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$_2$O$_2$ 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$_2$O$_2$/CO$_2$ compared to the use of H$_2$O$_2$ alone or CO$_2$ alone is due to the role of the percarbonate entity HCO$_4^-$ formed by reaction between H$_2$O$_2$ and CO$_2$. Oxidation by large amounts of H$_2$O$_2$ 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$_2$O$_2$ and leaving the effect of the predominant CO$_2$ accentuates the cracking reactions.

1. Introduction

Oxidation of hydrocarbons is a key challenge in petrochemical industrial processes due to the efficient conversion from cheap petroleum feedstocks to value-added oxygenated compounds (Liao et al 2014, Labinger 2016, Silva et al 2017, Nesterov et al 2018, Xu 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 hydroperoxide 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 (Wu et al 2008, Dobras and Orlíška 2018). This method, although selective produces large amounts of waste water alkaline or sulfur. The expensive and uneconomic 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 (Sundaravel et al 2013, Liu et al 2016). In terms of efficiency and eco-friendly sustainability, hydrogen peroxide is the suitable oxidant compared to other oxidizing agents, but its cost limits its application at industrial scale. To minimize its cost, it can be used in a mixture with CO₂. 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, 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 (Katrynio et al 2013). This is why they have been widely used in the field of oxidation catalysis. (Lechner et al 2016, Chen et al 2018). 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 is 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 (CoPW₁₂O₄₀) supported on activated carbon for the oxidation of cumene by H₂O₂ in the presence of CO₂. 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 the addition of Co(OAc)₂ as a cocatalyst enhanced significantly the oxidation of cyclohexene. Satokawa et al reported that Co(II) complex of 2-pyrazine carboxylic acid encapsulated in the Y-zeolite showed higher conversion of cyclohexene leading to 2-cyclohexen-1-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 PW₁₂O₄₀⁰³⁻ with the cobalt element as counter-cation.

2. Experimental

2.1. Materials
Cumene, C₆H₁₂ 99.8% purchased from Sigma Aldrich and sodium tungstate, Na₂WO₄.2H₂O, (96%). Tetraethyle ammonium bromide (TEABr), (>99%) from Merck-Schuchardt. Activated carbon (activated decolorizing powder) and CoSO₄.7H₂O from British Drug Houses Ltd (BDH) Chemicals Ltd, Poole, England.

2.2. Preparation of the catalysts
2.2.1. Bulk Co₁.₅PW₁₂O₄₀
12-Tungstophosphoric acid H₃PW₁₂O₄₀.13H₂O was prepared according to a well-known method (Rochiccioli-Delcheff et al 1983).

Co₁.₅PW₁₂O₄₀ (abbreviated CoPW) was prepared by proton substitution of the H₃PW₁₂O₄₀ heteropolyacid. This substitution is as follows. To an aqueous solution of H₃PW₁₂O₄₀ a required amount of Ba(OH)₂.8H₂O (to neutralize the 3 protons) is added slowly. Then, the required amount of Ba(OH)₂.8H₂O 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 Co₁.₅PW₁₂O₄₀
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 follows:100 mg sample of AC was dispersed in 100 ml of nitric acid (65%) and heated for 5 h at 80 °C with stirring. The desired amount of carbon support was dispersed in 100 ml of nitric acid (65%) and heated for 5 h 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 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 N₂ 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 CO₂ 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 1 μM). 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 × 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⁻¹).

### 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 1(b)) 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 (Fanning and Vannice 1993, Zhuang et al 1994, Shanmugharaj et al 2007, 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 (figure 1(a)) shows bands at 1080.2, 982.9, 883.2 and 766.8 cm⁻¹. These bands which are assigned to the stretching modes vas (P—O₃), vas (W—O₃), vas (W—O₃—W), and vas (W—O₃—W), (Oₐ, oxygen atom bound to 3W atoms and the central P atom; O₈₉ and O₉₉, bridging oxygen atoms; Oₐ₉, 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 1(b), 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.

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 2(a)), 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 2(b)) correspond to (002), (100), (004) and (110) diffractions respectively of hexagonal graphite (Zhang et al 2002, Sun et al 2005, Delidovich and Palkovits2016). 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.

3.1.3. Elemental analyses

Elemental analysis of CoPW was done by ICP and the results were reported in table 1(a). 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 (Eid et al 2013, Grama et al 2014). The amount of CoPW loaded on AC support was determined by considering the intensity of this band. The results (table 1(b)) showed that the experimental amount of CoPW (0.315 g/0.100g) was very close to the nominal one loaded on AC support (0.350 g/0.100g)

3.1.4. Surface morphology and Surface Area

The surface morphology of the activated carbon before and after treatment with HNO₃ 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 m$^2$ g$^{-1}$, whereas the acid treated activated carbon has a surface area of 628.69 m$^2$/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 (Soudani et al 2013, Bernal et al 2018, Rehman et al 2019). 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$_3$ which are probably fixed at the entrance of the micropores leading to a reduction in the pore volume.

3.2. Catalytic activity
AC-CoPW activity was evaluated for the oxidation of cumene by H$_2$O$_2$/CO$_2$ oxidizing system. The experiments were conducted at 75°C for 7 h 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$_2$O produced by H$_2$O$_2$ 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.

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 h under a CO$_2$ 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-
Table 2. Effect of AC support on cumene oxidation. Reaction conditions: $T = 75\, ^\circ\text{C}$; $P(\text{CO}_2) = 0.55\, \text{MPa}$; (H$_2$O$_2$/Cumene: 2.5) volume ratio; $t_r = 7\, \text{h}$; m(cat) = 0.75 g and m(co-catalyst) = 0.25 g.

| Catalyst   | Conversion (%) | 1  | 2  | 3  | 4  | 5  | 6  | 7  | Conversion per g of CoPW |
|------------|----------------|----|----|----|----|----|----|----|--------------------------|
| 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.

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: $T = 75\, ^\circ\text{C}$; $P(\text{CO}_2) = 0.55\, \text{MPa}$; (H$_2$O$_2$/cumene:2.5) volume ratio; $t_r = 7\, \text{h}$; m(cat) = 0.75 g and m(co-catalyst) = 0.3 g.

| Oxidant     | Conversion (%) | Ph = O | Ph-PrOH | Ph-Ol | Cracking |
|-------------|----------------|--------|---------|-------|----------|
| CO$_2$      | 3.5            | 27.7   | 40.0    | 2.8   | 29.5     |
| H$_2$O$_2$  | 12.9           | 31.9   | 53.2    | 6.1   | 8.7      |
| H$_2$O$_2$/CO$_2$ | 31.7 | 33.7   | 58.1    | 2.6   | 5.5      |

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 (Gokce and Aktas 2014, Abdulrasheed et al 2018). Indeed, the unsupported CoPW catalyst has only Lewis type acid sites, 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).

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$_2$O$_2$/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$_2$O$_2$/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$_2$O$_2$ alone and H$_2$O$_2$/CO$_2$ mixture. The results (table 3) show that in the case of oxidation by CO$_2$ alone and H$_2$O$_2$ alone, the conversions obtained are 3.53% and 12.9% respectively. Interestingly when cumene was oxidized by H$_2$O$_2$/CO$_2$ mixture, the conversion increased significantly (31.7%). The improvement in the oxidation of cumene by the H$_2$O$_2$/CO$_2$ oxidizing system is the result of two factors. The first is the effective activation of H$_2$O$_2$ 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$_2$O$_2$ with CO$_2$. For the activation of H$_2$O$_2$ by Co$_{1.5}$PW$_{12}$, it has been reported that in the presence of tungstate-based systems, oxidation by H$_2$O$_2$ leads to high reactivities and low activities for the non-productive decomposition of H$_2$O$_2$ (Mizuno et al 2008). Among the tungstate-based systems, the Peroxotungstate [PO$_4$(WO(O$_2$)$_2$)$_2$]$^{3-}$, also called Venturelo complex has been postulated as being a catalytically active species in the oxidation of various reactions (Ishii et al 1988, Duncan et al 1995, Qi et al 2011). Venturello et al 1983 reported that in aqueous H$_2$O$_2$, [PW$_{12}$O$_{40}$]$^{3-}$ led to the formation of the complex [PO$_4$(WO(O$_2$)$_2$)$_2$]$^{3-}$. This complex which is composed of two species [W$_4$O$_2$(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.
As for the effect of the percarbonate entity (HCO₄⁻) 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 HCO₄⁻ by the reaction of aqueous CO₂ and hydrogen peroxide (Beckman 2003). In the opinion of the author, the percarbonate species (HCO₄⁻) can be formed by the reaction of H₂O₂ with aqueous bicarbonate (HCO₃⁻) and this entity can epoxidize alkenes. It has also been reported by Hâncu et al 2002 that a biphasic aqueous H₂O₂/CO₂ mixture is an efficient epoxidizing system, where HCO₄⁻ is formed through various reactions of water, CO₂, and H₂O₂ and transfers of oxygen to alkenes (equations (2) and (3))

\[
\begin{align*}
{\text{PO}_4[\text{WO}_3]\text{H}_2}^{3-} + 24 \text{H}_2\text{O} &\rightarrow {\text{PO}_4[\text{WO}_2]\text{I}_4}^{3-} \\
+ 4\text{W}_2\text{O}_6\text{O}_2\text{I}_4\text{(H}_2\text{O}_2)\text{I}_2^{2-} + 8\text{H}^+ + 12\text{H}_2\text{O}
\end{align*}
\]

As for the effect of the percarbonate entity (HCO₄⁻) 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 HCO₄⁻ by the reaction of aqueous CO₂ and hydrogen peroxide (Beckman 2003). In the opinion of the author, the percarbonate species (HCO₄⁻) can be formed by the reaction of H₂O₂ with aqueous bicarbonate (HCO₃⁻) and this entity can epoxidize alkenes. It has also been reported by Hâncu et al 2002 that a biphasic aqueous H₂O₂/CO₂ mixture is an efficient epoxidizing system, where HCO₄⁻ is formed through various reactions of water, CO₂, and H₂O₂ and transfers of oxygen to alkenes (equations (2) and (3))

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &\rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{HCO}_3^- &\rightarrow \text{H}_2\text{O} + \text{HCO}_4^-
\end{align*}
\]

Truzzi et al 2019 mentioned that the acceleration of oxidation by HCO₃⁻/CO₂ on oxidations mediated by H₂O₂ are due to the percarbonate species (HCO₄⁻), an oxidant with two electrons stronger than H₂O₂ which is present in the H₂O₂/HCO₃⁻/CO₂ mixture. It was noted that small concentrations of HCO₄⁻ present in the mixtures are sufficient to significantly increase oxidation.

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 CO₂. Therefore, the optimal mass fraction 0.29 was selected for all subsequent investigations.

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 H₂O₂. The selectivity of Ph = O increased slightly, whereas that of Ph-PrOH and Ph-OH decreased slightly throughout the temperature range.

3.4.4. Effect of H₂O₂

Heteropolyoxotungstates are among the most suitable catalysts for H₂O₂ oxidation reactions. Indeed, the keggin heteropoly oxotungstates 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 H₂O₂. This makes the oxygen atoms of H₂O₂ more active and, therefore, the H₂O₂ activity for the oxidation reactions can be improved (Donoeva et al. 2009). This tempted us to examine the effect of H₂O₂ on cumene oxidation. Experiments with various proportions of H₂O₂ were carried out. The results (figure 6) show that increasing H₂O₂/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 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 H₂O₂. As for the selectivities of the reaction products, it can be noticed that increasing the concentration of H₂O₂ 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.

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 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.

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 H₂O₂, and therefore it is the effect of CO₂ that remains predominant (constant CO₂ pressure) thus leading to cracking reactions. This interpretation is supported by the increase in the selectivities of the products resulting from the cracking reactions (toluene, ethyl benzene, benzene and toluene) obtained.

3.4.7. Effect of CO₂ pressure
The effect of CO₂ on the course of the reaction was studied by varying the CO₂ 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 CO₂. 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 ($\text{HCO}_3^-$) which is responsible for oxidation by oxygen transfer. This result is very interesting 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.

4. Conclusions

The synthesis of 2-Phenyl-2-propanol and acetophenone was achieved by oxidation of cumene by $\text{H}_2\text{O}_2$ in the presence of $\text{CO}_2$. The reaction was catalyzed by 12-tungstocobaltate heteropolyanions ($\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$) supported on activated carbon in liquid phase.

Unlike the oxidation of cumene by $\text{O}_2$ gas, where cumene hydroperoxide is obtained in significant quantities, the oxidation of cumene by $\text{H}_2\text{O}_2$ leads only to traces of cumene hydroperoxide because of its decomposition in acidic aqueous medium.

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

The oxidation of cumene by $\text{CO}_2$, $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{CO}_2$ shows that when cumene was oxidized by $\text{H}_2\text{O}_2$ in the presence of $\text{CO}_2$, the conversion increased considerably. This synergetic effect is due to the formation of the percarbonate entity ($\text{HCO}_3^-$) which plays a key role in the oxidation reaction.

The conversion of cumene and selectivity of $\text{Ph-PrOH}$ can be controlled by selecting appropriate conditions. Higher $\text{CO}_2$ pressure and short reaction times favor $\text{Ph-PrOH}$ formation, whereas longer reaction times favor $\text{Ph} = \text{O}$ and $\text{Ph-OH}$.

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Conflicts of interest

The authors declare no conflict of interest.

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