

## Recent Developments in Zeolite-like Materials Synthesis and Characterisation\*

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In the last few years considerable effort has been directed at the targeted synthesis of zeolites and zeolite-like microporous materials with predetermined physical and catalytic properties. With new computational techniques, it has become possible to design templates for the synthesis of specific microporous structures with desired pore size and connectivities. With regard to zeolite-like materials, much attention has been focused on transition metal containing systems, like zincosilicates, titanosilicates and various metalloaluminophosphates with a potential to generate specific redox conditions, in addition to Brønsted and Lewis active catalytic centres. Experimental determination of subtle structural features such as the nature and position of the catalytically active metal sites, and the location, orientation and disorder of templates, metals or complexes within the microporous hosts has become possible using new characterisation techniques, mostly based on X-ray diffraction and the use of synchrotron and neutron radiation sources. *In situ* studies of the kinetics of nucleation, crystal growth and phase transitions or catalyst activation and operation at elevated temperatures have remarkably benefited from the new high-flux and well-collimated third-generation synchrotron radiation sources, and from the advances in the X-ray detector design and data handling.

**Key words:** zeolites, aluminophosphates, zincophosphates, molecular sieves, microporous materials, X-ray diffraction, synchrotron radiation.

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\* Dedicated to Professor Boris Kamenar on the occasion of his 70<sup>th</sup> birthday.

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## INTRODUCTION

The class of molecular sieves has been greatly extended during the last fifteen years by the discovery of zeolite-like aluminophosphates, metalloaluminophosphates, gallophosphates, zincophosphates, titanosilicates, zincosilicates and some other phosphate-based or silica-based microporous materials.<sup>1</sup> Their common feature is a three-dimensional, low-density, and open-framework structure consisting of  $\text{AlO}_4$ ,  $\text{PO}_4$ ,  $\text{SiO}_4$  or other metal-oxygen tetrahedra ( $\text{MO}_4$ ), linked to each other through bridging oxygen atoms.<sup>2</sup> Due to their well-defined channel and cavity systems with pore dimensions up to 15 Å, they are able to recognise and discriminate molecules with a precision of less than 1 Å, which makes them widely applicable in many industrial and research areas. Because of the presence of stable Brønsted acid sites ( $\text{P-OH-M}$ ,  $\text{Si-OH-Al}$ ) and Lewis acid sites (framework defects  $\text{MO}_3^-$ ,  $\text{AlO}_3^-$ ) in the negatively charged frameworks of  $\text{MAlPO}_4$ ,  $\text{SiAlPO}_4$ ,  $\text{MSiO}_4$  or  $\text{AlSiO}_4$  molecular sieves, they are extensively used as solid acid catalysts, adsorbents and ion exchangers in various types of organic shape-selective conversion and separation reactions in the chemical and petrochemical industries.<sup>3</sup> The importance of these materials has increased recently due to their activity as hosts to a range of other species, including small clusters of semiconductors, coordination complexes or metal clusters for optical and electronic applications.<sup>4</sup> The ability to modify their frameworks by transition metal substitution has enabled rich compositional and structural diversities, especially in the metalloaluminophosphate system (*e.g.*  $\text{M} = \text{Co}, \text{Zn}, \text{Mn}$  *etc.*), and has expanded the importance of these materials in industrial catalysis due to the formation of redox catalytic sites ( $\text{M}^{2+} \leftrightarrow \text{M}^{3+}$ ).<sup>5</sup>

The knowledge about the structures of these materials is essential for the understanding and prediction of their macroscopic physical and chemical properties. Size and connectivity of the channels and cavities determine their molecular sieving capability, and chemical composition and distribution of the framework and extra-framework (metal) active sites are of importance for catalytic, absorption or ion-exchange capacity. Framework topologies have been currently determined using powder/single-crystal X-ray/electron diffraction techniques, and also direct high-resolution electron microscopy,<sup>6</sup> depending on the size and quality of the crystals. Determination of the distribution of different metal atoms or other active centres over the framework of tetrahedral sites has been for a long time an almost insolvable problem in the structural chemistry of these systems. In addition to some newly developed NMR, electron paramagnetic resonance and diffuse reflectance spectroscopy, X-ray absorption and diffraction methods have recently proven to be successful and reliable for retrieving information about the nature and structure of the active sites.<sup>7</sup>

## SYNTHESIS OF NEW ZEOLITE-LIKE MICROPOROUS MATERIALS

Hydrothermal synthesis of the majority of zeolite-like materials is based on the use of template molecules as structure directing agents.<sup>1</sup> They incorporate in the structure pore openings during the synthesis and are subsequently removed by thermal treatment or soft chemical routes to obtain a microporous material. Recent advances in the hydrothermal synthesis of zeolites and zeolite-like materials have been based on the new synthesis routes that have become better directed by the use of carefully chosen templates or structure directing agents, sometimes synthesised specifically so as to induce a particular pore geometry. Using a design strategy concerning template charge, shape and framework-template interactions, it has already been possible to synthesise a series of open-framework (1) pure phase structures with (2) novel compositions and (3) controlled framework charges.

The first example of a recently developed *de novo design* computer methodology<sup>8</sup> is presented in Figure 1. It is a synthesis of a phase pure form of chabazite-like cobaltaluminophosphate, named DAF-5.<sup>9</sup> The charge on the 4-piperidinopiperidine template influenced the concentration of cobalt in the framework (two Co atoms per unit cell compensate for the 2+ charge of the template). From the results obtained it was concluded that the metal content in the framework could be controlled by the proper design of templates with suitable charge. The second example is a new microporous large-pore magnesium aluminophosphate STA-1 with 12-member ring channels in one direction and low framework density (13.4 tetrahedra per 1000 Å<sup>3</sup>).<sup>10</sup> It was prepared hydrothermally using linear diquinuclidinium ions [(C<sub>7</sub>H<sub>13</sub>N)-(CH<sub>2</sub>)<sub>n</sub>-(NC<sub>7</sub>H<sub>13</sub>)]<sup>2+</sup>; n = 7, 8, 9, which possessed flexible, charged and bulky end groups likely to form structures with interconnected pore space.

In a recent paper,<sup>11</sup> the template control of framework topology and charge in new phosphate- and arsenate-based sodalite analogues ZnGaP-SOD1, ZnGaAs-SOD1 and gallium substituted cobalt phosphate GCP-SOD1 was reported. Mixed inorganic cations were used in the synthesis to achieve a host-guest charge matching with tetramethylammonium and piperazine as the structure-directing agents, which resulted in framework structures with ordered distributions of tetrahedral Zn, Ga and P(As) atoms. The first two new sodalite analogues ZnGaP-SOD1 and ZnGaAs-SOD1 crystallise in a non-centrosymmetric space group, which is related to the fact that the template tetramethylammonium molecule is not centrosymmetric. In the GCP-SOD1 structure, a diprotonated piperazine cation is located at the centre of the sodalite cage and influences the framework Zn distribution (Figure 2).

Matching framework-template charges were also a crucial factor in the synthesis of a series of cobalt-phosphate-based zeolite analogues with high

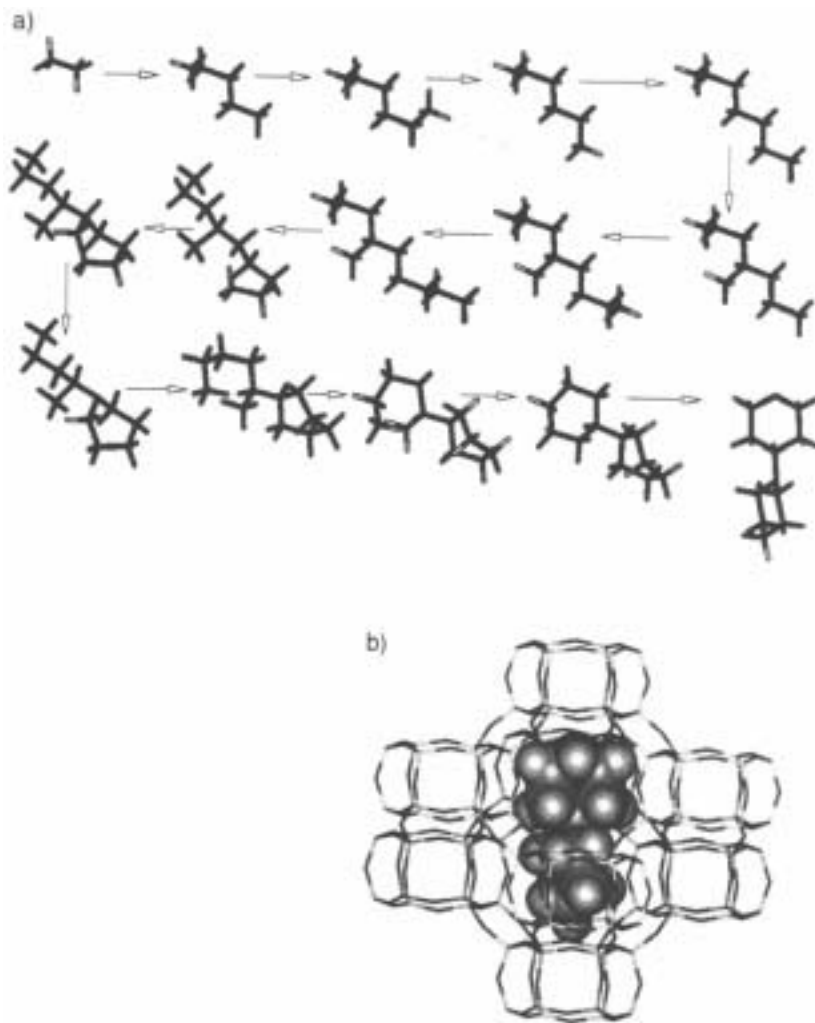


Figure 1. (a) Generation of 4-piperidinopiperidine from an ethane seed in a siliceous CHA unit cell with the program ZEBEDDE (*de novo design* methodology) and (b) energy-minimised location of 4-piperidinopiperidine in the CHA cage. The designed template has allowed a quick formation of CHA material in a phase pure form (reproduced with permission from Ref. 9).

levels of redox active metal sites.<sup>12</sup> Modified synthesis procedures were applied using  $\text{CoCO}_3$  and a non-aqueous ethylene glycol solvent system, since the water solvation and the hydrolysis reactions with transition elements were often seriously competing interactions, which could lead to interrupted and non-zeolitic frameworks. Cobalt-rich analcime, chabazite, sodalite,

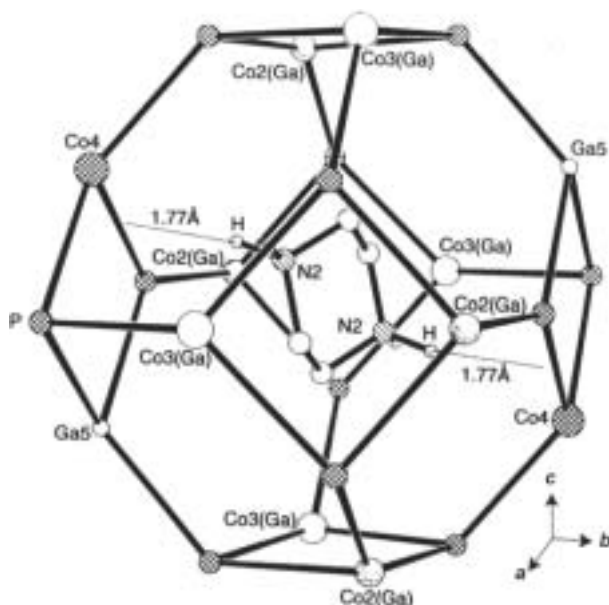


Figure 2. GCP-SOD1 structure: two positively charged  $\text{NH}_2^+$  groups are directed towards the most negative regions surrounding the pure cobalt sites (Co4); the pure gallium sites (Ga5) are adjacent to the pure cobalt sites (Co4) in order to achieve a more uniform charge distribution through the framework (reproduced with permission from Ref. 11).

thomsonite, gismondine, merlinoite and phillipsite phosphate-based zeolite analogues and two novel cobaltaluminophosphate structures, named ACP-1 and ACP-2,<sup>12</sup> with 8-member ring channels in one direction were prepared and characterised. Cobalt replaces up to 80% of Al or Ga in the frameworks.

There is currently a growing demand for zeolite-like molecular sieves with larger pore size and retained high shape selectivity.<sup>13</sup> Quite a few extra-large pore molecular sieves were successfully obtained in metallophosphate systems during the last ten years, such as  $\text{AlPO}_4\text{-8}$ <sup>14</sup> with 14-member ring channels, VPI-5<sup>15</sup> with 18-member ring channels, JDF-20<sup>16</sup> and cloverite [ $\text{Ga}_{96}\text{P}_{96}\text{O}_{372}(\text{OH})_{24}$ ] · 24RF, R = quinuclidinium<sup>17</sup> with 20-member ring channels, and iron phosphate ULM-15,<sup>18</sup> gallophosphate ULM-16<sup>19</sup> and a new vanadium phosphate  $\text{Cs}_3[\text{V}_5\text{O}_9(\text{PO}_4)_2]$ <sup>20</sup> with 16-member ring channels. However, most of them are thermally unstable and only  $\text{AlPO}_4\text{-8}$  and VPI-5 can be prepared as truly zeolitic frameworks, without 5- or 6-coordinated framework atoms and terminal or bridging OH, F and  $\text{H}_2\text{O}$  groups. Additionally, all of these materials contain channels with the largest pore size in only one dimension (except for cloverite) and some of these structures have no other

channels intersecting the main channel, which might be less desirable for commercial applications because of diffusion limitations. An approach to prepare materials for industrial applications with multidimensional channel systems and large cages, like the most widely used catalysts zeolite X and Y (FAU) with multidimensional 12-ring channel system, was reported recently.<sup>21</sup> Three new open-framework structures of metal (Co, Mg, Zn, Mn) substituted aluminophosphates and gallophosphates designated UCSB-8, UCSB-10 and UCSB-6<sup>21</sup> were synthesised using linear diamines,  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  ( $n \geq 7$ ) and polyether diamines with spatially competing hydrophilic and hydrophobic regions, a fact considered to be very important in the generation of large cages and pores. The templates used have backbones which fill the middle of the cage and have a smaller affinity than the amine groups for the charged inorganic species that ultimately make up the charged framework walls. The polyether diamines are also highly soluble, which is an additional advantage, since one of the biggest problems of the large organic templates is their insolubility in water. The large cage and the framework topology of one of the new structures, UCSB-8 with 12-ring apertures in two dimensions and 8-ring apertures in the third, is presented in Figure 3. Other proposed strategies for the preparation of extra-large pore materials include (1) the use of alternative solvent media, since it is unlikely that a low-density molecular sieve material could be synthesised in water because the formed crystals will float to the surface upon nucleation and make the subsequent growth difficult, and (2) the use of precursors with larger building units, such as layered materials, which could be transformed into three-dimensional structures (*e.g.* ferrierite, VPI-5).<sup>13</sup>

Exploitation of novel or modified media for the crystal growth and preparation of large-pore microporous materials has been notably progressing in the last few years. Addition of anions, particularly fluoride ions, into reaction mixtures, assuming their directing and templating roles and beneficial effects on nucleation and crystal growth rate, has led to a number of new structures, such as the well-known gallophosphate cloverite with 13 Å channels, oxyfluorinated microporous phosphate-based compounds named ULM-n<sup>22</sup> and many others. Very recently, a new gallium phosphate DIPYR-GaPO with 14-ring channels and 4-, 5- and 6-coordinated gallium was synthesised from the  $\text{HF-Ga}_2\text{O}_3\text{-P}_2\text{O}_5$  system.<sup>23</sup> Another interesting approach is the use of reverse micelles as nucleation sites in the synthesis of zincophosphates with sodalite and faujasite topology.<sup>24</sup> The micelles are prepared by dissolving small amounts of water in a nonpolar hydrocarbon solvent with the help of the surfactant (sodium bis(2-ethylhexyl)sulfosuccinate). In the synthesis of certain metal-substituted gallophosphates having sodalite-, laumontite-, and gismondine topologies, tetraethoxysilane  $[\text{Si}(\text{OEt})_4]$  was used as a mineraliser and ethylene glycol as solvent.<sup>25</sup> Addition of small

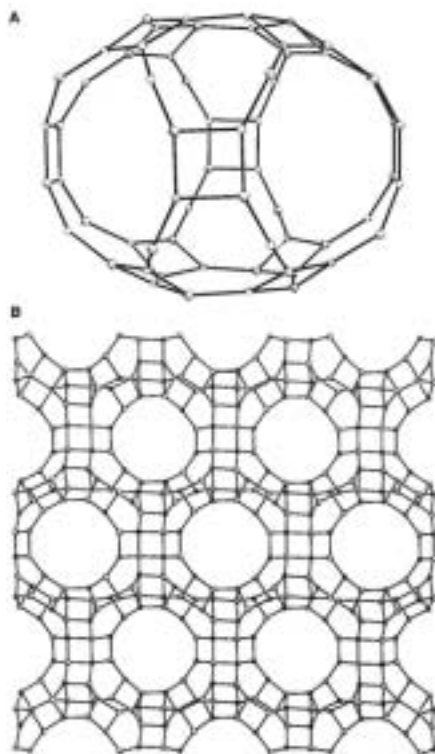


Figure 3. The large cage in metal-substituted aluminophosphate and gallophosphate structures UCSB-8 (SBE structure type) built of 64 T-atoms and bound with four 12-ring windows (top) and the 12-ring channels viewed down the *a* or *b* axis (bottom) (reproduced with permission from Ref. 21).

amounts of  $\text{Si}(\text{OEt})_4$  to the gel has helped the production of single-crystal rather than polycrystalline MGaPO products. The anticipated causes of the mineralising activity of  $\text{Si}(\text{OEt})_4$  have been the change of the gel precursor viscosity and the decrease of the number of available nucleation sites.

The urge for silica-based zeolite-like materials synthesis is based on the fact that they usually have a much higher thermal stability as catalysts than phosphates. Until very recently, the faujasite 12-ring channels were the largest among the silica-based materials. The first silica-based material with 14-member ring channels was UTD-1, synthesised in 1996 with an organometallic structure directing agent  $[(\text{Cp}^*)_2\text{Co}]\text{OH}$  ( $\text{Cp}^* = \text{Me}_5\text{C}_5$ ).<sup>26</sup> The material, which possesses a one-dimensional channel system, is thermally stable up to 1000 °C. This leads to the conclusion that the extra-large pore rings are not the major cause for the thermal instability of porous materi-



als.<sup>13</sup> The CIT-5<sup>27</sup> with 14-ring channels, SSZ-42<sup>28</sup> with 12-ring channels and the highly faulted SSZ-31 structure with elliptical one-dimensional large channels of approximately  $8.6 \times 5.7 \text{ \AA}$ ,<sup>6</sup> are some examples of the newly synthesised large-pore silica-based structures. Another new class of zeolite-type materials are titanosilicate molecular sieves, including ETS-4  $[\text{Na}_9\text{Si}_{12}\text{Ti}_5\text{O}_{38}(\text{OH}) \cdot 12\text{H}_2\text{O}]$ <sup>29</sup> with zorite structure and one-dimensional 12-ring channels, ETS-10<sup>30</sup> with three-dimensional 12-ring pore system and TS-1 with ZSM-5 topology, which all exhibit 4- or 6-coordinated framework Ti atoms and are exceptionally good catalysts. The unique catalytic properties, the high activity and the catalyst stability have led to a series of works on the use of titanium substituted silicate- and phosphate-based materials such as Ti-Beta,<sup>31</sup> TAPSO-5<sup>32</sup> and TAPSO-37.<sup>33</sup> The largest pore size of the newly synthesised zincosilicates, which are also very interesting potential catalysts, are 9-member rings.<sup>34</sup> A short literature review of these and other new silica-based and also some phosphate-based structures was published recently.<sup>35</sup>

There are also other fields of extensive zeolite-like materials research. One of them is the synthesis of chiral framework structures for potential applications involving enantioselective separation and catalysis. The first potentially useful chiral material was zeolite  $\beta$ , or rather, one of its polymorphs. So far, only a few small-pore chiral zincophosphates<sup>36,37</sup> and a layered chiral aluminium phosphate<sup>38</sup> have been reported. Numerous research studies have also focused on the synthesis of materials with new chemical compositions, although many of these efforts have resulted in materials with non-tetrahedral and interrupted, unstable frameworks. An interesting new material is, *e.g.*, an open-framework tin(II) phosphate built from three-coordinated Sn(II) and  $\text{PO}_4$  tetrahedra forming 8-ring channels in one direction.<sup>39</sup>

Considerable attention is still concentrated on silica- and phosphate-based mesoporous materials with 20–100 Å pore sizes, ordered channels, and disordered walls and their use in absorption and catalysis;<sup>40</sup> however, they are unstable and exhibit only partly ordered structures. Recent advances in the synthesis, characterisation and applications of mesoporous molecular sieves are due to a better understanding and exploitation of the mechanism of formation of these materials. A liquid crystal templating mechanism is commonly used, which allows the tailoring of their composition, pore size, structure and texture.<sup>41</sup> Well-documented, simplified preparations of these materials have allowed for the study of their application in fields ranging from a catalytic conversion of large molecules to their functioning as a nanoscopic host where polymers, atomic arrays of metal atoms and electronic materials can reside. Besides new structures and methods of synthesis, there have been great efforts to incorporate catalytically active elements, especially titanium, into mesoporous frameworks.<sup>40</sup>



## USE OF SYNCHROTRON RADIATION IN ZEOLITE-LIKE MATERIALS RESEARCH

The knowledge of framework topology and framework/extra-framework cation positions offers a crucial insight into the adsorption and catalytic properties of zeolites and zeolite-like microporous materials. The conventional diffraction methods, however, which normally yield complete answers about the structure properties of ordered crystalline materials, are not always able to provide structural information for zeolite-like structures with sufficient reliability. They have specific structural features such as (1) low concentration and often random distribution of metal active sites over the framework or extra-framework positions, (2) disordered extra-framework molecules and cations, (3) stacking faults and (4) large mosaic spread of imperfect small crystals.

Most of these problems have been currently overcome by the use of powerful synchrotron X-ray sources.<sup>42</sup> In particular, the third-generation sources like the European Synchrotron Research Facility (ESRF), Advanced Photon Source (APS) and Spring-8 have been used for a wide range of different applications and studies of materials with complex stoichiometries, such as high- $T_c$  superconductors, magnetic materials and microporous materials. The development and use of area detectors, like image plates (IP) and charge coupled device systems (CCD), with high sensitivity, wide dynamic range (valid for IP) and large dimensions have additionally reduced the measurement time and enabled fast data collection, even in the case of more sensitive samples.

A variety of new and improved methods have been devised in powder diffraction, microcrystallography, anomalous dispersion, time-resolved and *in-situ* studies, all of which are also applicable to the study of zeolite-like materials. Applications of synchrotron radiation include: (1) the *ab-initio* solution and refinement of unknown crystal structures from very high-resolution powder data, (2) *in-situ* studies of phase transformations as a function of temperature or pressure, (3) *in-situ* studies of reaction kinetics and chemical synthesis, and (4) determination of cation distribution in mixed systems and oxidation states in mixed-valence compounds by the use of resonant scattering techniques.

The first problem that appears in the structure determination of zeolites and zeolite-like materials is their usual appearance as microcrystalline powders. Therefore, the single crystal X-ray diffraction methods cannot be used. In the last few years, however, many new zeolite-type structures have been determined using high resolution synchrotron powder data and new powerful computer programs.<sup>43</sup> The powder diffraction method has been used for a long time only as a fingerprint technique for identification pur-

poses. Now, it can be applied to the refinement of atomic coordinates of complex structures and for *ab-initio* structure solutions, with the use of traditional direct and Patterson methods or of techniques based on previous structural and chemical information (geometrical modelling, Monte Carlo method, simulated annealing, *etc.*).<sup>44</sup> The very recent studies of zeolite-like materials that involve high-resolution synchrotron powder diffraction structure solutions are silicates UTD-1<sup>26</sup> and SSZ-31,<sup>6</sup> and titanosilicate ETS-4.<sup>29</sup> The powder methods have been successfully applied to a large number of zeolite and zeolite-like structures, where the location of non-framework species was of interest, such as the position of the crown ether molecules in the ECM-2 structure.<sup>45</sup>

Synchrotron radiation has also enabled the study of micrometer-sized crystals of microporous materials, due to the very high intensities of X-ray sources.<sup>46</sup> The use of area detectors in microcrystal diffraction has allowed more data to be collected in shorter times and has thus reduced difficulties due to low signal-to-noise ratios, which have often accompanied data collections on microcrystals. It has now become possible to routinely solve the structures from 1000  $\mu\text{m}^3$  crystals and in the near future even smaller crystals, with dimensions of 1–5  $\mu\text{m}$ , should give reliable results about the atomic structure of materials. Some recent examples of zeolite-like structure determinations include the structure solution and refinement of magnesium aluminophosphate STA-1 from a  $30 \times 30 \times 30 \mu\text{m}$  crystal,<sup>10</sup> structure redetermination of  $\text{AlPO}_4\text{-CHA}$  from a  $15 \times 20 \times 30 \mu\text{m}$  crystal<sup>47</sup> and the DAF-5 structure analysis on a  $30 \times 30 \times 30 \mu\text{m}$  crystal<sup>9</sup>, with a description of the disorder of 4-piperidinopiperidine. Although single-crystal methods are preferable for X-ray structure determinations, the quality of the results obtained with advanced powder diffraction methods is already comparable.

Anomalous dispersion methods, which employ the tuneability of synchrotron X-ray sources, have proved to be very successful in the structure determination of many inorganic materials composed of elements, adjacent in the periodic table and the same crystallographic sites, sometimes with a partial occupancy of less than 10%.<sup>48</sup> With data collections in the vicinity of and far from the absorption edge of the investigated element, and with subsequent comparison of the two data sets, one can evaluate the position of the element in the structure (see Figure 7). The method has been applied to single-crystal and powder data and also to a wide range of elements possessing an absorption edge accessible to synchrotron X-rays (Mn K-edge 1.89643 Å, Co K-edge 1.60815 Å, Zn K-edge 1.28340 Å, *etc.*). Collection of multiple sets of scattering data on a same sample generally requires a very high collection time efficiency because of the limited stability of the materials in the high-energy synchrotron X-ray beam and limited synchrotron time.

Consequently, the great success of the anomalous dispersion experiments in recent years, especially for powder samples, has been due to high speed area detectors, which allow the entire pattern at one wavelength to be collected in a few minutes. The anomalous dispersion method has already been used for determination of the local structure of metal active sites in zeolite-like catalysts. Studies based on the use of highly calibrated synchrotron radiation have confirmed the incorporation of Fe in the zeolite L framework,<sup>49</sup> helped to determine the local structure of Fe in Fe-ZSM-5 aluminosilicate and Ti in titanosilicate ETS-10,<sup>50</sup> as well as the distribution of Zn cations in Zn-NaY zeolite.<sup>51</sup> The advantage of the anomalous dispersion method is also a simultaneous determination of the long range order of the unknown crystalline material and the local structure of elements investigated.

Resonant X-ray techniques like anomalous dispersion have already overcome comparable neutron studies, which have been used for a long time in the structure analysis of materials to distinguish between elements with a similar X-ray scattering power or to determine partial occupancies of elements at one crystallographic site. In spite of the new high flux neutron sources, like ILL in Grenoble and ISIS in England, neutron intensities are, as compared to synchrotron radiation, still too weak for some of the more detailed diffraction experiments. Nevertheless, neutron powder diffraction is used for the determination of atomic positions and thermal parameters of lighter elements (framework H atoms and structurally disordered template molecules) in microporous materials.<sup>52</sup>

The most exciting field of recent research that has been enhanced by the development of new radiation sources are the time-resolved and *in-situ* studies of catalysts under operating conditions, their crystallisation processes, and their phase transformations. The *in-situ* studies provide information on the crystallisation routes during the solidification, so the production of zeolite materials becomes more explicit and reliable. Information on the structural changes in the catalysts during catalyst activation, operation and final inactivation, can serve for better applications of the catalyst and better outcomes of the reactions.<sup>7,53</sup> There are numerous examples in recent literature of the time-resolved *in-situ* X-ray diffraction studies of microporous materials, *e.g.* crystallisation of different MAPO materials from amorphous gels.<sup>54</sup> Very interesting are also X-ray absorption spectroscopic or combined X-ray absorption and diffraction studies of structural changes induced by calcination and subsequent reduction of different catalysts, such as CoAPO-44, CoAPSO-44 and DAF-2,<sup>55</sup> or CoAPO-5, CoAPO-18, and CoAPO-36 catalysts,<sup>56</sup> using Co K-edge data. The shifts in Co K-absorption edge spectra to a higher energy, which are shown in Figure 4, reflect an increase in the Co oxidation state.<sup>53</sup> The changes in Co–O bond distances from

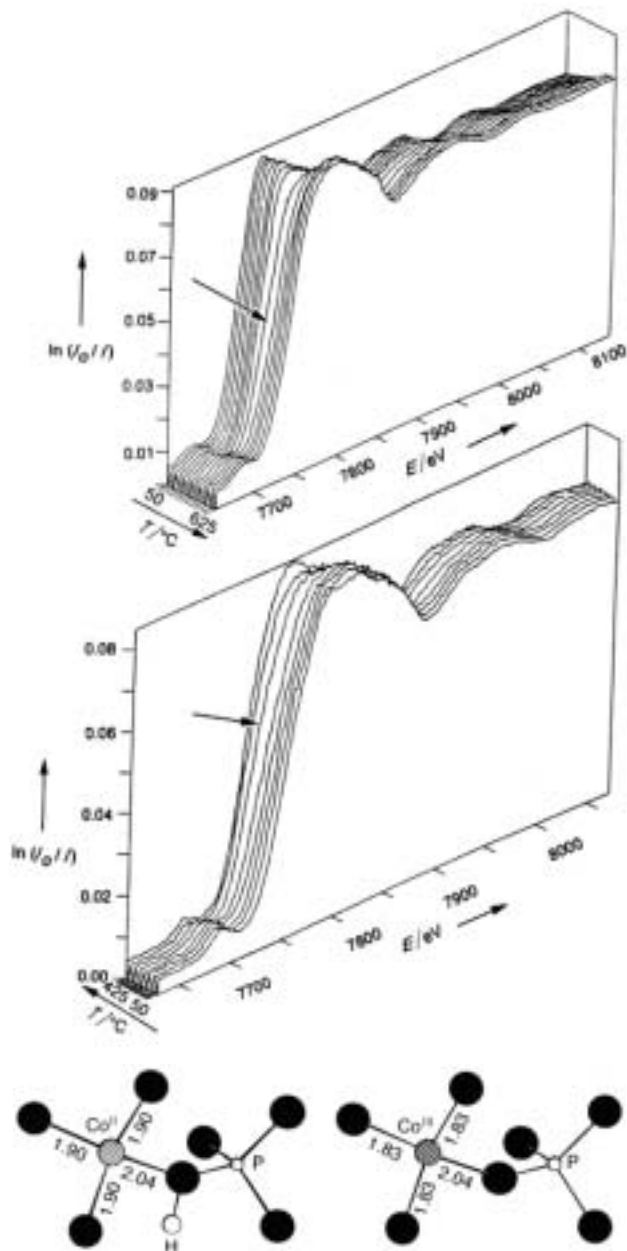


Figure 4. EXAFS spectra of CoAPO-18 redox catalyst (top) and schematic picture of  $\text{Co}^{2+}/\text{Co}^{3+}$  atoms local structures (bottom). A shift in K-edge spectra of cobalt (measured in fluorescence) during initial heating in air to burn off the template (upper spectrum) and during reduction to activate the catalyst (lower spectrum) is due to  $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$  transformation (reproduced with permission from Refs. 53 and 57).

1.90 to 1.83 Å prior to and after oxidation in CoAPO-18 catalyst are consistent with the proposed local structure of cobalt  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ .<sup>57</sup> Another illustrative example is the long range  $\text{Ni}^{2+}$  migration as the response of the Ni-exchanged zeolite Y activation to cyclomerisation, which has been monitored *in-situ* by X-ray diffraction (Figure 5).<sup>53,58</sup>

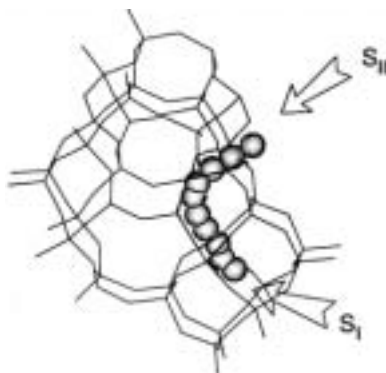


Figure 5. Schematic trajectory for migration of  $\text{Ni}^{2+}$  ions from  $S_I$  to  $S_{II}$  sites during the activation of the Ni-zeolite Y catalyst obtained by synchrotron *in-situ* diffraction and EXAFS studies. Migration of  $\text{Ni}^{2+}$  ions from  $S_I$  to  $S_{II}$  sites is evidently a prerequisite for catalytic activity (reproduced with permission from Ref. 53).

Energy-dispersive X-ray diffraction techniques or Laue techniques have undergone a renaissance with the full-white beam synchrotron sources and to some extent with the new neutron radiation sources, and have also been applied in the study of microporous materials crystallisation.<sup>59</sup> The Laue technique has enabled a very rapid collection of data, has made time-resolved experiments routinely available within time ranges of 100 picoseconds, and has been a promising method for the study of dynamic processes in zeolite-like materials. With further technical developments of synchrotron insertion devices, it would be possible to investigate sub-picosecond processes.<sup>60</sup>

#### OUR RESULTS IN THE SYNTHESIS AND STRUCTURAL CHARACTERISATION OF PHOSPHATE-BASED MOLECULAR SIEVES

Our principal interest in recent years has been focused on the synthesis and characterisation of phosphate-based zeolite-like materials. As mentioned before, they have a well-defined micropore system of zeolitic type; however,

the surface selectivity differs significantly from that of silica molecular sieves or zeolites. Their acidity is a complicated function of framework charge, structure, and nature of the (metal) atoms in the framework or extra-framework sites. Nevertheless, these phosphate derivatives have already been used as catalysts in many chemical reactions.<sup>3</sup> The latest results from our laboratory include: (1) determination of the site of incorporation of cobalt in a chiral zincophosphate framework by multiple wavelength anomalous dispersion crystallography, (2) a study of framework flexibility in chabazite-like aluminophosphate system using X-ray powder diffraction, and (3) »ship-in-bottle« syntheses and characterisation of aluminophosphates with encapsulated metal complexes.

The CoZnPO-CZP material with framework composition  $\text{Na}_6[\text{Co}_{0.2}\text{Zn}_{0.8}\text{-PO}_4]_6$  belongs to the group of small-pore zeolite-like molecular sieves with a high negative charge of the framework. The structure was initially determined using single crystal Mo-K $\alpha$  laboratory data (Figure 6).<sup>36,61</sup> However, due to the lack of scattering contrast between cobalt and zinc at the Mo-K $\alpha$

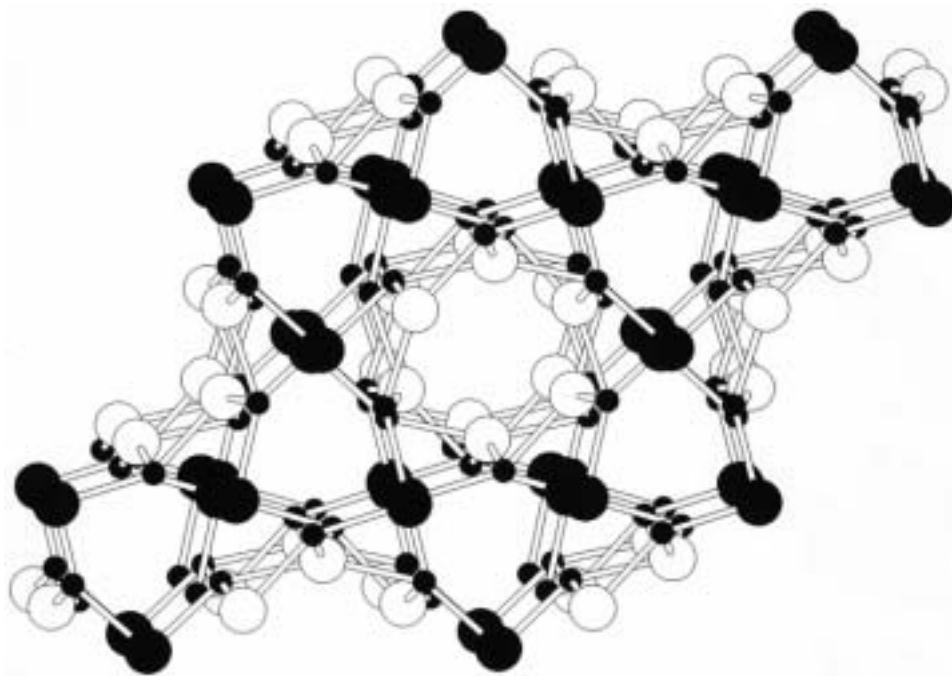


Figure 6. Schematic presentation of microporous CoZnPO-CZP framework and positions of two crystallographically different Zn sites according to two different types of 6-ring channels. Big black circles represent Zn1, big white circles Zn2 and small black circles P atoms. The structure is hexagonal [ $P6_522$ ,  $a = 10.464(4)$ ,  $c = 15.056(6)$  Å].

wavelength, the location of the isomorphously substituted cobalt over the two crystallographically different zinc sites could not be determined unambiguously. In order to determine the site(s) substituted by cobalt, synchrotron X-ray data were collected close to the K absorption edges of zinc and cobalt, and also at a wavelength of 1.45 Å. Subsequent calculation of  $f'$  difference Fourier maps allowed the pinpointing of both zinc and cobalt positions (Figure 7).<sup>62</sup>

The results clearly showed that Co was present predominately at the Zn1 site, which was located in one of the two different 6-ring channels, as

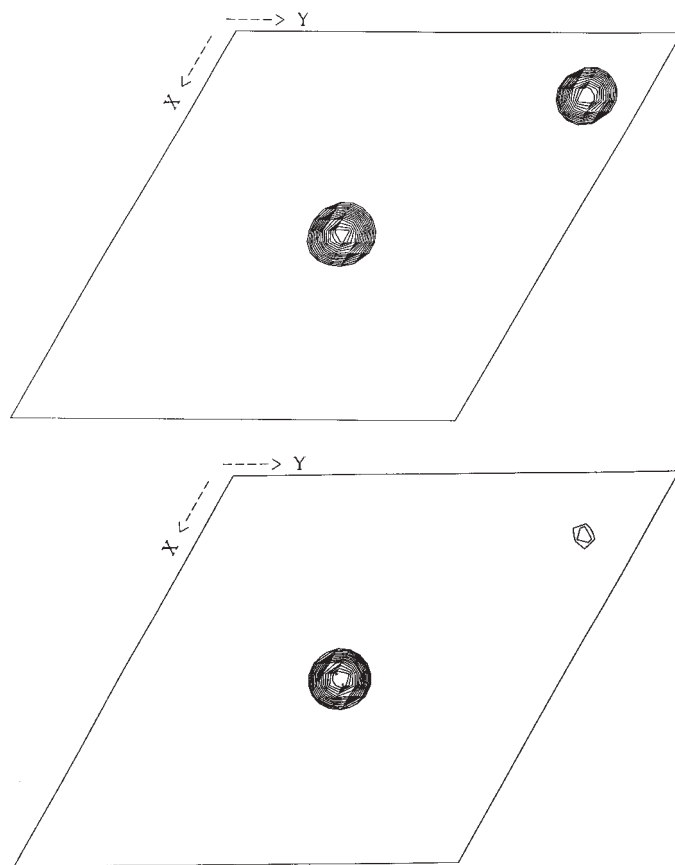


Figure 7. Zn K-edge (top) and Co K-edge (bottom) dispersive difference Fourier maps calculated using three synchrotron data sets ( $\lambda = 1.2846$  Å (Zn K-edge), 1.45 Å (reference) and 1.6083 Å (Co K-edge), which were collected at the Elettra X-ray diffraction beamline for the CoZnPO-CZP compound, revealed the presence of Zn at two and Co at one site (the small peak at the Zn2 site is at the noise level). Co isomorphous substitution thus takes place predominantly at one Zn framework site.



shown in Figure 6. The experiment was one of the first and most illustrative examples of the use of anomalous dispersion methods in the characterisation of active metal sites in zeolite-like materials.

Triclinic precursors of rhombohedral chabazite-like aluminophosphates  $\text{AlPO}_4\text{-34}$ ,  $\text{CoAPO-34}$  and  $\text{MnAPO-34}$  were successfully synthesised in the presence of HF, which was added to reactive aluminophosphate gels.<sup>63</sup> The  $\text{F}^-$  ions were found to be the crucial factor for a successful synthesis of  $\text{AlPO}_4\text{-34}$  material and remained encapsulated in the structure after the synthesis, forming bridges with two Al atoms (increasing in this way the Al coordination number from 4 to 6). The crystal structure of the as-synthesised  $\text{AlPO}_4\text{-CHA}$  was first determined from X-ray powder diffraction data in 1992<sup>64</sup> and redetermined in 1994 using synchrotron data.<sup>47</sup> Our studies of the crystal structures of calcined and rehydrated samples of  $\text{AlPO}_4\text{-CHA}$  revealed a very interesting behaviour of the materials.<sup>65</sup> Upon calcination at 500 °C, the triclinic structure of the as-synthesised phase [ $P\bar{1}$ ,  $a = 9.330(5)$ ,  $b = 9.209(4)$ ,  $c = 9.182(4)$  Å,  $\alpha = 87.56(3)$ ,  $\beta = 101.05(2)$ ,  $\gamma = 93.24(3)^\circ$ ] transforms into the rhombohedral one [ $R\bar{3}$ ,  $a = 9.329(2)$  Å,  $\alpha = 94.31(1)^\circ$ ], consistent with that of natural aluminosilicate chabazite.<sup>66</sup> However, the calcined sample is very moisture sensitive and upon hydration a change in chabazite structure occurs, which transforms the rhombohedral phase into a new triclinic one [ $P1$ ,  $a = 9.010(2)$ ,  $b = 9.279(2)$ ,  $c = 9.584(2)$  Å,  $\alpha = 95.23(1)$ ,  $\beta = 104.93(1)$ ,  $\gamma = 95.33(1)^\circ$ ], with terminal water molecules on the Al atoms, as shown in Figure 8. Hydration was found to be a reversible process, since thermal evacuation of the hydrated sample caused a complete return to the chabazite material, without any loss of crystallinity (Figure 9). In comparison with the MAPO materials prepared in a nonfluoride medium, our materials exhibited higher thermal stability up to 600 °C. Furthermore, it was found that at 20 °C the rehydrated triclinic phase reversibly transformed into another slightly different triclinic phase [ $P1$ ,  $a = 9.041(2)$ ,  $b = 9.336(2)$ ,  $c = 9.527(2)$  Å,  $\alpha = 94.97(1)$ ,  $\beta = 104.12(1)$ ,  $\gamma = 96.53(1)^\circ$ ], as it can be seen in Figure 9. This was an additional confirmation of the exceptional flexibility, stability and applicability of the synthesised material.

Transition metal complexes have recently been studied as possible templates in the crystallisation of porous solids as well as compounds useful for preparing novel materials.<sup>67</sup> A variety of coordination geometries and oxidation numbers of transition metals, associated with the precise and uniform size of voids in open-framework structures, as well as reactivity of the transition metal complexes make them useful for a number of chemical processes, especially for adsorption and catalysis. We have successfully synthesised and characterised two aluminophosphate molecular sieves with Ni(II) complexes encapsulated inside the channels or cavities of the host structures.

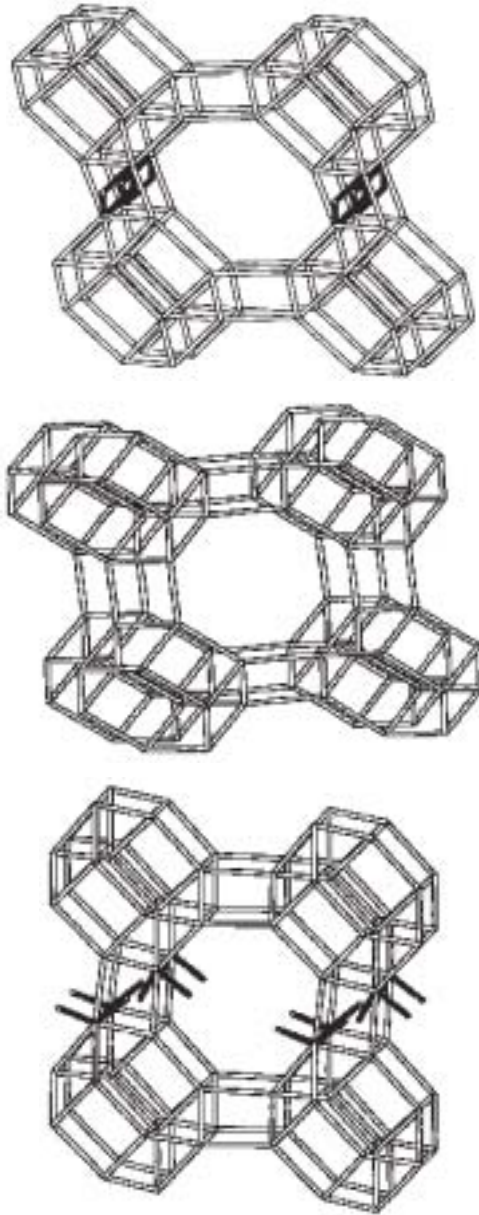


Figure 8. The structure of as-synthesised (top), calcined (middle) and rehydrated (bottom)  $\text{AlPO}_4\text{-CHA}$  material. In the as-synthesised sample there are bridging F atoms (darker Al-F-Al bonds), in the calcined sample the structure contains only tetrahedral Al and P, and in the rehydrated sample there are two terminal water molecules coordinating one of the three crystallographically different Al atoms in the structure (darker Al-H<sub>2</sub>O bonds).

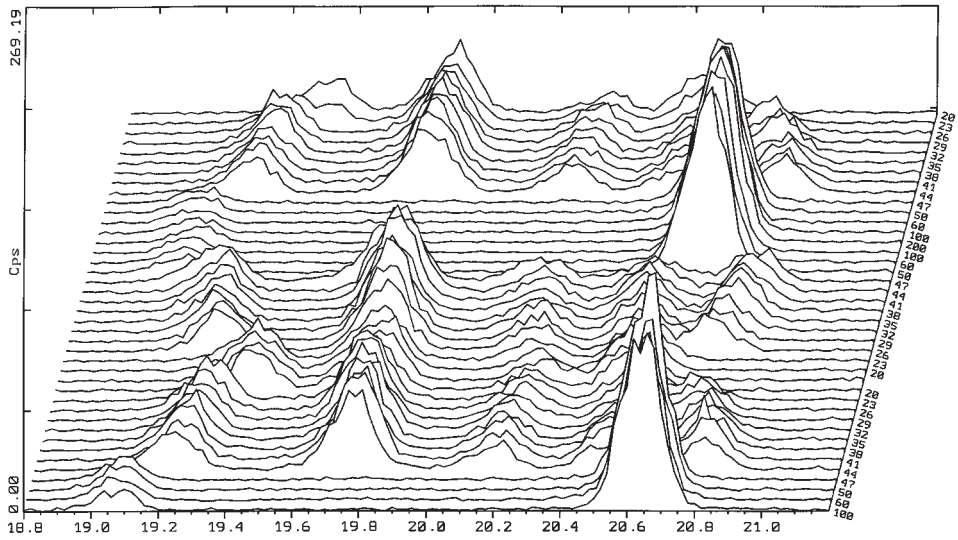


Figure 9. *In-situ* study of the reversible structural changes in the  $\text{AlPO}_4\text{-CHA}$  structure using a high-resolution laboratory diffractometer. Rhombohedral-triclinic and triclinic-triclinic phase transformations occur at 45 and 20 °C.

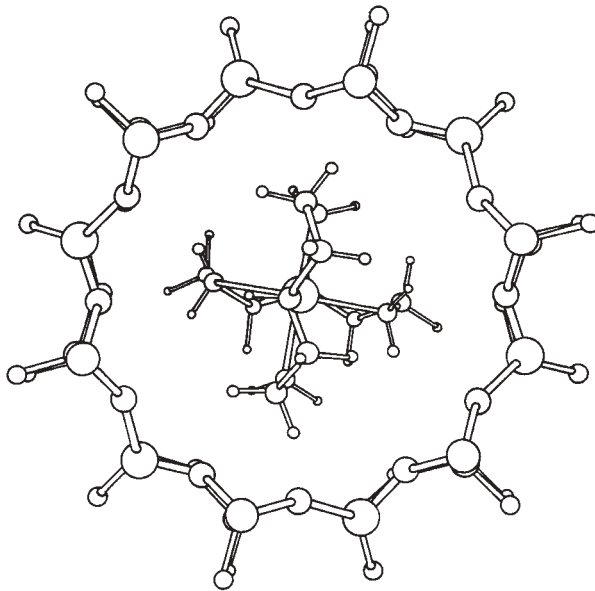


Figure 10.  $[\text{Ni}(\text{ten})_2]^{2+}$  inside a channel of  $\text{AlPO}_4\text{-5}$  in a view down the channel axis. The complex almost exactly fits the channel dimensions and is held inside the channel mainly by van der Waals forces.

The tris(1,2-diaminoethane)nickel(II) complex was found to be a novel template for the preparation of the chabazite-like  $\text{AlPO}_4\text{-34}$  molecular sieve.<sup>68</sup> During crystallisation the complex undergoes a ligand exchange, thus increasing the stabilisation of AlPO's chabazite structure by hydroxyls that have exchanged one 1,2-diaminoethane (en) molecule from the Ni(II) coordination sphere. The exchanged complex  $[\text{Ni}(\text{en})_2(\text{OH})_2]$  remains in the chabazite host and causes a triclinic deformation of the rhombohedral chabazite framework. Upon calcination, the triclinic phase completely transforms into the rhombohedral chabazite-like  $\text{AlPO}_4\text{-34}$ . The synthesis and structure of an  $\text{AlPO}_4\text{-5}$  molecular sieve with bis(di(2-aminoethyl)amine)nickel(II) complex ( $\text{Ni}(\text{ten})_2$ ) encapsulated in the structure have also been studied recently (Figure 10).<sup>69</sup> The encapsulation of the complex occurs during the crystallisation of  $\text{AlPO}_4\text{-5}$  and can be described as formation of a »bottle around the ship«. X-ray diffraction analysis shows that the encapsulation causes a change of unit cell parameters of the  $\text{AlPO}_4\text{-5}$  lattice, indicating the complex-host interactions. Geometry considerations suggest that  $\text{Ni}(\text{ten})_2$  remains in the  $\text{AlPO}_4\text{-5}$  host because it almost exactly fits into channel dimensions and is held inside the channel mainly by van der Waals forces.

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## SAŽETAK

### Noviji dosezi u sintezi i opisu svojstava materijala od vrste zeolita

*Nataša Zabukovec Logar, Ljubo Golič i Venčeslav Kaučič*

U nekoliko posljednjih godina znatni su naponi bili usmjereni na ciljanu pripremu zeolita i mikroporoznih materijala sličnih zeolitima s unaprijed zadanim fizikalnim i katalitičkim svojstvima. Uz pomoć novih računalnih tehnika bilo je moguće oblikovati obrasce za sintezu specifičnih mikroporoznih struktura željene veličine pora i međusobne povezanosti šupljina. U usporedbi s materijalima sličnim zeolitima velika se pažnja usmjerila na sustave koji sadrže prijelazni metal kao što su cinkosilikati, titanosilikati i različiti metaloaluminofosfati. Za njih je značajno da imaju mogućnost stvoriti posebne redukcijsko-oksidacijske uvjete, pored toga što posjeduju Brønstedova, odnosno Lewisova aktivna katalitička središta. Eksperimentalna određivanja istančanih strukturnih značajki poput prirode i položaja katalitičkih aktivnih položaja metala kao i smještaj, prostorno usmjerenje i nered obrasca, metala ili kompleksa unutar mikroporoznog domaćina postala su moguća korištenjem novih tehnika od kojih je većina utemeljena na rentgenskoj difrakciji i upotrebi sinkrotronskih i neutronske izvora zračenja. *In situ* istraživanjima kinetike nukleacije, rasta kristala i faznih prijelaza ili aktivacije katalizatora i postupaka pri povišenim temperaturama uvelike su koristili novi izvori sinkrotronskog zračenja treće generacije s vrlo visokim fluksom i fino kolimiranim snopom, kao i unapređenja postignuta u oblikovanju detektora zračenja i obradbi eksperimentalnih podataka.