Clean Alternative for Adipic Acid Synthesis Via Liquid-Phase Oxidation of Cyclohexanone and Cyclohexanol Over $H_{3-2x}Co_xPMo_{12}O_{40}$ Catalysts with Hydrogen Peroxide

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Abstract Adipic acid (AA) was synthesized from the oxidation of cyclohexanol (-ol), cyclohexanone (-one) and cyclohexanol/cyclohexanone (-ol/-one) mixture over a series of $H_{3-2x}Co_xPMo_{12}O_{40}$ (x: 0.0–1.5) Keggin-type polyoxometalates as catalysts in the presence of hydrogen peroxide (30 %) under mild conditions (90 °C, 20 h) and in solvent free. The heteropolysalts were prepared from $H_3PMo_{12}O_{40}$ and Ba(OH)₂ using the cationic exchange method and characterized by Infrared and diffuse reflectance UV–Vis spectroscopies, X-ray diffraction and TG analyses. The catalytic tests showed that salts are more efficient than the corresponding heteropolyacid and among the $H_{3-2x}Co_xPMo_{12}O_{40}$ (x: 0.25–1.5) series, $H_1Co_1PMo_{12}$ exhibits the highest AA yield for whole substrates, with ca. 76, 53 and 43 % from oxidation of -one, -ol and -ol/-one, respectively.

Keywords Keggin-type polyoxometalates · Cyclohexanol · Cyclohexanone · Hydrogen peroxide · Adipic acid

1 Introduction

Adipic acid (AA) is the main precursor for nylon-6,6, its production involves two steps [1-7]. The first one

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corresponds either to cyclohexane oxidation in the presence of air to a cyclohexanone/cyclohexanol mixture, phenol hydrogenation to cyclohexanol in the presence of molecular hydrogen or cyclohexane hydration to cyclohexanol (Asahi process). Cyclohexane, phenol or cyclohexene can be obtained from oxidation or hydrogenation of benzene. In the second step, the cyclohexanone/cyclohexanol mixture or cyclohexanol is oxidized to AA in the presence of nitric acid as oxidant and Cu–V–O as catalyst. In addition to AA, there is formation of succinic, glutaric and oxalic acids as by-products and nitrogen oxides gases (NO_x) as co-products. Among these gases, N₂O constitutes the major source of polluting species.

Currently, the development of a green protocol, as alternative non- HNO_3 pathway for the AA synthesis seems to be the objective of the research. Many attempts have been made to substitute the traditional process, using nitric acid, by catalytic systems more friendly using oxidants, respectful of environment, such as air, molecular oxygen or hydrogen peroxide.

The AA synthesis from cyclohexane using only one ecofriendly and cost-effective step was examined by several authors. With a radical catalyst as *N*-hydroxyphthalimide (NHPI) combined with Mn(acac)₂ or Co(OAc)₂ and molecular oxygen as oxidant, the best catalytic performance was obtained in the presence of the cobalt (73 % of AA selectivity at 73 % of cyclohexane conversion) [8]. Bonnet et al. have proposed a method for the AA production by air oxidation of cyclohexane, using different lipophilic carboxylic acids (3,5-di-tert-butylbenzoic, 4-tertbutylbenzoic or 4-trifluoromethylbenzoic acids) as catalytic systems and metallic precursors (cobalt, manganese) as co-catalysts. In this case also, the best catalytic results were obtained with the cobalt element (~70 % of AA selectivity) [9]. Among tested Anderson-type polyoxometalates (POMs) as catalysts

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for aerobic oxidation of cyclohexane to AA, Lü et al. [10] have found that $[(C_{18}H_{37})_2N(CH_3)_2]_6Mo_7O_{24}$ is the most effective with 87 % of AA selectivity at 10 % of conversion.

The hydrogen peroxide as an oxidizing agent was used for the AA synthesis from cyclohexene oxidation on materials based on tungsten [11] and peroxotungstates peroxomolybdates [12], mesoporous silicates doped with titanium [13–15] and based phosphomolybdic and phosphotungstic heteropolyacids (HPAs) complexes [16] as catalysts. High AA yields have been obtained with these processes.

The AA synthesis from the cyclohexanone oxidation in the presence of hydrogen peroxide has also been the subject of several studies. With tetrabutylammonium salts of P/W or P/Mo HPAs, it was found that HPAs react catalytically in the presence of aqueous hydrogen peroxide; whereas, they react only stoichiometrically without it [17]. Since hydrogen peroxide convert the reduced-form (blue) of the HPA produced by the substrate oxidation, to the oxidized-form (yellow). H_2O_2 plays the role of a promoter or a reoxidizing reagent for the HPA after substrate oxidation. The AA production by the liquid-phase oxidation of cyclohexanone with molecular oxygen was examined in presence of Mn(OAc)₂/Co(OAc)₂ catalysts [18] and μ 3-Oxo-bridged Co/Mn cluster complexes, CoMn₂(O) [19], in acetic medium. High catalytic activity and AA selectivity were observed with these catalytic systems. With HPAs of composition H_{3+x}PMo_{12-x}V_xO₄₀ (x: 1, 2), it was found that the use of acetic acid as co-solvent led to a strongly enhanced cyclohexanone conversion with respect to the reaction carried out with water-only solvent [20]. It was also reported in this study that the cyclohexanone oxidation proceeds via a redox mechanism, in presence of water-only solvent and a radical-chain autoxidation mechanism prevailed, in presence of acetic acid as co-solvent. With H₂O₂ as oxidant and Dawson-type heteropolytungstate as catalyst, the AA yield could reach 14.0 % from the cyclohexanone oxidation in absence of organic solvents, acidic additives and phase transfer agents [21].

In the liquid phase oxidation processes, the use of hydrogen peroxide requires an acidic environment that can come from the organic or inorganic acids. However, the use of the liquid acids can have a negative impact on the environment by generating more waste water volume. To overcome these drawbacks, it would be interesting to introduce the Keggin-type phosphomolybdic POMs as catalysts for liquid phase oxidative reactions. They have the advantage of possessing acid and oxidative properties that can be controlled according to the constituent elements and the requirements of the reaction. Thus, the acidity as well as the oxidizing power needed for the reactions could come from the POMs only. On the other hand, the partial substitution of protons of the HPA $(H_3PMo_{12}O_{40})$ by a transition metal could be also more attractive, because the oxidizing power can be enhanced.

In a previous study [22], we have used Keggin-type heteropolysalts of formula $M_xPMo_{12}O_{40}$ (M: Fe, Ni, Co and x: 1 or 1.5) as catalysts in the AA synthesis from liquid-phase oxidation of cyclohexanol (-ol), cyclohexanone (-one) or a cyclohexanol/cyclohexanone mixture (-ol/-one) in the presence of hydrogen peroxide (30 %) and in the absence of solvent. It was shown that Co-based catalyst exhibits the highest AA yield for whole substrates (-ol, -one and -ol/-one). In the present work, the AA synthesis using the same conditions will be studied over a series of soluble polyoxometalates of formula $H_{3-2x}Co_x$ PMo₁₂O₄₀, noted Co_xPMo₁₂, (x: 0.0–1.5), in order to examine the effect of x value on AA yields.

2 Experimental

2.1 Catalysts Preparation

 $H_3PMo_{12}O_{40}$ (noted Co_0PMo_{12}) was prepared in accord with classic method [23] and $H_{3-2x}Co_xPMo_{12}O_{40}$ (noted Co_xPMo_{12} , with x = 0.25–1.5) heteropolysalts were synthesized in two steps. In the first step, $Ba_xPMo_{12}O_{40}$ was prepared by addition of $Ba(OH)_2$ to an aqueous solution of $H_3PMo_{12}O_{40}$ in stoichiometric ratios (according to the Eq. (1)) and in the second step $BaSO_4$ was precipitated by cobalt sulfate via cationic exchange between Ba^{2+} and Co^{2+} (according to Eq. (2)). After filtration, the resulting heteropolysalt solution was evaporated to dryness at 50 °C under vacuum.

$$\begin{array}{rl} H_{3}PMo_{12}O_{40} + & x Ba(OH)_{2} \rightarrow H_{3-2x}Ba_{x}PMo_{12}O_{40} \\ & + & 2x H_{2}O \end{array} \tag{1}$$

$$\begin{array}{l} H_{3-2x} \textbf{Ba}_{x} PMo_{12}O_{40} + \ x\textbf{CoSO}_{4} \\ \rightarrow H_{3-2x} \textbf{Co}_{x} PMo_{12}O_{40} + x \ BaSO_{4} \downarrow \end{array} \tag{2}$$

2.2 Characterization

Infrared spectroscopy of KBr pellets was recorded on a PERKIN-ELMER (Spectrum One) apparatus. The resolution was fixed at 2 cm⁻¹ and the number of scans at 32. Before analysis, the diluted solids (1.5 mg) in KBr (150 mg) were pressed into pellets at 4 tons/cm². Diffuse reflectance UV–Vis spectra were recorded at room temperature using two apparatus: (1) a Perkin-Elmer Lambda19 spectrometer, equipped with a 60 mm integrating sphere coated with barium sulphate, the spectra were recorded with a sweep speed in wavelength of 240 nm/min, between 170 and 800 nm; and (2) a Jasco V-650 spectrophotometer, with a

sweep speed in wavelength of 200 nm/min, between 190 and 900 nm. X-ray diffraction patterns (XRD) were recorded at room temperature using a Siemens D5000 diffractometer equipped with a copper anticathode Cu K α ($\lambda = 1.5418$ Å), the indexing of the diffraction lines and phase identification were performed using the EVA software including a ICDD-JCPDS database. TGA analysis was performed on a TGA 2050, 626 Polarecord Metrohm apparatus with a rate of heat of 5 °C/min from 25 to 600 °C (to prevent the MoO₃ sublimation) under nitrogen.

2.3 Catalysis

The synthesis method is based on that described in the literature [17]. The liquid-phase oxidation of cyclohexanol (-ol), cyclohexanone (-one) or mixture of -ol and -one was carried out at 90 °C, using a 100 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The whole is stirred at 800 rpm. The reaction mixture is constituted by a calculated amount of catalyst and substrate (15 mmol); where into one drop of hydrogen peroxide (30 %) was added whenever the polyoxometalate showed a color change (from yellow or light green to blue). The reaction time was determined to be a time in that an appropriate amount of hydrogen peroxide in the dropping funnel had been consumed that corresponds to oxidation of substrate. The reaction time was found to be of 20 h. It is noteworthy that beyond 90 °C, hydrogen peroxide may decompose. The resultant homogeneous mixture was cooled at 0 °C overnight. AA, one of oxidation products, was isolated as white crystals and identified by FT-IR spectroscopy and melting point (~ 151 °C). The AA yield is given by the following relationship: R % = AA mass formed/theoretical AA mass.

3 Results and Discussion

3.1 Catalysts Characterization

The FT-IR characteristic bands of the Keggin structure of both HPA and Co_xPMo_{12} series were observed in the low wavenumber region (500–1,100 cm⁻¹) (Fig. 1). According to Rocchiccioli-Deltcheff et al. [24], the bands at 1,066–1,065, 964–962, 872–868, 788–782 and 596–594 cm⁻¹ are assigned to $v_{as}(P-O_a)$, $v_{as}(Mo-O_d)$, $v_{as}(Mo-O_b-Mo)$ (vertex junction), $v_{as}(Mo-O_c-Mo)$ (edges junction) and $\delta(P-O)$ vibrations, respectively. The comparison of the FT-IR frequency bands of Co_xPMo_{12} salts, with those of the parent acid (H₃PMo₁₂O₄₀) did not reveal significant difference within 1,500–250 cm⁻¹ range. This suggests that the Keggin primary structure remains intact after the partial substitution of protons of H₃PMo₁₂ acid by the Co²⁺ ions.

Figure 2 shows the UV–Vis spectra of $H_3PMo_{12}O_{40}$ and Co_xPMo₁₂ salt. The broad charge transfer band from oxygen to Mo(VI) appears between 250 and 500 nm. It was reported that this is the only ligand-metal charge transfer band that is observed in the case of POMs [25-27]. In presence of Co_xPMo₁₂, another band of lower intensity is observed between 500 and 600 nm, in particular for x > 0.75. For the other x values, the cobalt content in the POM don't exceed 2 %, therefore it is very difficult to observe this charge transfer band. This latter can be attributed either to d-d transition band of d^1 Mo(V) species in octahedral coordination and/or to d⁶ Co(III) species in octahedral coordination [19]. Same observations have been made by Mazari et al. [28, 29] in the presence of Co based salts of P/Mo HPA and by Dermeche et al. [26] in the presence of Sb or Sn based salts of P/Mo HPA. The existence of this band can be explained by a charge transfer between molybdenum and cobalt cations according to the following equation:

 $Mo(VI) + Co(II) \rightarrow Mo(V) + Co(III)$

Figure 3 shows that the XRD patterns of $Co_x PMo_{12}$ are similar to that of the parent acid, indicating that the salts crystallize in a triclinic structure as in the case of the acid. The partial or total substitution of the protons of H₃PMo₁₂ by Co²⁺ ion does not affect the crystal system of the POM.

Thermal analysis (TGA) was used in our case to determine the x value. The departure of water molecules of constitution resulting from the combination of protons with oxygen atoms of the solid is observed in the 300–500 °C range (figures not shown). The stoichiometric coefficients derived from TGA are close to those calculated theoretically (Table 1). These results confirm the reliability of the synthesis method (cation exchange) used in this work.

3.2 Catalytic Tests

The catalytic properties of soluble Keggin type salts, Co_xPMo_{12} , together with that of Co_0PMo_{12} , were examined in the liquid-phase oxidation of cyclohexanol (-ol), cyclohexanone (-one) and mixture of -ol and -one (-ol/-one) to AA, in the presence of hydrogen peroxide (30 %) under solvent-free conditions at 90 °C, using 15 mmol of substrate.

It is worth noting that the substrate oxidation did not proceed when the reaction mixture is constituted of substrate, catalyst and hydrogen peroxide simultaneously or when no catalyst was used. On the other hand, the oxidizing power of POM is generated only after addition of hydrogen peroxide (transition from blue to yellow). The pH values of the solution after reaction, tested by pH meter are around 2 for all catalytic tests, indicating that the reaction medium is acid.









In this work, only AA formation was taken into account. The other reaction products observed are the succinic and glutaric acids.

3.2.1 Cyclohexanol Oxidation

In order to optimize the reaction conditions, the mass effect of catalyst on AA yield was examined over the following POMs: Co_1PMo_{12} , $Co_{1.25}PMo_{12}$ and $Co_{1.5}PMo_{12}$. The data of Table 2 show that regardless the x value, an increase of the catalyst mass from 0.0313 to 0.0625 g leads to an increase in the AA yield, from ca. 39 to 53 %, ca. 23 to 38 % and ca. 20 to 34 % in the presence of Co_1PMo_{12} , $Co_{1.25}PMo_{12}$ and $Co_{1.5}PMo_{12}$, respectively. Whereas, a second increase of catalyst mass by a factor of 2 (from 0.0625 to 0.1250 g) decreases the AA yield, in particular for x > 1, from ca. 38 to ca.32 % for Co_{1.25}PMo₁₂ and from ca. 34 to ca.30 % for Co_{1.5}PMo₁₂. This decrease of the AA yield is probably caused by an increase of yields of other acids, due to a competition between the different acids. As, the highest AA yield was obtained with a mass of 0.0625 g, the study of the other parameters will be examined with this mass value.

Figure 4 shows obtained AA yields with $Co_x PMo_{12}$ (x: 0.0–1.5) catalysts from cyclohexanol oxidation. The cobalt salts are more effective than the corresponding HPA with AA yields of ca. 23–53 % against ca. 16 %. The effect of the x value variation on AA production shows that the AA yield increases from ca. 23 to ca. 53 % when x passes from 0.25 to 1. Beyond this value (x = 1), it decreases to ca. 34 %. These results demonstrate the influence of cobalt



Fig. 3 X-ray patterns of Co_0PMo_{12} **a**, $Co_{0.25}PMo_{12}$ **b**, $Co_{0.5}PMo_{12}$ **c**, $Co_{0.75}PMo_{12}$ **d**, Co_1PMo_{12} **e**, $Co_{1.25}PMo_{12}$ **f** and $Co_{1.5}PMo_{12}$ **g** materials

Table 1 Theoretical and experimental formulas of CoxPMo12 solids

Theoretical formula	Experimental formula	nH_2O*	
H _{3.00} Co _{0.00} PMo ₁₂ O ₄₀	H _{3.08} Co _{0.00} PMo ₁₂ O ₄₀	13	
H _{2.50} Co _{0.25} PMo ₁₂ O ₄₀	H _{2.35} Co _{0.32} PMo ₁₂ O ₄₀	12	
H _{2.00} Co _{0.50} PMo ₁₂ O ₄₀	H _{1.91} Co _{0.55} PMo ₁₂ O ₄₀	12	
H _{1.50} Co _{0.75} PMo ₁₂ O ₄₀	H _{1.45} Co _{0.78} PMo ₁₂ O ₄₀	12	
H _{1.00} Co _{1.00} PMo ₁₂ O ₄₀	H _{0.87} Co _{1.07} PMo ₁₂ O ₄₀	12	
H _{0.50} Co _{1.25} PMo ₁₂ O ₄₀	$H_{0.52}Co_{1.24}PMo_{12}O_{40}$	14	
H _{0.00} Co _{1.50} PMo ₁₂ O ₄₀	$H_{0.04}Co_{1.48}PMo_{12}O_{40}\\$	16	

* Number of H2O molecules of crystallization

Table 2AA yields (%) as a function of catalyst mass in cyclohexanol oxidation

Co _x PMo ₁₂	Catalyst mass (g)				
	0.0313	0.0625	0.125		
Co ₁ PMo ₁₂	38.8	52.5	51.6		
Co _{1.25} PMo ₁₂	23.3	37.9	32.1		
Co _{1.5} PMo ₁₂	19.6	33.8	29.6		

Reaction conditions: T_{react} : 90 °C, $n_{-ol} = 15$ mmol (V (-ol) = 1.63 mL), agitation rate: 800 rpm, reaction time: 20 h

atom number in the POM on AA yields. The highest AA yield (ca. 53 %) is obtained with Co_1PMo_{12} .

3.2.2 Cyclohexanone Oxidation

The AA yields obtained in the presence of the acid form, Co_0PMo_{12} , from the -one or -ol oxidation, are of ca. 16 %



0.75

x value

1

1.25

1.5

Fig. 4 Adipic acid yields as a function of the Co atoms number in $H_{3-2x}Co_xPMo_{12}O_{40}$ solids in cyclohexanone (*blue square*) and cyclohexanol (*red square*) oxidation (T_{react} : 90 °C, $m_{cat} = 0.0625$ g, $n_{-ol \text{ or -one}} = 15 \text{ mmol}$ (V (-ol) = 1.63 mL and V (-one) = 1.58 mL), agitation rate: 800 rpm, reaction time: 20 h)

0

0.25

0.5

and appeared to be independent of the nature of the substrate (Fig. 4). While, with cobalt salts, whatever the x value, the AA yields obtained from the -one oxidation are much higher than those obtained from the -ol oxidation with ca. 32–76 against ca. 23–53 %. These results seem predictable, since the ketone (-one) is oxidized directly to the acid products, while the alcohol (-ol) is oxidized initially to -one and subsequently, to the acid products.

As in the case of the -ol oxidation, it is apparent from Fig. 4 that the AA yield increases from ca.16 to 76 % when x rises from 0 to 1. Beyond this value (x = 1), it decreases until ca. 53 %. The most effective catalyst, in the cyclohexanone oxidation to AA is also Co_1PMo_{12} .

3.2.3 Oxidation of Cyclohexanone/Cyclohexanol Mixture

It was reported in the literature that AA can be produced from a mixture constituted of cyclohexanone (50 %) and cyclohexanol (50%) [1–5]. Hence, in this work, the influence of the addition of cyclohexanol (10-50 %) to the reaction mixture constituted of cyclohexanone and catalyst on the AA yield was studied. Co1PMo12O40, the most effective catalyst, was tested in this reaction. The catalytic activity data are presented in Table 3. In the absence of -ol, the AA yield is very high (ca. 76 %). In contrast, an increase of the percentage of -ol from 10 to 50 % in the reaction mixture caused a decrease of AA yield from ca. 76 to 43 %. The latter value (ca. 43 %) is lower than that obtained with the -ol alone (ca. 53 %). This observation of the decrease of AA yield has already been reported by other authors [19]. This result can be explain by the low rate of alcohol oxidation to AA compared with that of the ketone oxidation (-ol \rightarrow -one \rightarrow AA). After 20 h of

Table 3 Adipic acid yields as a function of the compositon of cyclohexanone/cyclohexanol mixture over $Co_1PMo_{12}O_{40}$

Substrate (-one/-ol)	100 / 0	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	0 / 100
AA yield (%)	75.5	69.5	61.6	57.8	50.2	42.9	52.5
n .		-	00.00		0.040		

Reaction conditions: T_{react} : 90 °C, $m_{cat} = 0.0625$ g, $n_{-olone} = 15$ mmol, agitation rate: 800 rpm, reaction time: 20 h

reaction, the amount of AA obtained from the ketone oxidation is therefore greater than that obtained from the alcohol.

The obtained results indicate that the presence of cobalt in the catalyst system increases strongly the AA yield. Some studies have already reported that cobalt-based systems are effective in the oxidation of cyclohexanone and cyclohexanol to AA [8, 9, 18, 19, 22].

In this study, the highest AA yield (ca. 53 % from -ol oxidation and ca. 76 % from -one oxidation) is obtained with one proton and one cobalt atom per Keggin unit (H₁Co₁ $PMo_{12}O_{40}$). This chemical composition allowed to have an acidic environment necessary for both reduction of H2O2 and cleavage of C-C bond of substrate and an oxidative environment favoring AA formation, with the oxidation of terminal carbon atoms. Therefore, a bifunctional catalytic system, with appropriate acidic and oxidizing properties, is very important for optimizing AA production from -ol, -one or -ol/-one mixture, in the presence of hydrogen peroxide and in the absence of solvent or additive acid. These results are in agreement with the literature works [11, 18–20], reporting that the AA synthesis from oxidation of cyclohexene, cyclohexanone or cyclohexanol in presence of H₂O₂, is not only an oxidation reaction, but also an acid-catalyzed reaction.

The efficiency of these catalysts is related to the fact that the reduced blue POM, obtained after the substrate oxidation reaction, can be reused for the same reaction by addition of one drop of hydrogen peroxide that converted it immediately to the oxidized form (yellow POM). The catalytic cycle is finished when the POM catalyst is no longer reduced, indicating that the substrate was completely consumed. These observations have already been noted by Nomiya et al. [17] which have also shown the reoxidizing effect of hydrogen peroxide on the POM.

The importance of gradual addition of H_2O_2 after each reduction of the catalyst by the substrate is confirmed by preliminary tests. It was shown that the reaction did not take place when the initial mixture composed of catalyst, H_2O_2 and substrate (-ol or -one) was stirred vigorously at 90 °C for 20 h.

These results suggest that the substrate oxidation in the presence of hydrogen peroxide would involve a similar mechanism to that of type Mars-van Krevelen. In this mechanism, it is admitted that during an alkane oxidation with molecular oxygen in presence of metal oxide as catalyst, there is an oxygen atom insertion from the crystal lattice to organic molecule. So, there is reduction of the catalyst. Then, its reoxidation will occur by the molecular oxygen of the gas phase. In liquid-phase oxidation, the substrate (alcohol or ketone) consumes oxygen that would come from POM, and then reduced POM is oxidized by H_2O_2 according to the following mechanism:

Substrate + $POM_{ox} \rightarrow oxygenated products + POM_{red}$

 $POM_{red} + H_2O_2 \rightarrow "peroxo-POM_{ox}" + H_2O$

It was also reported that the presence of H_2O_2 , in addition to its function to oxidize the POM, lead to the formation of "peroxo-POM_{ox}" intermediate species, that would probably be the active species in the AA formation [17, 30].

It appears also from this study, that the efficiency of cobalt salts, compared to that of parent acid, in both -ol and -one oxidation to AA, is probably due to an increase of the oxidizing power of POM after Co introduction and to the simultaneous presence of Mo(VI)/Mo(V) and Co(III)/Co(II) couples as observed by UV spectroscopy. Thus, the tow oxidative forms, Mo(VI) and Co(III) are involved in the substrate oxidation.

4 Conclusion

In this work, a series of POMs of formula $H_{3-2x}Co_x$ PMo₁₂O₄₀ (x: 0.0–1.5) was prepared, characterized and tested in the AA synthesis in the presence of H₂O₂, under mild conditions (90 °C, 20 h) and in solvent free.

The study of the physico-chemical characterization of Co_xPMo_{12} (x = 0.0–1.5) solids showed that the cationic cobalt position does not disturb the Keggin anion symmetry or the triclinic system of $H_3PMo_{12}O_{40}$ acid, whatever the number of introduced Co atoms by POM. The UV spectroscopy evidenced the presence of both Mo(VI)/Mo(V) and Co(III)/Co(II) couples and the TGA, the proton number per Keggin unit.

This study showed that cobalt salts are more efficient than parent acid in the direct catalytic oxidation of cyclohexanone, cyclohexanol and cyclohexanone/cyclohexanol mixture to AA with hydrogen peroxide, a clean oxidant, without any solvent. The POMs act as both an acidifying and an oxidant agent. Using this green method, a ca. 76 % yield of AA has been achieved with $H_1Co_1PMo_{12}O_{40}$ from cyclohexanone oxidation.

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