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Ordered Porous Materials as Media for the Organization of Matter on the Nanoscale

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Ordered porous inorganic compounds can now be synthesized with pore sizes between 0.3 nm and several tens of nanometers. The sharp pore size distribution of such materials and the ordered pore arrangement open possibilities for using them to organize matter on the nanometer scale. This overview highlights different aspects of this topic, using four selected examples: the spatial organization of molecules with high molecular hyperpolarizability to create a frequency-doubling element; the encapsulation of a laser dye which results in a new class of solid-state lasers; the encapsulation of small metal clusters in mesoporous ordered oxides; and the encapsulation of semiconductor clusters in such oxides. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Zeolites, which are crystalline, microporous aluminosilicates, have been known as minerals since the 18th century. Major technical applications started after synthetic zeolites became available in the 1950s. Zeolites are used in several application areas, for instance as ion exchangers in detergents, or as acid catalysts in the petroleum industry. Following the successes in the synthesis of aluminosilicate materials between the 1950s and the 1980s, other framework compositions could be prepared, such as the aluminophosphates, which also form three-dimensional frameworks consisting of tetrahedral TO_4 units (T = Al, P). The structures of these alumophosphates often have zeolitic analogues, but some of the structures are novel and have not been prepared in the aluminosilicate system. With an aluminophosphate, the so-called VPI-5,[1] the range of accessible pore sizes had been expanded to about 1.2 nm from the former maximum of about 0.75 nm present in zeolites of the faujasite family. Another breakthrough was achieved in the early 1990s when scientists of the Mobil Oil Corporation[2] and a Japanese group[3] independently discovered a family of aluminosilicate materials with ordered pore systems, the M41S family, in which the pore size can reach 10 nm. Many different framework compositions are nowadays available for this class of porous materials.

Ordered pore systems with pores of molecular dimensions are highly attractive host systems for the incorporation and organization of other species. Guest/host systems based on such porous crystals have therefore found considerable interest, from a scientific point of view as well as for possible applications[4–6]. The following discussion will focus on four examples highlighting the possibilities which these host systems offer for the organization of molecules and clusters on the nanometer scale.

FREQUENCY-DOUBLING SYSTEMS

Frequency doubling in zeolite-based guest/host systems was first discovered by Cox and Stucky in 1988.[7] They investigated the optical properties of several such materials, using different hosts as well as different guest molecules. High doubling efficiencies were observed with *p*-nitroaniline (PNA) as guest molecule, and molecular sieves with unidimensional channel systems as host, such as the aluminophosphate $AlPO_4$-5, a molecular sieve with a channel diameter of approximately 0.75 nm. The experiments on the PNA system are especially

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interesting, since the PNA crystal does not give rise to frequency doubling. The individual molecules have a hyperpolarizability different from zero, but the packing in the crystal is a centrosymmetric arrangement of individual molecules. This leads to cancellation of the contributions from different molecules, and there is no net effect and thus no macroscopic non-zero χ^2. Incorporation of the PNA molecules into the channel system of the molecular sieves, however, clearly breaks the symmetry on the macroscopic scale, so that second-harmonic generation (SHG) is observed.

These experiments were later repeated in more detail on single crystals by Caro *et al.*[8] and Caro and Marlow.[9] The first system investigated by this group was again PNA in $AlPO_4$-5 with its channels running along the long crystal axis (*c*-axis). Experiments on single crystals with polarized incident light revealed that the PNA is well ordered in the channel system of the molecular sieve (Fig. 1). If the plane of polarization of the incident light is parallel to the *c*-axis of the $AlPO_4$-5 crystal, maximum SHG is observed; if the polarization plane is perpendicular to the *c*-axis, no SHG signal is obtained. The observed dependence of the SHG intensity on the orientation of the crystal with respect to the polarization of the incident laser light proves that the net orientation of the PNA molecules has a predominant component along the channel axis of the molecular sieve.

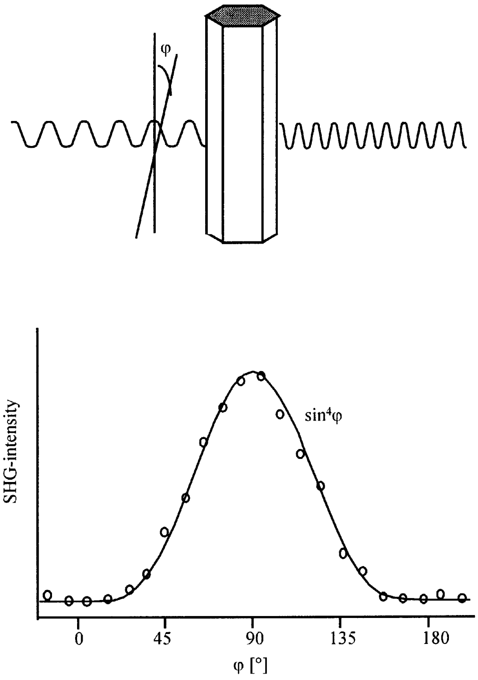

Figure 1 Principle of the SHG experiment on a single crystal of the PNA/$AlPO_4$-5 composite (top); dependence of the intensity of the SHG signal on the angle ϕ between the polarization plane of the incident laser light and the long crystal axis of the $AlPO_4$-5 crystal (bottom). Redrawn from Ref. 8.

The extent of this orientation has been analysed by Raman spectroscopy[10,11] and polarized IR microspectroscopy.[12] Figure 2 (top) shows a sketch of possible extreme orientations of the PNA molecules in the molecular sieve crystals, together with the expected polarized IR spectra. Figure 2 (bottom) shows experimental spectra of the PNA/$AlPO_4$-5 composite at a relatively low loading where only little interaction between individual PNA molecules occurs. As a comparison of Fig. 2, top and bottom, immediately shows, the PNA molecules are oriented primarily with their twofold rotation axis parallel to the channel axis of the molecular sieve. A more detailed analysis reveals that the average deviation from the perfectly parallel orientation is 13°. This is in close agreement with the Raman data. At higher loading, hydrogen bonding becomes evident in the IR spectra, and analysis becomes more difficult.

Which factor controls the relatively perfect alignment of the PNA molecules is still an open question. In order to give rise to observable SHG, it is not only necessary that the orientation of all molecules in one channel is identical, the same orientation needs to be present in all channels, or at least in the majority of the channels. Two explanations seem to be possible: the macroscopic polarity of the crystals could be responsible for the alignment, or the surface properties of the crystals could allow entry of the molecules into the channel system in only one orientation. A set of elegant measurements of the pyroelectric effect on a single crystal by Marlow and co-worker[13] suggests that entry into the channel system occurs with the nitro group of the PNA molecule first. The sign of the pyroelectric effect changes in the middle of the crystal if the crystal is heated spotwise with a laser, which means that there is a mirror plane in the crystal centre with respect to the PNA orientation (note: centrosymmetry on this length scale is not critical with respect to the SHG effect). This experiment suggests that the PNA molecules enter the pore system from both sides with the nitrogroup entering first. However, if the crystals were twinned with the two twins growing from the center rotated by 180° against each other, the orientation by the macroscopic dipole of the crystals might still be the

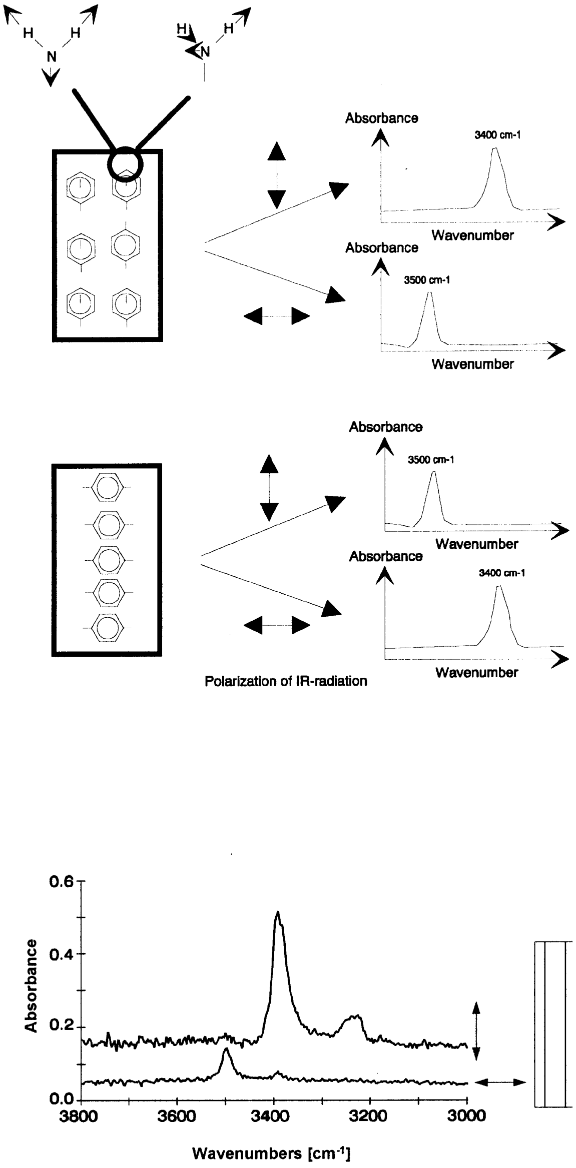

Figure 2 Schematic drawing of the effect of possible extreme orientations of the PNA molecules in the molecular sieve on the observed spectra in the NH-stretching region, if the composite is analysed with polarized IR radiation (top); experimental spectra obtained with polarized radiation (bottom). The arrow indicates the polarization plane with respect to the crystal. The experimental spectra strongly resemble the situation where the molecular long axis coincides with the crystal long axis. Redrawn from Ref. 12.

major influence. This question has not been unambiguously answered yet.

The PNA/$AlPO_4$-5 problem is not suitable for the construction of a frequency doubling device, since phase matching can not be achieved due the optical properties of the composite[14]. However, other guest species with more than one none vanishing tensor component in the hyperpolarizability tensor are more suitable for this purpose. p-Dimethylamino benzonitrile, again in the molecular sieve $AlPO_4$-5, is such a system. Detailed analysis of this system revealed that phase matching can be achieved[15]. Whether or not technical frequency doubling systems based on molecular sieves will be developed in the future remains open. One obstacle is still the difficulty in reaching high reproducibility in host crystal quality, which is absolutely necessary for the mass production and the technical use of such devices.

A new class of solid state lasers

The morphology of some molecular sieve crystals suggests their use as optical resonators in lasers. Here again the $AlPO_4$-5 system seems to be promising. The hexagonal prism with its planparallel ends could be directly used as a laser cavity if the ends would be coated, for instance with a dielectric multilayer, to create a mirror. The resonator with planparallel mirrors is certainly not optimal with respect to the laser quality, but the synthesis of such crystals in large amounts would be very easy, and thus the development of laser materials based on this class of substance is an interesting challenge. Such laser materials could offer several advantages. They would provide a highly flexible matrix, since many different guest species could be incorporated. Due to the open channel system the guest species could be further modified, for instance through complexation, and the integration of additional functions in one crystal could be possible, for instance by introducing additional frequency-conversion systems.

Synthesis of the host material in sufficiently high optical quality is relatively difficult. The structure of $AlPO_4$-5 is easy to synthesize, but usually the material forms as a fine, polycrystalline powder, which is not suitable for optical applications. A synthesis of high-quality $AlPO_4$-5 was developed by Finger and Kornatowski,[16] but in this synthesis procedure a special aluminium source (AlOOH-sol; CTA Säureschutz) was used which is no longer available. Although many parameters need to be optimized in order to synthesize high-quality $AlPO_4$-5, the aluminium source is the crucial component. In order to substitute the original aluminium source, many different (over 100)

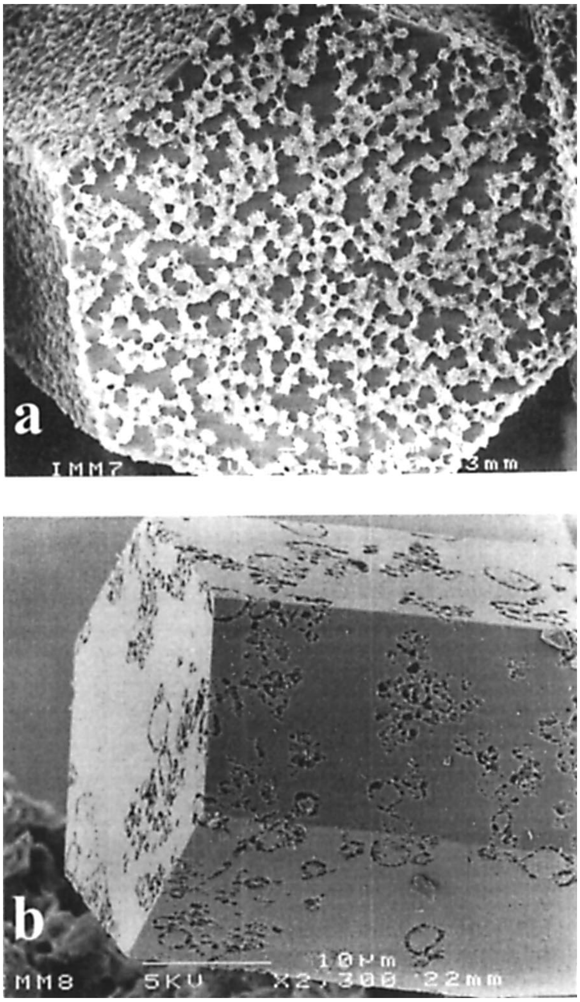

Figure 3 SAPO-5 crystals after 24 h exposure to Nd^{3+} solution at pH = 5 (a) and pH = 2.5 (b), both at room temperature (from Ref. 18).

aluminium sources, either commercially available or self-prepared, were tested by Demuth,[17] who eventually found that a precipitated pseudo-hydrargillite had similar properties with respect to the resulting crystal shape of $AlPO_4$-5 as the original aluminium source. The reason for these strong differences between different precursors is not clear, yet. It might be related to the release rates of suitable building blocks for the $AlPO_4$-5 synthesis.

With this optimized host system it was first attempted to prepare laser materials comparable with conventional solid-state lasers, such as the ruby laser with chromium as the active species, or the Nd:YAG with Nd^{3+} as the active species. Ion exchange to introduce the laser-active species is not directly possible for $AlPO_4$-5, since due to the electroneutral framework, no exchangeable cations are present, in contrast to the aluminosilicate zeolites. However, it is possible to incorporate silicon into the AlPO-framework, where the silicon substitutes primarily for phosphorus. Thus, for each silicon incorporated, one negative framework charge is created which leads to ion-exchange properties. The resulting silicoaluminophosphates are then called SAPOs. Problems were encountered when it was attempted to introduce Nd^{3+} as well as Cr^{3+} into the SAPO-5 by an ion-exchange procedure from solution. At too high a pH, the oxides of the laser-active species precipitated on the external surface of the molecular-sieve crystals (Fig. 3a); if the pH was lowered, the SAPOs partly dissolved (Fig. 3b). There was no intermediate pH range where the exchange was successful without damage to the crystals; complexation with various ligands during exchange did not provide a solution either.

Introduction of the laser-active ions into the pore system was finally achieved via direct incorporation during the synthesis. If the hydroxides of neodymium or chromium are precipitated together with the aluminium for the aluminium source, the use of such a precursor leads to crystals loaded with the active ions, as electron microprobing proved on a crystal embedded in a polymer and polished to remove the outer surface. Such crystals show the typical optical absorption behaviour of Cr^{3+} (after calcination also Cr(VI)), or Nd^{3+}. For the chromium-loaded materials the emission could also be observed which is shown in Fig. 4 together with the emission spectrum of a ruby single crystal. The spectrum of the chromium-loaded SAPO-crystal is very broad and resembles more that of a chromium doped glass, suggesting a distribution of chromium species in the crystal. In addition, the intensity scale is different for the two spectra; the luminescence from the ruby is very much higher than that from the Cr-SAPO.[18]

Laser luminescence, however, could never be induced in these samples; for the neodymium-modified materials not even the normal, unamplified luminescence was observed. This is most probably due to the fact that water or OH groups in the vicinity of the luminescing ions leads to vibrational relaxation of the excited states. Both luminescence frequencies, that for neodymium as well as that for chromium, are in the range of overtones of the OH vibrations, so that de-excitation occurs.

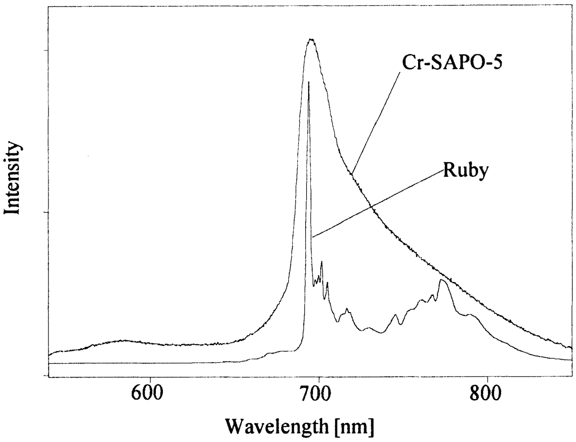

Figure 4 Luminescence spectra of Cr-SAPO-5 and ruby single crystal. Excitation wavelength 532 nm, measurement at 295 K. The spectrum of the ruby is reduced by a factor of approx. 1000 (from Ref. 18).

It was therefore attempted to introduce organic laser-active species into the channel system of the $AlPO_4$-5.[19] Most laser dyes conventionally used for dye lasers are too bulky to fit into the pore system. However, some dyes with an elongated molecular shape are available. We decided to incorporate the dye with the commercial name 'Pyridine 2' {1-ethyl-4-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]pyridinium}. Incorporation works best if the dye is added to the synthesis gel for the molecular sieve. Loadings in the region of 0.05 wt% can be achieved. Analysis of the resulting crystals with polarized light reveals that the dye is encapsulated in the crystal with a high degree of orientation (Fig. 5). Only if the light is polarized parallel to the crystal axis does the red absorption colour of the composite show up. If the polarization plane lies perpendicular to the crystal *c*-axis, no absorption occurs. This proves that the dye molecules are fairly perfectly oriented along the channel axis of the molecular-sieve crystals.

Luminescence is polarized as well, as could be expected from the absorption spectra. The regular luminescence is broad in the red spectral range, as is the luminescence of the Pyridine 2 molecule in solution. However, these crystals do not only show the regular luminescence, but also amplification by a stimulated emission. If the composite is irradiated with the frequency-doubled line of a Nd:YAG, the normal broadband luminescence spectrum is observed at low intensities of the exciting radiation. At a certain threshold level, though, very narrow spikes, the width of which is below the resolution of the instrumentation, show up and increase more in intensity than the background with increasing intensity of the excitation beam (Fig. 6). This is a clear indication for an amplification process such as occurs in lasers.[20] In more detailed experiments it has been shown that the amplification does not proceed along the crystal axis, but rather a whispering-gallery mode develops with internal reflection of the light at the hexagonal faces of the crystals.[20] A longitudinal mode could not develop because the molecular dipole moment change has its predominant component along the long molecular axis, so that light can be emitted only perpendicularly to the long crystal axis.

The discovery of this new class of solid-state laser materials opens the possibilities of introducing other dye molecules into molecular sieves, of varying the type of molecular sieve, of introducing additional species into the pore system in order to modify the optical properties, and many more. In addition, many of these crystals could be arranged to produce more complex devices. The materials seem to be well suited for a fine tuning of the properties, so that solid-state-like lasers with the properties of dye lasers might be developed.

INCORPORATION OF PREFORMED, LIGAND-STABILIZED METAL CLUSTERS INTO MESOPOROUS HOSTS

As stated in the Introduction, the discovery of the M41S materials in the early 1990s extended the pore sizes available in ordered porous materials into the 1–10 nm range. This pore size range corresponds to the sizes of ligand-stabilized metal clusters, such as the closed-shell clusters developed in Schmid's group.[21] Incorporation of such clusters in well-defined pore systems could stabilize the clusters against agglomeration, which easily occurs if the clusters lose their ligand sphere. Therefore this technique could be interesting for preparing supported catalysts with a stable dispersion of the noble-metal particles.

MCM-41, the most intensively investigated member of the M41S family, consists of a hexagonal packing of unidimensional pores. The pores are separated from each other by walls approximately 1 nm thick, which consist of amorphous silica. The crucial component in the synthesis mixture is a surfactant. Originally, a long-

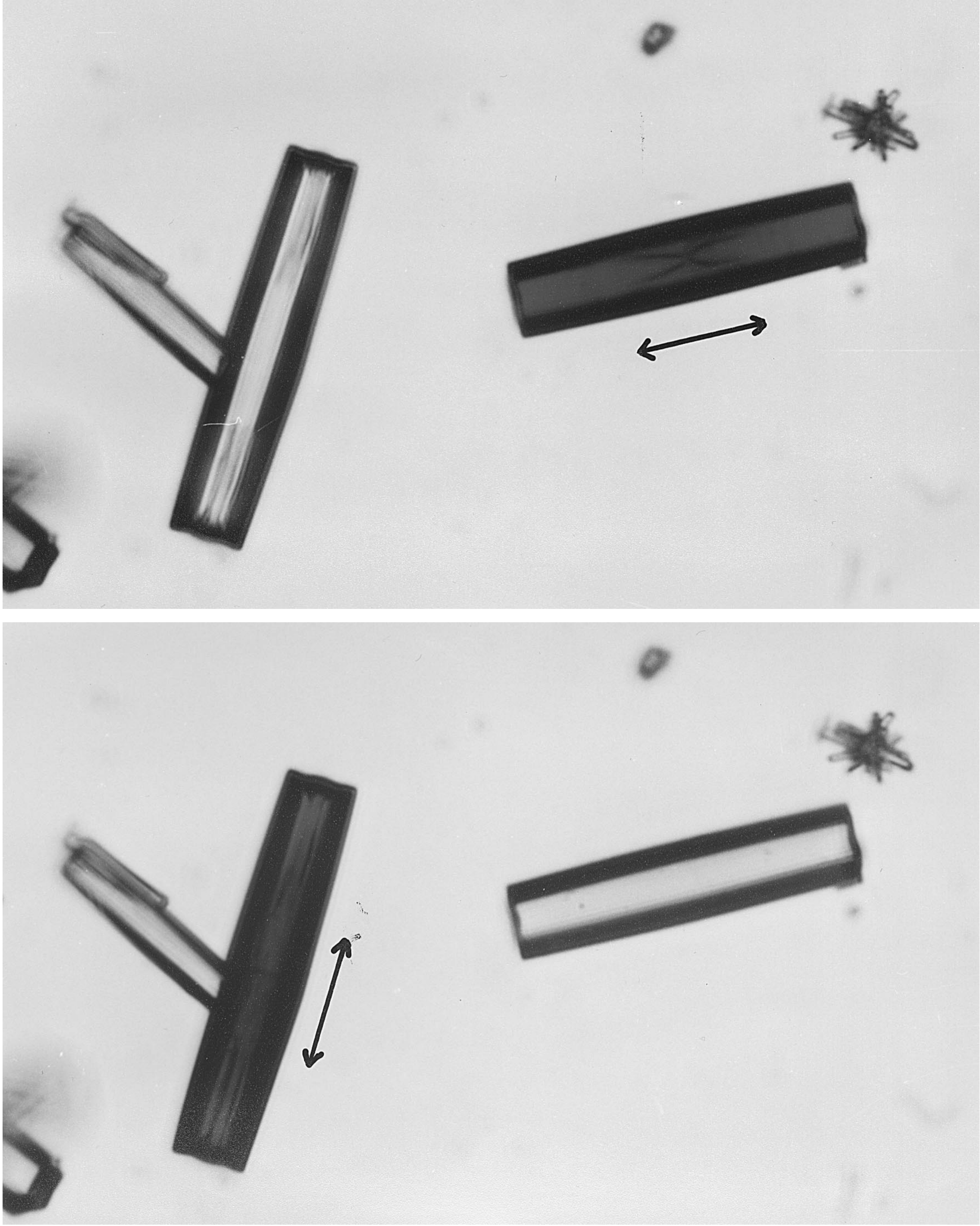

Figure 5 Optical micrographs of Pyridine-2-loaded A1PO$_4$-5 crystals using polarized light. The arrows indicate the direction of polarization. The dark crystals have a red colour in the optical microscope; the light crystals are transparent. Crystal size is approximately 100 μm.

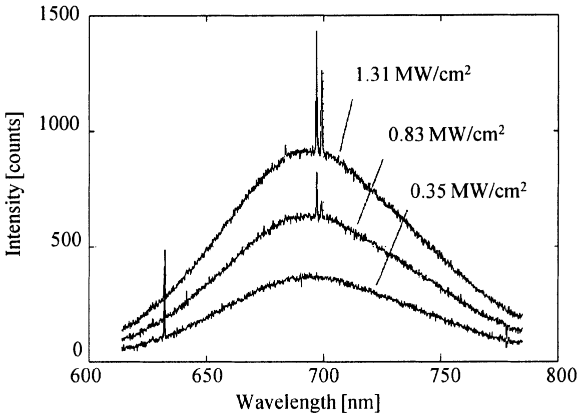

Figure 6 Luminescence of Pyridine-2-loaded A1PO$_4$-5 crystals after irradiation with a frequency-doubled Nd:YAG at 532 nm. The sharp spikes in the centre of the broadband emission indicate the laser action. The spike on the left is stray light from an HeNe laser.

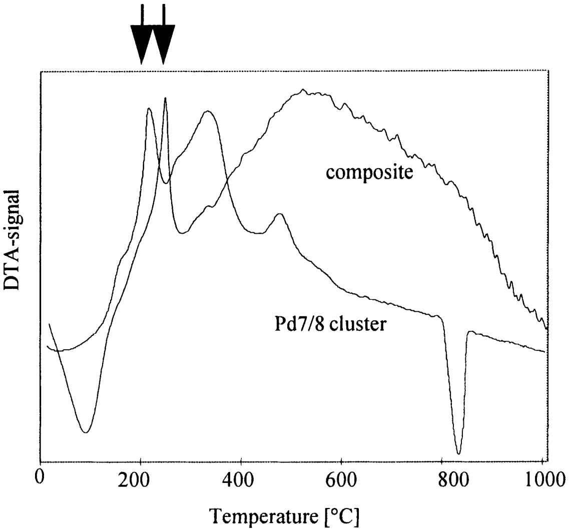

Figure 7 DTA traces of pure Pd 7/8 clusters and Pd 7/8 clusters incorporated into MCM-41 by incipient wetness impregnation. The arrows indicate the exotherms attributed to the removal of the ligands.

chain hydrocarbon with a trimethylammonium headgroup was used, but by now many different surfactants have been proved to work as well.[22] The materials form in a cooperative process, where silicate species in solution interact with the surfactant molecules and form supramolecular ordered arrays, which often resemble liquid-crystalline phases known from surfactant chemistry.[23]

Several different pathways for the incorporation of ligand-stabilized metal clusters into these ordered pore systems seem feasible. These include equilibrium adsorption and incipient wetness, where the mesoporous silica is mixed with the clusters dissolved in a suitable solvent which is then evaporated, or the incorporation during the synthesis. For the last pathway, the clusters have to be stable under the conditions of synthesis of the mesoporous oxide, which, however, can be very mild (room temperature, pH around 11).

Since we use CO oxidation with air in the gas phase as the catalytic test reaction, gold and palladium clusters are the best candidates for incorporation into the pore system. Most experiments were performed with the five-shell palladium cluster (nominal composition $Pd_{561}Phen_{36}O_{200}$) or a mixture of the seven- and eight-shell clusters, which are prepared by reduction of palladium acetate in solution in the presence of phenanthroline as stabilizing ligand. During the preparation different clusters form, but the five-shell and the seven eight-shell clusters can be isolated.

It is possible to incorporate the clusters into the pore system by all three techniques mentioned above. The clusters are stabilized in the pore system, compared with the free cluster. Figure 7 shows the differential thermal analysis traces of the free clusters and of the clusters incorporated in the pore system. The exotherm close to 200 °C can be attributed to the ligands leaving the cluster surface. This process is shifted to about 20–40°C higher temperatures when the clusters are incorporated in the channel system. This was shown for several different samples prepared by different pathways.

TEM analysis also proves the incorporation of the clusters in the channel system. Figure 8 shows a representative TEM picture of a sample resulting from incipient wetness impregnation. One can see that over large regions the clusters are homogeneously distributed; especially noteworthy is the fact that no higher concentration of clusters is observed near the edges of the particle. This is a clear indication that the clusters are present in the pores of the material and not on the external surface. However, in some parts of the sample the metal clusters are concentrated in apparently disordered structures. It is not clear, so far, whether the clusters have a higher tendency to be adsorbed on these parts of the samples or whether the sample is partly destroyed by the clusters.

The materials thus prepared are, as expected, catalytically highly active in CO oxidation. Figure

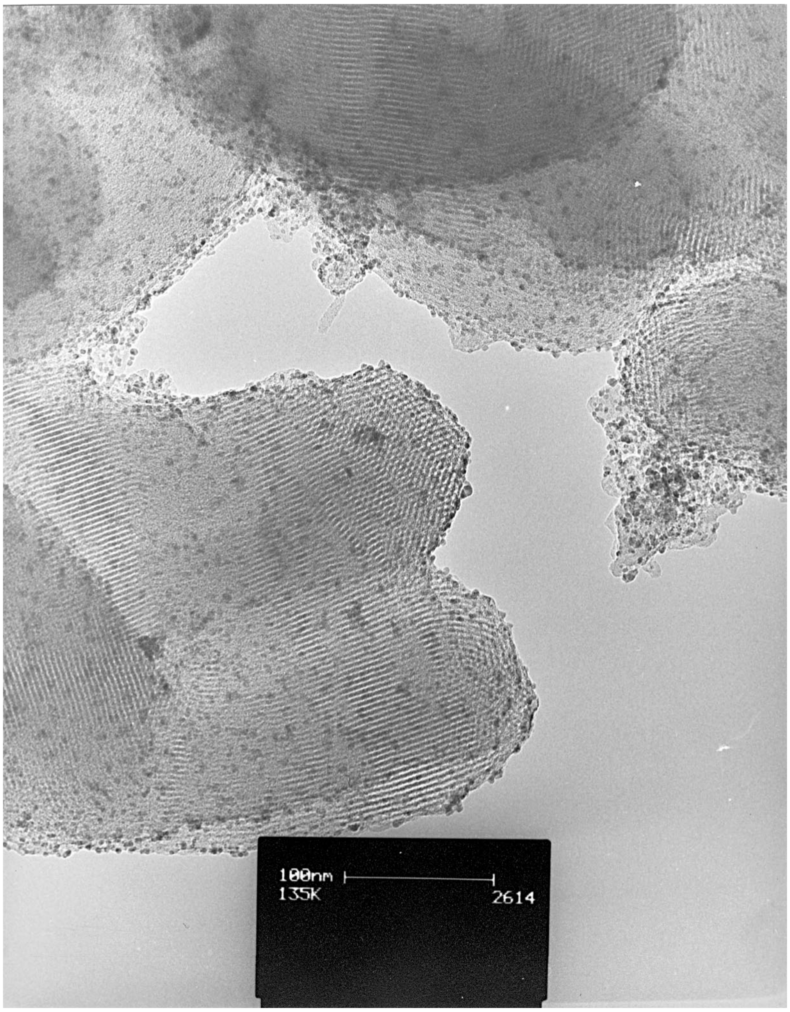

Figure 8 Transmission electron micrograph of an MCM-41 sample loaded with Pd 7/8 clusters by incipient wetness impregnation.

9 shows the conversion vs. temperature plots for differently prepared Pd/SiO_2 catalysts. The ignition temperature at which the conversion curves have a steep slope is dependent on the dispersion of the noble metal: the higher the dispersion, the lower the ignition temperature. The most active catalysts are prepared by equilibrium adsorption from solutions containing palladium salts, such as $Pd(NH_3)_4(NO_3)_2$. This preparation results in particle sizes below the detection limit in X-ray diffraction, i.e. smaller than 2 nm. The cluster-containing catalysts have a somewhat lower activity which is due to their larger crystallite sizes. The particle diameter without the ligand shell is around 2.4 nm, which is well in accordance with the catalytic performance. The ignition temperature is still very low compared with other palladium containing catalysts. No growth of the particles was observed during the catalytic experiments, which shows that the support indeed stabilizes the palladium particles.

The strength of this preparation pathway lies not so much in the fact that a high dispersion can be achieved. This is possible for many metals with much cheaper and simpler methods, as shown above. However, if a catalytic reaction is structure-sensitive, i.e. reaction pathways are dependent on the arrangement of the surface atoms, then very well-defined particles could be advantageous. Ligand-stabilized metal clusters can now be prepared from many different metals and even bimetallic particles can be formed. There is also a

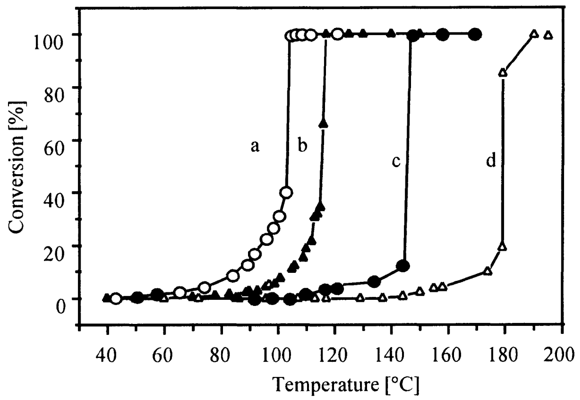

Figure 9 Oxidation of CO in air over different palladium catalysts in an open-flow reactor: 1% CO in air, gas hourly space velocity = 25 000 h^{-1}. Trace a (○) incipient wetness with $Pd(NH_3)_4(NO_3)_2$, 3 wt%; trace b (▲), ion exchange with $Pd(NH_3)_4(NO_3)_2$, 2 wt%; trace c. (●), incipient wetness with Pd 7/8 clusters; trace d (△), *in situ* synthesis with $Pd(NH_3)_2Cl_2$.

range of different compositions in the ordered mesoporous oxides; for instance, the catalytically important materials zirconia[24] and titania[25] are available. If a catalyst as described above is desired, the ingredients for its preparation would be available. Particle sizes of the metal as well as pore sizes of the supports can be tailored, so that the properties of both components can be adjusted to each other.

INCORPORATION OF SEMICONDUCTOR CLUSTERS INTO MESOPOROUS HOSTS

As in the field of ligand-stabilized metal clusters, similar progress has been made in the field of semiconductor clusters, mainly with II–VI semiconductors such as CdS, PbS, CdTe and so forth.[26] These clusters have some remarkable properties, such as a size-dependent absorption edge due to the changes in the band gap, and they often show strong luminescence. In some fortunate cases it has been possible to crystallize the clusters and thus obtain detailed information on their structure,[27,28] which can often be described in terms of sections from the bulk structure.

The luminescence of the semiconductor clusters is strongly dependent on the surface properties of the clusters, since the surface can trap charge carriers which are then lost for the luminescence process. Therefore, CdS clusters have to be coated with a protecting layer, such as CdO, to obtain high quantum yields for luminescence. The pore walls of MCM-41-type materials might act in a similar way, if the sizes of the semiconductor particle and the pores are exactly matched.

In order to study pathways to prepare such guest host systems and to study the properties, first a more stable luminescent semiconductor cluster has been incorporated in MCM-41. The CdTe clusters show a relatively strong luminescence, the colour of which is determined by the particle size of the clusters.[29] It was thus attempted to incorporate CdTe clusters into the pore system of MCM-41 by *in situ* incorporation during the synthesis as well as by equilibrium adsorption.

The clusters were synthesized, according to published procedures, from Al_2Te_3 as a source for an HTe^- solution from which the clusters were precipitated with cadmium in the presence of 1-mercaptoglycerol as ligand. Preparation of the clusters following this pathway led to formation of green-emitting CdTe with a particle size of approximately 2–2.5 nm. The luminescence spectrum after irradiation with the 254 nm mercury line is shown in Fig. 10. MCM-41 synthesized following published procedures could be loaded with these clusters by equlibrium adsorption. The loading of the mesoporous oxides with clusters is very low, below 0.1 wt%. However, the resulting powder luminesces, showing a luminescence spectrum almost identical to that of the parent cluster solution.

It was also attempted to incorporate clusters *in*

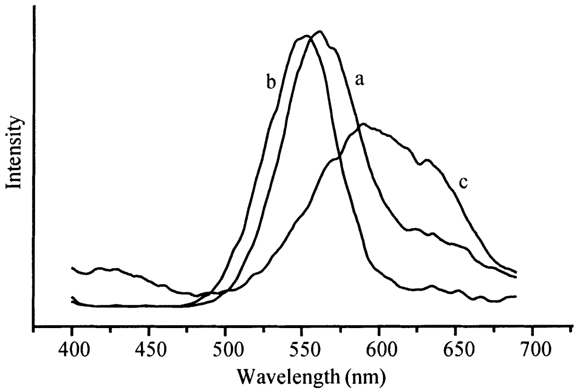

Figure 10 (a) Luminescence spectra of CdTe clusters; (b) CdTe-clusters loaded onto MCM-41; (c) an MCM-41/CdTe cluster composite prepared by adding the clusters to the MCM-41 synthesis solution.

situ during the synthesis. In order to achieve this, a solution of the CdTe clusters prepared as described above was added to the synthesis mixture for MCM-41, which contained fumed silica, sodium waterglass and cetyltrimethylammonium bromide. The resulting mixture was exposed to the synthesis temperature of 90 °C for two days. After this treatment the clusters had changed: the emission spectrum was appreciably red-shifted (Fig. 10), which is a clear indication that the clusters had grown. This was probably due to the extended treatment at 90 °C.

The clusters are strongly stabilized by adsorption onto MCM-41. While the luminescence of pure isolated clusters is lost after heating at 180 °C, the composite retains the green luminescence even after treatment at 400 °C. Some change, however, takes place, since after treatment at such temperatures a blue phosphorescence is also observed, the origin of which is not yet known.

It is so far not clear whether the clusters are located in the pore system. Comparison experiments with clusters supported on fumed silica also showed an appreciable thermal stabilization of the clusters. The luminescence of the MCM-41-based system, however, was more intense than that of the composite based on fumed silica.

CONCLUSION AND OUTLOOK

The four examples discussed above show that interesting composite systems can be prepared with ordered porous materials such as zeolites, aluminophosphates or MCM-41 as hosts. These composites can have properties which neither of the components exhibits. At the moment it is still an open question whether technical devices can be constructed based on such systems. However, the recent advances in the preparation of nanoscale clusters as well as nanoscale pores open the possibility of matching the sizes of the two in order to create novel guest host systems in which the nanostructures are ordered in a highly regular array. For this purpose not only molecular-sieve materials but also block copolymers or anodized alumina might be used, which expands the range of accessible composite properties even further.

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