Process intensification by combination of activated carbon supported catalysts and alternative energy sources

Intensificación de procesos combinando catalizadores de carbón activado soportados y fuentes de energía alternativas

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Abstract

Activated carbons are well known for their catalytic properties and for being used as a catalyst support in heterogeneous catalysis. Activated carbons possess most of the desired properties of a catalyst support; inertness towards unwanted reactions, stability under regeneration and reaction conditions, suitable mechanical properties, tunable surface area, porosity, and the possibility of being manufactured in different size and shape.

On the other hand, the intensification of chemical transformations into valuable products through microwave and ultrasound activation has attracted particular attention in chemical industries in recent decades. Industrial chemical transformations are conventionally carried out by conductive heating by using an external heat source; a slow and inefficient way of transferring energy into the system. On the contrary, microwave irradiation and ultrasound are efficient ways of activating chemical systems. The short reaction time and expanded reaction range offered by microwave and ultrasound activation are appropriate in the development of new strategies for chemical transformations in industrial chemistry. In addition, the combination of activated carbon supported catalysts and microwave and ultrasound activation provides a peculiar activity and selectivity not reproducible under conventional thermal activation in a discontinuous batch reactor.

Resumen

Los carbones activados son bien conocidos por sus propiedades catalíticas y por ser utilizados como soportes en catálisis heterogénea. Los carbones activados poseen muchas de las propiedades deseadas para un soporte catalítico; inactividad hacia reacciones no deseadas, estabilidad bajo condiciones de regeneración y de reacción, buenas propiedades mecánicas, área superficial modificable, porosidad, y posibilidad de ser fabricados en diferentes tamaños y formas .

Por otra parte, la intensificación de transformaciones químicas en productos de alto valor añadido a través de la activación de microondas y los ultrasonidos ha despertado especial interés en las industrias químicas en las últimas décadas. Las transformaciones químicas industriales se llevan a cabo normalmente mediante calentamiento térmico convencional por conducción térmica utilizando una fuente de calor externa, una forma lenta e ineficiente de transferir energía al sistema. Por el contrario, la irradiación microondas y los ultrasonidos son una forma eficaz de activar los sistemas químicos. El corto tiempo de reacción y la gran reactividad mostrada por la activación microondas y la activación por ultrasonidos resultan apropiadas para el desarrollo de nuevas estrategias para las transformaciones orgánicas en la química industrial. Además, la combinación de catalizadores soportados sobre carbón activado y la activación por microondas y ultrasonidos, proporciona valores de actividad y selectividad característicos, no reproducibles bajo activación térmica convencional en un reactor discontinuo tipo *batch*.

1. Introduction

Industrial chemistry has widely assumed the concept of *Green chemistry* to achieve the fundamental scientific tasks of protecting the environment and human health while simultaneously accomplish commercial profitability [1]. One of the main approaches for achieving this goal is to promote the use of the catalysis. Nowadays, catalysis is of crucial importance for chemical industrial processes [2]. In particular, supported catalysts are of special interest because they allow a higher activity and stabilization due to the fine dispersion of small metallic particles. In addition, they also provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal. In the past, the lack of fundamental understanding of many aspects of the use of carbon in catalysis caused a limited employ of carbon as catalyst and still more as catalyst support. The continuous studies conducted to understand all aspects of the physical and chemical characteristics of carbon materials, and especially of activated carbons (AC); surface area, porosity, and the possibility of controlling the surface chemistry of such materials, is the origin of important researches carried out in industrial chemistry [3-5]. In particular, ACs exhibit optimum properties, performance and stability in both acidic and basic media that let them to be used as catalyst support in multitude of different applications in chemical industries. It has been shown that although the surface area and the shape of carbon porosity may be very important in the preparation and properties of the corresponding catalysts, the role of carbon surface chemistry is also extremely important. All these aspects have to be taking into account when designing an AC supported catalyst.

Other approaches to promote the *Green Chemistry* are to explore alternative reaction conditions and reaction media to perform the desired catalytic chemical transformations with minimal by-products, and if possible, eliminate the use of conventional organic solvents. Some of the important alternative tools include the use of microwave and ultrasound as alternative energy sources.

Microwave enhanced chemistry is based on the

efficient heating of materials by microwave dielectric heating effects. Microwave irradiation produces efficient internal heating (in-core volumetric heating) by direct coupling of microwave energy with the molecules of solvent, reagents and catalyst present in the reaction mixture. This phenomenon is dependent on the ability of these specific materials to absorb microwave energy and convert it into heat. Microwave heating usually increases with the dielectric constant of the solvent, and for instance in the presence of hydroxyl groups. Short reaction times (high-speed synthesis), and unique reactive features of microwave-assisted synthesis are ideally suited to the increasingly demanding chemical industry affording high conversions and peculiar selectivities [6,7]. As previously commented, AC catalysts have been used to catalyze efficiently organic synthesis, because of their extended surface area, microporous structure, and high degree of surface reactivity. In addition, carbon materials under microwave activation are very efficient absorbers of microwave energy and convert easily that energy into heat (very "lossy" materials).

On the other hand, ultrasound, an efficient means of activation in synthetic chemistry, have been employed for decades with varied success to accelerate numerous catalytic reactions in homogeneous as well as in heterogeneous systems [8]. This high-energy input enhances mechanical effects in heterogeneous processes and induces new reactivities leading to the formation of unexpected chemical species. In general, sonication presents beneficial effects on the chemical reactivity, besides accelerating the reaction reduces the induction period, and enhance the catalyst efficiency [9]. The sonochemical phenomena is 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 [10,11]. Cavitation is a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid. Cavitation induces very high local temperatures and pressures inside the bubbles (cavities), leading to a turbulent flow of the liquid enhancing mass transfer. The remarkable phenomenon of cavitation makes sonochemistry inimitable.

In sonochemistry, ultrasound forms very fine emulsions in liquid-liquid systems. In case of liquid-solid systems as it is the case of using AC supported catalysts, a cavitation bubble collapses violently (asymmetrically) near the solid surface of the carbon catalyst forming liquid jets targeted at surface (microjets) (Figure 1). These high-speed jets of liquid are driven into the surface of a carbon particle causing localized high temperatures and pressures improving the liquid-solid mass transfer [12]. Kinetic studies of catalyzed heterogeneous reactions show that ultrasound activation increases the reaction rate and determine if this rate is limited by pore diffusion or if it is chemically controlled [13,14]. The ultrasound energy enhances the reaction rate and affects mainly the preexponential factor A in the Arrhenius equation by increasing the number of collisions of reactant molecules, not changing almost the final activation energy. In case of heterogeneous systems, several explanations justify the increase of reaction rate and selectivity observed; the deformation of the AC catalyst surface that exposes fresh, the highly active surface and the reduction of the diffusion length in the catalyst pores. The local turbulent flow associated with acoustic streaming improves mass transfer between the liquid phase and the surface, increasing the reaction rates. Moreover, ultrasound is capable of cleaning and smoothing the catalyst surface. The intensity of cavitation and therefore reaction rates and/or yields can be affected by the ambient conditions of the heterogeneous system (acoustic power, frequency, system vapour pressure, solvent, ultrasonic intensity, external temperature and pressure, dissolved gases, buffer, sample preparation, etc.) [15].

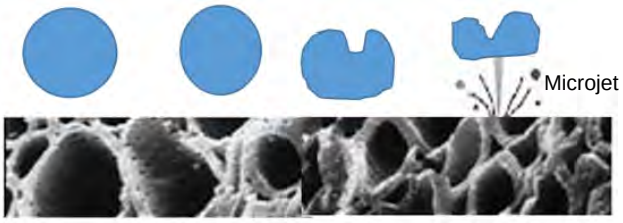


Figure 1. Asymmetric cavitacional collapse of a bubble near the surface of an activated carbon in sonochemistry.

Figura 1. En sonoquímica, colapso asimétrico cavitacional de una burbuja cerca de la superficie de un carbón activado.

2. Microwave assisted organic reactions catalyzed by AC supported catalysts

Basic AC supported catalysts, such as Na- and Cs-Norit or their binary combinations, have been tested in the *N*-alkylation of imidazole and benzimidazole with medium-chain and long-chain alkyl halides (1-bromobutane, 1-bromohexane, 1-bromononane or 1-bromododecane) under microwave activation [16,17]. The main products obtained in the synthesis were the corresponding *N*-alkyl imidazole derivatives, which are key intermediates in the synthesis of important anticonvulsant and bactericidal pharmaceuticals. We have also reported successfully the microwave-assisted *N*-propargylation of imidazole using propargyl bromide [18]. As mentioned previously, carbon materials absorb efficiently microwave energy and convert it into heat. Under these reaction conditions, the reaction temperature during the synthesis increases considerably, the conversion and selectivity of the reaction remarkably improved.

In our group we have also explored the effect of microwaves in the activation of alkaline promoted carbons to perform the *N*-substitution of 2-pyrrolidinone with 1-heptanal (Scheme 1) [19]. The combination of the basicity of the AC catalyst and the microwave activation led to the selective construction of C-N bonds for the synthesis of *N*-1-heptenyl-2-pyrrolidinone derivatives. The product obtained, *N*-substituted-γ-lactam, is used in the synthesis of important neuroexcitatory pharmaceuticals. The substantial enhancing effect in the yield provoked by combination of both microwave irradiation and AC catalysts can generalize for the production of similar fine chemicals. In addition, although a large number of works deals with microwaves activation, only a relatively small number of papers reports the influence of the reaction conditions on the rate and yields of chemical reactions. However, it is important that those parameters are well tuned and controlled

to maximize the microwave effects. In particular, we have found that among all the experimental procedures induced by heterogeneous media employed for the synthesis of numerous chemical compounds, the combination of microwave irradiation with AC catalysts offers interesting prospects and excellent yields under very mild conditions.

3. Ultrasound-assisted organic reactions catalyzed by AC supported catalysts

The ultrasonic activation is possible to apply in the preparation of fine chemical intermediates, which serve as precursors in many industrial processes. ACs have been employed as selective catalysts in the sonochemical activation of this type of reactions [20] since their microporous structure, high degree of surface reactivity, extended surface area and separation make them suitable catalysts to carry out this type of reactions [21]. In addition, the presence of alkaline promoters on the surface of the ACs results in the generation of basic sites on their structures [22] promoting in particular base catalyzed reactions. The combination of activated carbon catalysts and ultrasounds has proved to be very useful in the synthesis of important fine chemical intermediates as the following.

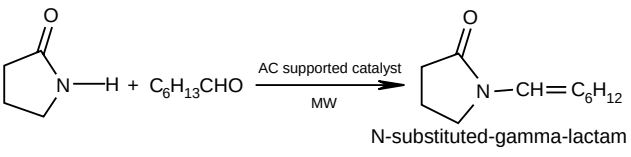
In our group we have synthesized α,β-unsaturated nitriles by sonochemical activation of carbonylic compounds with malononitrile using two basic carbons as catalysts (Na^+– and Cs^+–Norit) (Scheme 2). A substantial enhancing effect in yields and selectivities was observed when the basic AC catalysts were activated under ultrasonic waves. This work was the first, reported in literature, in using ACs as catalysts in combination with ultrasounds. As we commented previously, in the sonochemical phenomena, the ultrasonic irradiation has several additional enhancement effects when one of the phases is a solid and especially when this solid acts as catalyst. The microjects of liquid formed under cavitation, bombard the solid surface of the AC catalyst. This fact causes the exposition of unreacted surfaces of the carbon, increasing the interphase surface able to react. Thus, the ultrasound activation shows a positive effect in the reactivity of a chemical reaction, improving the conversion values if compared with those obtained under conventional thermal activation (batch reactor) [23].

We have also proved that nitrogen alkylation occurs easily under sonochemical conditions over alkaline-promoted carbon catalysts [24-26]. We reported the alkylation of imidazole with 1-bromobutane under ultrasound activation over alkaline ACs. The main products *N*-alkylimidazoles are important intermediates in the synthesis of antiviral pharmaceuticals. In the case of the bimetallic basic AC catalysts (NaK-Norit, NaCs-Norit and KCs-Norit), prepared by impregnation of a Norit AC with the correspondent binary combination of Na, K and Cs salts, an important enhancing effect was found; 73.3% yield in 60min at room temperature compared to around 30% under conventional thermal activation in an oil bath [27]. It could be observed that imidazole conversion increases in parallel with increasing the basicity of the catalyst.

On the other hand, chalcones are very common chemicals in natural products chemistry and its synthesis is typically carried out via Claisen–Schmidt condensation of aromatic aldehydes with acetophenone under conventional thermal activation. However, several problems are always present due to the long reaction times, the cost of expensive catalysts or difficult work-up. In this context, sonochemistry is presented as a good alternative as offers shorter reaction times and easier work-up procedures to obtain chalcones with higher yields. Our group carried out successfully the synthesis of chalcones with antibacterial activity over alkaline-doped carbons (Na-Norit and Cs-Norit) in absence of any solvent *via* Claisen-Schmidt condensation between benzaldehyde and acetophenone under ultrasound activation [28]. In this green procedure (organic solvent free), chalcones were selectively produced in very high yields (up to 90%). Under these experimental conditions, the formation of environmental hazardous residues is avoided. These solid catalysts can compete with the traditionally used NaOH.

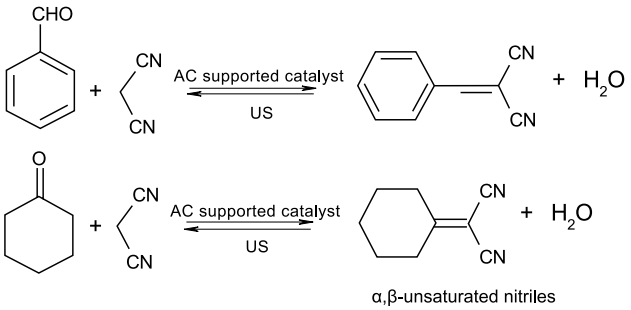
4. Conclusions

The potential of alternative sources of energy (microwave and ultrasound) as tools for process intensification appears to be very promising as it leads to intensification of many processing steps including mass transfer, heat transfer, chemical reaction and separation processes. The present work concentrates in the synthesis of fine chemical intermediates using microwave and ultrasound as method of activation of these chemical reactions. We summarize the degree of process intensification



Scheme 1. Microwave-assisted synthesis of N-substituted-gamma-lactams using alkaline activated carbon supported catalysts.

Esquema 1. Activación por microondas de la síntesis de gamma lactamas N-sustituidas utilizando catalizadores alcalinos de carbón activado soportados.



Scheme 2. Condensation of malononitrile with benzaldehyde (top) orcyclohexanone (bottom) to synthesize a,b-unsaturated nitriles under ultrasound activation over basic activated carbon supported catalysts.

Esquema 2. Condensación de malonitrilo con benzaldehído (arriba) o ciclohexanona (abajo) para sintetizar nitrilos a,b-insaturados bajo activación ultrasónica utilizando catalizadores de carbón activado soportados con propiedades básicas.

achieved in several chemical transformations under these reaction conditions when compared with the conventional approach. In addition, we studied the influence of using a solid catalyst under these activation conditions, and in particular, an activated carbon supported catalyst. Different external parameters related with microwave and sonochemistry have to be well tuned and controlled, to maximize the microwave and sonochemical effects on chemical reactions. In this way, a significant enhancement in the yields of the desired product can be achieved under mild reaction conditions.

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