Cyclohexanone Oxidation over H₃PMo₁₂O₄₀ Heteropolyacid via Two Activation Modes Microwave Irradiation and Conventional Method

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Abstract

The adipic acid (AA), important precursor for Nylon production, was synthesized from cyclohexanoneoxidation by two ways, microwaves irradiation and conventional method (under reflux) using H₃PMo₁₂O₄₀ heteropolyacid as catalyst in the presence of hydrogen peroxide. In the order to increase the AA yield, several parameters as cyclohexanone/catalyst ratio, H₂O₂ concentration, solvent nature (H₂O, CH₃CO₂H, and CH₃OH, CHCl₃ and CH₃CN) and cyclohexanol addition to cyclohexanone were examined. For both activation modes, the highest AA yields are of 26-28%. Whereas, with microwaves irradiation, the time gain is much more attractive 30 min compared to 20 h. Copyright © 2019 BCRC Group. All rights reserved

Keywords: H₃PMo₁₂O₄₀ heteropolyacid; Oxidation; Hydrogen peroxide; Cyclohexanone; Adipic acid; Microwave irradiation

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1. Introduction

The adipic acid (AA), whose the production is more than 2 Mt/year, is a key intermediate particularly for the nylon 6,6 manufacture. Moreover, AA is used as an additive in cosmetics, gelatins, lubricants, fertilizers, adhesives, insecticides, paper, and waxes [1]. It is produced from oxidation of cyclohexanol or cyclohexanol/cyclohexanone mixture in the presence of nitric acid (50-60%) (Figure 1) [2-4]. This protocol presents serious environmental constraints due to the nitric acid reduction that leads to nitrous oxides gases (NOₓ). Among them, N₂O, the more toxic gas, is vented to the atmosphere with a proportion equivalent to that of adipic acid (1 N₂O mole/AA mole). It has been shown that N₂O

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contributes to the ozone layer destruction and to the greenhouse effect. Its potential effect, in global warming, is 310 times higher than that of CO₂ [5].

So, the development of a protocol for the AA synthesis that enters into the green chemistry field in the absence of co-catalyst, phase transfer compound and surfactant and in addition a reduction of energy consumption as alternative to the industrial protocol becomes a necessity. Thus, many attempts have been made to substitute nitric acid by oxidant less harmful and less corrosive as air, molecular oxygen or hydrogen peroxide. Among these oxidants, hydrogen peroxide is the most attractive for liquid phase oxidation processes, because it is easier to manipulate and in addition its reduction leads only to the water formation. However, its use requires an acidic medium that can come from an organic or inorganic acid, compound harmful to the environment [6,7].

The introduction of a catalyst as Keggin-type polyoxometalate (POM) possessing simultaneously acidic and redox properties, can overcome this disadvantage. On the other hand, these properties can modulate according to the elements nature constituting the POM and the reaction needs. Moreover, it was reported that put together, POM and H₂O₂ lead to the formation of peroxy species that are considered as the active species in the reactions as epoxidation of olefins [8,9], oxidation of alcohols [9-11] and aromatics [12,13].

In our previous studies, we have evidenced the important role of H₂O₂ in the process of the cyclohexanone oxidation in the presence of Keggin type phosphomolybdates. These latter are of yellow color at the oxidized state corresponding to Mo(VI). When, they oxidize the substrate, they become blue, attesting thus the reduction of the POM (Mo(VI) to Mo(V)). Hydrogen peroxide oxidizes in its turn the reduced POM to give “peroxo-POMₐ” species of yellow color indicating that the redox process is reversible. The peroxo-POMₐ species could be the active species in the adipic acid formation [14-16]. It is noted that the protons necessary to the H₂O₂ reduction come from the POM.

It is generally known that the use of microwave radiation in organic synthesis permits a gain of both reaction time and energy consumption compared to conventional method (heating reflux). To our knowledge, until now, the AA synthesis using the microwaves irradiation method was not reported in the literature. The challenge is to use it for the AA synthesis from cyclohexanone (-one) or cyclohexanone/cyclohexanol (-one/-ol) mixture, hydrogen peroxide as oxidant and H₃PMO₁₂O₄₀ as catalyst in free solvent.

2. Materials and Methods

2.1 H₃PMO₁₂O₄₀ Preparation

H₃PMO₁₂O₄₀ was prepared according to Tsikdinov’s method [22]. This latter passes through that of its disodium salt, Na₄HPMO₁₂O₄₀. The first step, the Na₄HPMO₁₂O₄₀ preparation was started. To a solution containing 145.15 g (0.6 mol) of Na₃MoO₄, 2H₂O [ACROS10102-40-6, 99%] dissolved in 210 mL of water, 4.1 mL of H₃PO₄(8.9 M) [MERCK 9031556, 75%] and 142 ml of HClO₄ (5.85 M) [FLUKA 342259-11194, 70%] were added. After cooling (exothermic reaction), Na₄HPMO₁₂O₄₀ precipitates. After filtration and drying, ca. 95 g of salt were recovered. In a second step, 95 g of Na₄HPMO₁₂O₄₀ are dissolved in 164 mL of acidified water with 41.5 mL of HCl (0.17M) [FLUKA 7647-01-0, 37%]. The solution is placed in a separating funnel with 150 mL of diisopropyl ether [PANREAC 200-467-2]. Three phases are formed, the densest contains the etherate of H₃PMO₁₂O₄₀ acid. After recovery of this phase, the solution is stirred at room temperature to remove the ether. After dissolving of solid in a minimum of water, H₃PMO₁₂O₄₀ acid is recovered in the form of translucent yellow crystals after ca. 24h (ca. 81 g).

2.2 H₃PMO₁₂O₄₀ Characterization

Infrared spectroscopy (1200-400 cm⁻¹) was performed on a Nicolet spectrophotometer, using diamond ATR technique. X-Ray diffraction patterns (XRD) were recorded at room temperature on a Siemens D5000 diffractometer equipped with copper anticathode Cu-Kα (λ = 1.5418 Å), the indexing of the diffraction lines and the identification of the phase were carried out using the EVA software which includes a High score database. Diffuse reflectance UV-Vis spectra were recorded at room temperature using a Perkin-Elmer Lambda 19 spectrometer in 0.1 cm quartz cell. Solution ³¹P NMR spectra were recorded on a Bruker AC 300 apparatus at 121.5 MHz. Chemical shifts were referenced to 85% H₃PO₄.

2.3 Catalytic Test

H₃PMO₁₂O₄₀ (PMO₁₂) was tested in liquid phase oxidation of cyclohexanone in the presence of H₂O₂ (30%) under conventional heating (CM) at 90 °C and under microwave activation (MI) at 100 watt. The oxidation of cyclohexa-
none leads to adipic, glutaric and succinic acids. In this work, we are interested only to adipic acid formation which is separated from the other products by cold crystallization (4 °C) [17].

Substrate and catalyst were introduced into a flask equipped with a reflux condenser for both conventional method and microwave irradiation heating. The reaction principle consists to oxidize the substrate by the catalyst. The reduction of catalyst is manifested by the passage from Mo(VI), yellow color of POM, to Mo(V), blue color characteristic of reduced POM "heteropolyblues". The reduced POM is then oxidized by hydrogen peroxide which in its turn reduced to water. It is noted that the color change was observed after about 10min and few seconds for conventional method and microwave irradiation heating, respectively. The reaction is finished when the POM catalyst is no longer reduced, indicating that the substrate was completely consumed. The mixture was cooled at 4 °C overnight and adipic acid was recovered as white crystals.

The purity of AA was verified by measure of its melting point (152 °C) and by its IR spectrum. The AA yield was calculated in Equation (1).

\[
\text{Yield}_{AA} (\%) = 100 \times \frac{w(\text{AA})_{\text{exp}}}{w(\text{AA})_{\text{the}}} 
\]

3. Results and Discussion

3.1 Catalyst Characterizations

IR spectrum of the fresh $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ heteropolyacid (Figure 2) shows the characteristic vibration bands of phosphorus-oxygen and metal-oxygen bonds of Keggin anion, [PMo$_{12}$O$_{40}$]$^{3-}$, in the spectral range, 1200-400 cm$^{-1}$ [18]. Thus, the characteristic vibration bands observed at 1066, 965, 870, and 789 cm$^{-1}$ correspond to $\text{n}_{\text{as}}$(P–O$_a$), $\text{n}_{\text{as}}$(Mo–O$_d$), $\text{n}_{\text{as}}$(Mo–O$_b$–Mo), and $\text{n}_{\text{as}}$(Mo–O$_c$–Mo), respectively.

The XRD diffractogram of the heteropolyacid (Figure 3) shows lines located at 2θ of 7.92, 8.90, 9.30, 27.78, 28.36, and 29.00°, showed characteristic of a triclinic structure corresponding to hydrate H$_3$PMo$_{12}$O$_{40}$.13H$_2$O [19]. The UV-Visible spectrum of H$_3$PMo$_{12}$O$_{40}$ (Figure 4) shows a large charge transfer band, metal-oxygen, with two components at 210 and 310 nm associated to the presence of different
of POM oxygen’s and to interanionic charge transitions [20,21].

3.2 Catalytic Results

The reaction of cyclohexanone oxidation to adipic acid, using conventional method (reflux heating) in the presence of Keggin-type phosphomolydates, has already been the subject of several studies [14-16,22-24]. In this work, microwaves irradiation (MI), as a new activation mode, was introduced to test the feasibility of this reaction using \( \text{H}_3\text{PMo}_{12}\text{O}_{40} \) (noted PMo_{12}) as catalyst.

Preliminary catalytic tests carried out with powers of 100, 180, and 300 watt and reaction times varying between 5 and 60 min, have showed that 100 watt and 30 min are the best parameters to obtain optimal AA yield. While, previous works performed under conventional heating mode have showed that 20 h is the required reaction time to obtain optimal AA yield [14-16,22-24]. These results evidenced that the use of microwaves irradiation permits to reduce reaction time from 20 h to 30 min and to reduce energy.

3.2.1 Cyclohexanone oxidation

Effect of PMo_{12} mass

In this work, the reaction of cyclohexanone oxidation to adipic acid was carried out for the first time under microwaves irradiation in the presence of PMo_{12} catalyst, already tested in conventional method (reflux heating). For comparison, Table 1 shows the obtained AA yields from CM and MI, as a function of the catalyst mass. The reaction time is of 20 h for CM and 30 min for MI and in the case of MI, the tests were realized about 7 times. The AA was recovered as crystallites with CM and as crystallites or gel with MI. The results show that the two modes lead to similar AA yields (26-32 and 26-27% for CM and MI, respectively) with increase of the catalyst mass from 0.03 to 0.09 g. With a catalyst mass of 0.12 g, the AA formation was not observed in the case of MI contrarily to that of CM (30% of AA yield). Under microwave irradiation heating, the reaction mixture (cyclohexanone and catalyst) becomes solid (gel) with a dark blue color, reflecting a strong reduction of the heteropolyacid. A strong temperature increase was hence observed (>140 °C), as result of the strong electronic interaction of catalyst with substrate. It was known that the POMs are reservoir of electrons. Therefore, the optimal catalyst mass that can be used for MI, must not exceeded 0.09 g for 30 mmol of substrate.

The gel dissolved in ethanol then crystallized in an aqueous medium presents a characteristic IR spectrum of AA (Figure 5). From these observations, it can be conclude that the microwave irradiation method can be used for

| Catalyst mass (g) | AA yield (%) | CM | MI |
|------------------|--------------|----|----|
| 0.03             | 28           | 26 |    |
| 0.06             | 26           | 26 |    |
| 0.09             | 32           | 27 |    |
| 0.12             | 30           | /  |    |

Table 1. Adipic acid yield (%) as a function of catalyst mass (Conditions: n-one: 30 mmol, \( \text{H}_2\text{O}_2 \): 30% (CM: \( \text{T}_{\text{react}} \): 90 °C, \( t = 20 \) h; MI: puissance: 100 watt, \( t = 30 \) min)

| \([\text{H}_2\text{O}_2] \) (%) | AA yield (%) | CM | MI |
|-------------------------------|--------------|----|----|
| 20                            | 16           | 12 |    |
| 30                            | 28           | 26 |    |
| 40                            | 22           | Gel|    |
| 50                            | 17           | Gel|    |

Table 2. Adipic acid yield (%) as function of \( \text{H}_2\text{O}_2 \) concentration (Conditions: \( m_{\text{cat}} \): 0.03 g, n-one: 30 mmol, (CM: \( T_{\text{react}} \): 90 °C, \( t = 20 \) h; MI: puissance = 100 watt, \( t = 30 \) min)

Figure 4. UV-Vis spectra of fresh \( \text{H}_3\text{PMo}_{12}\text{O}_{40} \)

Figure 5. IR Spectra of adipic acid obtained from MI (a) and CM (b) activation
the production of AA.

Effect of substrate amount

The AA yield variation as a function of the substrate amount (15–30 mmol) was reported in Figure 6. In the case of conventional method, an increase up to 30 mmol led to a strong AA yield decrease from 28 to 15% and under micro-wave irradiation, the AA yield is of ca. 26% whatever the one amount. From these observations, 30 mmol will used for the subsequent of the study.

Effect of H$_2$O$_2$ concentration

The results of the Table 2 show that the AA yields are similar for both activation modes with 12-16 and 26-28% for H$_2$O$_2$ concentrations of 20 and 30%, respectively. Up to, an AA yield decrease from 28 to 17% was observed for CM and in the case of MI, a gel was formed. The formation of this latter is one of the constraints encountered to determine correctly its yield. From these results, it can be concluded that a H$_2$O$_2$ concentration of 30% is the most appropriate.

Table 3. AA yield (%) as function of mixture composition -ol/-one (Conditions: $m_{cat}$ : 0.03 g, n-one: 30 mmol, H$_2$O$_2$ : 30% (CM: $T_{react}$ : 90 °C, $t$ = 20 h; MI: puissance: 100 watt, $t$ = 30 min))

| -one/-ol (%) | AA yield (%) |
|--------------|--------------|
|              | CM          | MI          |
| 100/0        | 28          | 26          |
| 75/25        | 20          | 21          |
| 50/50        | 14          | Traces      |
| 25/75        | 7           | Traces      |
| 0/100        | 0           | Traces      |

Figure 6. AA yield (%) as a function of the substrate amount under MI and CM activation modes ($m_{cat}$ : 0.03 g, H$_2$O$_2$ : 30% (CM: $T_{react}$ : 90 °C, $t$ = 20 h; MI: puissance = 100 watt, $t$ = 30 min))

Effect of solvent nature

The -one oxidation was carried out in the presence of protic (H$_2$O, CH$_3$CO$_2$H, and CH$_3$OH) and aprotic solvents (CHCl$_3$ and CH$_3$CN). The effects of the solvent nature and the activation mode on the AA yield were examined. For CM, the reaction time is 20 h and for MI, 30 min, Figure 7 shows that for both activation modes, similar AA yields (24-28%) were obtained in solvent free and in the presence of CH$_3$CN and also with CH$_3$COOH solvent (12-15%). Whereas, in the presence of solvents as H$_2$O, CHCl$_3$, and CH$_3$OH, the adipic acid formation was not observed. These results show that the highest AA yield (28% for CM and 26% for MI) was obtained without solvent, evidencing thus the green profile of the AA synthesis in our reaction conditions. The negative effect only observed with the protic solvents can be attributed to their action on the catalyst, either by fixing of its protons (the solvent would behave as a base) or by diluting the reaction medium, which would reduce the proton action of H$_3$PMo$_{12}$O$_{40}$, necessary for the activation of cyclohexanone which involves a tautomeric keton-enol equilibrium.

3.2.2 Cyclohexanone/cyclohexanol mixture oxidation

The effect of -one/-ol mixture composition on AA yield (Table 3) was also examined under reflux and microwave irradiation with different ratios (0/100, 25/75, 50/50, 75/25, 100/0). In the case of CM, a progressive AA yield decrease from 28 to 0% was observed when the alcohol percentage increases from 0 to 100%. Under MI, AA could only be quantified when the -one/-ol ratio is 75/25 (21% of AA yield). The obtained results evidenced the negative effect of the alcohol presence in the reaction mixture. Similar observations already reported by other
authors, have been attributed to its slower oxidation rate compared to that of ketone and probably to the formation of hydrogen bonds between the C=O group of the ketone and the hydrogen of the C–OH group of cyclohexanol that have for consequence to decelerate the oxidation process [2,3,14,15,22].

3.3 Characterization of the Used Catalyst

Figure 8 shows the obtained 31P NMR results before and after cyclohexanone oxidation carried out under MC. The observed peak at -4.4 ppm is characteristic of the heteropolyacid, H3PMo12. After oxidation reaction, two peaks appear at -5.52 and -3.14 ppm indicating the

![Scheme 1. Proposed mechanism of oxidative conversion of cyclohexanone by H3PMo12O40/H2O2](image)

![Figure 8. 31P NMR of H3PMo12O40 before (a) and after (b) cyclohexanone oxidation under CM activation mode](image)
formation of new species. It was already reported that in the presence of hydrogen peroxide, the POM leads to peroxo-species identified by $^{31}$P NMR as $[\text{PO}_{4}][\text{WO}(\text{O}_{2})_{2}]_{4}$ and $[\text{PO}_{4}][\text{WO}(\text{O}_{2})_{2}]_{2}$ in the case of the $\text{H}_{3}\text{PW}_{12}\text{O}_{40}$ [25-29]. It was also showed that the peroxo-species are in equilibrium with $[\text{PW}_{12}\text{O}_{40}]^{4-}$ during the substrate oxidation [30]. From these observations, it can be conclude that the peroxo-phosphomolybdates are the active species for adipic acid formation.

The cyclohexanone oxidation to AA passes through two intermediate stages of oxidation. The first concerns the substrate conversion into oxidation products by the POM. The reduction of this latter results of an oxygen atom transfer from POM to the substrate, accompanied by the reduction of Mo(VI) to Mo(V). It is admitted that only 2 atoms of Mo per Keggin anion, undergo a reduction. This first step is visualized by the change of color from yellow, characteristic color of POM in its oxidized form (POMox), to blue, characteristic color of the POM, in its reduced form (POMred). In the second step, H$_2$O$_2$ intervenes to oxidize simultaneously the reduced phase of the POM and to form peroxo-species (oxidized peroxo-POMox). It has been reported in several studies that transition elements with high oxidation states (V(V), Nb(V), Mo(VI), and W(VI)) have a high affinity towards H$_2$O$_2$ [31-35]. This has as for consequence the formation of peroxocomplexes highlighted by several techniques (X-ray diffraction, FTIR, and Raman spectroscopies). These complexes, with an oxidizing power stronger than that of H$_2$O$_2$, have been shown to be very active in several reactions [8-24,29]. In our case, we could admit that the reduced POM, from the first stage, oxidizes and simultaneously forms peroxocomplexes “peroxo-POMox”. These latter oxidizes in their turn the products coming from the first stage to more oxygenated compounds such as acids among them the adipic acid [36]. On the other hand, it is admitted that the protons of $\text{H}_{3}\text{PMo}_{12}\text{O}_{40}$ intervene for the cyclohexanone activation through a tautomeric keton-enol equilibrium. From all these observations, the plausible mechanism of AA synthesis, according with the literature [37] is represented on Scheme 1.

4. Conclusions

This study on the oxidation of cyclohexanone to adipic acid (AA) using two modes of activation, reflux heating and microwave irradiation, $\text{H}_{3}\text{PMo}_{12}\text{O}_{40}$ heteropolyacid as catalyst and hydrogen peroxide as oxidant, showed the negative effects of the addition of protic or aprotic solvent and cyclohexanol to cyclohexanone on AA yield. For both methods, the best AA yields (26-28%) were obtained in the absence of solvent, with H$_2$O$_2$ (30%) and 30 mmol cyclohexanone. The microwave mode allows a saving of time (30 min against 20 h) and significant energy compared to the conventional mode.

References

[1] Van de Vyver, S., Román-Leshkov, Y. (2013). Emerging catalytic processes for the production of adipic acid. Catal. Sci. Technol., 3: 1465-1479.

[2] Castellan, A., Bart, J.C.J., Cavallaro, S. (1991). Synthesis of adipic acid via the nitric acid oxidation of cyclohexanol in a two-step batch process. Catal. Today, 9: 285-299.

[3] Castellan, A., Bart, J.C.J., Cavallaro, S. (1991). Nitric acid reaction of cyclohexanol to adipic acid. Catal. Today, 9: 255-283.

[4] Kapteijn, F., Rodriguez-Mirasol, J., Moulijn, J.A. (1996). Heterogeneous catalytic decomposition of nitrous oxide. Appl. Catal. B: Env., 9: 25-64.

[5] Pérez-Ramüre, J., Kapteijn, F., Schöffel, K., Moulijn, J.A. (2003). Formation and control of N$_2$O in nitric acid production: Where do we stand today? Appl. Catal. B: Env., 44: 117-151.

[6] Jin, P., Zhao, Z., Dai, Z., Wei, D., Tang, M., Wang, X. (2011). Influence of reaction conditions on product distribution in the green oxidation of cyclohexene to adipic acid with hydrogen peroxide. Catal. Today, 175: 619-624.

[7] Shang, M., Noël, T., ang, Q., Su, Y., Miyabayashi, K., Hasebe, V.H.S. (2015). 2- and 3-Stage temperature ramping for the direct synthesis of adipic acid in micro-flow packed-bed reactors. Chem. Eng. 260: 454-462.

[8] Kholdeeva, O.A., Maksimchuk, N.V., Maksimov, G.M. (2010). Polyoxometalate-based heterogeneous catalysts for liquid phase selective oxidations: Comparison of different strategies. Catal. Today, 157: 107-113.

[9] Ishii, Y., Yamawaki, K., Ura, T., Yamada, H., Yoshida, T., Ogawa, M. (1988). Hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridinium chloride. Epoxidation of olefins and allylic alcohols, ketonization of alcohols and diols, and oxidative cleavage of 1,2-diols and olefins. J. Org. Chem., 53: 3587-3593.

Copyright © 2019, BCREC, ISSN 1978-2993
[10] Zhang, S.J., Zhao, G.D., Gao, S., Xi, Z.W., Xu, J. (2008). Secondary alcohols oxidation with hydrogen peroxide catalyzed by \([n-C_{65}H_{35}N(CH_3)_3]_2\)PMo12O40: Transform-and-retransform process between catalytic precursor and catalytic activity species. *J. Mol. Catal. A: Chem.*, 289: 22-27.

[11] Tundo, P., Romanelli, G.P., Vázquez, P.G., Aricò, F. (2010). Multiphase oxidation of alcohols and sulfides with hydrogen peroxide catalyzed by heteropolymolybdates. *Catal. Commun.*, 11: 1181-1184.

[12] Zhang, F.M., Guo, M.P., Ge, H.Q., Wang, J. (2007). Hydroxylation of Benzene with Hydrogen peroxide over Highly Efficient Molybdenophosphonic Heteropoly Acid Catalysts. *Chin. J. Chem. Eng.*, 15: 885-898.

[13] Zhao, P.P., Wang, J., Chen, G.J., Zhou, Y., Huang, J. (2013). Phase transfer hydroxylation of benzene with \(\text{H}_2\text{O}_2\) catalyzed by a nitrile-functionalized pyridinium phosphovanadomolybdate. *Catal. Sci. Technol.*, 3: 1394-1404.

[14] Mazari, T., Benadjji, S., Tahar, A., Dermeche, L., Rabia, C. (2013). Liquid phase synthesis of adipic acid using Keggin-type phosphomolybdates catalysts. *Mat. Sci. Eng.: B*, 3: 146-152.

[15] Tahar, A., Benadjji, S., Mazari, T., Dermeche, L., Marchal-Roch, C., Rabia, C. (2015). Preparation, characterization and reactivity of kagam type phosphomolybdates, \(\text{H}_3\text{S}_{2}\text{Ni}_{3}\text{PMo}_{12}\text{O}_{40}\) and \((\text{NH}_3)\text{S}_{2}\text{Ni}_{3}\text{PMo}_{12}\text{O}_{40}\), for adipic acid synthesis. *Catal. Lett.*, 145: 569-575.

[16] Moudjahed, M., Dermeche, L., Benadjji, S., Mazari, T., Rabia, C. (2015). Dawson-type polyoxometalates as green catalysts for adipic acidsynthesis. *Mol. Catal. A: Chem.*, 414: 72-77.

[17] Chavan, S.A., Srinivas, D., Ratnasamy, P. (2002). Oxidation of cyclohexane, cyclohexanone, and cyclohexanol to adipic acid by a non-\(\text{HNO}_3\) route over \(\text{Co/Mn}\) cluster complexes. *J. Catal.*, 212: 39-45.

[18] Rocchiccioli-Delcheff, C., Fournier, M., Franck, R., Thouvenot, R. (1984). Vibrational investigations of polyoxometalates. 4. valence force fields of anions related to the lindqvist structure. *J. Mol. Struct.*, 114: 49-56.

[19] D’Amour, H., Allmann, R. (1976). Ein Kegginkomplex mit erniedrigter Pseudosymmetrie in der struktur des \(\text{H}_3[\text{PMo}_{12}\text{O}_{40}]\) \((\text{15}-\text{14})\text{H}_2\text{O}\). *Kristallogr. Cryst. Mater.*, 143 (1-2).

[20] Mazari, T., Roch-Marchal, C., Hocine, S., Salhi, N., Rabia, C. (2010). Oxidation of propane over ammonium-transition metal mixed Keggin phosphomolybdate salts. *J. Nat. Gas Chem.*, 19: 54-60.

[21] Cavani, F., Etienne, E., Mezzegori, R., Pigamo, A., Trifirò, F. (2001). Improvement of catalytic performance in isobutane oxidation to methacrylic acid of Keggin-type phosphomolybdates by preparation via lacunary precursors: nature of the active sites. *Catal. Lett.*, 75: 99-105.

[22] Benadjji, S., Mazari, T., Dermeche, L., Salhi, N., Cadot, E., Rabia, C. (2013). Clean alternative for adipic acid synthesis via liquid-phase oxidation of cyclohexanone and cyclohexanol over \(\text{H}_3\text{S}_{2}\text{Co}_{3}\text{PMo}_{12}\text{O}_{40}\) catalysts with hydrogen peroxide. *Catal. Lett.*, 143: 749-755.

[23] Mouheb, L., Dermeche, L., Mazari, T., Benadjji, S., Essayem, N., Rabia, C. (2018). Clean adipic acid synthesis from liquid-phase oxidation of cyclohexanone and cyclohexanol using \((\text{NH}_4)\text{Al}_{3}\text{PMo}_{12}\text{O}_{40}\) \((\text{A}: \text{Sh}, \text{Sn}, \text{Bi})\) mixed heteropolysalts and hydrogen peroxide in free solvent. *Catal. Lett.*, 148: 612-620.

[24] Mouanni, S., Mazari, T., Benadjji, S., Dermeche, L., Marchal-Roch, C., Rabia, C. (2018). Simple and green adipic acid synthesis from cyclohexanone and/or cyclohexanol oxidation with efficient \((\text{NH}_3)\text{H}_2\text{M}_{3}\text{PMo}_{12}\text{O}_{40}\) \((\text{M}: \text{Fe}, \text{Co}, \text{Ni})\) catalysts. *Bull. Chem. React. Eng. Catal.*, 13: 386-392.

[25] Salles, L., Aubry, C., Thouvenot, R., Robert, F., Doremieux-Morin, C., Chottard, G., Ledon, H., Jeanin, Y., Bregault, P. (1994). \(13^P\) and \(13^S\)W NMR spectroscopic evidence for novel peroxy species in the \(\text{H}_3[\text{PW}_{12}\text{O}_{40}]\).cntdot.yH\(_2\text{O}/\text{H}_2\text{O}_2\) system. synthesis and x-ray structure of tetrabutylammonium \((\text{mu}_.\text{hydrogen phos})\) \((\text{mu}_.\text{peroxo})\)bis (oxoperoxoxygenate) \((2-)\): a catalyst of olefin epoxidation in a biphasic medium. *J. Inorg. Chem.*, 53: 871-878.

[26] Ducan, D.C., Chambers, C., Hecht, E., Hill, C.L. (1995). Mechanism and dynamics in the \(\text{H}_3[\text{PW}_{12}\text{O}_{40}]\)-catalyzed selective epoxidation of terminal olefins by \(\text{H}_2\text{O}_2\). formation, reactivity, and stability of \([\text{PO}_4\text{[WO}_{4}]_2\text{]})^4^+\). *J. Am. Chem. Soc.*, 117: 681-691.

[27] Kuznetsova, L.I., Kuznetsova, N.I., Maksimovskaya, R.I., Aleshina, G.I., Koscheeva, O.S., Utkin, U.V. (2011). Epoxidation of butadiene with hydrogen peroxide catalyzed by the salts of phosphotungstic anions: relation between catalytic activity and composition of intermediate peroxo complexe. *Catal. Lett.*, 141: 1442-1450.

[28] Mengs, L.Y., Zhai, S.R., Sun, Z.C., Zhang, F.Z., Xiao, Y., An, Q.D. (2015). Green and efficient synthesis of adipic acid from cyclohexene over recyclable \(\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{PEHA/ZrSBA-15}\) with platelet morphology. *Micro. Meso. Mat.*, 204: 123-130.
[29] Amitouche, D., Haouas, M., Mazari, T., Mouanni, S., Canioni, R., Rabia, C., Cadot, E., Marchal-Roch, C. (2018). The primary stages of polyoxomolybdate catalyzed cyclohexanone oxidation by hydrogen peroxide as investigated by in situ NMR. Substrate activation and evolution of the working catalyst. *Appl. Catal. A Gen.*, 561: 104-116.

[30] Zhang, S., Zhao, G., Gao, S., Xi, Z., Xu, J. (2008). Secondary alcohols oxidation with hydrogen peroxide catalyzed by \[n\cdot C_{16}H_{33}N(CH_{3})_{3}]_{3}PW_{12}O_{40}:\] Transform-and-retransform process between catalytic precursor and catalytic activity species. *J. Mol. Catal. A: Chem.*, 289: 22–27.

[31] Luisa-Ramos, M., Justinoa, L.L.G., Burrowsa, H.D. (2011). Structural considerations and reactivity of peroxocomplexes of V(V), Mo(VI) and W(VI). *Dalton Transactions.*, 40: 4374-4383.

[32] Bortolini, O., Conte, V. (2005). Vanadium (V) peroxocomplexes: Structure, chemistry and biological implications. *J. Inorg. Biochem.* 99: 1549-1557.

[33] Kamata, K., Kuzuya, S., Uehara, K., Yamaguchi, S., Mizuno, N. (2007). \[\mu\cdot n_1^{\prime}:n_1^{\prime}:-\text{Peroxotungstate} \] Catalytically Active for Epoxidation of Olefins. *J. Inorg. Chem.*, 46: 3768-3774.

[34] Barrio, L., Campos-Martin, J.M., Fierro, J.L.G. (2007). Spectroscopic and DFT study of tungstic acid peroxocomplexes. *J. Phys. Chem. A* 111: 2166-2171.

[35] Taube, F., Andersson, L, Toth, I., Bodor, A., Howarth, O., Pettersson, L. (2002). Equilibria and dynamics of some aqueous peroxomolybdate catalysts: a \[^{17}O\] NMR spectroscopic study. *Chem. Soc. Dalton. Trans.*, 4451-4456.

[36] Istadi, I., Amin, N.A.S. (2005). Co-generation of \[C_2\] Hydrocarbons and Synthesis Gases from Methane and Carbon Dioxide: A Thermodynamic Analysis. *Journal of Natural Gas Chemistry*. 14(3): 140-150.

[37] Vafaeezadeh, M., Hashemi, M.M. (2014). Simple and green oxidation of cyclohexene to adipic acid with an efficient and durable silica-functionalized ammonium tungstate catalyst. *Catal. Commun.*, 43: 169-172.