Influence of peroxometallic intermediaries present on polyoxometalates nanoparticles surface on the adipic acid synthesis

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ABSTRACT

The cyclohexene oxidation by hydrogen peroxide catalysed by polyoxometalates (POM) has been shown as an adequate green route for the adipic acid synthesis. In this study, it has been demonstrated that POM's salts are effective catalysts for this reaction and how peroxopolyoxometalates intermediaries are the truly responsible species of the POM's salts catalytic activity and solubility. However, the latter can be reduced by calcining the catalyst previously. Polyoxomolybdates salts generally present a higher activity than polyoxotungstenates salts. Finally, it must be remarked the positive effect exerted by the acetic acid stabilising the peroxide of hydrogen against its decomposition.

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1. Introduction

From an industrial point of view, the 1,6-hexanoic acid or adipic acid is the most important dicarboxylic acid: around 2.5 millions of tons of this crystalline white solid are produced per year worldwide, mainly for its application as precursor in the nylon production. The industrial production of adipic acid is carried out through cyclohexanol and cyclohexanone oxidation – "KA oil" – with nitric acid. However, this process is not environmentally-friendly, since it generates a huge amount of greenhouse gases, of which N_2O is the most important one. N_2O is obtained as a by-product during the two oxidation stages that occur in the adipic acid production.

In the current chemical industry framework, the production processes have to comply with restrictive environmental standards and the technologies implemented should be sustainable from an energetic and environmental point of view. These premises have led to the so-called Green Chemistry. In this sense, the present strategies of improvement are focussed both on the substitution of nitric acid by other oxidant and the use of more economic chemical precursors.

Considering the oxidant, nitric acid could be replaced by hydrogen peroxide (H_2O_2). In fact, during the last decades the oxidation of organic compounds with hydrogen peroxide catalysed by metals has focussed considerable attention as a feasible alternative to environmentally harmful oxidants [1,2]. Hydrogen peroxide is a clean

oxidant, although, often, some problems arise associated to its use, such as decomposition, thus losing "oxidative capacity" [3]. For this reason, the majority of investigations are aimed at developing active catalysts for the chemical process but inactive towards hydrogen peroxide decomposition.

Considering the precursor, adipic acid can be also obtained directly from cyclohexene, thereby removing the step of conversion of cyclohexene to cyclohexanone and ciclohexanol. Cyclohexene oxidation with hydrogen peroxide usually involves epoxidation of the double bond, followed by the transformation of the intermediate to a diol. Subsequently, multiple oxidation steps take place, such as Baeyer–Williger-like reactions and subsequent hydrolysis to yield, finally, the adipic acid [4,5].

A key question concerning this reaction when conducted under aqueous medium deals with the solubility of hydrogen peroxide. This oxidant is not soluble in most of the organic solvents. For this reason, the utilisation of phase transfer compounds (PTCs) [4] is required. Despite of the use of PTCs increases yield of oxidation reactions involving organic compounds, those are relatively expensive and harmful for industrial applications, when huge amounts of these compounds are required.

Finally, it has to be taken into account that hydrogen peroxide, by itself, is not able to oxidise cyclohexene double bond. Therefore, as already mentioned above, the use of an effective catalyst under a biphasic medium is needed. Under these experimental conditions, it is worth mentioning the peroxotungstate catalysts developed by Venturello et al. [6], for which a high efficiency towards alkenes epoxidation with hydrogen peroxide, under a liquid biphasic system assisted with PTCs, has been reported [7].

Following these results, several polyoxometalates have been used as effective catalysts for homogeneous peroxidation with hydrogen peroxide [8–10]. It must be pointed out that, for this reaction, polyoxometalates act as catalyst precursors: monomeric, dimeric, and tetrameric peroxo-type species are generated by the reaction of the precursor with hydrogen peroxide, being those the catalysts for the reaction of epoxidation.

Regarding the adipic acid production, Noyori et al. [4] have obtained excellent results in the cyclohexene conversion to adipic acid, under homogeneous phase, replacing nitric acid by hydrogen peroxide as oxidant agent and using sodium tungstate (Na_2WO_4) as catalyst. Based on these results, attempts have been made of dispersing POM salts catalyst onto several mesoporous silicas [11,12]. Unfortunately, the catalytic tests indicate that only a small portion of the acidic and redox sites available are active for the reaction, and some leaching (13–14%) or surface coverage of the catalysts after their use takes place [11].

With these premises, the objective of the present work is to analyse the uselfulness of heteropolysalts that are active towards the conversion of cyclohexene to adipic acid under the experimental conditions mentioned above, for which they should be insoluble in the biphasic reaction medium.

2. Experimental

2.1. Materials and methods

The catalysts used in this work, based on Keggin's structures, ($[PMo_{12}O_{40}]^{-3}$ and $[PW_{12}O_{40}]^{-3}$ anions, POM), were prepared in our laboratories. These catalysts were obtained both in its acid form and as heteropolysalts, from caesium, ammonium and quaternary amine cations [13]. Due to their solubility in the reaction medium, heteropolyacids were supported onto an activated carbon fiber A20 (PMo/A20) whose preparation procedure is described in previous work [14]. In addition, other heteropolysalts were synthesised but replacing one of the addenda atoms (M = W or Mo) by other transition metal (M = W or Mo): $[FePM_{11}O_{39}]^{-5}$, $[CoPM_{11}O_{39}]^{-5}$, $[NiPM_{11}O_{39}]^{-5}$, $[PM_{10}V_2O_{40}]^{-5}$ following the procedures found in the literature [15–17].

The oxidation of cyclohexene was conducted in a glass reactor ($27\,cm^3$ of inner volume) located inside of a stainless steel vessel ($45\,cm^3$ of inner volume) coupled to a manometer to monitor the system pressure. For the reaction, $1\,cm^3$ of cyclohexene, $5\,cm^3$ of hydrogen peroxide (30%), $1\,cm^3$ of solvent (acetonitrile), $0.2\,cm^3$ of anhydrous acetic acid and a certain amount of catalyst, ranging from 10 to 120 mg, were mixed. A small magnet of teflon was added to the mixture and the whole system was immersed in a polyethylene glycol thermostatic-bath, at different temperatures, ranging from 40 to 90 °C. Preliminary results confirmed that 75 °C and a stirring speed of 800 rpm were the most suitable conditions. A reaction time of 6 h was selected as the optimum value, thus allowing complete conversion but minimising hydrogen peroxide decomposition. In addition, other reaction times, both shorter (0.5–3 h) and longer (until 24 h), were tested for comparative purposes.

Concerning the solvent, preliminary tests also demonstrated that acetonitrile yielded higher yield than other conventional solvents such as: methanol, anhydride acetic, toluene, dimethyl sulfoxide, acetonitrile. The solvent plays a role both and assisting POM stability towards its solvolysis against the hydrogen peroxide [18]. Complementary, acetic acid was added to the reaction medium as a source of protons, which seems to be essential for the oxidation reaction based on different authors' studies [19–22].

The reutilisation of the catalysts was approached, using the catalyst in a consecutive reaction. For that, upon completion of reaction time, the mixture was filtered, recovering the catalyst.

Then, it was washed several times with an acidic water solution until reaching pH 3. Subsequently, the catalyst was dried in a vacuum oven at 100 °C for 24 h. Finally, prior to its reuse in a new cycle, it was weighted. The loss weights were used to estimate the amount of catalyst solubilised during the reaction. In addition, for Cs-containing heteropolysalts, the importance of a previous step of calcination in air at 375 °C (1 h) was analysed.

2.2. Characterisation

The elemental analyses of POM, the fresh, calcined and used catalysts are listed in Table S1. The results obtained show that the elemental contentss are closed to the expected theoretical values on all POM. The experimental P/Mo and P/W ratios are in agreement with the exclusive presence of the Kegging compound, indicating that no significant decomposition takes place either during the calcination, or during the oxidation process.

The porous texture of the catalysts was analysed by physical adsorption of gases (N_2 at −196 °C and CO_2 at 0 °C), using two different volumetric equipments (Autosorb-B and Autosorb-6, respectively). Previously, the samples were degasified for 4 h at 150 °C.

The identification of the reaction products of the oxidation of cyclohexene into adipic acid was performed by taking an aliquot of the solution ($20\,\mu L$) at the end of the reaction time and analysing by a GC (Agilent 6890 provided with an HP-1 column of size $30\,m \times 250\,\mu m \times 0.25\,\mu m$) coupled to a mass spectrometer Agilent 5975 MS. Once identified all the reaction products, the conversion and the evolution of the reaction products were quantitatively estimated by a FID-GC (Agilent 6890), after proper calibration procedures. Regarding the amount of hydrogen peroxide decomposed, it was calculated from the subtraction of initial amount set of the reacted and the non-reacted quantities.

With the aim of determining if the structural or chemical properties of the catalysts were modified after the reaction, the fresh, calcined and used catalysts were analysed by different techniques, i.e. FT-Raman and UV–vis-spectroscopy. It is important to outline that other characterisation techniques such as: elemental analysis, XRD, SEM, TEM, DRIFT and TG techniques were also used, although these did not provide any significant differences among the fresh, calcined and used catalysts (the results obtained with the above mentioned techniques are summarised in the Supplementary Information). FT-Raman spectra were carried out with a FT-Raman (Bruker RFS/100) spectrophotometer using a laser with an excitation source (1064 nm, Nd-YAG). The UV–vis spectra were conducted using a UV–vis/NIR spectrophotometer (Jasco V-670), ranging wavelength values from 190 to 600 nm.

3. Discussion results

3.1. Study of the efficiency of the catalyst towards H_2O_2 consumption

Although the air is the most economic oxidant agent, for the reaction under study is not efficient enough. As already mentioned in the introduction, H_2O_2 is a clean and environmentally-friendly oxidant (only generates H_2O as by-product) and it is relatively cheap. However, it presents the disadvantage of its instability against decomposition. Many substances catalyse its decomposition, including most of the transition metals and their compounds. For this reason, it is important to pay attention to this issue. Not only because of economic reasons (not all the amount of oxidant takes part into the reaction) but also because of safety reasons (O_2 generated due to hydrogen peroxide decomposition can originate overpressure inside the reactor). As far as these authors concern,

Table 1
Data of pressure inside the reactor (bar) during the reaction along with the percentage of hydrogen peroxide decomposed, in parentheses, for different experimental conditions (amount of catalyst = 4×10^{-5} mole; $1\,cm^3$ of cyclohexene, $5\,cm^3$ of hydrogen peroxide (30%), $1\,cm^3$ of solvent (acetonitrile)).

Salt POM	Reaction time (h)		
	1	2	6
Without POM (90 °C)	1	3	8 (17)
Without POM (80 °C)	0	1	3 (6)
Without POM (75 °C)	0	1	2 (4)
HPMo/A20	3	6	9 (19)
HPMo/A20 2nd cycle	1	2	5 (10)
PFeMo	18 (38)	–	–
PCoMo	15 (32)	–	–
PNiMo	3	6	10 (21)
VPMo	4	7	12 (25)
$(N(C_3H_7)_4)_3PMo_{12}O_{40}$	2	6	9 (19)
$(N(C_3H_7)_4)_3PMo_{12}O_{40}$ (acetic)*	1	2	3 (6)
$(N(C_3H_7)_4)_3PMo_{12}O_{40}$ (acetic) 2nd cycle	0	1	3 (6)
$(NH_4)_3PMo_{12}O_{40}$ (acetic)	0	1	3 (6)
$(NH_4)_3PW_{12}O_{40}$ (acetic)	0	1	2 (4)
$Cs_3PMo_{12}O_{40}$ (acetic)	2	5	6 (13)
$Cs_3PMo_{12}O_{40}$ (cal. 375 °C) (acetic)	1	2	4 (8)
$Cs_3PW_{12}O_{40}$ (acetic)	1	2	4 (8)
$Cs_3PW_{12}O_{40}$ (cal. 375 °C) (acetic)	0	1	2 (4)

* $0.2\,cm^3$ of anhydrous acetic acid.

Fig. 1. Effect of the amount of the catalyst on the cyclohexene conversion reached after 6 h for two selected catalysts (reaction temperature = 75 °C; $1\,cm^3$ of cyclohexene, $5\,cm^3$ of hydrogen peroxide (30%), $1\,cm^3$ of solvent (acetonitrile); $0.2\,cm^3$ of anhydrous acetic acid).

this aspect is hardly analysed in the literature. In this work, the hydrogen peroxide decomposition was determined by measuring the pressure values in the reactor. A selection of experimental conditions (reaction times, temperatures, catalysts . . .) and their corresponding pressure values measured during the reaction are presented on Table 1.

First of all, it can be pointed out that the H_2O_2 decomposition is thermally favoured. Thus, in the absence of catalyst, its decomposition is accelerated at temperatures above 75 °C, which is evident from the increased pressure in the reactor. On the other hand, the higher activity of the A20-supported catalyst in the first cycle, towards the hydrogen peroxide decomposition, could be related to a higher presence of surface oxygenated groups, as reported for this type of supports in previous work [14]. Thirdly, the use of POM with the addenda atom substituted by other transition metal (PCoMo, PNiMo, PFeMo, PVMo), usually employed in oxidation reactions due to the promoting effect of the catalytic activity [3,17,23,24], are inappropriate when H_2O_2 is used as oxidant, because accelerate considerably this decomposition.

In the case of using the series of caesium heteropolysalts, the extent of H_2O_2 decomposition reaction is reduced, even more if the catalysts are calcined previously. Ammonium heteropolysalts are characterised by low decomposition activity as well.

It is interesting to highlight that the presence of acetic acid in the reaction medium assists the stabilisation of H_2O_2 towards its decomposition [18–21]. It is well known the effect exerted by certain acids to stabilise H_2O_2, which has been attributed to a possible modification in its ionisation, and, mainly, to a decrease in the population of OOH· species, which are intermediates of H_2O_2 decompositions. On the other hand, this compound is more stable under acid medium due to the formation of hydrogen bonds. Interestingly, this stabilisation effect does not take place with the heteropolyacids, despite they are stronger Brønsted acids [25] than acetic acid. This could be also related to the influence of transition metals within the POM structure on the H_2O_2 decomposition.

3.2. Study of the amount of catalyst for the reaction

For this study, CsPMo (heterogeneous phase reaction) and its corresponding acid, HPMo (homogeneous phase reaction), were selected. The conversion results obtained after 6 h of reaction at
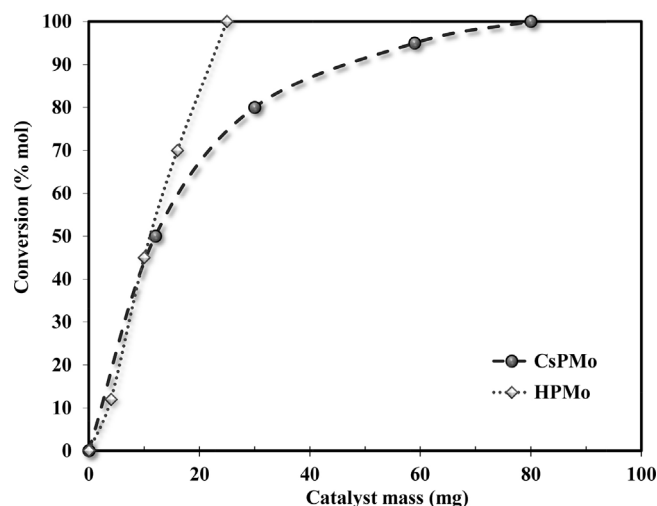
75 °C are shown on Fig. 1. First of all, it should be noted the important role of CsPMo as catalyst, and in general all the most of the heteropolysalts (PMo and PW-type salts) used in this study, as well as their respective HPMo and HPW. In the absence of the catalyst (corresponding to catalyst mass of zero on Fig. 1), the reaction does not take place under these experimental conditions. It is important also to remark the high catalytic activity that exhibits this salt. Conversions of 50% are achieved with low amounts of catalyst under heterogeneous conditions (12 mg), similar to that achieved under homogeneous conditions (with HPMo). As expected, for higher amounts of catalyst, higher conversions are reached under homogeneous conditions for identical amounts of catalyst. Nevertheless, the catalytic activity presenting by the heteropolysalt is relatively high. Only 1.5×10^{-5} mol are required for the HPMo and 3.6×10^{-5} mole in the case of CsPMo, to achieve a 100% conversion. As a result of this study, 4×10^{-5} mole of catalyst will be used for the rest of the catalytic tests, ensuring enough mass of catalyst.

3.3. Influence of the reaction time

The evolution of the conversion achieved over reaction time using HPMo (homogeneous phase) and CsPMo (heterogeneous phase) is illustrated on Fig. 2. As can be seen, the evolution of the conversion over time follows the trend of a sigmoid curve, which is typical of processes that require a catalyst induction period. This might be related to the formation of peroxometallic intermediates on the surface of CsPMo nanoparticles (and, in general of other similar salts) [3,20,26,27]. Because, after catalyst pre-treatment with hydrogen peroxide, the induction period disappears, this experimental observation supports the above hypothesis.

In order to verify the presence of peroxometallic species on the surface of catalyst, the used catalyst was analysed by FT-Raman. It must be pointed out, which DRIFT, XRD and TG patterns do not show any differences between fresh and used catalyst (see Figs. S1, S3 and S5). Fig. 3 compiles the comparison among both spectra (obtained from fresh and used CsPMo). The Raman spectra indicate that the catalyst structure before and after the reaction is the same, characteristic of the Keggin structure [28,29].

A detailed inspection of the spectra reveals the expected modes of these compounds: $994\,cm^{-1}$ (υ_s Mo=O$_d$), $978\,cm^{-1}$ (υ_{as} Mo=O$_d$), $913–880\,cm^{-1}$ (υ_{as} Mo—O$_b$—Mo), $610–595\,cm^{-1}$ (υ_s Mo—O$_c$—Mo) and $247\,cm^{-1}$ (υ_s Mo=O$_a$). The most relevant
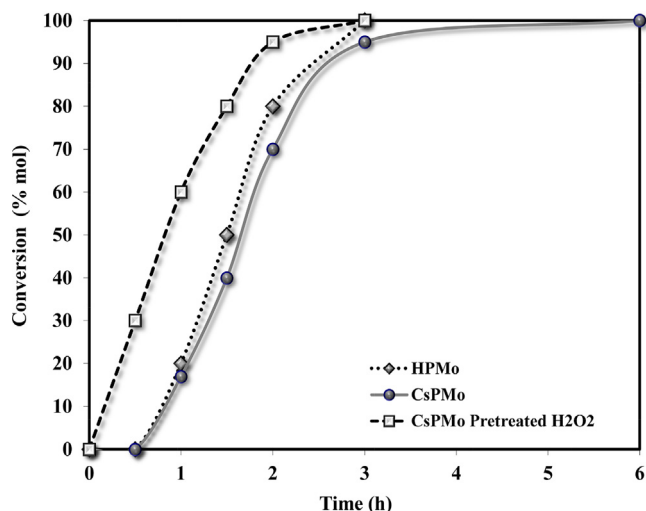
Fig. 2. Conversion of cyclohexene versus time using as catalyst HPMo and its salt CsPMo, fresh and pretreated with H_2O_2. (reaction temperature = 75 °C; amount of catalyst = 4×10^{-5} mole; 1 cm^3 of cyclohexene, 5 cm^3 of hydrogen peroxide (30%), 1 cm^3 of solvent (acetonitrile); 0.2 cm^3 of anhydrous acetic acid).

difference among both spectra is the emergence of a new peak at 853 cm^{-1} for the case of the used catalyst, which is attributed to a υ_s (O—O) [30,31], located close to the O—O vibration characteristic of H_2O_2, (which appears at 877 cm^{-1}) [32]. All these results suggest, on the one hand, the existence of peroxo species on the surface of catalyst and, on the other hand, the existence of other species, with a low nuclearity, which have been transferred to the solution due to the low intensity of this peak.

3.4. Study of the dependence between the degree of conversion and the solubility of the catalyst: Comparison with various POM

3.4.1. Influence of the type of POM on the extent of conversion

In order to analyse the influence of the nature of the POM on the extent of conversion, a large number of PMo and PW-type salts have been selected. Conversion values under optimum conditions are compiled on Table 2.

It can be said that, regardless the type of cation accompanying the Keggin structure, the Mo-based compounds present higher catalytic activity than those based on W. This is in agreement with

Table 2

Conversion of the cyclohexene (molar %) for the reaction during 6 h at 75 °C using several POM-based catalysts (amount of catalyst = 4×10^{-5} mole; 1 cm^3 of cyclohexene; 5 cm^3 of hydrogen peroxide (30%); 1 cm^3 of solvent (acetonitrile); 0.2 cm^3 of anhydrous acetic acid).

Salt	Conversion (% mol)
$H_3PMo_{12}O_{40}$	100
$H_3PW_{12}O_{40}$	100
$(NH_4)_3PMo_{12}O_{40}$	100
$(NH_4)_3PW_{12}O_{40}$	75
$(N(C_2H_5)_4)_3PMo_{12}O_{40}$	80
$(N(C_2H_5)_4)_3PMo_{12}O_{40}$ 2nd cycle	100
$(N(C_3H_7)_4)_3PMo_{12}O_{40}$	70
$(N(C_3H_7)_4)_3PMo_{12}O_{40}$ 3rd cycle	90
$(N(C_4H_9)_4)_3PMo_{12}O_{40}$	30
$(N(C_4H_9)_4)_3PMo_{12}O_{40}$ 3rd cycle	50
$(Ph_3PC_3H_7)_3PMo_{12}O_{40}$	3
$(Ph_3PC_3H_7)_3PMo_{12}O_{40}$ 3rd cycle	5
$Cs_3PMo_{12}O_{40}$	95
$Cs_3PMo_{12}O_{40}$ calcined	100
$Cs_3PMo_{12}O_{40}$ calcined 3rd cycle	100
$Cs_3PW_{12}O_{40}$	50
$Cs_3PW_{12}O_{40}$ calcined	75
$Cs_3PW_{12}O_{40}$ calcined 3rd cycle	80

the higher oxidant character of the $[PMo_{12}O_{40}]^{-3}$ anion [33]. Second, the type of cation influences dramatically on the degree of conversion achieved, the larger the cation, the lower the conversion of the corresponding salt. As a representative example, the conversion reached with the propiltriphenylphosphonium salt is very low. Thirdly, the results indicate an enhancement of activity for the used catalyst (if compared with the fresh catalyst). Both behaviours are in agreement with the existence of peroxo species on the surface of the nanoparticles originated after the interaction of H_2O_2 with the $[PMo_{12}O_{40}]^{-3}$. In this way, the decrease of the conversion observed with the increase of the cation size, must be related to steric impediments and accessibility problems of the reactants to reach $[PMo_{12}O_{40}]^{-3}$-surface. As commented previously, the increase in conversion after one cycle is explained by the existence of peroxo groups originated during the course of the reaction, thus diminishing the "induction" period. Finally, results in Table 2 shows the positive effect of the calcinations step for Cs-salts.

In order to analyse the effect of the cation on the conversion, the porous texture of the catalysts was analysed by means of the N_2 and CO_2 isotherms at −196 °C and 0 °C, respectively. Fig. 4 contains the N_2 isotherms obtained. The corresponding parameters estimated from these isotherms are listed on Table 3.
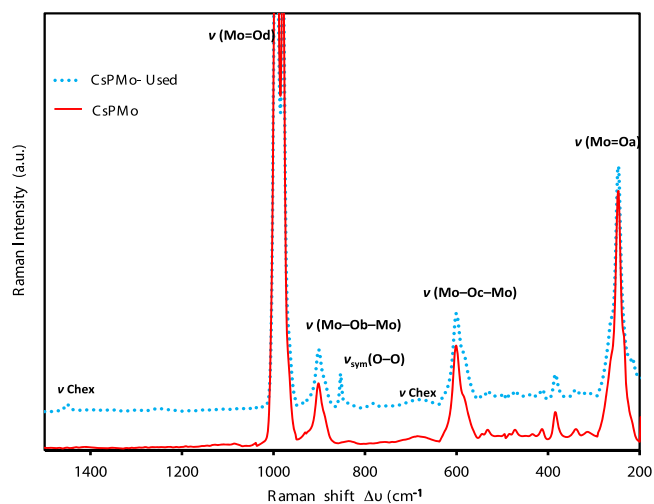

Fig. 3. FT-Raman Spectra of CsPMo, both fresh and used catalyst (after corresponding reaction to obtain adipic acid: reaction temperature = 75 °C; 6 h; amount of catalyst = 4×10^{-5} mole; 1 cm^3 of cyclohexene, 5 cm^3 of hydrogen peroxide (30%), 1 cm^3 of solvent (acetonitrile); 0.2 cm^3 of anhydrous acetic acid).
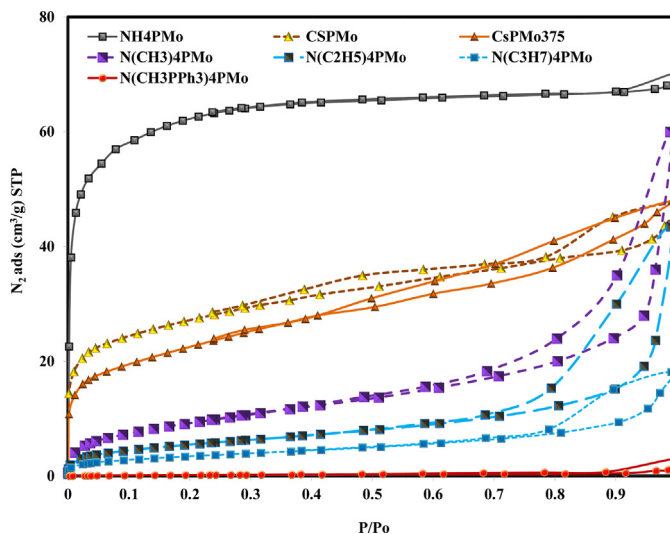

Fig. 4. Nitrogen adsorption isotherms at −196 °C of representative POM-salts.

Table 3
Textural properties of X₃[PMo₁₂O₄₀] salts.

Salt	S_{BET} (m²/g)	V_{N_2} [a]	V_{CO_2} [b]	V_{Meso} [c]	V_{Total} [d]
		(cm³/g)			
NH₄PMo	225	0.113	0.095	0.005	0.120
CsPMo	102	0.053	0.042	0.020	0.073
CsPMo-375	80	0.042	0.041	0.030	0.073
(N(CH₃)₄)PMo	37	0.017	0.015	0.075	0.093
(N(C₂H₅)₄)PMo	24	0.010	0.011	0.057	0.067
(N(C₃H₇)₄)PMo	14	0.006	0.011	0.022	0.028
(Ph₃PC₃H₇)PMo	2	0	0	0.004	0.004

[a] Total specific microporous volume.
[b] Specific narrow microporosity volume (<0.7 nm).
[c] Mesopore volume.
[d] Total specific porosity volume.

Considering the textural parameters obtained, NH₄PMo salt would be, a priori, the most appropriate catalyst, due to its large BET surface area, followed by the CsPMo salt. This is clearly seen by the good correlation among conversions and BET surface area values of the catalysts. Thus, the decrease of conversion values in the quaternary amines series is in agreement with the decrease in porosity, being relevant for the case of the (Ph₃PC₃H₇)PMo salt, which presents neither porosity nor catalytic activity. This is in agreement with the XRD patterns of this salt, which has a semi-amorphous structure, characterised by the absence of reflections in the range of 2θ where the rest of compounds show typical peaks (see Fig. S2). However, the non-existence of the micropore volumes does not mean that the reaction cannot take place, because these nanoparticles present external surface. Actually, the average size of 100–300 nm for these POMs (see TEM images Fig. S4) provides external surface areas of around 5–15 m²/g, close to those show by mixed commercial catalysts based on molybdenum oxide supported on alumina. Therefore, the low conversion values for the quaternary amines series should be attributed to steric impediments. Very low values are seen for (Ph₃PC₃H₇)⁺-salts. This voluminous cation seems to hinder the approach of either the H₂O₂ or of the cyclohexene to the POM surface.

3.4.2. Dependence of the solubility with the type of POM

The second requirement to be fulfilled by POM-salts is the insolubility in the reaction media. However, a certain amount of catalyst is solubilised in the course of the reaction. Table 4 compiles the cumulative percentage of catalyst mass transferred to the solution, which is highly dependent on the nature of the catalyst.

As expected, HPA-type compounds are completely soluble in the aqueous reaction medium. In the case of ammonium salts, these

Table 4
Cumulative percentage of catalyst mass, referred to the initial amount of catalyst (%), transferred to the solution after different cycles. Reaction during 6 h at 75 °C using several POM-based catalysts (amount of catalyst = 4 × 10⁻⁵ mole; 1 cm³ of cyclohexene; 5 cm³ of hydrogen peroxide (30%); 1 cm³ of solvent (acetonitrile); 0.2 cm³ of anhydrous acetic acid).

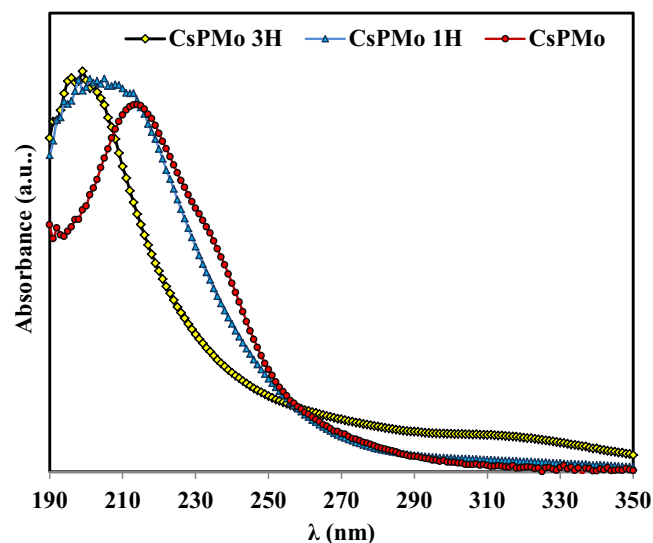| Salt POM	Number of cycle		
	1	2	3
H₃PMo₁₂O₄₀	100	–	–
H₃PW₁₂O₄₀	100	–	–
(NH₄)₃PMo₁₂O₄₀	70	100	–
(NH₄)₃PW₁₂O₄₀	30	60	100
(N(C₂H₅)₄)₃PMo₁₂O₄₀	40	85	–
(N(C₃H₇)₄)₃PMo₁₂O₄₀	20	40	55
(N(C₄H₉)₄)₃PMo₁₂O₄₀	10	15	25
(Ph₃PC₃H₇)₃PMo₁₂O₄₀	0	2	5
Cs₃PMo₁₂O₄₀	25	60	100
Cs₃PMo₁₂O₄₀ (cal. 375 °C)	12	25	40
Cs₃PW₁₂O₄₀	10	15	25
Cs₃PW₁₂O₄₀ (cal. 375 °C)	3	5	10

Fig. 5. UV spectra of the CsPMo catalyst in the solution of the reaction at different times: 0 h, 1 h and 3 h of reaction. (Reaction temperature = 75 °C; amount of catalyst = 4 × 10⁻⁵ mole; 1 cm³ of cyclohexene, 5 cm³ of hydrogen peroxide (30%), 1 cm³ of solvent (acetonitrile); 0.2 cm³ of anhydrous acetic acid).

also present a high solubility, mainly those based on PMo. Previous results confirmed that H₂O₂ was responsible of the solubility of these salts [10,29]. In this sense, analysing comparatively the results listed on Tables 2 and 4, it can be seen that exists a certain correlation among the extent of conversion and the high values of solubility. All these results point out to the fact that, after the formation of peroxo species onto the polyoxometalates nanoparticles surface, these are transferred to the solution, therefore, H₂O₂ is suggested to be the cause of the solubility of these salts [10,29].

In order to confirm this assumption, a study by means of UV–vis absorption spectroscopy was carried out in the solution at different reaction times. The obtained spectra are presented on Fig. 5. The fresh catalyst shows an absorption band (around 220 nm) and a shoulder (around 245 nm) related to a charge transfer band of O²⁻ ligand to Mo⁶⁺, associated to Od—Mo and Ob/Oc—Mo bonds, respectively [24,34,35]. After an hour of reaction, the peak at 220 nm shifts to lower wavelengths, while the shoulder at 245 nm disappears. After 3 h of reaction, the peak at 220 nm has shifted even more, up to about 200 nm. In addition, the emergence of a broad band about 290–350 nm takes place. These experimental observations have been also reported by other authors [24,36].

The correct identification of these bands is difficult owing to the different interpretations found in the literature [37–40]. Jannibello et al. [37] stablish relationships between the electronic transitions in the range of 250–300 nm with the existence of surface tetrahedral Mo—O complexes. Other authors assign the bands found at 300–320 nm to Mo₇O₂₄-type species, meanwhile the bands at 320–340 are assigned to MoO₃ isolated particles [38,39]. Other studies point out that the band registered at 330 nm is related to polyperoxomolibdate species, (e.g. [MoO(O₂)₃]₂₂ y [Mo(O₂)₄]₂₂) [40,2]. All these modification suggest a possible change of the fresh catalyst's Keggin structure by the hydrogen peroxide action, thus becoming a mixture of peroxoanions and other Keggin species degraded, both in the solution and on the surface of the nanoparticles. In this sense, the fact that the elemental analyses (Table S1) and the XRD patterns (see Fig. S3) show similar results in the case of the fresh and reused solid catalyst, supports the idea that the peroxoanions species are only on the surface of the nanoparticles, thus being the reused catalyst almost identical to the fresh catalyst from the chemical and structural point of view.

Table 5
Conversion of the cyclohexene and products selectivity after 6 h of reaction in different cycles, at 75 °C, using 4×10^{-5} mole of $Cs_3PMo_{12}O_{40}$ calcined. Data obtained in the presence and in the absence of acetic acid (0.2 cm^3 anhydrous acetic acid). (1 cm^3 of cyclohexene; 5 cm^3 of hydrogen peroxide (30%); 1 cm^3 of solvent (acetonitrile)).

Cycle	Conversion (% mol)	Selectivity (% mol)[a]			
		Epoxide	Diol	Cetone	Adipic
1st Acetic	100	7		1	80
2nd Acetic	100	11	4	3	73
3rd Acetic	100	12	2	3	69
1st	70	13	9	25	18
2nd	65	12	13	20	17
3nd	60	14	9	16	14

[a] Based on the initial cyclohexene moles.

3.5. Effect of the type of POM in the selectivity of the reaction products

The whole results obtained indicate that the $[PMo_{12}O_{40}]^{3-}$ anion, presents considerable advantages versus the $[PW_{12}O_{40}]^{3-}$ anion, exhibiting higher catalytic activity and a higher selectivity towards the adipic acid (product of superior oxidation state) due to the higher oxidizing power of Mo-containing anion compared with W-containing anion. In addition, the effect of the cation with which is combined the anion, also affects, not only the stability of the corresponding salt, but also the selectivity towards the desired reaction product. In this case, Cs^+ is the most suitable.

The reutilisation of the catalyst was analysed and the results are shown on Table 5. It can be seen that the selectivity of the catalyst, but not its activity, decreases after its use. This can be interpreted either as a decrease in the oxidising power of the active sites, after successive cycles, or those centres remaining, are characterised by a low oxidant capacity or high resistance to form the surface peroxo groups.

It must be remarked the relevant role of the acetic acid in the reaction medium, because both a decrease in the conversion and a low selectivity towards the desired reaction products are observed in the absence of this acid. These results, joined to those data compiled in Fig. 1 (higher stability of H_2O_2) demonstrate the necessity of the acetic acid for the reaction under study [19–22].

4. Conclusions

The obtained results indicate that the use of $[PMo_{12}O_{40}]^{3-}$ based heteropolysalts, due to their stronger oxidising power, lead, mainly, to the highest oxidation state product: adipic acid. In addition, the cation with which the anion is combined, affects not only to the stability of the corresponding salt, avoiding its solution during the catalytic reaction, but also to the selectivity.

The Cs^+ salt seems to be the most suitable.

It has been demonstrated the essential role played by acetic acid in the context of this reaction; it stabilises hydrogen peroxide against its decomposition and favours the selectivity towards the obtaining of adipic acid.

The peroxometallic intermediates, whose formation on the surface of the nanoparticles has been demonstrated by UV–vis and FT-Raman spectroscopic techniques, have been revealed as the real active sites of the reaction. Their existence allows us to explain the solubility of the catalysts during the course of the reaction as well. In this sense, the presence of large cations, up to a certain size, which still allows development of the porosity in the salts, results to be beneficial both for the occurrence of the reaction and the decrease of the solubility of the catalysts. The most appropriate cations seem to be caesium and quaternary amines.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata. 2014.07.023.

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