Synthesis and characterization of ε-Keggin-type Cobaltomolybdate-based 3D Framework Material

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ε-isomer of Keggin-type polyoxomolybdates are composed of one central XO_4 tetrahedron and twelve surrounding MoO_6 octahedra with T_d symmetry (Figure 1a).[1] Three oxygen atoms of four hexagonal faces of the ε-Keggin POM are able to bind to many metal ions such as transition metals and lanthanide metals (Figure 1b).

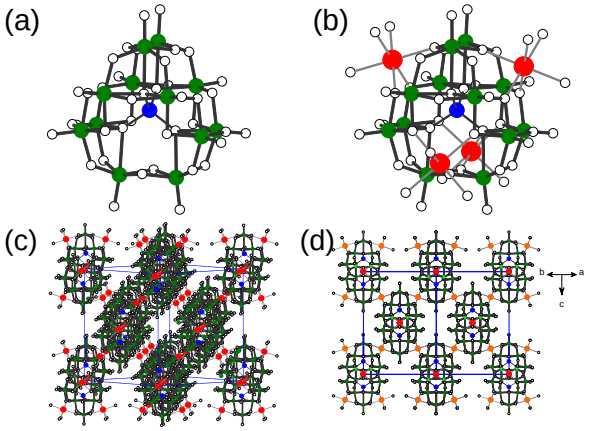

Fig. 1 Ball-and stick representation of (a) and (b) ε-Keggin-type molecule and (c) and (d) framework structure.

We have reported the first all-inorganic 3D framework where ε-Keggin polyoxovanadomolybdate, [ε-$VMo_{9.4}V_{2.6}O_{40}$], was linked by Bi^{III} cations to form a 3D framework with a zig-zag 3D pore system (denoted as **Mo–V–Bi oxide**) (Figure 1c)[2]. The **Mo–V–Bi oxide** is thermally stable, and the opened pores are analyzable by the gas adsorption-desorption technique. This compound can also be used as an acid catalyst[2].

Here, we describe the preparation and structural characterization of a new member of all-inorganic ε-Keggin POM-based 3D frameworks with cobalt ions (Co^{II}), NaH_9[ε-$Co^{II}Mo^{V}_8Mo^{VI}_4O_{40}Co^{II}_2$], denoted as **Na–Mo–Co oxide**[3].

Investigation of reaction conditions (pH of the solution, reaction temperature, reaction time etc.) indicates that once–produced $CoMoO_4$-$0.75H_2O$[4] without Mo metal was transferred to the desired **Na-Mo-Co oxide** by heating at 170 °C for 24 hours in the presence of Mo metal (Figure 2).

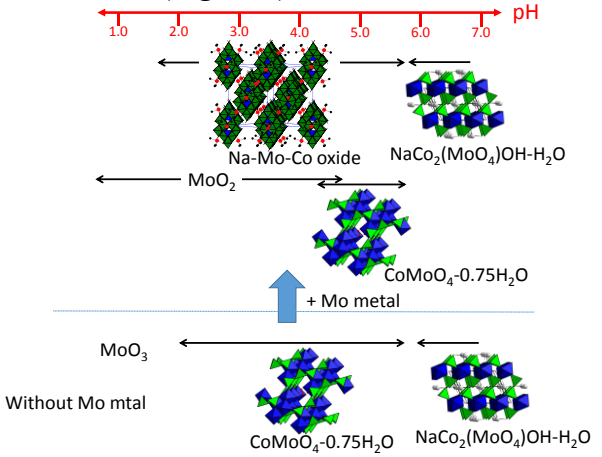

Fig. 2 Relationship between pH and products of hydrothermal reactions of aqueous solutions of Na_2MoO_4 and $CoCl_2$ at 170 °C for 24 hours with and without Mo metal.

We also present purification of this mixed oxide and characterization using powder XRD, IR, Raman, HAADF-STEM (Fig. 3), and XAFS.

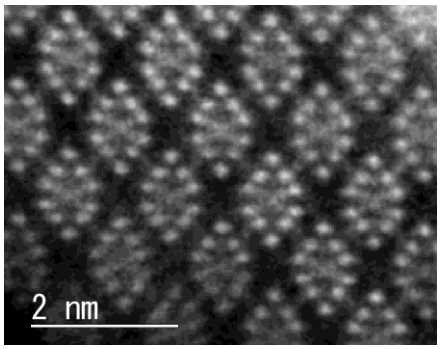

Fig. 3 HAADF-STEM image of **Na-Mo-Co oxide**

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