



## Influence of Reaction Conditions on the Catalytic Oxidation of Cyclohexene with Molecular Oxygen Using a Series of Keggin-Type Polyoxometalate

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### ABSTRACT

A series of kegginn-type polyoxometalates namely;  $H_3PMo_{12}O_{40}$ ,  $H_3PW_{12}O_{40}$ ,  $Fe_{1.5}PW_{12}O_{40}$  and  $Co_{1.5}PW_{12}O_{40}$  were prepared, characterized and tested for the oxidation of cyclohexene by molecular oxygen in acetonitrile medium. The oxidation gives 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexene oxide, however, 2-cyclohexen-1-one was the major product. The  $Co_{1.5}PW_{12}O_{40}$  catalyst showed the highest catalytic activity for the oxidation reaction and it was chose to study the effect of varying  $O_2$  pressure, time, temperature and catalyst weight. The highest percentage of cyclohexene conversion and selectivity of the major product 2-cyclohexen-1-one was obtained at 5bar of  $O_2$  pressure, 4h, 70 °C, and 900mg of  $Co_{1.5}PW_{12}O_{40}$  catalyst.

**Key words:** Polyoxometalate, cyclohexene, molecular oxygen, catalytic oxidation, Reaction conditions.

### INTRODUCTION

Allylic oxidation of olefins is a very attractive processes for the obtention of  $\alpha,\beta$ -unsaturated alcohols and ketones which are important transformation due to the presence of a highly reactive carbonyl group. In particular the oxidation products of cyclohexene (CyH) has an important position among the oxidation of olefinic compounds. Cyclohexene is a raw material to produce fine chemicals since its allylic products i.e. 2-cyclohexen-1-ol, 2-cyclohexen-1-one have a

great importance in industrial processes and find several applications as intermediates for the manufacture of useful chemicals<sup>1-5</sup>. 2-cyclohexen-1-ol (enol) is important in natural product synthesis and it can converted to phenol without co-products. 2-cyclohexen-1-one (enone) has its main industrial application in the synthesis of medication, pesticides, insect pheromone and adipic acid which used in the production of nylon-6. The epoxidation product of cyclohexene i.e. cyclohexene oxide (epoxy) is also a key intermediate in synthesis of fine chemicals, its importance come from high

reactivity due to the opening of the highly strained three-membered ring. Therefore, it is of great interest to develop a more efficient catalyst for the cyclohexene oxidation process.

Several transition metal compounds have been employed as catalysts such as Polyoxometalates (POM). POM are molecular metal-oxygen clusters with discrete structures, they have gained importance due to their distinctive electrochemical, magnetic, medicinal and catalytic properties. Catalysis is the most significant domains of interest due to POMS properties such as oxidative stability, adjustable oxidation states, possible activation of various oxidants and inherent acidity<sup>6,7</sup>. The oxidation and acid functions of POMS are of great importance in catalysis, because the redox and acidic properties can be controlled at atomic or molecular levels<sup>8-10</sup>.

The use of molecular oxygen O<sub>2</sub> as oxidant is considered to be green since no toxic by-products are produced in these reactions. O<sub>2</sub> is a cheap and green oxidant, it is more readily convenient oxidant for the oxidation reactions but it is relatively unreactive toward the strong bonds of C-H and C=C unless activated by highly effective catalysts or severe reaction conditions<sup>2,11,12</sup>.

In this paper the oxidation of cyclohexene using O<sub>2</sub> as an oxidizing agent in the presence of POM was studied. The effect of O<sub>2</sub> pressure, temperature, time, and catalyst weight on conversion and selectivity were also investigated.

## EXPERIMENTAL

### Preparation of the catalysts

The heteropolytungstate Co<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub> (CoPW), Fe<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub> (FePW) were prepared from 12-tungstophosphoric acid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. The H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (HPW) and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (HPMo) acids were prepared according to the method of Deltcheff *et al.*<sup>13</sup>. The salt forms were obtained from their counterpart heteropolyacids, as precipitate by adding slowly the required amount of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (to neutralize the three protons) to the aqueous solution of the heteropolyacid, and then the required amount of MSO<sub>4</sub>·XH<sub>2</sub>O was added (M=Co,Fe). After eliminating the formed BaSO<sub>4</sub> precipitate, the

obtained solution was allowed to stand for few days at 40°C. The salt was recovered from the solution by filtration.

### Catalytic measurement

The reactions were conducted in a stainless steel autoclave equipped with magnetic stirring. The autoclave was thermostated by circulating water which was pumped from a thermostat adjusted at the required temperature. The typical reaction procedure unless otherwise stated was: 10 mL of cyclohexene, 5 mL acetonitrile (solvent) and 200 mg of CoPW catalyst were charged into the autoclave. A 5 bar pressure of O<sub>2</sub> was injected into the autoclave and the system was stirred and heated at 70 °C for 4h.

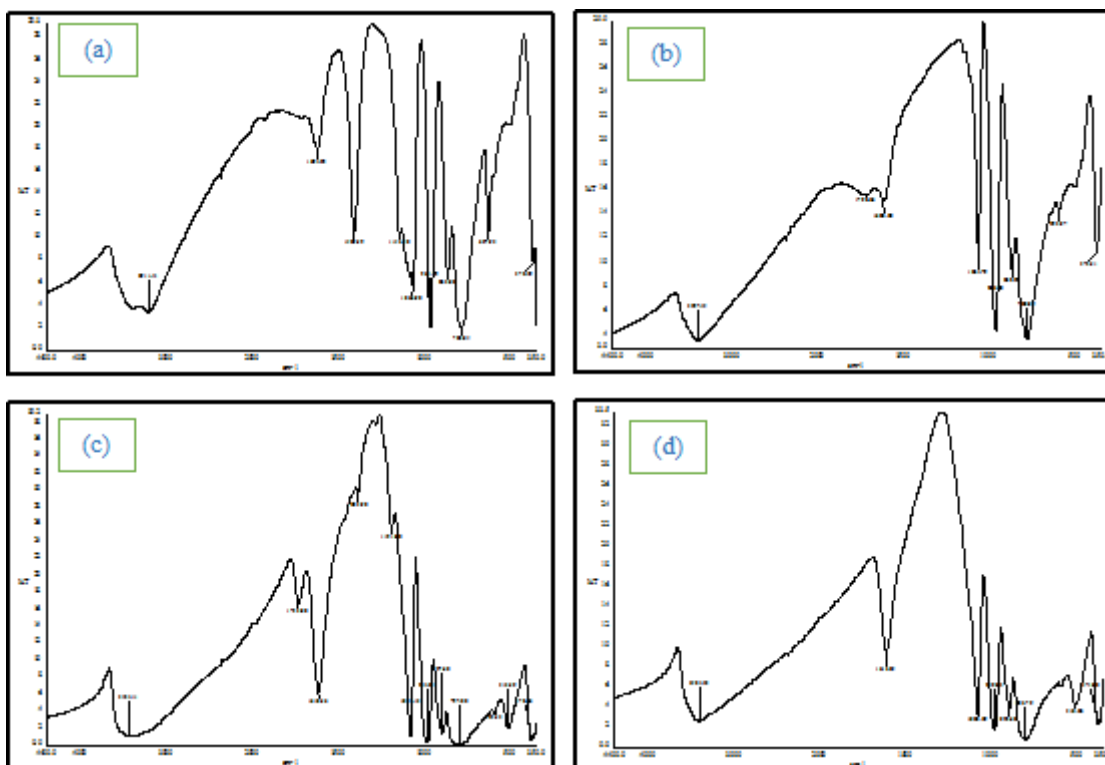
The resulting solution was analyzed with a PYE UNICAM gas chromatograph equipped with a flame ionization detector and a capillary column (HP-PLOT Q 30 m length and 0.53 mm internal diameter). The detector and injector temperature was set at 250°C and the total run time was 50 min. The identification of the oxidation reaction products was achieved occasionally by Gas Chromatography coupled with a mass selective detector (GC-MS). A Thermo Trace GC Ultra gas chromatograph equipped with AI 3000. For the separation of target compounds, a TR-5 MS-SQC capillary column (30 m length x 0.25 mm internal diameter, phase thickness 0.25 μm) was used with helium as the carrier gas (at a flow rate of 1 ml/min) and the products standard peaks were identified by the device software. From the GC/MS, the oxidation products of cyclohexene (CyH) were two major products 2-cyclohexen-1-one (enone) and 2-cyclohexen-1-ol (enol) and cyclohexene oxide (epoxy) as minor product.

## RESULTS AND DISCUSSION

### Characterization of POM catalysts

Fourier transform infrared (IR) spectra of the samples were recorded with a Shimadzu FTIR Spectrometer 8400S. The IR spectra of the HPW, HPMo, CoPW and FePW catalysts are shown in Fig. 1. The majority of the characteristic bands of the Keggin POM structure are found in the fingerprint region between 500-1200 cm<sup>-1</sup><sup>13,14</sup>. The vibrations were observed in the following spectral regions:

- The stretching vibration of the central  $\text{PO}_4$  tetrahedron at  $\sim 1080 \text{ cm}^{-1}$ .
- Stretching vibration involving the central M atom and the terminal O atom ( $\text{M}-\text{O}_t$ )  $\sim 980 \text{ cm}^{-1}$  where (M=W or Mo).
- $\text{M}-\text{O}_b$ -M bridges (inter bridges between corner sharing octahedral)  $\sim 890 \text{ cm}^{-1}$
- $\text{M}-\text{O}_e$ -M bridges (inter bridges between edge sharing octahedral) i.e. inside a  $\text{M}_3\text{O}_{13}$  set  $\sim (800-790 \text{ cm}^{-1})$



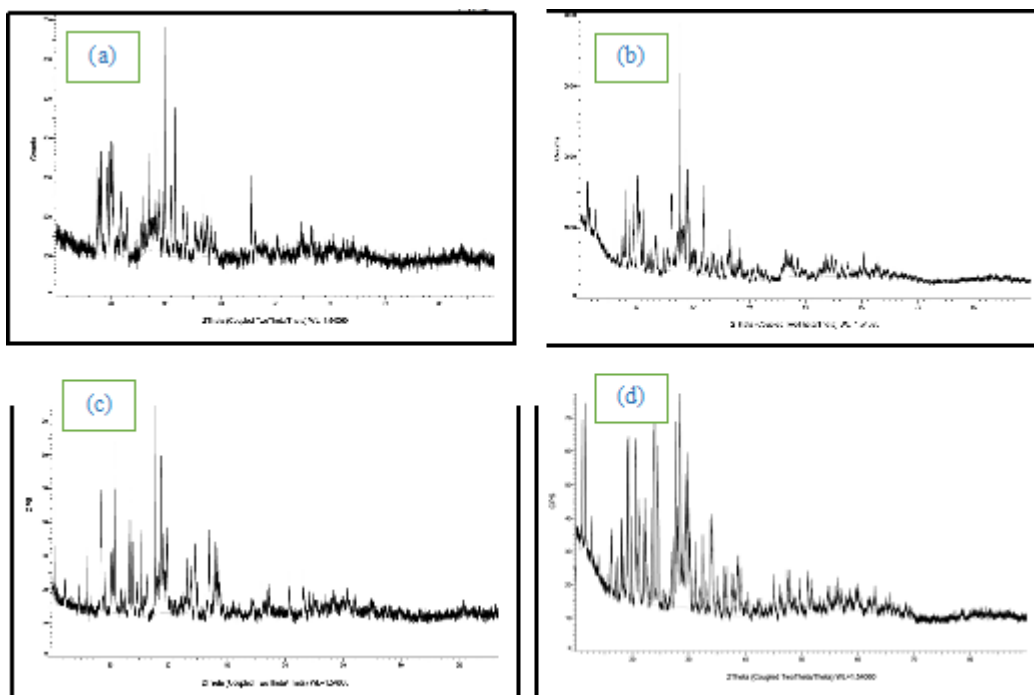
**Fig. 1: IR Spectra for a) HPW, b) HPMo, c) CoPW and d) FePW**

The powder X-ray diffraction (XRD) patterns were obtained on Siemens D5000 diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 0.15418 \text{ nm}$ ) radiation. The X-ray diffractograms of HPW, HPMo, CoPW and FePW are illustrated in Fig. 2. The results showed the presence of diffraction peaks at  $2\theta$  ranging in ( $7^\circ$ – $10^\circ$ ), ( $16^\circ$ – $23^\circ$ ), ( $25^\circ$ – $30^\circ$ ), and ( $31^\circ$ – $38^\circ$ ). These diffraction characteristic peaks ranges can be assigned to POM having keggin structure<sup>15</sup>. The diffractograms of HPW and HPMo show that the solids exhibited a degree of crystallinity. The substitution of the protons by cobalt and iron ions increased the intensity of almost all diffraction peaks of acid. The XRD pattern suggests that the 12-tungsto-phosphoric acid secondary structure undergoes structural transformation when the acidic protons are replaced by cobalt and iron cations. This might be due to the fact that the most of the

sandwiched water molecules in the form of  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  interacting with Keggin polyanions by hydrogen bonding are lost<sup>15-18</sup>. This type of interactions is known to make structural transformations that can be detected by powder X-ray diffraction<sup>19</sup>.

#### **Effect of Catalyst Type (Addenda and Counter Ions)**

POM generally consist of W and Mo as addenda atoms. Due to the high valence of these elements, POM can act as effective catalysts for the oxidation reaction. The large positive charge of the metal make these compounds capable of accepting electron pairs in vacant d orbitals and form stable  $\text{M}=\text{O}$  complex with  $\text{O}_2$ <sup>20,21</sup> which make the oxygen atom more electrophilic and therefore readily attacked the reaction site which results in the



**Fig. 2: XRD for a) HPW, b) HPMo, c) CoPW and d) FePW**

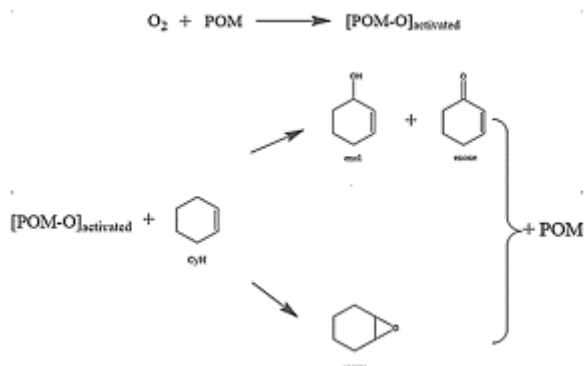
oxidation to form products. The general reaction pathway is presented in **Scheme 1**. The allylic oxidation and epoxidation are competitive process in the oxidation of CyH and often occurs simultaneously<sup>2,12</sup>. Previous studies have revealed that for the catalytic oxidation of CyH the abstraction of the allylic hydrogen to give allylic oxidation products is easier compared to its epoxidation.

For the investigation of the effect of the addenda atoms (Mo and W) on cyclohexene oxidation, the catalytic behaviors of HPMo and HPW heteropolyacids were compared. The results of the conversion and the product distribution are depicted in Fig.3. It can be seen that the catalyst having W as an addenda atom in HPW is more active than the catalyst that has Mo as an addenda atom HPMo. In fact, the conversion obtained over HPW (35%) was higher than that obtained over HPMo (27%). This is because that the peroxotungstate species, generated by the reaction of HPW with O<sub>2</sub> is catalytically very active. As for the selectivity the results showed that Mo addenda atoms form more enone (59.2%) than W addenda atoms (51%), the enone formation obtained by HPMo higher than that obtained by HPW is due to the fact that the potential

redox of Mo is higher than W one. Whereas, W elements form epoxide (11.6%) while Mo (0%) did not these results suggest that acid character of the W catalyst which is more than Mo leads to the epoxide<sup>9,22</sup>. For the enol compound it was formed by both Mo and W elements with almost the same selectivity.

The effect of the counter cation (H<sup>+</sup>, Co<sup>2+</sup> and Fe<sup>2+</sup>) on the cyclohexene oxidation has been achieved by comparing the catalytic behavior of HPW, CoPW and FePW. As shown in Fig.3, it can be seen that the substitution of the protons by the cobalt or by the iron cations, both the conversion and the selectivity for enone and enol (allylic products) were increased in decrement of the epoxide. This was agreed with previous published data<sup>12</sup> which usually used catalysts based on cobalt, iron and copper for allylic oxidation of olefins.

Since the POMs catalyst having Co as a counter cation and W as addenda atoms was found to be the best catalyst of the tested series, CoPW was selected for further investigations.



Scheme 1: Suggested reaction pathway for cyclohexene oxidation by  $O_2$  in the presence of POM

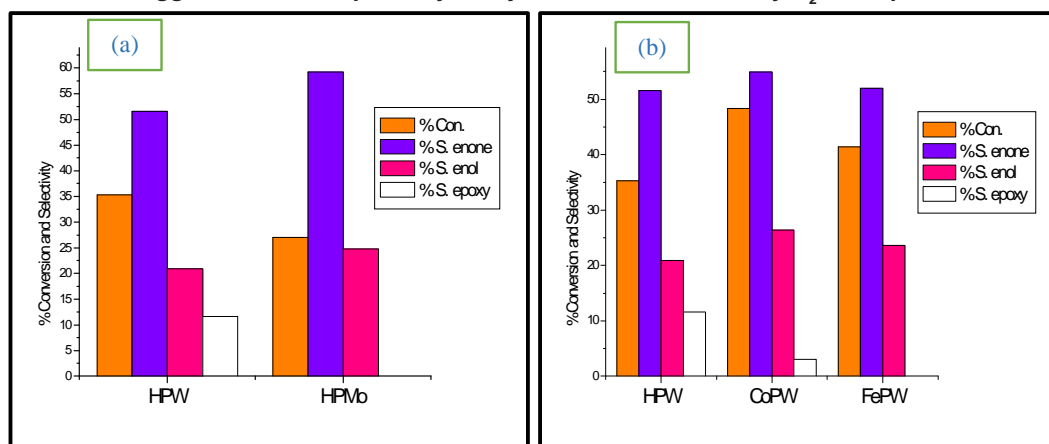


Fig. 3 (a): Effect of the addenda atom (W, Mo) on CyH conversion and products selectivity, b) Effect of the counter cation ( $H^+$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ) on CyH conversion and products selectivity.

#### Effect of Catalyst Weight

As seen in Fig. 4 when the weight of the catalyst increased from 200mg - 900mg the conversion increase from 53% to 98%. This suggests that CoPW functions as an active site for the oxidation and with the increase of catalyst amount the number of active sites available for the reaction to progress increases<sup>23</sup>. Since CoPW catalyst prefers to form enone (Fig. 3), when the CoPW weight increases a gradual increase in enone and decrease in enol selectivity were also noticed, while for epoxy no significant change in its selectivity was observed. An experiment without catalyst (blank run) was carried out and no conversion was obtained which indicates that  $O_2$  by itself will not aid the oxidation of CyH in the absence of catalyst.

#### Effect of $O_2$ Pressure

Upon increasing the oxygen pressure  $P(O_2)$  from 1 - 5 bar the oxidation of CyH improved

from 29% to 53% (Fig. 4). The presence of excess oxidant favored further oxidation and when  $P(O_2)$  increases the concentration of the active species (catalyst + oxidant) increases and as a consequence the rate will increase. For the products selectivities (Fig. 5), it can be seen that the  $O_2/CoPW$  system prefers to attack the allylic bond in CyH to form enone and enol rather than the C=C bond to form epoxy. There is a slight increase in the selectivity of the major product enone; a maximum value was achieved at  $P(O_2) = 5\text{ bar}$  while for enol and epoxy a decrease in selectivity was observed due to further oxidation to other products.

#### Effect of Reaction Time

The reaction was carried out at different periods (0.5, 1, 2, 3 and 4 h), generally the conversion of CyH increases with time and this is due to the reason that more time is required for the formation of reaction intermediates (substrate

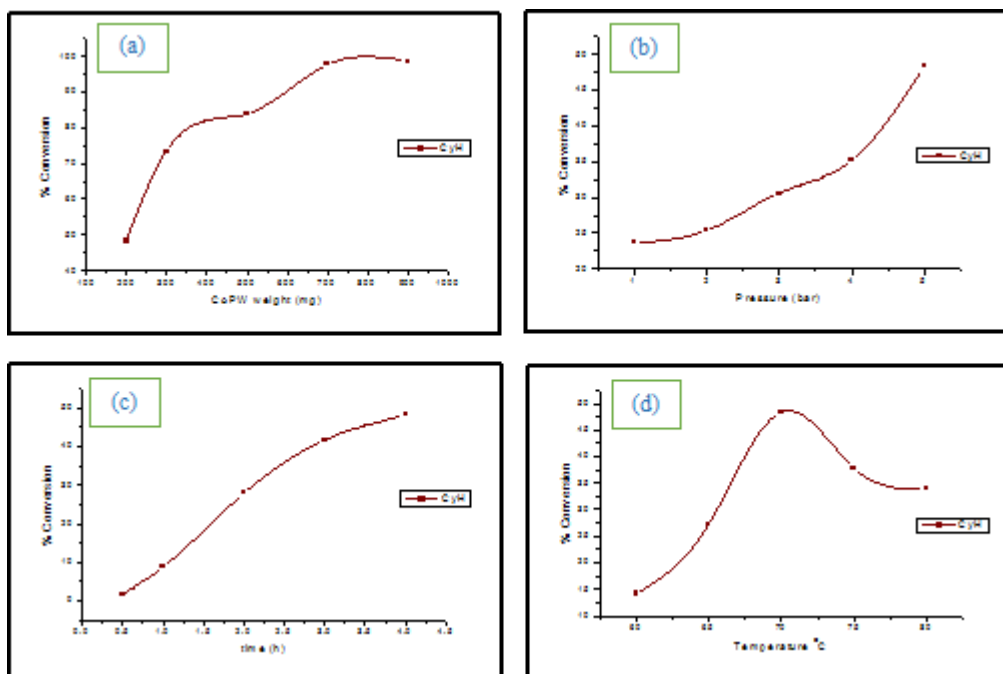


Fig. 4: Effect of reaction conditions on CyH conversion, (a) catalyst weight, (b) O<sub>2</sub> pressure, (d) time and (c) temperature

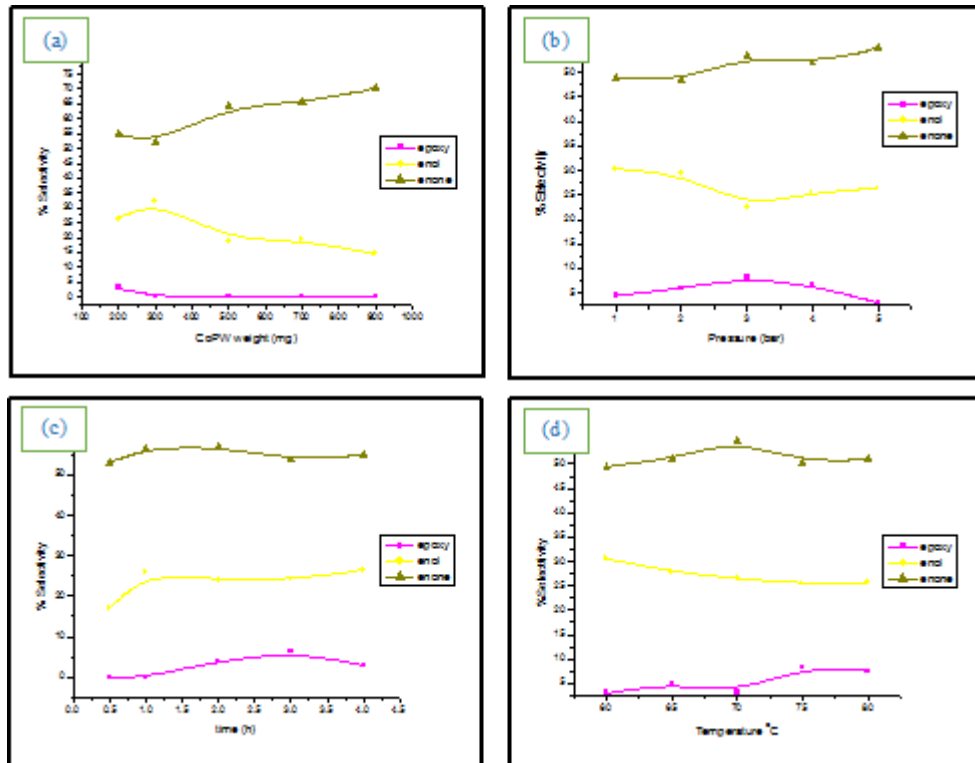


Fig. 5: Effect of reaction conditions on products selectivity, (a) catalyst weight, (b) O<sub>2</sub> pressure, (d) time and (c) temperature.

+catalyst) which is finally converted to the products. As for the selectivity of the products there is a slight increase with time. The results also show that the O<sub>2</sub>/CoPW prefer mostly to attack allylic bond in CyH to form enone and enol and thus limit the C=C epoxidation products i.e. epoxy.

#### Effect of Reaction Temperature

The conversion of CyH was increased almost linearly with temperature up to 70 °C and a further increase in temperature resulted in the decrease of CyH conversion Fig. 4. Since the CoPW is thermally stable the decrement in conversion at reaction temperature above 70 °C was not due to the catalyst decomposition. The oxidation of CyH well increase with temperature from 60 to 70 °C and this agree with the view point of kinetic. The decrease of conversion after 70 °C may be due to that most reactions with O<sub>2</sub> gives a considerable amount of heat and the increase of reaction temperature is unfavorable from the view point of thermodynamic.

As for the selectivity Fig. 5 it remains almost steady for enone and enol but it increased up for epoxy beyond 70°C, this may be related to the activation energy of C=C i.e. higher temperature reaction favor reaction with higher activation energy.

#### CONCLUSION

For the oxidation of CyH by O<sub>2</sub> in acetonitrile it was found that all these catalysts HPW, HPMo, FePW and CoPW led to enone, enol and epoxy. The results showed that W addenda atoms and Co<sup>2+</sup> counter cations was the best for the CyH conversion and the enone formation. The effect of various reaction conditions showed that there was a slight change in the products selectivity and enone was the major product in all cases. The best conversion of CyH and selectivity for enone were obtained at P(O<sub>2</sub>)=5bar, 4h, 70°C, and 900mg of CoPW catalyst.

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