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The effect of ultrasound on the N-alkylation of imidazole over alkaline carbons: Kinetic aspects

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1. Introduction

Ultrasonic irradiation leads to the acceleration of numerous reactions in homogeneous or heterogeneous systems [1]. Furthermore, significant improvements can be realized with regards to the yields [2–4].

The sonochemical phenomena are originated from the interaction between a suitable field of acoustic waves and a potentially reacting chemical system; the interaction takes place through the intermediate phenomenon of the acoustic cavitation. Three important factors have to be considered when an ultrasonic induced reaction is performed: the acoustic field, the bubbles field and the chemical system [5,6].

The chemical effects of ultrasounds have been attributed to the implosive collapse of the cavitation period of the sound waves. The bubbles are generated at localized sites in the liquid mixture that contain small amounts of dissolved gases. Trapped within a microbubble, the reactants are exposed to a high pressure and temperature upon implosion, the molecules are fractured forming highly reactive species with a great tendency to react with the surrounding molecules. When one of the phases is a solid, the

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ABSTRACT

N-Alkylimidazoles have been synthesized by sonochemical irradiation of imidazole and 1-bromobutane using alkaline-promoted carbons. The catalysts were characterized by X-ray photoelectron spectroscopy, thermal analysis and nitrogen adsorption isotherms. Under the experimental conditions, N-alkylimidazoles can be prepared with a high activity and selectivity. It is observed that imidazole conversion increases in parallel with increasing the basicity of the catalyst. For comparison, the alkylation of imidazole has also been performed in a batch reactor system under thermal activation. © 2010 Elsevier B.V. All rights reserved.

ultrasonic irradiation has several additional enhancement effects and this is especially useful when the solid acts as catalyst [7,8]. So, the cavitation effects form microjects of solvent which bombard the solid, increasing the interphase surface able to react. In general, the sonication presents beneficial effects on the chemical reactivity, such as to accelerate the reaction, to reduce the induction period, and to enhance the catalyst efficiency [9].

The objective of this contribution is to investigate the kinetics and the mechanism of the imidazole alkylation reaction (Scheme 1) catalyzed by basic carbons under both ultrasound and conventional thermal activation. The authors have previously proved that this reaction can be carried out over acid zeolites and under ultrasound activation following a different reaction mechanism [10]. In this report, the authors study the influence of different external parameters in this reaction such as basicity (alkaline promoter on the carbon), porosity, and amount of catalyst and reaction temperature. The combination of these parameters of the catalysts enabled to be used for the highly selective synthesis of N-alkylimidazoles.

The N-alkylation of heterocycles, particularly imidazole, has been reported as a key route to prepare important bactericidal, fungicidal [11] and anticonvulsant [12] compounds.

Activated carbons have been employed as selective catalysts in related reactions, because of their microporous structure, high degree of surface reactivity and extended surface area [13].

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Scheme 1. Alkylation of imidazole with 1-bromobutane.

Moreover, the inclusion of alkaline promoters on the carbons results in the generation of basic sites on their surface [14,15].

2. Experimental

2.1. Catalysts preparation and characterization

RX-1-EXTRA Norit carbon from Norit Company was treated with the corresponding aqueous alkaline chloride solution (2 M) at 353 K for 1 h. The liquid/solid ratio was 10. The samples were filtered and washed with distilled water until chloride free (AgNO₃ test). After drying at 373 K, overnight, the resulting carbons were pelletized, crushed and sieved to particle size of 0.074–0.140 mm diameter.

The two series of alkali-loaded catalysts are named: M-N (Na-Norit, K-Norit and Cs-Norit), and MM'-N (NaK-Norit, NaCs-Norit and KCs-Norit). The ash contents of the catalysts were obtained by thermogravimetric analysis (TG/DTA Seiko System 320). The pH of the samples was measured following the method described by Rivera-Utrilla and Ferro-García [16] using an Omega pH-meter, model PHB-62.

Specific surface areas of the carbon samples were determined by nitrogen adsorption isotherms at 77 K, applying the BET method [17] in a Micromeritics ASAP 2010 Volumetric System. Volume adsorbed in the different types of pores was calculated by the DFT (density functional theory) method [18] by means of DFT plus software.

Photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and MgK α (*hv* = 1253.6 eV, 1 eV = 1.6302 × 10⁻¹⁹ J) Xray source. The powder samples were pressed into aluminum holders and mounted on a sample rod placed in the pretreatment chamber of the spectrometer. After outgassing 1 h at room temperature, they were placed into the analysis chamber. The residual pressure in the ion-pumped analysis chamber was maintained below 5×10^{-9} Torr during data acquisition. The intensities of C1s, O1s, and Na1s or Cs 3d_{5/2} peaks were estimated by calculating the integral of each peak after smoothing and subtraction of the "S"-shaped background and fitting the experimental curve to a combination of Gaussian and Lorentzian lines of variable proportion. The binding energies (BE) were reference to the major C 1s component at 284.9 eV, this reference giving BE values with an accuracy of ± 0.1 eV.

2.2. Reaction procedure

2.2.1. Ultrasonic induced reactions

Imidazole (5 mmol) and 1-bromobutane (15 mmol) were mixed in a flask suspended into the ultrasonic bath (Selecta Ultrasound-H, with a heating system, 40 kHz of frequency, and 550 W of power). Then, the corresponding catalyst was added and the reaction started. The reactions were carried out at the reaction temperatures: 293, 313 and 333 K, respectively in the absence of any solvent.

2.2.2. Thermal induced reactions

Similar procedure was adopted for conventional thermal heating. The samples were magnetically stirred, in a batch reactor

in the absence of any solvent. Then, the catalyst was added to the reaction mixture and the reaction started.

The reaction was followed by gas chromatography-mass spectrometry (GC-MS), using a 60-m-long phenyl-silicone capillary column and a flame ionization detector. The conversion is expressed in terms of amount of **A** product (Scheme 1).

In previous experiments, it was found that for stirring speeds above 1000 rpm, and particle sizes of diameter minor than 0.250 mm, nor diffusion processes control exists, either external or internal [15].

3. Results and discussion

3.1. Catalyst characterization

The pH of samples is given in Table 1. The pristine carbon, RX-1-EXTRA Norit, exhibits a basic pH (8.0) that increases only slightly in the sample exchanged with sodium, but considerably in the Cs-Norit sample (pH = 10.3). In spite that the amount of cesium in the solid is around one-third of the sodium cation, the higher basicity of the Cs ions could be the cause of the increase observed in the pH of the cesium samples. The pH of the series MM'-N is within the values of M-N series, being all of them around 10 pH units.

As it was above mentioned the amount of sodium ion into the Norit is around 3 times the amount of cesium ions. This is expected because the surface of the active carbon has a determined density of active groups [17] which interact with the M^+ ions by electrostatic forces during the adsorption–impregnation process. For steric hindrance, mainly at the micropores of the substrate, it is obvious that the Na⁺ ions (ionic radius = 0.095 nm) can access the centers located at the micropores, whereas the Cs⁺ ions (ionic radius = 0.169 nm) have to overcome a diffusional barrier.

Table 1Some characterization data of the catalysts.

Catalyst	pН	Ash (%)	M ₂ O (%)	Metal (at-g/100 g cat.)
Norit	8.0	3.1	-	-
Na-N	8.4	4.8	1.7	0.055
Cs-N	10.4	5.5	2.4	0.017
K-N	10.1	5.1	2.0	0.035
NaK-N	9.8	5.2	2.1	-
NaCs-N	10.0	5.3	2.2	-
KCs-N	10.4	4.4	1.3	-

Table 2

Specific area (S_{BET}) and adsorbed volume data obtained by DFT.

Sample	$S_{\rm BET}~(m^2/g)$	$V_{\rm micropore}~({\rm cm}^3/{\rm g})$	$V_{\rm mesopore}~({\rm cm}^3/{\rm g})$	$V_{\rm tot}~({\rm cm^3/g})$
Norit	1450	0.467 (81.8%)	0.094 (16.5%)	0.571
Na-N	1375	0.440 (77.2%)	0.111 (19.5%)	0.570
Cs-N	1447	0.460 (84.7%)	0.074 (13.6%)	0.543
NaK-N	1415	0.455 (74.8%)	0.135 (22.2%)	0.608
NaCs-N	1338	0.434 (78.2%)	0.104 (18.7%)	0.555
KCs-N	1416	0.463 (80.9%)	0.095 (16.6%)	0.572

Values in parenthesis indicate the percentage of each type of pore in carbon sample. Micropore: $\emptyset < 20$ Å; mesopore: 20 Å $< \emptyset < 500$ Å. V_{tot} : volume adsorbed by pores $\emptyset < 2000$ Å.



Fig. 1. N₂ adsorption isotherm of pristine Norit carbon.

Norit carbon used as pristine solid has a high specific surface area $(1450 \text{ m}^2/\text{g})$ and the total adsorbed volume of nitrogen $(0.571 \text{ cm}^3/\text{g})$ (Table 2). The pore size distribution of this carbon is principally micropores (81.8%) with an important contribution of mesopores (16.5%). This data is reflected in N₂ isotherms profile (Fig. 1), which is type I in BDDT classification [18]. The hysteresis loop, classified as type H4 [18], is typically of activated carbons as it is explained by the slit-shaped pores, present in the carbon [19,20].

The impregnation with different alkaline metals does not change significantly the specific surface area characteristics of the substrate (Table 2). The isotherm curves show the same profile, and slight differences in specific surface area and micropore volume (Table 2). The Cs-N sample presents the higher value of surface area and nitrogen adsorption into the micropores.

In order to get a more precise idea about the chemical state and the relative dispersion of the alkaline metals at the surface of the carbon, a study of the different samples by X-ray photoelectron spectroscopy was carried out. The binding energies of C 1s and O 1s core levels and the characteristic inner levels of the alkaline elements are given in Table 3, together with the M/C atomic ratios, determined from the peak intensities and the tabulated sensibility atomic factors [18]. The C 1s core level is complex, in which several components can be revealed. A major peak at 284.9 eV and another three (four in the case of the Norit pristine) centered at higher binding energies can be discerned. The peak located at 284.9 eV can be assigned to the C-C bonds of graphitic-like structure of the carbon, and even to H-containing species (-CH-), because the small chemical shift of these last species with respect to the first ones makes it difficult to distinguish. A second peak with a 15-23% ratio of the total area is observed around 286.4 eV, which can be associated with C-O bonds in alcohols or ethers. The third component close to 288 eV. in general less intense than the former, is attributed to ketonic species (C=O) and the last one, above 289 eV, to more oxidized (-COO-) or carbonates species [21]. In the Norit sample, besides this peak, which is observe at 290.6 eV, another component around 292.5 eV is detected. This last peak, due to a shake-up satellite $(\pi \rightarrow \pi^*)$ produced in the photoionization process of graphitic structure, is not observed in the alkaline-containing samples.

Similarly, the O 1s line profile is quite complex, especially in the Norit sample and several components can be distinguished. The first component centered at 531 eV, can be assigned to C–O and/or COO species of the carbonaceous support [21]. The second one, at 532 eV, is attributed to the hydroxides (and carbonates) of the corresponding alkaline metals. In the Norit sample, another two components above 533 eV are observed, which could be assigned

Table 3

Binding energies (eV) of core electrons and atomic ratios calculated by XPS.

Catalyst	C 1s	O 1s	<i>M</i> (BE)	M/C atomic ratio		
				Na	Cs	К
Norit	284.9 (57) 286.4 (23) 288.9 (7) 290.6 (6) 292.5 (7)	531.2 (29) 532.5 (41) 533.9 (19) 535.2 (11)	-	-		
Na-N	284.9 (57) 286.2 (15) 287.5 (15)	530.9 (44) 532.7 (56)	1072.5ª	0.0050		
K-N	289.4 (13) 284.9 (70) 286.8 (30)	531.0 (24) 532.8 (51) 534.5 (25)	293.0 ^b			0.0030
Cs-N	284.9 (59) 286.5 (20)	530.9 (47)	723.9 ^c		0.0027	
	288.1 (10) 289.7 (11)	532.6 (53)				
NaK-N	284.9 (74)	531.4 (25)	1071.2ª; 292.9 ^b	0.0002		0.0005
	286.6 (20) 288.3 (6)	533.0 (44) 534.8 (28)				
NaCs-N	284.9 (73)	531.4 (27)	1071.2ª; 723.9 ^c	0.0001	0.0001	
	286.6 (18) 288.3 (9)	533.0 (45) 534.8 (28)				
KCs-N	284.9 (74)	531.4 (25)	292.8 ^b ; 723.9 ^c		0.0001	0.0006
	286.6 (18) 288.3 (8)	533.0 (47) 534.8 (28)				

Values in parenthesis indicate the percentage of each peak.

^a Na 1s.

^b K 2p_{3/2}.

^c Cs 3d_{5/2}.

to molecular water [21], probably with different interaction degrees with the surface.

The binding energies of the inner electrons of the alkaline elements fit well with hydroxide species, although carbonates species cannot be discarded, due to the proximity of the binding energies of these last species. Nevertheless, it does not mean that Na⁺ and Cs⁺ are not ion exchanged on surface negative groups. As it is known, the surface of carbon materials presents negative groups that easily interact with alkaline cations when the corresponding ion exchange treatment is carried out. This ion exchange generates the active sites. By contrast, the exposure to ambient condition can generate a partial carbonation of the surface by reaction with CO₂, as detected by XPS. This is a frequent process in basic solid materials. Hence, the alkaline carbon is considered as the true catalyst [21].

With respect to the M/C atomic ratio, this ratio diminishes when the size of the alkaline cation increases as a consequence of the less exchange in the case of cesium than in the case of sodium, as determined by thermogravimetric analysis. However, the XPS results show a slight cesium enrichment at the surface, because the M/C ratio is around 2.4 times less for the cesium than for the sodium, meanwhile the content in metal (at-g M/100 g carbon) determined by thermogravimetric analysis is 3 times higher for the Na-Norit than for the Cs-Norit.

3.2. Sonochemical synthesis of N-alkylimidazoles

Under our experimental conditions, N-substituted imidazole of type **A** is selectively obtained. The mass spectrum of the reaction product confirms that **A** (MS m/s: 124 (M⁺), 97, 81, 55(100), 41) is



Scheme 2. Reaction mechanism between imidazole and electrophiles.



Fig. 2. Alkylation of imidazole (5 mmol) with 1-bromobutane (15 mmol) using 0.025 g of alkaline-promoted carbons under sonochemical activation at 298 K. (A) M-N series and (B) MM'-N series.

produced. Under base catalysis, imidazole reacts with electrophiles at the N-position (Scheme 2). The nature of the products depends upon the choice of the alkylating conditions and of catalyst type. As we have shown, alkaline-promoted carbons are appropriate materials to catalyze basic organic reactions showing, under our experimental conditions, basic sites up to $pK_a = 16.5$ [22]. Considering that the NH group of imidazole presents a $pK_a = 14.5$, these carbons could be appropriate catalysts to perform the alkylation [23].

3.2.1. Kinetic study

The alkylation of imidazole with alkyl halides proceeds under both acid [10] and basic (Scheme 2) media following a different reaction mechanism. In Table 4 is shown the kinetic parameters

Table 4

Kinetic rate constants for the alkylation of imidazole (5 mmol) with 1-bromobutane (15 mmol) under sonochemical activation using alkaline carbons (0.05 g).

Catalyst	<i>T</i> (K)	Batch k $(\times 10^4 \text{ M}^{-1} \text{ s}^{-1} \text{ g}_{cat}^{-1})$	Ultrasounds k (×10 ⁴ M ⁻¹ s ⁻¹ g ⁻¹ _{cat})
Na-Norit	293	0.82	3.65
	313	2.00	9.85
	333	2.78	15.3
Cs-Norit	293	2.28	7.48
	313	4.36	8.61
	333	5.11	18.7
K-Norit	293	1.68	4.37
	313	2.11	8.57
	333	3.53	8.87
NaCs-Norit	293	2.22	7.18
	313	3.10	7.80
	333	4.79	8.77
KCs-Norit	293	2.36	7.27
	313	4.32	7.95
	333	4.89	9.10
NaK-Norit	293	1.83	4.80
	313	2.26	7.52
	333	3.06	8.99

obtained from the alkylation of imidazole reactions under both conventional thermal and sonochemical activation by using different basic solid catalysts. In the present work N-substituted imidazole (**A**) was obtained as the only product of the alkylation of imidazole. The reaction proceeds with 100% selectivity to N-butylimidazole under all reaction conditions. The reported selectivity was determined in the following way [yield of desired product]/([yield of detected product] + [detected reactant]). The total balance calculated to carbon atoms was in all cases better than 98%.

The results obtained in Table 4 were obtained by fitting a pseudo-first order kinetic model considering that one of the reactant is in excess [10], in our case 1-bromobutane concentration, not showing any significant change during the reaction. From these results it can be said that Na-Norit catalyst is approximately half as active as catalysts containing caesium, these are Cs-, NaCs-and KCs-Norit and slightly lower than that containing potassium, this is NaK-Norit. It can be observed that the rate constants decrease in the order: Cs-Norit > KCs-Norit > NaCs-Norit > NaK-Norit.

Under our experimental conditions, the reaction was neither controlled by external nor internal diffusion as it was confirmed by using different particle sizes of the catalysts (0.074, 0.140 and 0.250 mm) and different stirring rates (600 and 1500 rpm). From the Arrhenius equation, the activation energies were also calculated. The results obtained for the five catalysts employed in this study confirm that the reaction rate is not limited by pore diffusion and that it is controlled chemically ($E_a > 20$ kJ/mol).

3.2.2. Influence of external parameters

3.2.2.1. Influence of the basicity of the catalyst and temperature. The alkylation of imidazole with 1-bromobutane was performed on both series of catalysts, M-N and MM'-N at different temperatures. As an example the conversions at 333 K are given in Fig. 2.

From these results it can be said that the order of activity is

 $Na-N < K-N < NaK-N < NaCs-N < KCs-N \approx Cs-N$.



Fig. 3. Alkylation of imidazole with 1-bromobutane under sonochemical activation with 0.025 g of catalyst after 60 min at different reaction temperatures. (A) M-N series and (B) MM'-N series.

Cs-N is around 1.3 times more active than Na-N. Thus, conversions of 99% are reached in only 120 min of reaction when Cs-N is the catalyst at 333 K. Closer conversions (around 93%) are obtained when the catalyst is doped with K and Cs (KCs-N). The activity of the samples NaK-N and NaCs-N is intermediate between Cs-N and Na-N catalysts. This trend indicates that the type of promoter is decisive to define the basicity of these catalysts. Moreover, the reaction is extremely sensitive to slight modification of the catalyst basicity. Thus, the Lewis basic character is determined by the alkaline dopant. The same trend is observed at 293 and 313 K. Fig. 3 displays the conversion values at 120 min of reaction as an example of the influence of the temperature on the ultrasonic induced reactions. As this figure shows, from the results obtained at 293 and 313 K, the conversion increases with the reaction temperature, keeping the selectivity 100% in all cases due to the cavitation phenomena during the sonochemical reactions. However no significant changes in the conversion are observed when temperature of sonication is increased from 313 to 333 K. This fact confirms some previous works in the literature [10,25] which describes that a liquid sonicated at a temperature near the boiling point of the medium, enhanced effect is diminished or even no important sonochemical effect may be expected.

As expected, an increase of the reaction temperature implies an increase of the yield of the N-alkylimidazole, keeping the selectivity 100% in all cases. High yields (between 75% and 99%) are obtained when Cs-N is employed as catalyst.

3.2.2.2. Influence of the catalyst amount. In order to study the effect of the catalyst amount, imidazole was alkylated with 1-bromobutane using two different amounts of catalyst (0.025 and 0.050 g). The results are shown in Table 5.

Table 5

Alkylation of imidazole (5 mmol) with 1-bromobutane (15 mmol) under sonochemical activation. Influence of the catalyst amount. M-N and MM'-N series. Reaction temperature: 293 K.

Catalyst	Time (min)	Conversion (%	Conversion (%)	
		0.025 g	0.050 g	
Na-N	15	22.2	32.4	
	30	27.5	39.6	
	60	33.7	41.8	
	120	60.7	70.6	
Cs-N	15	40.1	44.6	
	30	53.6	57.3	
	60	70.3	78.3	
	120	80.4	87.3	
K-N	15	24.2	32.0	
	30	28.9	50.1	
	60	40.2	63.4	
	120	49.1	72.2	
NaK-N	15	25.3	35.6	
	30	30.1	53.2	
	60	42.6	65.6	
	120	50.2	74.7	
NaCs-N	15	37.0	45.0	
	30	52.6	52.6	
	60	60.6	72.5	
	120	80.0	86.7	
KCs-N	15	40.0	45.3	
	30	52.3	53.2	
	60	63.6	73.3	
	120	81.3	87.0	

In general, under ultrasound activation the conversion increases by a factor of 1.2 when duplicates the catalyst amount.

3.2.2.3. Comparison of ultrasonic activation with thermal activation: influence of the reaction temperature. The effect of the reaction temperature has been studied during the alkylation of imidazole with 1-bromobutane under ultrasonic waves and in a batch reaction system using different amounts of catalysts. As an example, Figs. 4 and 5 show the activity of the catalyst at 60 min of reaction using 0.05 g of the two series of catalysts.

The comparison evidences that the ultrasonic activation enhances N-alkylation of imidazole much better than thermal activation at any temperature since higher conversion levels are reached at the same reaction times. The improvement of the reactivity is more drastic at low temperatures. This can be explained due to the fact that an increase of the temperature will raise the vapor pressure of the liquid medium of the ultrasonic bath, leading to an easier cavitation but to a less violent collapse, which makes the cavitation less effective [24]. On the other hand, a



Fig. 4. Alkylation of imidazole with 1-bromobutane under sonochemical and thermal activation with 0.05 g of catalyst after 60 min at different reaction temperatures. (A) Na-N and (B) Cs-N.



Fig. 5. Alkylation of imidazole with 1-bromobutane under thermal (A) and sonochemical (B) activation with 0.05 g of catalyst after 60 min at different reaction temperatures for the catalysts of the MM-N series.



Fig. 6. Alkylation of imidazole with 1-bromobutane under thermal and sonochemical activation with 0.025 g of catalyst at 293 K (A) and 333 K (B) on Cs-N catalyst.

further factor to be considered is that at temperatures near boiling point of the ultrasonic liquid medium, a large number of microbubbles are generated concurrently in it, acting as a barrier to the sound transmission. These bubbles dampen the effective ultrasonic energy from the source that enters the reaction liquid medium. Thus, our experimental results confirm some previous works published in the literature [25], which describe that when a liquid is sonicated at a temperature near its boiling point, enhanced effect are diminished or even any important sonochemical effects may be expected.

As a final example, the evolution of the reaction under sonochemical and thermal activation at 293 and 333 K using the Cs-N carbon, which is the most basic catalysts are displayed in Fig. 6. It is evidenced that at lower temperatures, the differences of activity between ultrasound and thermal activation are higher than at higher temperatures again because there is no sonochemical effect during the ultrasound activation when the temperature is increased up to 333 K. In any case our basic carbons turned out as suitable catalysts to carry out the proposed reaction under both conventional thermal and ultrasound activation, in short times and under mild conditions being also able to be reused in four cycles of reaction without important changes in the final yield of the reaction.

4. Conclusions

The effect of ultrasound waves in the activation of alkalinepromoted carbons has been explored in the alkylation of imidazole with 1-bromobutane. It was found that there is a substantial enhancing effect in the yield when ultrasound was used to activate the reaction. Enhancement effect on the reaction rate by combining the basicity of the carbon catalysts and ultrasound is presented as an alternative method for the production of Nsubstituted imidazoles and, in general, for the production of other fine chemicals due to the mild conditions that this system offers. In spite of the large body of work dealing with sonocatalysis, only a relatively small number of papers report the influence of the reaction conditions on the rate and yields of chemical reactions. It is well documented that, external parameters have a great influence on the cavitation and, since the cavitation is necessary to induce sonochemical reactions. It is important that those parameters are fine tuned and controlled, to maximize the sonochemical effects. We have found here that among all the experimental procedures induced by heterogeneous media employed in this synthesis, the combination of ultrasound irradiation with alkaline carbons offers interesting prospects because excellent yields are achieved under very mild conditions.

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