

Preparation and characterization of Keggin-type heteropolysalts, $\text{Co}_x\text{PMo}_{12}\text{O}_{40}$ ($x = 0-1.5$)

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1. INTRODUCTION

Polyoxometalates (POMs), based transition-metal oxide clusters, have received much attention in various fields such as catalysis, photochemistry, nonlinear optics, biology and medicine [1]. Their physico-chemical, acidic and oxidative properties can be adjusted according with the nature of constituent elements [2]. In the field of catalysis, the most studied POMs are those with the Keggin. They were tested in wide variety of reactions in homogeneous and heterogeneous phases. In the redox processes, the nature of counter- cation in the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ system can play a significant role. Thus, it has been shown that using Fe(III), vanadyl(VO^{2+}), antimony (Sb^{3+}) or cobalt (Co^{2+}) counter-cation develop a more favourable distribution of both reduced Mo(V) and oxidized Mo(VI) sites [3]. In the present work we report the synthesis and characterization using several techniques of Keggin-type heteropolysalts of composition $\text{H}_{3-2x}\text{Co}_x\text{PMo}_{12}\text{O}_{40}$ ($x = 0 - 1.5$) denoted as $\text{Co}_x\text{PMo}_{12}$.

2. EXPERIMENTAL

2.1. Materials

$\text{Co}_x\text{PMo}_{12}$ was synthesized by a cation exchange carried out in two stages: in the first step $\text{Ba}_x\text{PMo}_{12}\text{O}_{40}$ was prepared from addition of $\text{Ba}(\text{OH})_2$ to an aqueous solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in stoichiometric ratios, and in the second step BaSO_4 precipitates after addition of cobalt sulphate. After filtration, the solution was drained to 50°C . $\text{Co}_x\text{PMo}_{12}$ salts were conserved with any washing.

2.2. Characterization

Infrared spectroscopy of the solids was recorded on an ATR Thermo scientific Nicolet apparatus. Solution ^{31}P NMR spectra were recorded on a Bruker AC300 apparatus at 121.5 MHz, temperature with a Siemens D5000 diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418^\circ\text{A}$). Thermal analysis (TG) were carried out using a Perkin Elmer Similtaneous Thermal analyzer STA 6000 and the studies of the morphology of salts using JEOL JSM-5800LV Scanning MicroscopIe (SEM).

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Table 1. IR vibration wave numbers (cm^{-1}) of the polyoxometalate.

$\text{Co}_x\text{PMo}_{12}$	γPOa	$\gamma\text{M} = \text{Od}$	$\gamma\text{MO}_b\text{M}$	$\gamma\text{MO}_c\text{M}$
X = 0	1060	962	870	785
X = 0.25	1062	964	875	787
X = 0.5	1062	966	876	791
X = 0.75	1060	964	876	791
X = 1	1060	962	874	791
X = 1.25	1062	964	877	791
X = 1.5	1060	962	876	791

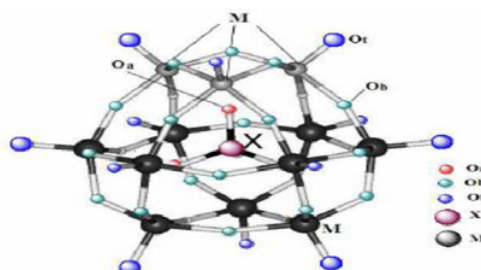


Figure 1. Structure of Keggin unit.

3. RESULTS

3.1. ATR spectroscopy

The IR vibration wave numbers solids are summarized in Table 1. In the low wave number region ($1100-500\text{cm}^{-1}$), the characteristic bands of the Keggin structure were obtained. According to Rocchiccioli-Deltcheff et al [4], the bands at 1065, 962, 865, 793 and 561cm^{-1} correspond to $\nu_{\text{as}}(\text{P}-\text{Oa})$, $\nu_{\text{as}}(\text{Mo}-\text{Od})$, $\nu_{\text{as}}(\text{Mo}-\text{Ob}-\text{Mo})$, $\nu_{\text{as}}(\text{Mo}-\text{Oc}-\text{Mo})$ and $\nu(\text{P}-\text{O})$ vibrations, respectively. In Keggin type unit (Fig. 1), Oa refers to oxygen atom common to PO_4 tetrahedron and one trimetallic group Mo_3O_{13} ; Ob connects two trimetallic groups, Oc binds two octahedral MoO_6 inside a trimetallic group and Od is the terminal oxygen atom. The whole structure has Td symmetry and corresponds to α isomer. This suggests that primary structure remains intact after the partial and /or the total protons substitution.

Chemical shifts are referenced to 85% H_3PO_4 . X- ray diffraction (XRD) patterns were recorded at room.

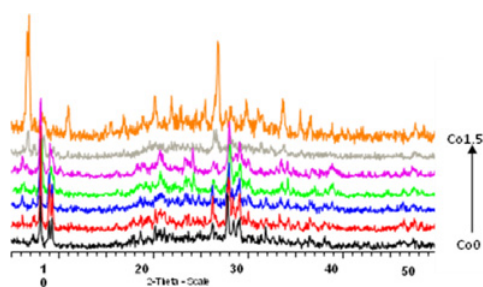


Figure 2. XRD patterns of $\text{Co}_x\text{PMo}_{12}$ solids.

Table 2. Comparative salts formula.

Theoretical formula	TG deduced formula
$\text{H}_{3.0}\text{Co}_0\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{3.0}\text{Co}_{0.0}\text{PMo}_{12}\text{O}_{40}$
$\text{H}_{2.5}\text{Co}_{0.25}\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{2.53}\text{Co}_{0.23}\text{PMo}_{12}\text{O}_{40}$
$\text{H}_2\text{Co}_{0.5}\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{1.96}\text{Co}_{0.52}\text{PMo}_{12}\text{O}_{40}$
$\text{H}_{1.5}\text{Co}_{0.75}\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{1.57}\text{Co}_{0.71}\text{PMo}_{12}\text{O}_{40}$
$\text{H}_{1.0}\text{Co}_{1.0}\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{0.94}\text{Co}_{1.03}\text{PMo}_{12}\text{O}_{40}$
$\text{H}_{0.75}\text{Co}_{1.25}\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{0.6}\text{Co}_{1.2}\text{PMo}_{12}\text{O}_{40}$
$\text{H}_{0.0}\text{Co}_{1.5}\text{PMo}_{12}\text{O}_{40}$	$\text{H}_{0.0}\text{Co}_{1.5}\text{PMo}_{12}\text{O}_{40}$

3.2. XRD analysis

The X-ray diffractograms of $\text{Co}_x\text{PMo}_{12}$ are similar to that of the parent acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Fig. 2), that crystallizes in the triclinic system. These results agree with those of IR spectroscopy showing that the ions occupy the counter-ion position in the polyoxometallate.

3.3. ^{31}P NMR

Solution ^{31}P NMR spectrum of $\text{Co}_x\text{PMo}_{12}$ exhibits only one peak at around -3.18 , -3.27 , -3.36 , -3.4 , -3.31 , -3.31 and -3.50 ppm for $x=0-1.5$ respectively. These results evidenced the purity of the heteropolysalts and also show that the chemical shift of ^{31}P is very sensitive to the value of x .

3.4. Thermal analysis (TG)

The TG curves of all salts show two steps of weight loss. Before 200°C , the weight loss was attributed to crystallization water desorption and between $200-250^\circ\text{C}$, water desorption. The latter weight loss allows to calculate the number of protons and therefore to deduce the value of x . Deduced formula for cobalt salts were in good agreement with the theoretical ones (Table 2).

3.5. UV-Visible

In the UV-Vis spectra of $\text{Co}_{1.5}\text{PMo}_{12}$ salt, (Fig. 3), a large band in the domain of wavelengths $200-450$ nm was observed associated to ligand-metal charge transfers from oxygen to Mo(VI) in the Keggin anion [2,5,6]. In addition to this broad absorption band, another large charge transfers band was observed above $500-600$ nm that may be attributed to the d-d transition band of

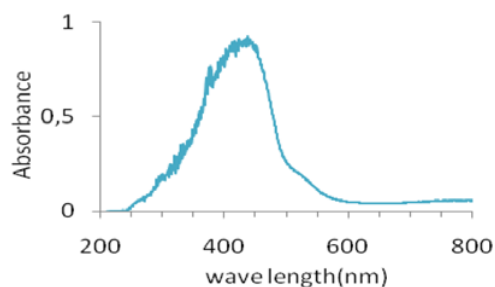


Figure 3. UV-Visible spectra of $\text{Co}_{1.5}\text{PMo}_{12}$.

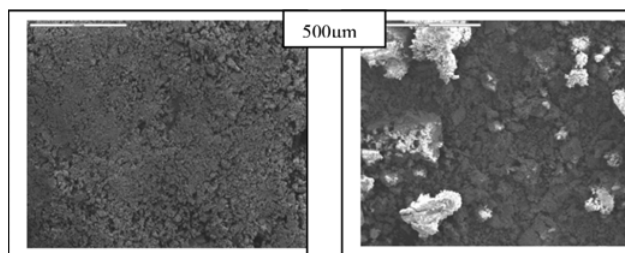


Figure 4. SEM images of $\text{H}_3\text{PMo}_{12}$ and $\text{Co}_{1.5}\text{PMo}_{12}$.

d^1 Mo(V) species in octahedral coordination [6]. This result suggested a partial reduction of Mo (VI) to Mo(V) corresponding to the electron exchange occurring between Co(II) and Mo(VI) as follows:



3.6. SEM analysis

From electron microscopy measurement, $\text{H}_3\text{PMo}_{12}$ and $\text{Co}_{1.5}\text{PMo}_{12}$ show different morphologies as a consequence of the substitution of protons by the Co^{2+} ions (Fig. 4).

4. CONCLUSION

The results showed that the gradual cationic exchange method allows to obtain a series of compounds, $\text{H}_{3-2x}\text{Co}_x\text{PMo}_{12}\text{O}_{40}$ ($x=0-1.5$), whose properties could be adjusted according to the value of x .

References

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