



DOI: 10.1002/adfm.200600925

Transparent Zeolite-Polymer Hybrid Materials with Adaptable Properties**

By Stéphane Suárez, André Devaux, Jorge Bañuelos, Olivia Bossart, Andreas Kunzmann, and Gion Calzaferri*

We report here on a simple preparation procedure for highly transparent zeolite-polymer hybrid materials and polymer covered zeolite L monolayers. Wrapping up zeolites containing, e.g., dye molecules as guest species with alkoxysilane derivatives results in an efficient dispersion of the nano particles into the organic liquid monomer. The following copolymerisation process leads to a hard, insoluble and transparent material containing zeolites. Optical properties such as colour, luminescence, refractive index or photochromism can be adapted by simply changing the type and amount of the guest in the zeolite crystals, while transparency is maintained.

1. Introduction

Molecular sieves have been shown to be ideal host materials for the supramolecular organisation of dye molecules, complexes or clusters. An increased chemical or thermal stability of the inserted species can often be observed in such host-guest materials. The defined geometry of the cavities and channels can be transferred to the spatial arrangement of guest species, thereby generating highly organised materials. Further functionalities can be added by assembling such host-guest systems into well-defined macroscopic structures on various supports^[1–5] and by promoting communication between guests and external species or devices.^[5,6] The large variety in pore structure and morphologies provided by different types of molecular sieves offers many possibilities for the design of host-guest systems with specific properties.^[7] Readers are referred to ref. [8] for a review on chromophores in porous silicas and minerals. Aspects of photochemistry as well as the inclusion of naphthalene and anthracene into zeolite L have recently been extensively reviewed by Hashimoto et al., [9,10] pyrene-zeolite L composites were investigated by Liu and Thomas.^[11]

We have been using zeolite L in most of our experiments as it has proven to be a very versatile host material. Zeolite L crystals are cylindrically shaped, porous aluminosilicates featuring a hexagonal symmetry. The size and aspect ratio of the crystal can be tuned over a wide range. [12] A single crystal consists of many one dimensional channels oriented parallel to the cylinder axis. For example, a crystal of 600 nm diameter consists of approximately 100 000 strictly parallel channels. These can be filled with suitable organic guests. Geometrical constrains of the hosts framework lead to supramolecular organisation of the guests in the channels. Thus very high concentrations of monomeric dye molecules can be realized. An interesting side effect of including dyes into zeolite crystals is the protection of these molecules against chemical attack, photobleaching or thermal decomposition. For example, the light sensitive compound 1,6-diphenylhexatriene is considerably stabilised when inserted into zeolite L. This stabilisation effect is the result of a lack of space in the channel for a trans to cis isomerisation of the molecule, a step necessary for the photoinduced degradation. [13] Photochromism can occur inside the channels, if there is enough space to accommodate the isomerisation step.^[14] Protection from chemical attack is observed in many cases where reactive molecules have to overcome a large diffusional barrier or where anions such as hypochlorite cannot enter the negatively charged channels.^[15] García et al. observed that inclusion of α,ω-diphenylallyl cations (DPP) into ZSM-5 leads to a major increase in their stability against reaction with water. [16] It was suggested that the phenyl caps of the included DPPs are acting as molecular stoppers, protecting the positive DPP centres from attack by external nucleophilic reagents.[16] The substantially increased stability of organic dye molecules in zeolites opens possibilities for developing new kinds of pigments. High brightness can be created by inclusion of fluorescent molecules and a large variety of colours becomes accessible through combination of two or more dyes. Further functionality can be added by interfacing the dye-zeolite L materials to external species or devices. Such an interface can be

Department of Chemistry and Biochemistry, University of Bern 3012 Bern (Switzerland)

E-mail: gion.calzaferri@iac.unibe.ch

Dr. A. Kunzmann Optical Additives

Dorfli 9, 5603 Staufen (Switzerland)

^[**] This work was supported by the Kommission für Technologische Innovation (KTI) project 2005-07 and the Clariant Research Project Dye-Loaded Zeolites. We would like to thank Dr. Massoud Dadras of the Service de Microscopie et Nanoscopie (University of Neuchâtel, Switzerland) for measuring the high resolution TEM images, Dr. D. Pflieger from Clariant for providing some of the chemicals used in this study, and Beatrice Frey for the SEM measurements.



^[*] Prof. G. Calzaferri, Dr. S. Suárez, Dr. A. Devaux, Dr. J. Bañuelos, Dr. O. Bossart