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Research Article

Simple and Green Adipic Acid Synthesis from Cyclohexanone and/or Cyclohexanol Oxidation with Efficient $(NH_4)_xH_yM_zPMo_{12}O_{40}$ (M: Fe, Co, Ni) Catalysts

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Abstract

The oxidation of cyclohexanone and/or cyclohexanol to adipic acid (AA) was performed at 90 °C with a reaction time of 20 h, in the presence of H_2O_2 as oxidant and transition metal substituted ammonia polyoxometalates of formula, $(NH_4)_xH_yM_zPMo_{12}O_{40}$ (M: Fe, Co, or Ni, and x = 2.5 or 2.28) as catalysts. The catalytic results showed that the AA yield is sensitive to the transition metal nature and to the reaction conditions (sample weight and substrate amount). The $(NH_4)_{2.29}H_{0.39}Co_{0.16}PMo_{12}O_{40}$ was found to be the better catalytic system toward AA synthesis from cyclohexanone oxidation, with 40% of AA yield

Keywords: Keggin mixed salts; Oxidation; Hydrogen peroxide; Cyclohexanone; cyclohexanol; Adipic acid

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1. Introduction

The worldwide demand for clean chemical processes for adipic acid synthesis has expanded greatly in recent decades. So, the development of catalytic oxidation systems with environmentally benign oxidants as air [1], molecular oxygen [2,3], or hydrogen peroxide [4-6] that can reduce the use of toxic and hazardous substances is the sought aim. It was noted that with these oxidants, the active oxygen species content is high with 100% for molecular oxygen and 47% for hydrogen peroxide. Hydrogen peroxide is the oxidant that has received much attention because it is safer in storage and operation, with water as the sole by product.

Adipic acid (AA) is of a great interest, in the manufacture of nylon-6,6 polyamide [7]. Its in-

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dustrial production takes place on two steps, cyclohexane oxidation to a mixture of cyclohexanol and cyclohexanone (noted KA oil) in presence of air (first step) then the KA oil is oxidized to AA by nitric acid (second step). The nitric acid used is the source of NO_x emission whose most harmful is the N_2O [8-10].

Polyoxometalates (POMs), large family of anionic metal-oxygen clusters, having chemical properties such as strong oxidative powers and strong Brönsted and Lewis acidities have especially received much attention in the area of the oxidation catalysis [11-14]. The POMs based on molybdenum, particularly, can act as effective catalysts for the H_2O_2- and O_2-based green oxidations [15-17]. Furthermore, they are oxidatively stable and can undergo stepwise multi electron redox process without any structural modification. With transition-metal-substituted POMs, it was reported that their remarkable catalytic activities were due to the multifunctional character of multimetallic active sites as simultaneous activation of oxidants and substrates, reaction intermediates stabilization, oxygen-transfer and multielectron transfer [15-17]. In previous studies, we have underlined the efficiency of transition-metal-substituted POMs [18-21] as catalysts in the clean oxidation of cyclohexanone and mixture of cyclohexanone/cyclohexanol to adipic acid in the presence of hydrogen peroxide without solvent, phase-transfer agents and adding acid.

In this study, a series of substituted POMs of formula, $(NH_4)_xM_zH_yPMo_{12}O_{40}$ (M: Fe, Co, or Ni, and x = 2.5 or 2.28) were synthesized and characterized by elementary analysis, Fourier Transform Infrared (FT-IR) and UV-Visible spectroscopies, Nitrogen physisorption and X-ray Diffraction (XRD) analysis. Their catalytic activity was examined through cyclohexanone and/or cyclohexanol oxidation to AA with 30% of H_2O_2 in free solvent conditions. The effects of the POM composition and the reaction conditions were examined.

2. Materials and Methods

2.1 Heteropolysalts preparation

$H_3PMo_{12}O_{40}.nH_2O$ acid was prepared by the conventional method of Tsigdinos [22]. The ammonium salt, $(NH_4)_3PMo_{12}O_{40}$ was prepared from a mixture of 2.4 mmol of $H_3PMo_{12}O_{40}$ acid and 3.6 mmol of urea, previously ground finely. The powder undergoes heat treatment for 18 h under N_2 flow (7 mL/min) [20]. Mixed ammonium salts $(NH_4)_xH_yM_zPMo_{12}O_{40}$ (noted $MPMo_{12}$) were prepared according to the method described by Mizuno *et al*. [23]. It consists to adding, in stoichiometric ratios, an aqueous solution of $M(NO_3)_2$ (0.16 M) with M^{n+}: Co^{2+} or Ni^{2+} or $Fe(NO_3)_3$ (0.24 M) to aqueous solution of $H_3PMo_{12}O_{40}$ (0.06 M) followed by a solution of NH_4Cl (0.08 M). The precipitate was dried at 50 °C under vacuum with a rotary evaporator and recovered.

2.2 Polyoxometalates Characterization

POMs elemental analysis was performed on an atomic emission spectrometer (AES) type Perkin Elmer, Optima 2000 D.VS. Porosity measurements were carried out with liquid N_2 on a Micromeritics ASAP 2010 instrument. IR analysis was performed on a Nicolet 550 Fourier transform spectrometer. UV-Vis spectra were recorded on a UV-Vis Near IR spectrometer, of model Perkin Elmer, Lambda 19. The X-ray diffractograms were carried out on a Siemens D-5000 diffractometer.

2.3 Catalytic test

The adopted experimental method is based on that described in the literature [6]. An amount of substrate (cyclohexanone or/and cyclohexanol) and a given mass of catalyst were introduced into a necked flask fitted with a condenser and placed in an oil bath heated at 90 °C. The mixture (substrate and catalyst) stirred at 800 rpm, of light yellow or green, color of oxidized POM (POMox), was turned blue, color of reduced POM (POMred). The H_2O_2 (~ 30%) was then added in portions of 1 mL under stirring until the mixture returns its initial color (yellow or green) that corresponds to the catalyst reoxidation (POMox). POMox oxidizes a second time the substrate and the cycle was repeated until the disappearance of the solution bluing (total consumption of the reagent). The reaction time is ~ 20 h for all reactions. The reaction mixture was then placed in cold (4 °C) for ~ 4 days. Adipic acid, one of the reaction products was recuperated in the form of white crystals, washed with saturated AA solution and dried.

3. Results and Discussion

3.1 Heteropolysalt characterization

Elemental analysis of the salts was performed after heat treatment at 300 °C under air for 24 h to remove residual nitrates. Table 1 shows analysis results. The stoichiometric coefficients were calculated on the basis of 12 Mo atoms per Keggin unit. The atoms numbers of phosphorus (1 per Keggin unit), transition

metal and nitrogen per mole of salt, deduced from the analysis are in agreement with those introduced experimentally. Exception for $FePMo_{12}$ salt, where the number of analyzed nitrogen atom (1.64) is lower than corresponding theoretical value (2.28). This difference can be explained by the loss of NH_4^+ ions during the heat treatment prior to analysis.

Table 2 shows that the different structural parameters depend on the nature of the metal element in the polyoxometalate. Thus, the specific and the micropore surfaces and the pore and the micropores volumes of $CoPMo_{12}$ salt are largely superior to those of $NiPMo_{12}$ and $FePMo_{12}$ salts. The observed difference in the structural parameters between $CoPMo_{12}$ and the two others salts can be related to the existence of both Co(II) and Co(III) based ammonia salts as seen in UV analysis. $FePMo_{12}$ has the highest average pore diameter. Nitrogen adsorption-desorption isotherms of different salts (figures not shown) are of Type II and their hysteresis of Type B showing that salts are mesoporous. These results are confirmed by the average pore diameter value ($20 < d < 500$ Å).

IR spectra (Figure 1) of $MPMo_{12}$ salts have the characteristic vibration bands of the Keggin anion in the 1100-300 cm^{-1} spectral range [24], corresponding to $n_{as}(P–O_a)$, $n_{as}(Mo=O_d)$, $n_{as}(Mo–O_b–Mo)$ and $n_{as}(Mo–O_c–Mo)$ located at 1060-1064, 960-965; 866-880 and 776-799 cm^{-1}, respectively. In addition, another vibration band associated to ammonium ions was observed around 1400 cm^{-1}. All spectra of $MPMo_{12}$ are similar to that of $(NH_4)_3PMo_{12}O_{40}$ (spectrum not shown) suggesting the conservation of $[PMo_{12}O_{40}]^{3-}$, Keggin unit.

In UV-Visible spectroscopy, a broad absorption band of oxygen–molybdenum(VI) charge transfer was observed in the 250-500 nm region for all $MPMo_{12}$ salts (Figure 2) [25]. In addition to this band, another of lower intensity was observed in the 620-720 nm region in the presence of $CoPMo_{12}$ salt, attributed either to the d-d transition of d^1 Mo(V) species in octahedral coordination and/or to d^6 Co(III) species also in octahedral coordination, suggesting that the $CoPMo_{12}$ salt is partially reduced. An exchange of electrons between Mo(VI) and Co(II) probably took place.

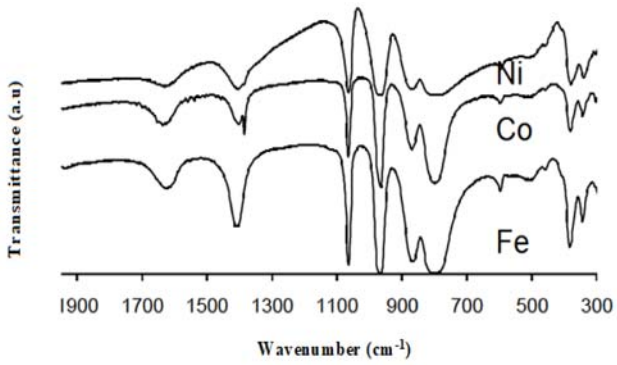

Figure 1. FT-IR spectra of $MPMo_{12}$ salts

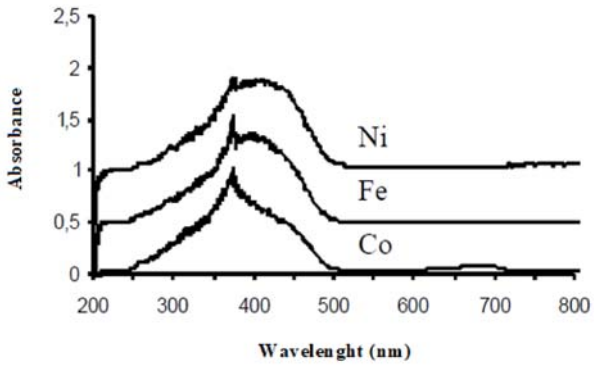

Figure 2. UV-Visible spectra of MPMo12 salts

Table 1. Elemental analysis of the $MPMo_{12}$ heteropolysalts: () Theoretical stoichiometric coefficient

$MPMo_{12}$	Composition (%)				Coefficient		
	P	Mo	M	N	P	M	N
$FePMo_{12}$	1.61	59.12	0.74	1.10	1.01 (1)	0.25 (0.24)	1.64 (2.28)
$CoPMo_{12}$	1.63	58.87	0.50	1.64	1.02 (1)	0.16 (0.16)	2.29 (2.5)
$NiPMo_{12}$	1.66	58.75	0.45	1.75	1.05 (1)	0.15 (0.16)	2.46 (2.5)

Table 2. Physical properties of $MPMo_{12}$ salts

Solid	S_{BET} ($m^2.g^{-1}$)	Micropore volume ($cm^3.g^{-1}$)	Micropore surface ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Average pore diameter (Å)
$FePMo_{12}$	25	6.2×10^{-3}	14.3	2.1×10^{-2}	35.4
$CoPMo_{12}$	123	4.6×10^{-2}	105.8	6.8×10^{-2}	21.9
$NiPMo_{12}$	29	1.1×10^{-2}	25.6	1.5×10^{-2}	20.3

The X-ray diffractograms of $MPMo_{12}$ (Figure 3) are isotypes to that of $(NH_4)_3PMo_{12}O_{40}$, that crystallizes in a cubic structure (JCPDS 09-0412) with a lattice parameter a = 11.634 Å and the Pn3m space group. This result suggests that the partial substitution of ammonium ions by the transition metal ions did not affect the crystal lattice of $(NH_4)_3PMo_{12}O_{40}$ salt.

3.2 Catalytic tests

The catalytic properties of $(NH_4)_3PMo_{12}O_{40}$ and $MPMo_{12}$ salts were examined in the AA synthesis from the oxidation of cyclohexanone, cyclohexanol and mixture of these substrates in presence of H_2O_2 (30%) and in solvent free. The oxidation of these substrates leads to several products. This work has focused only on the AA that is the only product that crystallizes in cold (4 °C). Its purity was verified by measuring of its melting point (~152 °C) and recording of its FT-IR spectrum.

It is worth noting that the substrate oxidation did not take place when the reaction mixture is constituted of substrate, catalyst and hydrogen peroxide simultaneously or in absence of catalyst. On the other hand, the oxidizing power of POM is generated only after addition of hydrogen peroxide (transition from blue to yellow).

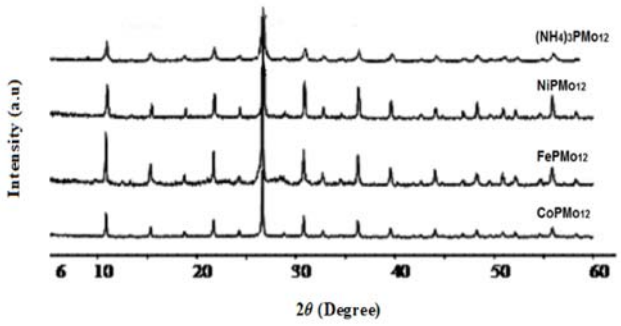

Figure 3. RX diffractograms of $(NH_4)_3PMo_{12}$ and $MPMo_{12}$ salts

The pH values of the solution after reactions are around 2 for all catalytic tests, acidity necessary to the H_2O_2 reduction. It is to highlight that the ammonium salts are not soluble when they are in contact with the substrate (-one, -ol and –one/-ol) and they become soluble after the addition of H_2O_2 oxidant. Their solubility can be attributed to the formation of metal-peroxo species as it has already been reported by other authors with metal ions with d^0 electronic configuration as: Ti(IV), V(V), and W(VI) [26-28]. In this study, the effects of catalyst mass, substrate amount and polyoxometalate composition on the adipic acid yield were examined.

In order to optimize the adipic acid synthesis conditions, a detail study, was carried out with no substituted catalyst, $(NH_4)_3PMo_{12}O_{40}$. The oxidation of cyclohexanone and that of cyclohexanol were performed with different catalyst mass (0.0313; 0.0625 and 0.125 g) and different substrate mole number (15, 30, or 60 mmol). The highest AA yield (39%) was obtained from cyclohexanone oxidation, with catalyst mass of 0.0625 g and substrate amount of 30 mmol. These operation conditions will be applied for the following catalytic tests.

Table 3 shows that AA yield (Y_{AA}) is sensitive to both POM composition and substrate nature. With the alcohol, the partial substitution of ammonium ions by nickel and cobalt ions favored the AA production with yields of 23 and 25 %, respectively, against 17%. Whereas, $FePMo_{12}$ is inactivate. This may be explained by homolytic decomposition of H_2O_2 as HO· radicals, mechanism promoted by the Fe^{3+}/Fe^{2+} Fenton system as reported by other authors [18,29]. With the ketone, the AA yields are better (14-40 against 0-25%), predictable result, ketone oxidation is easier than that of alcohol. $(NH_4)_3PMo_{12}$ and $CoPMo_{12}$ have a similar catalytic behaviour with about 40% against 33 and 14% of AA yield for $NiPMo_{12}$ and $FePMo_{12}$, respectively. The highest activity obser-

Table 3. Adipic acid yields in function of the polyoxometalate composition, in cyclohexanone and cyclohexanol oxidation

Catalyst	Conversion (%)	H_2O_2 amount (mL)	AA yield (%) from cyclohexanol	H_2O_2 amount (mL)	AA yield (%) from cyclohexanone
$(NH_4)_3PMo_{12}$	100	13	17	10	39
$FePMo_{12}$	100	10	00	8	14
$CoPMo_{12}$	100	16	25	12	40
$NiPMo_{12}$	100	11	23	13	33

Conditions: T_{react} = 90 °C, m_{cat} = 0.0625 g, $n_{alcohol\ ou\ ketone}$ = 30 mmol ($V_{alcohol}$ = 3.26 mL, V_{ketone} = 3.16 mL), Agitation rate: 800 rpm, reaction time = 20 h.

ved in the presence of Co and Ni based POMs compared to that of Fe based POM can be attributed to the more acid character of ferric ions that would defavor the ketone oxidation towards the AA formation.

The AA synthesis was also performed from the oxidation of cyclohexanone/cyclohexanol mixture in presence of $(NH_4)_3PMo_{12}O_{40}$ and $CoPMo_{12}$ catalysts, using the optimized operating conditions above. The obtained results (Table 4) show that the addition of alcohol to ketone has negative effect on AA formation regardless of the catalyst composition. This observation has already been reported in the presence of methyleyhylcetone as oxidant and Co/Mn based complexes as catalysts [3] and hydrogen peroxyde as oxidant and Keggin phosphomolybdic salts substituted with cobalt or nickel as catalysts [18,19]. The following sequence was observed: Y_{AA} (cyclohexanone) > Y_{AA} (cyclohexanone / cyclohexanol) > Y_{AA} (cyclohexanol).

From obtained results, it can be concluded that the hydrogen peroxide have for role to oxidize the reduced form of POM and simultaneously to form "peroxo-POMox" species as observed with Ti(IV), V(V) and W(VI) metals that have led to metal- peroxo species [26-28]. These "peroxo-POMox" species would probably be the active species in the AA formation.

In order to verify the efficiency of $CoPMo_{12}$, several catalytic test cycles were realized. After recovery of the adipic acid crystals (first cycle), 30 mmol of cyclohexanone were added to the filtrate and the oxidation reaction was occurred under the optimized conditions. The obtained results after five cycles are reported in Figure 4. A progressive adipic acid yield decrease from 40% (first cycle), 24% (second cycle), 11% (third cycle) and 5% (fourth cycle), to 0% (last cycle), was observed. This can be interpreted as a decrease in the oxidizing power of the active sites, after successive cycles, and to the water content increase resulting from the H_2O_2 reduction. However, it is highlight that this study evidenced the remarkable catalytic performance of $CoPMo_{12}$, with a total AA yield sum of 80% after four cycles.

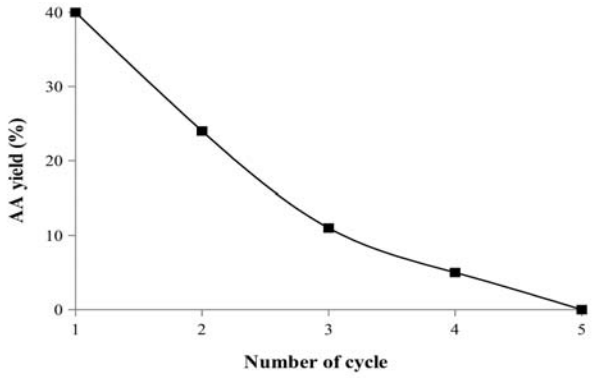

Figure 4. Adipic acid yields after several reaction cycles (catalyst: $CoPMo_{12}$, T_{react} = 90 °C, $n_{substrate}$ = 30 mmol, Agitation rate: 800 rpm, reaction time = 20 h)

4. Conclusions

The physico-chemical characterizations showed that $(NH_4)_xH_yM_zPMo_{12}O_{40}$ (M: Fe, Co, or Ni) POMs prepared are of Keggin-type. $(NH_4)_xH_yM_zPMo_{12}O_{40}$ (M: Co or Ni) are efficient in the AA synthesis, with as oxidant, hydrogen peroxide, in the absence of solvent and at a low reaction temperature (90 °C), conditions that fall within the field of "Green chemistry", compared to those used in the "nitric acid" polluting conventional method. The highest AA yield was obtained from the cyclohexanone oxidation with $CoPMo_{12}$ (40%), using 0.0625 g of catalyst and 30 mmol of substrate and can be reused four times without loss of catalytic activity.

Table 4. AA yields as a function of composition of cyclohexanone/cyclohexanol (-one/-ol) mixture over $(NH_4)_3PMo_{12}$ and $CoPMo_{12}$

(-One/-ol) ratio	H_2O_2 amount (mL)	AA yield (%) $(NH_4)_3PMo_{12}$	H_2O_2 amount (mL)	AA yield (%) $CoPMo_{12}$
100/0	13	39	14	40
90/10	12	37	11	34
80/20	11	30	8	30
70/30	10	36	12	30
60/40	9	27	10	27
50/50	11	34	13	28
0/100	13	17	13	25

Conditions: T_{react} = 90 °C, m_{cat} = 0.0625 g, $n_{substrate}$ = 30 mmol, Agitation rate: 800 rpm, reaction time = 20 h

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