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ZEOLITES AND RELATED MICROPOROUS MATERIALS: STATE OF THE ART 1994

PART C

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Nitrido Zeolites - a Novel and Promising Class of Compounds

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1. Summary

The synthetic approach to nitrido zeolites has been opened up by the synthesis and characterization of the P-N-sodalite class of compounds. A variety of compounds with a general formula $M_{7-x}H_{2x}[P_{12}N_{24}]X_{2-y}$ with M = Zn^{2+}, Co^{2+}, Ni^{2+} etc. and X = F^-, Cl^-, Br^-, I^- has been obtained. Striking features of these compounds are high chemical and thermal stability as well as an intense colour in some cases.

2. Introduction

The importance of zeolites as catalysts, molecular sieves, adsorbents, and ion exchangers has increased considerably in recent years. The substitution of silicon and/or aluminium in the zeolite framework by other elements like B, P, Ge, Ga, As, Sb, Ti etc. made it possible to tailor the specific properties due to the demanded applications [1,2]. In contrast, the substitution of the anion substructure, for example by replacing oxygen by other electronegative elements, has been almost completely neglected.

The search for a combination of two elements isosteric with the corresponding combination of silicon and oxygen leads to phosphorus(V) nitrides. In this class of substances we found several compounds with P-N-substructures analogous to well known silicates (Figure 1).

Examples are the ortho-anion $[PN_4]^{7-}$ in Li_7PN_4 [3], cyclo-silicate analogous anions in $Li_{12}P_3N_9$ [4], or the $^3_\infty[PN_2^-]$-network in HPN_2 [5] or $LiPN_2$ [6]. Even the synthesis of a zeolite-like framework is possible and here we present the broad synthetic approach and the characterization of the P-N-sodalite class of compounds.

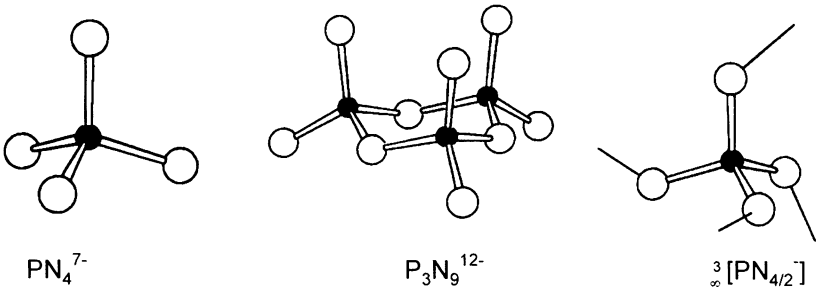

Figure 1. Condensation of PN_4 - tetrahedra in phosphorus nitrides

3. Syntheses

The synthesis of a zeolite-like framework structure $^3_\infty[PN_{4/2}^-]$ is possible [7] when, for the in situ preparation of ammonia in the high-pressure ammonolysis of P_3N_5, Zn_3N_2 is treated with ammonium chloride [Eq. (1)]. Under the given experimental conditions a phosphorus(V) nitride is formed with a molar ratio P:N = 1:2, while at the same time zinc and chlorine are incorporated into the solid through $ZnCl_2$, which is volatile at the reaction conditions (Figure 2). The reaction then proceeds quantitatively to afford $Zn_5H_4[P_{12}N_{24}]Cl_2$ [Eq. (2)].

$$Zn_3N_2 + 6\ NH_4Cl \xrightarrow{400°C} 8\ NH_3 + 3\ ZnCl_2 \quad (1)$$

$$4\ P_3N_5 + 4\ NH_3 + 5\ ZnCl_2 \xrightarrow{640°C} Zn_5H_4[P_{12}N_{24}]Cl_2 + 8\ HCl \quad (2)$$

A step by step exchange of the hydrogen atoms in the product obtained is possible in a subsequent reaction with additional $ZnCl_2$ in which HCl is liberated [Eq. (3)].

$$Zn_5H_4[P_{12}N_{24}]Cl_2 + 2\ ZnCl_2 \xrightarrow{700°C,3d} Zn_7[P_{12}N_{24}]Cl_2 + 4\ HCl \quad (3)$$

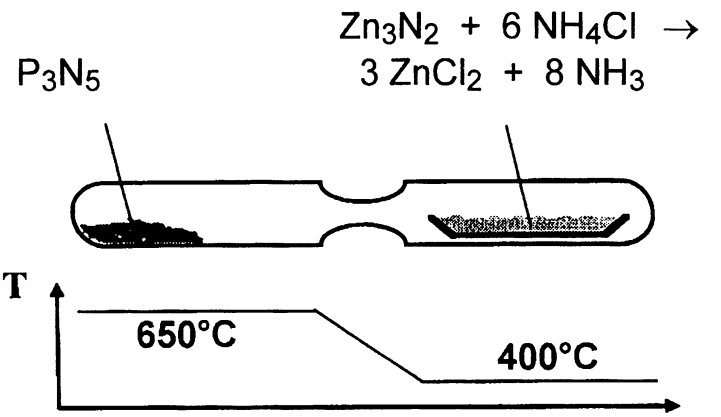

Figure 2. Compartmented ampoule for the in situ preparation of NH_3

The synthetic method described previously is not suitable for the preparation of modified P-N-sodalites containing other metal cations, (e.g. alkaline earth metals, transition metals, lanthanides).

P-N-sodalites $M_5H_4[P_{12}N_{24}]Cl_2$ (M = Zn,Co,Ni) can be obtained remarkably easy by reacting corresponding amounts of the metal chloride MCl_2, hexachloro-cyclotriphosphazene $(PNCl_2)_3$, and ammonium chloride [Eq. (4)].

$$5\ MCl_2 + 4\ (PNCl_2)_3 + 12\ NH_4Cl \xrightarrow{700°C,2d} M_5H_4[P_{12}N_{24}]Cl_2 + 44HCl \qquad (4)$$

This reaction is carried out in sealed ampoules and the batch size is limited by the amount of HCl formed. An alternative procedure involves the use of a molecular phosphorus component in which the chlorine atoms are completely replaced by amino groups $[\{PN(NH_2)_2\}_3]$ [Eq.(5)]. In this case the product is the hydrogen-free P-N sodalite $M_7[P_{12}N_{24}]Cl_2$ [8].

$$7\ MCl_2 + 4\ (PN(NH_2)_2)_3 \xrightarrow{700°C,2d} M_7[P_{12}N_{24}]Cl_2 + 12\ NH_4Cl \qquad (5)$$

A particularly elegant method for the preparation of P-N-sodalites modified in various ways is the reaction between phosphorus(V) nitride imide HPN_2 and the corresponding metal halide MX_2 [Eq. (6)], which affords compounds with a large number of different metal cations and halide ions (e.g. M = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb; X = Cl, Br, I) [8].

$$5\ MX_2 + 12\ HPN_2 \xrightarrow{700°C,2d} M_5H_4[P_{12}N_{24}]X_2 + 8\ HX \qquad (6)$$

By using the methods described above it has been possible to obtain a wide variety of P-N sodalites. As well as divalent cations such as Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, trivalent cations such as Cr^{3+}, Fe^{3+}, and even monovalent cations such as Cu^{+} can be incorporated. In all cases phase widths are observed in which a fraction of the metal ions can be replaced by the corresponding number of hydrogen cations, which are then covalently bonded to nitrogen atoms of the P-N-skeleton.

In all P-N-sodalites described before, the β-cages contain a halogen anion surrounded by metal cations. However, the presumption for the applications of zeolite framework structures are empty holes and channels. So we tried to synthesize sodalites without the central halogen atom, exhibiting "empty" β-cages. Recently we succeeded by the simple reaction [9] of phosphorus nitride with zinc nitride [Eq. (7)].

$$2\ Zn_3N_2 + 4\ P_3N_5 \xrightarrow{850°C,7d} Zn_6[P_{12}N_{24}] \qquad (7)$$

4. Characterization

The powder diffraction diagram of $Zn_7[P_{12}N_{24}]Cl_2$ indicates a cubic structure. The similarity to the powder diagram of sodalite $Na_8[Al_6Si_6O_{24}]Cl_2$ is evident [10]. In the system of $Zn_{7-x}H_{2x}[P_{12}N_{24}]Cl_2$ we observed a phase width in which the number of zinc atoms varies between 4 and 7. With decreasing amount of hydrogen atoms in the P-N-sodalite, the cubic lattice constant increases, as shown in Table 1.

Table 1
Refined lattice constants of P-N-sodalites

compound	lattice constant [pm]	reference
$Zn_{4.8}H_{4.4}[P_{12}N_{24}]Cl_2$	821.61(4)	[11]
$Zn_{5.5}H_{3.0}[P_{12}N_{24}]Cl_2$	822.56(1)	[11]
$Zn_{6.1}H_{1.8}[P_{12}N_{24}]Cl_2$	823.11(3)	[11]
$Zn_7[P_{12}N_{24}]Cl_2$	824.21(1)	[7,8]
$Zn_6[P_{12}N_{24}]$	823.35(2)	[9]
$Zn_{6.8}[P_{12}N_{24}]Cl_{1.6}$	828.00(6)	[11]

The Rietveld refinement of the crystal structure of $Zn_7[P_{12}N_{24}]Cl_2$ confirmed the suspected analogy [7,8]. It shows that phosphorus and nitrogen form a sodalite-like framework of corner-sharing PN_4 tetrahedra (Figure 3). It is constructed from $[P_4N_4]$- and $[P_6N_6]$- rings (P-N 163.6(7) pm, P-N-P 125.8(4)°). In the center of each ß-cage is a Cl^--ion, tetrahedrally coordinated by Zn^{2+}-ions (Zn-Cl 259.6(2) pm). The Zn^{2+}-ions are pseudo-tetrahedrally coordinated by one Cl^--ion and three N-atoms (Zn-N 196.0(8) pm).

The hydrogen atoms bonded to nitrogen atoms can be detected by IR-spectroscopy. The N-H stretch is observed near 3100 cm^{-1}. Typical vibrations of the P-N-framework are found at 1270, 1075, 890 and 580 cm^{-1} (Figure 4).

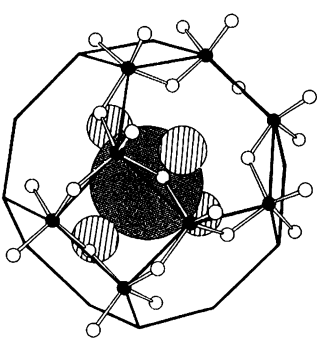

Figure 3. Section of the crystal structure of $Zn_7[P_{12}N_{24}]Cl_2$
P: black, N: white, Cl: gray, Zn: striped.

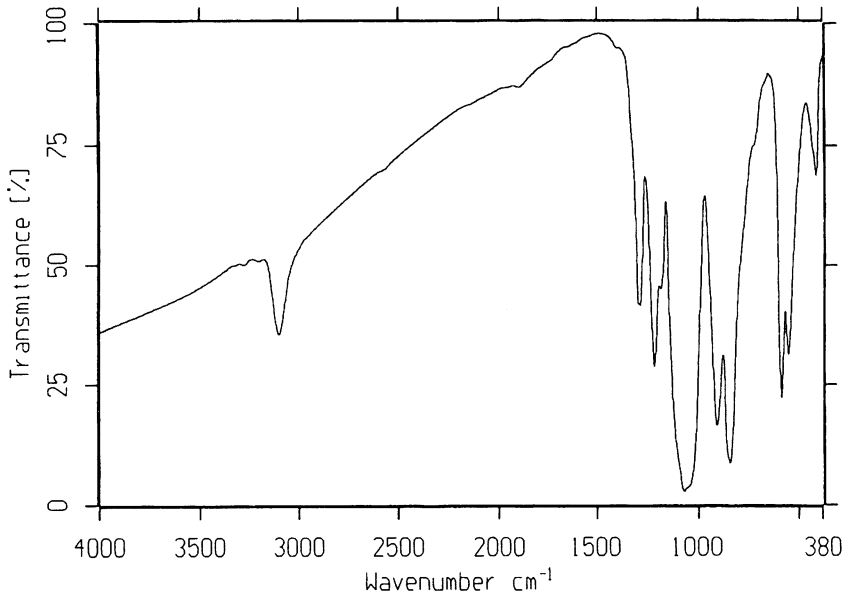

Figure 4.
IR-spectrum of $Zn_{7-x}H_{2x}[P_{12}N_{24}]Cl_2$ compounds

P-N-sodalites are thermally stable up to 800 °C (in a nonoxidizing atmosphere) and are inert towards all common solvents as well as hot acids and bases. Only in a special autoclave system $Zn_7[P_{12}N_{24}]Cl_2$ decomposes in dilute sulfuric acid (190 °C, 10 bar, 2 d; the phosphorus(V) nitride hydrolyses to ammonium hydrogen phoshate [11]).

A striking property of some P-N-sodalites are the intense colour (blue (Co,Ni), brown (Fe), dark green (Cr)). These P-N-sodalites with the composition $M_{7-x}H_{2x}[P_{12}N_{24}]X_2$, M = Co^{2+}, Ni^{2+}, X = Cl^-, Br^-, I^- have been characterized by their UV-VIS-spectra. To rationalize the UV-Vis-spectra it is assumed that the vicinity of the transition metal can be approximated by the cationic complex $[MX(NH_3)_3]^+$ which is solely responsible for the colour of the solid. The spectrum of the Co-P-N-sodalite, $Co_{7-x}H_{2x}[P_{12}N_{24}]Cl_2$ for example, has absorption maxima around 6000, 9000 and 15000 cm^{-1} as shown in Figure 5. In comparision to the well investigated complexes $[CoX_4]^{2-}$ which exhibits two maxima around 6000 cm^{-1} ($^4A_2 \rightarrow {}^4T_1(F)$ - transition) and 15000 cm^{-1} ($^4A_2 \rightarrow {}^4T_1(P)$ - transition) the additional maximum in the UV-VIS-spectrum of the Co-sodalite is due to the decrease in symmetry. The fine

structure of the absorption peaks are due to spin-orbit coupling leading to additional splitting of the energy levels. Extended Hückel and Ligand-Field-Calculations are used to explain the spectra [12].

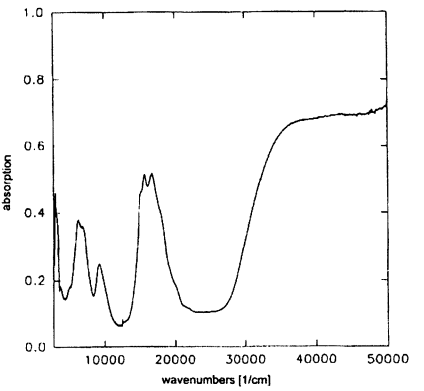

Figure 5.
UV-VIS-spectrum of $Co_{7-x}H_{2x}[P_{12}N_{24}]Cl_2$

5. Discussion, Conclusions

The synthesis of P-N-zeolites appears particularly attractive with respect to desirable material properties and the modification of known zeolite materials. The intense colour of some P-N-sodalites suggests that they may find use as pigments. Quantum mechanical calculations could help to predict the colour of unknown P-N-sodalites.

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