Solid State Sciences 12 (2010) 1866–1869

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

# Synthesis of Keggin-type polyoxometalate crystals

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ARTICLE INFO

*Article history:*
Received 30 November 2008
Received in revised form
16 May 2009
Accepted 10 January 2010
Available online 22 January 2010

*Keywords:*
Polyoxometalates
Crystals
Self-assembly
Keggin
Vanadomolybdates

ABSTRACT

Vanadium-containing polyoxometalates (POM) were synthesized under acidic conditions and characterized by XRD, FT-IR, $^{51}$V MAS-NMR, EXAFS-XANES and SEM.

POM crystals were successfully grown under acidic atmosphere, thus forming a self-assembled structure. This self-organized structure was constituted by cubic crystals having between 20 and 80 μm in size.

Both $^{51}$V MAS-NMR, EXAFS-XANES and PM6 calculations suggest that non-covalent interactions, such as hydrogen bonding, or shared vanadium atoms of non-complete coordination are the driving force of the self-assembly process.



## 1. Introduction

Spontaneous self-organization of matter shows the high capacity of nature to structure itself when specific conditions are present. The design and control of chemical systems over multiple-length scales from the molecular to the macro-scale thus represent one of the greatest challenges of contemporary science. In particular, the ability to understand how molecules organize, and thus build supramolecular architectures to produce functional nano-systems and nanomachines. Supramolecular chemistry deals with the association of two or more chemical species and is based on molecular non-covalent interactions [1,2].

These interactions often confer to the supramolecular structure new chemical and physical properties [3]. The nano-objects of supramolecular chemistry are both defined by the nature of the individual building blocks, and by the type of interactions which hold them together. The driving force for the assembly process can be hydrogen bonding, electrostatic forces, Van der Waals forces, metal-ion coordination, etc.

Heterogeneous catalysis can also take advantage from the peculiar properties of self-assembled catalysts [4,5]. Hence, these materials can be useful for the conception of new structured catalysts and reactors. Indeed, self-assembled catalysts can avoid the use of an inert binder to pack isolated crystals in catalytic beds, thus ensure improved heat and mass transfers. One can therefore reasonably hope to achieve a higher catalyst activity which may be accompanied by a raise in selectivity.

Due to their simple synthesis procedure and thermal stability, polyoxometalates (POM) having the Keggin structure are often used in acid catalysis. These acid polyoxometalates are molecular clusters formed by different metal oxides with the general formula $H_3PM_{12}O_{40}$. A central $PO_4$ tetrahedron, is surrounded by $12MO_6$ octahedra (M = Mo, W) arranged in four groups of three edge-sharing $M_3O_{13}$. Each group shares a common oxygen atom, together with the central $PO_4$ tetrahedron. It is possible to substitute $Mo^{6+}$ or $W^{6+}$ ions by $V^{5+}$, thus creating an excess of negative charge which has to be compensated [6]. Heteropolyacids are ionic crystals in the solid state, consisting of large polyanions (primary structure: $PM_{12}O_{40}^{3-}$), counter cations, and water of crystallization. This creates the so-called secondary structure $H_{3+n}PV_nM_{12-n}O_{40}\cdot xH_2O$ [7]. In addition, the arrangement of the particles, their morphology and pore structure generate the tertiary structure [7,8].

The aim of the present study is to produce organized tertiary structure of V-containing POM, while developing a suitable synthesis procedure. We have focused our work on the understanding of the assembly process by experiments and PM6 calculations.

## 2. Experimental

12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$), furnished by Fluka was used without further purification. V-containing POM were

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doi:10.1016/j.solidstatesciences.2010.01.022

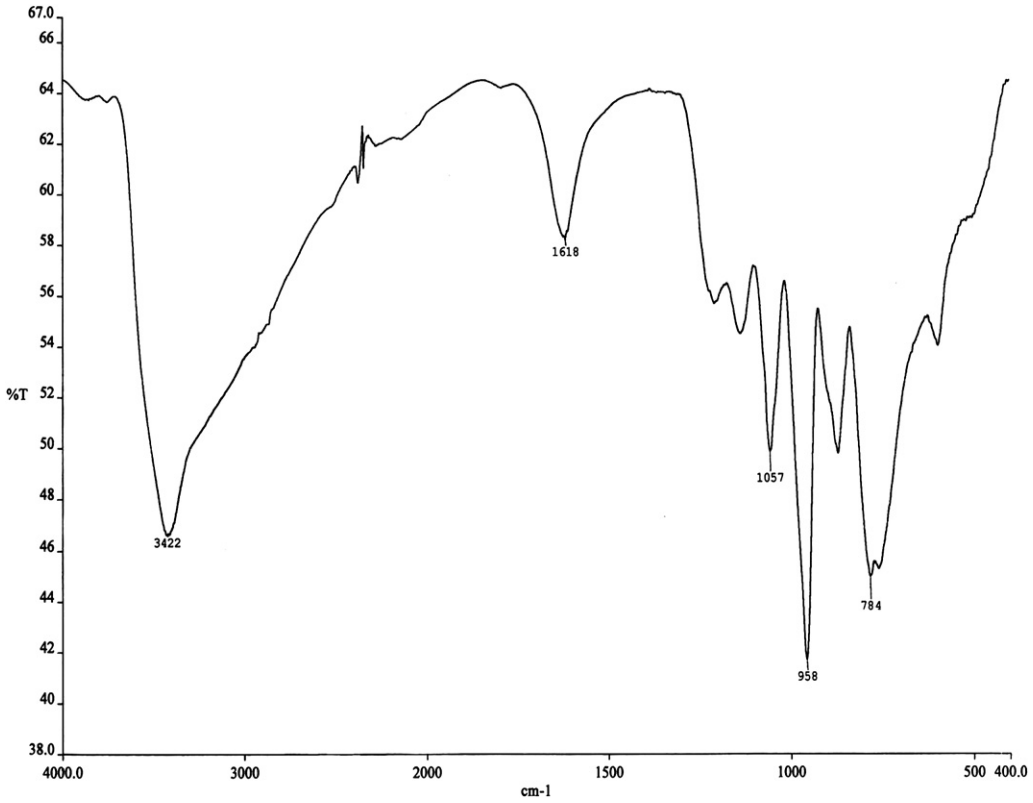


**Fig. 1.** FT-IR of $H_5V_2Mo_{10}O_{40}$ polyoxometalate.

prepared by acidification with sulfuric acid of an aqueous solution containing an alkali metal salt of the molybdate or vanadate, and subsequent isolation of the material via ether extraction. Heteropolyvanadates (HPV) have therefore been synthesized by mixing aqueous solutions of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$, Fluka, 99.5 wt%), disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$, Fluka, 99 wt%), and sodium metavanadate ($NaVO_3$, Fluka, 98 wt%). Under vigorous stirring, concentrated sulfuric acid was added dropwise to acidify the solution. The red-colored solution was cooled to 273 K, and kept 2 h at this temperature before being extracted by diethyl ether. The resulting HPV–etherate complex was finally placed in a dessicator under sulfuric acid vapors for several days to allow a slow recrystallization of the POM.

X-ray diffraction (XRD) patterns were acquired on a D8 Advance Bruker AXS powder diffractometer ($\theta/2\theta$) using monochromatized Cu-$K_\alpha$ radiation in the range of 2θ from 5° to 60°. FT-IR measurements were performed with a Perkin–Elmer spectrum BX apparatus, using KBr pellets. Scanning Electron Microscopy (SEM) was operated on a JEOL FEG 6700F microscope working at 9 kV accelerating voltage.

Solid state $^{51}V$ MAS-NMR was performed on a Bruker Avance III 400WB spectrometer at a spinning frequency of 28 kHz, with a 2.5 mm probe. $V_2O_5$ was used as a reference with a chemical shift of −610 ppm.

XANES and EXAFS measurements were carried out at the vanadium K-edge (5465 eV) in fluorescence mode at room

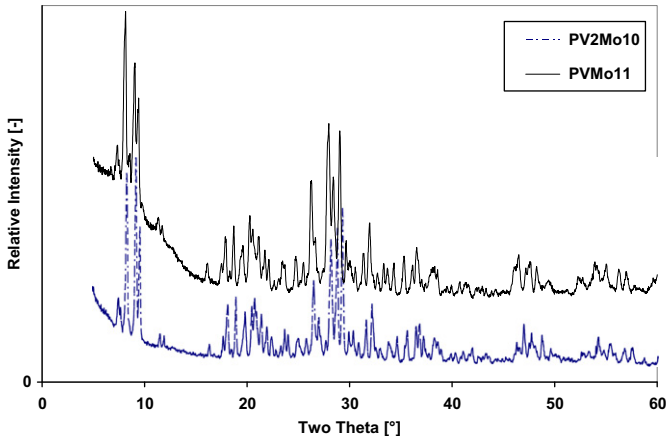


**Fig. 2.** XRD patterns of $V_1$ and $V_2$ polyoxometalates.

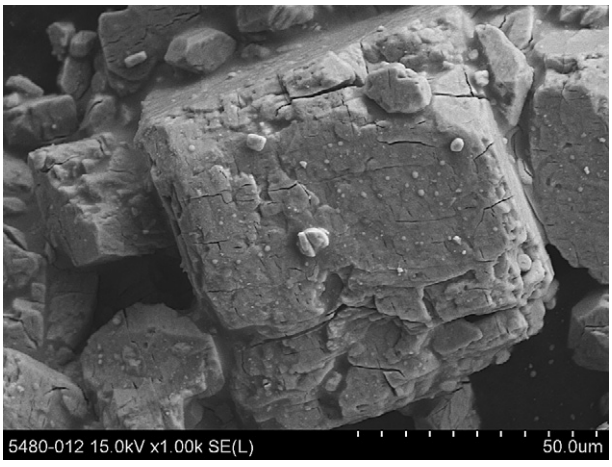


**Fig. 3.** SEM image of self-organized $H_5PV_2Mo_{10}O_{40}$ material.