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Activated carbon supported $Co_{1.5}PW_{12}O_{40}$ as efficient catalyst for the production of 1, 2 cyclohexane diol by oxidation of cyclohexene with H_2O_2 in the presence of CO_2

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ABSTRACT

Vicinal diols are important building blocks for chemicals and pharmaceuticals. Currently, they are produced from olefins using solvents and harmful oxidants unfavorable from an environmental and economic point of view. This work lies on the synthesis of 1,2 cyclohexane diol from cyclohexene by a green route. To achieve it, a series of Cobalt Keggin heteropolyanion salt ($Co_{1.5}PW_{12}O_{40}$) loaded on activated carbon with different contents was prepared, characterized and tested for the synthesis of diol. The effect of various parameters such as reaction temperature, reaction time and CO_2 pressure on the reaction was studied. The effect of reaction temperature in the range 60-80 °C showed that high temperatures favor diol formation while low temperatures favor cyclohexanone and a segmented concave Arrhenius graph was observed. The results of this work showed that oxidation by H_2O_2 in the presence of CO_2 is an efficient oxidant system for the production of 1.2 cyclohexane diol over carbon activated carbon supported $Co_{1.5}PW_{12}O_{40}$. Thanks to CO_2 as a soft oxidizing agent, a conversion of 96.9% and a selectivity in 1, 2 cyclohexane diol of 64.2% was obtained. This simple, safe and environmentally method could be an alternative green route for vicinal diols production from alkenes.
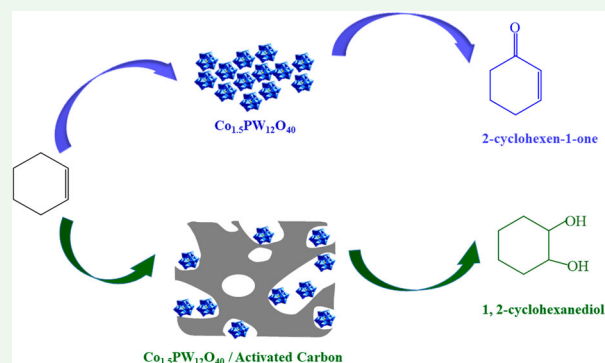
Introduction

Diols are considered to be useful intermediates because of the various potential applications of the products obtained. In particular, vicinal diols are used as basic elements in the synthesis of pharmaceutical products (*1,2*), cosmetics, (*3*), carbonyl compounds (*4*) and liquid crystals (*3*). They are also used as auxiliaries for asymmetric synthesis (*5*). Consequently, several methods for their synthesis such as reduction of ketones and hydroxy α-diketones, hydrolysis of epoxides and oxidation of olefins have been reported (*6–10*). However, in these methods, several steps are performed, solvents and hazardous substances as oxidants such as OsO_4/N-methylmorpholine-N-oxide, $RuCl_3$ / $NaIO_4$, $KMnO_4$ and organometallic complexes have been used (*9,11,12*). $KMnO_4$ was generally used in excess and this leads to the formation of several undesirable by-products (*12*). The OsO_4/co-oxidant system is considered to be the most effective. Unfortunately, the high cost and toxicity are the main disadvantages for industrial application and from the point of view of green chemistry (*13*). It is worth remembering that the growing demand for diols and the environmental concerns require the use of heterogeneous and an environmentally catalytic systems and oxidant agents. A process using environmentally friendly reagents such as H_2O_2 and O_2 in the oxidation

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of olefins is highly appreciated. Both are clean and cheap but it is evident that O_2 is the ideal oxidant to be used. However, O_2 is rarely used because it is kinetically inert and requires harsh conditions of temperature and/or pressure to be activated (*14*). H_2O_2 is a highly efficient oxidant with an active oxygen content of 47.1 wt% (*15*) but it can decompose dangerously if used in high concentrations. Its decomposition must be controlled because the reaction produces gaseous oxygen and heat (100.4 kJ / mol). H_2O_2 is considered as a green oxidant because it only produces H_2O as a by-product. This is why it is widely used in the chemical industry and in environmental protection (*16–18*). Although many reactions can be obtained using O_2, the use of H_2O_2 as an oxidant has the advantage of carrying out reactions under milder conditions. Although the oxidation of olefins is often inefficient because various products could be obtained along at higher conversions, an appropriate choice of the catalyst and oxidant system can orient the oxidation towards the desired product with an optimal conversion and selectivity. Therefore, it would still be highly desirable to develop a new efficient and clean method for the dihydroxylation of olefins. Dalmizrak et al (*9*) have used $KMnO_4/H_2O_2$ oxidant system in a water-acetone mixture for the dihydroxylation of olefins. In the opinion of the authors, using H_2O_2 as a co-oxidant is primordial to synthesize vicinal cis-diols with a high yield. In the present research work, an easy, safe and green method for the synthesis of 1, 2-cyclohexanediol by dihydroxylation of cyclohexene was reported. The synthesis was achieved by using H_2O_2 in the presence of CO_2 as soft oxidant under mild reaction conditions. The reaction was catalyzed over activated carbon-supported $Co_{1.5}PW_{12}O_{40}$ in a solvent-free reaction. The CO_2 / H_2O_2 mixture was selected as the oxidizing system because it has been reported that in this mixture, the percarbonate entity HCO_4^- can be formed by reaction between CO_2 and H_2O_2 and this percarbonate species is responsible for the transfer of oxygen to alkenes (*19*). Moreover, chemistry of CO_2 has become a more attractive area of research. It is cheap, nontoxic and it is considered as an alternative and economical feedstock (*20,21*). Hydrogen peroxide is a very attractive green oxidant, as H_2O is the by-product (*22–24*). Therefore, our method using CO_2 / H_2O_2 as oxidizing system is a greener approach compared to the usual oxidation methods used. In fact, in most of the many important industrial processes, a very undesirable, highly toxic by-product is released into the environment. Hydrogen peroxide (H_2O_2) does not have these inherent problems. It is considered as an important chemical in environmentally friendly methods in the chemical industry (*25–29*). Thus, this research work is a novel protocol for the practical

and green synthesis of vicinal diols compared to the usual methods.

Experimental

Materials

Activated carbon (activated decolorizing powder) and $CoSO_4.7H_2O$ from British Drug Houses Ltd (BDH) Chemicals Ltd, Poole, England. Sodium tungstate, $Na_2WO_4.2H_2O$ (98% purity) and H_2O_2 (30% in aqueous solution) were obtained from WINLAB. Cyclohexene (> 99.5%) was purchased from BDH. All other chemicals were of analytical grade and used as received.

Preparation of the catalysts

$Co_{1.5}PW_{12}O_{40}$

$H_3PW_{12}O_{40}$ heteropolyacid acid was prepared according to the well-known method described in the literature (*30*). The $Co_{1.5}PW_{12}O_{40}$ salt (noted CoPW) was prepared from the heteropolyacid by replacing the three protons with the cobalt cation (Co^{2+}). Typically, a desired amount of $H_3PW_{12}O_{40}$ was dissolved in water and the required amount of $Ba(OH)_2.8H_2O$ (to neutralize the three protons) was added slowly to the aqueous solution of heteropolyacid under stirring. Then, after the required amount of $CoSO_4.7H_2O$ was added and the $BaSO_4$ formed was removed by filtration. The resulting solution was allowed to stand for a few days at 4 °C for crystallization of the CoPW salt.

Immobilization of $Co_{1.5}PW_{12}O_{40}$ on activated carbon

The activated carbon (AC) used as a support has been oxidized by nitric acid to create oxygenated groups allowing the fixation of the CoPW heteropolyanions. The procedure is as follows: A mass of 0.1 g of carbon suspended in 100 ml of nitric acid (65%) was heated for 5 h at 80°C and then cooled to room temperature. The oxidized carbon was then washed several times with deionized water (until pH 7 was reached) and dried at 100°C overnight. The oxidized AC prepared was then added to the required amount of prepared CoPW already dissolved in acetone with stirring for half an hour. Then the temperature was raised to 60°C to remove the excess acetone and the prepared catalyst was dried in an oven at 80°C. By using this method, a series of AC supported CoPW catalysts with various CoPW loading were prepared. They are denoted AC-CoPW-x where x is the percentage weight of CoPW in AC-CoPW catalyst: AC-CoPW-50; AC-CoPW-60; AC-CoPW-67; AC-CoPW-75.

Catalysts characterization

The as-synthesized in AC-CoPW catalysts were characterized by FTIR, XRD, polarography and TGA. FTIR spectra were recorded with an infrared spectrometer SHIMADZU FT- IR NICOLET- 6700 $(4000-400 \text{ cm}^{-1})$ as KBr pellets. The XRD powder patterns were performed on an Ultima IV, X-ray diffractometer: Rigaku using Cu-Kα radiation. The polarography measurements were carried out with a METROHM 797 VA COPMUTRACE (Version1.2) equipped with three electrodes. The analyzes were performed using a saturated calomel electrode (SCE) as the reference electrode and a mercury drop electrode as the working electrode. The sample was dissolved in an aqueous mixture of 1 M HCl / dioxane (50/50 v / v) with a mass of 30 mg of sample in 50 ml of solution, i.e. a concentration of approximately 0.05 M. Under these conditions $[PW_{12}O_{40}]^{3-}$ shows reversible waves in the range $[-0.15-0.800 \text{ V}]$. Thermogravimetry analysis (TGA) was performed on a Perkin-Elmer TGA/DSC instrument. The analysis was conditioned at constant heating rate 10°C/min and the temperature from 25 to 800°C in air. Transmission electron micrographs were recorded on a JEOL JEM-2100F field emission electron microscope (JEOL, Japan) with an acceleration voltage of 110 kV.

Catalytic dihydroxylation

The experiments were carried out in a stainless steel jacketed vessel equipped with a pressure gauge, manometer controls for pressure settings. The jacketed vessel was connected to a circulator water bath to adjust the temperature. A mixture consisting of 10 ml of cyclohexene, 10 ml hydrogen peroxide (30% in aqueous solution), 5 ml of acetonitrile (solvent) and 0.2 g of catalyst was charged in the vessel. The mixture was heated to 70°C then pressurized to 0.5 MPa. under stirring. After 4 h of reaction, the mixture was cooled and analyzed with a gas phase chromatograph (PYE UNICAM) equipped with a flame ionization, a catharometer detector and a capillary column (HP-PLOT Q length 30mID 0.53 mm). The qualitative analysis of the products was carried out occasionally by Gas chromatography-mass spectrometry (GC-MS) using a Thermo Trace GC Ultra gas chromatograph (AI 3000) equipped a TR-5 MS-SQC capillary column (30 m x 0.25 mm i.d., phase thickness 0.25 μm).

Results and discussion

Catalysts characterization

FTIR

The spectra of the AC-CoPW-x samples are depicted in Figure 1. It is seen from the figure that the main four
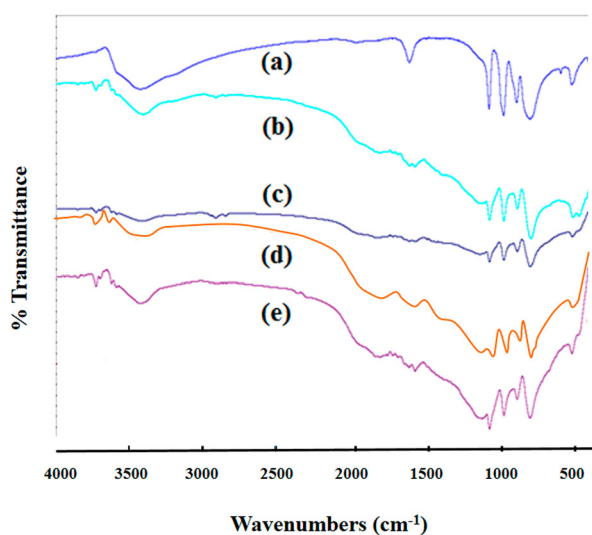

Figure 1. FTIR spectrum of: (a) CoPW; (b) AC- CoPW-50; (c) AC-CoPW-60; (d) AC-CoPW-67; (e) AC-CoPW-75.

characteristic bands of the Keggin structure are present. The main characteristic bands of the Keggin structure are observed at 917 cm^{-1} (γas P-Oa), at is 970 cm^{-1} (γas W-Od), at 850 cm^{-1} (γas W-Ob-W) and at 767 cm^{-1} (γas W-Oc-W). This result, therefore, shows that for all the samples, the solid CoPW has maintained its Keggin structure on the AC support. This result is in agreement with that of (30,31). The presence of HPW on the surface of the AC-HPW catalysts was confirmed in the FTIR.

X-Ray diffraction

XRD spectra of the AC-CoPW-x series are depicted in Figure 2. The results showed that each sample exhibits a pattern related to the kegging structure. In fact, it has been reported in the literature that kegging-type heteropolyanions exhibits a peak in each range of 2θ, 16°–23°, 25°–30°, and 31°–38° (32,33). Thus, the preservation of the Keggin structure in the synthesized catalysts was confirmed by FTIR and XRD.

Thermogravimetry analysis

The thermal stability of the unsupported and the AC supported CoPW was subjected to thermogravimetric analysis (TGA). The TGA of AC-CoPW-x series curves are presented in Figure 3. TGA curve for unsupported CoPW shows three thermal events with total weight loss 9%. The first mass loss, between 25 and 100°C, was due to release of physically adsorbed water and some of the hydrating water molecules (2% wt loss). The second mass loss occurred between 100 and 220 °C (and corresponded to the formation of the anhydrous catalyst with 4% wt loss). Finally, the third step occurred
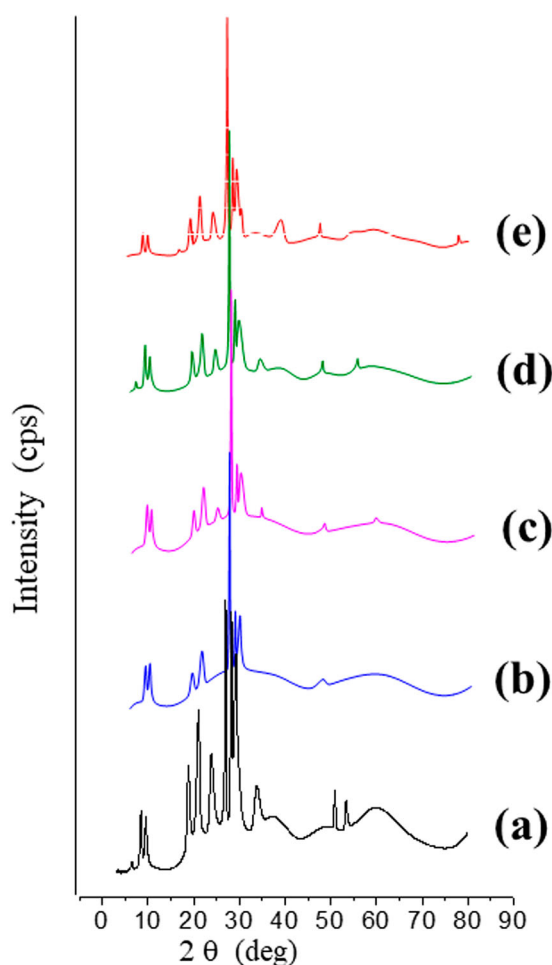
Figure 2. XRD spectrum of: (a) CoPW; (b) AC- CoPW-75; (c) AC-CoPW-67; (d) AC-CoPW-60; (e) AC-CoPW-50.

Figure 3. TG curves of: (a) CoPW; (b) AC-CoPW-75; (c) AC-CoPW-67; (d) AC-CoPW-60; (e) AC-CoPW-50. Analysis at constant heating rate 10°C/min in flowing air in air.

of loss. The total wt loss % are 6, and 5 for AC-CoPW-60; AC-CoPW-67 respectively compared to 9% for CoPW. From TGA analysis, it can be concluded that on deposition low content of CoPW on AC support may be considered slightly more stable with reduction of weight loss % than pure unsupported CoPW due to the strong anion-support interaction. However, the amount of CoPW on AC surface plays an important role to optimize the catalyst stability and thus its efficiency as a catalyst in a given reaction.

Polarography

The amount of CoPW loaded on the AC support was determined by polarography. The results reported in Table 1 showed that the nominal concentrations are very close to the experimental concentrations.

Catalytic activity

The catalytic activity of the AC-CoPW-x was evaluated for the reaction of the dihydroxylation of cyclohexene. The experiments were carried out under a CO_2 pressure of 0.5 MPa at 70°C during 4 h. The reaction products were analyzed by GC and GC-MS. The results showed that 1, 2-cyclohexanediol was obtained as major product. 2-cyclohexen-1-one and 2-cyclohexen-1-ol (abbreviated

over a wide temperature range (approximately 220–700 °C), which is related to the decomposition of the Keggin anion by the formation of the anhydride ($PW_{12}O_{38.5}$) followed by total transformation in the oxides (P_2O_5 and WO_3) (34). The TGA of GC-CoPW-50 presented different curves and substantially different weight loss compared to the unsupported catalysts (CoPW). This sample showed basically two thermal events. The first mass loss occurred between 50 and 250 °C (1.5% wt. loss), which is associated to the removal of physically adsorbed water and hydrating water molecules. A second weight loss took place between 500 and 700°C, corresponds to the crystallization of new oxide phases produced from Keggin structure decomposition (1.5% wt. loss). In addition, the thermal degradation of the Keggin unit (KU) followed by crystallization of the resulting oxides occurred at a higher temperature comparison with parent salt (CoPW). Otherwise, TGA curves for both AC-CoPW-60; AC-CoPW-67; AC-CoPW-75 were almost the same main decomposition processes as for the parent salt (CoPW) with a slight difference in the total weight
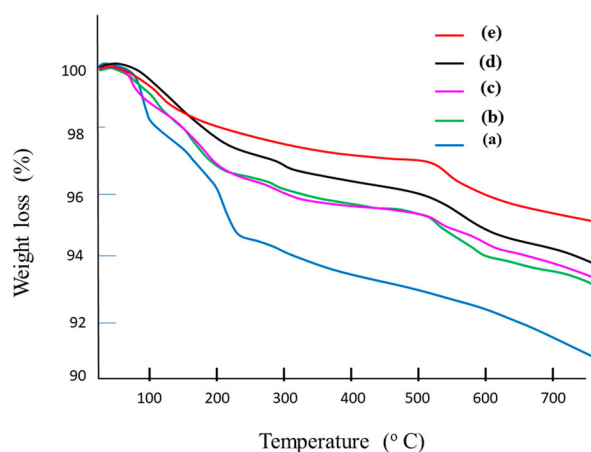
Table 1. Comparison between the nominal wt. (%) and the experimental wt. (%) of CoPW loaded on the AC support. The experimental wt. (%) were measured by polarography.

Catalyst	Nominal wt. (%)	Experimental wt. (%)
AC- CoPW −50	50	51
AC- CoPW -60	60	59
AC- CoPW -67	67	70
AC- CoPW -75	75	75

as diol, enone and enol respectively) were obtained as minor products. Cyclohexene oxide (abbreviated as epoxide), cyclohexanol, 1, 2-cyclohexanedione, 3-hydroxy cyclohexanone and 1,2,3-cyclohexanetriol are observed as traces.

Effect of AC support

The high solubility of heteropolyanions in polar media and their low surface area ($1-10 m^2/g$) affects their applications to catalyze non polar organic compounds. To overcome these drawbacks, supports with a high specific surface and which can act as an interface between the polar and non-polar phases are used to significantly increase their catalytic reactivity. Among the supports which have these properties, AC is the most preferred for industrial applications because of its low cost, its high specific surface and its large capacity of adsorption of CO_2 (35). This is the reason why we studied the effect of the AC support on the dihydroxylation of cyclohexene in the presence of CO_2. Another reason also is to heterogenize the catalyst and thus allow its reuse. To clarify the role of AC, the CoPW catalyst and the AC-CoPW-75 catalyst were tested for the dihydroxylation of CyH and their catalytic activities were compared. The experiments were conducted at 70°C for 4 h under a CO_2 pressure of 0.5 MPa. The obtained results (Table 2) showed that AC-CoPW enhanced both the conversion of CyH and selectivity of diol compared to bulk CoPW. The increase in the conversion can be explained by the increase in the concentration of the percarbonate species HCO_4^-. In fact, it has been reported that HCO_4^- which is formed in H_2O_2/CO_2 mixture through the reactions of CO_2, H_2O, and H_2O_2 (eq 1and 2) is an efficient epoxidizing system acting by transfer oxygen to olefins (19).
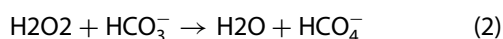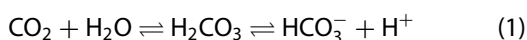
$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (1)$$

$$H2O2 + HCO_3^- \rightarrow H2O + HCO_4^- \quad (2)$$

According to the Equations (1) and (2), the concentration of HCO_4^- depend on amount of CO_2. The higher the amount of CO_2, the higher the concentration of percarbonate species. It has been mentioned that the enhancement of the reaction rate by HCO_3^-/CO_2 for oxidation mediated by H_2O_2 is due to the percarbonate species (HCO_4^-), which is an oxidant with two electrons stronger than H_2O_2 (36). According to the author, small concentrations of HCO_4^- present in the mixtures are sufficient to significantly increase oxidation. It is worth remembering that AC has a large capacity for adsorbing CO_2 (35). It is therefore evident that it contributes enormously to the increase in the concentration of HCO_4^- which plays an important role in the oxidation leading to the epoxides and to the oxidation of the alkenes (35). As for the increase in the selectivity of the diol, this could be due to the fact that the surface of the functionalized AC contains hydroxyl and carbonyl groups which have an acid character (37). These acidic groups, in the presence of H_2O (H_2O_2 / H_2O) lead to the formation of the diol.

Effect of CoPW loading

The effect of the CoPW loading on the conversion and products yields is illustrated in Figure 4. It can be seen from the figure that the conversion rate depends on the CoPW content. Indeed, for low content, the conversion rate increases rapidly. When the CoPW content increases from 0.50% by weight to 67% by weight, the conversion increases from 15.0% to 82.7%, on the other hand for high contents, the conversion rate increases only very slowly. This decline of the conversion rate at high contents can be explained by the fact that at high contents, the CoPW is poorly dispersed on the support. It is agglomerated and this decreases the amount exposed to catalyze the reaction. Our results were corroborated by many research reported in the literature. In a study of effect of the dispersion of supported vanadia (V_2O_5/TiO_2) on the selective catalytic reduction of NO, Fushun et al. (38) explain the decrease in activity at high coverage by the formation of V_2O_5 crystallites which have reduced the amount of V_2O_5 on the surface. Pojanavaraphan et al. studied steam reforming of methanol over the gold (Au) supported on CeO_2-Fe_2O_3 (39). They found that the catalytic activity increased when the Au content increased from 1% to 3% and then dropped for the content of 5%. The active catalyst of 3% Au content has a high dispersion and an optimal size of the gold particles. Patel et al. (40) studied the catalytic reduction of NO by CO over a series of CuO supported on mesoporous silica SBA-15 with copper loadings of 4.01–10.1 wt%. The highest activity was obtained over the catalyst containing
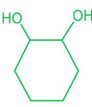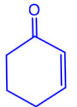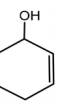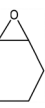
Table 2. Reactivity of the unsupported catalyst (CoPW) and the activated carbon supported catalyst (AC-CoPW-75). Reaction conditions: reaction temperature = 70°C; reaction time:4 h; P_{CO2} = 0.5 MPa.

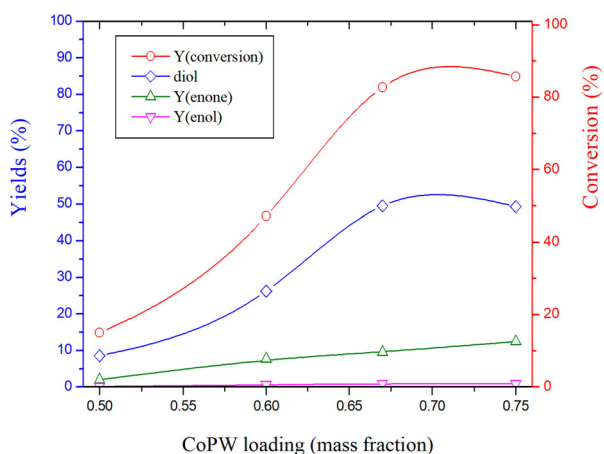|		Selectivity (%)			
Catalyst	Conversion (%)	HO⬡OH	⬡=O	⬡OH	epoxide
AC-CoPW-75	85.8	57.5	14.5	1.0	0.1
CoPW	70.5	11.1	49.6	21.6	0.0

Figure 4. Effect of CoPW loading on the conversion and yields. Reaction conditions: m(cat) = 200 mg; reaction temperature: 70°C; reaction time: 4 h; P(CO$_2$): 0.5 MPa.

8.67 wt% Cu. An increase in the Cu loading to 10.1 wt% led to a decrease of the activity. The explained the decline of the activity by the formation of bulk CuO aggregates and a Cu$_2$O phase at high Cu contents. Mohan Reddy et al. studied the ammoxidation of 2-methylpyrazine (MP) to cynopyrazine (CP) over a series of catalysts with various contents of vanadium incorporated into the ammonium salt of 12-molybdophosphoric acid (AMPV) supported on titanium dioxide (*41*). They reported that the conversion of MP increased with increasing the APMV up to 20 wt.%. to reach a maximum (92%) then decreased. At higher loading, the supported catalyst behaves like unsupported AMPV. As for the variation of the product yields, the results showed that like the conversion, the yields of the reaction products also depend on the content of CoPW on the support. When the CoPW content increases from 0.50 to 0.67, the diol yield increases from 8.6% to

49.5%, but when the content increases from 0.67 to 0.75, the yield varies from 49.5% to 49.3%, this is to say a very slight decrease. This decrease in yield of the diol occurs in favor of the yield of enone. This can be explained by the fact that at high loading, the CoPW agglomerated on the support (Figure 5) behaves as if it was not supported and favors enone product (see Table 2). Meanwhile, the enol yield remained almost constant regardless of the loading. These very small variations in the yields of the reaction products, when the CoPW content varies, results in almost constant selectivities (Figure 6).

In the following, we will further explore the effect of reaction conditions including effect of reaction time, catalyst amount, reaction temperature and catalyst reuse on the cyclohexene dihydroxylation over AC-CoPW-75 catalyst.

Effect of reaction time

The effect of reaction time was investigated from 0.5 to 4 h, while keeping the reaction conditions. The obtained results (Figure 7) showed that increasing reaction time increased the conversion considerably. The conversion increased from 8.9% to 85.8% in 4 h of reaction. On the other hand, the diol and enone selectivity increased only slightly. In fact, the selectivity of diol and enone increased from 51.8% to 57.5% and from 13.9% to 14.5% which represents a small variation for 4 h of the reaction. The increase of the diol and enone selectivity was accompanied by a slight decrease in enol and epoxide. The selectivities decreased from 4.3% to 2.0% and from 1.0% to 0.1%.

The change of the reactants and product concentrations versus time is illustrated in Figure 8. The fact that the increase in the concentration of the diol with
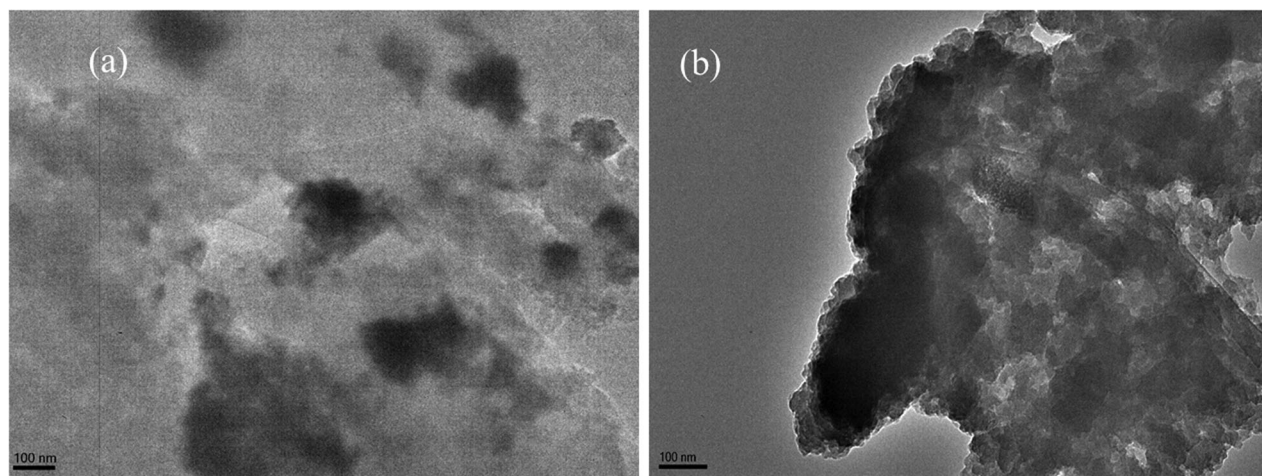

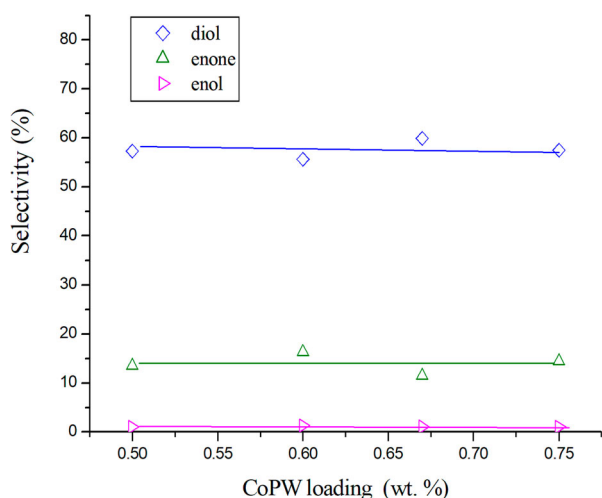**Figure 5.** TEM images of **(a)** dispersed AC-CoPW-50 (low loading) and (b) agglomerated AC-CoPW-75 (high loading).

Figure 6. Effect of CoPW loading on the selectivities. Reaction conditions: m(cat) = 200 mg; reaction temperature = 70°C; reaction time:4 h; P_{CO2} = 0.5 MPa.

the reaction time occurs at the same time as the conversion, from the beginning of the reaction and that the selectivities have remained constant, confirms that the diol, enone and enole were formed directly from cyclohexene by parallel reactions. Taking into account the results presented in Figures 7 and 8, a reaction pathway (Scheme 1) was suggested.

Effect of reaction temperature

The effect of the reaction temperature was investigated by varying the temperature from 60°C to 80°C and the results are depicted in Figure 9. It is seen from the figure that the conversion dependent strongly on the reaction temperature. In the temperature range from
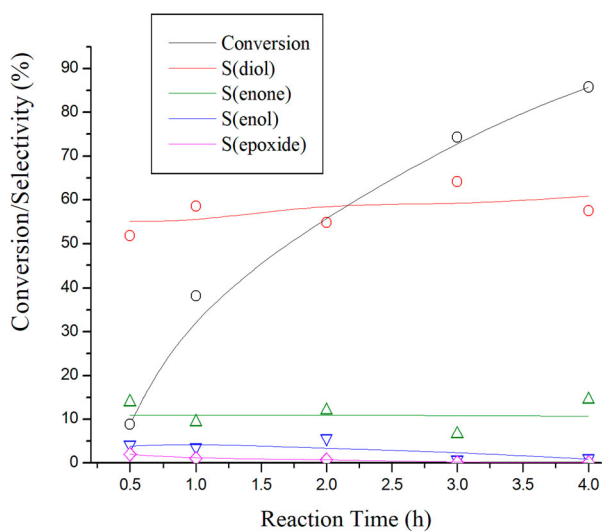
60°C to 75°C, the conversion increased from 46.2% to 95.9% respectively. This represents an increase of ≈ 51.8%. While in the temperature range from 75°C to 80°C, the change is not significant. The conversion varied from 95.9% to 96.9% which represents an increase of ≈1.1% only. The conversion remaining almost unchanged at high temperature could be due to the decrease in the solubility of CO_2 in the reaction mixture phase. In fact, an increase in temperature increases the conversion but at the same time, it decreases the solubility of carbon dioxide in the reaction mixture. A similar finding has been reported in the literature (42,43). The conversion remaining unchanged could also be due to the decomposition of hydrogen peroxide into oxygen and water. In fact, it has been reported that at higher temperatures, the efficiency of using H_2O_2 decreases owing to accelerated decomposition of H_2O_2 into oxygen and water (44). The effective decomposition of hydrogen peroxide is the reaction catalyzed by the transition metal ions generating the highly reactive hydroxyl free radical (45). From the above results, it appears that the reaction temperature is an important factor affecting both the conversion and product selectivies. Higher temperatures appeared to favor selectivity towards cyclohexane diol to the detriment of deep oxidation product (enone).

The Arrhenius plot for the cyclohexene oxidation by CO_2-H_2O_2 mixture over AC-CoPW is depicted in Figure 10. As seen in the figure, the change of the reaction rate with the reaction temperature does not follow the usual Arrhenius equation, but showed two segments. The Arrhenius plot exhibits two slopes, suggesting that

Figure 7. Variation of product selectivity with reaction time. Reaction conditions: reaction temperature: 70°C; P(CO₂): 0.5 MPa,
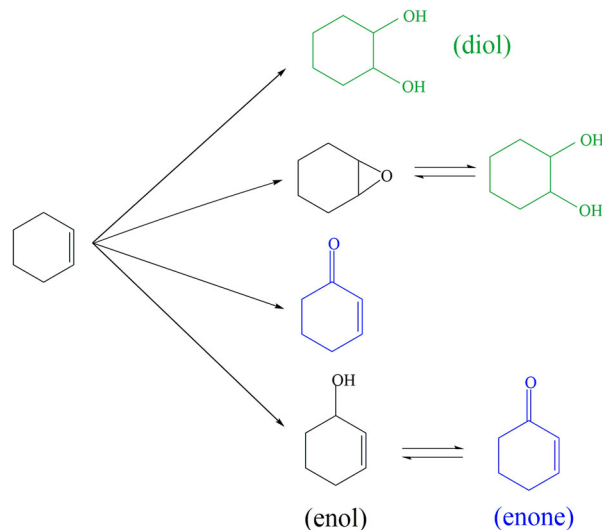
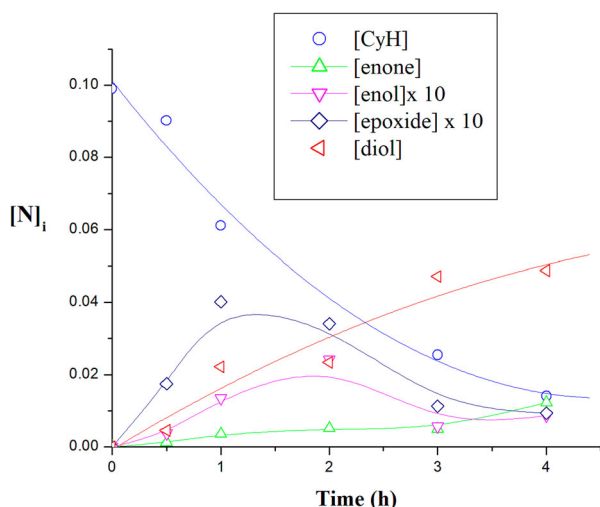**Scheme 1.** Suggested reaction pathway for CyH oxidation by CO_2 / H_2O_2 mixture over activated carbon supported CoPW catalyst.

Figure 8. Variation of te number of moles of reactant and products with time. Reaction conditions: m(cat) = 200 mg; reaction temperature = 70℃; P_{CO2} = 0.5 MPa.

the reaction occurred at least in two steps. At the temperatures below 70℃, the apparent activation energy of the reaction is 12.4 kJ/mol, whereas at the temperatures higher than 70℃, the apparent activation energy is 64.4 kJ/mol. Nonlinear Arrhenius curves, similar to that obtained in this work have been reported in the literature (46–48). *Mdleleni et al* (46) have studied the temperature effects on the hydroformylation and hydrogenation of cyclohexene over Rhodium supported on poly(4-vinylpyridine) (Rh/P4VP) catalyst over the range 85-120℃. They obtained a nonlinear (a convex Arrhenius) curve. According to the authors, the convex Arrhenius plots obtained suggest a change in the rate-limiting step between consecutive reactions as the temperature is varied from 85℃ to 120℃. The authors obtained a segmented Arrhenius curve. Above 70℃, the activation energy determined is 9.3 kcal / mol. Between 55 and 60℃, the calculations give an activation energy of 25.8 kcal / mol. Based on the fact that the reaction step with the highest activation energy "predominates" at a lower reaction temperature, ie the step with the highest large Ea, is rate limiting at lower temperature, and inversely the lower apparent activation energy process becomes the rate limiting at higher temperature. This interpretation suggests that the change in rate limiting step occurs between consecutive reactions and does not represent a case of two competing reaction paths. Pardey *et al*. (48) reported the influence of the reaction temperature on the catalytic hydroformylation of 1-hexene to aldehydes The reactions were catalyzed by rhodium(I) [Rh(COD)(2-pic)2]PF6 complex immobilized on the microporous aminated P(4-VP) under water gas shift reaction conditions over the range 70 –110 ℃.
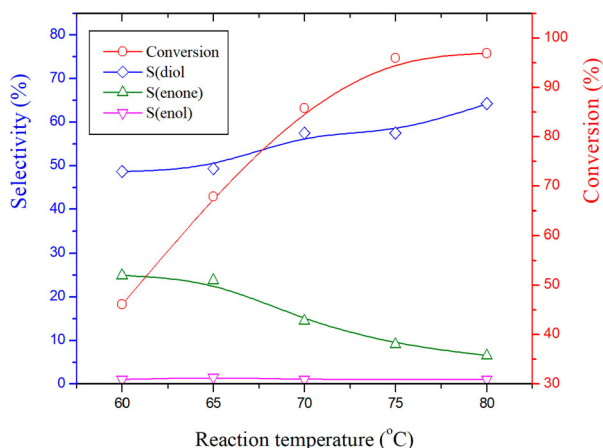

Figure 9. Effect of reaction temperature on the conversion and product selectivities. Reaction conditions: m(cat) = 200 mg; reaction time 4 h; P(CO₂): 0.5 MPa.

The results of hydroformylation process show a segmented concave upward Arrhenius plot with a lower apparent activation energy (Ea) at temperatures above 90 ℃ (Ea1 = 53.7 kJ/mol) than temperatures below 90 ℃ (Ea2 = 123.3 kJ/mol). By observing a decrease in the apparent activation energy at high temperature, in the hydroformylation process system in which there are several competitive reactions, such as hydroformylation, isomerization and the water gas shift reaction, the authors concluded that a decrease in activation energy with an increase in temperature may be a reflection of intrinsic kinetics (49). Yamaguchi et al. (47) studied the Hydrolysis of Cellulose by a Solid Acid Catalyst in the temperature range 50–120 ℃. The obtained results indicate that the conversion of cellulose into glucose does not increase in proportion to reaction temperature above 90 ℃ and the Arrhenius plot obtained showed
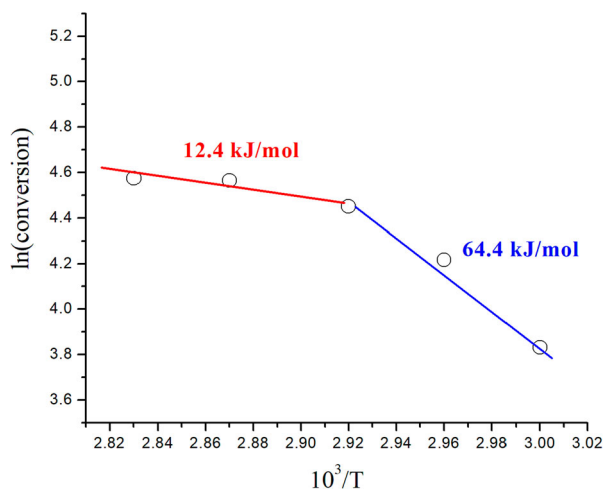

Figure 10. Temperature dependence (Arrhenius plot) for the oxidation of CyH by CO₂/ H₂

Table 3. Catalytic performance of the fresh and used catalyst. Reaction conducted at 70°C for 4 h over AC- CoPW -75 catalyst.

Catalyst	Conversion	Selectivity (%)		
		Diol	enone	enol
fresh	85.8	57.5	14.6	1.0
used	80.1	63.2	7.9	0.9

two slopes: above and below 80–90 °C. Based on the fact that the amounts of by-products, such as levoglucosan, acetic acid, formic acid and levulinicacid, do not increase significantly, even above 90 °C. The authors believe that neither dehydration nor decomposition of the glucose produced can explain the decrease in the formation of glucose above this temperature. In their opinion the possible explanation is the degradation of cellulose as a reagent. They based their interpretation on the fact that the cellulose is denatured in hot concentrated strong liquid acids such as H_2SO_4. In our case, since diol and enone products were formed by competitive reactions, one possible explanation is the decrease in the solubility of CO_2 at high temperature resulting in the decrease in the concentration of the percarbonate entity HCO_4^- responsible for the transfer of oxygen to alkenes (*19*).

Catalyst recycling

The reusability of the CoPW-AC-75 catalyst in the oxidation of cyclohexene was examined. The experiments were carried out at 70°C for 4 h under 0.5 MPa CO_2 pressure. After the first run, the catalyst was separated from the reaction mixture by centrifugation, washed with acetone several times and dried in oven to remove the impurities deposited on the catalyst. The recovered catalyst was used for the CyH oxidation under the same reaction conditions. The obtained conversion and selectivities on fresh and used catalysts are presented in Table 3. It can be seen from the table, that after utilization, the catalyst has lost about 6.6% of its initial conversion without significant change on diol and enol selectivity. As for the selectivities, the results showed that enone selectivity was halved in favor of diol. This decrease in the enone selectivity can be attributed to the decrease of CoPW content on the AC as a result of CoPW leaching. The results presented in table shows clearly that CoPW favors enone formation as observed in the investigation of the support effect.

Conclusion

The oxidation of cyclohexene by CO_2 /H_2O_2 oxidant mixture over activated carbon-supported $CoPW_{12}O_{40}$

Keggin-heteropolyanions was investigated. From this study, the following main points emerge:

The use of activated-carbon supported heteropolyanions catalyst improves significantly both the conversion and selectivity of diol compared to the unsupported heteropolyanions.

The effect of the reaction temperature has shown that the reaction is highly dependent on temperature. An unusual plot of Arrhenius has been observed. Obtaining a downward concave Arrhenius plot for a reaction system showing parallel reactions suggests that the decrease in conversion is due to the decrease in CO_2 solubility in the reaction system which has resulted in a decrease in the concentration of percarbonate species.

The use of CO_2 as a cheap, available and safe feedstock for the synthesis of 1, 2 diols, makes our process an easy economic process.

This simple, safe and environmentally method could be an alternative to the more expensive and less environmentally friendly traditional method used for the preparation of diols.

Disclosure statement

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Notes on contributors

Dr Ramyah Radman, has prepared her PhD under the supervision of Professor Ahmed Aouissi at King Saud University in Riyadh Saudi Arabia and she obtained her PhD in 2015. Her research interests include catalysis and kinetics.

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