CHABAZITE: FROM A "BOILING STONE" TO THE NANO-OXIDE CARRIER

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INTRODUCTION

Chabazite (CHA) is one of the most widespread natural zeolites. Also, it is one of the first zeolites to be studied as an ion-exchanger [1]. The main feature of the chabazite structure is the so-called “chabazite cage” consisting of parallel stacks of six-membered double rings (D6R) in the sequence ABC. The D6R units are linked by tilted four-rings. The aluminosilicate network is a nanoporous three-dimensional framework with ellipsoidal apertures having dimensions of about 0.37x0.42 nm, which classifies the chabazite-like aluminophosphates as molecular sieves with small pore openings.

Zeolites have now various applications such as ion-exchange, heat-exchange, adsorbtion and catalysis. The CHA-type zeolites exhibit excellent adsorptive properties and therefore chabazite finds use in commercial adsorbents for natural gas drying [2].

Natural chabazites however are variable in chemical composition which significantly affects their applications [3]. Moreover, zeolitic tuff must be purified and that is usually economically too expensive. In this sense synthetic zeolites have many advantages. At the begining of the 1990's very extensive research in the field of zeolite synthesis led to the discovery of novel compounds with zeolite structures. Among them porous aluminophosphates are the most important class.

In this paper we report novel applications of the zeolite framework. We have found that the chabazite-like aluminophosphate lattice could serve not only as a carrier for fine nano-sized particles but it can also be a reactor which enables their formation.

EXPERIMENTAL

The aluminophosphate was prepared hydrothermally in an aqueous medium using *tris*(ethylenediamine)nickel(II) chloride and di-n-butylamine [4].. Only the Ni(II) complex was captured in the aluminophosphate host.

Thermal decomposition of the as-synthesized material was studied using a SDT Q-600 simultaneous DSC-TGA instrument (TA Instruments). The samples (mass app. 10 mg) were heated in a standard alumina 90 μl sample pan. Experiments were carried out under air with a flow rate of 0.1 dm^3 min^{-1}.

The thermal processing of the as-synthesized material was performed by heating the sample under air up to 550 °C at a heating rate of 10 °C min^{-1}. The sample was then heated isothermally at 550 °C during 30 min. The constant weight of the residual pale-yellow product (Ni-CHA) confirmed that the calcination under these conditions was complete.

For the transmission electron microscopy (TEM) analysis the Ni-CHA samples were ground to a fine powder in an agate mortar with alcohol. The suspension containing the sample was deposited onto the lacey carbon-coated TEM sample supports. TEM studies were performed using a 200 kV TEM (JEM-2100 UHR, Jeol Inc., Tokyo, Japan) equipped with an ultra-high resolution objective lens pole-piece having a point-to-point resolution of 0.19 nm, being sufficient to resolve the lattice images of NiO and $AlPO_4$ in the low-index zone axes. From the TEM images, diameters of the NiO particles were measured in order to determine their average size. Due to a relatively small size of the NiO nanoparticles, the selected area electron diffraction (SAED) on multiple nanocrystals was preformed to obtain the diffraction rings with the structure-specific *d*-values.

RESULTS AND DISCUSSION

The as-synthesized aluminophosphate product posseses a deformed chabazite structure [5]. Upon crystallization *tris*(ethylenediamine)nickel(II) ion exhibits not only the templating feature in connecting and arranging the tetrahedral Al- and P-structural units but also plays a co-structuring role. By losing one ethylenediamine ligand from its coordination sphere upon hydrothermal crystallization, Ni(II) ion forms an unseal P-O-Ni-O-P bridge across the chabazite cage. This causes a triclinic deformation of the aluminophosphate framework, which upon calcination transforms into the aluminophosphate with rombohedral chabazite lattice. Figure 1 shows the view down the *a* crystallographic axis of the crystal structure.

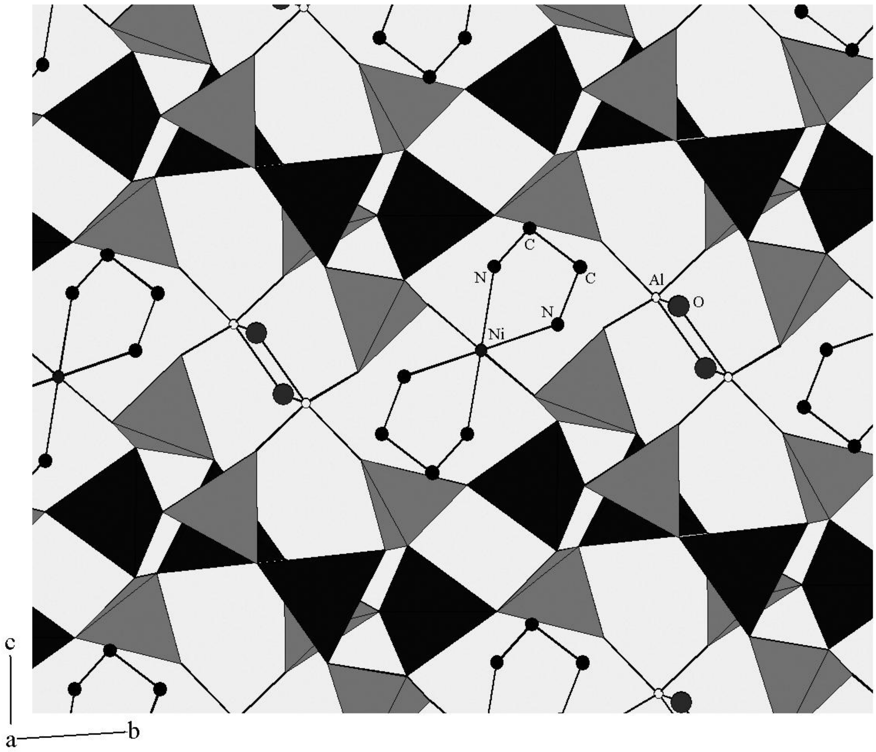

Figure 1. Schematic view of the aluminophosphate lattice with captured Ni(II) complex down the *a* crystallographic axis. The AlO_4 tetrahedra are darkly shaded, and the PO_4 tetrahedra are lightly shaded. Hydrogen atoms have been omitted for clarity.

In the as-synthesized aluminophosphate lattice, two thirds of aluminum are present as AlO_4 tetrahedra, while one third is five–coordinate due to the presence of the double Al–OH–Al bridges. Octahedrally coordinated nickel atoms are an integral part of the aluminophosphate lattice, being surrounded by two bidentately coordinated ethylenediamine ligands and by two oxygen atoms from the adjacent PO_4 tetrahedra.

The thermal decomposition of the Ni(II) complex was studied by TG analysis. The decomposition occurs in two main stages (Fig. 2). The first one displays in the 180-420 ºC range. It corresponds to the dehydroxylation process. The complex shape of the TG and DTG curves in that temperature region suggests that the dehydroxylation is a multi-step process. The second stage occurs above 420 ºC and it belongs to the loss of two ethylenediamine molecules (deamination). The DTG curve in that temperature region displays a sharp single maximum centered at 530 °C showing that the deamination is a single step process. The residual (Ni-CHA) is pale-yellow powder.

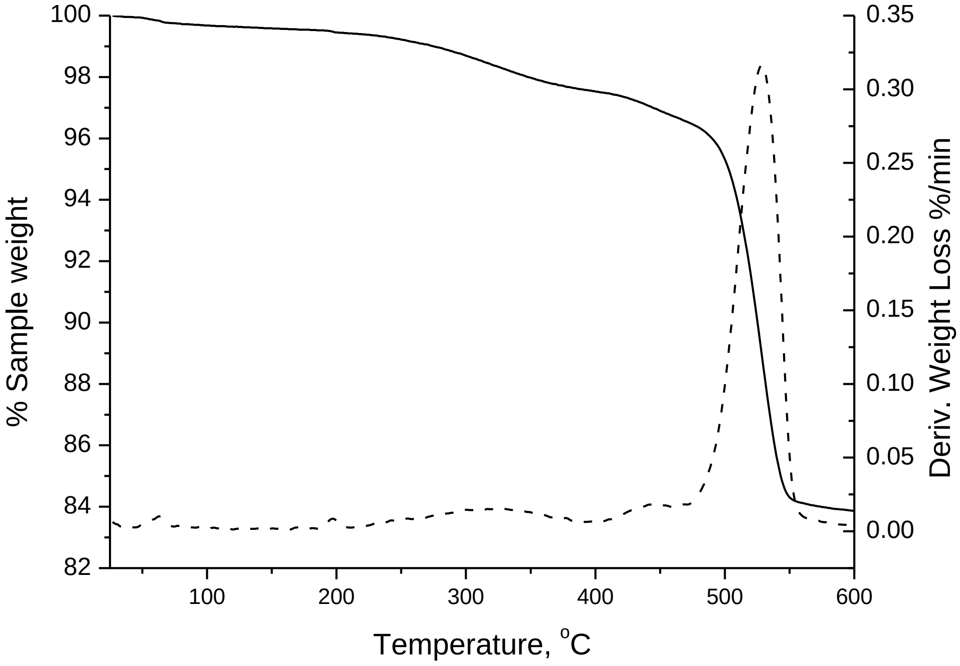

Figure 2. TG (solid) and DTG (dash) curves of as-synthesized material

The Ni-CHA contains a chabazite-like $AlPO_4$-34 [5] and a nickel oxide phase which was confirmed by the TEM analysis.

Fig. 3(a) shows a TEM image of a typical area of the Ni-CHA. The dark spots belong to the nickel oxide phase. NiO is present in the form of spherical nanocrystalline particles, homogeneously dispersed in the chabazite matrix. The sizes of NiO crystallites are between 2-7 nm, with the average particle measuring ~ 5 nm in diameter. This value is similar to that reported for Ni(diethylenetriamine)$_2$-$AlPO_4$-5 where the 6 nm nickel oxide particles, inhomogeneously distributed, were also obtained by calcination [6]. No preferential faceting of the cubic NiO crystals (rock-salt structure) can be observed, implying a rapid crystallization.

The TEM image indicates that NiO is formed in such a manner that it does not enter the channels of $AlPO_4$-34, nor it in anyway interacts with the hosting chabazite lattice nor deforms it. Since the size of NiO particles exceeds the pore size of the chabazite framework, it seems likely that the process of NiO crystallization occurs outside the pores. However, small size of the NiO particles indicates that the pore openings play a significant role in the prevention of further agglomeration. As a comparison, an average particle size (calculated from the peak broadening using the Scherrer equation) of NiO obtained by thermal decomposition of Ni(ethylenediamine)$_3SO_4$ was found to be about 17.5 nm [7].

The SAED pattern recorded over multiple NiO particles, shown in Fig. 3(b), corresponds to the cubic NiO structure (i.e. JCPDF # 78-0643) with additional reflections stemming from the underlying aluminophosphate chabazite-like matrix. The $AlPO_4$-34 has crystallized in multiple randomly oriented and intergrown domains, which is obvious from their different orientation in the TEM image in Fig. 3(a). Individual $AlPO_4$-34 domains are from 100 nm to more than 500 nm in size. Under longer exposure to the electron beam (i.e. more than 20 seconds) $AlPO_4$-34 became fairly unstable and amorphous, especially in very thin sections of the crystal.

Fig. 3(c) shows partly overlapping NiO spherical particles located at the edge of the amorphous aluminophosphate matrix (in a very thin crystal foil, less then 5 nm in thickness). In suitably oriented particles it was possible to resolve the lattice images corresponding to the cubic structure of NiO.

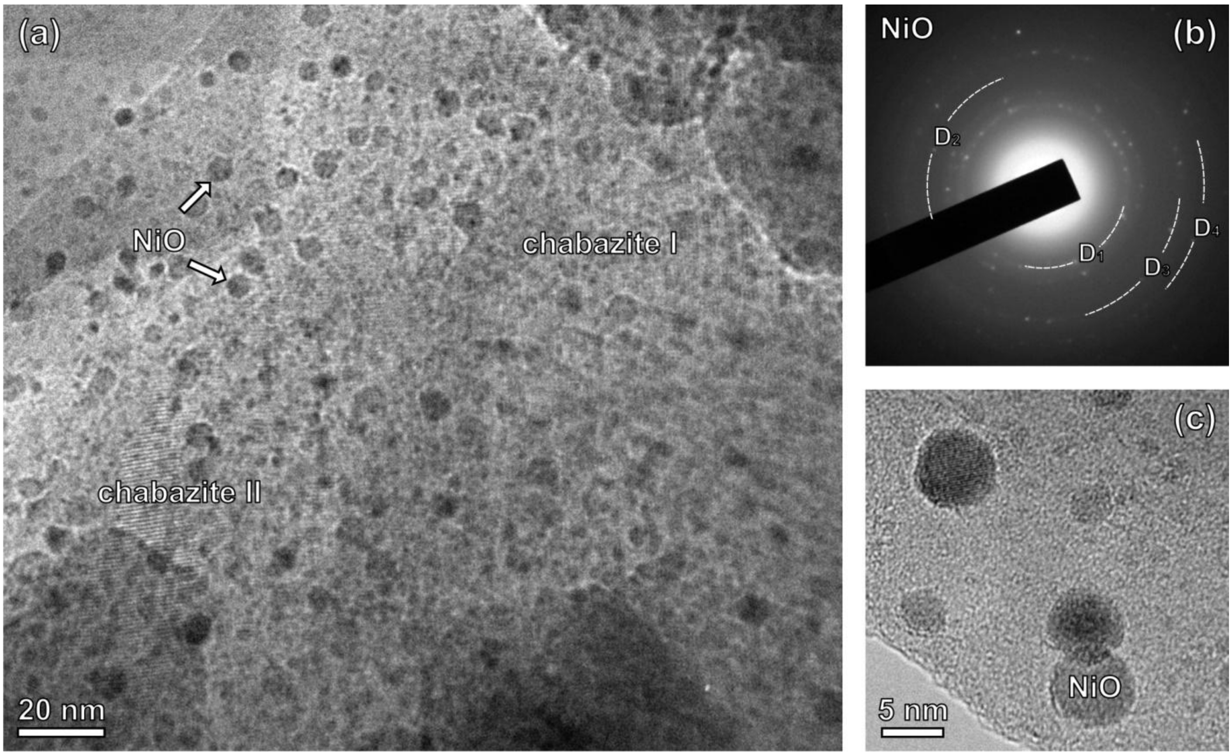

Figure 3. TEM images of the NiO-containing $AlPO_4$-34 processed in air. (**a**) NiO crystallizes on the surface in form of spherical nanoparticles (dark spots ~ 5 nm in diameter). $AlPO_4$-34 has crystallized in multiple overlapping domains (I+II). (**b**) SAED pattern recorded over a larger area shows diffraction rings with *d*-values corresponding to cubic NiO. (**c**) Isolated NiO particles are randomly distributed and show a high degree of crystallinity.

In order to check for a possible structural interaction of the aluminophosphate matrix with the NiO phase we have oriented one of the $AlPO_4$-34 crystalline domains into the lowest-index orientation, where the largest *d*-spacings of the crystal are visible. Glancing the lattice image at an acute angle (Fig. 4) along the rows of white dots does not reveal any major distortions or lattice defects that might have resulted from epitaxial intergrowth of NiO with the aluminophosphate crystal. This leads to the conclusion that, under experimental conditions used in this experiment, the NiO phase does not interfere with the $AlPO_4$-34 crystal on the structural level.

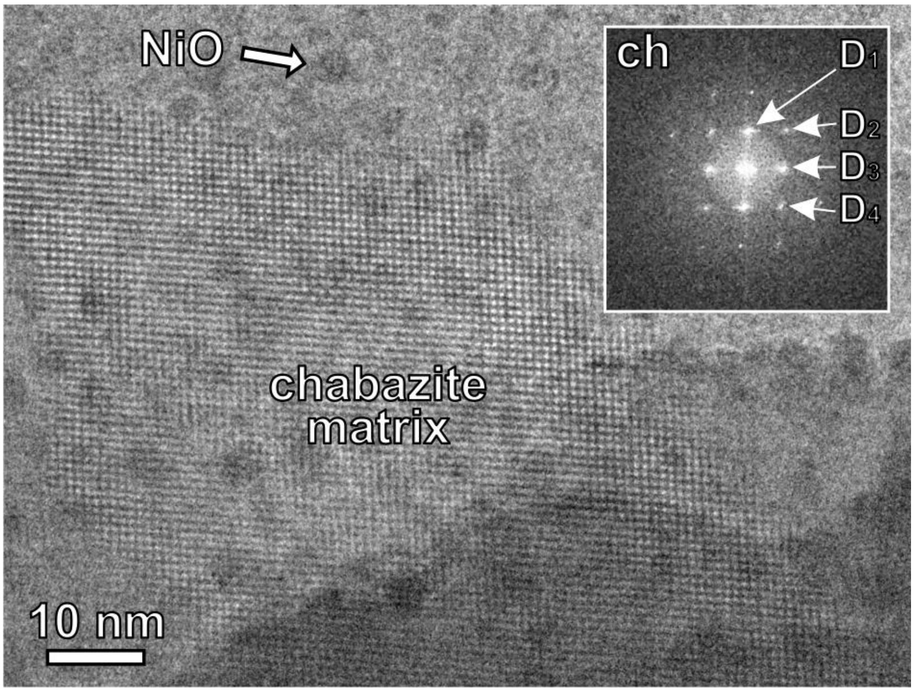

Figure 4. The high-resolution TEM image of the NiO-containing $AlPO_4$-34 in the low-index orientation shows the symmetry of $AlPO_4$-34 unit cell. An FFT spectrum (inset in the upper right corner) from the crystalline foil indicates the rhombohedral unit cell with an a-parameter of ~ 0.9 nm and $\alpha \sim 95.5\ ^\circ$ in accord with the crystallographic parametra of $AlPO_4$-34. The NiO particles are indicated by arrows.

CONCLUSION

The amine Ni(II) complex exhibits not only unique structural-directing role in the crystallization of porous aluminophosphate with chabazite framework but also acts as precursor for obtaining very fine nano-oxide particles. Upon thermal treatment the complex captured inside the aluminophosphate lattice decomposed in two stage processes. The deamination occurs at about 530 ^oC in a single step. The residual contains the chabazite-like aluminophosphate and nano-sized nickel oxide particles with an average size of about 5 nm. The TEM analysis shows that the NiO phase does not interfere with the aluminophosphate crystal on the structural level.

The constraints imposed by small pore openings of the chabazite lattice seems to be crucial in the prevention of agglomeration of nano particles. Preliminary results concerning the thermal decomposition of *bis*(di(2-aminoethyl)amine)nickel(II) complex ion encapsulated in the $AlPO_4$-5 [8] show that nickel oxide particles forms on the aluminophosphate surface are of about 10 nm in size ($AlPO_4$-5 belongs to aluminophosphate structural types with large pore openings).

The study shows that the thermal decomposition of amine complexes of Ni(II) encapsulated inside the microporous aluminophosphate host can be a suitable method for obtaining fine nano-oxide particles.

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