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Sonocatalysis and alkaline-doped carbons: An efficient method for the synthesis of chalcones in heterogeneous media

Carlos Javier Durán-Valle[a], Isabel M. Fonseca[b], Vanesa Calvino-Casilda[c], María Picallo[c],
Antonio José López-Peinado[c], Rosa María Martín-Aranda[c,*]

[a] *Dpto. de Química Inorgánica, Facultad de Químicas, Avda de Elvas s/n, Universidad de Extremadura, E-06070 Badajoz, Spain*
[b] *REQUIMTE, CQFB, Departamento de Química, Faculdade de Ciências e Tecnología, Universidade Nova de Lisboa,*
Campus da Caparica, 2829–516, Portugal
[c] *Dpto. de Química Inorgánica y Química Técnica, Facultad de Ciencias, Universidad Nacional de Educación a Distancia (UNED),*
C/Senda del Rey 9, E-28040 Madrid, Spain

Abstract

The Claisen–Schmidt condensation between benzaldehyde and acetophenone has been carried out for the preparation of chalcones. Two basic activated carbons (Na- and Cs-Norit) have been used as catalysts. The order of activity is Na-Norit < Cs-Norit. Chalcones have been synthesized by sonochemical irradiation. The effect of the ultrasound activation has been studied. Cs-doped carbon is presented as the optimum catalyst, giving excellent activity for this type of condensation. A substantial enhancing effect in the yield was observed when the carbon catalyst was activated under ultrasonic waves. This "green" method (combination of alkaline-doped carbon catalyst and ultrasound waves) has been applied to the synthesis of several chalcones with antibacterial properties achieving, in all cases, excellent activities and selectivities. 4′-Hydroxy and 4′-carboxy-chalcones have been prepared under mild conditions by sono-activation of the carbon catalyst. A comparative study under non-sonic activation has showed that the yields are lower in silent conditions, indicating that the sonication exerts a positive effect on the activity of the catalyst. Cs-Norit carbon catalyst can compete with the traditional NaOH/EtOH when the reaction is carried out under ultrasounds. The role of solvent in this reaction was studied with ethanol. High conversion was obtained in absence of solvent. The carbons were characterized by thermal analysis, nitrogen adsorption and X-ray photoelectron spectroscopy.

Keywords: Chalcone synthesis; Sonocatalysis; Basicity; Activated carbons as catalysts; Claisen–Schmidt condensation

1. Introduction

The members of chalcone and flavonid family have attracted a great deal of interest due to their applications as antibacterial, anti-inflammatory and anticancer pharmacological agents [1–3]. Chalcones are important intermediates in the synthesis of many pharmaceuticals. They are commonly synthesized via the Claisen–Schmidt condensation between acetophenone and benzaldehyde. This reaction is catalyzed by acids and bases under homogeneous conditions. Homogeneous reactions present several hurdles, such as catalyst recovery and waste disposal problems. In this respect, heterogeneous catalysts are considered as an eco-friendly alternative. The utilization of heterogeneous catalysts for the production of chalcones was reported in literatures [4–10]. But there is no report for the use of activated carbons as catalysts in combination with ultrasounds.

Recently, activated carbons have been employed to catalyze fine chemicals reactions, because their extended surface area, microporous structure and high degree of surface reactivity [11–13]. Thus, this type of materials is competitive with other traditionally employed catalysts for organic synthesis, such as zeolites, clays or supported oxides.

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* Corresponding author.
E-mail address: rmartin@ccia.uned.es (R.M. Martín-Aranda).

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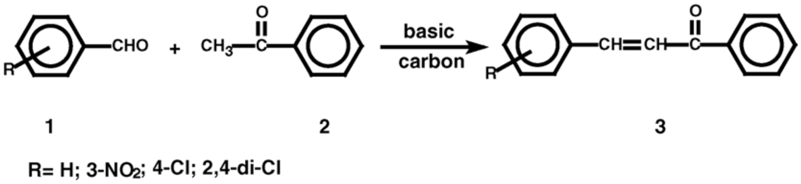


Scheme 1. Claisen–Schmidt condensation between benzaldehyde (**1**) and acetophenone (**2**).

It has been shown that carbons have basic sites, which are able to catalyze reactions needing weak and medium basic strengths. Moreover, the activity can be modified changing the countercation [14,15]. In this context, the present study reports the chalcone synthesis using alkaline activated carbons as solid-base catalysts.

The importance of minimizing the impact that chemical proccesing has on the environment is growing, with an increased appreciation of the need to reduce pollution and depletion of our finite environmental resources. Optimal use of material, energy and consequent waste management can be recognised as important factors for environmental protection. Industrial chemistry is widely adopting the concept of "Green Chemistry" to meet the fundamental scientific challenges of protecting human health and the environment while simultaneously achieving commercial profitability. Some of the important alternative tools include the use of ultrasounds as an alternative source. The short reaction time and expanded reaction range that is offered by ultrasound assisted synthesis are suited to the increased demands in industry, in particular, in the pharmaceutical industry. In this sense, ultrasonic irradiation leads to the acceleration of numerous catalytic reactions as well as in homogeneous and heterogeneous systems [16] and significant improvements can be realized with regards to the yields [17,18]. The sonochemical phenomena originate 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 [19,20].

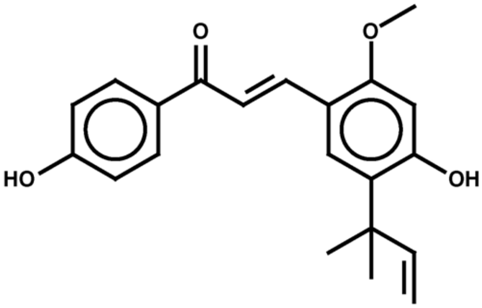
The chemical effects of ultrasounds have been attributed to the implosive collapse of the cavitation period of the sound waves. The bubbles are generated at localized sites in the liquid mixture that contain small amounts of dissolved gases. Trapped within a microbubble, the reactants are exposed to a high pressure and temperature upon implosion, fracturing the molecules, forming highly reactive species with a great tendency to react with the surrounding molecules. When one of the phases is a solid the ultrasonic irradiation has several additional enhancement effects, which are particularly convenient when the solid acts as catalyst [21,22]. The cavitation effects form microjects of solvent, which bombard the solid surface. This effect causes the exposition of unreacted surfaces of 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 [23].

The present paper reports the experimental results obtained in a heterogeneous reaction (benzaldehyde condensation with acetophenone, liquid phase) catalyzed by alkaline-doped carbons (solid phase) under ultrasonic activation and in the absence of any solvent (Scheme 1). For comparison, the results obtained under thermal activation are also presented. We have also investigated the influence of different factors during the reaction, such as basicity of the catalyst, catalyst amount and reaction temperature.

Finally, the method employed in this study (combination of sonocatalysis and alkaline-doped carbon) has been used for the synthesis of commercial chalcones with the structure of Licochalcone A (Scheme 2) with exhibit pharmacological activities against *Staphylococcus aureus* [24].

No new classes of antibiotics have been introduced in the market since the Nalixidic acid in 1962 until the introduction of Linezolid in 2000. Compounds with a chalcone-based structure type Licochalcone A (Scheme 2) and oxygenated chalcones was shown to present activity against Gram-positive strains of bacteria. Recently, Nielsen et al. [25] published a study that identifies the groups responsible for the antibacterial effect of Licochalcone A against *S. aureus*. It was shown that the 4′-hydroxy group in the ring was essential for the activity. Nevertheless, the major obstacle in the development of this type of compounds is the low solubility of chalcones. They changed the proteolytic properties of the 4-hydroxy group making it more acidic and exchanging the hydroxy group with carboxylic acids. All the chalcone products described by Nielsen et al. were prepared using 1.5 eq. of sodium hydroxide in ethanol.

In the present study, we present the application of a new catalytic method for the synthesis of this type of chalcones



Scheme 2. Licochalcone A.

(sonocatalysis with alkaline-doped carbon), which is presented as a ‘‘green’’ procedure.

2. Experimental

2.1. Catalysts preparation

An activated carbon, RX-1 EXTRA Norit, has been employed as pristine carbon. Two alkaline carbons have been prepared by ionic exchange of Na and Cs using 0.43 and 0.075 M solutions of sodium and cesium carbonates, respectively, with 2 wt% metal content for about 60 h at 353 K. In both cases, the liquid-to-solid ratio was 10 by weight. The samples were filtered and washed to give a carbonate-free material. After drying for 16 h at 383 K, the carbons were crushed and sieved to 0.250 mm particle size.

2.2. Catalysts characterization

The Norit RX-1 EXTRA carbon is a well-characterized steam activated peat-char [26,27]. Specific surface areas of the carbon samples were determined by N_2 adsorption isotherms at 77 K, applying the BET method [28] in a Micromeritics ASAP 2010 Volumetric System. Volume adsorbed in the different types of pores was calculated by the Density Functional Theory (DFT) method [29] by means of DFT plus software. Table 1 shows the specific surface areas and the adsorbed volume obtained for both catalysts.

Photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R spectrometer.

The ash contents of the studied catalysts were obtained by thermogravimetric analysis (TG/DTA Seiko System 320). The calculated metal contents (Table 2) indicate that the exchange capacity of Norit RX-1 EXTRA carbon for sodium is around three times the exchange capacity for cesium.

The pH’s of the samples studied were measured following the method described by Rivera and Ferro [30] using an Omega pH-meter, model PHB-62.

2.3. Reaction procedure

2.3.1. Ultrasonic induced reactions

Benzaldehyde (5 mmol) and acetophenone (5 mmol) which are liquid reactants, were mixed in a flask in the absence of solvent (or with 5 ml of ethanol). The flask was suspended into the ultrasonic water bath at the reaction temperature (303, 313 and 323 K). The corresponding catalyst was then added (0.3 or 0.6 g of alkaline carbon) and the reaction times started. The reactions were performed in an ultrasonic bath (Selecta Ultrasound-H) with a heating system, 40 kHz and 550 W.

Table 1
Specific area (S_{BET}) and adsorbed volume data obtained by DFT

Sample	S_{BET} (m^2/g)	$V_{micropore}$ (cm^3/g)	$V_{mesopore}$ (cm^3/g)	V_{tot} (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

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

Table 2
Characterization of the catalysts

Catalyst	pH	Ash (%)	M_2O (%)	Metal (at g/(100 g catalyst))
Norit	8.0	3.1	–	–
Na-Norit	8.3	4.8	1.7	0.055
Cs-Norit	10.3	5.5	2.4	0.017

2.3.2. Thermal induced reactions (non-sonic reactions)

The conventional heating experiments were carried out in a batch reactor. The same ratio of reactants than that for ultrasound activation is used. The mixture was heated up to the reaction temperature (303, 313 and 323 K). The reaction was followed by gas chromatography-mass spectrometry, using a 60-m long phenyl-silicone capillary column and a flame ionization detector. The conversion is expressed in terms of amount of chalcone (**3**) in wt% (Scheme 1).

2.3.3. Synthesis of Licochalcone A derivatives

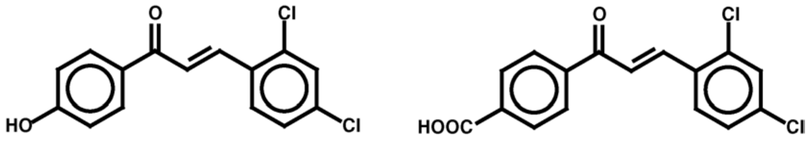
4-Hydroxy-2,4-dichloro-chalcone and 4-carboxy-2,4-dichloro-chalcone were obtained according to the general procedure under sonication or thermal activation (Scheme 3).

3. Results and discussion

3.1. Catalysts characterization

Norit carbon used as pristine carbon has a high specific surface area (1450 m^2/g) and a total adsorbed volume of N_2 of 0.571 cm^3/g in pores up to 2000 Å (Table 1). The pore size distribution of this carbon is principally micropores (81.1%) with an important contribution of mesopores (16.5%). The impregnation with the alkaline metals does not change the surface characteristics of the substrate. The Cs-N sample presents the higher value of surface area and nitrogen microporosity adsorption. Table 2 summarizes the pH and the metal contents of the catalysts. The pristine carbon, RX-1 EXTRA Norit, exhibits a basic pH (8.0), which increases only slightly in the sample exchanged with sodium, but considerably in the Cs-Norit sample. In spite of the exchange capacity for the cesium being around three times less than the capacity of the sodium, the highest basicity of the first cation could be responsible for the increase observed in the pH of the sample (10.3).

In order to get a more precise idea about the chemical state and the relative dispersion of the alkaline metals at the


4 **5**

Scheme 3. 4′-Hydroxy-2,4-dichloro-chalcone (**4**) and 4′-carboxy-2,4-dichloro-chalcone (**5**).

surface of the carbon, a surface analysis 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 [31]. Peak synthesis procedures revealed several components in the C 1s core level. A major peak at 284.9 eV and another three (four in the case of the Norit pristine) centered at high 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. The H-containing species (–CH–) should be included in the same peak, due to the small chemical shift between these species and the C–C ones. 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. 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. In the Norit RX-1 sample, besides this peak, which is observed 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, is not observed in the alkaline-containing samples.

Similarly, the O 1s line profile is quite complex, especially in the Norit sample. The first component centered at 531 eV, is due to C–O and/or COO species of the carbonaceous support. The second one, at 532 eV, is attributed to the hydroxides (and carbonates) of the corresponding alkaline metals. In the Norit carbon sample, another two components above 533 eV are observed, which could be assigned to molecular water, probably with different interaction degree with the surface or different localization, for example, at the external surface and micropores.

Table 3
Binding energies (eV) of core electrons and atomic ratios calculated by XPS

Catalyst	C 1s	O 1s	*M*	M/C atomic ratio
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-Norit	284.9 (57) 286.2 (15) 287.5 (15) 289.4 (13)	530.9 (44) 532.7 (56)	1072.5[a]	0.0050
Cs-Norit	284.9 (59) 286.5 (20) 288.1 (10) 289.7 (11)	530.9 (47) 532.6 (53)	723.9[b]	0.0027

Values in parenthesis indicate the percentage of each peak.

[a] Na 1s.

[b] Cs $3d_{5/2}$.

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 the latter 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 contains 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 CO_2, as detected by XPS. This is a frequent process in basic solid materials. Hence, the alkaline carbon is considered as the true catalyst.

With respect to the M/C atomic ratios, they tend to diminish when the size of the alkaline cation increases as a consequence of the lower exchange in the case of cesium, 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 three times higher for the Na-Norit than for the Cs-Norit carbon.

3.2. Claisen–Schmidt condensation on alkaline-doped activated carbons

The Claisen–Schmidt condensation between benzaldehyde (**1**) and acetophenone (**2**) (Scheme 1) was first carried out at 303 and 313 K, in absence of solvent using 0.3 and 0.6 g, respectively, of alkaline-doped carbons for 5 h. The reaction gives *trans*-chalcone (**3**). The reaction was also carried out using ethanol as solvent. The yield of chalcone is showed in Fig. 1 and compared with the obtained using ultrasound activation. No side products were observed, indicating that the Cannizaro reaction or ketone autocondensation do not take place under these experimental

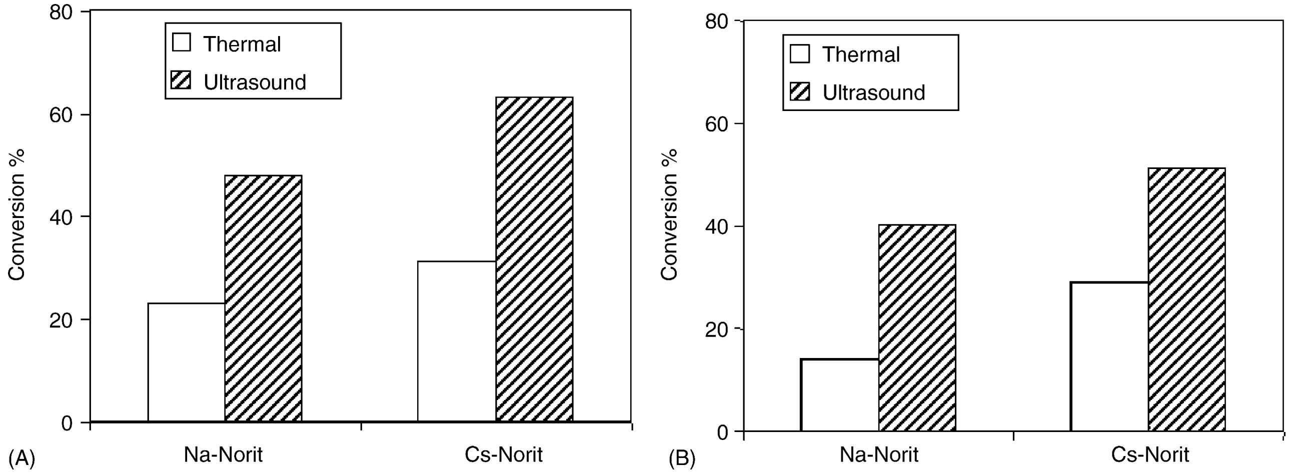


Fig. 1. Influence of the solvent during the chalcone formation using as catalysts Na- and Cs-Norit (0.3 g). (A) Dry media. (B) Solvent. Ethanol: 5 ml; reaction time: 120 min; reaction temperature: 303 K.

conditions. In Fig. 1, it can be observed a clear improvement in the catalytic activity when the reaction takes place in absence of solvent. It is also observed that ultrasounds enhance the activity, keeping constant the selectivity. This increase of activity due to ultrasounds is attributed to the cavitation phenomena during the induced sonochemical reactions. This trend is observed at 303, 313 and 323 K, using 0.3 or 0.6 g of both carbon catalysts (Na- or Cs-Norit).

In Fig. 2, yields of chalcone (**3**) versus time at 303 K are presented. These results show that the order of activity is Na-Norit < Cs-Norit under sono-activation or thermal-activation. Thus, conversions around 75% are obtained when the catalyst is doped with Cs. This trend indicates that the type of promoter can modulate the basicity of the carbon surface and, so the Lewis basic character of the carbon is determined by the alkaline dopant. The same trend is observed at 313 and 323 K. The reaction was negligible when undoped pristine carbon was employed as catalyst under identical conditions.

The comparison between ultrasound and thermal activation evidences that the sono-activation enhances the Claisen–Schmidt condensation between benzaldehyde and acetophenone 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, closer to room temperature. 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. On the other hand, a 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 literature [32], 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.

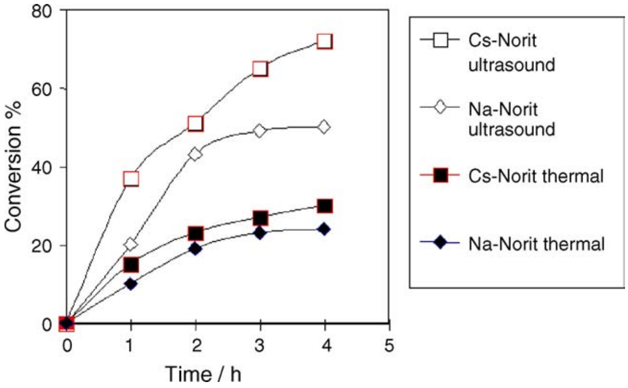


Fig. 2. Effect of the alkaline dopant during the condensation between acetophenone and benzaldehyde at 303 K in the presence of 0.3 g of catalyst. Na- and Cs-Norit. Solvent: 5 ml ethanol.

Based on the results showed in the previous part of the work, we carried out the Claisen–Schmidt condensation between different substituted benzaldehydes and acetophenones under sono-activation of the alkaline-doped carbon and a wide variety of chalcones were prepared. The condensations were carried out at different reaction temperatures using the most active carbon catalysts (Cs-Norit). Table 4 displays the yields of chalcones obtained at 303 K. It can be observed that yields between 55 and 90% are achieved in 5 h, while selectivity is around 99% in all the cases.

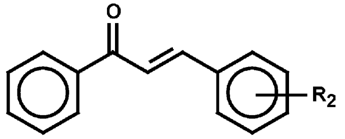
3.2.1. Preparation of chalcones with antibacterial activity using alkaline-doped carbon under sonochemical activation

Claisen–Schmidt condensation of hydroxy acetophenones or carboxy acetophenones has been described in the literature using basic catalysts [33]. Licochalcone A has antibacterial activity against *Staphylococcus aureus*. The

Table 4
Yields of chalcones under ultrasonic activation

Catalyst	R_2	Yield (%)
Na-Norit	$3\text{-}NO_2$	55
	4-Cl	79
	2,4-di-Cl	83
Cs-Norit	$3\text{-}NO_2$	60
	4-Cl	89
	2,4-di-Cl	90

Reaction temperature: 303 K and catalyst: Cs-Notrit (0.6 g)



exchange of the 4′-hydroxy group with carboxy acids increases aqueous solubility of the chalcones improving their in vitro antibacterial activity against *Staphylococcus aureous*. Traditionally, the synthesis of these chalcones is carried out by Claisen–Schmidt condensation between benzaldehyde and acetophenone using 1.5 eq. of sodium hydroxide in ethanol reflux. However, a ‘‘green’’ methodology would avoid the use of organic solvents and liquid catalysts. In the present study, we optimize the use of activated carbons as solid-base catalysts under ultrasound activation. Using this method, it has been possible improve the yield of chalcones which exhibit antibacterial activity, such as 4′-hydroxy- and 4′-carboxy-Licochalcone A derivatives. Fig. 3 shows the conversion values obtained. Using the Cs-Norit carbon, the preparation of these types of chalcones has been achieved successfully. In fact, with this catalyst and under ultrasound activation, it is possible to achieve 25% conversion of 4′-hydroxy and 50% conversion of 4′-carboxy-chalcone. It is important to remark that conversions around 13% for 4′-hydroxy-chalcone and 46% for 4′-carboxy-chalcone are obtained in 18 h and NaOH/EtOH reflux.

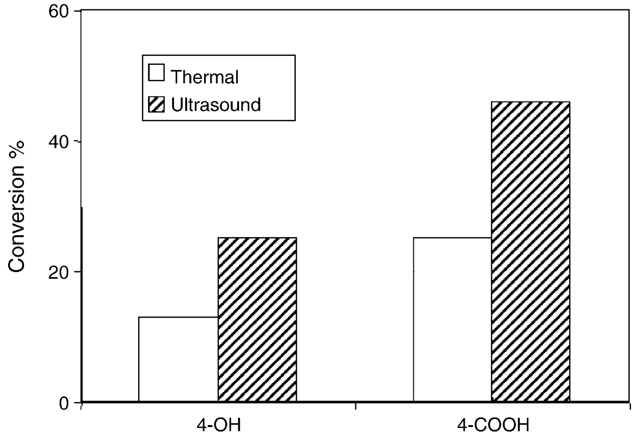


Fig. 3. Influence of the ultrasound activation versus non-sonic activation during the solventless synthesis of 4′-hydroxy and 4′-carboxy-chalcones. Reaction temperature: catalyst: Cs-Norit (0.6 g). Reaction time: 5 h.

For comparison purposes, the reactions were also performed under thermal activation using the same reaction conditions. In this case, lower conversions (around 15 and 25%) were obtained, indicating that the effect of ultrasound waves exerts a positive effect in the activation of the carbon catalyst. It was found a substantial enhancing effect in the yield of chalcone when ultrasound was used.

4. Conclusions

Alkaline carbons were found to be very efficient catalysts for the Claisen–Schmidt condensation. The basicity of the carbon is enhanced by the presence of the alkaline metal on the surface. The effect of ultrasound waves in the activation of alkaline-doped carbons has been explored in this condensation between benzaldehyde and acetophenone. It was found that there is a substantial enhancing effect in the yield when ultrasound was used. Under these experimental conditions, the formation of environmental hazardous residues is avoided. Alkaline-doped carbon catalysts can successfully be employed to obtain chalcones with antibacterial activities. These solid catalysts can compete with the traditionally used NaOH. Enhancement effect on the reaction rate by combining the basicity of the carbon with ultrasounds is presented as an alternative method for the production of differently substituted chalcones and, in general, for the production of other fine chemicals due to the mild conditions that this method offers.

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