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# Euro Green Chemistry 2019-Cyclohexanone Oxidation over $H_3PMo_{12}O_{40}$ Heteropolyacid via Two Activation Modes Microwave Irradiation and Conventional Method-CHERIFA RABIA-Université Mouloud Mammeri

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**Introduction:**

The adipic acid (AA), whose the manufacture is supplementary than 2 Mt/year, is a key intermediate mainly for the nylon 6,6 manufacture. Moreover, AA is used as an additive in cosmetics, gelatins, lubricants, fertilizers, adhesives, insecticides, paper, and waxes .It is formed from oxidation of cyclohexanol mixture in the presence of nitric acid (50-60%). This protocol presents severe environmental causes due to the nitric acid lessening that leads to nitrous oxides gases (NOx). Among them, $N_2O$, the more toxic gas, is vented to the atmosphere with a proportion equal to that of adipic acid. It has been contribute to the ozone layer damage and to the greenhouse effect. It is an effect, in global warming, is 310 times more than that of $CO_2$.

So, the expansion of a protocol for the AA synthesis that enters into the green chemistry ground in the lack of co-catalyst, phase transfer compound and surfactant and in addition a lessening of energy consumption as another to the industrial protocol becomes a requirement. So many attempts have been made to substitute nitric acid by oxidant fewer harmful and fewer corrosive as air, molecular oxygen or hydrogen peroxide. Out of 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 usage requires an acidic medium that can come from an organic or inorganic acid, compound risky to the environment. The introduction of a catalyst as Keggin-type polyoxometalate possessing at the same time acidic and redox properties can conquer this disadvantage. Alternatively, these properties can alter according to the elements nature constituting the POM and the reaction needs. Moreover, it was reported that put together, POM and $H_2O_2$ lead to the development of peroxo species that are considered as the active species in the reactions as epoxidation of olefins oxidation of alcohols and aromatics.

In our earlier studies, we have evidence the important role of H2O2 in the procedure of the cyclohexanone oxidation in the incidence of Keggin type phosphomolybdates. These latter are of yellow color at the oxidized state corresponding to Mo(VI). When, they oxidize the substrate, they turn out to be blue, attesting thus the lessening of the POM (Mo(VI) to Mo(V)). Hy-drogen peroxide oxidizes in its revolve the reduced POM to give "peroxo-POMox" species of yellow color representing that the redox process is reversible. The peroxo-POMox" type could be the active variety in the adipic acid formation. It is most important that the protons necessary to the H2O2 lessening come from the POM. It is usually known that the use of microwave radiation in organic synthesis permit a gain of both reaction time and energy utilization compared to conventional method (heating reflux). As of our knowledge, in anticipation of now, the AA synthesis using the microwaves irradiation method was not reported in the literature.

**Materials and methods**

**$H_3PMo_{12}O_{40}$ Preparation:**

$H_3PMo_{12}O_{40}$ was organized according to Tsig-dinos's method. This latter flow through that of its disodium salt, $Na_2HPMo_{12}O_{40}$. The primary step, the $Na_2HPMo_{12}O_{40}$ preparation started. To a solution containing 145.15 g (0.6 mol) of $Na_2MoO_4$. $2H_2O$ [ACROS10102-40-6, 99%] dissolved in 210 mL of water, 4.1 mL of $H_3PO_4$ (8.9M) [MERCK 9031556, 75%] and 142 ml of $HClO_4$ (5.85 M) [FLUKA 342259-11194, 70%] were added.

After filtration and drying, ca. 95 g of salt were improved. In a second step, 95 g of $Na_2HPMo_{12}O_{40}$ are dissolved in 164 mL of acidified water with 41.5 mL of HCl (0.17M) [FLUKA 7647-01-0, 37%]. The solution is kept in a separating funnel with 130 mL of diisopropyl ether [PANREAC 200-467-2]. Three processes are formed; the densest contains the etherate of $H_3PMo_{12}O_{40}$ acid. After improvement of this phase, the solution is stirred at room temperature to remove the ether.

**Results and Discussion**

**Catalyst Characterizations:**

IR spectrum of the fresh $H_3PMo_{12}O_{40}$ heteropolyacid shows the quality vibration bands of phosphorus-oxygen and metaloxygen bonds of Keggin anion, $[PMo_{12}O_{40}]^{3-}$, in the spectral variety, 1200-400 cm-1. Then, the characteristic vibration bands noticed at 1066, 965, 870, and 789 cm-1 correspond to nas(P–Oa), nas(Mo–Od), nas(Mo–Ob–Mo), and nas(Mo–Oc–Mo), respectively. The XRD diffractogram of the heteroployacid performance lines situated at 2θ of 7.92, 8.90, 9.30, 27.78, 28.36, and 29.00°, showing characteristic of a triclinic structure equivalent to hydrate $H_3PMo_{12}O_{40}.13H_2O$.

**Catalytic Results:**

The reaction of cyclohexanone oxidation to adipic acid, by means of conventional method (reflux heating) in the presence of Keggin-type phos-phomolydates, has already been the subject of several studies. In this job, microwaves irradiation (MI), as novel activation mode, was initiate to test the availability of this reaction using $H_3PMo_{12}O_{40}$ (noted $PMo_{12}$) as catalyst.

This work is partly presented at 10th World Congress on Green Chemistry and Technology, July 10-11, 2019, Paris, France.

Preliminary catalytic tests approved out with powers of 100, 180, and 300 watt and reaction times changeable between 5 and 60 min, have showed that 100 watt and 30 min are the best parameters to get optimal AA results. While, previous works perform under conventional heating mode have showed that 20 h is the required reaction time to get optimal AA results. These results evidence that the use of microwaves irradiation permits to decrease reaction time from 20 h to 30 min and to decrease energy.

The cyclohexanone oxidation to AA flows through two mediate stages of oxidation. The first concerns the substrate change into oxidation products by the POM. The decrease of this later results of an oxygen atom transfer from POM to the substrate, accompanied by the decline of Mo(VI) to Mo(V). It is admitted that only 2 atoms of Mo per Keggin anion, undergo a reduction.

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