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Clean Adipic Acid Synthesis from Liquid-Phase Oxidation of Cyclohexanone and Cyclohexanol Using $(NH_4)_xA_yPMo_{12}O_{40}$ (A: Sb, Sn, Bi) Mixed Heteropolysalts and Hydrogen Peroxide in Free Solvent

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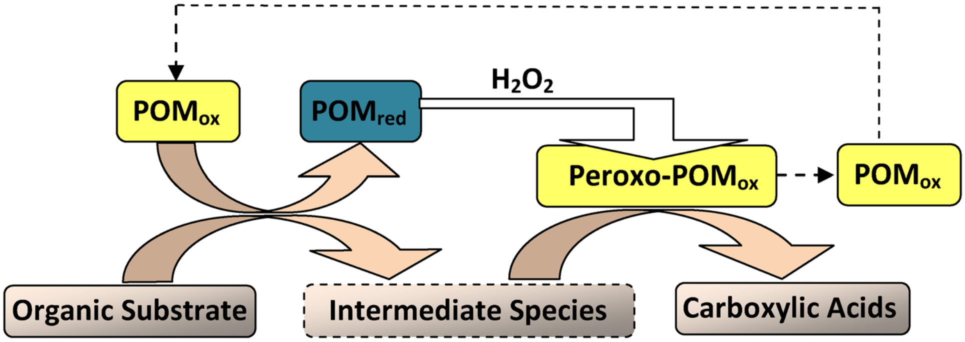
Abstract

Clean synthesis of adipic acid (AA) from oxidation of cyclohexanone, cyclohexanol or mixture cyclohexanol/cyclohexanone, was carried out at 90 °C, in the presence of hydrogen peroxide (30%) in free solvent, using Keggin-type polyoxometalates, $(NH_4)_xA_yPMo_{12}O_{40}$ (A^{n+}=Sb^{3+}, Bi^{3+} or Sn^{2+}), as catalysts. HPLC analysis of reaction mixture showed the formation of adipic, succinic and glutaric acids and unidentified products. The salts were found to be effective for AA synthesis. Whatever the composition of the catalyst, the alcohol oxidation favors the formation of the unidentified products, unlike the ketone oxidation which favors that of the adipic acid. $(NH_4)_{0.5}Sn_{1.25}PMo_{12}O_{40}$ led to the highest AA yield (56%) from cyclohexanone oxidation, after 20 h of reaction. In addition, ^{31}P NMR analysis showed that it has conserved the Keggin structure contrary to others catalysts and that it can be used at least 3 times with reaction times of 20 h, without regeneration. From different catalytic tests and ^{31}P NMR data, reaction pathways have been proposed. The active species could be peroxo-polyoxometalates.

Graphical Abstract



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

1 Introduction

In the current chemical industry framework, adipic acid, important precursor in the nylon production is obtained from oxidation of a mixture of cyclohexanone and cyclohexanol (KA oil) by nitric acid [1–4]. However, the reduction of this latter leads to nitrogen oxides gases as by-products. Among them, NO_2 and NO are recycled and N_2O_5 and N_2O are vented to the outside, thus contributing to global warming and ozone depletion.

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To avoid these drawbacks, many research groups are trying to develop a process environmentally friendly, to substitute nitric acid by oxidants such as air, molecular oxygen [5–7] or hydrogen peroxide [8–13], so-called "Green Chemistry". The hydrogen peroxide is the oxidant that has focused a considerable attention for the adipic acid synthesis, because its reduction leads only to water as by-product. The used catalysts are peroxotungstates, peroxomolybdates, peroxotungstate-organic complexes [8–11], silica-functionalized ammonium tungstate [12] and alumina supported Fe_2O_3, mesoporous nanoparticles [13].

Nevertheless, hydrogen peroxide, very sensitive to reaction conditions, decomposes easily to water and oxygen molecular, therefore its oxidizing power is found reduced. To prevent its decomposition, several authors have suggested the addition of co-catalysts, phase transfer compounds and surfactants [8–11]. However, despite the obtained high AA yields, the presence of these harmful reactants, that are relatively expensive, makes the process of AA production, less environmentally friendly.

Polyoxometalates (POMs), particularly those based on molybdenum are known for their strong oxidizing power, stability and high resistance to oxidizing conditions. In addition, to facilitate the oxygen transfer to the substrate, POMs may undergo multi-electron redox process without any structural modifications [14–16]. Although, their catalytic performance has been established, for oxidation of alkenes and alcohols in presence of the hydrogen peroxide [17–23], their degradation over time was also observed. It was showed by ^{31}P NMR that the hydrogen peroxide led to the POM decomposition into peroxo-species as $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $\{PO_4[WO(O_2)_2]_2\}^{2-}$, in the case of the $H_3PW_{12}O_{40}$ use [24–27].

So, to make more efficient the use of both POM and hydrogen peroxide, Nomiya et al. [28], have adopted a strategy that consists to perform the catalytic oxidation at two-steps. In the first step, the reaction takes place between the organic substrate and POM catalyst, leading to reaction products and reduced form of the catalyst that is of blue color, characteristic color of POM, in its reduced state. In the second one, the reduced catalyst is oxidized by the hydrogen peroxide that is manifested by a color change from blue to yellow, characteristic color of POM, in its oxidized state. The latter continues to react with the remaining substrate and so on until the reagent is exhausted or total reduction of POM. This process was already used in our previous works to examine the catalytic properties of Keggin type transition metal substituted POM series of formula $M_xPMo_{12}O_{40}$ (M: H, Ni, Co, Fe), $H_{3-2x}Co_xPMo_{12}O_{40}$ and $H_{3-2x}Ni_xPMo_{12}O_{40}$ (x: 0.25–1.5) [29–31] and Dawson-type POM series of formula $K_6P_2Mo_xV_yW_{18-x}O_{62}$ (x:5,6 and y:0) and (x:5 and y:1) [32] for adipic acid synthesis. It is a clean process that does not require the addition of reagents as solvent, co-catalysts, phase transfer compounds, surfactants and/or acid.

As, it was shown that the presence of a less metallic element than molybdenum in the POM, modified the redox properties with a better distribution of both reduced Mo(V) and oxidized Mo(VI) sites and in addition, facilitated electron transfer during redox process [33, 34], our choice was made on element introduction as antimony, bismuth or tin. Thus, in this work, the ammonium salts of 12-molybdophosphoric acid were partially substituted by these elements. The POMs have as formula $(NH_4)_{2.988}Bi_{0.004}PMo_{12}O_{40}$ (noted $NH_4BiPMo_{12}O_{40}$), $(NH_4)_{0.75}Sb_{0.75}PMo_{12}O_{40}$ (noted $NH_4SbPMo_{12}O_{40}$) and $(NH_4)_{0.5}Sn_{1.25}PMo_{12}O_{40}$ (noted $NH_4SnPMo_{12}O_{40}$). This salt series was tested in the adipic acid synthesis from the liquid phase oxidation of cyclohexanone, cyclohexanol or cyclohexanol/cyclohexanone mixture at 90 °C, using hydrogen peroxide (30%). The operation conditions to optimize the AA yield were determined. The effects of chemical composition and reaction time on AA yield were examined. Reaction products were analyzed by HPLC and the POMs were characterized after catalytic test by ^{31}P NMR spectroscopy. The physico-chemical characterizations of these materials were published previously [35].

2 Experimental

2.1 Synthesis

$(NH_4)_3PMo_{12}O_{40}$ (noted $NH_4PMo_{12}O_{40}$) and the series of mixed ammonium salts $(NH_4)_xA_yPMo_{12}O_{40}$ with $A^{n+}=Sb^{3+}$, Bi^{3+} or Sn^{2+} (noted $NH_4APMo_{12}O_{40}$) were precipitated at pH 1 from ammonium heptamolybdate, phosphoric acid and ACl_3 (Sb or Bi) or ACl_2 (Sn) with added hydrochloric acid, according with the method described in literature [34, 35]. $NH_4PMo_{12}O_{40}$ and $NH_4BiPMo_{12}O_{40}$ are yellow and $NH_4SbPMo_{12}O_{40}$ and $NH_4SnPMo_{12}O_{40}$ are light green.

2.2 Catalytic Test

The adipic acid synthesis method is that described by Nomiya et al. [28]. The liquid-phase oxidation of cyclohexanone (-one), cyclohexanol (-ol) or -one/-ol mixture was carried out at 90 °C, using a 100 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture consists of calculated amounts of catalyst and substrate. Whenever the catalyst exhibited a change in color from yellow or light green to blue, the hydrogen peroxide (30%) was added by fraction of 0.5 mL until the color change from blue to the initial color of catalyst and so on. The reaction mixture was stirred at 1000 rpm. The catalytic cycle is finished when the POM catalyst is no longer reduced after 20 h, indicating that the substrate was completely consumed. Hydrogen peroxide (30%) concentration was verified by potassium permanganate method prior to use. It is noteworthy that beyond 90 °C, hydrogen peroxide may be decomposed.

To further verify the adipic acid yield, two separate experiments were tested, with each catalyst. The reaction mixture of the first one is analyzed by HPLC to determine the substrate conversion and the selectivities of reaction products. The reaction mixture of second experiment, after completion of the reaction, is set to 4 °C overnight and the adipic acid is recovered as crystals. These latter were identified by melting point (152 °C) and FT-IR and ^{1}H-NMR spectroscopies.

The two experiments will allow to compare the AA yields calculated as follows:

$$\text{AA yield (\%)} = \left[\text{substrate conversion (\%)} \times \text{AA selectivity (\%)}\right] / 100, \text{ for firstexperiment}$$

$$\text{AA yield (\%)} = \text{AA recovered mass} \times 100 / \text{theoretical AA mass, for secondexperiment}$$

The selectivities of products were calculated as follows:

$$\text{Selectivity (\%) ofidentified product} = \text{product mole number} \times 100/\text{substratemole number}$$

$$\text{Selectivity (\%) ofunidentified products} = [\text{substratemole number} - \sum \text{identified products mole number}] \times 100/\text{substratemole number}$$

2.3 Analysis

^{31}P MAS NMR spectra of used catalyst were recorded at room temperature on a Bruker Avance 400 spectrometer. 85% H_3PO_4 was used as an external reference.

The reaction products were analyzed by HPLC (Dionex Varian 380-LC) equipped of a 107H Corgel column and a RID. Sulfuric acid diluted in degassed water is used as mobile phase.

The ^{1}H-NMR spectrum of adipic acid was recorded over Bruker Ascend 400 spectrometer (^{1}H-NMR 128 scans). Dimethylsulfoxide-d_6 (DMSO-d_6) was used as solvent.

The FT-IR spectrum of adipic acid was recorded over a Fourier Transformer Shimadzu FTIR-8400 on the 4000–400cm^{-1} range.

3 Results and Discussion

The catalytic performances of the series of Keggin-type salts, $(NH_4)_xA_yPMo_{12}O_{40}$ (A^{n+}=Sb^{3+}, Bi^{3+} or Sn^{2+}) together with $H_3PMo_{12}O_{40}$ and $(NH_4)_3PMo_{12}O_{40}$, were examined in the liquid-phase oxidation of -ol, -one and equimolar mixture (-ol/-one) at 90 °C, in the presence of hydrogen peroxide (30%) in free solvent.

Several preliminary tests were carried out with $NH_4SnPMo_{12}O_{40}$ catalyst. In the following different mixtures: (i) POM + H_2O_2, (ii) -one + POM and (iii) -one + POM + H_2O_2, a blue color characteristic to reduced POM (Mo(VI) → Mo(V)) was observed. The (i) mixture demonstrates that the POM has an oxidative power more high than that of H_2O_2. This latter is oxidized to molecular oxygen. The protons, required to H_2O_2 oxidation, come from the ammonium ions of POM ($(NH_4)_{0.5}Sn_{1.25}PMo_{12}O_{40}$). In the case of (ii) mixture, the reaction take place, the substrate was oxidized, but AA was not obtained suggesting that probably intermediates species were formed. In (iii) mixture, both substrate and H_2O_2 were oxidized by the POM but in this case also, AA was not obtained. In conclusion, for that the hydrogen peroxide to be able to act as an oxidant, it must be added after reduction of the catalyst by the substrate. These observations were already signaled in previous works [20–23]. It should be noted that in the absence of catalyst, AA was obtained as traces from -one oxidation by hydrogen peroxide.

Moreover, it should be emphasized that the $(NH_4)_xA_yPMo_{12}O_{40}$ salts are not soluble in the presence of substrate, but they become soluble in the reaction medium, after addition of H_2O_2. The decomposition of this latter, very sensitive to contact of the metal surface, could involve the formation metal-peroxo species as observed in the presence of metal ions with electronic configurations d^0 [24, 25, 36, 37]. Therefore, the formation of metal-peroxo species can be the cause of the solubility of ammonium salts.

HPLC analysis of reaction mixture showed the formation of adipic (AA), succinic (SA) and glutaric (GA) acids, in addition of unidentified products (UPs). An example of chromatogram obtained from -one oxidation, in the presence of $NH_4SbPMo_{12}O_{40}$ catalyst, is given in Fig. 1. In the present work, we were particularly interested to the AA formation. Figure 2 shows the characteristic ^{1}H-NMR and FT-IR spectra of AA.

In order to fix the molar ratio, $n_{catalyst}/n_{-one}$, leading to the highest AA yield, the catalytic tests were carried out with $NH_4SnPMo_{12}O_{40}$. As shown in Table 1, there is a parallel between the results, so the AA yield increases from 22 to 56% with the -one conversion from 77 to 100% and with the $n_{catalyst}/n_{-one}$ molar ratio from 1.08×10^{-3} to 4.30×10^{-3}. From these results, all catalytic tests were carried out with

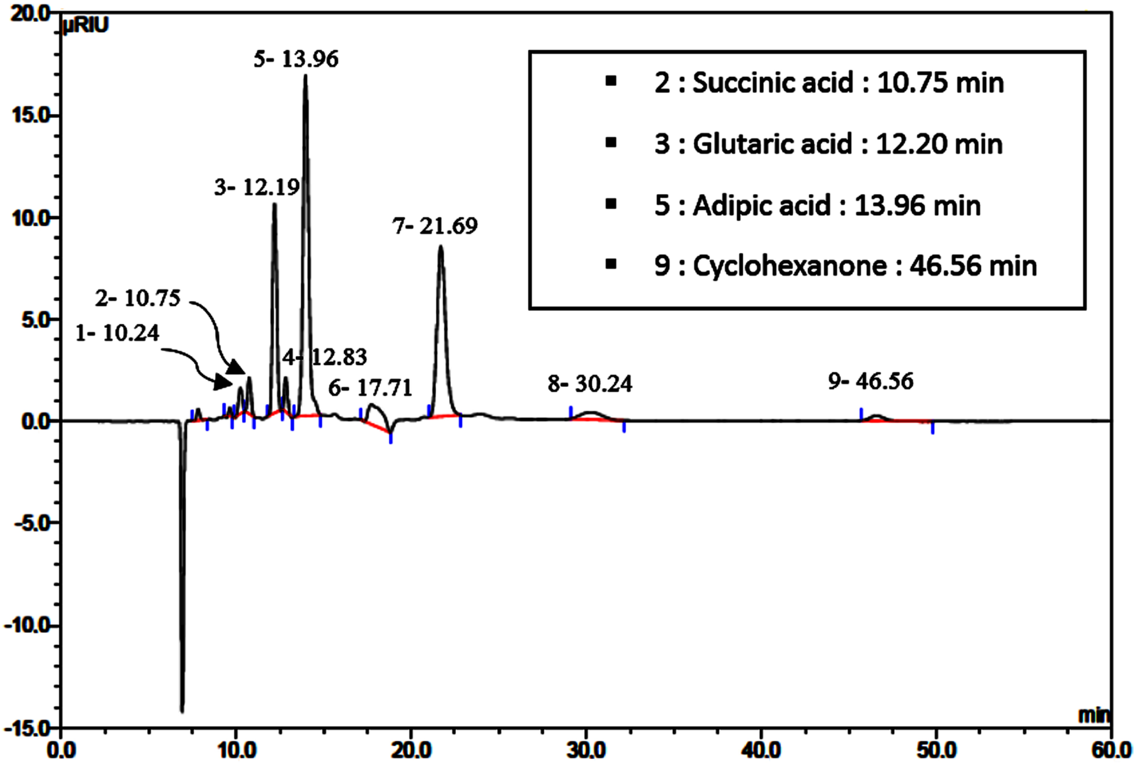
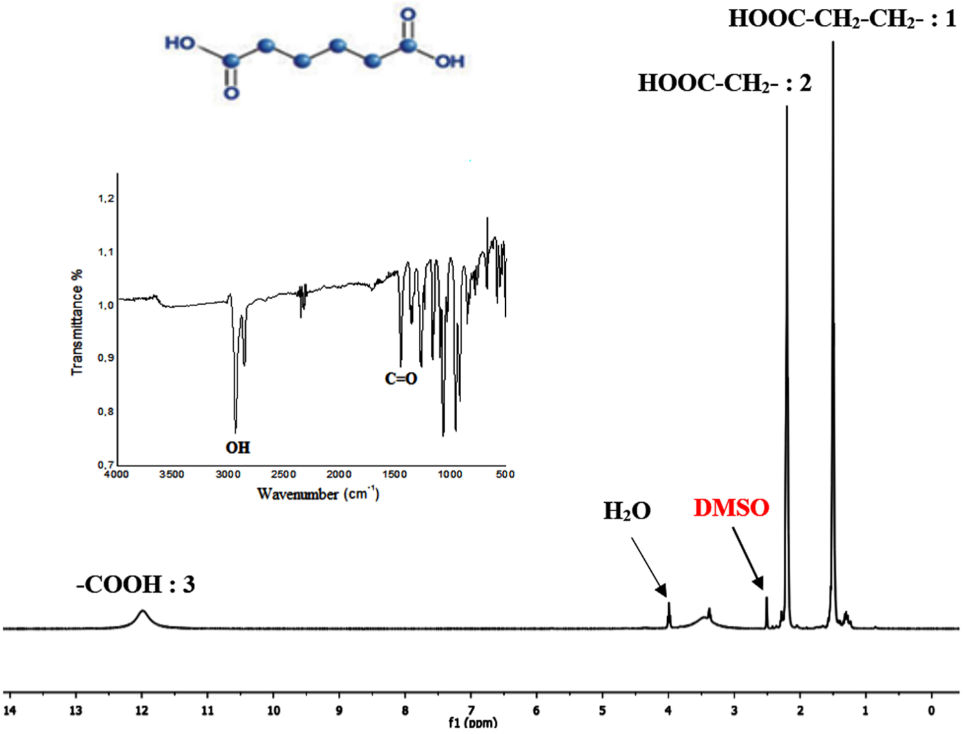


Fig. 1 HPLC chromatogram of reaction products obtained from cyclohexanone oxidation, catalyst: $NH_4SbPMo_{12}O_{40}$, $n_{catalyst}/n_{substrat}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

Fig. 2 ^{1}H-NMR and FT-IR spectra of adipic acid



a $n_{catalyst}/n_{-one}$ molar ratio of 4.30×10^{-3} corresponding to 125 mg catalyst and 15 mmol of substrate.

3.1 Cyclohexanone Oxidation

Figure 3 shows that the -one conversion is total after 5 h of reaction for $NH_4SnPMo_{12}O_{40}$, $NH_4SbPMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ evidencing the high activity of POMs. The catalytic results summarized in Table 1, were recovered after 20 h of reaction. The counter-cation has an influence on reaction product distribution. Thus, the AA formation is favored in the presence of substituted salts with yields of 42, 47 and 56% for $NH_4BiPMo_{12}O_{40}$, $NH_4SbPMo_{12}O_{40}$ and $NH_4SnPMo_{12}O_{40}$ respectively against 31 and 38% for $H_3PMo_{12}O_{40}$ and $NH_4PMo_{12}O_{40}$ respectively. Glutaric acid appears particularly in the presence of $NH_4BiPMo_{12}O_{40}$, $NH_4SbPMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ (25, 24 and 7% of yield respectively). Whatever the used POM, succinic acid is obtained with a low yield (≤ 4%) while the unidentified products are obtained with a high yield sum varying between 22 and 61%. In literature, only the formation of both glutaric and succinic acids as major by-products were reported [8–11]. The results obtained indicate that the catalytic process used in this work makes the action of both POM and H_2O_2 more efficient with high cyclohexanone conversion, but with also more unidentified products.

Table 1 AA yield and conversion as function of $n_{catalyst}/n_{-one}$, catalyst: $NH_4SnPMo_{12}O_{40}$, reaction time: 20 h, reaction temperature: 90 °C

$n_{catalyst}/n_{-one}$ (10^3)	Conversion (%)	AA yield (%)
4.30	100	56
2.16	99	38
1.44	85	31
1.08	77	22

It should be emphasized that the obtained AA yields after its cold crystallization are similar to those obtained by HPLC analysis as shown in Table 2, with respectively, 56 and 57% for $NH_4SnPMo_{12}O_{40}$, 47 and 48% for $NH_4SbPMo_{12}O_{40}$, 42 and 42% for $NH_4BiPMo_{12}O_{40}$, 38 and 38% for $NH_4PMo_{12}O_{40}$ and 31 and 35% for $H_3PMo_{12}O_{40}$. From these results, it appears that the crystallization allows practically to recover the totality of AA.

3.2 Cyclohexanol Oxidation

Figure 3b shows that -ol conversion in presence of $NH_4SnPMo_{12}O_{40}$ is practically total (97–100%) after 5 h

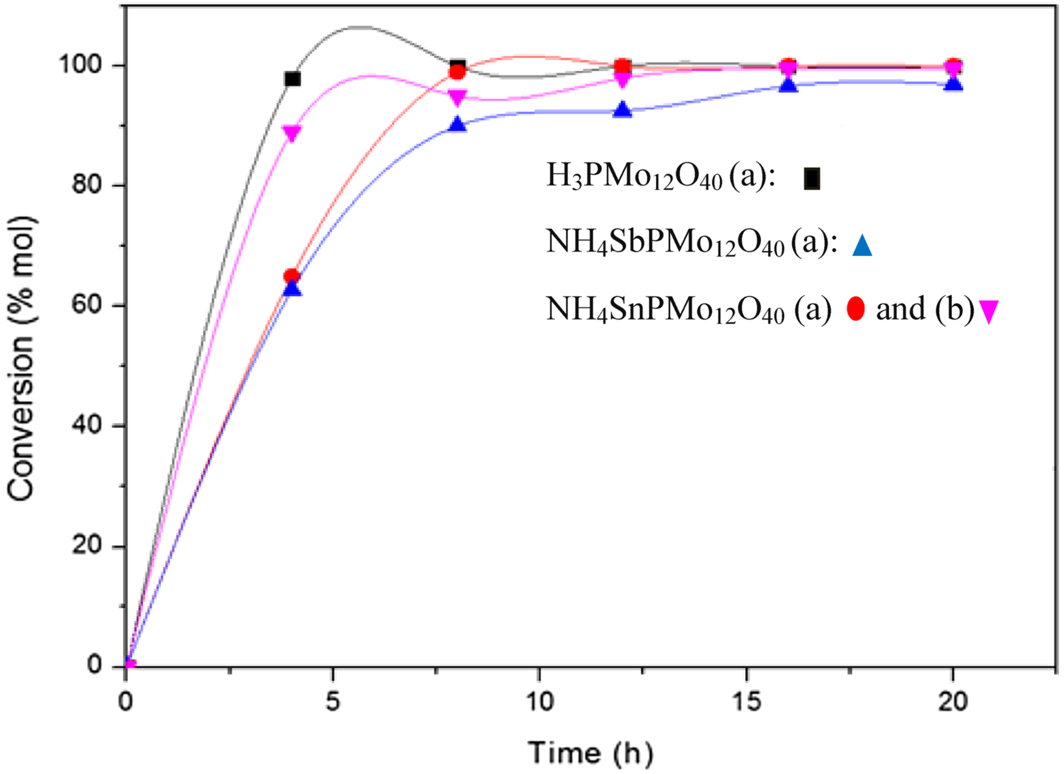


Fig. 3 Conversion of cyclohexanone (**a**) and cyclohexanol (**b**) as function of the reaction time. $n_{catalyst}/n_{substrat}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

Table 2 Catalytic performances of POMs for cyclohexanone oxidation, $n_{catalyst}/n_{-one}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

Catalysts	Cold crystallization of AA	HPLC analysis				
	AA Yield (%)	Conversion (%mol)	Selectivities (yields) (%)			
			AA	GA	SA	UPs
$H_3PMo_{12}O_{40}$	35	100	31(31)	7 (7)	1 (1)	61 (61)
$NH_4PMo_{12}O_{40}$	38	100	38(38)	1 (1)	< 1 (< 1)	61 (61)
$NH_4BiPMo_{12}O_{40}$	41	96	44(42)	26 (25)	3 (3)	27 (26)
$NH_4SbPMo_{12}O_{40}$	48	97	48(47)	25 (24)	4 (4)	23 (22)
$NH_4SnPMo_{12}O_{40}$	57	100	56(56)	< 1 (< 1)	< 1 (< 1)	43 (43)

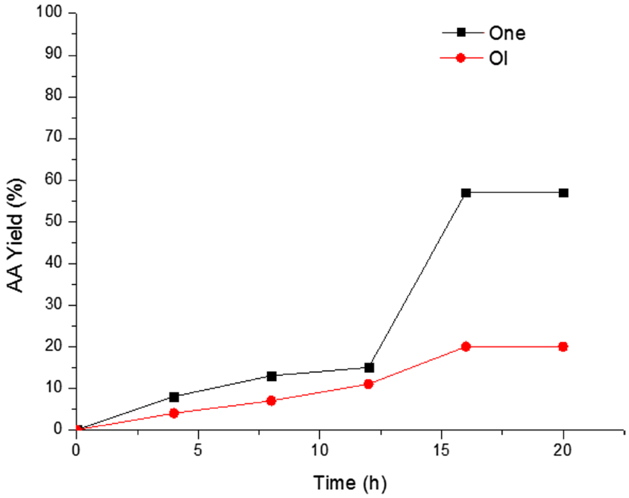


Fig. 4 Adipic acid yield as function of reaction time, catalyst: $NH_4SnPMo_{12}O_{40}$; Substrate: -one and -ol, $n_{catalyst}/n_{substrat}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

of reaction as in the case of the -one conversion. It is noted that, after 4 h of catalytic test, the -ol conversion is more important than that of -one (ca.90 against ca.65%). These results indicate that the alcohol oxidizes more readily. However, the curves of the Fig. 4 show a slow progression of AA production with the time from -ol oxidation, while it is brutal beyond 10 h from -one oxidation. The AA yield does not exceed 17% in the first case, while it achieves ca.60% in the second one. The observations made from the Figs. 3 and 4, are confirmed by the results of Tables 2 and 3, that show high yields toward unidentified products (UPs) from -ol oxidation (80%) compared to those obtained from -one oxidation (43%).

The AA yields obtained after its cold crystallization are similar to those obtained by HPLC analysis as shown in the Table 2, $H_3PMo_{12}O_{40}$ (5–6%), $NH_4PMo_{12}O_{40}$ (6–7%), $NH_4BiPMo_{12}O_{40}$ (2–2%), $NH_4SbPMo_{12}O_{40}$ (10–10%) and $NH_4SnPMo_{12}O_{40}$ (17–17%). These results are consistent with those observed with the ketone oxidation which confirms that the AA loss after crystallization is negligible.

Whatever the composition of the catalyst, the obtained AA yields from -ol oxidation are much lower than those obtained from -one oxidation (2–17 against 31–56%), whereas, the unidentified products represent 80–96 against 22–61% of yields. These results, showing that the formation of UPs favored from -ol oxidation, can be explained by the presence of the more reactive hydroxyl group than the ketone group, so the oxidation of the alcohol will lead to more products.

3.3 Oxidation of Cyclohexanol and Cyclohexanone Mixture

In the industrial process, adipic acid is obtained from oxidation of KA oil (mixture of cyclohexanol(50%) and cyclohexanone(50%)) by nitric acid [2–4]. In this context, the POMs were used for KA oil oxidation in the same operation

Table 3 Catalytic performances of POMs for cyclohexanol oxidation, $n_{catalyst}/n_{-one}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

Catalysts	Cold crystallization of AA	HPLC analysis				
	AA yield (%)	Conversion (%mol)	Selectivities (yields) (%)			
			AA	GA	SA	UPs
$H_3PMo_{12}O_{40}$	6	97	6 (5)	1 (1)	< 1 (< 1)	93 (90)
$NH_4PMo_{12}O_{40}$	7	97	7 (6)	1 (1)	< 1 (< 1)	92 (90)
$NH_4BiPMo_{12}O_{40}$	2	99	2 (2)	< 1 (< 1)	< 1 (< 1)	97 (96)
$NH_4SbPMo_{12}O_{40}$	10	98	10 (10)	1 (1)	< 1 (< 1)	89 (87)
$NH_4SnPMo_{12}O_{40}$	17	100	17 (17)	3 (3)	< 1 (< 1)	80 (80)

conditions ($n_{catalyst}/n_{substrat}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C) and AA was recovered by cold crystallization. The obtained AA yields, from oxidation of -one, -ol and -ol/-one, are displayed in Fig. 5. The results show that the AA formation is very sensitive to the substrate nature, thus, for all catalysts, the highest AA yields were obtained from -one oxidation with 35–57% against 17–39 and 2–17% from -ol/-one oxidation and -ol oxidation, respectively. Regardless of the substrate nature, the tin based catalyst led to best catalytic performances with AA yields of ca.57, 39 and 17% against ca. 48, 34 and 10% for $NH_4SbPMo_{12}O_{40}$ and ca. 41, 25 and 2% for $NH_4BiPMo_{12}O_{40}$, obtained from oxidation of -one, -ol/-one and -ol respectively. The observed low AA yields from oxidation of -ol/-one mixture compared to those obtained from -one oxidation can be attributed to the formation of hydrogen bonds between the C=O group of -one and the hydrogen of C–OH group of -ol, that makes difficult the oxidation of both substrates. Therefore, the alcohol has inhibited the -one oxidation. Results are in agreement with those observed in literature [29–32, 38].

All these results showed that the introduction of Sn, Sb or Bi as counter ion into the polyoxometalate is favorable to the AA formation. Indeed, the high catalytic activity of POM, partially substituted by an element less metallic than transition metal, Mo, can be attributed to the multifunctional character of active sites (Lewis acid and oxidative) associated to the presence of redox couples, Mo(VI)/Mo(V) and Sn(IV)/Sn(II), Sb(V)/Sb(III) or Bi(V)/Bi(III) as reported in previous work [35] and the presence of a Brönsted acidity coming from ammonium ions. These different sites intervene simultaneous in the activation of substrate, oxidant (H_2O_2) and oxygen-transfer and multielectron transfer. The better catalytic performance exhibited by $NH_4SnPMo_{12}O_{40}$ can be lied to the high Sn atom number (1.25 against 0.75 and 0.004 atoms per Keggin unit for Sb and Bi respectively) and its high reducibility, leading thus to a better distribution of ions with different states of oxidation.

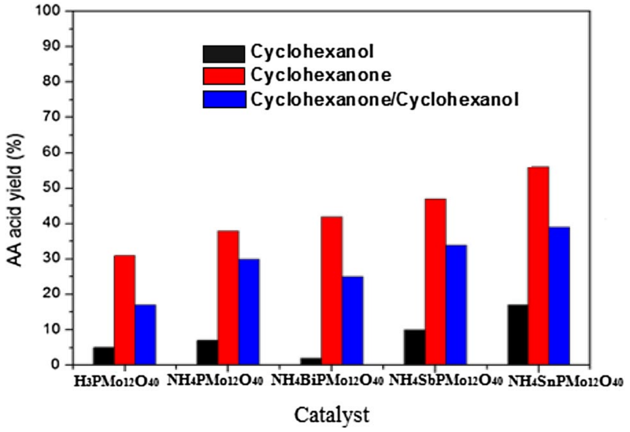


Fig. 5 Adipic acid yield as function of the POM composition, substrate: -one, -ol and -one/-ol, $n_{catalyst}/n_{substrat}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

3.3.1 Characterization of the Used Catalyst

^{31}P NMR results of $H_3PMo_{12}O_{40}$, $NH_4BiPMo_{12}O_{40}$ and $NH_4SbPMo_{12}O_{40}$, used catalysts (Table 4) exhibit, after 20 h of reaction, chemical shifts at −0.48, −0.46 and at −1.68 ppm, respectively, values, different to those of fresh POMs that were observed at −4.4 ppm, characteristic value of the oxidized species, $[PMo_{12}O_{40}]^{3-}$, [35, 39]. These results evidenced the presence of new phosphorous based species. It was reported that in the presence of hydrogen peroxide, POMs usually decomposes into peroxo-based metalate complexes. In the case of $H_3PW_{12}O_{40}$, the identified species by ^{31}P NMR were principally $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $\{PO_4[WO(O_2)_2]_2\}^{2-}$ [24–27, 40]. Whereas in our case, this is the reduced POM by the substrate that reacts with H_2O_2, confirmed by blue-to-yellow color change. This color change can suggested that H_2O_2 could simultaneously oxidize the reduced POM and form peroxo-oxidized POM species (noted peroxo-POM_{ox}). These latter could react with intermediates species yielding oxygenated products whose adipic acid. It was emphasized that peroxo-based POM species can play a key role in oxidation reactions of organic substrates [26, 27]. In the case of $NH_4SnPMo_{12}O_{40}$, one peak located at −4.1 ppm was observed, demonstrating that the Keggin structure was conserved with probably a substitution of some oxygen atoms bridge, (O^{2-}), by oxygen “peroxo” (O_2^{2-}) in a symmetrical manner which would explain the chemical shift value of −4.1 close to 4.4 ppm. These observations seem indicate that $NH_4SnPMo_{12}O_{40}$ can undergo stepwise multielectron redox process without any structural modification contrarily to $H_3PMo_{12}O_{40}$, $NH_4BiPMo_{12}O_{40}$ and $NH_4SbPMo_{12}O_{40}$.

3.4 Catalyst Stability

$NH_4SnPMo_{12}O_{40}$ catalyst was reused in order to test its catalytic stability. After each catalytic cycle, the adipic acid is recovered after cold crystallization, then 15 mmol of cyclohexanone were added to reaction mixture and the

Table 4 ^{31}P NMR results of POMs before and after ketone oxidation

POMs	δ (ppm) of fresh catalyst	δ (ppm) after catalytic test
$H_3PMo_{12}O_{40}$	−4.4	−0.22
$NH_4BiPMo_{12}O_{40}$	−4.4	−0.46
$NH_4SbPMo_{12}O_{40}$	−4.4	−1.68
$NH_4SnPMo_{12}O_{40}$	−4.4	−4.0

oxidation reaction was carried out with the soluble used catalyst, under the optimized conditions. Each cycle lasts 20 h. The catalytic activity results are represented in Fig. 6. A progressive decrease of adipic acid yield from 56 to 0% is observed after five reaction cycles. The significant decrease in AA yield after each cycle would probably arise from the action of several factors such as the decrease in acidity from ammonium ions, which results in reduction of the oxidizing power of H_2O_2 (the protons being necessary for its reduction), and subsequently decrease of peroxo species, active sites, necessary for the formation of oxygenated products. These results showed that $NH_4SnPMo_{12}O_{40}$ catalyst can be used at least 3 times with reaction times of 20 h, without regeneration.

3.5 Reaction Pathways

It is known that clusters POMs are good electron acceptors exhibiting fast reversible multielectron redox transformations under mild conditions. In the case of molybdenum based POMs, the color is sensitive to the oxidation state of Mo. Thus, the POM changes from yellow, characteristic of Mo (VI), to blue, characteristic of Mo (V), in the presence of reducing compound without any structural modification. It should be pointed out that only two Mo(VI) per Keggin anion can undergo a reduction and therefore, result POM with mixed valence. The change of color would allow us to propose possible reaction pathways.

From the method of Nomiya et al. [28] that allows to visualize the different catalytic oxidation steps and ^{31}P NMR results that show the formation of a new specie attributed to peroxo-POM_{ox}, the following pathways could can be proposed:

$$\text{Organic substrate} + \text{POM}_{\text{ox}} \rightarrow \text{POM}_{\text{red}} + \text{intermediatespecies} \tag{1}$$

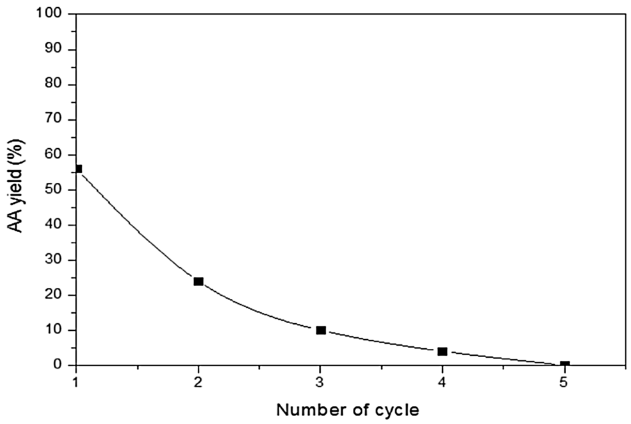


Fig. 6 Adipic acid yields after several reaction cycles, catalyst: $NH_4SnPMo_{12}O_{40}$, $n_{catalyst}/n_{-one}$ molar ratio: 4.30×10^{-3}, reaction time: 20 h, reaction temperature: 90 °C

$$\text{POM}_{\text{red}} + \text{H}_2\text{O}_2 \rightarrow \text{peroxo} - \text{POM}_{\text{ox}} \tag{2}$$

$$\begin{aligned}&\text{Peroxo}-\text{POM}_{\text{ox}} + \text{intermediate species}\\&\qquad \rightarrow \text{reaction products} + \text{POM}_{\text{ox}}\end{aligned} \tag{3}$$

The first stage (Eq. 1) occurs between the organic substrate (-one) and POM, leading to reaction product intermediates and to the reduced form of the catalyst (blue color). In the second stage (Eq. 2), the reaction takes place between reduced POM (noted POM_{red}) and hydrogen peroxide leading to simultaneously oxidation of reduced POM (yellow color) and formation of peroxo-oxidized POM (noted peroxo-POM_{ox}), active species. This second step can be considered as the rate-determining step. The color change from blue to yellow can last 10 min. After a time of 9–10 h, no color change was observed suggesting that in the reaction mixture, only peroxo-POM_{ox} species are present. These latter react with intermediate species to give oxygenated products and oxidized POM (POM_{ox}) (Eq. 3). The total reaction time must be of 20 h, required time to obtain the maximum AA yield. Whatever the stage, the predominant mechanism is of the redox type, with direct involvement of the POM in the reaction in oxidized, reduced and peroxo species forms. In conclusion, these observations would indicate that the formation of the oxygenated compounds would be initiated only after addition of hydrogen peroxide and the POM alone is not able to oxidize the organic substrate, to oxygenated compounds.

This proposition of reaction pathways is according with those reported by others authors which have suggested that the peroxo species could be the key active catalytic intermediate, in the one-step oxidative cleavage of cyclohexene to adipic acid [8, 10, 11, 41] and in the liquid phase oxidation reactions of the alkenes and alcohols [24, 25].

4 Conclusion

In this work, the heteropolysalts, $(NH_4)_xA_yPMo_{12}O_{40}$ (A^{n+}=Sb^{3+}, Bi^{3+} or Sn^{2+}), in the presence of hydrogen peroxide (30%), were found to be very active for both cyclohexanone and cyclohexanol oxidation with 96–100% of conversion. For all catalysts, the formation of adipic acid is favored from cyclohexanone oxidation while that of unidentified products from cyclohexanol oxidation. Among, the tested catalysts, $(NH_4)_{0.5}Sn_{1.25}PMo_{12}O_{40}$ is the most effective towards adipic acid with 56% of yield. The high catalytic activity of $(NH_4)_xA_yPMo_{12}O_{40}$ salts can be due to the multifunctional character of active sites and to the presence of peroxo-polyoxometalate species.

This green process of AA production can be an alternative to that of current industrial using nitric acid as oxidant.

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