

TRANSITION METAL COMPLEXES SUPPORTED ON NATURAL ZEOLITES: NEW COMPOSITE MATERIALS FOR INNOVATIVE APPLICATIONS

A. Godelitsas

ISchool of Science, National and Kapodistrian University of Athens, Zografou campus, 15784 Athens, Greece
E-mail: agodel@geol.uoa.gr

Zeolites constitute a major group of crystalline microporous -in fact nanoporous- materials including both natural (more than 50) and synthetic species (more than 100, also referred as molecular sieves). Their structure is characterized by a three-dimensional aluminosilicate framework adjusting the formation of intracrystalline micropores -channels- which normally host exchangeable cations (e.g. Ca^{2+}) and mobile H_2O -molecules. The size of the channels (generally $<20 \text{ \AA}$) regulating the sorptive properties of the materials, is related to the framework density (FD, in $\text{Tsites}/1000 \text{ \AA}^3$) and the cation exchange capacity (CEC, in $\text{meq}/100 \text{ g}$) depends on the Si/Al ratio controlling the available negatively-charged extraframework sites. Similar synthetic microporous -nanoporous- materials known as zeotypes possess a relevant fundamental framework but with T-sites occupied by different elements (e.g. Al-P, Si-Ti), while the framework of the so-called porosils (silicalites) is built up exclusively by Si-tetrahedra. However, all natural zeolites are typical aluminosilicate solids exhibiting a higher FD in comparison to other tectosilicate phases such as feldspars, and are low-cost industrial minerals (mostly found in tuffs and basalts) with several commercial applications.

The zeolitic materials are not frequently used as synthesized or as obtained from the nature (unmodified), but their physicochemical properties are refined by chemical and/or thermal treatment. One of the novel procedures to obtain modified zeolites is the gradual loading of the crystals with transition metals and organic substances, which leads to complexes supported on the aluminosilicate zeolitic substrate. The coordination and organometallic compounds can either be encapsulated inside the micropores -nanopores- (intrazeolite complexes) or arranged on the surface of the crystals (surface complexes). The surface complexes are anchored by chemical bonds to active (Brønsted or Lewis) surface sites, whereas the intrazeolite ones are hosted into the channels allowing the zeolite to act as a “solid solvent”. In the latter case, the guest complexes principally retain all of their properties and, being isolated in the micropores playing the role of “inorganic molecular-scale microreactors”, are often more stable under dimerisation, auto-oxidation, clustering and thermal-degradation conditions. Moreover, in both cases the supported complexes are considered as “new” (not existing as individual chemical compounds) if oxygen-atoms of the zeolite lattice participate in the first coordination sphere. The above described solid systems constitute in fact an entirely new class of composite materials with great technological interest.

The existing literature [see e.g. 1-3] on synthetic zeolites (e.g. FAU-type) provides evidence for peculiar applications such as the shape/size-selective catalysis and even the biomimetic catalysis where the supported in the micropores „ship-in-a-bottle“ complexes behave as the enzymes in the protein structure. These materials are the so-called zeozymes contributing to the establishment of the supramolecular solid-state science.

The relevant research [see e.g. 4-11] already performed using naturally occurring species is comparably limited and refers to FAU-type zeolites as well as to HEU-type zeolites (clinoptilolite/heulandite series, which are the most abundant zeolites on Earth). Different

intrazeolite and surface complexes (e.g. Ni²⁺-pyridine and Cu²⁺-diethyldithiocarbamate; Figure 1) have been investigated in respect of the above zeolites, whereas novel uses of the obtained composite solid materials have been pointed out, including the development of specific sorbents & catalysts, environment-friendly pesticides & insecticides, and modern pharmaceuticals & nutrients.

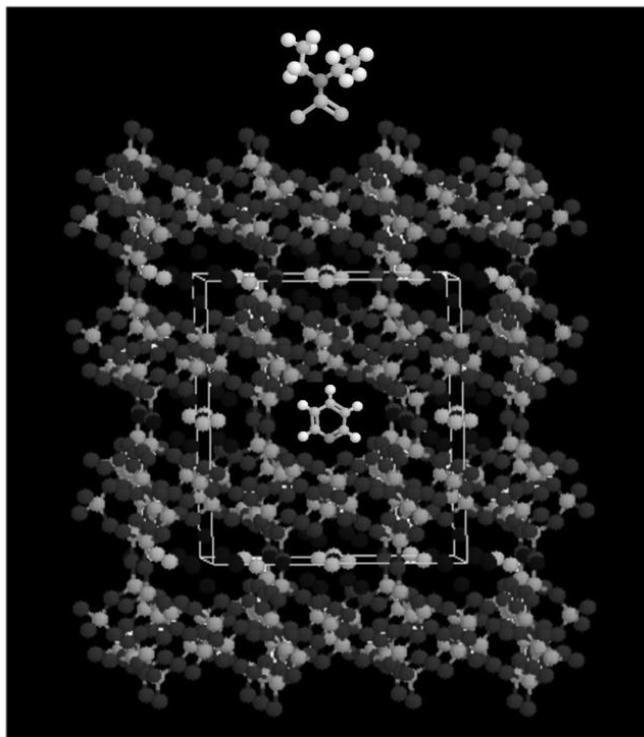


Figure 1. Examples of intrazeolite and surface complexes (e.g. Ni²⁺-pyridine and Cu²⁺-diethyldithiocarbamate) with regard to the structure of HEU-type zeolites.

REFERENCES

- [1] G.A.Ozin and C.Gil, *Chem. Rev.*, 1989,**89**, 1749-1764.
- [2] P.C.H. Mitchell, *Chem. & Ind.*, 1991, **6**,308.
- [3] R. Parton et al., in *Zeolite Micropor. Solids*, E.G. Derouane et al. Eds., 1992, 555
- [4] H.D. Simpson and H. Steinfink, *J. Am. Chem. Soc.*, 1969, **91/23**, 6225-6229.
- [5] H.D. Simpson and H. Steinfink, *J. Am. Chem. Soc.*, 1969, **91/23**, 6229-6232.
- [6] A. Godelitsas, D. Charistos, J. Dwyer, C. Tsipis, A. Filippidis, A. Hatzidimitriou and E. Pavlidou, *Micropor. Mesopor. Mater.*, 1999, **33**, 77-87.
- [7] B. Concepcion-Rosabal, J. Balmaceda-Era and G. Rodríguez-Fuentes, *Micropor. Mesopor. Mater.*, 2000, **38**, 161-166.
- [8] A. Godelitsas, D. Charistos,] A. Tsipis, C. Tsipis, A. Filippidis, C. Triantafyllidis, G. Manos and D. Siapkias, *Chem. Eur. J.*, 2001, **7**, 3705-3721.
- [9] T. Armbruster, P. Simoncic, N. Dobelin, A. Malsy and P. Yang, *Micropor. Mesopor. Mater.*, 2003, **57**, 121-131.
- [10] A. Godelitsas, D. Charistos, C.Tsipis, P. Misaelides, A. Filippidis and M. Schindler, *Micropor. Mesopor. Mater.*, 2003, **61**, 69-77.
- [11] A.Godelitsas and Th. Armbruster, *Micropor. Mesopor. Mat.*, 2003, **61**, 3-24.