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Synergistic effect between CO₂ and H₂O₂ on ethylbenzene oxidation catalyzed by carbon supported heteropolyanion catalysts

<https://doi.org/10.1515/gps-2018-0003>

Received January 7, 2018; accepted July 10, 2018; previously published online August 27, 2018

Abstract: A series of Keggin heteropolytungstate salts (M_{1.5}PW₁₂O₄₀, M=Cu, Co, Zn and Fe) were prepared and characterized utilizing inductively coupled plasma spectrometry (ICP), Fourier transform infrared (FTIR) spectra, and ultraviolet-visible (UV-Vis) light spectroscopy. The as-prepared catalysts were tested for the oxidation of ethylbenzene by using carbon dioxide/hydrogen peroxide (CO₂/H₂O₂) as the oxidizing agent system under solvent-free conditions. The results indicated that the heteropolytungstates catalyzed the side chain oxidation of ethylbenzene leading to acetophenone as a major product. The effect of various reaction parameters on ethylbenzene oxidation over the best catalyst of the series, namely Co_{1.5}PW₁₂O₄₀ loaded on activated carbon (AC), was investigated. It was found that the selectivity depends strongly on the reaction temperature. Higher reaction temperatures reduce the conversion due to the decomposition of H₂O₂. Oxidation by a large amount of H₂O₂ decreases the conversion owing to a decrease of the solubility of ethylbenzene in an aqueous medium, and favors the oxidation of the reaction products, which are more soluble in an aqueous medium. The increase of the CO₂ pressure improves both the conversion and the selectivity of acetophenone due to the involvement of the percarbonate species (HCO₄⁻) responsible for oxidation by oxygen transfer.

Keywords: activated carbon; carbon dioxide; heteropolyanions; hydrogen peroxide; oxidation.

1 Introduction

The conversion of alkylbenzenes into carbonyl compounds is one of the most important processes in petrochemistry. In fact, the resulting products such as aldehydes, ketones, and carboxylic acids are widely used in the production of resins, plastics, fine chemicals, and pharmaceuticals and serve as versatile building blocks of many biologically active compounds [1, 2]. Regarding the oxidation of alkylbenzenes, that of ethylbenzene has been the subject of considerable interest. This led researchers to test various oxidants such as molecular O₂ [3, 4], tert-butyl hydroperoxide [5, 6] and hydrogen peroxide (H₂O₂) [7, 8]. Taking into account that many of the oxidation systems have serious drawbacks, such as the use of toxic reagents [7, 9–12], relatively high operation temperatures [7, 10], and low ethylbenzene concentration [11, 13], researchers have placed emphasis in their research works to develop economic and environmental processes. Therefore, it seems interesting to use environmentally benign oxidants such as carbon dioxide (CO₂), O₂, and H₂O₂. In the last decades, CO₂ has attracted growing attention as a soft oxidizing agent. However, when used alone, CO₂ favors cracking and dehydrogenation reactions rather than oxidation reactions, whereas when used along with an oxygen donor source, the oxydehydrogenation reaction occurs. This synergistic effect is useful for the creation of carbonyl groups in hydrocarbons. Aqueous H₂O₂ is the proper oxidant since it produces water as the only by-product, and is easy to treat after reactions. Moreover, it has been found to form peroxocomplexes with molybdenum and tungsten heteropoly compounds [14, 15]. It is worth noting that several homogeneous heteropolyanion based catalysts have proven their performance in oxidation reactions owing to their redox and acid–base properties that can be adjusted by varying the heteroatom, counter anion, and addenda atoms [16–18]. It has been reported that in the oxidation of alkenes, the Keggin heteropolyanion is only a precursor to the real catalyst, {PO₄[M(O)(O₂)₂]₃}³⁻ and/or [M₂O₃(O₂)₂(H₂O₂)₂]²⁻ (M=Mo, W), formed by treating the heteropolyanions with aqueous H₂O₂ [9, 15]. It is worth noting that several heteropolyanion based catalysts have proven their performance in

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oxidation reactions owing to their redox and acid–base properties that can be adjusted by varying the heteroatom, counter anion, and addenda atoms [16–18]. Moreover, these kinds of materials do not undergo deactivation by water [19, 20]. Kanjina and Trakarnpruk [16] studied the oxidation of ethylbenzene with H₂O₂ in acetonitrile over Co-substituted heteropolytungstate tetra-*n*-butylammonium salt. The reactions were carried out for 24 h using an H₂O₂/ethylbenzene molar ratio of 10. Under these conditions, the oxidation of ethylbenzene yielded acetophenone and 1-phenylethanol. They obtained a high selectivity to acetophenone (93%). Based on the fact that the reaction was totally inhibited in the presence of 2,6-di-*tert*-butyl-4-methylphenol as a radical scavenger, they deduced that the reaction occurred in a radical process.

Oxidation of ethylbenzene with H₂O₂ in various solvents over vanadium containing mixed addenda heteropolyanions of the general formula, XV_{*n*}M_{12-*n*}O₄₀ (X = P or Si; M = Mo or W and *n* = 1, 2) catalysts was also investigated [21]. The highest conversion (31.3%) was obtained when acetic acid was used as a solvent. In this case, the oxidation yielded the carbonyl compound (aldehydes or ketones) as the major reaction product. Benzyl acetate was obtained with smaller amounts. In the opinions of the authors, the reaction proceeds by homolytic cleavage of H₅PV₂Mo₁₀O₄₀-peroxo intermediates. The formed hydroperoxy and hydroxy radicals initiate the formation of benzyl radicals, which leads to acetates or alcohols and aldehydes or ketones products. Unfortunately, like all homogeneous systems, they have some disadvantages, such as difficulties in recycling catalysts and the purification of products. Therefore, their exploration as heterogeneous catalyst systems is promising. The most commonly used route for the preparation of heterogeneous polyoxometalate catalysts is by loading polyoxometalates in porous materials. In the present work, the oxidation of ethylbenzene by the CO₂/H₂O₂ oxidizing system over bulk and activated carbon (AC) supported Keggin heteropolyanion catalysts was investigated.

2 Materials and methods

2.1 Materials

Sodium tungstate, Na₂WO₄·2H₂O (96%) and ethylbenzene, C₈H₁₀ (99.8%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Tetraethylammonium bromide (TEABr), (>99%) was purchased from Merck-Schuchardt (Hohenbrunn, Germany) and AC (activated decolorizing powder) was purchased from BDH Chemicals Ltd. (Poole, England).

2.2 Preparation of the catalysts

2.2.1 Unsupported catalysts: The H₃PW₁₂O₄₀ heteropolyacid was prepared according to the method by Deltcheff et al. [22]. The heteropolytungstate salts, namely, Co_{1.5}PW₁₂O₄₀, Cu_{1.5}PW₁₂O₄₀, Fe_{1.5}PW₁₂O₄₀ and Zn_{1.5}PW₁₂O₄₀ (abbreviated as FePW, CoPW, CuPW and ZnPW, respectively) were prepared as precipitates by slowly adding the required amount of Ba(OH)₂·8H₂O (to neutralize the three protons) to the aqueous solution of the H₃PW₁₂O₄₀ heteropolyacid. Then, the required amount of MSO₄·xH₂O was added (M = Co, Cu, Fe, or Zn), leading to the formation of insoluble barium salt, which was removed by filtration. The resulting solutions were allowed to stand for a few days at 4°C to allow the precipitation of the salts, which were then recovered from the solution by filtration.

2.2.2 AC supported Co_{1.5}PW₁₂O₄₀: To bind Co_{1.5}PW₁₂O₄₀ on AC support, oxygenated groups (functionalization) were created by using concentrated nitric acid according to the following steps: a 0.1 g sample of carbon was suspended in 100 ml nitric acid (65%), and heated for 5 h at 80°C, then cooled at room temperature. The treated AC was then washed with deionized water to pH 7, and dried at 100°C overnight. The resulting functionalized AC was then added to the desired amount of the prepared CoPW already dissolved in acetone under stirring for 30 min. After removing the excess acetone by heating at about 60°C, the prepared catalyst was dried in an oven at 80°C. The as-prepared catalyst was denoted AC-CoPW.

2.3 Characterization of the catalysts

The characterization of the as-prepared catalysts was performed utilizing inductively coupled plasma spectrometry (ICP) and Fourier transform infrared (FTIR) spectra. Elemental analyses were carried out under ICP measurements using a Perkin Elmer Nexion 300D spectrometer. IR spectra were recorded with an infrared spectrometer, SHIMADZU FTIR NICOLET-6700 (4000–400 cm⁻¹) as KBr pellets. The ultraviolet-visible (UV-Vis) spectra (in H₂O) were obtained with a double beam UV-Vis spectrophotometer (Philips 8800).

2.4 Catalytic oxidation

The oxidation reactions were performed in a stainless steel autoclave equipped with a magnetic stirring bar. The temperature of the autoclave was adjusted by a heating jacket. Typically, a mixture of 10 ml of ethylbenzene, 25 ml of H₂O₂ (30% in aqueous solution), and 0.75 g of catalyst was magnetically stirred at the desired temperature and CO₂ pressure. After the required time, the mixture was cooled, sampled, and analyzed with a gas phase chromatograph (Thermo Scientific Trace GC Ultra) equipped with a thermal conductivity detector and a flame ionization detector. The products were separated with a TR-5 capillary column (inner diameter 0.53 mm, film 1 μm). The products were identified by gas chromatography coupled with mass spectrometry (GC-MS) using a Thermo Scientific Trace GC Ultra gas chromatograph equipped with an AI 3000 autoinjector. For the separation of target compounds, a TR-5 MS-SQC capillary column (30 m × 0.25 mm inner diameter, 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 Catalyst characterization

3.1.1 Unsupported catalysts

Elemental analysis of the series of unsupported heteropolyanion salt catalysts was performed by ICP-MS and the results are reported in Table 1. The results were adjusted considering 1 atom of phosphorous per Keggin unit according to the nature of the Keggin structure and were found to be in good agreement with the expected ones for tungsten and counter ions.

The FTIR spectra of the unsupported heteropolyoxometalates are shown in Figure 1. The main characteristic features of the Keggin structure are observed at 917 cm^{-1} (ν_{as} P-Oa), at 970 cm^{-1} (ν_{as} W-Od), at 850 cm^{-1} (ν_{as} W-Ob-W) and at 767 cm^{-1} (ν_{as} W-Oc-W). These results are in agreement with those reported in the literature for Keggin heteropolyanions [22, 23]. In the Keggin structure, Oa is the oxygen atom common to PO_4 tetrahedron and one trimetallic group Mo_3O_{13} , Ob is the oxygen shared by two trimetallic groups, Oc binds two octahedral groups MoO_6 of the trimetallic group and Od refers to the terminal oxygen atom.

3.1.2 AC supported $Co_{1.5}PW_{12}O_{40}$

Regarding the FTIR of the carbon supported cobalt-heteropolytungstate, it can be seen from Figure 2 that the characteristic bands of Keggin heteropolyanions are present, which indicates that loaded CoPW on the AC had preserved its Keggin structure. Analysis of Keggin CoPW heteropolyanions in H_2O by UV-Vis spectroscopy showed an absorbance at 254 nm [24–26]. The intensity of this band was used to determine the amount of CoPW loaded on AC support. The obtained results showed that the nominal amount of CoPW loaded on AC support ($0.350\text{ g}/0.100\text{ g}$) was very close to the experimental amount ($0.315\text{ mg}/0.1\text{ mg}$).

3.2 Catalytic activity

The unsupported and AC supported heteropolyoxometalate salts with Co, Fe, Cu, and Zn as counter anions were tested for the oxidation of ethylbenzene by using CO_2/H_2O_2 as an oxidizing agent system. The reactions were carried out in the liquid phase at different reaction conditions. Analysis using GC-MS showed that the oxidation by CO_2/H_2O_2 led

Table 1: Elemental analysis of the as-prepared unsupported heteropolyanion salt catalysts.

$M_{1.5}PW_{12}$ (theoretical formulas)	P (molar ratio)	M	W
$Fe_{1.5}PW_{12}$	1	1468	11,945
$Co_{1.5}PW_{12}$	1	1512	11,974
$Cu_{1.5}PW_{12}$	1	15,145	13,201
$Zn_{1.5}PW_{12}$	1	1347	12,340

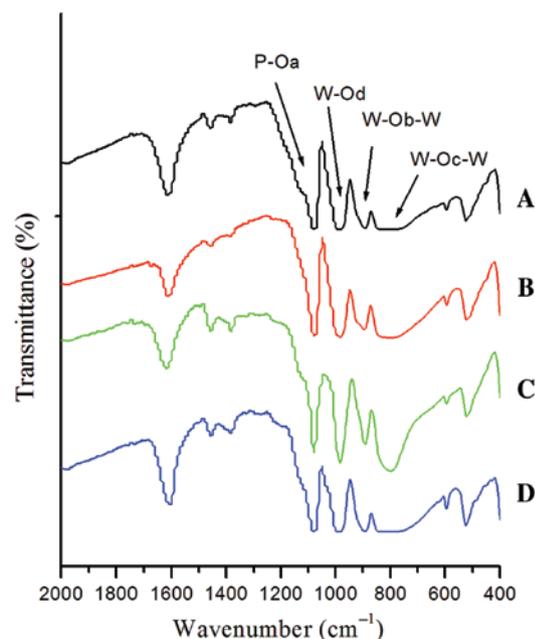


Figure 1: Fourier transform infrared (FTIR) spectra of the as-prepared MPW_{12} series of catalysts: (A) Co, (B) Cu, (C) Fe, (D) Zn.

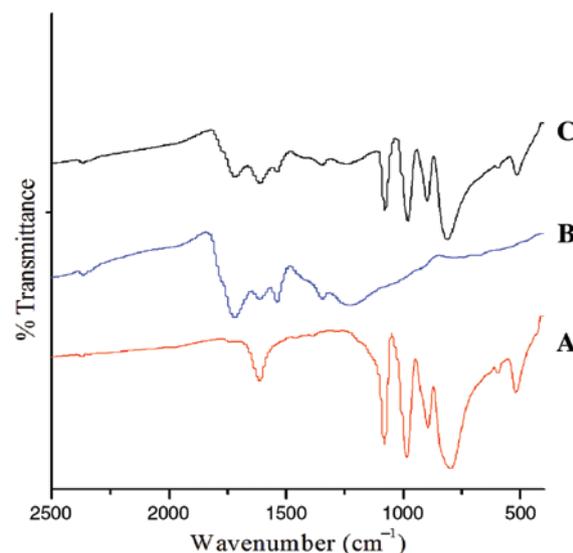
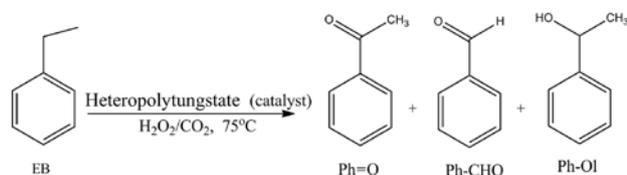


Figure 2: Fourier transform infrared (FTIR) spectrum of the (A) unsupported $Co_{1.5}PW_{12}O_{40}$ (CoPW), (B) functionalized activated carbon (AC) and (C) AC supported CoPW (AC-CoPW).



Scheme 1: Main products formed through oxidation of ethylbenzene by CO₂/H₂O₂ oxidizing agent system over heteropolytungstate catalysts.

to acetophenone, benzaldehyde and 1-phenylethanol as the main products. Toluene and benzene were obtained as minor products (Scheme 1).

3.2.1 Catalytic activity of the unsupported catalysts

FePW, CoPW, CuPW and ZnPW heteropolyoxometalate salts were tested for the oxidation of ethylbenzene by using CO₂/H₂O₂ as an oxidizing agent system. The reactions were carried out in the liquid phase using 10 ml of ethylbenzene and 25 ml of H₂O₂ at 70°C under 0.55 MPa CO₂ pressure for 7 h, using 0.35 g of a heteropolyoxometalate catalyst and 0.10 g of TEABr (co-catalyst). The results of the effects of the counter anions on the conversion and the product distribution are summarized in Table 2. It can be seen that all of the catalysts of the series led to acetophenone as a major product. CoPW heteropolytungstate, which has Co²⁺ as a counter anion, led to the highest conversion and highest selectivity in carbonyl compounds (acetophenone and benzaldehyde) compared to the rest of the catalysts.

Table 2: Effect of heteropolyoxometalate cation on ethylbenzene oxidation.

Catalyst	Conversion	Selectivity (%)				
		Acetophenone	Benzaldehyde	1-Phenylethanol	Benzene	Toluene
CoPW	3.70	51.8	16.8	3.87	20.8	4.72
CuPW	2.54	46.7	9.27	9.82	25.1	7.79
FePW	2.73	53.7	8.68	5.97	22.5	6.79
ZnPW	2.26	48.7	1.54	8.09	24.4	7.87

Reactions catalyzed by 0.35 g of catalyst and 0.10 g of tetraethylammonium bromide (TEABr) (co-catalyst) at 70°C under 0.55 MPa CO₂ pressure during 7 h; H₂O₂/ethylbenzene = 2.5.

Table 3: Effect of activated carbon (AC) support on ethylbenzene oxidation.

Catalyst	Conversion (%)	Selectivity (%)				
		Acetophenone	Benzaldehyde	1-Phenylethanol	Benzene	Toluene
CoPW	14.7	58.8	3.67	20.4	9.4	3.24
AC-CoPW	23.9	65.5	9.39	14	7.69	0.83

Reactions conditions: T = 75°C; P(CO₂) = 5.5; (H₂O₂/ethylbenzene) volume ratio = 2.5; tr = 7 h; m(cat) = 0.75 g and m (co-catalyst) = 0.25 g.

3.2.2 Effect of AC support

The high solubility of heteropolyanions in polar media and their low surface area (1–10 m²/g) limit their applications. To overcome these drawbacks, solid supports with high surface areas are used to heterogenize the heteropolyanions and to increase their surface areas, and therefore to improve their catalytic reactivity. For this purpose, the most active catalyst of the series was loaded on AC support and its catalytic activity was compared to its unsupported counterpart CoPW. The oxidation reaction of ethylbenzene (25 ml of H₂O₂ and 10 ml of ethylbenzene) was carried out at 75°C for 7 h, and the results are shown in Table 3. As can be seen, the AC support improved both the conversion and selectivity of carbonyl compounds (acetophenone and benzaldehyde). The significant increase in the conversion might be due to the fact that AC support increased the accessibility of the catalyst to ethylbenzene molecules (organic phase). Regarding the increase in the carbonyl compound selectivities, this might be because the surface of functionalized AC contains hydroxyl and carbonyl groups which have an acidic character, which is favorable for the oxidation to carbonyl formation.

3.3 Catalytic activity of AC-CoPW catalyst

To optimize the conversion and selectivity for the oxidation of ethylbenzene, the most active catalyst, AC-CoPW, was selected for investigating the effect of the co-catalyst,

reaction temperature, concentration of H₂O₂, amount of catalyst, reaction time and CO₂ pressure.

3.3.1 Effect of co-catalyst

The influence of the co-catalyst (TEABr) on the conversion and selectivity was examined. The results obtained (Figure 3) show that when the mass fraction of the co-catalyst increased from 0.16 to 0.25, the conversion increased from 20% to 40%. That is, it doubled. Beyond 0.25, the conversion remained unchanged. Contrary to conversion, the selectivity to acetophenone remained unchanged when the mass fraction of the co-catalyst varied from 0.16 to 0.25, and then decreased beyond 0.25. By contrast, the selectivity of 1-phenylethanol increased to the detriment of benzaldehyde over the whole range of the mass fraction. The obtained results indicate that the co-catalyst slowed the oxidation rate. This result is in agreement with that of Hâncu et al. [27] who reported that percarbonate (HCO₄⁻) can be formed through various reactions of H₂O, CO₂, and H₂O₂, or directly by the reaction of H₂O₂ with CO₂, and it is responsible for the transfer of oxygen to alkenes. In the opinion of the authors, in a hydrophobic organic solvent (CO₂) and a hydrophobic alkene (cyclohexene), this species might be transport limited. To explore the use of a phase transfer catalyst to enhance the reaction, the authors found that using tetraheptylammonium bromide at 1 mol % loading (relative to the cyclohexene) doubled the yield, whereas using 0.5 mol % produced little yield enhancement at 40°C. As a result of the above studies indicating that 0.25 was the optimum mass fraction, this catalyst/co-catalyst ratio was employed for all further investigations.

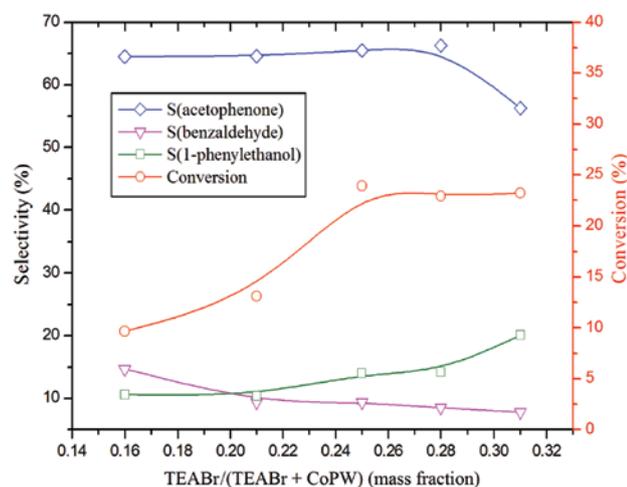


Figure 3: Effect of co-catalyst on the conversion and product selectivities over Co_{1.5}PW₁₂O₄₀ (CoPW) catalyst. Reaction conditions: (H₂O₂/ethylbenzene) volume ratio = 2.5; T = 75°C; P(CO₂) = 5.5; tr = 7 h.

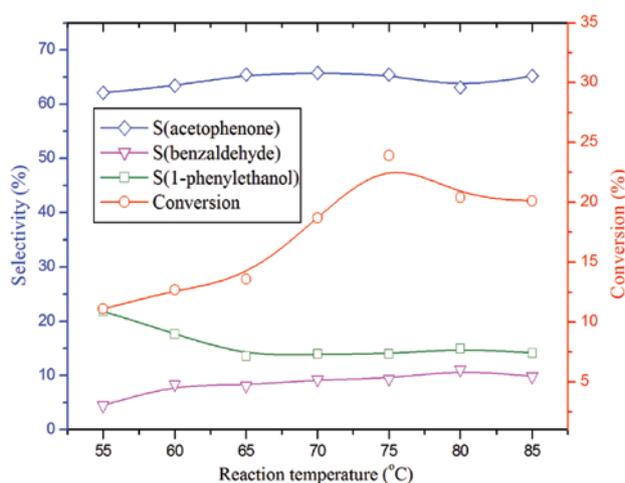


Figure 4: Effect of reaction temperature on the conversion and selectivity over activated carbon supported Co_{1.5}PW₁₂O₄₀ (AC-CoPW) catalyst. Reaction conditions: (H₂O₂/ethylbenzene) volume ratio = 2.5; P(CO₂) = 5.5; tr = 7 h; m(cat) = 0.75 g and m(co-catalyst) = 0.25 g.

3.3.2 Effect of reaction temperature

The effect of the reaction temperature on ethylbenzene oxidation was studied in the temperature range between 55°C and 85°C, and the results are shown in Figure 4. The results indicate that oxidation of ethylbenzene strongly depends on the reaction temperature. An increase in temperature up to 75°C improved the conversion, while a further increase up to 85°C caused a decrease in the conversion. The conversion decay observed for temperatures above 75°C could be attributed to the decomposition of H₂O₂ [10, 28]. Regarding the change of the selectivities, it can be seen that both the selectivities in acetophenone and benzaldehyde increased when the temperature was increased from 55°C to 75°C. Then, they remained almost unchanged from 75°C to 85°C. Conversely, the selectivity of 1-phenylethanol decreased when the temperature increased from 55°C to 75°C. This may be the result of further oxidation of 1-phenylethanol to acetophenone and benzaldehyde. Taking into account the above results, it can be concluded that 75°C is the optimum reaction temperature for acetophenone production.

3.3.3 Effect of H₂O₂

The dependence of the conversion and selectivity of the products on H₂O₂/ethylbenzene volume ratios is shown in Figure 5. It can be seen that increasing the H₂O₂/ethylbenzene volume ratio increased the conversion until it reached a maximum value of 25.2% at a volume ratio of 2,

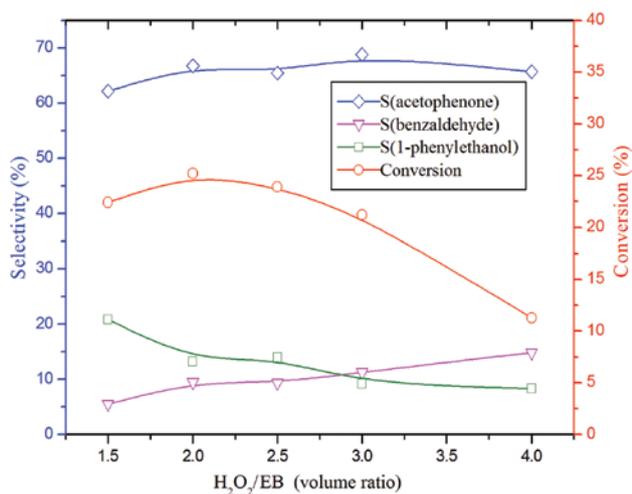


Figure 5: Effect of H₂O₂/ethylbenzene volume ratio on the conversion and selectivities over activated carbon supported Co_{1.5}PW₁₂O₄₀ (AC-CoPW) catalyst. Reaction conditions: T=75°C; P(CO₂)=5.5; tr = 7 h; m(cat)=0.75 g and m (co-catalyst)=0.25 g.

after which it decreased gradually. The conversion (11.3%) obtained at a volume ratio of 4 represents a loss of 55.2% compared to the obtained maximum value. These results can be explained by the fact that a large amount of H₂O₂ led to the oxidation of the products instead of the ethylbenzene reactant. Indeed, for large amounts of H₂O₂, the solubility of the ethylbenzene decreases considerably in the resulting (H₂O/H₂O₂) medium, which can lead to an increase in the transfer mass resistance, whereas the oxygenated products, which are more soluble, are easily oxidized. This suggestion is corroborated by the dependence of the selectivity of the products on the H₂O₂/ethylbenzene volume ratio, where a decrease of 1-phenylethanol selectivity in favor of that of acetophenone and benzaldehyde when the concentration of H₂O₂ increases, is clearly observed. Similar results were reported by Neuman and Levin-Elad [29] and Tuel et al. [30]. In the opinions of the authors, one possible major reason for a lower conversion is probably that the large excess of H₂O₂ led to deep oxidation of the products; the other is that H₂O₂ catalyzes H₂O₂ decomposition.

3.3.4 Effect of the amount of catalyst

The effect of the catalyst amount on ethylbenzene oxidation was investigated in the range 0.75–1.25 g. In the absence of the catalyst, no significant conversion was observed, which indicates that H₂O₂ alone is unable to oxidize ethylbenzene to a considerable extent. In the presence of the catalyst, the results (Figure 6) show that ethylbenzene conversion increased as the catalyst amount increased. It is worth noting that for all catalyst amounts,

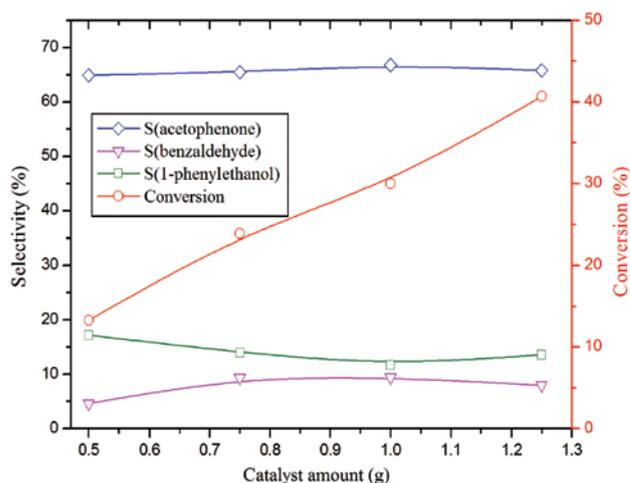


Figure 6: Effect of catalyst amount on the conversion and product selectivities. Reaction conditions: (H₂O₂/ethylbenzene) volume ratio = 2.5; T=75°C; P(CO₂)=5.5; tr = 7 h.

acetophenone was obtained as the major product with a selectivity of about 65%. Regarding 1-phenylethanol, it can be seen that its selectivity decreases slightly in favor of that of benzaldehyde. This is expected because the increase of conversion increases the consecutive reactions, that is to say, 1-phenylethanol consumption in favor of acetophenone and benzaldehyde formation.

3.3.5 Effect of reaction time

The effect of the reaction time on ethylbenzene oxidation is depicted in Figure 7. The selectivity of acetophenone and benzaldehyde increased with time up to 9 h.

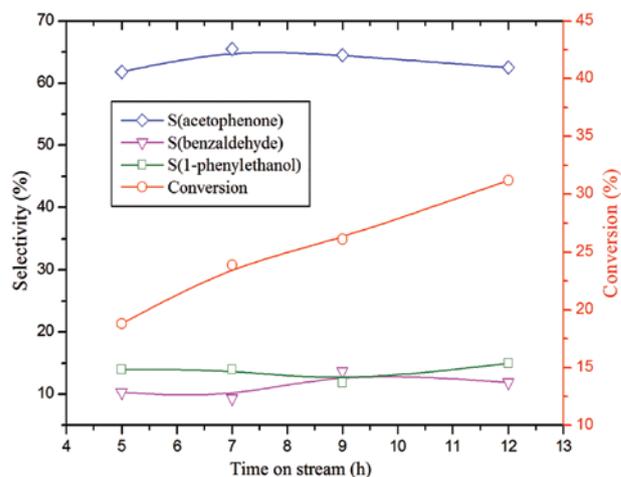


Figure 7: Variation of the conversion and product selectivities with reaction time. Reaction conditions: (H₂O₂/ethylbenzene) volume ratio = 2.5; P(CO₂)=5.5; m(cat)=0.75 g and m (co-catalyst)=0.25 g.

Beyond 9 h of reaction, a slight decrease of their selectivities was observed. Conversely, 1-phenylethanol selectivity decreased up to 9 h, and then it increased for the rest of the reaction time. In general, when the conversion increased, the consecutive reactions become significant, thus we can expect an increase in acetophenone and benzaldehyde. However, this is not the case; the results showed a continuous increase of the conversion throughout the time, but a decrease in the selectivities of acetophenone and benzaldehyde after 9 h. This result suggests that the effect of H₂O₂ was weakened (consumed) and only the effect of CO₂ as a soft oxidant remained because it is always supplied at the same pressure.

3.3.6 Effect of CO₂ pressure

The effect of CO₂ pressure was explored, and the results are depicted in Figure 8. It can be seen from the figure that increasing CO₂ pressure increased the conversion until it reached a maximum value of 24.5% at a pressure of 0.55 MPa. Further increase of CO₂ pressure did not significantly change the conversion value. As for the variations of the selectivities, it can be seen that in the 0–1.5 pressure range, the selectivity of 1-phenylethanol decreased in favor of that of acetophenone and benzaldehyde, which reached values of 69.5% and 10.4%, respectively. Beyond 0.15 MPa, the selectivities obtained remain almost unchanged. The above results showing that the conversion of ethylbenzene obtained with the oxidizing H₂O₂/CO₂ system was higher than that obtained with H₂O₂ alone (14.7%) and with CO₂ (1.7%) alone and under N₂ (16.2%), suggest the

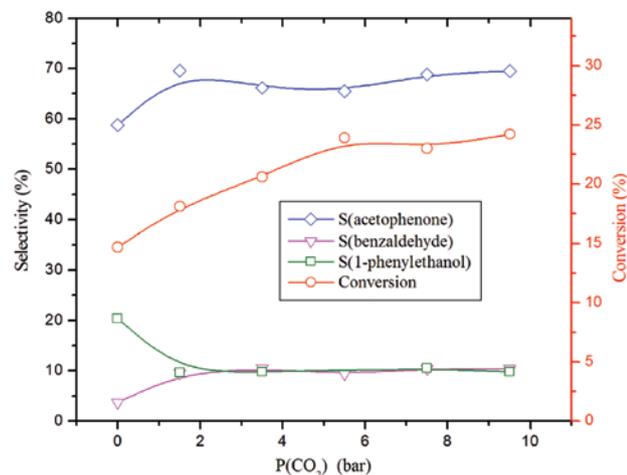


Figure 8: Effect of CO₂ pressure on conversion and PO selectivity. Reaction conditions: (H₂O₂/ethylbenzene) volume ratio = 2.5; tr = 7 h; m(cat) = 0.75 g and m (co-catalyst) = 0.25 g.

existence of a synergistic effect between H₂O₂ and CO₂. This synergistic effect can be explained by the fact that at high CO₂ pressures, the concentration of the percarbonate species (HCO₄⁻) responsible for oxidation by oxygen transfer increases with the increase of CO₂ amount, which obviously increases with the increase of CO₂ pressure; this leads to the increase in acetophenone and benzaldehyde amounts (deep oxidation) to the detriment of 1-phenylethanol (weak oxidation). These results are corroborated by those presented by Hâncu et al. [27]. In fact, by studying the epoxidation of alkenes by the H₂O₂/CO₂ system, the authors pointed out that the percarbonate species (HCO₄⁻) is responsible for the transfer of oxygen to alkenes. In the opinion of the authors, the percarbonate species (HCO₄⁻) can be formed by various reactions between H₂O, CO₂ and H₂O₂, or directly by the reaction between H₂O₂ and CO₂. Our results are also corroborated by those reported by Yao and Richardson [31] who reported that H₂O₂ reacts with aqueous bicarbonate (HCO₃⁻) to form percarbonate (HCO₄⁻), and that this species can epoxidize alkenes and oxidize sulfides.

4 Conclusion

In this work, the oxidation of ethylbenzene on a series of heteropolytungstate salts was investigated. The most active catalyst of the series was loaded onto an AC support. It was found that AC improves the conversion and selectivity of acetophenone. The increase of acetophenone selectivity may be due to acidic sites on the surface of the functionalized AC, which is favorable to oxidation reactions.

An optimization of the reaction conditions was studied and it was found that high reaction temperatures reduce the conversion due to the decomposition of H₂O₂. Oxidation by a large amount of H₂O₂ decreases the conversion because of the low solubility of ethylbenzene in the aqueous phase. The CO₂ pressure has a significant influence on both the conversion and product selectivities. Increasing CO₂ pressure increases the conversion owing to the synergistic effect between CO₂ and H₂O₂. This synergistic effect is due to the involvement of the percarbonate species (HCO₄⁻) responsible for oxidation by oxygen transfer.

The optimum conditions for the production of acetophenone are carrying out oxidation of ethylbenzene at 75°C, under a high pressure of CO₂ and using an H₂O₂/ethylbenzene volume ratio of 2.

Acknowledgements: This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

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