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Porous carbon: A versatile material for catalysis

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ABSTRACT

Heterogeneous catalysis is an exciting field in constant development. New and improved catalysts that can both be effective and economical are always on demand. Activated carbons may well play an important role in this field, as they are a cheaper alternative while more environmentally benign. In this paper, a brief overview of the effort developed in the application of activated carbon as heterogeneous catalysts in various reactions is presented. Functionalised activated carbon has been used as catalyst for fine chemical reactions. Gas-phase reactions for NO, N_2O and CO_2 conversions were thoroughly studied using activated carbon as catalyst support. In situ characterization techniques proved to be valuable tools to understand carbon gasification mechanism.

1. Introduction

Heterogeneous catalysis is an exciting field in constant development and mutation. Catalysts are indispensable for numerous processes and may represent the pivotal optimization step towards sustainability, both economic and environmental. In particular, solid catalysts have been considered an important feature of the green chemistry approach for sustainable progress.

In view of the many disadvantages presented by the traditionally employed catalysts in several procedures, much attention has been devoted to the development of new and improved heterogeneous catalysts. Besides shortcomings as high reaction temperature, prolonged reaction time, low conversion, low regioselectivity and non-reutilization, homogeneous processes may have additional difficulties in separation and purification of the products.

Authors research work has been devoted to this subject and a considerable amount of studies have been developed around heterogeneous catalysis, with special attention for fine chemical synthesis in the scope of green chemistry. Zeolites [1–5], mesoporous silicates [6–9] and polymeric membranes [10,11] have been tested and optimized for several synthetic reactions of industrial relevance. Biodiesel production [12] esterification reactions [13] and free fatty acid esterification [14–16] using catalytic membranes for process intensification by integrating in a single step reaction and separation/purification, has also been object of study.

Among the solids studied, attention has been given to porous carbon, a versatile and very environmentally friendly material. Some of this material characteristics makes them particularly suitable for several applications due to its large specific surface area, high porosity, excellent electron conductivity and relative easy surface chemical tuning. One of the first application that comes to mind is adsorption [17,18], and in fact much attention have been devoted to this subject by the authors. Being water a valuable resource with increase need of care, residual water treatment is a relevant field of research, highlighted by the new emergent pollutants consequent of our ever changing life style. Thus, different carbon materials, particularly biomass waste derived carbons have been used in the removal of pharmaceutical and related compounds, such as paracetamol and ibuprofen [19], iopamadiol [20], caffeine [21] and diclofenac [22], as well as heavy metals [23–25]. Therefore, biomass wastes, particularly lignocellulosic wastes, have proved to be suitable, low-cost and abundant alternatives to the conventional raw materials for porous carbons production. Moreover, the use of bio-wastes as feedstock to produce carbons is a potential pathway to solve the waste management problems of several industries dealing with this type of wastes [26,27].

The high surface area and high chemical and physical stability of activated carbons also makes them useful, interesting and cheaper alternative materials to be used as catalysts or as catalyst support [28–30].

As catalyst supports one main area of application has been the hydroprocessing of petroleum feedstocks [31]. Also, much work has been done in the application of carbon materials in hydrogenation reactions [32], environmental catalysis [33] and more recently photocatalysis [34,35], electrocatalysis [36] and fuel cells

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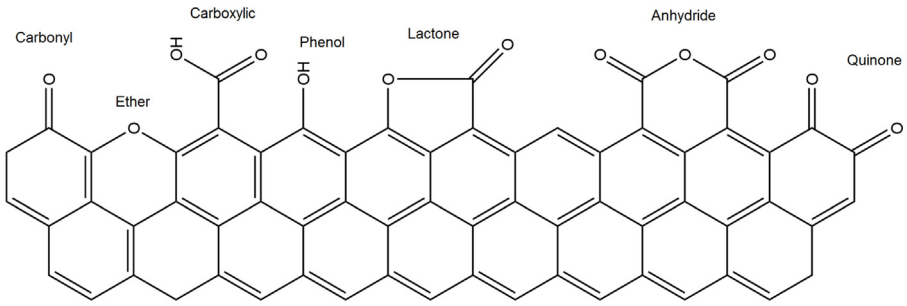

Fig. 1. Scheme of the surface oxygen groups in the carbon.

Adapted from [61].

[37]. Activated carbon has also been studied as catalyst support for the reduction of NO, N_2O and CO_2 [38–45], a subject to which the authors have dedicated much attention.

Activated carbon as catalysts relies in the presence of heteroatoms which form functional groups, that will be the active sites incorporated in the carbon structure. This metal-free heterogeneous catalysis using carbon materials has also been refer to as carbocatalaysis [29]. Several reactions such as oxidative dehydrogenation of hydrocarbons [46], dehydration and dehydrogenation of alcohols [47], NOx reduction [48,49], SOx oxidation [50,51], ozonation [52], catalytic wet air oxidation [53,54] used carbon as catalyst.

The goal of the present paper is to present an overview of different possible applications of activated carbon in the catalytic field, focused on the areas of expertise of the authors.

2. Application in fine chemical synthesis

2.1. Activated carbon as catalyst

Many fine chemical synthesis reactions are catalyzed by acids. Traditionally, such reactions are performed in the presence of strong inorganic acids, in homogeneous phase. As mentioned before, acids like sulfuric acid, nitric acid or hydrochloric acid have many disadvantages for the process, although having fast kinetics and high conversions, they often present low selectivity. Additionally, these are corrosive and aggressive compounds very demanding on the equipment, and with a post reaction treatment that can be tedious, complicated and potentially very harmful for the environment. Among the many heterogeneous catalysts that have been developed and employed as acid catalyst in fine chemical synthesis, activated carbon is a most friendly, and economic alternative [30].

During activated carbon preparation, two main processes can be used: physical or chemical activation, and each one can strongly affect the surface of the resulting material depending on the chemical agent and the activation conditions [55]. Physical activation is a two-step process, which means that the raw material is first carbonized in the absence of oxygen in a process named as pyrolysis (usually at temperatures between 400 and 850 °C) followed by activation of the resulting char from the carbonization step with oxidant gases such as steam or CO_2 (around 600–1000 °C) [26,56]. Chemical activation can be a one-step or two-step method; it involves the impregnation of the precursor (the biomass or the resulting char from the first step of carbonization) with the chemical agent (dehydrating agents and/or oxidants) followed by heating under inert atmosphere at temperatures between 400 and 800 °C [26,56]. Also, physical and chemical activation can be used simultaneously.

When producing biomass-derived activated carbons, the type of starting material or precursor also influences significantly the characteristics and properties of the surface of the resulting carbon [57].

Activated carbons are very versatile materials with interesting tuneable properties, where is possible the tailoring of the porous structure and of the surface chemistry. Materials with very different characteristics may be prepared by modification treatments, thus allowing fine-tuning of the physical-chemical properties to obtain the desired catalytic performance. An important feature of the activated carbon is the presence of functional groups on the surface of the material which are particularly relevant for these specific catalytic reactions. The nature, type and concentration of such groups will determine its application as acid catalysts since some of these groups can act as active sites [30].

Oxygen functional groups are most important in this context. The type and concentration of these groups can be modified by oxidative agents, either in gas-phase or in solution, and through thermal treatments, being tuned by careful selection of the preparation conditions [58].

It has been well established that it is possible to have several oxygenated groups in different amounts at the surface of the activated carbon (Fig. 1): carboxylic acids, carbonyl, quinone, ether, phenol, lactone [59–61].

There are several treatments that can be performed to obtain an oxidised carbon surface: The most common are treatment in liquid phase with acids, typically HNO_3, H_2SO_4 or a mixture of both; treatment with hydrogen peroxide H_2O_2, or treatment with gases, such as N_2 doped with O_2 or air, or even N_2O and ammonia (NH_3), where also other heteroatoms may be introduced.

The identification and quantification of surface functional groups and their relation to catalytic activity can be established through X-ray Photoelectron Spectroscopy (XPS) and Temperature-Programmed Desorption Mass Spectrometer (TPD/MS) studies.

Matos et al. [62] studied the methoxilation of α-pinene by using three HNO_3 oxidised carbon materials: a meso-microporous activated carbon prepared from olive stones (CBN), a xerogel carbon (CMN) and a commercial microporous carbon (NoritN), as acid catalysts in yielding α-terpinyl methyl ether as main product of the reaction. Even though some effect of the textural properties could be observed, the results indicated that the most important feature of these catalysts was the surface chemistry (Fig. 2). The olive stone based carbon was obtained by chemical activation with phosphoric acid and resulted in a biomass catalyst with better characteristics for the reaction studied, due to the introduction of phosphate groups during its synthesis. The catalytic activity increased in the order NoritN < CMN < CBN, showing that the textural properties also have some influence. All catalyst showed good selectivity towards the α-terpinyl methyl ether.

Another biomass based carbon was prepared using palm kernel shell as raw material, a low value residue of the palm oil industry. The solid acid catalyst was prepared by treatment with concentrated sulfuric acids after carbonization. The obtained solid acid