Nitric acid-oxidized carbon for the preparation of esters under ultrasonic activation

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Temperature-programmed desorption, X-ray photoelectron spectroscopy (XPS) spectroscopy and catalytic test reaction have been applied to investigate acid sites in a microporous activated carbon (Norit RX 1 Extra). Treatment with HNO_3 generates acid sites in the pristine carbon. XPS data show an increase of the amount of carboxyl and hydroxyl groups on the activated carbon surface. The thermodesorption profiles of the material corroborate the XPS data and indicate the presence of hydroxyl groups of carboxylic acids. The results obtained by these methods indicate the presence of acid sites. Thus, the acidity of the carbon was tested in the esterification of organic acids with alcohols. The pristine carbon presents no activity. By contrast, the treated carbon presents enough acidity to carry out the reaction achieving conversion values of around 45% for the reaction of benzoic acid with ethanol in a batch reactor. Such a value increases if the reaction is carried out under ultrasound activation, affording conversion values of around 85%. The selectivity of the reactions is high, around 95%. Only in the case of 1-octanol are some side-products observed, due to the oxidation of the alcohol.

KEY WORDS: nitric acid-oxidized carbons; acid catalysis; fine chemistry; esterification; sonocatalysis.

1. Introduction

Solid and liquid acid catalysts are used extensively in the petroleum and chemical processing industries, and there is a significant opportunity to improve many of these processes by replacing the current liquid-phase systems with solid acid catalysts [1]. Liquid acid systems, such as H_2SO_4, $AlCl_3$ and BF_3, are corrosive and present waste disposal problems [2]. While liquid acid catalysts are widely used in industry, they have low specificity and they are, thus, limited for reactions requiring high selectivity. The catalytic processes involving the synthesis of fine chemicals produce much lower volumes of products than those in petroleum refining and petrochemistry, but these are important speciality products (medicines, food additives and other products) [3,4]. From an engineering standpoint heterogeneous catalysts are the easiest catalysts to handle because they are stable at high temperature and are phase separated from the reactants and products. Thus, they find widespread use in industry. Esterification reactions have numerous applications and are classically catalyzed by acids in liquid- and gas-phase systems [5–8]. Esters of carboxylic acids are important, since they are used in the production of fine and speciality chemicals such as fragrances, pharmaceuticals and pesticides [9].

Many solid acids have been used in catalytic reactions (zeolites, clays, etc.) [10–12]. Activated carbons are porous materials, which are generally used as adsorbents [13], catalysts or catalyst supports [14,15]. Activated carbons exhibit acid–base properties and their acid or base character depends on the history of their origin and on the temperature and conditions under which they were activated (figure 1). Attempts have been made to identify and estimate the surface acidity of acid carbons using several physicochemical techniques [16]. The textural and chemical properties of active carbons, such as their porous structure, surface reactivity and extended surface area, mean that this type of material can also act as a catalyst in organic synthesis [17].

Ultrasonic irradiation accelerates numerous catalytic reactions [18] and significant yield improvements can be achieved [19]. The sonochemical phenomena originate

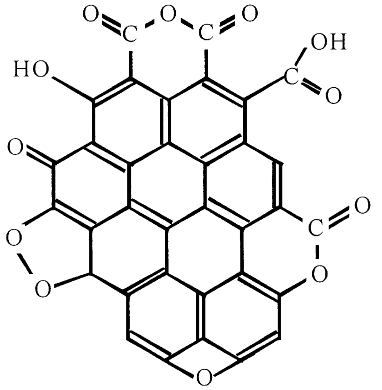

Figure 1. Some surface groups of the carbon.

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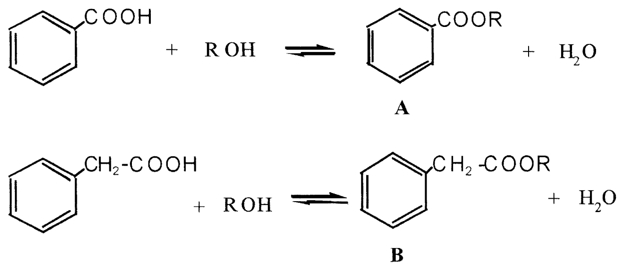

Scheme 1. Esterification of benzoic and phenylacetic acids with alcohols.

from the interaction between a suitable field of acoustic waves and a potentially reacting system; the interaction takes place through the intermediate phenomenon of acoustic cavitation.

The present study investigates the preparation, characterization and application of an HNO_3-oxidized activated carbon as a catalyst in the esterification of organic acids with alcohols (scheme 1). Moderate temperatures have been employed in the liquid-phase reactions. The aim is to demonstrate that the HNO_3 treatment generates enough acidity in the material for it to be used as an acid catalyst. For comparison, the results obtained under ultrasonic activation are also presented.

2. Experimental

2.1. Materials

2.1.1. Catalysts (surface treatment)

A commercial microporous activated carbon, RX1 Extra Norit, denoted as **N**, was used as the carbon substrate. The pristine carbon was treated with HNO_3 (10% weight concentration), as described in the literature [20–23]. This treatment is well known as very efficient for introducing surface oxygen groups on activated carbons. The mixture (carbon and acid) was stirred and heated at 353 K until most of the acid was evaporated. The carbon/(10% HNO_3) ratio was 1 g/10 ml. The treatment was repeated three times. The resulting carbon (**NN**) was washed with doubly distilled water using a Soxhlet apparatus until the pH was 6. After drying for 16 h at 383 K the carbon sample was crushed and sieved to 0.074–0.140 mm particle size.

2.1.2. Reactants

Ethanol, 1-butanol, 1-octanol, benzoic acid and phenylacetic acid were of reagent grade, obtained from Fluka.

2.2. Catalyst characterization

The BET areas of the carbon samples were determined by nitrogen adsorption at 77 K, taking 0.162 nm^2 as the cross-sectional area of the adsorbed nitrogen molecule. An automatic Micromeritics ASAP 2010 volumetric system was used to obtain the corresponding gas adsorption isotherms. The relative pressures reached were lower than 1×10^{-5}. The accuracy of the BET area measurement was 5%.

To obtain the micropore volumes, the Dubinin–Radushkevich equation [24] was applied to the corresponding CO_2 adsorption isotherms at 273 K. The cross-sectional area for the CO_2 molecule was taken as 0.17 nm^2.

Temperature-programmed desorption (TPD) experiments were performed using a Seiko SSC/5200 thermobalance system under N_2 atmosphere and a gas flow of 50 $cm^3\,min^{-1}$. The heating rate was 10 K min^{-1}. An online mass spectrometer (Baltzers, QMG 421) measured the gases evolving from the activated carbons during the desorption in the TG system.

The surface groups were determined quantitatively following the Boehm method [25]. One gram of carbon was placed in 50 ml of the following CO_2-free solutions: sodium hydroxide (neutralizes carboxylic, lactonic and phenolic groups), sodium carbonate (neutralizes carboxylic and lactonic groups), sodium bicarbonate (neutralizes carboxylic groups) and hydrochloric acid (neutralizes basic sites). The flasks were shaken for 24 h and then filtered. The excess base or acid was titrated with HCl and NaOH, respectively.

2.3. Reaction procedure

2.3.1. Thermally induced reactions

Prior to any experiment it was confirmed that, under our experimental conditions, the reactions were controlled by neither external nor internal diffusion, by using different particle sizes (0.074–0.140 mm) and different stirring rates (1000 and 3500 rpm). Blank runs confirmed that the reaction was negligible in the absence of catalyst. In a typical esterification reaction, 5 mmol of the corresponding carboxylic acid (benzoic acid or phenylacetic acid) were mixed with 3 ml of alcohol without any solvent. The mixture was kept in a Pyrex flask under stirring while heating to the reaction temperature (333 K). The reaction time started when the catalyst was added. Samples were taken periodically and the evolution of the reaction between 1 and 11 h was followed using a KNK-3000-HRGC Konik gas chromatograph fitted with a 60 m phenylsilicone capillary column and a flame ionization detector. The conversion was expressed in terms of the amount of ester obtained in wt% (see scheme 1).

2.3.2. Ultrasonically induced reactions

An amount of 5 mmol of the corresponding carboxylic acid (benzoic acid or phenylacetic acid) was mixed with 3 ml of alcohol without any solvent. The mixture was introduced in a flask that was suspended in an ultrasonic bath at the reaction temperature (333 K). The reaction time started when catalyst was added. The reactions were performed in the ultrasonic bath (Selecta Ultrasound-H) with a heating system at a frequency of 40 kHz and power of 550 W. Samples were taken periodically and the evolution of the reaction was monitored by GC between 1 and 11 h.

3. Results and discussion

3.1. Characterization of the carbons

The textural properties of the activated carbons are listed in table 1. The oxidation of the pristine carbon with HNO_3 slightly decreases the micropore volume and the specific surface area, from 1917 to 1785 $m^2 g^{-1}$. The fact that the micropore volume measured by CO_2 adsorption (V_{CO_2}) is lower than that obtained by N_2 adsorption ($V_{N_2(P/Po=0.01)}$) indicates the presence of relatively large micropores where CO_2 adsorbs without pore filling at the low relative pressures at which the isotherm is measured [26]. In many cases, when an activated carbon is oxidized with HNO_3 a drastic decrease in surface area and micropore volume is observed. This may be due either to a preferential fixation of oxygen groups at the entrance of the pores [22] or to the destruction of the pore walls by the oxidizing treatment [27]. Vinke *et al.* [28] proposed that when the pore system of oxidized carbon remains intact, the basal planes of the activated carbons are not affected by nitric acid. Therefore, the oxygen surface groups are expected to be located at the edges of the basal planes. This could be confirmed by the almost identical values of the micropore width (L) calculated from the Dubinin–Radushkevich equation for both carbons (table 1).

The titration results of the carbon surfaces are also presented in table 1. As can be observed for the as-received activated carbon, surface carboxylic, lactonic, phenolic and basic groups have been detected in small amounts by such a method. When the activated carbon is oxidized the total acidic groups increase by 10 times. This increase is mainly due to the formation of carboxylic and phenolic groups. These results are in agreement with those of Pittman *et al.* [29] who found that the oxidizing treatment with HNO_3 generates carboxyl, phenolic and hydroxyl groups at the carbon surface.

Table 2
Binding energies (eV) of inner electrons, their relative participation and atomic ratios determined by XPS

Sample	C 1*s*		O 1*s*		O/C atom
	BE	%	BE	%	
N	284.9	57			0.055
	286.4	23	531.2	29	
	288.9	7	532.5	41	
	290.6	6	533.9	19	
	292.5	7	535.2	11	
NN	284.9	51			0.154
	286.4	27	531.2	30	
	288.9	10	532.7	48	
	290.6	5	534.1	15	
	292.5	7	535.4	7	

The results of the curve fitting of the XPS measurements are summarized in table 2. The C 1*s* peaks are assigned to functional groups as follows [30]: 284.9 eV to aromatic carbons, 286.4 eV to carbons in keto–enol equilibrium, 288.9 eV to carboxylic groups and 290.6 eV to carbonates. The peaks obtained from the deconvolution of the O 1*s* peak are assigned in the following way [31]: 531.2 eV to carbonyl oxygen atoms in esters, amides and anhydrides, 532.5–532.7 eV to oxygen atoms in hydroxyls or ethers, 533.9–534.1 eV to oxygen atoms in carboxyl groups and 535.2–535.4 eV to adsorbed water. As table 2 shows, the treatment with HNO_3 increases threefold the O/C ratio of the **NN** as compared with the **N** carbon. In fact, an increase of the total intensity of the peaks assigned to such functional groups is observed.

The thermodesorption profiles of the **NN** carbon are shown in figure 2. The CO_2 desorption may result from the decomposition of carboxyl, anhydride and lactonic surface groups, whereas the CO desorption may result from the decomposition of phenolic, carbonyl, quinone, pyrone and anhydride surface groups [32,33]. The CO_2 profile shows three peaks at 573, 693 and 913 K. The peak that appears at 573 K is assigned to the decomposition of carboxylic groups [23,34]. The H_2O profile peak

Table 1
Textural characteristics of activated carbons and Bohem titration: total basic groups (B_G), total acidic groups (A_G), carboxyl groups (C_G), lactonic groups (L_G), phenolic groups (P_G) in meq $(100\,g)^{-1}$

Sample	S_{BET}	$V_{N_2(P/Po=0.01)}$	V_{CO_2}	L (Å)	B_G	A_G	C_G	L_G	P_G
N	1917	0.553	0.340	12.6	25	4.9	1.7	2.4	0.8
NN	1785	0.510	0.323	12.2	31	79.0	35.0	5.88	38.12
NN after reaction	1780	0.508	0.319	12.3	30	79.5	35.6	5.8	38.12

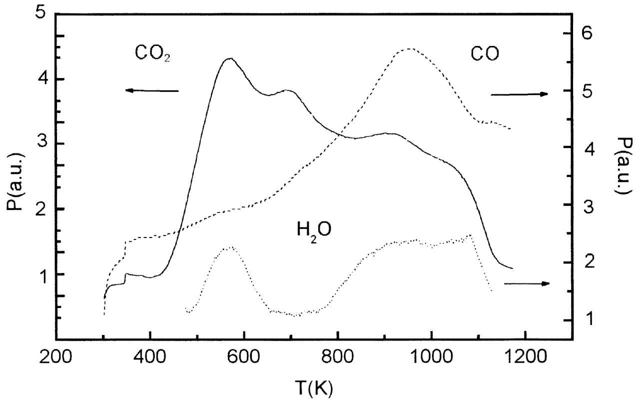

Figure 2. Thermodesorption profiles of **NN** activated carbon.

that appears at this temperature due to the hydroxyl groups of the carboxylic acid groups confirms this assignment. The identification of the peaks at 693 and at 913 K in the CO_2 profile is not so clear. Otake *et al.* [23] assigned the desorption peaks at 900 K to anhydrides. However, Zielke *et al.* [31] have assigned the desorption peaks at 623–673 K to anhydrides and lactones, and those near 823–873 K to peroxides. The anhydrides decompose into one CO molecule and one CO_2 molecule, thus the desorbed amounts of CO and CO_2 would be equal. The deconvolution of the CO_2 and CO profiles using a Gaussian multi-peak function shows that the desorbed amounts are not equal. Also, the difference in temperatures is too high. Thus, the peaks that appear at 693 and 913 K in the CO_2 profiles are tentatively assigned to lactonic and peroxidic groups [27]. The peak that appears at 953 K in the CO profile is assigned to phenol groups [27]. The wide peak of the H_2O profile that appears at similar temperatures further supports this idea. Concerning the surface oxygen groups characterization, the results obtained are slightly different depending on the technique used (titration, XPS or TPD). However, all of them afford the same trend. There is an increase of the oxygenated groups (particularly carboxylic and phenolic groups) produced as a consequence of surface HNO_3 treatment.

The titration results of oxygen surface groups remain constant after reaction (table 1). This indicates that the carbon surface acidic groups are not esterified by the reactant.

3.2. Synthesis of esters

The esterification of phenylacetic acid and benzoic acid with ethanol, 1-butanol and 1-octanol was carried out at 333 K on both catalysts (**N** and **NN**). The reaction conversion was negligible in the absence of catalyst, and the pristine carbon (**N**), which was not subjected to the nitric acid treatment, afforded less than 6% conversion in all cases. As shown in tables 3 and 4, the conversions increased as the chain lengths of the alcohols decrease, suggesting that the chain length of the alcohol had a negative effect on the reactions. Other authors have observed this fact [7]. However, in our study the alcohol to aromatic acid ratios differ.

The oxidized carbon (**NN**) appears to be a very active catalyst for the liquid-phase esterification of benzoic acid (pK = 4.21) and phenylacetic acid (pK = 4.30) with alcohols. Moderate conversion values are obtained for both organic acids when 0.3 g of **NN** catalyst are employed in a batch reactor system, affording less than 45% yield in any case. However, conversions of around 85% and 65% are obtained for the esterification of

Table 3
Esterification of phenylacetic acid (5 mmol) with alcohols (3 ml) at 333 K using 0.3 g of nitric acid-oxidized carbon as catalyst

Alcohol	Time (h)	Conversion (%)	
		Thermal	Ultrasound
Ethanol	3	5	12
	5	15	27
	7	20	39
	9	29	54
	11	35	65
1-Butanol	3	3	8
	5	9	21
	7	13	29
	9	19	36
	11	24	43
1-Octanol	3	1	0
	5	5	3
	7	9	10
	9	14	19
	11	19	25

Table 4
Esterification of benzoic acid (5 mmol) with alcohols (3 ml) at 333 K using 0.3 g of nitric acid-oxidized carbon as catalyst

Alcohol	Time (h)	Conversion (%)	
		Thermal	Ultrasound
Ethanol	3	9	21
	5	22	45
	7	36	69
	9	40	79
	11	43	84
1-Butanol	3	6	9
	5	17	21
	7	31	35
	9	35	42
	11	39	54
1-Octanol	3	4	6
	5	9	12
	7	16	24
	9	23	32
	11	29	42

phenylacetic and benzoic acids, respectively, when the reactions are activated by ultrasound. As the characterization underlines, the nitric acid treatment of the Norit carbon generates acid sites strong enough to promote this acid-catalyzed reaction. Selectivities of around 95%, except in the case of 1-octanol, were obtained. In this case, oxidation to 1-octenal was detected as a secondary product of the reaction (less than 6%) under sonocatalysis.

4. Conclusions

HNO_3-oxidized Norit RX1 Extra activated carbon is an active and selective catalyst for esterification reactions. The HNO_3 treatment generates mainly carboxyl and phenolic hydroxyl groups on the carbon surface. The oxygen surface groups are located at the edges of the basal planes. The esterification of benzoic and phenylacetic acids with alcohols can be successfully carried out on nitric acid-oxidized carbon. The increase of the alcohol chain length had a negative influence on the conversion. Ultrasound enhances the yields of the corresponding esters, affording 85% yield when benzoic acid reacts with ethanol after 11 h. This method can be extended to the preparation of esters that serve as products or precursors for industrial processes. High activity and selectivity are obtained, indicating that nitric acid-oxidized carbon presents appropriate textural and chemical characteristics to be used as a catalyst for fine chemicals production under mild conditions.

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