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Carbon support treatment effect on Ru/C catalyst performance for benzene partial hydrogenation

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ABSTRACT

Ru/C catalysts were prepared from commercial activated carbon submitted to different treatments. The catalysts were prepared by incipient wetness impregnation, through an aqueous solution of the precursor RuCl₃·xH₂O. After impregnation, some catalysts were submitted to direct reduction treatment under H₂ flow at the temperature of 150 °C, in order to evaluate the effects of activation. The supports were characterized by N₂ adsorption, Boehm and potentiometric titration. The X-ray photoelectron spectroscopy was used to study the supports and catalysts surfaces, while scanning electron microscopy allowed us to determine the chemical composition and observe the catalysts morphology. Ru/C catalysts performance was evaluated within the hydrogenation reaction of benzene in liquid phase, using a Parr reactor. The reaction was conducted under total pressure of 5.0 MPa of H₂, at a temperature of 100 °C with water in the reaction medium. The obtained results indicate that the Ru/C system catalytic performance is influenced for determined functional groups present on the activated carbon surface. The carbonyl groups decrease the activity and selectivity of the reactions, while an increase of the carboxylic groups leads to more active catalysts and the highest yield of cyclohexene.

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1. Introduction

The partial hydrogenation of benzene is a chemical reaction employed in the productive sector and environmental protection. The cyclohexene obtained can be industrially used for several syntheses of compounds, as for instance nylon. Moreover, due to severe restrictions regarding the presence of aromatic toxic compounds in oil-derivative fuels, this reaction represents a promising alternative treatment, without significant loss of octane [1]. Hydrogenation reaction of benzene characteristically occurs in successive and exothermic (benzene \rightarrow cyclohexene \rightarrow cyclohexane) stages and it is highly favorable for cyclohexane production.

Therefore, through kinetic strategies higher selectivity can be obtained for the intermediary product. In such reaction, rutheniumbased catalysts have led to higher yields of cyclohexene [2,3], especially in the presence of water in the reaction medium [4]. Although some studies highlight a better performance of ruthenium mass catalysts [5], researches are still being carried out to develop supported catalysts, aiming at reducing their costs and exploring possible potentialities of metal–support interaction [6]. Activated carbon is considered an inert material if compared to other catalytic supports. Nevertheless, the formation of active sites, constituted by heteroatoms (O, N and H) is responsible for the acidity or basicity of the solid, as well as for their redox properties [7]. Particularly, the presence of oxygen on the carbon surface may influence the catalyst hydrophilicity and, as a consequence, influence the yield of the desired product, affecting the precursor-support interaction during the catalyst preparation. In liquid reaction medium, water and hydrophilic catalysts have been widely utilized to inhibit the hydrogenation of the formed cyclohexene [8]. The main role of water is to withdraw cyclohexene from the surface of the hydrophilic catalyst, reducing its undesired hydrogenation. By studying benzene hydrogenation in liquid state, applying Pt catalysts prepared from activated carbon modified with nitric acid and N₂, Aksoylu et al. [9] noticed that such treatments led to more active and selective catalysts. In this context, the purpose of this article is to study the influence of treatment applied to support in the performance of Ru/C catalysts to partial benzene hydrogenation in liquid state.

2. Experimental

2.1. Preparation of supports and catalysts

This study used a commercial carbon (Clarimex 061) produced by Brascarbo Agroindustrial Ltd. This solid, denominated

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Table 1

Treatments applied to original carbon C(OR).

Support	Treatment
C(N2/300)	Heating at 10 °C/min under a flow of 250 mL of N_2 /min up to the temperature of 300 °C, maintained for 7 h
C(N2/400)	Heating at 10 °C/min, under a flow of 250 mL of N ₂ /min, up to the temperature of 400 °C, maintained for 7 h
C(HN25)	Oxidation in aqueous solution of 2 mol of HNO ₃ /L, under stirring at 25 °C for 3 h. Washing in distilled water until reaching neutral pH and drving at 100 °C
C(HN90)	Oxidation in aqueous solution of 8.6 mol of HNO ₃ /L, under reflux at 90 °C for 20 h. Washing in distilled water until reaching neutral pH and drying at 100 °C
C(HN90-N2/300)	Oxidation in aqueous solution of 8.6 mol of HNO_3/L , under reflux at 90 °C for 20 h. Washing in distilled water until reaching neutral pH and drying at 100 °C. Heating at 10 °C/min, under a flow of 250 mL of N ₂ /min, up to the temperature of 300 °C. maintained for 7 h
C(H2O2)	Oxidation in aqueous solution of 2 mol of H_2O_2/L , under stirring at 25 °C for 3 h Washing in distilled water until reaching neutral pH and drying at 100 °C
C(KOH)	Oxidation in aqueous solution of 16 mol of KOH/L, under stirring maintained for 10 min, at room temperature. Drying at 100 °C for 14 h, followed by heating at 110 °C for 14 h, under flow of 150 mL of N ₂ /min up to 300 °C, maintained for 1 h. Washing in aqueous solution of 0.5 mol HCl/L and later in hot water. Washing in distilled water at room temperature, until reaching neutral pH, and drying at 100 °C [10]

original carbon C(OR), was submitted to the treatments described in Table 1.

Ru/C catalysts were prepared by applying the incipient impregnation, using an aqueous solution of RuCl₃·xH₂O from Aldrich Chem. Co., so as to obtain a metal mass fraction of 5 wt%. After the impregnation, the solids were left at room temperature for about 12 h, and dried in a heater at 80 °C for 24 h. Next, some of the catalysts were submitted to direct reduction treatment at 150 °C for 3 h, under a flow of a N₂/H₂ (98%/2%) mixture.

2.2. Characterization of supports and catalysts

N₂ adsorption, Boehm titration and point of zero charge (PZC) were utilized to characterize the supports, while X-ray photoelectron spectroscopy (XPS) was applied to characterize supports and catalysts.

 N_2 adsorption (Brunauer, Emmet, Teller method) was performed at its normal boiling temperature (-196 °C), in a Micromeritics Tristar dynamic equipment model ASAP 2010. The adjustment of experimental points was performed by employing the classic BET model.

Based on neutralization (acid–base) [11], Boehm titration was used to quantify some of the functional groups existing on carbon surface.

PZC, defined as the pH at which carbon surface has neutral charge, was determined by the potentiometric titration, utilizing a digital Analyser pHmeter model 300M.

XPS spectra were obtained with a HA100 VSW hemispherical analyzer, operating in stable transmission mode (44 eV transition energy). Al K α radiation (1486.6 eV) was applied and the chamber pressure was lower than 2×10^{-8} mbar.

The scanning electron microscopy with microprobe for spectrometry of Energy Dispersive X-ray analysis (SEM+EDX) was used aiming at quantifying the main elements found in the catalysts as well as to observing their morphology. The analyses were performed with a Leica device model LEO 440i. The initial stage consisted of metalizing the catalyst to form a thin layer of gold atoms on it with 92 Å film thickness. The analyses were performed by employing 3 MA current for 180 s.

Table 2
Activated carbon textural characteristics.

Support	$Sg(m^2/g)$	Pv (cm ³ /g)		
		Micro	Meso	Total
C(OR)	900	0.13	0.63	0.76
C(N2/300)	790	0.10	0.59	0.69
C(N2/400)	870	0.13	0.60	0.73
C(HN25)	910	0.16	0.58	0.74
C(HN90)	480	0.09	0.27	0.36
C(HN90-N2/300)	460	0.08	0.28	0.36
C(H2O2)	870	0.14	0.56	0.70
C(KOH)	70	0.008	0.082	0.09

Total = micropores + mesopores.

2.3. Catalytic tests

Benzene hydrogenation reactions were performed in a slurry type Parr reactor with total capacity of 300 mL. A 200 mg catalyst mass was introduced into the reactor, along with 30 mL of water and 5 mL of n-heptane as internal standard. The catalyst activation was performed in situ, at 100 °C, under flow of H₂ for 45 min. Next, the reactor was charged at 5 MPa of working pressure, and 25 mL of benzene were introduced into the reaction medium. During the reaction, a pressure accumulator tank and regulator valve permitted the maintenance of a constant hydrogen pressure inside the reactor. The velocity of 1.500 rpm was adopted for being considered sufficient to avoid mass transport limitation and the reaction was conducted at the constant temperature of 100 °C. During the reaction, organic phase aliquots were drawn (around 6 samples per test) through gas phase chromatography, in order to determine its composition. Chromatographic analyses used CG 151-40 capillary column of 25 m length in phase FI-53 of polydimethylsiloxane, connected to a chromatograph with flame ionization detector, model HP 5890.

The initial reaction rate was determined from benzene consumption. Benzene conversion (X) was calculated according to its classical definition, while yield of cyclohexene (R) was calculated considering the following definition:

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R = \frac{\text{No of mols of formed cyclohexene}}{\text{No of mols of formed cyclohexene}}
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No of initial mols of benzene

Thus, cyclohexene selectivity (*S*) can be obtained through the relation S = R/X.

3. Results and discussion

3.1. Carbon textural characteristics

Table 2 shows the values for specific surface area (Sg) and pore volume (Pv) obtained for the studied carbons.

With regard to the reference original carbon C(OR), the achieved results indicate that treatments performed with nitric acid at 90 °C and with potassium hydroxide lead to a significant reduction of the carbon specific area, especially in the base. Such effect comes along with an accentuated reduction of the total pore volume. According to Castilla et al. [12] and Castelló et al. [13], a severe oxidation may destroy the carbon porous structure, considerably increasing the number of acid groups and making the basic groups disappear.

According to Castilla et al. [12], treatment with nitric acid may to lead to carbons with pore of walls thinner and therefore more easily destroyed. According to these authors, two mechanisms can act in the process of breaking of the walls of the pores, after treatment with a strong oxidizing agent. The first way is through the oxidation of surface terminal groups, where a decrease in the area of the coal may occur due the formation of acid mellitus $[C_6(COOH)_6]$. The second mechanism occurs through mechanical destruction of the

Table 3	
Distribution of surface functional group	s.

Support	Concentration of surface functional groups (meq/g)			
	C _X	L	Ph	C _N
C(OR)	0.58	0.03	0.49	1.4
C(N2/300)	0.57	0.13	0.39	1.2
C(N2/400)	0.49	0.03	0.71	1.3
C(HN25)	0.77	0.05	0.58	1.2
C(HN90)	1.60	0.30	0.52	0.46
C(HN90-N2/300)	0.92	0.35	0.98	0.36
C(H2O2)	0.99	0.11	0.50	0.98
C(KOH)	0.38	0.92	0.74	0.45

 C_x = carboxylic groups; L = lactones; Ph = phenolic groups; C_N = carbonyls.

pores due to surface tension of the oxidant solution. In the case of carbon treated with KOH, pores with thinner walls may have been originated from the breaking of bonds in the matrix carbonic with rearrangement of the aggregates, leading to the collapse and destruction of pores. In addition, the use of a high amount of KOH in the preparation of activated carbon may inhibit the formation of CO_2 and of potassium compounds, preventing the gasification of carbon with the consequent formation of porosity [13], usually observed for low concentrations of base.

On the other hand, the treatments applied barely affected the textural characteristics of the original carbon C(OR).

3.2. Characteristics of carbon surface

Table 3 shows the distribution of surface functional groups determined by Boehm titration, as verified in the carbons studied here. The results indicate that adsorptive carbons have acid surface functions, in the form of non-carbonylic (carboxylic groups, lactones and phenolic groups) and carbonylic (carbonyls) groups. The level of acid strength of acid functional groups is ordered as follows: carboxylics > lactones > phenolic groups > carbonyls.

With reference to exclusively thermal processes (physical), the comparison between the applied treatments show that wet activation processes (chemical) create oxygenated groups in a more uniform way on the activated carbon surface, which means that the quantity of non-carbonylic groups (carboxylic groups, lactones and phenolic groups) is very similar to the quantity of carbonylic groups. Among wet activation process, the nitric acid treatment at 90 °C leads to the acquisition of the highest quantity of non-carbonylic acid sites on the carbon surface (2.42 meq/g).

The acidity of the different functional groups of carbon is not only a function of the surface group nature (pKa fixed value), but also of their carbon chain position. Usually, such groups facilitate the adsorption process, contributing to the increase in the adsorbent material hydrophilicity [14]. In addition, they can promote ruthenium dispersion on the activated carbon, leading to more active catalysts Fig. 1.



Fig. 1. Thermodynamics aspects of the benzene hydrogenation reaction.

Table 4

pH at point of zero charge (PZC).	
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Support	pH at PZC
	r ···· ·
C(OR)	2.75
C(N2/300)	2.40
C(N2/400)	2.44
C(HN25)	2.13
C(HN90)	1.87
C(HN90-N2/300)	2.35
C(H2O2)	2.25
C(KOH)	8.50

Determining pH at PZC through potentiometric titration of the different supports allows the identification of changes on the original carbon surface. In amphoteric carbon, such as the original carbon C(OR), the surface is positively charged when pH < PZC and negatively charged when pH > PZC.

The achieved results for the different carbon supports are shown in Table 4.

Prepared carbons show lower PZC values than the original one C(OR), except for C(KOH) solid. The carbons obtained through nitric acid, C(HN25) and C(HN90) treatment show the lowest values for pH of PZC; the value diminishes as the acid treatment temperature increases. In the case of carbon prepared with potassium hydroxide, C(KOH), there is an elevated increase of pH value of PZC, which indicates a strong basic characteristic of this support.

Results obtained for pH of PZC lead to the following acidity order: C(HN90) > C(HN25) > C(H2O2) > C(HN90-N2/300) > C(N2/300) > C(N2/400) > C(OR) > C(KOH).



Fig. 2. XPS spectra for C 1s for activated carbon C(OR) and C(HN90).



Fig. 3. The spectra of XPS for C 1s and Ru 3d for Ru/COR)NR and Ru/C(OR)R150 catalysts.

XPS analyses performed for supports C(OR), C(N2/300) and C(HN90) reveal the main occurrence of graphitic carbon (284.7 eV), correspondent to non-functional carbon, Csp² and Csp³, being Csp² the carbon from the aromatic chain and Csp³ the aliphatic carbon in hydrocarbonates. The existence of phenolic groups (282.6 eV), carbonyls (287.6 eV), carboxylic groups (289.1 eV), and nitrogenated groups bonded to carbon and electron π bonds in aromatic carbons (291.0 eV) is also noticed [15]. Quantifying the distribution of elements C, O and N was based on the intensity of characteristic peaks of the elements present and feature sensitivity factors (C 1s = 1.00; O 1s = 2.850; N 1s = 1.770).

The spectra of XPS for C1 s for the activated carbons C(OR) and C(HN90) are shown in Fig. 2(a and b).

In the case of C(OR) and C(N2/300) supports, there is no occurrence of nitrogenated compounds found in support C(HN90). In this solid, nitrogen is formed as NO₂ groups and nitrogenated functions. Such result is in accordance with what Salame and Bandosz [14–16] observed – the study verified the presence of nitronium and nitrate ions on the surface of the carbon prepared with nitric acid.

Furthermore, results reveal that support C(N2/300) does not show significant changes on its surface in comparison to the original carbon C(OR). At first impression, this would not be in accordance with the increase in quantity of lactones observed through Boehm titration.

However, such increase may not be detected through XPS analysis because the characteristic binding energies of lactone and phenolic groups are very similar. Nevertheless, the performed characterization demonstrates the conclusion that the treatments applied to the original carbon C(OR) change the solid surface, promoting an increase in the concentration of the surface functional groups.

3.3. Chemical composition of the catalysts

XPS analyses were also performed with the following catalysts: Ru/C(OR)NR, Ru/C(OR)R150, Ru/C(HN25)NR and Ru/C(HN90)NR. The results obtained for ruthenium in non-reduced (282 eV) Ru/C(OR) catalyst suggest that this metal is in the form of RuCl₃ (281.8 eV). The spectra of XPS for C 1s and Ru 3d for the different catalysts are shown in Figs. 3 and 4(a and b).

However, in catalyst Ru/C(OR) reduced to $150 \,^{\circ}$ C, ruthenium shows a binding energy of 281.6 eV, very close to this element in stages RuO₂ (281.5 eV) and RuCl₃. In this case, the absence of Ru⁰ (280.0 eV) is due to a limited oxidation of this element in the



Fig. 4. The spectra of XPS for C 1s and Ru 3d for Ru/C(HN25)NR and Ru/C(HN90)NR catalysts.

surface of the metallic particle, induced by the catalyst exposure to air [17].

For Ru/C catalysts whose supports were treated with nitric acid, C(HN25) and C(HN90), the XPS results suggest that metal ruthenium is in the forms of RuO₂ and/or RuO₃ (282.5 eV). As a matter of fact, both catalysts show different characteristics from the other analyzed solids, especially for the nitrogen present in two distinct types of nitrogenated functional groups (around 404.5 eV).

The presence of these two nitrogenated functional groups may contribute to an increase in the support acidity and promote the formation of Ru–NO₂ bond, modifying ruthenium behavior on the catalyst surface.

For the existing elements in the analyzed catalysts, the atomic ratios of the surface were calculated from the XPS spectra, experimentally obtained to the energy state of Ru $3d^{5/2}$, Cl 2p and C 1s. The results are shown in Table 5, along with global values obtained by EDX, for comparison purpose.

The obtained atomic ratios confirm a fine concordance between EDX and XPS analysis results. The results indicate that reduction treatment lessens the chlorine level in Ru/C(OR) catalyst [18]. In the case of non-reduced Ru/C systems, prepared from

supports treated with nitric acid (HNO₃) at 25 $^\circ\text{C}$ and 90 $^\circ\text{C}$, the quantity of chlorine diminishes as the treatment temperature rises.

Drastic reduction of chlorine level in Ru/C(HN90) catalyst may be due to the presence of a great quantity of carboxylic groups and different nitrogenated groups. In the absence of chlorine, the functional surface groups are favorable to the maintenance of the coordinated ruthenium.

Table 5

Global atomic ratios (EDX) and surface atomic ratios (XPS) to Ru/C catalysts.

Catalyst	Atomic ratio				
	Cl/Ru		Ru/C		
	EDX	XPS	EDX	XPS	
Ru/C(OR)NR Ru/C(OR)R150 Ru/C(HN25)NR Ru/C(HN90)NR	3.1 2.9 n.d. n.d.	3.3 2.2 3.8 0.15	0.0061 0.074 n.d. n.d.	0.0063 0.0085 0.0039 0.051	

n.d. = not determined; NR = non-reduced; R150 = reduced to 150 °C.



Fig. 5. Yield of cyclohexene throughout the reaction with non-reduced Ru/C catalysts.

3.4. Catalytic performances in benzene hydrogenation

Ru/C catalysts were evaluated with the purpose of studying the influence of treatment applied to support in the catalytic performance in hydrogenation reaction of liquid benzene.

When Ru/C(OR) catalyst was reduced to 150 °C, a decrease on cyclohexene performance was noticed throughout the reaction, in relation to the non-reduced catalyst. Such effect is due to the elimination of chloride by reduction treatment, since the presence of chloride may enhance the hydrophilic characteristic of the solid [19]. Therefore, the catalytic tests were conducted with non-reduced catalysts.

Results demonstrated in Fig. 5 indicate that all Ru/C catalysts, whose supports were treated, present higher cyclohexene yields than the catalyst prepared with the original carbon Ru/C(OR).

The increased cyclohexene yields can be explained based on an increase of the catalysts hydrophilicity, due to the higher quantity of surface oxygenated groups, formed by the treatments applied to the support, according to the results of carbon characterization.

In the case of supports treated with nitric acid, the obtained catalysts, Ru/C(HN25) and Ru/C(HN90), show a similar behavior with a high yield of cyclohexene for low conversions. Such differentiated behavior is related to the presence of nitrogenated functional groups formed by the treatment with nitric acid.

It is also important to observe the high yields obtained with Ru/C(KOH) catalyst, which may be related to the low specific area of the support [19].

As can be seen in Fig. 1, the constant k_1 is related to the rate of partial hydrogenation of benzene and, consequently, the formation of cyclohexene. In turn, the parameter k_2 is associated with the rate of hydrogenation of cyclohexene, for the formation of cyclohexane. Since k_3 is a constant rate on the direct hydrogenation of benzene to form cyclohexane.

Table 6 gives the values of the constants k_1 , k_2 and k_3 , obtained from the catalytic tests performed, considering a first-order reactions.

The results showed that the catalyst Ru/C(OR)NR, prepared with the original untreated carbon, has the higher value for the constant k_3 (220 m s⁻¹), which is much larger than the constants k_1 (24 m s⁻¹) and k_2 (36 m s⁻¹). This result indicates a high rate of direct hydrogenation of benzene to cyclohexane, to the detriment of the consecutive hydrogenation. Such behavior may be due both to the large amount of carbonyl groups, and the low concentration

Table 6

Values of rate constants for the hydrogenation reaction of benzene with Ru/C catalysts non-reduced.

Catalyst	$k_1 ({ m ms^{-1}})$	$k_2 ({ m ms^{-1}})$	$k_3 (m s^{-1})$
Ru/C(OR)NR	24	36	220
Ru/C(N2/300)NR	28	37	100
Ru/C(N2/400)NR	29	32	120
Ru/C(HN25)NR	30	75	70
Ru/C(HN90)NR	35	88	74
Ru/C(HN90-N2/300)NR	12	14	31
Ru/C(H2O2)NR	18	16	54
Ru/C(KOH)NR	33	50	110

of carboxylic groups defined for this support, which is consistent with that seen in Figs. 6 and 7.

Studies conducted with activated carbons [20] showed that several acidic carbon–oxygen groups provide a hydrophilic character of carbon and reduce the adsorption of benzene, which is nonpolar compound. When acidic surface groups are removed, and carbonyl functional groups and quinones predominate, the adsorption of benzene increases. A greater adsorption of benzene is due to the interaction between the π electron cloud of the aromatic ring of benzene and the partial positive charge of the carbonyl carbon atom. Complexes formed between benzene and carbonyl and quinone sites occur within the micropores of the carbon. Thus, the benzene present in the reaction medium can be easily adsorbed on



Fig. 6. Relationship between cyclohexene maximum yield and total quantity of carbonylic functional groups on the carbon surface.



Fig. 7. Relationship between cyclohexene maximum yield and total number of carboxylic functional groups on the carbon surface.

the catalyst surface, leading to the direct hydrogenation of benzene to cyclohexane.

In turn, in the case of the catalysts Ru/C(N2/300)NR, Ru/C(N2/400)NR and Ru/C(KOH)NR the constants k_1 and k_2 have values close to those obtained for the catalyst reference Ru/C(OR)NR. However, a lower value for the constant k_3 for these catalysts shows a decrease in the rate of direct hydrogenation of benzene, leading to a higher yield of cyclohexene. However, it should be noted that in the case of the catalyst Ru/C(KOH)NR, the highest selectivity of cyclohexene can also be due to lower specific surface area of solid. According to Rodrigues and Cobo [19], Ru catalysts with low surface area are more selective for the partial hydrogenation of benzene in the liquid phase.

For the catalysts treated with HNO₃, Ru/C(HN25)NR and Ru/C(HN90)NR, k_1 values remain around 30 m s⁻¹. However, in relation to previous cases, the values of k_2 (about 80 m s⁻¹) increase, while k_3 (around 70 m s⁻¹) decreases. This result indicates an increased rate of partial hydrogenation of benzene at the expense of its direct hydrogenation to cyclohexane.

Since the catalysts Ru/C(HN90-N2/300)NR and Ru/C(H2O2)NR had the lowest values for the constants determined. This result indicates a catalytic activity lower than that of other catalysts. However, the average value obtained for the relative selectivity between the formation of cyclohexene and cyclohexane, as reflected by the ratio $k_1/(k_2 + k_3)$, is around 0.26. This value is much higher than in the case of the solid reference Ru/C(OR)NR (0.09) and greater than the calculated for the other catalysts (around 0.20). The increase in selectivity at the expense of catalytic activity, suggests an increased hydrophilic character of these catalysts, induced by the treatments applied to the supports. In the system under study, the water added to the reaction medium has the role of the cyclohexene formed away from the catalytic surface, preventing the undesired hydrogenation to cyclohexane. In this case, a catalyst more hydrophilic is more easily engaged by a layer of water, which decreases the rate of mass transfer of benzene to the surface of the catalyst and therefore decreases the reaction rate observed.

3.5. Influence of the functional groups in the Ru/C catalysts performance

Aiming at evaluating the influence of the different functional oxygenated groups, found on the surface of activated carbon, on the performance of Ru/C; the establishment of a relation between the quantity of these groups and the catalytic performance in benzene hydrogenation reaction was realized.

Fig. 6 represents the achieved relation between cyclohexene maximum yield and the total quantity of carbonylic groups on the carbon surface area.

In this case, results show that the increase in the number of carbonylic functional groups tends to reduce cyclohexene maximum yield. The same effect was observed in catalytic activity, indicating that a great number of carbonylic groups may disfavor ruthenium dispersion on the support, leading to less active catalysts.

Fig. 7 shows the achieved relationship between the maximum yield of cyclohexene and the total quantity of carboxylic functional groups on the carbon surface. The results indicate that an increase in carboxylic functional groups tends to increase cyclohexene yield.

It is important to point out that the highest maximum yields of cyclohexene observed in supports C(KOH), C(HN90) and C(HN90-N2/300) are due to the decrease of these solids specific surface area along with the reduction in these supports pore volume. The reduction in micropore and mesopore volume may result in an increase

in the macropore volume, favoring the diffusion of the cyclohexene formed in the pores and, consequently, avoiding its undesired hydrogenation at cyclohexane.

With regard to catalytic activity, it was observed that the increase in the quantity of carboxylic groups tends to increase the initial reaction rate. Such effect is associated with an increase of ruthenium dispersion in the catalyst. As noted by Zhu et al. [21,22], ruthenium dispersion increases according to the quantity of carboxylic surface groups. Moreover, highly acid supports favor the catalytic activity of this reaction [23,24]. Adsorbed benzene in acid active sites of the support may also react with the adsorbed hydrogen on the metallic surface and consequently raise the catalytic activity. For this reason, supports with great quantity of carboxylic groups (strong acids) on their surface may contribute to a higher catalytic activity in benzene hydrogenation reaction.

4. Conclusions

The achieved results in the present study reveal that treatments applied to activated carbon may influence the performance of Ru/C catalysts in liquid benzene partial hydrogenation reaction.

The catalytic performance of Ru/C system is influenced by certain functional groups existing on the surface of the activated carbon. Carbonyl groups decrease the reaction activity and selectivity, whereas an increase of carboxylic groups leads to more active catalysts and higher yields of cyclohexene.

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