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RESEARCH ARTICLE

Catalytic Activity of Co_3O_4 Supported on Activated Carbon for Alcohols Oxidation

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Abstract: In this work, the catalytic performance of cobalt oxide supported on activated carbon was studied during the oxidation reaction of several aliphatic/aromatic primary or secondary alcohols. Good results for benzyl alcohol and benzyl alcohol derivatives conversion and selectivity were obtained, while aliphatic, primary, and secondary alcohols in the study exhibited low conversions. The influence of the use of sonication during the impregnation of cobalt species was also evaluated. The particle size, distribution and dispersion of cobalt oxide (Co_3O_4) were compared with the catalyst prepared conventionally. These results are essential for understanding more about the activity of this type of catalysts in the synthesis of aldehydes and ketones.

***Methods*:** Two powdered activated carbons, RX3 Extra provided by NORIT and G60 provided by Aldrich, were used as support of the catalysts. Cobalt oxide particles were deposited on the supports by means of the incipient wetness technique. A portion of this preparation was manually stirred (i), while another portion was subjected to sonication by 20 min (ii). The catalysts so synthetized were called: **Co/RX** and **Co/G60** as item (i); while **Co/RX-s** and **Co/G60-s** for item (ii). The performance and characterization of synthetized catalysts was studied with N_2 physisorption, AA (Atomic Absorption), SEM (Scanning Electron Microscopy) and H2-TPR (Temperature Programmed Reduction). Alcohols oxidation reaction was carried out at 80°C using 0.2 mmol of each alcohol, a mass of catalyst (0.1 g, 0.09 mol%) and 20 mL of toluene as solvent. Different types of alcohols were used: benzyl alcohol, 1-phenylethanol, 4-chlorobenzyl alcohol, cyclohexanol, 2-phenylethanol, 2-octanol, 1-heptanol, 1-octanol, 3-phenyl-1-propanol.

***Results*:** Co_3O_4 particles supported on activated carbon catalysts were prepared through incipient wetness method. According to the characterization results, the use of sonication is an important factor if used in the impregnation process. G60 and RX supports and Co/G60, Co/RX, Co/G60-s,Co/RX-s catalysts have a very high surface area (500-1900 m2 g-1). No differences were found on surface area between catalysts either using or not the sonication treatment. Cobalt loading by AA technique in each support showed a slight variation with the synthesis method. The cobalt content for Co/G60 and Co/RX catalysts was 9.5 and 9.6 % wt Co, respectively; while Co/G60-s and Co/RX-s was 9 % wt Co, indicating that ultrasound affects interaction between precursor and support. SEM analysis showed uniform distribution on the catalysts, when ultrasound is used during the synthesis. It is evidenced that the synthesized catalysts without the sonication treatment have more agglomerations, and consequently the particles are less distributed on the support surface. Excellent results were obtained in the oxidation of aromatic alcohols such as benzyl alcohol and benzyl alcohol derivatives, showing higher conversion and selectivity with **Co/G60-s** and **Co/RX-s** (100 % conversion and 99 % selectivity at 3 hours of reaction). It is believed that their chemical properties permit good dehydrogenation and the subsequent oxidation. On the contrary, the aliphatic primary and secondary alcohols by their structural and chemical characteristics do not demonstrate good conversions.

***Conclusion*:** Cobalt oxide-based catalysts supported on activated-carbon (Co/AC) showed good catalytic activity and selectivity during the alcohol oxidation. The use of sonication is an important factor if used in impregnation step, because it causes physicochemical changes by the cavitation and implosion processes, changing the nucleation and agglomeration of the active phase on support. This favors the catalytic development of the system mainly involved in quantity, dispersion and particle size. Excellent results were obtained in the oxidation of aromatic alcohols such as benzyl alcohol and benzyl alcohol derivatives, showing higher conversion and selectivity with this type of catalyst (Co/AC). The effect of sonication on the preparation of this type of catalysts might contribute to the study of the green oxidation reaction of alcohols with O_2 as oxidizing agent.

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1. INTRODUCTION

Aldehydes and ketones have been identified as raw material compounds in different industrial processes and fine chemistry [1, 2]. They may be obtained from alcohol oxidation, using conventionally oxidizing agents like chromium (IV) salts, but this reaction presents considerable difficulties by stoichiometric amounts [3-5]. These oxidants, besides being very expensive, generate wastes that pollute the environment and produce byproducts as carboxylic acids. Development of catalysts and oxidizing agents to minimize these

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drawbacks is necessary [6, 7]. Benign heterogeneous catalysts and environmentally friendly oxidizing agents greatly help to reduce the limitations in the alcohol oxidation reaction [8, 9].

In recent years, it has been important to study the selective oxidation of various types of alcohols into their corresponding aldehydes and ketones**.** Reports of Seok, S *et al.* [10] and Babak Karimi *et al.* [11] showed interesting results, some differences in the oxidation of different types of aliphatic and aromatic alcohols were observed. Yamaguchi and Mizuno [12, 13] have proposed the use of oxidizing agents like O_2 or air which generate H_2O as the unique byproduct, being the most promising work in these processes.

It has been developed heterogeneous catalysts based on transition metals like Pd [14, 15], Pt [16, 17], Rh [18, 19], Ru [20, 21], among others. However, although these catalysts present good activity and selectivity, they tend to be quite expensive. Thus, the use of low-cost metals such as Mn [22-25], Ni [9], Co [26-29], and their respective oxides have an industrial interest. Several materials have been used as catalyst supports for the alcohol oxidation reaction, due to their influence in different parameters physic-chemicals for example MCM-41[30], SBA-15 [31], ZrO_2 [32].

Activated carbon (AC) has well known properties: high superficial area, chemical surface that might be modified with different treatments, good stability, low cost, inertness in liquid reaction media, and porosity [22-24]. Zhu *et al.* [33, 34], demonstrated excellent results during oxidation of benzyl alcohol by using activated carbon supported cobalt oxide catalysts (Co_3O_4/AC) and previous studies [28] showed the importance of the type of support in the catalytic activity of cobalt species. The ultrasonic techniques for synthesis and preparation of solid catalysts have great importance [35-37], because they might affect the catalysts properties such as dispersion, particle size, morphology, among others either in a positive or a negative way, depending on the case. Some effects of the use of sonication treatment over the activated carbon, which improve the efficiency of support and the catalyst itself have been reported [38].

In this work, the catalytic performance of cobalt oxide supported on activated carbon was studied during the oxidation reaction of several aliphatic/aromatic primary or secondary alcohols. The influence of the use of sonication during the impregnation of cobalt species was also evaluated. The particle size, distribution and dispersion of cobalt oxide (Co_3O_4) were compared with the catalyst prepared conventionally.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation

Two powdered activated carbons, RX3 Extra provided by NORIT and G60 provided by Aldrich, were used as support of the catalysts. Cobalt oxide particles were deposited on the supports by means of the incipient wetness technique according to procedures described [28, 33, 34]. 0.5 g of $Co(NO_3)_2$• $6H_2O$ (MERCK, 99.9%) were dissolved in 5 mL of deionized water adding 1 g of carbonaceous support. Then proceeded as follows: (i) a portion of this preparation was manually stirred, while (ii) another portion was subjected to sonication by 20 min at 42 kHz and 100W (Branson Ultrasonics 2510), posteriorly both samples were dried in an oven (WTB-Binder 0,80Kw) at 110 °C during 12 h. Finally, the samples were treated in an inert atmosphere (N_2) at 350 °C for 2 h in a circular oven. The catalysts so synthetized were called: **Co/RX** and **Co/G60** as item (i); while **Co/RX-s** and **Co/G60-s** for item (ii) previously described.

2.2. Characterization

Brunauer-Emmet-Teller surface area (S_{BET}) and pore average sizes of the supports and catalysts were determined by nitrogen physisorption (N_2) at -196 °C following the BET model in Quantachrome Autosorb Automated equipment. 0.02 g of each sample was degassed in an inert atmosphere (N_2) at 150 °C during 3 h, before the measurement. Metal loading in the catalysts was determined by Atomic Absorption (AA) in Thermo-electron Series S equipment. 23 mg of sample were calcined at 900 °C to mineralize the carbonaceous support, and then it was digested with hydrochloride, nitric and hydrofluoric acids during 2 h at 180 °C. Finally, boric acid was added to complex the excess hydrofluoric acid. The solution obtained was measurement at λ= 240.7 nm. Average particle size was determined *via* Transmission Electronic Microscopy (TEM), images were obtained by an electronic microscope (JEOL 1200 EX) operating at 90 kV. Temperature Programmed Reduction with H_2 (H_2-TPR) measurements of catalysts were carried out by using 10% H_2/Ar as a reducing gas. The gas flow rate was 25 mL min^{-1} and was kept constant by using mass flow controllers at 10 °C min^{-1}. Calibration was made by reducing 30 mg of CuO powder (99%, Merck) under the same experimental conditions. Area under the peaks from hydrogen consumption was determined by the deconvolution using the Fityk programme. The electronic state of the surface species and their surface atomic ratios of catalysts were determined by X-ray Photoelectron Spectroscopy (XPS). XPS profiles of carbonaceous supports were made. Measurements were acquired in a VG-Microtech Multilab equipment with a MgKα (hv: 1253.6 eV) radiation source and a passing energy of 50 eV, following the Co $2p_{3/2,}$ N $2p_{3/2}$, O 1s, and C 1s peak binding energies (BE). The analysis pressure during data acquisition was kept at 5.10^{-7} Pa. Samples were treated by following the same pretreatment conditions for each catalyst. A careful deconvolution of the spectra was made and the areas of the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of 30-70% proportions, using the sensitivity factors of each element normalized the areas. The reference BE was the C 1s peak at 285.0 eV.

2.3. Catalytic Test

Reaction tests were performed in a semi-batch reactor with constant stirred. Equipment consist of a three-necked flask with thermometer, condensation tube and oxygen entry. Alcohols oxidation reaction was carried out at 80°C using 0.2 mmol of each alcohol, a mass of catalyst (0.1 g, 0.09 mol%) and 20 mL of toluene (Merck, 99.9%) as solvent. Different types of alcohols were used: benzyl alcohol (Merck, 99.5%), 1-phenylethanol (Merck, 97%), 4-chlorobenzyl alcohol (Sigma, 99%), cyclohexanol (Fisher

Scientific, reagent grade), 2-phenylethanol (Merck, 98%), 2-octanol (Alfa Aesar, 98%), 1-heptanol (Merck, 99%), 1-octanol (Carlo Erba, 99%), 3-phenyl-1-propanol (Sigma, 98%). As feed an oxygen flow of 50 mL min^{-1} was used as oxidizing agent. Reactant and products were analyzed by gas chromatography coupled to mass detector CG-MS (GC 6890 Series Y1530A) and a DB-VRX nonpolar capillary column.

3. RESULTS AND DISCUSSIONS

3.1. Characterization

XRD (X-ray Diffraction), TGA/MS (Thermogravimetric Analysis/Mass Spectrometry) and XPS (X-ray Photoelectron Spectroscopy) analysis of supports and catalysts were report in previous works [28]. According to the results, G60 and RX supports are amorphous. Further, the Co/AC catalysts evidence a crystalline phase as a cobalt oxide spinel (Co_3O_4). XPS results showed peaks at 779.5 and 780.8 eV that correspond to Co^{3+} and Co^{2+} surface species of Co_3O_4, which is very active for the reaction studied [29, 39]. TGA/MS analysis for G60 and RX showed a greater amount of functional groups, the catalysts prepared with these supports exhibited the best catalytic performance in the benzyl alcohol oxidation [28].

Table **1** presents the superficial properties for both the supports and catalysts, with and without the sonication treatment. It is well known that the carbonaceous support has a very high surface area (500-1900 m^2 g^{-1}) [40], according to this RX and G60 S_{BET} is high, as shown in Table **1**.

It can be seen that both catalysts have lower values of S_{BET}, compared to the supports, which suggests that the supported metallic particles are blocking an important fraction of the support surface area (23-24%) [37]. No differences were found on surface area between catalysts either using or not the sonication treatment, thus it was not the main factor. In the same way, RX and G60 supports showed the highest pore total volume, while Co/RX, Co/RX-s, Co/G60 and Co/G60-s catalysts present similar values (Table **1**); this suggests that no change occurs in the surface properties (S_{BET}) of the catalysts, using manual stirring or sonication during the preparation step.

Cobalt loading by AA technique in each support showed a slight variation with the synthesis method. The cobalt content for Co/G60 and Co/RX catalysts was 9.5 and 9.6 % wt Co, respectively; while for Co/G60-s and Co/RX-s was 9 % wt Co, indicating that ultrasound affects interaction between precursor and support. Cavitation processes affect functional groups on the activated carbon surface, which leads to less interaction between cobalt precursor and support, reducing the cobalt loading by leaching.

SEM analysis allowed seeing the morphology of the catalysts as well as distribution, dispersion and the average particle size. (Fig. **1**) illustrates two SEM images of the synthesized catalysts, in which morphological differences are observed.

A uniform distribution on the support surface is observed when ultrasound is used during the synthesis **(**Fig. **1** (**b**), (**d**)), while, it is evidenced that the synthesized catalysts without the sonication treatment have more agglomerations, and consequently the particles are less distributed on the support surface (Fig. **1** (**a**), (**c**)). This behavior is due to the effect of cavitation [41], which makes the particles of Co_3O_4 become well and uniformly dispersed on the support [42]. In addition, this process might remove impurities and some labile groups of the surface as well as a portion of the pore walls, especially the microspores, may be destroyed [38].

Fig. **2** shows the frequency histograms of the catalysts obtained by SEM. In this figure is observed that nanoparticles of supported cobalt oxide (Co_3O_4 <100 nm) were impregnated in the whole catalysts. Co/G60 and Co/G60-s catalysts present an average particle size between 20-30 nm. However, Co/G60-s present larger particle sizes indicating less uniformity, in comparison with its equivalent without sonication treatment.

In Fig. **2** (**c**, **d**), Co/RX and Co/RX-s catalysts have a more noticeable difference in particle size, approximately 30 nm were obtained for Co/RX, while for Co/RX-s average sizes were 40-50 nm. This behavior is observed in those catalysts that were prepared with sonication, causing greater size in particles of Co_3O_4; this might be caused mainly by cavitation and implosion that affects the crystalline structure of the precursor causing effects in both the nucleation and the sintering [42, 43].

Table 1. BET surface area, pore volume, H_2-TPR, and metal loading results for supports and catalysts.

Sample	S_{BET} (m^2 g^{-1})	V_μ (cm^3 g^{-1})	Metal Loading (% wt)	H_2-TPR					
				Co_3O_4-CoO		CoO-Co^0		AC	
				Area	T_{max} (°C)	Area	T_{max} (°C)	Area	T_{max} (°C)
RX	1524	0.883	--	--	--	--	--	42368	688
Co/RX	1007	0.666	9.6	46597	323	130148	444	127369	650
Co/RX-s	1011	0.657	9.0	23715	271	91935	433	117148	660
G60	978	0.940	--	--	--	--	--	41159	680
Co/G60	704	0.710	9.5	25978	267	68429	407	230143	604
Co/G60-s	729	0.738	9.0	18397	265	27753	388	269311	584

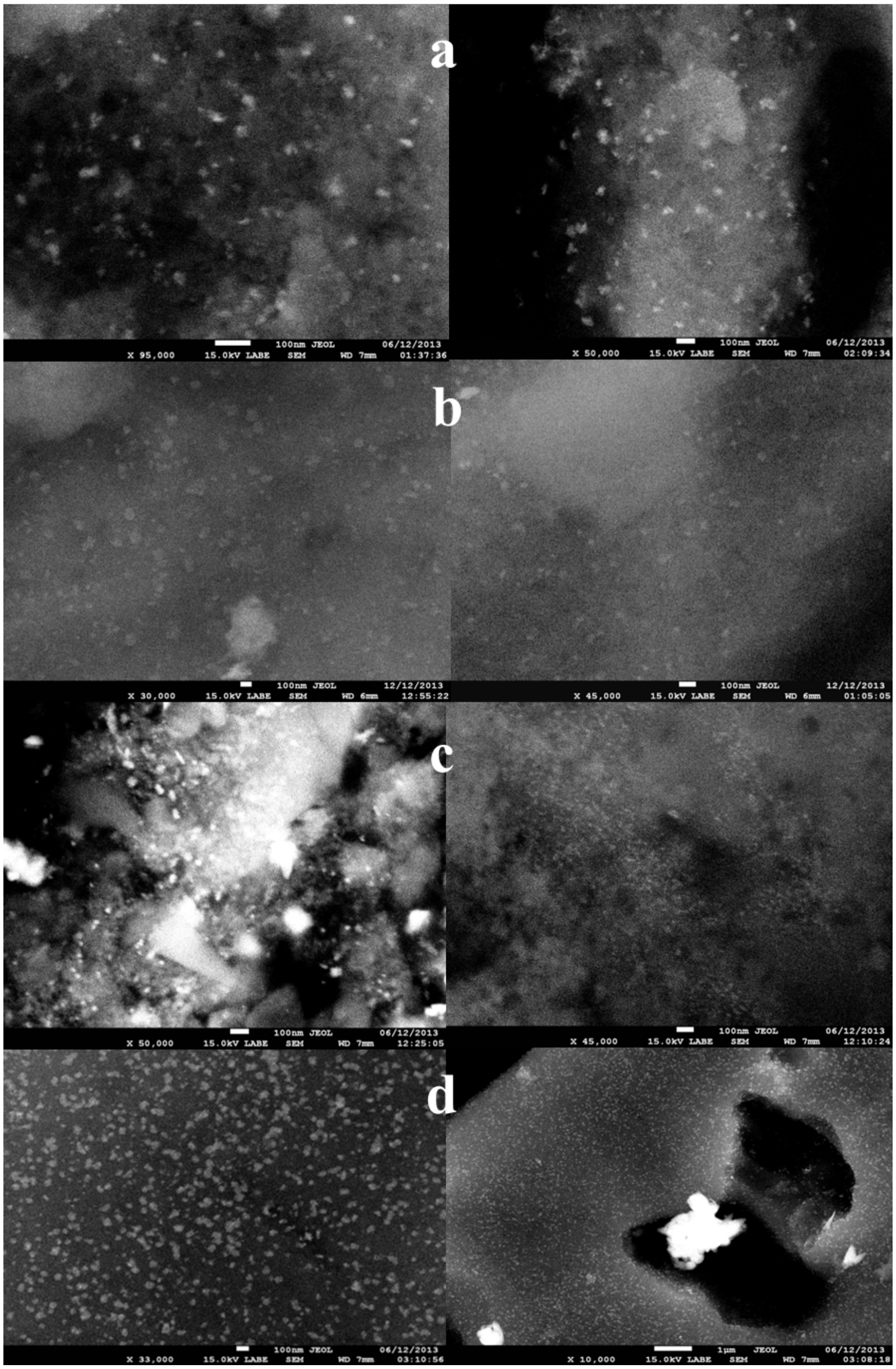


Fig. (1). SEM analysis for (**a**) Co/G60, (**b**) Co/G60-s, (**c**) Co/RX and (**d**) Co/RX-s catalysts.

H_2-TPR analysis helped to identify the oxidation states and the reducible character of impregnated cobalt species, as well as the amount of reducible species in the AC supports determined by deconvolution of TPR peaks. Area under the peaks, maximum temperature (T_{max}) and the assignment of each signal reducible species of cobalt for each catalyst are shown in Table **1**.

In Fig. **3** the H_2-TPR profiles for G60 and RX supports and catalysts, similar peaks for activated carbon reduction are evident, while in the catalysts differences are observed in the H_2-TPR profile in each case. The TPR for G60 and RX supports (Fig. **3** (**c**)) exhibits a single characteristic peak around 700°C caused by the reduction of surface functional groups such as carbonyls, carboxyls, phenols among others from the activated carbon [44, 45]. The H_2-TPR profile of the catalysts (Fig. **3** (**b**, **c**)) shows the presence of very similar peaks with differences in intensity along the whole TPR profile.

The reduction of cobalt species indicates the presence of Co_3O_4 [46]. Initially, a peak around 250-350 °C is attributed to the reduction of Co_3O_4 to CoO, later a second peak around 400-500 °C is attributed to the reduction of CoO to Co^0.

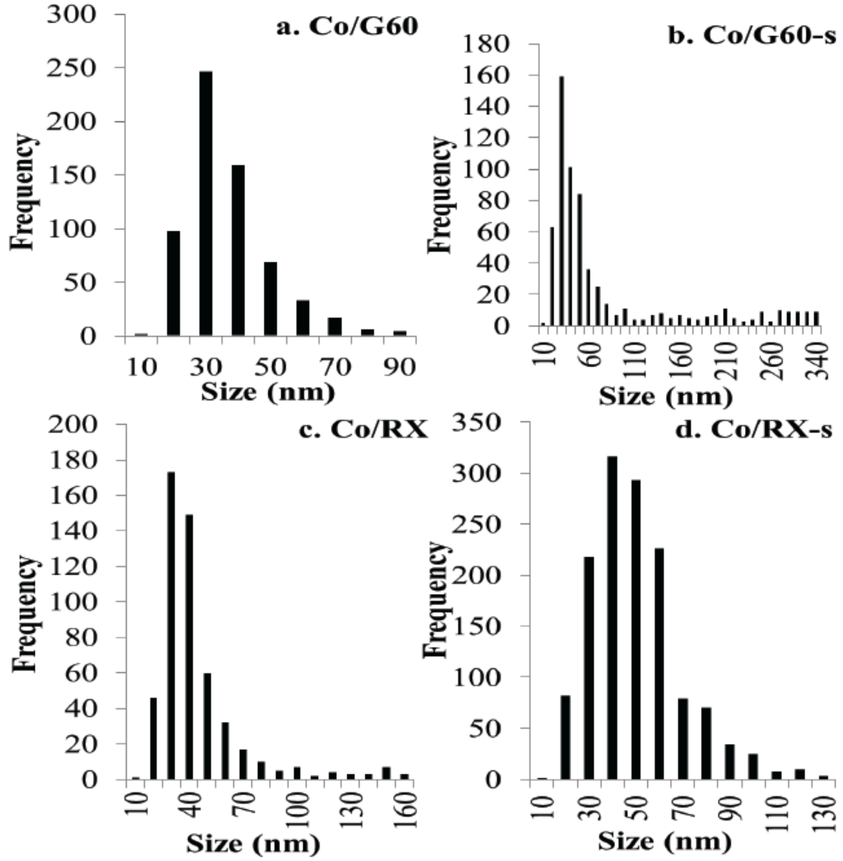


Fig. (2). Particle size distribution of the catalysts: **a**) Co/G60, **b**) Co/G60-s, **c**) Co/RX and **d**) Co/RX-s.

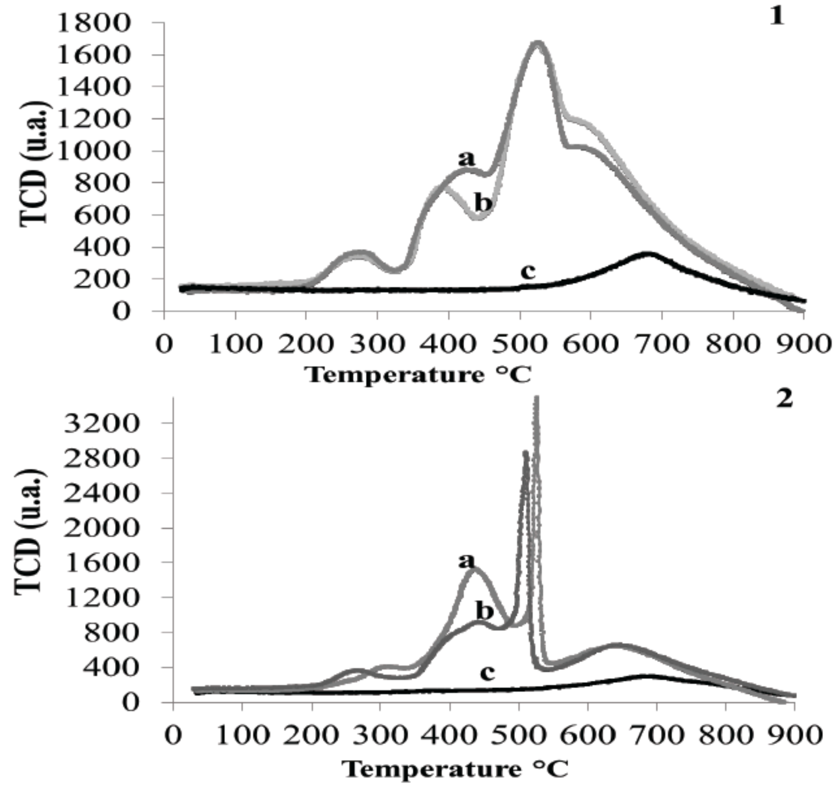


Fig. (3). H_2-TPR profiles for (1) **a**) Co/G60, **b**) Co/G60-s and **c**) G60; (2) **a**) Co/RX, **b**) Co/RX-s and **c**) RX.

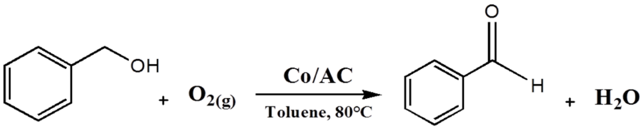
Similarly, a peak around 500 °C is observed which is attributed to the catalytic effect of the catalysts by the presence of the products of AC and hydrogen reduction [47, 48].

The reducibility of the species of these catalysts strongly depends on their particle size and/or interaction with the support [49]. In order to observe the degree of reducibility and the interaction with the support, the values of the area obtained and the peak temperature of the H_2-TPR are compared. Results show areas of higher hydrogen consumption for Co/G60 and Co/RX catalysts, indicating greater reducibility of the cobalt species, which may be related to greater amount of cobalt as determined by AA (Table **1**) and smaller particle size observed in SEM analysis (Fig. **2**).

On the other hand, Co/G60-s and Co/RX-s catalysts have lower hydrogen consumption, confirming a larger particle size; maximum reduction at low temperatures are still observed confirming a better distribution of these particulates on the catalyst as determined by SEM images Fig. **1**. The area and the maximum reduction temperature of the activated carbon supports depend on the amount of reducible functional groups [28]. In this case, it is evident that the catalysts with G60 support have a greater number of reducible functional groups and maximum reduction at lower temperatures, in comparison with catalysts with RX3 support. This indicates greater presence of functional groups in G60 support, making it an interesting parameter for both the activity and oxidizing power in the oxidation reaction of alcohols. Previous studies [28], showed the oxidant power dependence of the catalysts with greater presence of functional groups in the activated carbon supports in the presence of molecular oxygen.

3.2. Catalytic Activity

Benzyl alcohol (Scheme **1**) was chosen as a standard substrate in order to evaluate the synthesized catalysts and the performance of catalytic system.



Scheme **1**. Oxidation reaction of benzyl alcohol to benzaldehyde.

The catalytic results of this oxidation reaction can be observed in Table **2**, all catalysts had activity for this type of oxidation reaction, with high percentages of total conversion (*X*, %) and selectivity (*S*, %) towards the production of benzaldehyde.

Compared the catalysts synthesized from different activated carbon supports, it can be observe that Co/G60 catalyst showed higher activity that Co/RX, despite having a lower surface area (Table **2**), this difference is mainly due to the physicochemical properties of supports and their interaction with the active phase. However Co/G60-s and Co/RX-s exhibited the same activity. The previous studies showed greater activity in Co/G60 because it exhibited the best oxidative properties [28]. It can be also observed that this catalyst has a smaller average particle size, this generate a better interaction with the substrate showing greater synergism between the active phase and the G60 support.

When comparing the catalytic performance of the solids with and without sonication on the catalytic activity, it was observed that the catalysts synthesized with sonication have a higher activity, because they can totally oxidize the benzyl alcohol in less time maintaining its selectivity as shown in Fig. **4**. The increase in catalytic activity may be caused by both the dispersion and particle size of the active phase in the catalyst. As observed above, SEM images of the Co/G60-s and Co/RX-s catalysts show that the oxide particles are not agglomerated on the surface of the support and are evenly distributed. Even with lower cobalt content (Table **1**). This catalytic behavior is caused because there is greater availability of active sites throughout the specific area of the catalyst by improving the oxidative dehydrogenation caused by the Lewis acidity of the oxide with the alcohol and its subsequent oxygen oxidation [33]. However, it should not be ruled out the effect of surface chemistry and porosity of AC on both conversion and selectivity [33, 40].

Reaction Conditions: Alcohols (0.2 mmol), Co/AC (0.1g), Toluene, 80°C, O_2 (50 mL min^{-1})

While the catalysts without sonication showed smaller sizes of particles, they exhibited greater agglomeration causing less distribution which greatly decreases their catalytic activity, compared with the catalysts with sonication.

Table **3** shows the results of catalytic oxidation for other aromatic and aliphatic alcohols, with the most active catalysts (Co/G60-s and Co/RX-s), the influence of variation in the chemical structure, functionality, electronic and steric effects of substituents on the alcohol during oxidation was investigated. The oxidation of 4-chlorobenzyl alcohol showed high conversion rates (96%) and selectivity values (≥ 99%) and 2-phenylethanol also showed a strong behavior in undergoing oxidation despite the fact that it is a secondary alcohol and it needs a longer reaction time. The activity of

Table 2. Results of benzyl alcohol oxidation reaction.

Catalyst	**t (h)**	***X* (%)**	**S (%)**	**Activity** **mmol BA h^{-1} g^{-1}Co** $h^{-1}g_{Co}^{-1}$
Co/G60	3	88	>99	6.2
Co/G60-s	3	100	>99	7.4
Co/RX	3	57	92	4.0
Co/RX-s	3	100	>99	7.4

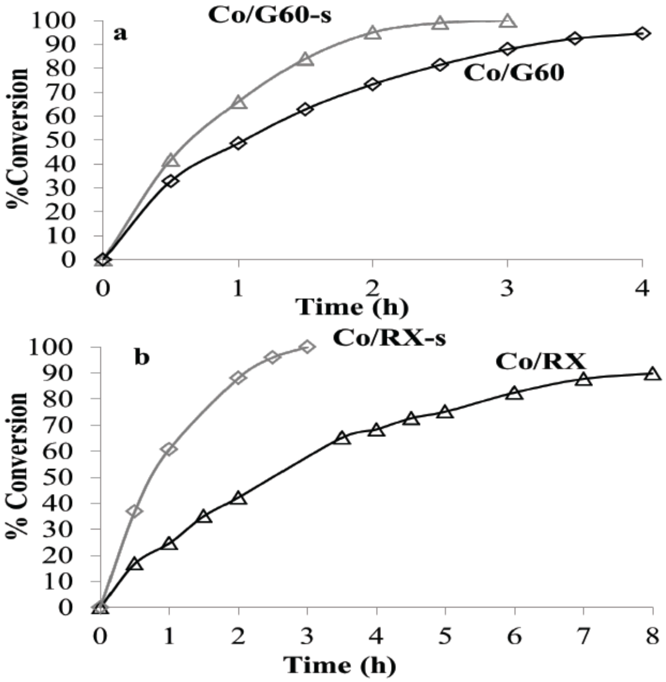
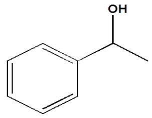
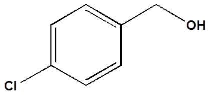
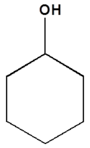
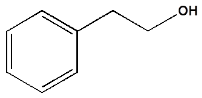
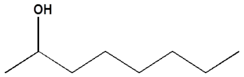
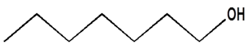
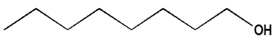
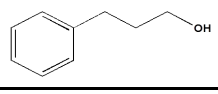


Fig. (4). Conversion of Benzyl Alcohol as a function of time (h) for **a**) (Δ) Co/G60-s (◊) and Co/G60; **b**) (◊) Co/RX and (Δ) Co/RX-s catalysts.

Table 3. Oxidation reaction of aromatic and aliphatic alcohols by O_2 catalyzed by Co/G60-s and Co/RX-s catalysts.

Substrat	Catalyst	t (h)	*X* (%)	S (%)
	Co/RX-s	8	60	100
	Co/G60-s	8	79	100
	Co/RX-s	5	96	92
	Co/G60-s	5	96	100
	Co/RX-s	7	15	100
	Co/G60-s	4	5	100
	Co/RX-s	9	6	60
	Co/ G60-s	9	9	75
	Co/RX-s	8	14	100
	Co/ G60-s	8	24	60
	Co/RX-s	7	5	100
	Co/ G60-s	7	7	100
	Co/RX-s	8	4	100
	Co/ G60-s	8	8	46
	Co/RX-s	6	3	100

Reaction Conditions: Alcohols (0.2 mmol), Co/AC (0.1g), Toluene, 80°C, O_2 (50 mL min^{-1})

the benzyl alcohol derivatives is provided by the electronic stability conferred by the presence of the aromatic ring and substituent groups such as –Cl. This substituent has two electronic effects on the phenyl ring: 1) resonance donation, and 2) inductive withdrawal [50]. In aromatic alcohols, halogen substituents in the *para* positions act as electron-donor groups and provide major resonance contribution due to the availability of their lone pairs, easily promoting the dehydrogenation of the alcohol and therefore its oxidation.

While the primary and secondary aliphatic alcohols showed low conversion rates, it might be caused by the poor Lewis acid character from the oxygen of the hydroxyl group of these molecules, in the case of 2-octanol, 1-octanol and 1-heptanol; the steric hindrance does not allow a good adsorption and subsequent dehydrogenation of the molecules decreasing their conversion.

CONCLUSION

Cobalt oxide-based catalysts supported on activated-carbon (Co/AC) showed good catalytic activity for selectivity oxidation of alcohols. The use of sonication is an important factor if used in impregnation process, because it causes physicochemical changes by the processes of cavitation and implosion, changing processes of both nucleation and agglomeration of the active phase on support, which favor the catalytic development of the system mainly involved in quantity, dispersion and particle size. Excellent results were obtained in the oxidation of aromatic alcohols such as benzyl alcohol and benzyl alcohol derivatives, showing higher conversion and selectivity with this type of catalyst (Co/AC); it is believed that their chemical properties permit good dehydrogenation and the subsequent oxidation, in difference with the aliphatic, primary and secondary alcohols, that by their own structural and chemical characteristics do not demonstrate good conversions. The effect of sonication on the preparation of this type of catalysts might contribute to the study of the green oxidation reaction of alcohols with O_2 as oxidizing agent.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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