

MS35-P05

Organometallosiloxanes and germoxanes as porous materials

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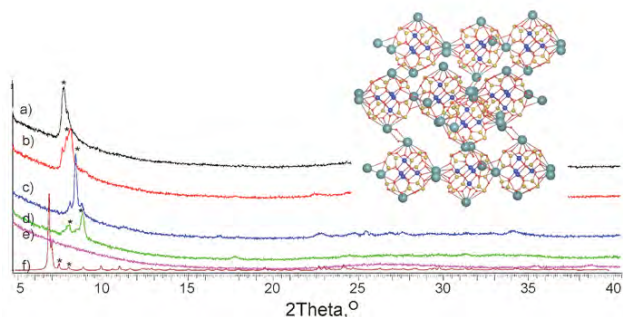
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Metallosiloxane $M_nM'_m[RSiO_{1.5}]_n$ and metalgermoxane $M_nM'_m[RGeO_{1.5}]_n$ cluster units (M = transition metal, i.e. Cu, Co, Ni, Fe, M' – alkali metal, i.e. Na, K, Cs, Rb, n = 2-7, m = 2 - 10) are relatively rigid polynuclear nanosized units possessing catalytic [1] and magnetic [2] properties. The shape and size of cluster units generally governed by the nature of transition metal and synthetic conditions, while the nature of alkali metal and solvent affect connectivity of these cages [3]. Rigidity of cages is responsible for realization of supramolecular and coordination architectures with open channels and voids up to 15 Å. Moreover, as coordination polymers are formed by M-O and M'-O interactions only, these porous architectures remain stable up to 400°C when the organic coating is decomposed [3a].

In this study we discuss the effect of M, M' and E (E = Si, Ge) nature on the shape and connectivity of cluster units, the topology and abundance of 1D, 2D and 3D architectures based on organometallosiloxanes and germoxanes, and synthetic pathways to form porous 2D and 3D nets. Multitemperature PXRD data of various compounds are compared to investigate thermal stability of the title compounds and their ability to form purely inorganic molecular sieves. The latter can be used for catalysis and gas sorption.

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References:

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Keywords: metallosiloxanes and metalgermoxanes, networks, topology

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Pressure-induced solid-state reactions of coordination polymers

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Metal-organic frameworks (MOF's) and Coordination Polymers (CP's) are classified as the interdisciplinary field between the coordination and inorganic chemistry. For decades, these porous materials have been thoroughly investigated because of their potential applications, such catalysis and sensing as well as the storage of fuel gases and water.¹ Presently, high pressure has become an established highly-efficient tool for inducing strong structural transformations in various compounds.² In particular high pressure can be applied for post-synthetic modification (PSM) of CP's. Several approaches have been used for PSM, but the category of pressure induced modifications has merely begun to emerge.

Herein we present 2-dimensional cadmium coordination polymer $Cd(APP)_2NO_3 \cdot NO_3$ [APP abbreviates 1,4-bis(3aminopropyl)piperazine], undergoing a pressure induced associative reaction to $cis-Cd(APP)_2(NO_3)_2$. Our high-pressure structural measurements revealed that at 0.4 GPa a rearrangement of the Cd-coordination sphere takes place, which is connected with the formation of a new additional coordination bond. As a result of this reaction, a nitrate anion, detached of the cation and located in the crystal void space in the phase I, is transferred to the metal center. Consequently, the cadmium liganacy increases from 6 to 7 in phase II. The high-pressure reactivity of CP's can be explained by three simple rules: involving the metal/ligand ionic radii ratio, the elimination of potential voids in the compressed structure as well as the vicinity from the metal center to reacting anions.

References:

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Keywords: Coordination Polymers; high pressure; new bond formation