Covalent Aryloxide Metal-Organic Network Materials

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Metal-organic coordination network (MOCN) materials formed from rigid organic spacers and metals of known coordination tendencies have become increasingly well known. Materials with large pores present possibilities for molecular recognition, separation and the catalytic transformation of guest molecules [1]. In addition, chiral nanoporous materials are an emerging area of research in this field. The vast majority of networks are formed from later transition metals and rigid carboxylate or pyridine based organic spacer ligands. A key feature of MOCN materials is that considerable structural predictive ability exists over traditional solid-state inorganic compounds in their design.

Here, we report results of continuing work on the synthesis and X-ray structural characterization of a unique class of early transition metal covalent metal-aryloxide network materials [2]. A prototypical example, $\{[Ti(OC_{12}H_8O)_{1.5}(O^iPr)(HO^iPr)]_2\}_n$, is formed by treating $Ti(O^iPr)_4$ with excess 4, 4'-biphenol at 100°C in tetrahydrofuran. The three-dimensional porous network solid is derived from six 4,4'-biphenoxide linkages connecting bioctahedral dititanium cores.

Substitution of various metal precursors, solvents (pyridine, ether, etc.), and bisphenolic spacer precursors (dihydroxynaphthalene, 4,4'''-dihydroxyquaterphenyl, etc.) has afforded an array of one-, two- and three-dimensional materials. We have also made use of chiral alkoxide precursors to obtain crystalline network materials. In general, coordinating solvents such as pyridine decrease network dimensionality. The effect of network dimensionality on the olefin polymerization activity of the materials has been shown to decrease in the order 3-D > 2-D > 1-D > 0-D (amorphous polymer or molecular analog).

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