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Selective oxidation of cumene into 2-phenyl-2-propanol and acetophenone over activated carbon supported $Co_{1.5}PW_{12}O_{40}$ Material.

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Abstract

This article reports the oxidation of cumene by H_2O_2 in the presence of CO_2. It describes the role played by carbon dioxide on the course of the reaction. The reaction was catalyzed by unsupported $Co_{1.5}PW_{12}O_{40}$ and supported on activated carbon. The prepared materials were characterized by ICP, IR, XRD and UV. Analysis of the reaction products by gas chromatography coupled with mass spectrometry and gas chromatography showed that 2-phenyl-2-propanol and acetophenone were the main products of the reaction. Activated carbon significantly increases conversion by increasing $Co_{1.5}PW_{12}O_{40}$ accessibility to cumene molecules. The improvement in the conversion and selectivities of 2-phenyl-2-propanol and acetophenone by the use of the oxidizing system H_2O_2 / CO_2compared to the use of H_2O_2 alone or CO_2 alone is due to the role of the percarbonate entity HCO_4^- formed by reaction between H_2O_2 and CO_2. Oxidation by large amounts of H_2O_2 decreases the conversion by decreasing the solubility of cumene in the resulting aqueous medium. An increase in the reaction time resulting in a decrease in the concentration of H_2O_2 and leaving the effect of the predominant CO_2 accentuates the cracking reactions.

Keywords: cumene, carbon dioxide, hydrogen peroxide, polyoxometalates, activated carbon

1. Introduction

Oxidation of hydrocarbons is a key challenge in petrochemical industrial processes due to the efficient conversion from cheap petroleum feed stocks to value-added oxygenated

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compounds (Liao et al., 2014, Labinger, 2016, Xu et al., 2018, Silva et al., 2017, Nesterov et al., 2018). Oxidation of cumene into 2-phenyl-2- propanol (Ph-PrOH) and acetophenone (Ph=O) is one of such reactions. Ph-PrOH and Ph=O products are important intermediates. Ph-PrOH is used as a fragrance ingredient in many compounds such as cosmetics, shampoos, toilet soaps household cleaners and detergents (Fahlbusch et al., 2003). Ph=O is a raw material for the production of pesticides perfumes, pharmaceuticals, resins and alcohols (Alcántara et al., 2000). Currently, 2-phenyl-2-propanol is obtained as a by-product in the production of propylene oxide by using Cumene hydroperoxide in an industrial process (Liu et al., 2006, Tsuji and Oku, 2006). Currently Cumene hydroperoxide was industrially synthesized by using air as oxidant and Cumene hydroperoxide as initiator under high temperature and pressure. (the operating temperatures are 353–393 K; the pressures are 100–600 kPa of air). To prevent the decomposition of the hydroperoxde produced, alkaline solution was used to neutralize the acids formed (Hsu and Cheng, 1998, Suresh et al., 2000) . Besides Low degrees of conversion equal to 20% and selectivity to hydroperoxide of 90–95%, are achieved there are still some drawbacks such as poor safety (Dobras and Orlińska, 2018, Wu et al., 2008). This method, although selective produces large amounts of waste water alkaline or sulfur. The expensive and unecological post-treatment of wastewater and the 2-step synthesis of 2-phenyl-2-propanol make the process unattractive. Thus, it would be more beneficial to develop a cleaner synthetic route by using an environmentally friendly oxidizing agent. The most commonly used oxidants for oxidation reactions are tert-butyl hydroperoxide, hydrogen peroxide and nitric acid. However, these oxidants have serious drawbacks and are not very desirable for use in industrial applications. The use of tert-butyl hydroperoxide and nitric acid produces a large amount of organic pollution and waste. Hydrogen peroxide produces water by decomposition, which contributes to the deactivation of several catalysts (Liu et al., 2016, Sundaravel et al., 2013). In term of efficiency and eco-friendly sustainability, hydrogen peroxide is the suitable oxidant compared to these oxidizing agents, but its cost limits its application at industrial scale. To minimize its cost, it can be used in a mixture with CO_2. In fact, it has been reported that when hydrogen peroxide is used with carbon dioxide its efficiency increased (Hâncu et al., 2002, Nolen et al., 2002). Among the catalysts used in oxidation reactions,

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polyoxometalates have proved their effectiveness thanks to their oxidizing and acidic properties that can be adjusted to catalyze specific reactions by the choice of heteroatom, counter-anion and addenda atoms (Katryniok et al., 2013). This is why they have been widely used in the field of oxidation catalysis. (Chen et al., 2018, Lechner et al., 2016). In addition, they are water tolerant (Okuhara, 2002). Unfortunately, when they are used in the liquid phase and in the polar medium, they have the disadvantages of homogeneous catalysts, that is to say, difficulties of recycling and purification of the products. Therefore, their utilization as heterogeneous catalytic systems are promising ways. One of the methods used to heterogenize polyoxometalates is to load them on a support. In this work, we report the catalytic activity of a Keggin-type polyoxometalate ($CoPW_{12}O_{40}$) supported on activated carbon for the oxidation of cumene by H_2O_2 in the presence of CO_2. Cobalt was selected as a cation, because cobalt based catalysts are among the catalysts that have shown high catalytic activities in oxidation reactions. Li et al., 2012 reported that that the addition of $Co(OAc)_2$ as a cocatalyst enhanced significantly the oxidation of cyclohexene. Satokawa et al. reported that Co(II) complexe of 2-pyrazine carboxylic acid encapsulated in the Y-zeolite showed higher conversion of cyclohexene leading to 2-cyclohexen-l-one and 1,2-epoxycyclohexane as the major products (Chutia et al., 2009). Moreover, the industrial production of cyclohexanone and cyclohexanol mixture used in the manufacture of nylon is achieved by oxidation of cyclohexane using cobalt naphthenate salt catalyst (Musser, 2000). Thus, it would be interesting to explore a catalyst having advantages of $PW_{12}O_{40}]^{3-}$ with the cobalt element as counter-cation.

2. Experimental

2.1. Materials

Cumene, C_9H_{12} 99.8% purchased from Sigma Aldrich and sodium tungstate, $Na_2WO_4.2H_2O$, (96%). Tetraethyle ammonium bromide (TEABr), (>99%) from Merck-Schuchardt. Activated carbon (activated decolorizing powder) and $CoSO_4.7H_2O$ from British Drug Houses Ltd (BDH) Chemicals Ltd, Poole, England).

2.2. Preparation of the catalysts

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

12-Tungstophosphoric acid $H_3PW_{12}O_{40}.13H_2O$ was prepared according to a well-known method (Rocchiccioli-Deltcheff et al., 1983).

$Co_{1.5}PW_{12}O_{40}$ (abbreviated CoPW) was prepared by proton substitution of the $H_3PW_{12}O_{40}$ heteropolyacid. This substitution is as follows. To an aqueous solution of $H_3PW_{12}O_{40}$, a required amount of $Ba(OH)_2.8H_2O$ (to neutralize the 3 protons) is added slowly. Then, the required amount of $Ba(OH)_2.8H_2O$ was added, resulting in the formation of insoluble barium salt, which was removed by filtration. The filtrate is allowed to stand for a few days at 4 ° C to allow precipitation of the CoPW salt which is then recovered from the solution by filtration.

2.2.2. Supported $Co_{1.5}PW_{12}O_{40}$

The attachment of the CoPW heteropolyanions onto the activated carbon (AC) support necessitates the creation of oxygenated groups on the support, and what was done by oxidation was created by oxidation with concentrated nitric acid.

The preparation of the supported catalyst was achieved as follow:100 mg sample of AC was dispersed in 100 ml of nitric acid (65%) and heated for 5 hours at 80 ° C with stirring. The desired amount of carbon support was dispersed in 100 ml of nitric acid (65%) and heated for 5 hours at 80 ° C with stirring. The mixture containing the activated carbon is allowed to cool to room temperature, then filtered and washed with deionized water at pH 7 and dried at 100 ° C overnight. A desired amount oxidized AC was then added to the desired amount of CoPW already dissolved in acetone and the mixture was kept under stirring for 30 min. Then after it was heated at about 60°C to remove the excess acetone and dried overnight in an oven at 80°C. the supported catalyst was denoted AC-CoPW.

2.3. Characterization of the catalysts

The catalysts were characterized by Fourier transforms infrared (FT-IR) spectra, X-ray diffraction (XRD), inductively coupled plasma spectrometry (ICP) and UV-Vis. IR spectra were recorded by means of an infrared spectrometer SHIMADZU FT- IR

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NICOLET- 6700 (4000−400 cm^{-1}). XRD characterization were carried out employing an Ultima IV X-ray Rigaku diffractometer using Cu-Kα radiation. ICP measurements using a Perkin Elmer Nexion 300D Spectrometer. UV-Vis characterization was achieved by means of double beam UV-Vis spectrophotometer (Philips 8800). Surface area measurement BET was determined using NOVA 2200e analyzer (Quantachrome, Japan) by the adsorption of N_2 at 77 K. Catalysts Surface morphology was analyzed by using a JSM-7600F (JEOL Ltd., Japan) scanning electron microscope (SEM).

2.4. Catalytic oxidation

The experiments were carried out in a stainless steel autoclave equipped with a pressure gauge and manometer controls for pressure settings. The temperature of the autoclave was adjusted by a heating jacket. The temperature of the autoclave is controlled by a heating jacket. The procedure is as follow: a given amount of catalyst and co-catalyst (TBABr) were added to the cumene and hydrogen peroxide (30% in aqueous solution) solution. The mixture was stirred magnetically and heated to the desired temperature under CO_2 pressure. After the required time, the resulting mixture was cooled, sampled and analyzed. Qualitative analysis was achieved by a Gas Phase Chromatograph (Thermo Scientific Trace GC Ultra) equipped with a capillary column (TR 5, ID 0.53 mm Film 1μM). Quantitative analysis was done occasionally by Gas chromatography-mass spectrometry (GC-MS) using a Thermo Trace GC Ultra gas chromatograph AI 3000 equipped with a TR-5 MS-SQC capillary column (30 m x 0.25 mm i.d., phase thickness 0.25 μm) was used with helium as the carrier gas (at a flow rate of 1 mL/min).

3. Results and Discussion

3.1. Catalysts Characterization

3.1.1. Infrared Spectroscopy

Figure 1 shows the FT-IR spectra of the oxidized AC, CoPW and AC-CoPW catalysts. The spectrum of the oxidized AC (figure 1b) shows bands at 1346, 1730, and 1536 cm^{-1} which were assigned to C-O, C=O, and C=C groups, respectively. The peak at around 1730 cm^{-1} correspond to the C=O strength vibration in the COOH group (Shanmugharaj

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et al., 2007, Fanning and Vannice, 1993, Zhuang et al., 1994, Yang et al., 2017). This band could be due to either lactone groups (Fanning and Vannice 1993) or to carboxyl groups in aromatic compounds (Zhuang et al., 1994, Yang et al., 2017). Thus, these results show that the oxidation treatments have created oxygen groups, such as carboxylic and hydroxyl groups, on the carbon surface.

The spectrum of CoPW (figure1a) shows bands at 1080.2, 982.9, 883.2 and 766.8 cm^{-1}. These bands which are assigned to the stretching modes νas (P–O$_d$), νas (W–O$_d$), νas (W–O$_b$–W), and νas (W–Oc–W), (Oa, oxygen atom bound to 3W atoms and the central P atom; O$_b$ and Oc, bridging oxygen atoms; O$_d$, terminal oxygen) are characteristic of the keggin structure (Rocchiccioli-Deltcheff et al., 1983). As for the FT-IR spectrum of AC-CoPW, it can be seen in figure 1b, that besides the bands related to the carbon, the four characteristic bands of keggin structure are present. These latter indiquent that CoPW loaded on the AC has preserved its Keggin structure.
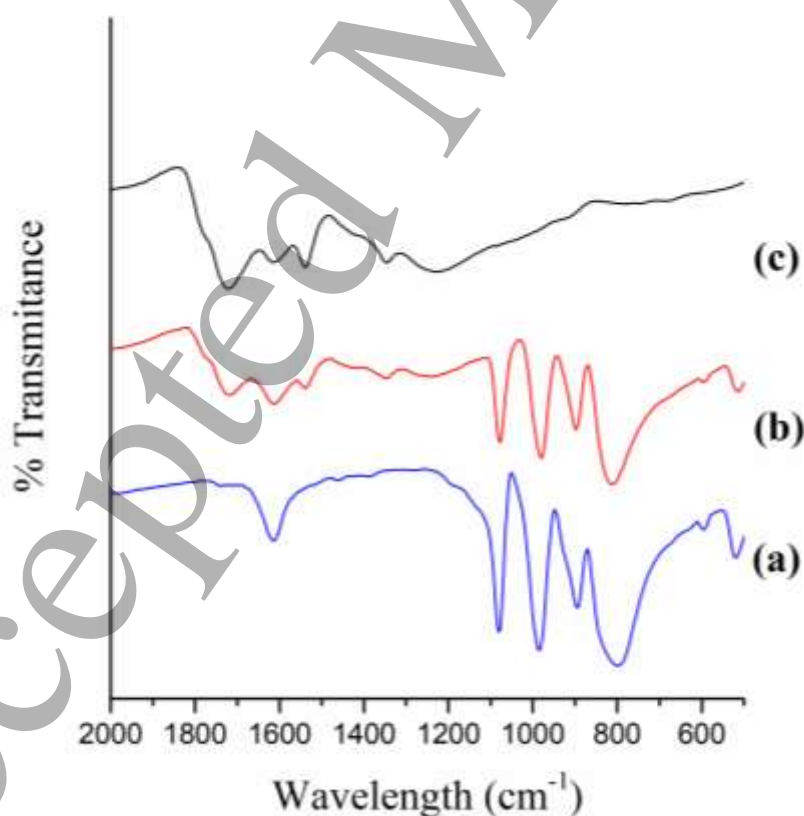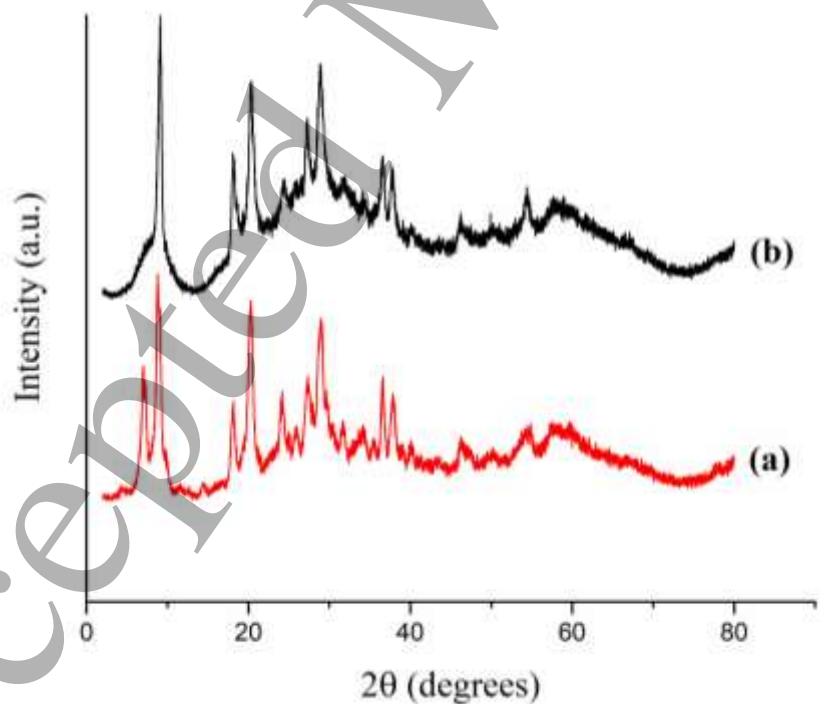
Figure 1. IR spectra of (a) CoPW; (b) AC-CoPW (c) AC

3.1.2. X-ray Diffraction

Figure 2 the X-ray diffraction patterns of the CoPW and AC-CoPW. The reflections at 9.8°, 21.0°, 26.2°, and 34.9°, observed in the patterns of CoPW (Figure 2a), indicated that this latter has both a Keggin structure (Fournier et al., 1992, Yoshimune et al., 2002). Indeed, the X-ray diffractions for the keggin structure show peaks in each of the four ranges of 2θ, namely 7-10°, 16-23°, 25-30° and 31-38°. The reflections observed at 26.1°, 43.1°, 53.5° and 78.7° 2θ for AC-CoPW (Figure 2b) correspond to (002), (100), (004) and (110) diffractions respectively of hexagonal graphite (Delidovich and Palkovits, 2016, Zhang et al., 2002, Sun et al., 2005). These reflections indicated that the graphitic structure of AC was preserved after oxidation treatment. Besides the reflections assigned to AC, characteristic peaks of CoPW are also observed. These results indicated that Keggin structure was preserved after loading on AC support. Thus, both XRD and FTIR characterizations showed that AC-CoPW catalyst was successfully synthesized.

Figure 2. XRD spectra of (a) CoPW and (b) AC-CoPW

3.1.3. Elemental Analyses

Elemental analysis of CoPW was done by ICP and the results were reported in Table 1a. The results which were determined by considering 1 atom of phosphorous per Keggin unit were found in a good agreement with the expected ones for tungsten and counter ion. Analysis of CoPW loaded on AC support was done by UV-visible in aqueous solution. It has been reported that CoPW in aqueous solution showed an absorbance at 254 nm (Grama et al., 2014, Eid et al., 2013). The amount of CoPW loaded on AC support was determined by considering the intensity of this band. The results (Table 1b) showed that the experimental amount of CoPW (0.315g/0.100g) was very close to the nominal one loaded on AC support (0.350g/0.100g)

Table 1. Elemental analysis data of the prepared CoPW and AC-CoPW

Catalyst	Nominal	Experimental
(a) P/Co/W (% mol)	1/1.5/12	1/1.52/11.97
(b) CoPW-AC (Wt.%)	0.350/0.100	0.315/0.100

3.1.4. Surface morphology and Surface Area

The surface morphology of the activated carbon before and after treatment with HNO_3 was analyzed by SEM. The results obtained (figure 3) showed that the activated carbon before treatment consisted of particles of variable sizes forming spaces between them (pores) whereas, for the activated carbon treated with nitric acid, the particles are agglomerated and the surface appeared as a porous mass. These results are confirmed by the surface area measurement. In fact, the activated carbon before treatment has a surface area of 1019.66 m² / g, whereas the acid treated activated carbon has a surface area of 628.69 m² / g. The treatment of the activated carbon with HNO_3 reduces considerably the specific surface area. These results are corroborated by those reported in the literature. In fact, many studies reported that nitric acid treatment reduces the specific surface area (Bernal et al., 2018, Rehman et al., 2019, Soudani et al., 2013). Soudani et al., 2013 reported that this reduction depends on the concentration of HNO_3. In the opinion of the author, this reduction is also due to the oxygen groups created by the treatment with HNO_3

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which are probably fixed at the entrance of the micropores leading to a reduction in the pore volume.
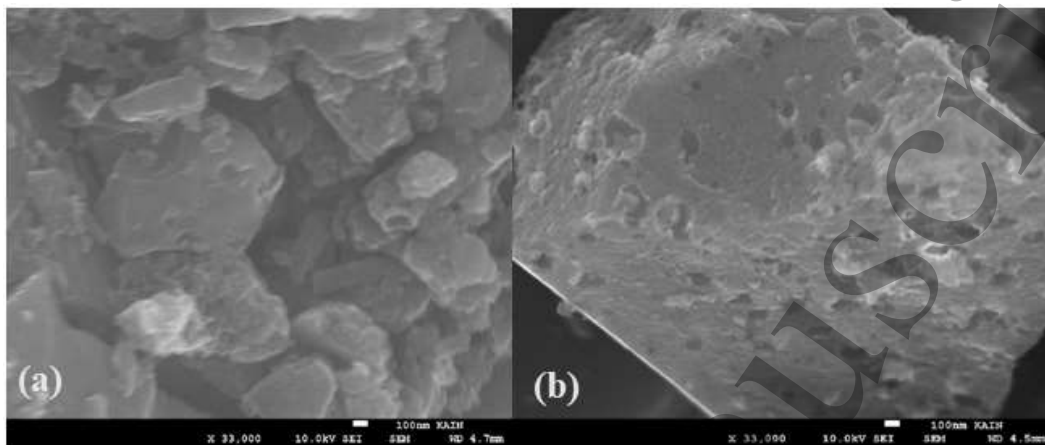
Figure 3. The SEM images of (a) activated carbon (AC) (b) oxidized activated carbon with HNO_3 (OAC).

3.2. Catalytic activity

AC-CoPW activity was evaluated for the oxidation of cumene by H_2O_2/CO_2 oxidizing system. The experiments were conducted at $75^{\circ}C$ for 7h under different pressures of CO_2. Analysis by GC-MS showed that the reaction led to acetophenone (Ph=O), 2-Phenyl-2-propanol (Ph-PrOH) and phenol (Ph-OH) as major products. Ethylbenzene, toluene, benzene and acetone were obtained as minor products (Scheme 1). Cumene hydroperoxide was observed as trace because of it decomposition in acidic aqueous medium (H_2O produced by H_2O_2 decomposition. This result is corroborated by that reported by (Praveen Kumar et al., 2010) where it has been mentioned that oxidation of cumene with oxygen generates cumene hydroperoxide which is then decomposed in acidic aqueous medium into phenol and acetone.

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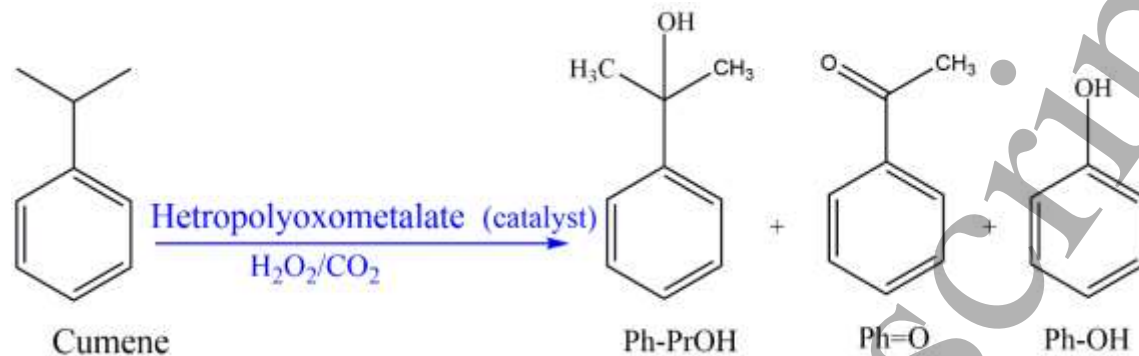
Scheme 1. Main products obtained by oxidation of cumene with H_2O_2 in the presence of CO_2 over AC-CoPW catalyst.

3.3. Effect of the Support

The effect of AC support on cumene oxidation was studied by comparing the unsupported CoPW catalytic activity and CoPW supported on AC. Catalytic tests were carried out at 75 ° C for 7 hours under a CO2 pressure of 0.55 MPa. The results (Table 2) show that AC support improved conversion. In fact, the conversion per gram of CoPW obtained over the bulk CoPW (29.1%) increased to (55.6%) when CoPW was supported on AC. This result indicated that the conversion was almost doubled (1.9 times). This considerable increase in conversion can be explained by the fact that the AC support increases the accessibility of the CoPW heteropolyanion to the cumene molecules (organic phase). As for the selectivities, the results show that of $Ph = O$ and that of Ph-CHOH remain almost unchanged. On the other hand, for the reaction catalyzed by the supported catalyst, the selectivity for PhOH decreased in favor of those of the other cracking products (ethylbenzene, toluene and benzene). In fact, when the reaction has been catalyzed by the unsupported CoPW catalyst, the selectivities for toluene, benzene and ethylbenzene obtained are respectively 0%, 0.6% and 1.1%. When the reaction was catalyzed by the supported catalyst OAC-CoPW, the selectivities obtained become 1.3%, 2.4% and 0.9% respectively. This could be due to the acidic oxygen groups (hydroxyl, phenolic and carboxyl) created on the surface of the activated carbon (Abdulrasheed et al., 2018, Gokce and Aktas 2014). Indeed, the unsupported CoPW catalyst has only Lewis type acid sites,

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whereas the supported catalyst ACA-CoPW has, in addition to these Lewis type acid sites, Brønsted type acid sites on the surface of the activated carbon. This clearly indicates that the Brønsted acid sites on the carbon support are responsible for the cracking reactions. This result is in agreement with those reported in the literature where it has been mentioned that the acidity of the support promotes cracking reactions (Wang et al., 2004). It has also been reported that Brønsted type acid sites effectively catalyze the cracking of cumene (Yue et al., 1998).

Table 2. Effect of AC support on cumene oxidation. Reaction conditions: $R_T = 75^oC$; $P(CO_2) = 0.55$ MPa; $(H_2O_2/$ Cumene: 2.5) volume ratio; $R_t = 7h$; m(cat) = 0.75g and m(co-catalyst) = 0.25g.

Catalyst	Conversion (%)	Selectivities [*] (%)							Conversion per g of CoPW
		1	2	3	4	5	6	7	
CoPW	21.8	33.1	57.0	6.4	1.9	0	0.6	1.1	29.1
CoPW/AC	31.7	33.7	58.1	2.6	1.1	1.3	2.4	0.9	55.6

[*]1, Ph=O; 2, Ph-PrOH; 3, PhOH; 4, Acet; 5, Toluene; 6, Benzene; 7, Ethylbenzene.
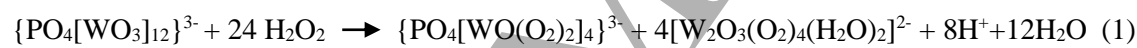
3.4. Effect of reaction conditions

In order to improve the yields of Ph-PrOH and Ph = O, an optimization of the reaction was carried out. For this purpose, the effect of the oxidizing system composition, the reaction temperature, the H_2O_2 / Cumene ratio, the amount of catalyst, the reaction time and the CO_2 pressure on the oxidation of Cumene was examined. The catalyst supports AC-CoPW, has been selected to catalyze the reactions.

3.4.1. Effect of H_2O_2 / CO_2 oxidizing system

The effect of the oxidizing system composition on the conversion and selectivities was examined by oxidizing cumene by CO_2 alone, H_2O_2 alone and H_2O_2 / CO_2 mixture. The results (Table. 3) show that in the case of oxidation by CO_2 alone and H_2O_2 alone, the conversions obtained are 3.53 % and 12.9% respectively. Interestingly when cumene was

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oxidized by H_2O_2/CO_2 mixture, the conversion increased significantly (31.7%). The improvement in the oxidation of cumene by the H_2O_2 / CO_2 oxidizing system is the result of two factors. The first is the effective activation of H_2O_2 by $Co_{1.5}PW_{12}$ and the second is the formation of a percarbonate species, a strong oxidant formed by the reaction of H_2O_2 with CO_2. For the activation of H_2O_2 by $Co_{1.5}PW_{12}$, it has been reported that in the presence of tungstate-based systems, oxidation by H_2O_2 leads to high reactivities and low activities for the non-productive decomposition of H_2O_2 (Mizuno et al., 2008). Among the tungstate-based systems, the Peroxotungstate $[PO_4(WO(O_2)_2)_4]^{3-}$, also called Venturelo complex has been postulated as being a catalytically active species in the oxidation of various reactions (Ishii et al., 1988, Qi et al., 2011, Duncan et al., 1995). Venturello et al., 1983 reported that in aqueous H_2O_2, $[PW_{12}O_{40}]^{3-}$ led to the formation of the complex $[PO_4\{W(O)(O_2)_2\}_4]^{3-}$. This complex which is composed of two species $[W_2O_2(O_2)_4]$ attached to the PO_4^{3-} anion- reacts with the olefin to give an intermediate which subsequently loses a molecule of water to lead to the reaction products and to regeneration of the catalyst.

$$\{PO_4[WO_3]_{12}\}^{3-} + 24\ H_2O_2 \longrightarrow \{PO_4[WO(O_2)_2]_4\}^{3-} + 4[W_2O_3(O_2)_4(H_2O)_2]^{2-} + 8H^+ + 12H_2O \quad (1)$$

As for the effect of the percarbonate entity (HCO_4^-) on the oxidation, it has been reported (Richardson et al., 2000) that this entity which is formed from hydrogen peroxide and sodium carbonate can oxidize alkene into epoxide. Beckman also postulated the formation of HCO_4^- by the reaction of aqueous CO_2 and hydrogen peroxide (Beckman, 2003). In the opinion of the author, the percarbonate species (HCO_4^-) can be formed by the reaction of H_2O_2 with aqueous bicarbonate (HCO_3^-) and this entity can epoxidize alkenes. It has also been reported by Hâncu et al., 2002 that a biphasic aqueous H_2O_2/CO_2 mixture is an efficient epoxidizing system, where HCO_4^- is formed through various reactions of water, CO_2, and H_2O_2 and transfers of oxygen to alkenes (eq 1and 2)

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (1)$$
$$H_2O_2 + HCO_3^- \longrightarrow H_2O + HCO_4^- \quad (2)$$
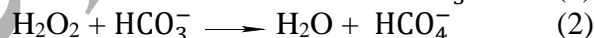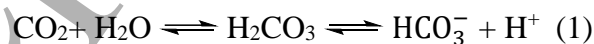
Truzzi et al., 2019 mentioned that the acceleration of oxidation by HCO_3^- / CO_2 on oxidations mediated by H_2O_2 are due to the percarbonate species (HCO_4^-), an oxidant with two electrons stronger than H_2O_2 which is present in the $H_2O_2/HCO_3^- /CO_2$ mixture. It was noted that small concentrations of HCO_4^- present in the mixtures are sufficient to significantly increase oxidation.

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Table 3. Effect of the composition of the oxidizing system on the conversion and selectivities of the products for the reaction catalyzed by AC-CoPW. Reactions conditions: T= 75°C; P (CO_2) = 0.55 MPa; (H_2O_2/cumene: 2.5) volume ratio; tr = 7hrs; m (cat) = 0.75g and m (co-catalyst) = 0.3g.

Oxidant	Conversion (%)	Selectivity (%)			
		Ph=O	Ph-PrOH	Ph-Ol	Cracking
CO_2	3.5	27.7	40.0	2.8	29.5
H_2O_2	12.9	31.9	53.2	6.1	8.7
CO_2/H_2O_2	31.7	33.7	58.1	2.6	5.5

3.4.2. Effect of Co-Catalyst

The effect of co-catalyst amount on cumene oxidation was investigated in the mass fraction ranging from 0.16 to 0.34. The results depicted in figure 4 showed that increasing the mass fraction from 0.16 to 0.28 increased the conversion from 9.5% to 31.7%. Beyond 0.28, there is no significant change. The selectivity of Ph-PrOH presented the same trend as the conversion. That is to say it increases when the mass fraction increases from 0.16 to 0.28 and then remains unchanged above 0.28. The increase in the selectivity of Ph-PrOH is to the detriment of that of Ph = O and Ph-OH which clearly indicate that the co-catalyst prevents the deep oxidation but favors the weak oxidation (formation of Ph-PrOH alcohol). Given the above results, it can be deduced that an appropriate amount of the co-catalyst contributes to the activation of CO_2. Therefore, the optimal mass fraction 0.29 was selected for all subsequent investigations.
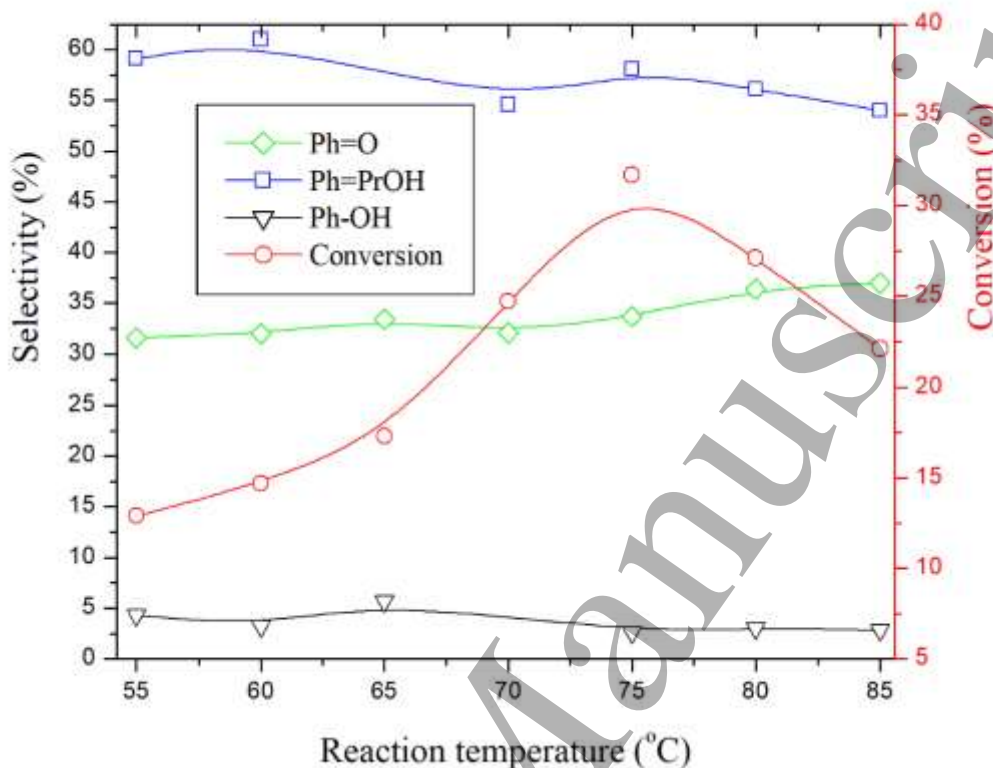
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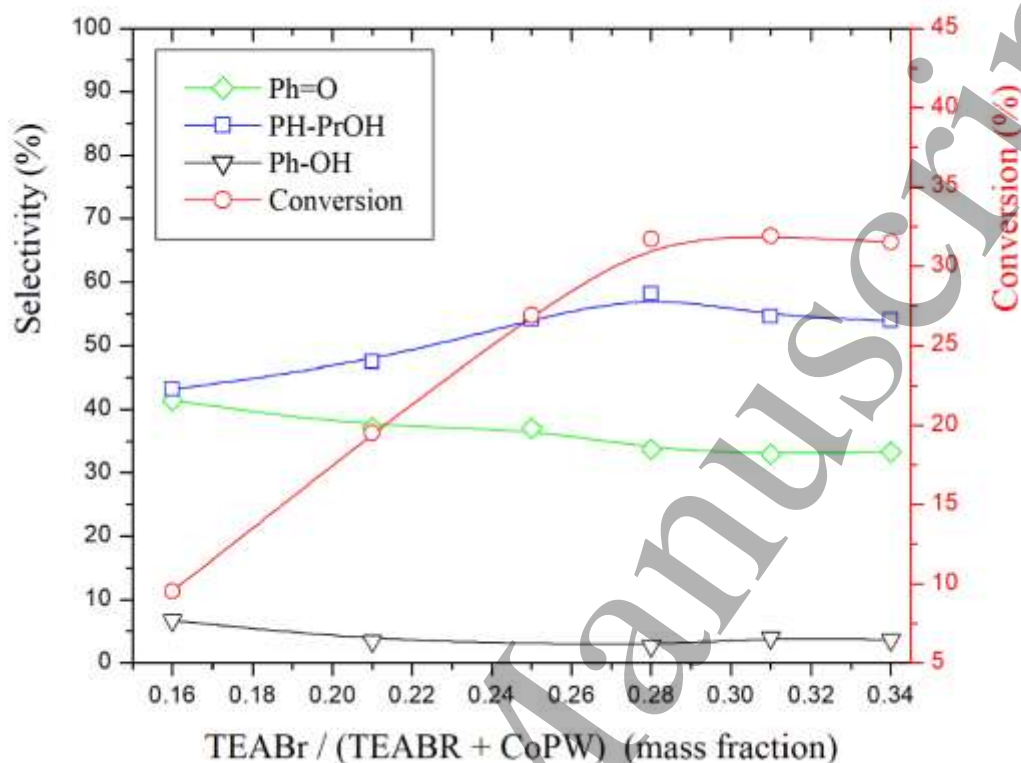
Figure 4. Effect of co-catalyst on the conversion and product selectivities over AC-CoPW catalyst. Reaction conditions: (volume ratio : H_2O_2/ Cumene = 2.5); $R_T = 75°C$; $P(CO_2) = 0.55$ MPa; $R_t = 7h$.

3.4.3. Effect of reaction temperature

The effect of the reaction temperature (R_T) on the conversion and selectivities is depicted in figure 5. The results showed that increasing reaction temperature to 75°C increased the conversion. Further increase in reaction temperature up to 85°C caused a decrease in conversion. The conversion decay observed for temperatures above 75°C could be attributed to the decomposition of H_2O_2. The selectivity of Ph=O increased slightly, whereas that of Ph-PrOH and Ph-OH decreased slightly throughout the temperature range.
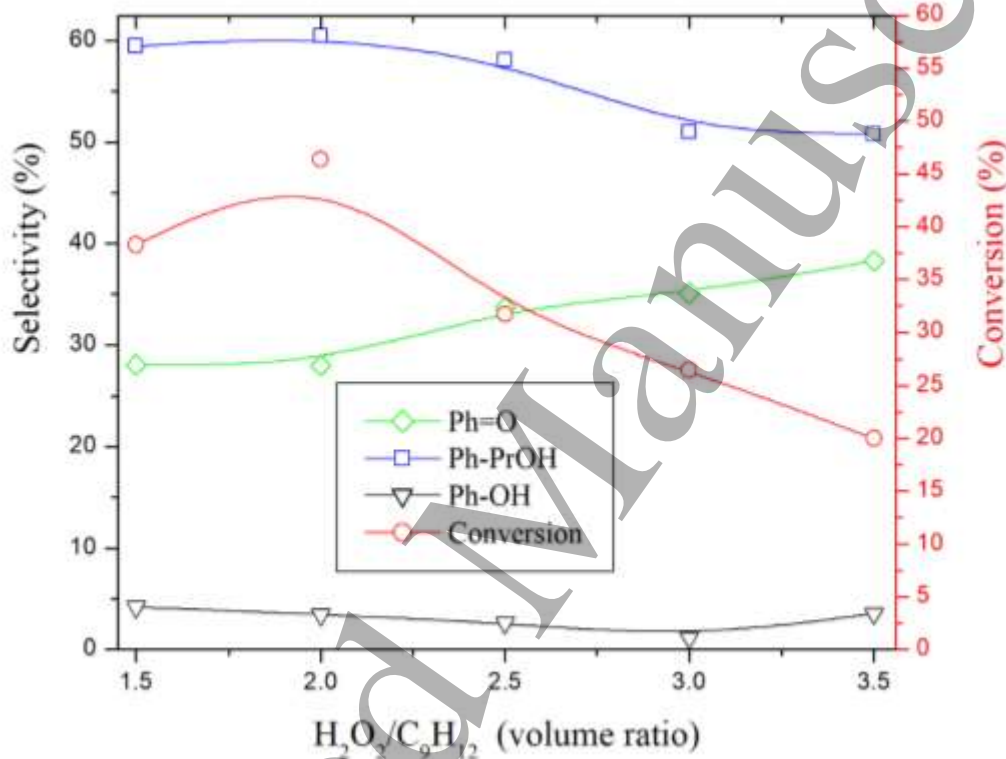
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Figure 5. Effect of reaction temperature on the conversion and product selectivities over AC-CoPW catalyst. Reaction conditions: (H_2O_2/ Cumene: 2.5) volume ratio; $P(CO_2) = 0.55$ MPa; $R_t = 7$h.

3.4.4. Effect of H_2O_2

Heteropolyatungstates are among the most suitable catalysts for H_2O_2 oxidation reactions. Indeed,the keggin heteropolyoxotungstates have 12 peripheral tungsten atoms (W) and each W atom has a large positive charge. This positive charge makes the heteropolytungstates capable of accepting electron pairs in vacant W orbitals to form a stable complex with H_2O_2. This makes the oxygen atoms of H_2O_2 more active and, therefore, the H_2O_2 activity for the oxidation reactions can be improved (Donoeva et al., 2009). This tempted us to examine the effect of H_2O_2 on cumene oxidation. Experiments with various proportions of H_2O_2 were carried out. The results (figure. 6) show that increasing H_2O_2/cumene volume ratio increased the conversion to a maximum value of 46.4% for a volume ratio of 2 and then gradually decrease to a value of 20.3 % for a

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volume ratio of 3.5. The decrease in conversion was due to the gradual decrease in cumene solubility in the polar medium which increases with the amount of H_2O_2. As for the selectivities of the reaction products, it can be noticed that increasing the concentration of H_2O_2 decreased, the selectivity of Ph-PrOH and PhOH in favor of Ph=O. This is expected since cumene is insoluble in the aqueous phase, it is the alcohols that are oxidized instead.

Figure 6. Variation of the conversion and product selectivities with volume ratio over AC-CoPW catalyst. Reaction conditions: $R_T = 75^{\circ}C$; $P(CO_2) = 0.55$ MPa; $R_t = 7h$.

3.4.5. Effect of catalyst amount

The effect of catalyst amount on cumene reaction was studied in the range 0.50-1.25g and the results are presented in figure 7. As expected, the conversion increases with the increase in the amount of the catalyst. On the other hand, the selectivity of the products depends on the conversion. It is well known that the increase in conversion increases the consecutive reactions. This is in agreement with our results. In fact, increasing the amount of catalyst increased both the conversion and Ph=O selectivity but decreased the

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selectivity of Ph-PrOH and phenol PhOH. This results indicated that Ph=O might be formed directly from cumene and from Ph-PrOH and/or phenol PhOH by consecutive reactions.
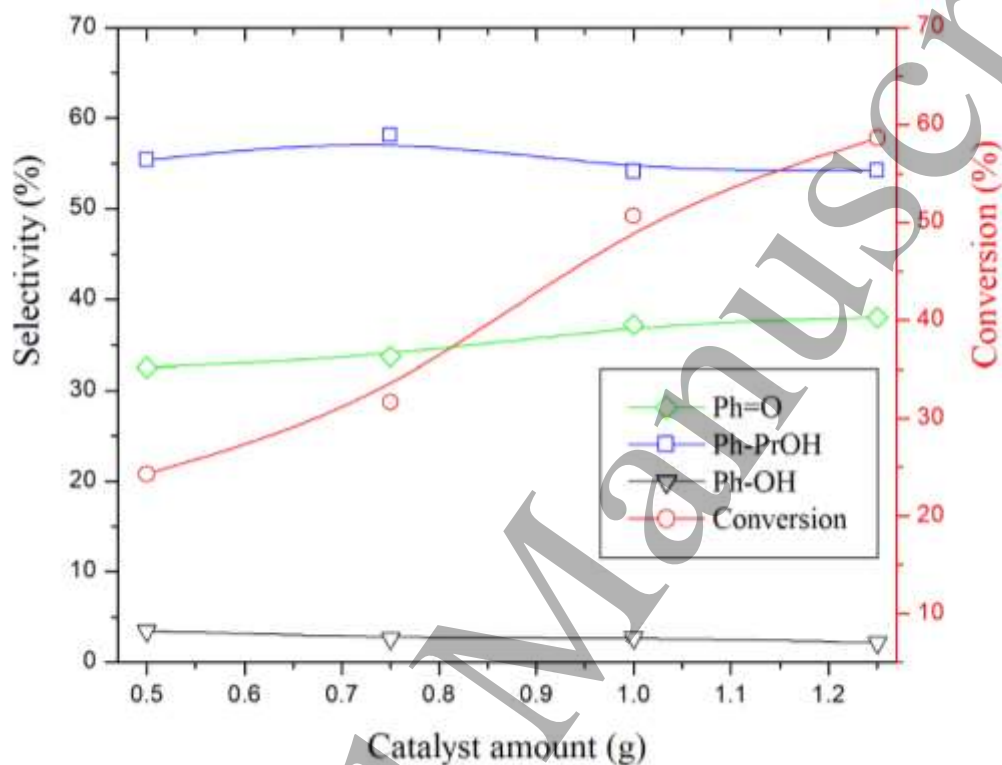

Figure 7. Variation of the conversion and product selectivities with catalyst amount over AC-CoPW catalyst. Reaction conditions: (H_2O_2/ Cumene) volume ratio =2.5; $P(CO_2) = 0.55$ MPa; $R_T = 75^{\circ}C$; $R_t = 7h$.

3.4.6. Effect of reaction time

The variation in conversion and selectivity as a function of time is shown in figure. 8. The results obtained show that the conversion increases linearly with the reaction time. With regard to the selectivity, it is noted that the selectivity for both Ph = O and Ph-PrOH has slightly decreased in favor of that of Ph-OH. This increase in the Ph-OH selectivity as a function of reaction time indicates the progress of the cracking reaction. This is explained by the decrease in the concentration of H_2O_2, and therefore it is the effect of CO_2 that remains predominant (constant CO_2 pressure) thus leading to cracking reactions. This

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interpretation is supported by the increase in the selectivities of the products resulting from the cracking reactions (toluene, ethyl benzene, benzene and toluene) obtained.
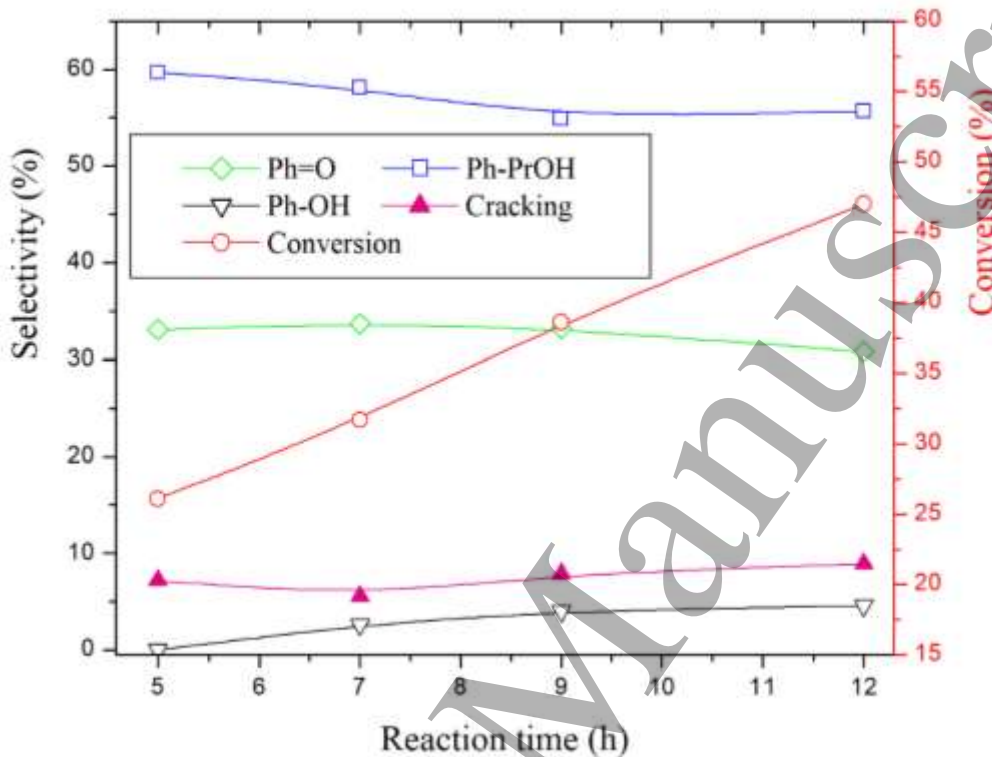

Figure 8. Variation of the conversion and product selectivities with reaction time over AC-CoPW catalyst. Reaction conditions: (H_2O_2/ Cumene) volume ratio=2.5; $R_T = 75^{\circ}C$; $P(CO_2) = 0.55$ MPa.

3.4.7. Effect of CO_2 Pressure

The effect of CO_2 on the course of the reaction was studied by varying the CO_2 pressure from 0M Pa to 0.55 MPa. The results obtained are illustrated in figure 9. It is noted from these results that the conversion increases rapidly with the pressure of CO_2. On the other hand, and what is very interesting is the increase of the selectivity of Ph-PrOH to the detriment of Ph = O and Ph-OH (products resulting from deep oxidation reaction and cracking). This result can be explained by the action of the percarbonate entity (HCO_4^-) which is responsible for oxidation by oxygen transfer. This result is very interesting

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because we observe an increase in conversion and selectivity at the same time and this is not the case in the majority of oxidation reactions.
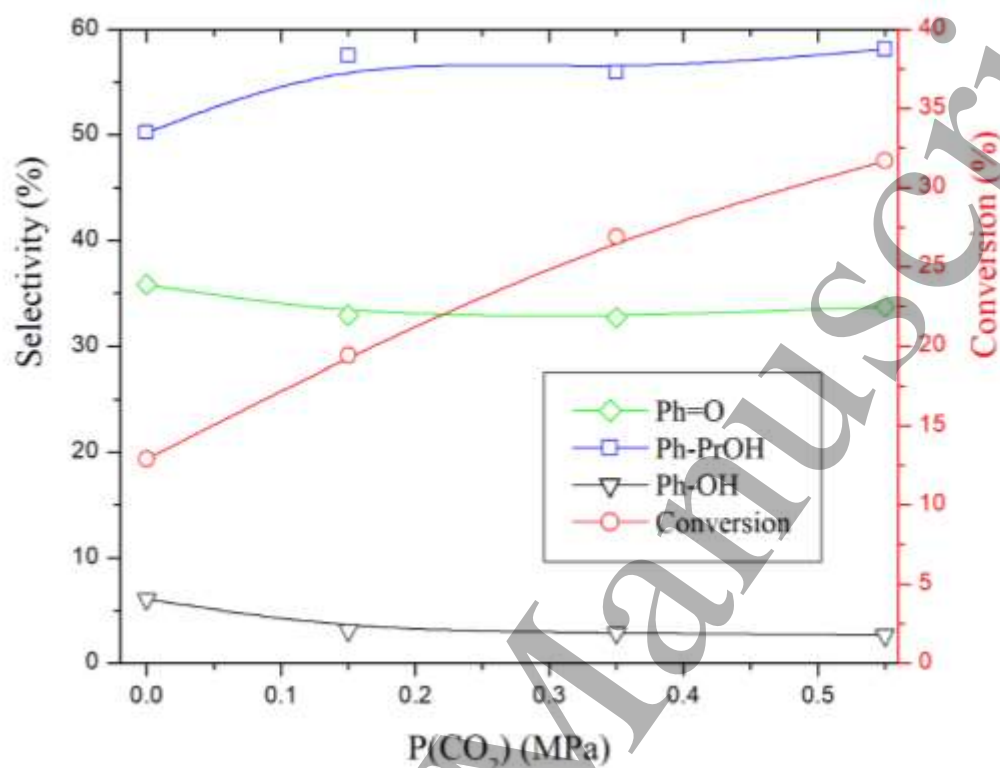
Figure 9. Variation of conversion and selectivities as a function of CO_2 pressure over AC-CoPW catalyst. Reaction conditions: (H_2O_2/Cumene: 2.5) volume ratio; $R_T = 75^{\circ}C$; $R_t = 7h$.

4. Conclusions

The synthesis of 2-Phenyl-2-propanol and acetophenone was achieved by oxidation of cumene by H_2O_2 in the presence of CO_2. The reaction was catalyzed by 12-tungstocobaltate heteropolyanions ($Co_{1.5}PW_{12}O_{40}$) supported on activated carbon in liquid phase.

Unlike the oxidation of cumene by O_2 gas, where cumene hydroperoxide is obtained in significant quantities, the oxidation of cumene by H_2O_2 leads only to traces of cumene hydroperoxide because of its decomposition in acidic aqueous medium.

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By increasing the accessibility of CoPW to cumene molecules (organic phase), the activated carbon support significantly improves conversion while keeping selectivities of Ph = O and Ph-PrOH almost unchanged.

The oxidation of cumene by CO_2, H_2O_2 and H_2O_2 / CO_2 shows that when cumene was oxidized by H_2O_2 in the presence of CO_2, the conversion increased considerably. This synegetic effect is due to the formation of the percarbonate entity (HCO_4^-) which plays a key role in the oxidation reaction.

The conversion of cumene and selectivity of Ph-PrOH can be controlled by selecting appropriate conditions. Higher CO_2 pressure and short reaction times favor Ph-PrOH formation, whereas longer reaction times favor Ph=O and Ph-OH.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

References

ABDULRASHEED, A., JALIL, A., TRIWAHYONO, S., ZAINI, M., GAMBO, Y. & IBRAHIM, M. 2018. Surface modification of activated carbon for adsorption of SO2 and NOX: A review of existing and emerging technologies. *Renewable and Sustainable Energy Reviews,* 94**,** 1067-1085.

ALCÁNTARA, R., CANOIRA, L., JOAO, P. G., SANTOS, J.-M. A. & VÁZQUEZ, I. 2000. Ethylbenzene oxidation with air catalysed by bis (acetylacetonate) nickel (II) and tetra-n-butylammonium tetrafluoroborate. *Applied Catalysis A: General,* 203**,** 259-268.

BECKMAN, E. 2003. Production of H 2 O 2 in CO 2 and its use in the direct synthesis of propylene oxide. *Green Chemistry,* 5**,** 332-336.

BERNAL, V., GIRALDO, L. & MORENO-PIRAJÁN, J. 2018. Physicochemical Properties of Activated Carbon: Their Effect on the Adsorption of Pharmaceutical Compounds and Adsorbate–Adsorbent Interactions. *C,* 4**,** 62.

20

CHEN, Q., SHEN, C. & HE, L. 2018. Recent advances of polyoxometalate-catalyzed selective oxidation based on structural classification. *Acta Crystallographica Section C: Structural Chemistry,* 74.

CHUTIA, P., KATO, S., KOJIMA, T. & SATOKAWA, S. 2009. Synthesis and characterization of Co (II) and Cu (II) supported complexes of 2-pyrazinecarboxylic acid for cyclohexene oxidation. *Polyhedron,* 28**,** 370-380.

DELIDOVICH, I. & PALKOVITS, R. 2016. Impacts of acidity and textural properties of oxidized carbon materials on their catalytic activity for hydrolysis of cellobiose. *Microporous and Mesoporous Materials,* 219**,** 317-321.

DOBRAS, G. & ORLIŃSKA, B. 2018. Aerobic oxidation of alkylaromatic hydrocarbons to hydroperoxides catalysed by N-hydroxyimides in ionic liquids as solvents. *Applied Catalysis A: General,* 561**,** 59-67.

DONOEVA, B. G., TRUBITSINA, T. A., MAKSIMOV, G. M., MAKSIMOVSKAYA, R. I. & KHOLDEEVA, O. A. 2009. Catalytic Properties and Stability of the Heteropolytungstate [P2W21O71 (H2O) 3] 6–in H2O2-Based Oxidations. *European Journal of Inorganic Chemistry,* 2009**,** 5142-5147.

DUNCAN, D. C., CHAMBERS, R. C., HECHT, E. & HILL, C. L. 1995. Mechanism and dynamics in the H3 [PW12O40]-catalyzed selective epoxidation of terminal olefins by H2O2. Formation, reactivity, and stability of {PO4 [WO (O2) 2] 4} 3. *Journal of the American Chemical Society,* 117**,** 681-691.

EID, A., BENLOUNES, O., HILAL, H. S., RABIA, C. & HOCINE, S. 2013. Dehydrocyclization of n-Hexane over Heteropolyoxometalates Catalysts. *Advances in Chemical Engineering and Science,* 3**,** 82.

FAHLBUSCH, K. G., HAMMERSCHMIDT, F. J., PANTEN, J., PICKENHAGEN, W., SCHATKOWSKI, D., BAUER, K., GARBE, D. & SURBURG, H. 2003. Flavors and fragrances. *Ullmann's Encyclopedia of Industrial Chemistry*.

FANNING, P. E. & VANNICE, M. A. 1993. A DRIFTS study of the formation of surface groups on carbon by oxidation. *Carbon,* 31**,** 721-730.

FOURNIER, M., FEUMI-JANTOU, C., RABIA, C., HERVÉ, G. & LAUNAY, S. 1992. Polyoxometalates catalyst materials: X-ray thermal stability study of phosphorus-containing heteropolyacids H 3+ x PM 12–x V x O 40· 13–14H 2 O (M= Mo, W; x= 0–1). *Journal of Materials Chemistry,* 2**,** 971-978.

GOKCE, Y. & AKTAS, Z. 2014. Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. *Applied Surface Science,* 313**,** 352-359.

GRAMA, L., BODA, F., FLOREA, A. G., CURTICĂPEAN, A. & MUNTEAN, D.-L. 2014. The UV and IR comparative spectrophotometric study of some saturated and lacunary polyoxometalates. *Acta Medica Marisiensis,* 60**,** 84-88.

HÂNCU, D., GREEN, J. & BECKMAN, E. J. 2002. H2O2 in CO2: Sustainable production and green reactions. *Accounts of chemical research,* 35**,** 757-764.

HSU, Y. F. & CHENG, C. P. 1998. Mechanistic investigation of the autooxidation of cumene catalyzed by transition metal salts supported on polymer. *Journal of Molecular Catalysis A: Chemical,* 136**,** 1-11.

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. *The Journal of Organic Chemistry,* 53**,** 3587-3593.

21

KATRYNIOK, B., PAUL, S. & DUMEIGNIL, F. 2013. Recent developments in the field of catalytic dehydration of glycerol to acrolein. *ACS Catalysis,* 3**,** 1819-1834.

LABINGER, J. A. 2016. Platinum-catalyzed C–H functionalization. *Chemical reviews,* 117**,** 8483-8496.

LECHNER, M., GÜTTEL, R. & STREB, C. 2016. Challenges in polyoxometalate-mediated aerobic oxidation catalysis: catalyst development meets reactor design. *Dalton Transactions,* 45**,** 16716-16726.

LI, Y., ZHOU, X.-T. & JI, H.-B. 2012. Cocatalytic effect of cobalt acetate on aerobic cyclohexene oxidation catalyzed by manganese porphyrin. *Catalysis Communications,* 27**,** 169-173.

LIAO, S., PENG, F., YU, H. & WANG, H. 2014. Carbon nanotubes as catalyst for the aerobic oxidation of cumene to cumene hydroperoxide. *Applied Catalysis A: General,* 478**,** 1-8.

LIU, T., CHENG, H., SUN, L., LIANG, F., ZHANG, C., YING, Z., LIN, W. & ZHAO, F. 2016. Synthesis of acetophenone from aerobic catalytic oxidation of ethylbenzene over Ti–Zr–Co alloy catalyst: Influence of annealing conditions. *Applied Catalysis A: General,* 512**,** 9-14.

LIU, X., LU, G., GUO, Y., GUO, Y., WANG, Y. & WANG, X. 2006. Catalytic transfer hydrogenolysis of 2-phenyl-2-propanol over palladium supported on activated carbon. *Journal of Molecular Catalysis A: Chemical,* 252**,** 176-180.

MIZUNO, N., YAMAGUCHI, K., KAMATA, K. & NAKAGAWA, Y. 2008. Activation of hydrogen peroxide by polyoxometalates. *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis.* Elsevier.

MUSSER, M. T. 2000. Cyclohexanol and cyclohexanone. *Ullmann's Encyclopedia of Industrial Chemistry*.

NESTEROV, D. S., NESTEROVA, O. V. & POMBEIRO, A. J. 2018. Homo-and heterometallic polynuclear transition metal catalysts for alkane CH bonds oxidative functionalization: Recent advances. *Coordination Chemistry Reviews,* 355**,** 199-222.

NOLEN, S. A., LU, J., BROWN, J. S., POLLET, P., EASON, B. C., GRIFFITH, K. N., GLÄSER, R., BUSH, D., LAMB, D. R. & LIOTTA, C. L. 2002. Olefin epoxidations using supercritical carbon dioxide and hydrogen peroxide without added metallic catalysts or peroxy acids. *Industrial & engineering chemistry research,* 41**,** 316-323.

OKUHARA, T. 2002. Water-tolerant solid acid catalysts. *Chemical reviews,* 102**,** 3641-3666.

PRAVEEN KUMAR, K., SELVIN, R., KUMARI, P., SELVA ROSELIN, L., ARUL, N. & BOUOUDINA, M. 2010. Selective decomposition of cumene hydroperoxide into phenol and acetone over nanocrystalline ZSM-5. *International Journal of Materials Engineering Innovation,* 1**,** 417-425.

QI, F., DE-KAI, Y., DAO-QUAN, W., XIAO-MEI, L., JIAN-JUN, Z., JIN-PING, W. & FU-HENG, C. 2011. Eco-friendly Synthesis of Cyclododecanone from Cyclododecatriene. *Green and Sustainable Chemistry,* 2011.

REHMAN, A., PARK, M. & PARK, S.-J. 2019. Current Progress on the Surface Chemical Modification of Carbonaceous Materials. *Coatings,* 9**,** 103.

RICHARDSON, D. E., YAO, H., FRANK, K. M. & BENNETT, D. A. 2000. Equilibria, kinetics, and mechanism in the bicarbonate activation of hydrogen peroxide: oxidation of sulfides by peroxymonocarbonate. *Journal of the American Chemical Society,* 122**,** 1729-1739.

ROCCHICCIOLI-DELTCHEFF, C., FOURNIER, M., FRANCK, R. & THOUVENOT, R. 1983. Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum (VI) and tungsten (VI) compounds related to the Keggin structure. *Inorganic Chemistry,* 22**,** 207-216.

SHANMUGHARAJ, A., BAE, J., LEE, K. Y., NOH, W. H., LEE, S. H. & RYU, S. H. 2007. Physical and chemical characteristics of multiwalled carbon nanotubes functionalized with

aminosilane and its influence on the properties of natural rubber composites. *Composites Science and technology,* 67**,** 1813-1822.

SILVA, G. C., CARVALHO, N. M., HORN JR, A., LACHTER, E. R. & ANTUNES, O. A. 2017. Oxidation of aromatic compounds by hydrogen peroxide catalyzed by mononuclear iron (III) complexes. *Journal of Molecular Catalysis A: Chemical,* 426**,** 564-571.

SOUDANI, N., SOUISSI-NAJAR, S. & OUEDERNI, A. 2013. Influence of nitric acid concentration on characteristics of olive stone based activated carbon. *Chinese Journal of Chemical Engineering,* 21**,** 1425-1430.

SUN, Z., LIU, Z., HAN, B., WANG, Y., DU, J., XIE, Z. & HAN, G. 2005. Fabrication of ruthenium–carbon nanotube nanocomposites in supercritical water. *Advanced Materials,* 17**,** 928-932.

SUNDARAVEL, B., BABU, C., PALANISAMY, B., PALANICHAMY, M., SHANTHI, K. & MURUGESAN, V. 2013. Praseodymium Incorporated AlPO-5 Molecular Sieves for Aerobic Oxidation of Ethylbenzene. *Journal of nanoscience and nanotechnology,* 13**,** 2507-2516.

SURESH, A. K., SHARMA, M. M. & SRIDHAR, T. 2000. Engineering aspects of industrial liquid-phase air oxidation of hydrocarbons. *Industrial & engineering chemistry research,* 39**,** 3958-3997.

TRUZZI, D. R., COELHO, F. R., PAVIANI, V., ALVES, S. V., NETTO, L. E. & AUGUSTO, O. 2019. The bicarbonate/carbon dioxide pair increases hydrogen peroxide-mediated hyperoxidation of human peroxiredoxin 1. *Journal of Biological Chemistry,* 294**,** 14055-14067.

TSUJI, J. & OKU, N. 2006. Process for producing cumene. Google Patents.

VENTURELLO, C., ALNERI, E. & RICCI, M. 1983. A new, effective catalytic system for epoxidation of olefins by hydrogen peroxide under phase-transfer conditions. *The Journal of Organic Chemistry,* 48**,** 3831-3833.

WANG, X., CARABINEIRO, H., LEMOS, F., LEMOS, M. & RIBEIRO, F. R. 2004. Propane conversion over a H-ZSM5 acid catalyst: Part 1. Observed kinetics. *Journal of Molecular Catalysis A: Chemical,* 216**,** 131-137.

WU, S., WANG, Y., WU, T., HU, W. & SHU, C. 2008. Evaluation of thermal hazards for dicumyl peroxide by DSC and VSP2. *Journal of Thermal Analysis and Calorimetry,* 93**,** 189-194.

XU, S., ZHANG, J., CHEN, B. & LEI, Z. 2018. Process intensification on the selective catalytic oxidation of cumene with ionic liquids. *Chemical Engineering and Processing-Process Intensification,* 130**,** 88-92.

YANG, J., HE, Q. S., NIU, H., CORSCADDEN, K. & CALDWELL, C. 2017. A comparative study on the performance of fiber-based biosorbents in the purification of biodiesel derived from camelina sativa. *Journal of Technology Innovations in Renewable Energy,* 5**,** 123-132.

YOSHIMUNE, M., YOSHINAGA, Y. & OKUHARA, T. 2002. Effect of alkaline metal on microporosity of acidic alkaline salts of 12-tungstophosphoric acid. *Microporous and mesoporous materials,* 51**,** 165-174.

YUE, Y., SUN, Y., XU, Q. & GAO, Z. 1998. Catalytic activities and properties of AlHMS mesoporous molecular sieves. *Applied Catalysis A: General,* 175**,** 131-137.

ZHANG, H.-B., LIN, G.-D., ZHOU, Z.-H., DONG, X. & CHEN, T. 2002. Raman spectra of MWCNTs and MWCNT-based H2-adsorbing system. *Carbon,* 40**,** 2429-2436.

ZHUANG, Q., KYOTANI, T. & TOMITA, A. 1994. DRIFT and TK/TPD analyses of surface oxygen complexes formed during carbon gasification. *Energy & fuels,* 8**,** 714-718.

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