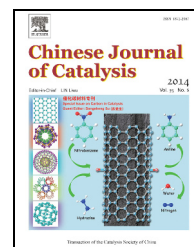


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Review (Special Issue on Carbon in Catalysis)

Proton catalysis with active carbons and partially pyrolyzed carbonaceous materials

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ABSTRACT

The development of environmentally friendly solid acid catalysts is a priority task. Highly oxidized activated carbon and their ion-substituted (saline) forms are effective proton transfer catalysts in esterification, hydrolysis, and dehydration, and thus are promising candidates as solid acid catalysts. Computations by the *ab initio* method indicated the cause for the enhanced acidity of the carboxylic groups attached to the surface of highly oxidized carbon. The synthesis of phosphorylated carbon was considered, and the proton transfer reactions catalyzed by them in recent studies were analyzed. The development of an amorphous carbon acid catalyst comprising polycyclic carbonaceous (graphene) sheets with $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic type OH-groups was carried out. These new catalysts were synthesized by partial pyrolysis and subsequent sulfonation of carbohydrates, polymers, and other organic compounds. Their high catalytic activities in proton transfer reactions including the processing of bio-based raw materials was demonstrated.

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1. Introduction

About a hundred years ago already, publications have appeared about the ability of activated carbon to accelerate electron transfer reactions, namely the oxidation of alcohols, olefins, sulfur dioxide in the gaseous phase, and others, as well as by oxalic and uric acids in aqueous solutions. Since then, interest in this phenomenon has increased, which is reflected in numerous articles with experimental and theoretical data and also in a number of fundamental reviews and specialized monographs [1–6].

However, these publications only partially covered the participation of activated carbon in acid-base catalytic reactions, in particular, the process of proton transfer, although there are reasons for comprehensive studies on activated carbon as a

recyclable solid acid material. It is common knowledge that the attack on carbon by strong oxidants leads to the grafting of carboxylic and phenolic groups onto the surface with plentiful mobile protons, which is a good reason to assign them to the category of highly porous solid acids. The oxidation of carbon is not the only way of introducing grafted acid groups onto their surface. Protonated surface functionalization can also be achieved by the phosphorylation of active carbon and other carbonaceous materials in the case of their heat treatment with phosphoric acid [7–10] or by the sulfonation with concentrated sulfuric acid (sulfonated carbon) [11–17].

In recent years, it has also been shown that the sulfonation of incompletely carbonized cellulose, starch, glucose and some polymers makes it possible to get hard carbon-based insoluble solid acids, which can potentially be used as a replacement for

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the homogenous sulphuric acid catalyst [11–17]. Meanwhile, mainly for historical reasons, oxidized, sulphonated, and phosphorylated carbon were studied mainly as cation exchangers with high selectivity towards multiply charged cations [18]. Only in recent years have they been studied for catalysis. The study of their catalytic activity in proton transfer reactions has been developed in the Ukraine since the 1960s by D. N. Strazhesko and I. A. Tarkovskaya and their colleagues, which was thereafter developed in the Institute for Sorption and Problems of Endoecology of the National Academy of Sciences of Ukraine with the participation of the authors of this article [18–22]. Somewhat later, these studies were also developed in papers [23–27] on the catalytic dehydration of alcohols.

From the viewpoint of modern trends concerning “green” approaches to acid-catalyzed chemical processes, the use of recyclable solid acid materials to replace the typically homogeneous acid catalyzed conditions has been recently promoted [28]. In fact, homogeneous catalysts (HCl, H₂SO₄) are difficult to separate from the reaction system, ecologically unfriendly, and cause equipment corrosion. On this view, many articles [11–17] have found that carbonaceous materials specifically modified by protonic groups are the best candidates among solid acids for various acid catalyzed reactions.

Unfortunately, the vast majority of publications on oxidized carbon that are dedicated to their catalytic properties are sketchy. Furthermore, they did not optimize the acidity of the surface functional groups of the oxidized carbon and evaluate the efficiency of these solid acids in various proton-transfer reactions. Therefore, this review will provide data covering the influence of various factors on proton mobility in the surface functional groups of activated carbon, as well as on their catalytic activity in the liquid phase and gas phase reactions of etherification, hydrolysis transesterification (biodiesel), dehydration, etc. In addition, we plan to analyze the studies dedicated to solid acid catalysts based on sulphonated and phosphonated carbon, and also different types of partly pyrolyzed carbonaceous materials.

2. Acidity of the surface functional groups of oxidized carbon

Incredible as it may seem, many publications dedicated to oxidized carbon in general have analyzed only the ratio of the total number of carboxylic and phenolic groups that determined the cation exchange (sorption) function of these carbon materials. Boehm titration with varying strength bases that are used for these analytical evaluations allows the reliable estimation of, for example, the ratio between these groups depending on the origin and oxidation conditions of the activated carbon. However, there were no thorough studies that evaluated the effect of carbon oxidation on the acidity of the functional groups. Meanwhile, it was assumed that the accumulation of electronegative –COOH groups on the surface layer of the carbon will increase the mobility of their protons. Nevertheless, the transmission of electrons in the condensed π -systems of carbonaceous material should be highly effective. A spectacular example of this effect can be seen in the data on benzoic and

o-phthalic acids containing, respectively, one and two carboxy groups associated with phenyl ring. Due to the electronic effect, the acidity of –COOH groups of *o*-phthalic acid is one order of magnitude higher than benzoic acid (pK_a 3.2 and 4.2 respectively). In oxidized carbon with a vast π -conjugation system, these effects should be present to a larger extent.

By taking into account all these conceptual aspects, in [29] we for the first time conducted a comprehensive study of the oxidation degree effect under atmospheric oxygen and nitric acid conditions on the structure and acidity of the surface functional groups of the carbonaceous materials. However, before proceeding to the presentation of these results, we shall first discuss the calculation methods of the ionization constants (pK_a values) of oxidized carbon and other carbonaceous materials with surface protonic groups.

2.1. pK_a of carbon oxidized to varying degrees

The same approaches that are traditionally used for the ionization constant determination of polymeric acids, namely, ion exchange resins, are also applicable for the quantitative evaluation of the acidity of the surface functional groups of carbon. Usually even for monofunctional cation exchangers, the ionization constant K_d varies continuously with the neutralization degree, which can be experimentally estimated from the shapes of the potentiometric titration curve of the polymeric acid by an alkali. According to ref. [30], the ionization constant of the polymeric acid (cation exchanger) is calculated from the equation

$$K_d = \frac{[H^+] \cdot [A^-]}{[HA]} \cdot f(z)$$

where $[A^-]$ and $[HA]$ are the content of ionized and non-ionized protonic groups in the ion exchanger, and z is the ratio of their content in the matrix. After a transformation to pK_a ($pK_a = -\log K_d$), we use the Henderson-Hasselbach equation:

$$pK_a = pH - n \log \frac{1-\alpha}{\alpha}$$

$$pK_a = pH$$

where α is the neutralization degree of the ion exchanger functional groups.

This equation gives the most reasonable results for neutralization degree values with $\alpha = 0.5$. In this case, the equilibrium pH of the solution (for potentiometric titration) is approximately equal to the pK_a value of the corresponding functional groups. In the case of multifunctional cation exchangers, to which oxidized carbon are also related, the pK_a values for some functional groups types can be obtained from the pH values because of the corresponding bend of the titration curves (extrema) for the same values of $\alpha = 0.5$. Using this approach, the author of [18] concluded that the values of the ionization constants K_d of oxidized carbon lay in the range from 10^{-2} to 10^{-10} (i.e., $pK_a = 2-10$). In the later studies for this purpose, the method used differential potentiometry [31].

In ref. [29], we investigated how the type of functional groups and their pK_a values depend on the degree of oxidation

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