10], or even expanded block-copolymers [11] as structure-directing agents. Recently, polymer-templated ordered silicas with cage-like mesostructure have been developed [12].

In the first chapter (Chapter 1.1) Behrens et al. present methods for the preparation of functional composites based on zeotypes. They incorporated different chromophors. As synthesis routes they used either an unspecific co-occlusion, where the guest species is just added to the zeolite synthesis gel containing an additional structure-directing agent (SDA), or a direct method, in which the modified functional guest species directly acts as SDA. The incorporated functional units obtained are arranged and protected by the inorganic framework leading to altered optical properties. These first examples concentrated on rather stable guest molecules, however, the development of milder synthesis methods, to introduce species with new magnetic properties for example, seems to be imminent.

A real “ship-in-the-bottle” synthesis of organic dyes in the cages of faujasite-type zeolites was carried out by Wöhrle et al. (Chapter 1.2). The developed methods use the fixation of a first educt with the host by acid–base interactions. Then the synthesis of the chromophore is achieved by reaction of the second educt, also introduced into the pores. The obtained loadings were as high as  $10^{-4}$  mol dye per gram zeolite. The host–guest interactions were studied for the encapsulated photochromic spiropyran as an example. Compared with organic polymer hosts in the matrix of a dealuminated zeolite Y, a dramatically improved stability of the switched state against thermal relaxation and an extreme high stability during photoinduced switching were found.

Ganschow et al. (Chapter 1.3) established a one-step procedure for the covalent anchorage of dyes at the pore walls of the mesoporous Si-MCM-41 and they achieved the stable crystallization inclusion of highly fluorescing dye molecules during the synthesis of microporous  $\text{AlPO}_4\text{-5}$  by using microwave radiation. It turned out that during the rapid microwave-assisted crystallization, a preferential accommodation of smaller chromophores takes place. Larger dye molecules enter later. Such accommodation enables directed energy transfer between the hosted dye molecules. The dye accommodation in porous minerals can be analyzed by bifocal microscopy (Chapter 4.3 by Seebacher et al.). In order to obtain optimized crystal geometries for micro-lasing (Chapter 4.6 by Benmohammadi et al.) the synthesis conditions were varied so that  $\text{AlPO}_4\text{-5}$  crystals with low length-to-width aspect ratios were formed.

The chapter of Kornatowski and Zadrozna (Chapter 1.4) deals also with the con-

trol of the crystal morphology of the  $\text{AlPO}_4\text{-5}$  molecular sieve and its derivatives. Their growth can be controlled to a high extent and extremely flat crystals with length-to-width aspect ratios reduced to about 0.1 and the crystal width enlarged to about  $120\ \mu\text{m}$  were obtained for the first time for CrAPO-5. The crystal length is reduced owing to the adsorption of organic and inorganic additional components/co-templates on the growing crystals.

Nanoporous crystals can also be used for the confinement of liquid crystals. This is demonstrated by Frunza et al. (Chapter 1.5) who studied the influence of the molecular sieve pore/cavity system on the phase transition characteristic and the host-guest interactions that stabilize the cyanobiphenyl liquid crystal molecules inside the pores. It has been found that size as well as shape and interconnectivity of the pores play an important role for the modification of properties of liquid crystals. Phase transitions characteristic of liquid crystals were only observed if the nanoporous hosts provide interconnected pores larger than 3 nm as they exist in extra large pore SBA-15 material.

Hybrid materials with adjustable content and molecular weight of the loaded organic polymer fraction can be synthesized by cationic host-guest polymerization of vinyl ether monomers within MCM-41 materials. The synthesis routes to reach this goal are discussed by Spange et al. in Chapter 1.6. The structures of the polymer chains in MCM-41 are identical to the pure, bulk polymers, whereas the glass-transition temperature is significantly different from those of the bulk fraction. The given synthesis procedures are suitable for producing flexible polymer chains within pores of inorganic materials to study their dynamics in confined geometry (compared to chapter 3.2 by Kremer et al.).

The next chapter by Behrens et al. (Chapter 1.7) report that it is possible to obtain functional mesostructured organic/inorganic hybrid materials directly by a self-assembly process in which the functional organic molecules act themselves as amphiphilic SDAs in a synthesis approach analogous to the preparation of M41S mesophases. Special structure-directing effects that cannot be observed with non-functional amphiphiles become apparent: aggregation tendencies between the functional amphiphiles can lead to a clear preference for only one type of mesostructure and the possibility of forming aggregates of different type can give rise to different mesostructures for different surfactants with similar lengths. The aggregation phenomena are influenced by interactions between the aromatic systems of the chromophore amphiphiles.

Besides organic dye molecules, various inorganic guest species also can be arranged and stabilized by encapsulation in nanoporous materials. The next two chapters give some examples of the development of composite materials with prospective new physical and especially optical properties.

In Chapter 1.8. Wark et al. discuss the arrangement of metal oxide species in the pores of molecular sieves either in mononuclear dispersion or as clusters or nanoparticles. The encapsulation was predominately achieved by post-synthetic treatment using chemical vapor deposition (CVD), ion exchange, and impregnation. The stabilized differently sized metal oxide species differ drastically in their behavior against reductive gases. The composites can be used for a sensing of gases