

MODIFIED MICROPOROUS AND MESOPOROUS MATERIALS

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SUMMARY

Transition metal-modified microporous zeolitic materials (silicate- and phosphate-based) are attractive catalysts due to their hydrothermal stability and high catalytic activity and selectivity. Metal-modified mesoporous materials with larger pore openings have been developed for catalytic processes where larger molecules are involved. The inclusion of nanosized particles of zeolitic microporous materials with larger external surface areas and high surface activity into mesoporous matrices, i.e. the preparation of microporous/mesoporous composites, substantially enhances the catalytic activity of mesoporous materials. The important feature of nanoporous solids based on a various metal oxides is also their ability to form thin films with nanometer-scale thickness. Examples of successful preparation and/or functionalisation of new nanoporous solids encompass microporous and mesoporous silicates (MnS-1, MnMCM-41, MnTUD-1), microporous and mesoporous aluminophosphates (FeAPO-36, FeHMA), microporous/mesoporous silicate composites ((Ti,Al)-Beta/MCM-41, (Ti,Al)-Beta/MCM-48, Ti-Beta/SBA-15) as well as cubic mesoporous aluminophosphate thin films. Studies of structure-property relations of new solids have included X-ray diffraction, spectroscopic (XAS, NMR) and electron microscopy characterisation techniques.

INTRODUCTION

Porous materials are classified into three categories, microporous with pore openings from 0.3 to 2 nm, mesoporous having pores between 2 and 50 nm, and macroporous with pores greater than 50 nm. [1] Microporous materials are exemplified by crystalline framework solids such as zeolites (aluminosilicates), whose crystal structure defines channels, cages, shapes and mutual positions of channels, i.e. micropores, of strictly regular dimensions. Mesoporous materials, exemplified by the silicate MS41 materials family, are amorphous solids exhibiting highly-ordered pore structures and large internal surface areas.

Microporous materials are mostly used as absorbents, ion-exchangers, molecular sieves and finally 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. [2] The most common reactions, where microporous acid-catalysts are involved, are fluid catalytic cracking, hydrocracking, aliphatic alkylation, isomerisation, transformation of aromatics and the conversion of methanol to hydrocarbons. Redox microporous 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 H₂O₂ using Ti- or Fe-substituted microporous catalysts. The discovery of mesoporous silicates attracted worldwide attention since they can incorporate relatively large-sized species

inside the pores. [3] The extensive research to expand their functionality and improve their hydrothermal and chemical stability by a modified and optimised synthetic or post-synthetic routes in recent years has already enabled their application in the field of catalysis. [4] Intensive research efforts have also been driven by the emerging applications such as biosensors, drug delivery, gas separation, energy storage and fuel cell technologies. Investigations in the field of mesoporous thin films are uprising fast due to their potential applications as chemical and optical sensors, shape-selective membranes and energy-storage devices. [5]

The incorporation of transition metals into silicate, aluminophosphate and similar inorganic frameworks generates or moderates catalytic activity of the materials. The incorporation of titanium into the framework of silicalite-1, for example, yields excellent catalysts with selective properties for epoxidation. [6] Metal-modified $\text{AlPO}_4\text{-}n$ 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. [7] Here we report on synthesis and structure studies of new micro- and mesoporous materials with the emphasis on the preparation of metal-modified nanosized zeolitic particles, microporous/mesoporous composites and zeolitic thin films.

SYNTHESIS OF ORDERED POROUS MATERIALS

Microporous materials are generally prepared hydrothermally from aqueous gels containing a source of the framework building elements (Si, Al, P, etc.), a mineraliser (OH^- , F^-) regulating the dissolution/condensation processes during the crystallization, and a structure-directing agent, usually an organic amine or ammonium salt. Ordered mesoporous silica- and nonsilica-based materials are also prepared hydrothermally by a variety of procedures using various structure directing agents, i.e. surfactants, like cationic cetyltrimethylammonium hydroxide or nonionic block copolymers. Precise adjustments of synthetic parameters, like silica source, temperature and the time of crystallisation or pH, affect the properties of final products, e.g. pore size or hydrothermal stability. Transition metals can be incorporated into microporous or mesoporous materials by a post-synthetic ion-exchange treatment or by direct framework substitution by the addition of transition metal cations into the synthesis gel.

An alternative to a classical hydrothermal synthesis is a microwave oven. The microwave heating is regarded as a novel synthesis tool for microporous and mesoporous materials because it offers several benefits, such as enhanced nucleation process, the promotion of faster crystallisation, rapid synthesis, the formation of uniform crystals, and small crystallites, facile morphology control, the avoidance of undesirable phases by shortening the synthesis time and so on. Recently, it was found that it provides an effective way to control the particle size distribution, crystal morphology, orientation, and even the crystalline phase. [8]

CHARACTERISATION OF ORDERED POROUS MATERIALS

The elucidation of structures of ordered porous materials is essential for the understanding and prediction of their macroscopic physical and chemical properties. In particular, the size and connectivity of the pores 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.

The conventional single-crystal and powder diffraction methods have been successfully used for structure determinations of crystalline microporous structures. Problems that can arise are mainly due to the small size of the crystallites that often require *ab initio* powder structure solutions and the low concentration and/or random distribution of metal active sites over the framework or extra-framework positions. The rapid development of synchrotron radiation sources has brought around a tremendous progress in XRD techniques and methods, e.g. anomalous dispersion methods for metal site determination. [9] With the availability of synchrotron radiation sources, X-ray absorption spectroscopy (XAS) techniques have also developed into a widely used tool for structural research of ordered porous materials. XAS analytical methods XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) provide structural information about local symmetry and the average oxidation number of selected atom. Since XAS is selective towards a particular element and sensitive only towards a short-range order, it is one of the most appropriate spectroscopic tools for microporous and mesoporous catalysts characterization. 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 (XAS) in a solid catalyst.

Nuclear magnetic resonance spectroscopy also offers a wealth of information on structural and dynamical properties of crystalline- as well as amorphous porous materials. The positions and local environments of framework and extra-framework atoms of porous solids can be determined by either studying NMR spectra of ^{29}Si , ^{27}Al , ^{31}P , ^{69}Ga or ^{71}Ga nuclei, or nuclei of charge-compensating ions like ^1H , ^{23}Na , ^7Li or ^{133}Cs .

EXAMPLES

1) Mn- AND Fe-MODIFIED MICROPOROUS AND MESOPOROUS SILICATES AND ALUMINOPHOSPHATES

The incorporation of transition metals into microporous and mesoporous frameworks modifies or generates acidic and/or redox properties in porous hosts. Metals that are most commonly used for the functionalisation of microporous and mesoporous hosts are titanium, iron, manganese, vanadium and cobalt.

Recently, manganese-containing redox molecular sieves have received considerable attention as catalysts for the selective oxidation of hydrocarbons using air/molecular oxygen as the oxidant. For instance, aluminophosphates of the type [M]APO-5 or -18 (M = Co, Mn, Fe, Cr, etc.) or manganese ion-exchanged zeolites were studied for the oxyfunctionalisation of cyclohexane. [10] However, manganese-containing catalysts based on nanoporous silica have only scarcely been investigated for aerobic hydrocarbon oxidations under solvent-free, liquid-phase conditions. We have prepared MnS-1, MnMCM-41, MnMCM-48 and MnTUD-1. Characterization by XRD and nitrogen sorption revealed the high quality of the materials with respect to long-range order and specific surface area. Local environment of Mn was characterized by using XAS. EXAFS analyses of Mn K edge absorption spectra of MnS-1, MnMCM-41 and MnMCM-48 revealed manganese cations coordinated to three oxygen atoms

at a distance of 1.91 Å and one oxygen atom at a longer distance of 2.19 Å. The short distance of 1.91 Å is consistent with the average tetrahedral Mn⁺³-O distance of 1.93(4) Å reported for MnAsO₄ as expected for an isomorphous substitution within the silicate framework. [11] XANES studies of Mn K edge absorption spectra revealed the average oxidation number of Mn in all three samples of 2.9±0.05 ($n(\text{Mn}^{2+})/n(\text{Mn}^{3+}) \cong 10/90$). Catalytic tests showed that manganese(III)-containing microporous and mesoporous silicas selectively catalyse the oxidation of alkyl aromatics in benzylic position to aromatic ketones in the absence of any initiator by using molecular oxygen as the terminal oxidant under mild, solvent-free, liquid-phase conditions. [12]

Both the acidity and redox properties can be modified also by inserting iron into the microporous and mesoporous hosts. 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. [13] In most studies, the framework Fe³⁺ is regarded as the major active agent in the catalytic reactions. We have prepared iron-substituted microporous aluminophosphate FAPO-36 and mesoporous aluminophosphate FeHMA that both exhibit redox behaviour and are good candidates for redox catalysts. [14] The local structure of framework iron in the template-free FAPO-36 was studied by XAS and revealed the incorporation of Fe³⁺ into tetrahedral framework sites. The acidity of FAPO-36 has been investigated by using CO adsorption-desorption FTIR spectroscopy on the oxidized and reduced material, confirming 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. XAS study of FeHMA, prepared by microwave synthesis, showed preferential octahedral coordination of Fe³⁺ on FeHMA although the presence of smaller amount of tetrahedrally coordinated Fe²⁺ was also detected. Mössbauer spectra of template-free FeHMA demonstrated the above mentioned dependence of tetrahedral/octahedral coordination upon specific conditions used (i.e. the presence/absence of adsorbed water) and the pronounced reversibility of Fe³⁺ ↔ Fe²⁺ redox transitions.

2) Ti-MODIFIED MICROPOROUS/MESOPOROUS COMPOSITES

Mesoporous silicates and their metal-modified analogues are not crystalline materials like microporous ones, they are amorphous or better glass-like, and they do not exhibit catalytic properties of microporous zeolitic materials. Their hydrothermal stability is low and metals are usually unstable within the frameworks. So, the oxidation strength of mesoporous catalysts is rather weak compared with traditional metal-modified microporous catalysts owing to the amorphous character of the mesoporous framework. Recent investigations have been focused on the preparation of microporous/mesoporous composites that combine performances of both microporous and mesoporous materials. The first attempt to prepare such a composite, i.e. the zeolite with FAU topology coated with a thin layer of mesoporous MCM-41, was reported in 1996. [15]

Here we report on the synthesis and characterization of three titanium-modified microporous/mesoporous composites (Ti,Al)-Beta/MCM-48, (Ti,Al)-Beta/MCM-41 and Ti-Beta/SBA-15 [16]. Microporous titanium silicates such as zeolites Ti-silicalite-1 and Ti-Beta are extremely efficient catalysts for the epoxidation of alkenes in the presence of aqueous H₂O₂ and *tert*-butyl hydroperoxide as oxidants. Catalytic efficiency is attributed to the unique

architecture of titanium centres that are isolated in the silicate framework. The composites (Ti,Al)-Beta/MCM-48 and (Ti,Al)-Beta/MCM-41 were prepared by a hydrothermal two-step synthesis procedure. In the first synthetic step, colloidal zeolite Beta particles were prepared that were in the second step combined with surfactant(s) solution. HRTEM was successfully used for the confirmation of the presence of micropores and mesopores at the same area of investigation for the first time in both composites. The aluminium-free Ti-Beta/SBA-15 composite material was prepared by the deposition of Ti-Beta nanoparticles onto SBA-15 material. The incorporation of titanium in the framework and thus the presence of Ti oxidation centres within the composite materials were confirmed by XAS. NMR investigations showed that acid sites related to framework aluminium were generated by the calcination of as-synthesized (Ti,Al)-Beta/MCM-48.

3) MESOPOROUS THIN FILMS

Mesoporous thin films are potential hosts for pure metal/metal oxide nanoclusters, and the combination with aluminophosphate or silicate framework with acidic properties, could lead to new materials with catalytic, electronic and sensing properties.

A novel thermally-stable large-pore aluminophosphate-based mesoporous thin films with cubic (*Im3m*) pore arrangements have been prepared by using nonionic block copolymer surfactants as mesostructure directing agents. Aluminophosphate solution was deposited onto a glass substrate under controlled conditions by dip-coating method. The mesostructure and thermal stability of thin films were investigated by small-angle X-ray scattering (SAXS) and confirmed by X-ray diffraction and high-resolution transmission electron microscopy. It has been shown that aluminophosphate-based thin films retained their ordered pore system up to 400 °C with small structural changes in inorganic framework when rising the temperature according to ²⁷Al and ³¹P NMR spectra. Transition metal-modified aluminophosphate films, interesting for catalytic applications, are expected to be produced under similar conditions.

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