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### The role of metal cations as template species in zeolite framework formation

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Zeolites are crystalline aluminosilicates used for many applications. Numerous zeolitic materials and topologies are known, but their formation, especially on molecular level and the stage of nucleation remains in the dark. Experience taught the formation of a specific framework critically depends on conditions like gel composition, temperature and time. Small changes in pH or variation of the metal cation can entirely change the obtained topology from one type to another or prevent crystallization at all. The cation effect most probably is due to their direct interaction with and stabilization of elemental aluminosilicate oligomers (AOs) and should depend on hardness, size and charge of the participating species. Strategies to study the stabilization of specific structural elements by metal ions are *in-situ* and *ex-situ* analysis of framework formation and transformation from one topology into another. Here we report the results of studies of the crystallization of two topologically related low silica zeolites from amorphous gels (FAU and LTA), [1], [2], and of the framework transformation of zeolite Y (FAU) into chabazite (CHA) [3].

Simultaneous *in-situ* XRD-Raman study of the crystallization of low silica zeolite X (FAU) and zeolite A (FAU) from amorphous gels have been performed. Both frameworks contain sodalite cages as a building unit linked via double 6-rings (D6R) in FAU and double 4-rings (D4R) in LTA. The oligomeric species in solution were monitored by UV-Raman, while the transition from amorphous to crystalline state was simultaneously recorded by XRD. A very important role has been assigned to the presence of K<sup>+</sup> in solution, directing the synthesis to the FAU topology. Probably, interaction with silica 4-rings (4Rs) blocks the pathway leading to the LTA structure [5]. Furthermore, the absence of 6Rs during FAU formation excluded the sodalite cage as a possible common building unit for both topologies.

As initial compound for the framework transformation of FAU into CHA served commercial zeolite Y with different ion contents (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, H<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>). NMR, powder XRD, and AAS were used for the characterization of the initial, intermediate and final materials. CHA and FAU topologies both contain edgewise connected double six rings (D6R) resulting in the sodalite cavity in FAU and chabazite cages in CHA. Surprisingly, the Na/Al ratio of the starting material was not as crucial as reported in literature [3]. Formation of CHA by decomposition of the Na-form of FAU was as successful as the transformation of NH<sub>4</sub><sup>-</sup>, H<sup>-</sup>, or K<sup>-</sup> forms of FAU in KOH. But the presence of Ca ions in the FAU structure fully prevented transformation. It has been observed that this cation has remarkable stabilizing effect on the FAU structure [4]. Presence of K<sup>+</sup> cations appeared as critical factor for CHA formation. With other alkalihydroxides synthesis of CHA failed.

Our investigation reveals the crucial role of nature and concentration of the cations play as template species in final zeolite framework formation.

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[1] G.H. Kuhl, *Zeolites* **1987**, *7*, 451-457. [2] R.W. Thompson et al., *J. Crystal Growth* **1982**, *56*, 711-722. [3] M. Bourgogne, et al., *US Patent* **1985**, *4*, 4503,024. [4] J.F.M. Denayer, et al., *Micropor. Mesopor. Mater.* **2007**, *103*, 11-

19. [5] A. Depla et al., *Phys. Chem. Chem. Phys.* **2011**, submitted.

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### A new approach to crystal-structure prediction

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The general failure to make reliable crystal structure predictions from chemical composition has long been identified as a continuing scandal in Crystallography [1]. Recent techniques have exploited the principle of minimum energy in conjunction with a combinatorial analysis, in a computational simulation, to obtain and classify a large number of arrangements on energy grounds. Despite limited success, the fact is that no scientific insight into the process of crystallization is gained. We therefore suggest a different approach which should provide intuitive insight into the factors affecting structure stability.

Brown and Shannon [2] showed a correlation between ‘cation-anion’ bond length and bond strength in crystals for a variety of chemical compositions and coordination numbers. This approach was developed further by Brown [3] [4] into Bond-Valence Theory, with two key rules: (1) the Valence-Sum Rule which states that the sum of the bond valences around an ion is equal to its formal valence, and (2) the Valence-Matching Principle which states that a chemical bond may form when the Lewis-acid strength of the cation matches the Lewis-base strength of the anion. The latter rule is of particular importance as it allows a prior examination of structure stability whereas, for example, Pauling’s rules [5] only allow a posterior examination. Brown [4] has shown how the valence-sum rule can be combined with what he calls Loop Equations to solve a bond network for the bond-valence values that exactly satisfy these equations. The question then becomes whether there is a specific combination of cations and anions that can adopt this arrangement.

The International Crystal Structure Database (ICSD) enables comprehensive evaluation of bond-valence ranges by surveying the database for dispersion of bondlengths for all combinations of atoms, oxidation states and coordination numbers. Sites of candidate structures can then be assigned suitable ion species. A logical path to crystal-structure prediction thus arises: (1) solve the valence-sum rule and loop equations to get ideal bond-valences for a particular bond topology and combination of formal charges at the various sites; (2) convert the resultant bond-valences to bond lengths for possible combinations of candidate ions; (3) if the resultant values lie within the observed dispersion of bondlengths for the candidate ions, the structure is possible with regard to bond-valence criteria. Competing structures of the same formula may then be evaluated in the usual way (distance-least-squares calculations followed by a Molecular Orbital Theory energy evaluation [6]). This procedure thus relies upon well-developed techniques that are applied in a novel way, avoiding the stochastic component of a computer simulation, and allowing careful analysis at any step of the process.

[1] J. Maddox, *Nature*, **1988**, 335, 201. [2] I.D. Brown and R.D. Shannon, *Acta Crystallographica*, **1973**, A29, 266-282. [3] I.D. Brown and D. Altermatt, *Acta Crystallographica*, **1985**, B41, 244-247. [4] I.D. Brown, **2002**, *The Chemical Bond in Inorganic Chemistry*, Oxford University Press. [5] L. Pauling, *Journal of the American Chemical Society*, **1929**, *51*, 1010-1026. [6] J.K. Burdett, **1980**, *Molecular shapes*. John Wiley & sons, New York

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