

Nanoporous Materials: From Catalysis and Hydrogen Storage to Wastewater Treatment

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Abstract

Porous inorganic solids have found great utility as catalysts and sorption media because of their large internal surface area, i.e. the presence of voids of controllable dimensions at the atomic, molecular, and nanometer scales. With increasing environmental concerns worldwide, nanoporous materials have become more important and useful for the separation of polluting species and the recovery of useful ones. Their prospective applications include the use as templates for the production of electrically conducting nanowires and also for highly selective biosensors and biomembrane materials. Inorganic-organic or hybrid nanoporous crystalline materials have recently attracted much attention and increasing interest due to their promising use in gas processing and hydrogen storage. This review covers our recent developments in the synthesis, characterisation and property evaluation of new nanoporous inorganic and some hybrid solids with the emphasis on the silica and phosphate-based frameworks by using hydrothermal and microwave procedures with X-ray diffraction, spectroscopic (XAS, NMR) and electron microscopy characterisation techniques. The functionalisation of nanoporous materials by physical and/or chemical treatments, studies of their fundamental properties, such as catalytic effects or adsorption and their applications, emphasising (1) catalysis, (2) hydrogen and energy storage, and (3) environmental pollution control are also reviewed.

Keywords: nanoporous materials, microporous materials, mesoporous materials, zeolites, inorganic-organic hybrids, catalysts, hydrogen storage, wastewater treatment;

Biographical Sketches



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1. Introduction

1.1. Nanoporous materials on micro- and meso-scale.

International Union of Pure and Applied Chemistry (IUPAC) classifies porous materials into three categories¹ - microporous with pores of less than 2 nm in diameter, mesoporous having pores between 2 and 50 nm, and macroporous with pores greater than 50 nm. The term nanoporous materials has been used for those porous materials with pore diameters of less than 100 nm. Many kinds of crystalline and amorphous nanoporous materials such as framework silicates and metal oxides, pillared clays, nanoporous silicon, carbon nanotubes and related porous carbons have been described lately in the literature.² This

review will focus on the microporous and mesoporous silica- and phosphate-based materials with ordered pore structures.

Microporous materials are exemplified by crystalline framework solids such as zeolites, whose crystal structure defines channels and cages, i.e. micropores, of strictly regular dimensions (Figure 1). They can impart shape selectivity for both the reactants and products when involved in the chemical reactions and processes. The large internal surface area and void volumes with extremely narrow pore size distribution as well as functional centres homogeneously dispersed over the surface make microporous solids highly active materials. Over the last decade, there has been a dramatic increase in synthesis, characterization and application of novel microporous materials.³ The

composition of crystalline microporous materials ranges from aluminosilicates to aluminophosphates and gallophosphates or recently discovered inorganic-organic hybrids.⁴

Zeolites, which represent the largest group of microporous materials, are crystalline inorganic polymers based on a three-dimensional arrangement of SiO_4 and AlO_4 tetrahedra connected through their oxygen atoms to form large negatively-charged lattices with Brønsted and Lewis acid sites. These negative charges are balanced by extra-framework alkali and/or alkali earth cations. The most known zeolites are silicalite-1, ZSM-5, zeolite Beta and zeolites X, Y, and A. The incorporation of small amounts of transition metals into zeolitic frameworks influences their properties and generates their redox activity. Zeolites with their well-organised and regular system of pores and cavities also represent almost ideal matrices for hosting nanosized particles e.g. transition metal oxides that can also be involved in catalytic applications.⁵

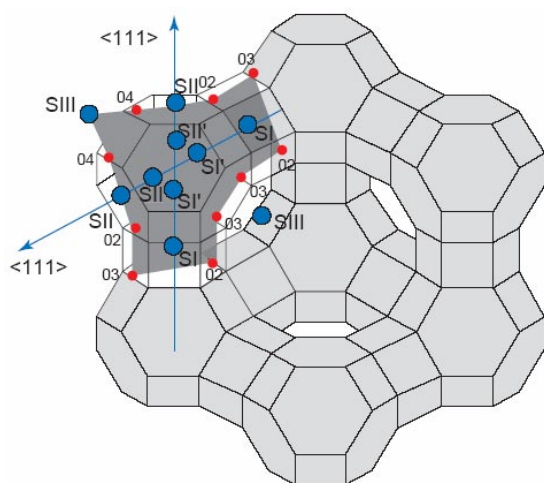


Figure 1: Structure and possible cation sites (SI, SII, etc.) in zeolite faujasite. Due to the presence of aluminium, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics [reproduced with permission from ref. 106].

The second largest known group of microporous materials is the aluminophosphate family, members of which were first synthesised in 1978 using amines as templates a.k.a. structure-directing agents. The aluminophosphate AlPO_4 frameworks are formed from vertex-sharing AlO_4 and PO_4 tetrahedra. The Al/P ratio is usually one, making the framework electrostatically neutral with no active sites present. The isomorphous substitution of framework aluminium or phosphorus atoms with divalent transition metals, such as Mn, Co, Fe, etc. generates negative framework sites and

makes these microporous materials very successful selective catalysts. An example of industrially very successful aluminophosphate catalyst is SAPO-34. Research has now progressed to form new microporous metallo-phosphates from many elements other than aluminium, such as gallophosphates and transition-metal phosphates, with differing chemistry and coordination geometry that have led to new structures and new possible applications.⁶

The careful selection of organic ligands as building blocks in the formation of novel metal-organic (MOF) and inorganic-organic (hybrid) microporous frameworks has recently opened a promising route to a variety of new advanced materials exhibiting the flexibility and functionality of organic and hydrothermal stability of inorganic components.⁷ The robustness of these networks depends on the strength and dimensionality of the bonds, i.e. the metal-ligand interactions. The research has focused on the metal phosphates carboxylates⁸ and metal carboxylates⁹, where carboxylate groups, like oxalates and higher dicarboxylates, have acted as a linker between inorganic moieties, usually PO_4 or MeO_4 and MeO_6 polyhedra ($\text{Me}=\text{Zn}, \text{Fe}, \text{Co}, \text{Cd}, \text{Mn}, \text{etc.}$).

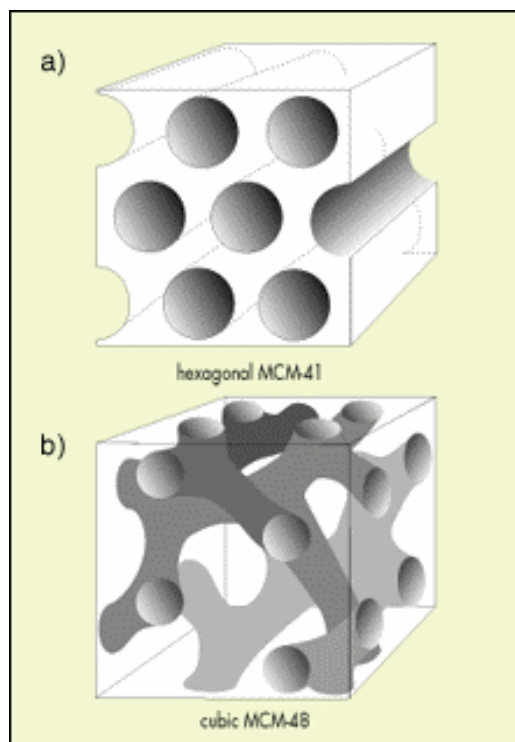


Figure 2: Mesoporous silicates were reported by Mobil Oil scientists in 1992; (a) MCM-41, which stands for Mobil Composition of Matter No. 41, shows a highly ordered hexagonal array of one-dimensional pores with a very narrow pore size distribution. The walls, however, very much resemble amorphous silica. (b) MCM-48 has a cubic mesostructure, i.e. arrangement of the pores.

The advantage of the shape confinements inside the pores of microporous materials can turn into severe limitations when large, bulky reactants have to be processed. These limitations seemed to be overcome by the discovery of MS41 family of silicate amorphous mesoporous materials with large internal surface areas and narrow pore size distributions by Mobil Oil scientists in 1992.¹⁰

Their most known and studied material is MCM-41 mesoporous silicate with one-dimensional hexagonal arrangement of the pores. The cubic MCM-48 material exhibits three-dimensional pore system that is more resistant to pore blocking and allow faster diffusion of reactants than a one-dimensional array of pores (Figure 2). The long-range ordering of the pores and the potential for isomorphous substitution with transition metals, enabling formation of catalytically-active centres, have incited applications in areas such as adsorption, separation and catalysis, especially in processes where bulkier molecules are used.¹¹ A variety of mesoporous silicates, aluminosilicates, aluminophosphates, and other transition metal oxides and phosphates have been developed and synthesised using several supermolecular assembly pathways.¹²

Most of the silica- and phosphate-based mesoporous materials have relatively lower catalytic activity and hydrothermal stability than their microporous analogues. This is attributed to the low acidity or low oxidation ability of catalytically active species that are strongly related to the amorphous nature of the pore walls and which severely hinder their practical applications.¹³ Additionally, molecular size exclusion or shape-selective processing is not as readily obtained on solids with amorphous pore walls because they usually have a broader distribution of pore sizes compared to microporous crystalline materials. Various strategies have been employed to overcome these problems. One of them is to combine major advantages of crystalline microporous and mesoporous material and prepare so-called microporous/mesoporous composites.¹⁴ Different methodologies have been described for their preparation.¹⁵ The two-step preparation of microporous/mesoporous solid, which encompasses the synthesis of nanosized microporous crystallites that are later organised in the mesoporous structure by using large surfactant molecules, has recently drawn greatest attention.

1.2. Designing nanoporous materials for clean technology, green chemistry, and sustainable development

There is an increasing need for cleaner fuels and industrial processes that would minimise the consumption of energy, production of waste, or the use of corrosive, explosive, volatile, and nonbiodegradable

materials and a range of nanoporous materials already meet the majority of these demands.¹⁶

Microporous materials are mostly used as heterogeneous acid and redox catalysts in petroleum industry and in the production of chemicals for various types of shape-selective conversion and separation reactions.¹⁷ They form the basis of new environment-friendly technologies, involving cheaper, more efficient and more environment-friendly ways for carrying out chemical reactions. Transition metal-modified microporous molecular sieves with aluminosilicate and aluminophosphate frameworks catalyse a wide variety of synthetically-useful oxidative transformations with clean oxidants such as hydrogen peroxide or oxygen under relatively mild conditions with the advantage of facile recovering and recycling, if compared to homogeneous liquid phase catalyst, like sulphuric acid.¹⁸ A number of applications in waste treatment processes, including removal of heavy metals and radioactive species, as well as ammonia, different phosphates and toxic gasses from water, soil and air are due to the unique structural and surface physico-chemical properties of microporous materials, such as excellent absorption and ion-exchange capacities. Among very recent applications of microporous materials are also optical-electronic devices, biological materials and implants, sensors, and membranes for gas separation.¹⁹ Gas sorption studies on new inorganic-organic (hybrid) and metal-organic (MOF) framework structures have shown their great potential in the field of solid state hydrogen storage technologies.²⁰

Somewhat less developed, but still highly important are applications of mesoporous solids. Expansion of the functionality and improved control over the hydrothermal and chemical stability of ordered mesoporous solids by modified and optimised synthetic or post-synthetic routes in recent years have been crucial for their increasing application in the fields of catalysis and also optics and semiconductor industry.²¹ Intensive research efforts have also been driven by the emerging applications such as biosensors, drug delivery, gas separation, energy storage and fuel cell technologies.²²

The main challenges in research of nanoporous materials include the understanding of structure-property relations and tailor-design of nanostructures for specific applications. A substantial progress has been made in the control of the pore shape and sizes and active sites' activity and distribution (Figure 3). Tailoring of acid catalysis and other processes over zeolites and zeolite-like materials is probably as close as one can get. For mesoporous solids the main goal, the control of homogeneous surface with single active sites, i.e. the regular distribution of active sites that would lead to an optimised catalytic performance, has still not been achieved.

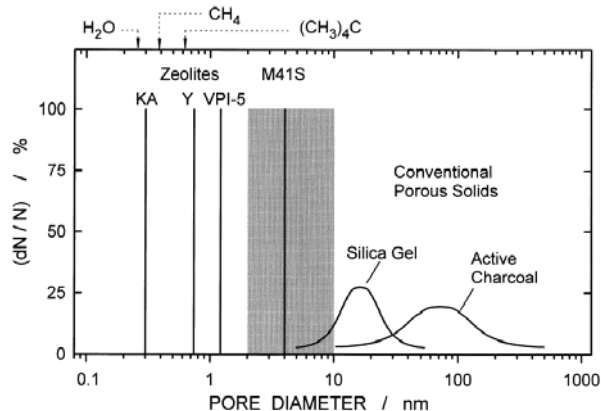


Figure 3: Typical pore diameter distributions of porous solids (KA is the K form of zeolite A; VPI-5 is a microporous aluminophosphate with 18-membered-ring pores; M41S is a family of mesoporous MCM materials). For comparison, the kinetic diameters of water, methane and neopentane are also indicated [reproduced with permission from ref. 107].

2. Catalysis

2.1. Microporous and mesoporous acid and redox catalysts

Catalysis by nanoporous materials nowadays covers a broad range of economically very important processes related to the upgrading of crude oil and natural gas as well as the profitable production of fine chemicals.²³ All reactions and conversions are based on the acid and redox properties and shape-selective behaviour of nanoporous materials. Acid-catalysed reactions are by far the most numerous and best-studied reaction type in which organic functional groups undergo an array of different transformations with nucleophilic

reagents in the presence of microporous solid acids as catalysts.²⁴ The most common reactions, where nanoporous acid-catalysts are involved, are fluid catalytic cracking, hydrocracking, dewaxing, aliphatic alkylation, isomerisation, oligometisation, transformation of aromatics and conversion of methanol to hydrocarbons. Redox nanoporous catalysts are also increasingly used for a variety of selective oxidations of various substrates of synthetic hydrocarbons, alcohols, and amines since these reactions can be performed under mild conditions in the liquid phase. An illustrative example is the clean production of adipic acid that is used in the production of nylon with the direct oxidation of cyclohexene with aqueous H_2O_2 using Ti- or Fe-substituted microporous catalysts.²⁵ The incorporation of tetravalent (e.g. Ti, V) transition metals into the framework of silicalite-1 forms excellent catalysts with selective properties for epoxidations.²⁶ The incorporation of trivalent (e.g. Cr, Fe) transition metals into the framework of silicalite-1 results in high-quality inorganic membranes used for catalytic membrane reactors. Metal-modified AlPO_4 - n catalysts (n denotes a specific structure type) have been shown to oxidise linear alkanes using molecular oxygen as reagents, rather than using more expensive oxidants such as organic hydroperoxides (Figure 4).²⁷

Transition metal-modified mesoporous materials with aluminosilicate and aluminophosphate framework are already reported to be good catalysts for acid-catalysed reactions and oxidations, hydroxylation and polymerisation reactions.²⁸ Nanocomposites built from highly dispersed nanoparticles of transition metal oxides, incorporated into intracrystalline voids have good catalytic performance in carbon monoxide and methanol oxidation,²⁹ although they do not exhibit catalytic properties comparable to those of

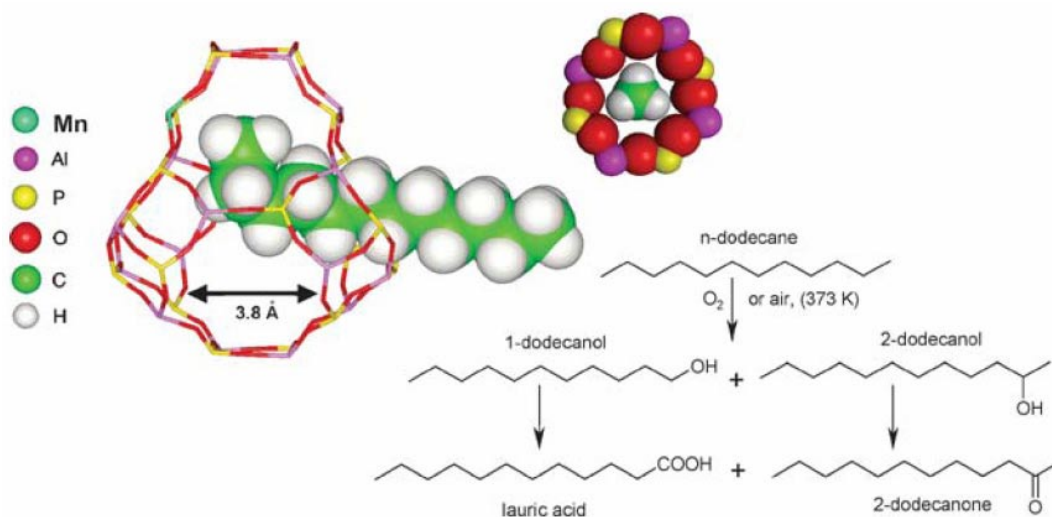


Figure 4: $\text{Me}^{3+}\text{AlPO-18}$ ($\text{Me} = \text{Mn}, \text{Co}$) is a regioselective oxidation catalyst that, in air or O_2 , preferentially oxyfunctionalises the terminal methyl group, as schematised here for n -dodecane [reproduced with permission from ref. 16].

microporous silicates. Hydrophilicity and low-metal dispersion of metal-modified or metal-functionalised mesoporous materials decrease their activity and selectivity in reactions using aqueous H_2O_2 as oxidant and the leaching of metal species from the solid disables the recovery of the catalyst.³⁰ Recently discovered microporous/mesoporous composites are expected to overcome these problems.

2.2. Ti-containing nanoporous silicates (Ti,Al)-Beta/MCM-48, (Ti,Al)-Beta/MCM-41

The field of porous titanium silicates is one of the fastest developing areas of porous materials.³¹ The materials possess remarkable catalytic activity in selective oxidation of organic compounds. Microporous titanium silicates such as zeolites Ti-silicalite-1 and Ti-Beta are extremely efficient catalysts for epoxidation of alkenes in the presence of aqueous H_2O_2 and *tert*-butyl hydroperoxide as oxidants, which is attributed to the unique architecture of titanium centres that are isolated in the silicate framework.³² By choosing different microporous zeolitic materials it is in general possible to tailor the catalyst with respect to the concentration of catalytically active titanium sites and to the access of molecules to these sites.

The dimensions of micropores within zeolitic structures limit the application of these catalysts to catalytic reactions with small molecules. Larger reactants could in principle be processed by using mesoporous titanium silicates such as Ti-MCM-41 or Ti-SBA-15.³³ Mesoporous silicates do not exhibit catalytic properties comparable to those of microporous silicates, with main drawbacks in leaching of titanium species from the pore walls, which affects the catalyst's function. Greater wall thickness of some of the mesoporous materials, like SBA-materials family, can also make part of titanium sites unavailable for the reactants. Titanium-modified microporous/mesoporous composites are thus promising catalytic materials combining stable active framework sites and large pores for processes with bulkier reactants and products. Up to now most of the literature in the field of composites has focused on the preparation of new composites with different methods but only a few of them have emphasised the modification with transition metals.^{34,14} The examples of modification with titanium are TiMMM-1³⁵, MTS-9³⁶, UL-TS-1³⁷ with highly active catalytic sites and Ti-JLU-20³⁸. They were all prepared with zeolite seed or zeolite nanoclusters of Ti-silicalite-1 (TS-1) and none of them with Ti-Beta zeolite precursor. Recently, we succeeded in the preparation of titanium containing microporous/mesoporous composites (Ti,Al)-Beta/MCM-41 (Figure 5)³⁹ and (Ti,Al)-Beta/MCM-48 (Figure 6).⁴⁰

The catalytic activity of Ti-Beta/MCM-41 composite in oxidation reactions and titanium leaching from the

framework was tested by the epoxidation of cyclooctene using *tert*-butyl hydroperoxide as the oxidant. Titanium leaching from the composite was not observed. The tests with bulkier molecules are in progress. The detailed structural characterisation revealed that the product was hydrothermally stable. (Ti,Al)-Beta/MCM-41 was synthesized hydrothermally in the presence of structure-directing agents cetyltrimethylammonium bromide (CTABr) and tetraethyl ammonium hydroxide (TEAOH). The presence of both micropores and mesopores in template-free (Ti,Al)-Beta/MCM-41 was detected by using X-ray diffraction, absorption/desorption of nitrogen and with a detailed HRTEM investigation. X-ray absorption studies (XANES and EXAFS analyses) showed the presence of Ti^{4+} cations coordinated to four oxygens. These results indicated framework Ti and thus the presence of Ti oxidation centres within the composite material. NMR investigations showed the presence of Brønsted and Lewis acid sites related to framework aluminium, which were generated by the removal of potassium and sodium ions from the (Ti,Al)-Beta/MCM-41 pores.

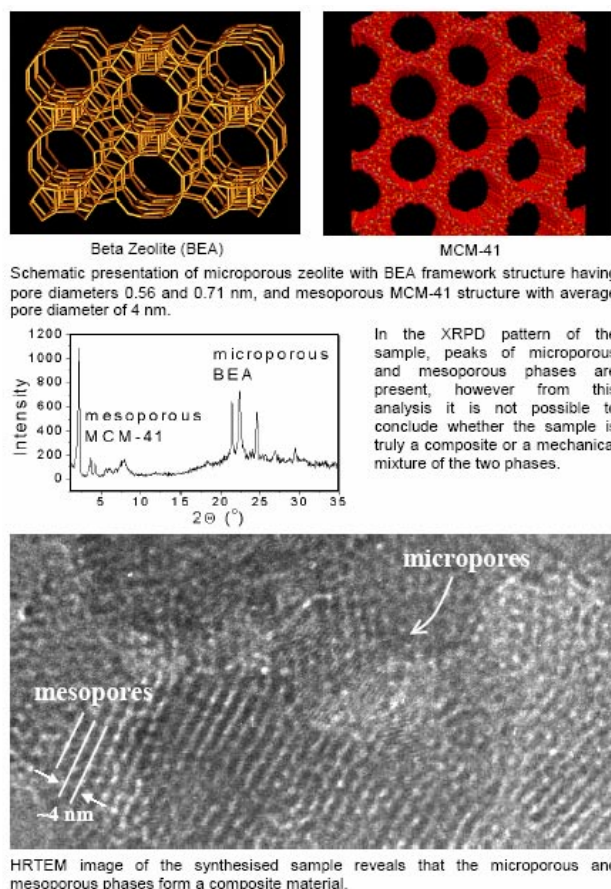
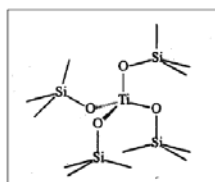
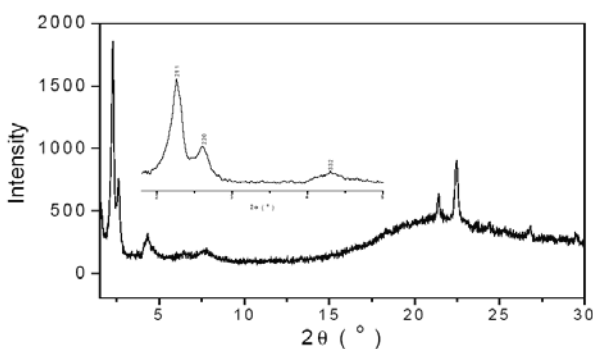


Figure 5: Synthesis and characterisation of (Ti,Al)-Beta/MCM-41 composite.

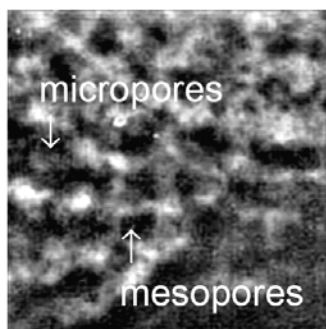
The (Ti,Al)-Beta/MCM-48 was also synthesized hydrothermally in the presence of

cetyltrimethylammonium bromide (CTABr) Triton® x-114 and tetraethyl ammonium hydroxide (TEAOH). Elemental analysis and X-ray absorption studies showed the presence of tetrahedral Ti^{4+} species that do not leach from the framework and represent oxidation sites in the material. However, aluminium in (Ti,Al)-Beta/MCM-48 is sensitive to thermal treatment, i.e. when removing template molecules from the pores by calcination. We thus have oxidation and not acid sites, what is an advantage, when one-step reactions are concerned.

XRD pattern confirms the presence of mesoporous cubic MCM-48 and microporous zeolite Ti-Beta phases. The inset represents the expansion of low-angle 2 θ region.



Titanium centres isolated in the silicate framework represent potential catalytic sites for oxidation reactions.



HRTEM image of the microporous/mesoporous silicate-based composite (Ti,Al)-Beta/MCM-48

Figure 6: Synthesis and characterisation of (Ti,Al)-Beta/MCM-48 composite.

2.3. Fe-containing nanoporous silicates and aluminophosphates (FeVPI-5, FAPO-36, FeHMA)

The substitution of iron is widely used to modify the original properties of porous catalyst hosts in micro- and mesoporous structures. Both the acidity and redox properties can be modified by inserting iron into the structure onto the framework sites or as extra-framework iron-complexes. Iron-containing microporous catalysts have been attracting considerable attention due to their remarkable activity in the reduction of nitrous oxides, oxidation of cyclohexane, oxidation of benzene to phenol, and the selective oxidation of methane.⁴¹ In most studies, the framework Fe^{3+} is proposed as the major active agent in the catalytic reactions. The most applicable iron-containing microporous catalysts are FeZSM-5 and Fe-silicalite-1.⁴² Among microporous

aluminosilicates FAPO₄-5, FAPO₄-11 and FeVPI-5 were reported to be catalytically active in the oxidation of aromatic compounds, such as hydroxylation of phenol and benzene, and epoxidation of styrene as well as the oxidation of naphthol.⁴³ The catalytic activity of FAPO-5 and FAPO-11 is comparable with that of Ti-silicalite-1 in some reactions. FeVPI-5 shows high activity in naphthol oxidation by H_2O_2 yielding the conversion of 14.5 %, while Ti-silicalite-1 is completely inactive owing to its small pore sizes. These results suggest that FeVPI-5 is a good candidate for the catalytic oxidation of large organic compounds. We have prepared two large-pore microporous aluminophosphates FeVPI-5⁴⁴ and FAPO-36⁴⁵ that exhibit redox behaviour and are good candidates for redox catalysts. Elemental analysis and X-ray absorption spectroscopy of hydrothermally synthesised FeVPI-5 indicated isomorphous substitution of framework aluminium by Fe^{3+} . The acidity tests of template free FeVPI-5, performed by IR spectroscopy and using CO adsorption at low temperature on the oxidized and on the reduced material, supplied evidence on the redox behaviour of framework iron in FeVPI-5. The local structure of the framework iron in the large-pore template-free FAPO-36 was studied by X-ray absorption spectroscopy and revealed the incorporation of Fe^{3+} into the tetrahedral sites of the framework. The acidity of FAPO-36 has been investigated by using carbon monoxide adsorption-desorption FTIR spectroscopy on the oxidized and on the reduced material, evidencing the redox behaviour. The net charge of the framework can be tuned by adjusting the oxidation state of iron, thus controlling the presence or absence of Brønsted acid sites on the sample.

Mesoporous systems with incorporated iron also attract interest, since the mesoporous host may accommodate larger molecules in the pores thus allowing catalytic processes for a broader variety of reactions.⁴⁶ Mesoporous iron-functionalised catalysts have been reported to have high catalytic activity, i.e. FeHMS and FeMCM-41 silicates⁴⁷ for phenol hydroxylation or FeSBA-1 silicate for phenol *tert*-butylation⁴⁸. Compared with the silicates/aluminosilicates, the low pH synthesis and the flexible network of mesoporous aluminophosphates are the main factors favouring the stabilisation of large amounts of trivalent iron in the matrix. Recently, we have reported the microwave synthesis of iron-substituted hexagonal mesoporous aluminophosphate FeHMA using cetyltrimethylammonium chloride (CTACl) as a template.⁴⁹ The local environment of iron incorporated in HMA investigated by X-ray absorption spectroscopy showed preferential octahedral coordination of Fe^{3+} although the presence of smaller amount of tetrahedrally coordinated Fe^{2+} was also detected. Mössbauer spectra of template-

free FeHMA demonstrated the above mentioned dependence of tetrahedral/octahedral coordination on the specific conditions used (i.e. presence/absence of the adsorbed water) and the pronounced reversibility of $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ redox transitions. From NMR analysis, parameters of Fe local structure obtained by Mössbauer spectroscopy and from literature data on microporous iron aluminophosphates we could conclude that Fe^{2+} and a part of Fe^{3+} are incorporated into the FeHMA framework. Water molecules are probably coordinatively bonded to framework Fe^{3+} cations.

Transformations in coordination and oxidation states of iron occurring under catalytic conditions are generally quite common. In this regard, the degree of the crystallinity of host is of primary importance. Coordination and redox properties of iron species present in strictly crystalline microporous systems may be distinctly different from the properties of iron located in mesoporous hosts possessing partly amorphous structure in their pore walls.⁵⁰

2.4. Mn-containing nanoporous silicates and aluminophosphates (MnS-1, MnHMA, MnMCM-41)

Manganese complexes are nowadays fast developing catalysts for epoxidation reactions.⁵¹ Many Mn-containing microporous and mesoporous materials have been reported; most of them comprise manganese on extra-framework positions as manganese complexes, and very few have manganese in the framework positions. One of them is MnAPO-5 material that was found to be a good catalyst for the ethylation of benzene.⁵² We have prepared and characterised manganese-containing silicalite-1 material MnS-1.⁵³ The material was synthesized hydrothermally in the presence of structure directing agent (template) tetraethylammonium hydroxide (TEAOH) for the first time. An incorporation of Mn into the framework sites of silicalite-1 was suggested by elemental, thermogravimetric and cation exchange analyses of template-free sample. X-ray absorption spectroscopic methods confirmed isomorphous substitution of Si^{4+} by Mn^{3+} in MnS-1. The presence of small amount of extra-framework Mn^{2+} could not be completely excluded. FT-IR spectroscopic studies of CO adsorption at 100 K on template-free MnS-1 revealed the Lewis acidity of the sample. No redox activity $\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+}$ was observed.

Recently, a number of manganese-functionalised mesoporous materials have been prepared. For example, MCM-41 supported catalysts, prepared by the template ion-exchange method, show high activity for the epoxidation of stilbene.⁵⁴ Gas-phase grafted Mn species provide higher activity in stilbene oxidation than impregnated Mn-MCM-41 when tert-butyl hydroperoxide was used as an oxidant.⁵⁵

In contrast, Mn impregnated MCM-41 showed higher activity than gas-phase grafted Mn-MCM-41 in diphenylmethane oxidation using air as an oxidant. The differences were attributed to the nature of the Mn centres. We have prepared and fully characterised two manganese-containing mesoporous materials, i.e. silica-based MnMCM-41⁵⁶ and hexagonal mesoporous aluminophosphate MnHMA (Figure 7)⁵⁷. We synthesised MnMCM-41 by direct hydrothermal method in the presence of cetyltrimethylammonium chloride (CTACl) as a template. Local environment of manganese incorporated in mesoporous silicate MCM-41 that was investigated by X-ray absorption spectroscopy showed the coexistence of Mn^{2+} and Mn^{3+} cations in both as-synthesised and template-free MnMCM-41 samples. Mn^{3+} cations in the template-free MnMCM-41 were incorporated into the framework and coordinated to three oxygens in the first coordination shell. Pulsed ESR (Electron Spin Resonance) and ESEEM (Electron Spin-Echo Envelope Modulation) investigations were in agreement with XANES and EXAFS studies. Thermally stable manganese-modified hexagonal mesoporous aluminophosphate (MnHMA) was synthesized hydrothermally in a microwave oven in the presence of cetyltrimethylammonium chloride (CTACl) as a template. X-ray Absorption Spectroscopy studies of local environment revealed that manganese in the as-synthesized and template-free MnHMA was present in the form of Mn^{2+} and Mn^{3+} ions in the ratio 40%/60% both coordinated with four oxygen atoms. EPR (Electron Paramagnetic Resonance) and ESEEM (Electron Spin Echo Envelope Modulation) revealed that Mn^{2+} in both as-synthesized and template-free products was located into the mesoporous aluminophosphate framework.

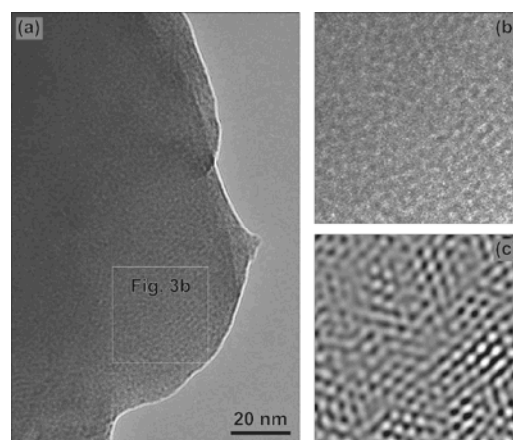


Figure 7: (a) A high-resolution TEM image of the as-synthesised MnHMA particle. (b) A close-up of the detail from the raw image in Fig. 6 (a) shows faint hexagonal features in some parts of the image. (c) FFT filtered image of this detail clearly reveals a close-packed hexagonal pattern disrupted with several dislocations and stacking faults, which have been partly induced by a relatively strong electron irradiation.

2.5. Hydrothermal and microwave synthesis of nanoporous catalysts

The design, synthesis and modification of nanoporous materials are challenging and have to be well controlled. Microporous materials are in general prepared hydrothermally from aqueous gels containing a source of the framework building elements (Si, Al, P, etc.), a mineraliser (OH⁻, F⁻) regulating the dissolution and condensation processes during the crystallisation, and a structure-directing agent or template, usually an organic amine or ammonium salt. Transition metals can be incorporated into microporous materials by post-synthetic ion-exchange treatment or by direct framework substitution by the addition of transition metal cations into the synthesis gel.⁵⁸ Our recent metal-substituted microporous products were prepared exclusively by a direct hydrothermal method that resulted in novel materials with stable active framework sites.

Ordered mesoporous silica- and nonsilica-based materials are also prepared hydrothermally by a variety of procedures and over a wide range of compositions using various different structure directing agents, i.e. surfactants.⁵⁹ The mechanisms of formation, although still a matter of discussion, are understood in principle, and the macroscopic morphology as well as the orientation of the pores can be controlled in fortunate cases. Adjustments of synthetic parameters crucially affect the properties of final products, i.e. their hydrothermal stability and pore sizes.⁶⁰ Using tetraethyl orthosilicate as an alternative silica source and by reducing the pH of the solution during synthesis an improved yield of MCM-48 with enhanced stability was reported.⁶¹

For the preparation of microporous/mesoporous composites three methodologies have been described in the literature.¹⁵ The first approach is to start the synthesis of mesoporous material and then add the template for the formation of microporous material. In this way the amorphous walls of mesoporous solid are expected to partly recrystallise into crystalline microporous walls. The second approach is based on the use of protozeolitic seeds containing small crystalline domains instead of fully crystalline microporous (zeolite) particles. These seeds are organized into the mesoporous structures by using different types of surfactants. In the third approach carbon-based particles are added as a secondary template into the reaction mixture. When the synthesis of microporous material is completed, they are removed by calcination leading to the formation of mesoporous zeolite single crystals. We have used the second approach in the preparation of (Ti,Al)-Beta/MCM-48 and (Ti,Al)-Beta/MCM-41 materials.

An alternative to a classical hydrothermal synthesis is a microwave oven. Studies in the last

decade suggest that microwave energy may have a unique ability to influence chemical processes. These include chemical and materials syntheses as well as separations. Specifically, recent studies have documented a significantly reduced time for fabricating zeolites, mixed oxide and mesoporous molecular sieves by employing microwave energy.⁶² In many cases, microwave syntheses have enabled the formation of new nanoporous structures. By reducing the times by over an order of magnitude, continuous production would be possible to replace batch synthesis. This lowering of the cost would make more nanoporous materials readily available for many chemical, environmental, and biological applications. Further, microwave syntheses have often proven to create a more uniform (defect-free) products than conventional hydrothermal synthesis. We have successfully used microwaves in the synthesis of two mesoporous aluminophosphates FeHMA and MnHMA.

2.6. Characterisation of structure porosity and acid sites in nanoporous catalysts (XRD, TEM, NMR, XAS)

The elucidation of the structures of nanoporous materials is essential for the understanding and prediction of their macroscopic physical and chemical properties. In particular, the size and connectivity of the channels and cavities determine their molecular sieving capability. The coordination, location, oxidation state and strength of bonding of the divalent and other transition metal ions in materials are directly related to their activity/selectivity in catalytic and other reactions.⁶³

The conventional single-crystal diffraction methods, which normally yield the most complete answers about the structure properties of ordered crystalline materials, are not always able to provide structural information with sufficient reliability for the microporous structures. The first problem is the small size of the crystals that often require *ab initio* powder structure solutions. The second problem is the low concentration and often random distribution of metal active sites over the framework or extra-framework positions that cannot be detected by conventional methods. The rapid development of synchrotron radiation sources has brought a tremendous progress in this field or research. The so-called micro-crystallography, dealing with a few micron-sized single-crystals and anomalous dispersion methods, has given new insights into the structural chemistry of microporous materials. It has also enabled the in-situ diffraction studies of the structural changes during crystallisation and phase transitions as a function of temperature or pressure and also in-situ studies of reaction kinetics by following the structural changes during the catalysis and other processes that are taking place on the microporous surfaces.⁶⁴ We have recently

written a review paper on the use of X-ray diffraction in the structure elucidation of microporous materials.⁶⁵ The equipment that we used in our studies comprise single-crystal Nonius Kappa CCD diffractometer with MnK α radiation, two powder diffractometers, Siemens D-5000 and PANalytical X'Pert PRO high-resolution diffractometer with CuK α radiation, and synchrotron radiation sources in Daresbury, UK and Elettra in Trieste, Italy.

High-resolution transmission electron microscopy (HRTEM) is essential in the characterisation of amorphous mesoporous solids, where X-ray diffraction methods cannot give reliable answers about solids' structural properties.⁶⁶ Using HRTEM methods we can determine the distribution and size of the mesopores. HRTEM and electron crystallography was for example used for the determination of the cubic structure of MCM-48 material.⁶⁷ Electron crystallography is an approach of electron microscopy where a three-dimensional image is synthesised from a set of two-dimensional images. We are extensively using high-resolution TEM microscope JEM 2010F UHR in the characterisation of new mesoporous products. HRTEM was used to confirm the presence of micropores and mesopores at the same area of investigation for the first time in TiBeta/MCM-48 and TiBeta/MCM-41 composites, which could not be performed with other characterisation methods. Additionally, good resolution images of mesoporous aluminophosphate MnHMA were collected using this method.

With the availability of synchrotron radiation sources, X-ray absorption spectroscopy (XAS) techniques have also developed into a widely used tools for structural research of nanoporous materials. XAS analytical methods XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) provide microscopic structural information of a sample through the analysis of its X-ray absorption spectra of selected atoms. XANES identifies local symmetry and the average oxidation number of selected atom. EXAFS provides the description of a short-range order for selected atom in terms of the number of neighbours, distances, and thermal and static disorder within the range of those distances. Since XAS is selective towards a particular element and sensitive only towards short-range order, it is one of the most appropriate spectroscopic tools for microporous and mesoporous catalysts characterisation. XAS studies of metal-modified zeolites and silica based mesoporous catalysts focused on the structural characterisation of framework metal species. EXAFS has become a powerful method to directly detect the isomorphous substitution of tetrahedrally coordinated framework atoms (Al, P or Si) by metal ions. Recently, we have studied Co and Mn in MeAPO-31⁶⁸, Zn and Fe

in MeAPO-34⁶⁹, Fe in FAPO-36, FeVPI-5 and FeHMA, and Mn in MnS-1, MnMCM-41 and MnHMA materials using data collected at two synchrotrons, Elettra in Trieste, Italy and DESY in Hamburg, Germany.

More examples on the use of X-ray absorption in the study of nanoporous materials are also listed in our recent crystallographic review.⁷⁰ Since the late 1980s XAS and XRD techniques using synchrotron sources gained more and more attention for in situ studies in heterogeneous catalysis.⁷¹ Combining in situ XRD and XAS is an excellent approach to obtain information on reaction-dependent changes of both long-range crystallographic order (XRD) as well as oxidation state and local coordination environment of particular elements (EXAFS) in a solid catalyst.

Magnetic resonance spectroscopy also offers a wealth of information on structural and dynamical properties of crystalline as well as amorphous nanoporous materials.⁷² The positions and local environments of framework and extra-framework atoms of porous solids can be determined by studying nuclear magnetic resonance (NMR) spectra of ²⁹Si, ²⁷Al, ³¹P, ⁶⁹Ga or ⁷¹Ga nuclei, or nuclei of charge-compensating ions like ¹H, ²³Na, ⁷Li or ¹³³Cs. The chemical shifts of these atoms in silicates and aluminosilicates depend on the number of silicon and aluminium atoms connected with a given SiO₄ tetrahedron. ²⁷Al is in principle a very favourable nucleus for NMR, since it has a 100 % natural abundance. The quantitative use of ²⁷Al NMR data allows the determination of relative proportions of 4-, 5- and 6- coordinated aluminium in zeolites. Recent development of multiple-quantum MAS (MQMAS) techniques, with which the resolution of spectra of quadrupolar nuclei can be dramatically improved, has given an additional momentum to the studies of aluminium local environment within aluminosilicates.⁷³ We have studied silicates and aluminophosphates modified by small amounts of transition metal ions of Ti, Mn, Fe, Co, and Zn at Slovenian NMR Centre on Varian 300 and 600 MHz equipment.⁷⁴ Recently, we showed that broadline ³¹P NMR can be employed for studying Ni(II), Fe(II/III) and Mn(III) incorporation, when the extent of substitution, i.e. Me/Al fraction, is above 1%.⁷⁵

3. Hydrogen storage

3.1. Nanoporous materials as adsorbents in hydrogen technology

In the search for alternative fuels, hydrogen is the ideal candidate as a clean energy carrier for both transportation and stationary applications. It is considered to be one of the best alternative fuels due to its abundance, easy synthesis, and non-polluting nature when used in fuel cells. For optimum hydrogen

storage, materials should meet the following criteria: high storage capacity, low dissociation temperature, moderate dissociation pressure, low heat of formation in order to minimise the energy necessary for hydrogen release, low cost, low weight, in particular for transport applications such as electric vehicles, and high stability against O₂ and moisture for long cycle life. The major challenges in the development of new hydrogen storage materials, with particular reference to batteries and fuel cells, are improved energy storage density, kinetics and cycle life, using readily available elements at a reasonable cost.⁷⁶

Hydrogen may be stored in solids by chemisorption or physisorption. For physisorption, new nanoscale materials with high specific surface area are needed. Gas adsorption characterisation of ordered organic-inorganic nanocomposites, i.e. mesoporous materials, was reviewed recently.⁷⁷ In the last five years, a new class of crystalline materials, which possesses a very low density and high surface area, the so-called metal-organic frameworks (MOFs) and related inorganic-organic (hybrid) materials, have been developed and synthesised and immediately attracted great attention in hydrogen storage community.⁷⁸ Rosi et al. recently reported interesting metallo-organic framework materials with hydrogen-sorption capacities at 78 K and ambient temperature under safe pressure (up to 20 bar) (Figure 8).⁷⁹ MOF-5 material showed 4,5 wt.% hydrogen absorption at 78 K and moderate pressures. In other similar structures, such as IRMOF-6 and IRMOF-8, the specific H₂ uptake is approximately doubled and quadrupled, respectively, compared to MOF-5 at room temperature and 20 bar pressure. The hydrogen-absorption capacity of these structures at room temperature is comparable to that of carbon nanotubes at cryogenic temperatures and can be fine-tuned by modifying the porosity of the structure with suitable linkers.

Metal-organic frameworks (MOFs) are crystalline inorganic-organic hybrid materials that consist of metal ions and organic molecules connected in space to produce an infinite one-, two, or three-dimensional framework.⁸⁰ The modularity of MOFs, specifically, the ability to modify the organic and/or inorganic components, offers a ready means to modify and control properties of such materials (e.g. inclusion, magnetism). The interior void spaces can be functionalised with organic groups using the proper synthesis design. A relatively new class of MOFs are inverted metal-organic frameworks (IMOFs) organically functionalised using principles of supramolecular chemistry.⁸¹ Similar characteristics have inorganic-organic (hybrid) nanoporous solids, which are usually built of inorganic layers that are covalently bonded with organic molecules to form framework structures. In some structures the organic moiety is an integral part of the layer. Different metal-phosphates, arsenates, vanadates, etc. modified with organic species, like dicarboxylic acids or nitrogen containing organic cations, have been reported recently, with the emphasis on the iron- and aluminium-oxalato phosphates.⁸²

3.2. The use of dicarboxylates in the synthesis of inorganic-organic and metal-organic frameworks

Dicarboxylic ligands seem to be a perfect choice, when designing new inorganic-organic porous structures with specific physico-chemical properties. They possess various binding or coordination modes, i.e. four different oxygens can form covalent bonds with inorganic moieties, the length of the hydrocarbon chain between the two carboxylic group can be increased, resulting in the framework with larger pores, and also the hydrocarbon chain can be additionally functionalised with different organic groups, depending on the selected applications. All of these lead to a variety of new structures with enhanced flexibility, compared to rigid inorganic microporous and mesoporous solids.

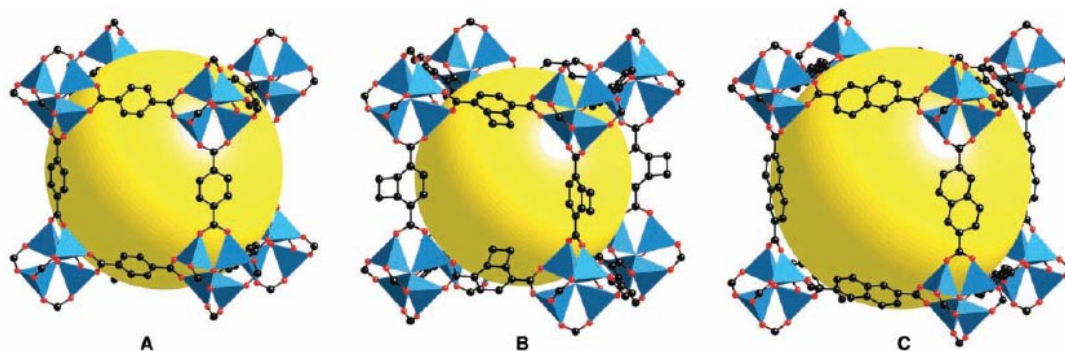


Figure 8: Structures of MOF-5 (A), IRMOF-6 (B), and IRMOF-8 (C) illustrated for a single cube fragment of their respective cubic three-dimensional extended structure. On each of the corners is a cluster [OZn₄(CO₂)₆] of an oxygen-centred Zn₄ tetrahedron that is bridged by six carboxylates of an organic linker (Zn, blue polyhedron; O, red spheres; C, black spheres). The large yellow spheres represent the largest sphere, e.g. gas volume, that would fit in the cavities without touching the van der Waals atoms of the frameworks [reproduced with permission from ref. 79].

The use of carboxylic ligands in the formation of porous frameworks has been reviewed recently in detail.⁸³ The emphasis was on oxalates, aliphatic dicarboxylates and some multifunctional carboxylates with two or more carboxylate arms.

We have studied a possible use of dicarboxylate ions in the formation of open-framework metal-phosphates.⁸⁴ Three dicarboxylic acids (oxalic, malonic and para-benzene dicarboxylic) were investigated as possible pillars in the formation of framework structures with extended structures in the presence of 1,2-diaminopropane as a structure-directing agent. In our research, only the oxalate ion has proved to be a suitable building block for the formation of hybrid networks. The terephthalate ion seems to possess the ability to be structurally involved in lattice formation, although not in networks of the hybrid type. The malonate ion in this system has not shown the propensity towards lattice formation, i.e. malonic acid merely exists as intercalated species inside a two-dimensional zincophosphate structure. This difference in behaviour of the malonate ion vs. oxalate ions could be related to their structural differences. Namely, the strict resonance-induced planarity of the free oxalate ion makes these anions in effect a rather rigid structural units of fixed geometries, which can therefore readily function as building blocks of hybrid network systems. In contrast, the complete rotational freedom around two C-C axes in the malonate ion renders this anion a very flexible species that can be present in reaction systems in a variety of conformations. It is this absence of structural rigidity that could prevent the malonate ion from being a suitable building block of hybrid network structures. The reason that the terephthalate ion does not participate in hybrid lattice formation was attributed to the lack of a significant chelate effect when this ion coordinates to a metal centre. However, we have prepared two new materials with metal-organic framework (MOF) using zinc, the terephthalate ion and 1,2-diaminopropane as a structure-directing agent.⁸⁵

3.3. Characterisation and structure analysis of crystalline hybrid and metal-organic structures

We have prepared and characterised a series of new crystalline structures, using different dicarboxylic acids in the hydrothermal synthesis. All syntheses were carried out hydrothermally by using 1,2-diaminopropane (DAP) as a structure-directing agent. Here, we will emphasise four new hybrid and MOF structures that were structurally analysed using single-crystal X-ray diffraction, i.e. alumino(oxalato)phosphate (APOX)⁸⁶, iron(III) phosphate-oxalate (FPOX)⁸⁷, zinc phosphate with intercalated malonic acid (ZPMAL)⁸⁸, and zinc terephthalate (Zn/DAP/TA)⁸⁵.

The crystallisation of the reaction mixture in which aluminium isopropoxide was used as the metal component and oxalic acid as dicarboxylic acid resulted in a new 3-D alumino(oxalato)phosphate (APOX) consisting of aluminophosphate layers which were pillared by oxalate ions. Oxalate ions are quadridentately bonded by participating in the coordination of AlO_6 and by bridging the layers. A hybrid 12-member ring channel is formed running through the structure and hosting diprotonated DAP and water molecules (Figure 9).

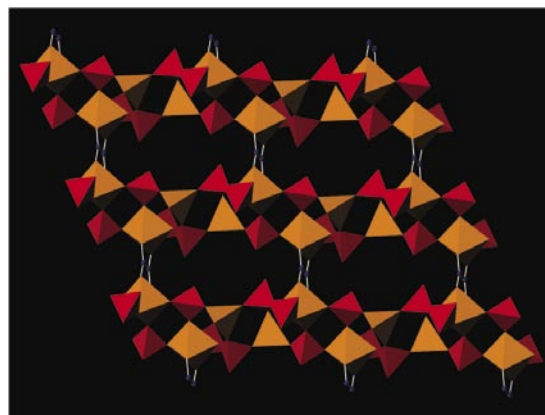


Figure 9: Structure of three-dimensional inorganic-organic (hybrid) framework; Three-dimensional APOX ($[\text{H}_3\text{NCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{NH}_3]_2[\text{Al}_4\text{P}_6\text{O}_{20}(\text{OH})_4(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$) structure (PO_4 tetrahedra are red, the AlO_4 tetrahedra and AlO_6 octahedra are orange). The APOX layers are connected through oxalate bridges (C-atoms are shown as blue circles) into a three-dimensional open-framework material. Template molecules are omitted for clarity. Single-crystal data: P-1, $a = 8.611(1) \text{ \AA}$, $b = 9.096(1) \text{ \AA}$, $c = 11.371(1) \text{ \AA}$, $\alpha = 104.811(1)^\circ$, $\beta = 111.368(1)^\circ$, and $\gamma = 94.248(1)^\circ$.

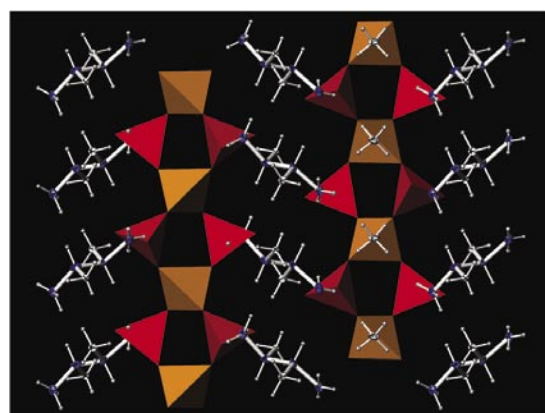


Figure 10: The one-dimensional aluminophosphate, $[\text{NH}_4^+][\text{H}_2\text{DAP}^{2+}][\text{Al}_3\text{P}_2\text{O}_8^{3-}]$, obtained in the presence of 1,2-diaminopropane (DAP). Ammonium cations and the doubly protonated DAP lie between the chains (C atoms are blue, N and H atoms are gray, PO_4 tetrahedra are red and AlO_4 tetrahedra are orange). Single crystal data: $\text{Pc}2_1n$ with $a = 8.2788(2)$, $b = 16.7882(3)$, $c = 8.6608(2) \text{ \AA}$.

According to thermal analysis results, it seems likely that in the APOX synthesis the (Al,O)- and (P,O)-polyhedra start to cross-link with oxalate ions around the DAP species at an early stage of crystallization. In this manner DAP is trapped and stabilized within the framework and does not undergo a partial decomposition observed in the absence of oxalate ions; i. e. under identical crystallisation conditions of a reaction mixture in which oxalic acid was not used, a chain-like aluminophosphate was obtained (Figure 10).⁸⁹

Open-framework iron(III) phosphate-oxalate (FPOX) was prepared from the reaction mixture analogous to that used in the APOX synthesis, but containing Fe^{3+} ions instead of Al^{3+} . The iron(III) phosphate layers are bridged by oxalate units bonded to octahedrally coordinated iron centres, resulting in the formation of large one-dimensional 12-member channels. The channels run perpendicular to the iron phosphate layers and contain DAP and water molecules. The doubly protonated DAP is positioned inside the channel in an asymmetric manner thus creating different environments for the Fe atoms situated across one another at the sides of the channel. This indicates that the amine component can also affect the magnetic properties of metallophosphates.

The use of malonic instead of oxalic acid yields a crystalline product (ZPMAL) only in the case when zinc ions are employed in the reaction mixture. However, malonic acid in ZPMAL is only an intercalated species together with DAP and ammonium cations (all of them being disordered over the same partly occupied sites). The zinc phosphate product has a two-dimensional crystal structure built up of parallel inorganic layers, which are held together through hydrogen bonding with the intercalated species. An eight-member ring channel runs through the macroanionic zinc phosphate sheet. During the crystallization of ZPMAL, the DAP species partly decomposed yielding NH_4^+ . This behaviour is similar to that observed in the chain-like aluminophosphate.

Terephthalate ions act as multidentate bridging ligands and have been used in many synthetic systems since they form short bridges via one carboxylic group or long bridges via the benzene ring. We have hydrothermally prepared and characterised a three-dimensional metal-terephthalate, again using DAP as a structure-directing agent (Figure 11). Zinc atoms are bonded to four oxygen atoms from the terephthalate group and two water molecules (Figure 12).

4. Wastewater treatment

4.1. Natural zeolites and ecological issues

The use of zeolitic materials for the environmental protection is stimulated by good physico-chemical

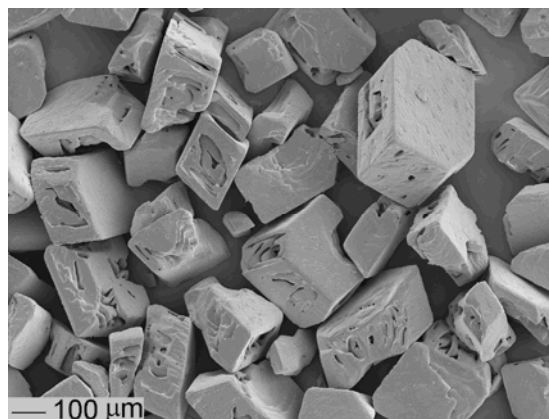


Figure 11: Metal organic material zinc 1,4-benzenedicarboxylate: synthesis and framework structure: crystalline product was prepared from a reaction system containing the zinc ions, the terephthalate ions (1,4-benzenedicarboxylate) and 1,2-diaminopropane in the molar ratio of 4:2:3, respectively. The product (Zn/DAP/TA) is thermally stable up to 400 °C.

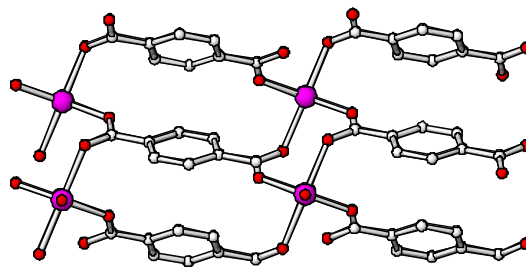


Figure 12: The Zn/DAP/TA structure comprises a 3-D network arising through interconnection of the square-pyramidal Zn units and terephthalate (BDC) ions. Each BDC is coordinated to four Zn atoms (Zn atoms are violet, C atoms grey and O atoms red). Single-crystal data: C 2/c, $a=17.9978(5)$, $b=6.3647(1)$, $c=7.2657(2)$, $\beta=91.467(1)^\circ$.

properties, e.g. selective sorption, by non-toxic nature, availability and low cost. A great deal of research on natural zeolites has been focused on the most commonly occurring types, especially clinoptilolite, mordenite and chabazite.⁹⁰ Natural zeolites are used in a wide range of environmental applications, including water purification, with the emphasis on the ammonia and heavy metal removal⁹¹, removal of radioactive ^{137}Cs and ^{90}Sr from low-level waste streams of nuclear installations⁹², and recently also for the removal of organic pollutants, like hydrochlorofluorocarbons (HCFCs) and petroleum products from water.⁹³ They can be used as barriers to contaminant migration or as binders in waste solidification systems.

There are increasing demands for healthier environment, with the emphasis on high-quality drinking water and on the removal of contaminants from industrial, agricultural and municipal wastewaters. Most technologies using natural zeolites for water and soil

purification are based on the unique cation-exchange behaviour of zeolites through which dissolved cations are removed from water or soil by exchanging with cations on a zeolites exchange sites. The most common cation in waters affecting human and animal health is NH_4^+ . It can be replaced with biologically acceptable cations, like Na^+ , K^+ or Ca^{2+} in the zeolite. Ammonia removal is very important to prevent oxygen depletion and algae bloom and due to its extreme toxicity to most fish species.⁹⁴ Additionally, it has detrimental effects on disinfections of water supplies and corrosive action on certain metals and construction materials. Nitric oxides, nitrates and ammonia/ammonium are very soluble in water and can quickly end up in ground and drinking water. Chabazite and clinoptilolite showed the best results for ammonia removal. Heavy metals are well known for toxicity and their disposal is a significant industrial waste problem. Clinoptilolite and mordenite proved to be very efficient for the removal of transition metals, like Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , etc., which are often present in industrially contaminated soil and water and can be very toxic even in concentrations as low as mg/L. Pb^{2+} , Cu^{2+} , Fe^{3+} , Cd^{2+} , and Cr^{3+} are especially common metals in industrial wastes that tend to accumulate in organisms, causing numerous diseases and disorders.⁹⁵ Clinoptilolite and mordenite also have very high selectivities for Cs^+ and Sr^{2+} and can therefore be used to remove trace amounts of both radioactive nuclei from nuclear process wastewaters and soil at the nuclear waste repositories or nuclear weapon test sites.⁹²

4.2. Mechanisms of heavy metals removal from industrial wastewaters

The contamination with heavy metals exists in aqueous waste streams of many industries, such as metal plating facilities, dyes and textile industry, mining operations, etc. The amount of heavy metals waste is increasing every year; they tend to accumulate in living organisms. Treatment processes for the removal of heavy metals from wastewater include coagulation, carbon adsorption, ion exchange, reverse osmosis, etc.⁹⁶ The sorption processes are the most attractive, since their application is simple, and they require mild operating conditions. The limiting factor could be the regeneration of the sorbing materials.

The sorption of heavy metals by natural zeolites is a complex process because of the inner and outer charged surfaces, imperfections on the surfaces, mineralogical heterogeneity and the presence of other non-zeolite phases that can also contribute to the overall sorption capacity. The extensive research of adsorption isotherms revealed that ion exchange or chemisorption on zeolites governs the immobilisation of metal cations in natural zeolite tuffs is governed by.^{97,92} Sorption of

metals by natural zeolites is governed by ion exchange or chemisorption. Following the ion exchange mechanism, ions present in the pores of zeolite crystalline lattices, like Na^+ , K^+ , Ca^{2+} etc. are substituted by metal ions from the solution. The chemisorption always results in the formation of stable inner-sphere or outer-sphere complexes, where functional groups on the zeolite framework (mainly OH) form strong chemical bonds with metal ions. In clinoptilolite and the majority of zeolites, ion-exchange processes generally dominate over chemisorption. The sorption of heavy metal by the zeolite is directly related to the charge of the zeolite framework, i.e. the quantity of aluminium present in the zeolite framework, the nature and concentration of the cationic species, the size and distribution of zeolite tuff particles, the solvent and the temperature.^{98,90} Higher temperature and cations with higher charges and small radii are preferred for the zeolite. The tendency of many heavy metals to undergo hydration may reduce the capacity of the zeolite for metal uptake due to the large diameters of the hydrated ions.

The possibilities of using natural zeolites for the heavy metals removal from wastewaters with the equilibrium and dynamic ion exchange studies of metals on natural and synthetic zeolites have been extensively studied. In most of the studies, chromium, which is a very toxic metal, especially in the 6+ oxidation state, irreversibly bonds to the zeolite.⁹⁹ The best results for lead uptake were achieved using phillipsite and chabazite and the regeneration of the absorbent can readily be done, e.g. by NaNO_3 solution. Cadmium can be removed from the wastewater using chabazite and exhausted beds regenerated with NaNO_3 solution.¹⁰⁰ Removal of zinc from wastewater is most efficient at lower Zn^{2+} concentrations using different zeolites, including clinoptilolite.¹⁰¹

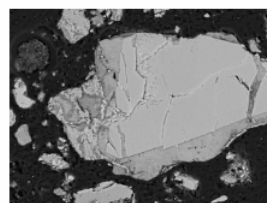
4.3. Structural studies and determination of sorption mechanisms of Cr, Zn and Fe on the clinoptilolite tuffs (XRD, XAS, XPS)

Clinoptilolite is the most abundant natural zeolite and is mainly found in specific types of sedimentary rocks (tuffs) in the form of small crystals (0.1–100 μm) associated with clays and other silicate and aluminosilicate phases of similar density. Detailed structural investigations using X-ray diffraction and complementary microscopic, spectroscopic and thermal techniques of metal-loaded clinoptilolites and its analogues have helped in answering many questions concerning sorption mechanisms. In a recent overview of structural studies of metal-loaded HEU-type zeolites (clinoptilolite and its structural analogue heulandite) the preferred sites of the ion-exchanged metals (Ag^+ , Pb^{2+} , Cd^{2+} , Mn^{2+} , Cu^{2+}) and the associated framework structural changes are listed.¹⁰²

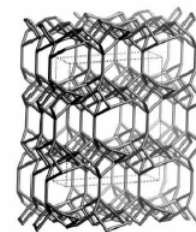
We have performed a detailed structural studies, i.e. microscopic, diffraction, photoelectron and X-ray absorption spectroscopic analyses, of Cr^{3+} -modified (Figure 13)¹⁰³, and Zn^{2+} - and $\text{Fe}^{2+/3+}$ -modified¹⁰⁴ natural clinoptilolite tuffs in order to improve the understanding of the sorption mechanism for particular metal.

Structural analysis of Cr^{3+} -modified natural zeolite sample from the deposit of Donje Jesenje (Croatia) was performed by using diffraction, spectroscopic methods, and electron microscopy with elemental analysis. X-ray diffraction confirmed the presence of up to 50% of clinoptilolite in the sample. X-ray absorption spectroscopy results confirmed that chromium cations in the sample were predominantly in the trivalent state, and that most probably arrange in the form of small polynuclear clusters in the pores of the clinoptilolite. The formation of Cr_2O_3 nanocrystallites as an alternative arrangement of octahedral chromium was excluded by the X-ray absorption spectroscopy results. The X-ray photoelectron spectroscopy depth analysis suggested a uniform distribution of chromium from the surface of the crystallites to the depth of 50(3) nm. The uniform distribution of Cr over the whole sample could indicate that the clustering of chromium polyhedra started only after smaller Cr^{3+} ions or mononuclear chromium complexes penetrated into the zeolite pores following the ion-exchange mechanism. The subsequent hydration of Cr^{3+} cations and formation of clusters is the most probable reason for the irreversibility of the chromium uptake by a posttreatment using NaCl or HCl solutions, since we are facing sterical problems during the process of desorption.

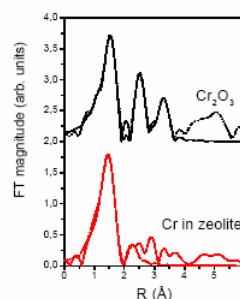
The Zn^{2+} -modified zeolite sample from a large sedimentary deposit in Vranjska Banja, Serbia and Montenegro, was also structurally investigated. It contains from 70 to 80 % of clinoptilolite. With elemental microporobe analysis (EDX) zinc was found only in the clinoptilolite phase, which again confirmed that zeolite is an active component in the zeolite tuff, and that the sorption processes do not occur on feldspar or other present phases. Pretreatment of zeolite tuff with NaCl or CaCl_2 solutions affected sorption mechanism and local structure of Zn^{2+} . Zn K-edge X-ray absorption spectra revealed zinc bonded to four oxygen atoms in distorted tetrahedral symmetry. On the other hand, zinc in pretreated samples bonds to six oxygens in distorted octahedral symmetry. X-ray photoelectron spectroscopy depth analysis showed that zinc is concentrated on the surface of the crystallites. At the depth of 50 nm from the surface, the concentration of Zn was half of that from the surface, which was not the case in chromium sorption. The Mössbauer spectroscopic analysis of $\text{Fe}^{2+/3+}$ -modified zeolite sample showed that the overwhelming part of iron ions was located in framework octahedral sites. A minor, 5% part of ions



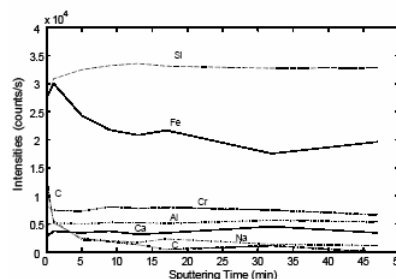
SEM picture of the polished crystallites: three major phases were detected, according to the colour contrast and EDS elemental analysis clinoptilolite, feldspar and quartz.



Zeolite clinoptilolite (HEU)



Fourier transforms of the k^2 -weighted Cr EXAFS spectrum calculated in the k range from 2.5 \AA^{-1} to 11.5 \AA^{-1} and reference Cr_2O_3 sample calculated in the k range from 3.5 \AA^{-1} to 12.5 \AA^{-1} (dashed line - experiment; solid line - best fit exafs model) revealed that Cr^{3+} cations bond to six oxygen atoms at the distance of $1.97(2) \text{ \AA}$ and two chromium atoms at the distance of $2.54(2) \text{ \AA}$.



In-depth dependence of intensities for some XPS peaks as a function of the sputtering time on the Cr-exchanged sample. From sputtering rate of about 1.1 nm/min measured on the Ni/Cr reference multilayer structure, the estimated depth is about 50 nm.

Figure 13: Structural investigation of Cr^{3+} -modified clinoptilolite tuff.

was located as Fe^{2+} in extra-framework octahedral sites, which was in accordance with previous studies of iron in clinoptilolites.¹⁰⁵

5. Conclusions and perspectives

Nanoporous materials, the basis for nanotechnologies, are one of the fastest developing fields in materials science. The applicability of microporous solids have been already proven many times and further development is expected in the targeted synthesis of new materials with specific and selective properties for known applications. New microporous frameworks suitable for effective hydrogen storage will definitely attract further special attention in the forthcoming years.

The synthesis of the mesoporous silicas MCM-41 and MCM-48 in 1992, using a supramolecular surfactant system as a template, provoked a boom in nanoporous materials. The surfactant templating method has since been extended to synthesize non-silica mesoporous

materials (e.g. metal oxides, organosilicas, and carbons). Many potential applications have been explored, from catalysis, separation, biology, environmental monitoring, and pharmaceuticals to clinical toxicology, but a gap in real industrial applications still exists. The great challenge facing the mesoporous materials community now is to transfer laboratory studies to industrial applications. Although the potential applications of such materials have been widely studied in many areas, more efforts are still needed for the continuing study of their practical applications to commercialise mesoporous materials in the future. The forthcoming practical applications in fields such as catalysis, separation, adsorption, drug delivery, electronic devices, low dielectric constant materials and beyond, will stimulate more research interests in this area, and more exciting and useful developments in mesoporous materials will also be delivered.

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Povzetek

Nanoporozni anorganski materiali so izredno uporabni kot katalizatorji in sorbenti, kar je posledica velike specifične površine in prisotnosti por točno določenih premerov, ki so primerljivi z dimenzijami atomov oziroma molekul. Z vedno večjo skrbjo za okolje postajajo nanoporozni materiali vedno pomembnejši in uporabni tudi za ločevanje in odstranjevanje okolju škodljivih snovi. Njihova uporaba se v prihodnosti kaže na področjih visokoselektivnih biosenzorjev, biomembran ter kot templatov pri pripravi prevodnih nanocerk. Velika pozornost je v zadnjem času namenjena novim anorgansko-organskim ali hibridnim poroznim materialom zaradi zelo obetajočih raziskav na področju shranjevanja vodika, ki je ena od najpomembnejših stopenj pri širši uporabi vodika kot alternativnega vira energije. V prispevku je podan pregled naših najnovejših raziskav na področjih priprave in določitve lastnosti anorganskih in nekaterih hibridnih nanoporoznih materialov, s poudarkom na silikatnih in fosfatnih ogrodjih, z uporabo hidrotermalne sinteze ali sinteze v mikrovalovni peči ter karakterizacijskimi metodami, kot so rentgenska difrakcija, spektroskopske metode (XAS, NMR) in elektronska mikroskopija. Prav tako je predstavljena funkcionalizacija nanoporoznih materialov s fizikalnimi in/ali kemijskimi postopki ter študij njihovih katalitskih ali sorpcijskih lastnosti z možnostmi uporabe v (1) katalizi, (2) pri shranjevanju vodika in (3) zmanjševanju onesnaženosti okolja.