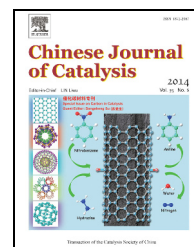


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Essay (Special Issue on Carbon in Catalysis)

Classification of carbon materials for developing structure-properties relationships based on the aggregate state of the precursors

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Modern carbon science lacks an efficient structure-related classification of materials. We present an approach based on dividing carbon materials by the aggregate state of the precursor. The common features in the structure of carbon particles that allow putting them into a group are discussed, with particular attention to the potential energy stored in the carbon structure from different rates of relaxation during the synthesis and prearrangement of structural motifs due to the effect of the precursor structure.

Keywords: Carbon material; Classification; Carbonization

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1. Introduction

The chemistry of carbon materials (CMs) seems terribly tangled for those who try to enter this domain for the first time. Moreover, this feeling can remain after several years of work. This is not surprising since there are almost one thousand types of pure carbon materials known at this moment, and there are even more types of modified and doped ones. Actually this field of science suffers from the lack of classification more than any other areas of materials chemistry.

Although works on the classification of carbon materials have been reported, however, our point of view is that they still do not cover all varieties of CMs and do not give the expected scientific insight into structure-properties relationships. Therefore, in this essay we present a short review on the current state-of-art in the classification of CMs and our suggestions for its improvement. We hope to start a wide discussion in the carbon community.

2. History

The first attempts to describe the structure of carbon were by Warren in 1936 [1,2] based on pioneering X-ray diffraction (XRD) experiments on non-crystalline carbon. The concept of "turbostratic" (meaning in-plane rotation of graphene sheets in graphite) carbon was introduced to explain the widening of peaks in XRD patterns. The next step was made by Rosalind Franklin in 1951 [3] when she explained the difference between graphitizing and non-graphitizing carbons (transformed or not into graphite on heating below 2000 K with no additional treatment, respectively) by the pre-orientation of graphite micro-crystallites in the bulk, which allowed or did not allow further rearrangement.

The works of Rosalind Franklin and co-workers formed the first classification of carbon materials by their relation to graphite as the most thermodynamically stable form. All materials were divided into graphitic (consisting solely of graphite particles) and non-graphitic. The latter materials were subdivided into graphitizing and non-graphitizing, as described above. This classification was purely phenomenological, but still valid. In the 1990s, it was modified to account for the curved carbon planes discovery, which formed a wide range of materials like fullerenes, carbon nanotubes (CNTs) and their derivatives. It was recognized that the crystallites are not necessarily planar [4,5], but the main idea of CMs as structurally reducible to graphene or graphene-derived building blocks remained.

However, with the passage of time, many differences in the properties of CMs have appeared that cannot be attributed to the orientation of the graphitic (even when formed by curved sheets) crystallites in the particle. It became obvious that some general rules besides the tendency to graphitize on heating should be proposed.

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3. Common problems

There are a series of problems that anyone making a classification of CMs will encounter. We list the most important of these.

1. One of the most popular trends in treating CMs is the reduction of their structure to graphene forms and their properties to the properties of edge groups or the graphene basal plane [6,7]. The cross-links between crystallites are usually neglected in their impact on the chemical and physical properties and they are treated simply as mechanical junctions. This shortcoming has a mainly historical origin since CMs were considered as "more or less graphite" for more than a century. Also, the simplified picture of "carbon as graphite" is much easier to comprehend, so many people are naturally inclined to take it as self-evident.

2. Sometimes people tend to reduce the chemistry of CMs to organic chemistry, which neglects their important properties due to their solid state chemistry and porosity. This happens quite often in the interpretation of the acid-base properties of CMs or the surface functionalization of CMs.

3. One should emphasize that "pure carbon" materials in the majority of cases contain not only carbon atoms but also some hydrogen atoms, and although their mass content is not very high, their atomic ratio may reach 30 atom%. The role of hydrogen in carbon materials is often wrongly underestimated, as it both affects the physical properties (especially magnetism-related ones) of the material and can be used for characterization (e.g. by ^1H NMR or echo EPR spectroscopy).

4. The terms used in CMs chemistry are ambiguous. This group of problems can be subdivided into two groups: those related to terms of amorphism and those related to the notation of the types and features of the CMs. For the former, the situation in the classification of amorphous matter and related phenomena is not acceptable. The approach to amorphous solids is still dominated by the concept of an overcooled liquid, which is valid for glasses but not for other types of amorphous materials (including CMs), and there is muddled use of terms like "amorphous", "disordered", "nano-crystalline", etc. The terms used in carbon science are also often not clearly defined (e.g. the term "carbonization" is also used as "pre-carbonization" depending on the area of application). The denotations of

CMs exist as an overlay of traditional names and trademarks, which are different for different manufacturers and research groups. One can look up a typical classification of CMs elsewhere [8] and observe that the origin of the CMs, their structure and some key properties are mixed together in the presenting of the classes of CMs. A typical approach in this case is to define the three "classic" allotropes of carbon (diamond, graphite, and carbyne), derive some of the CMs as defective diamond or defective graphite and put the rest of the materials into the general group of "nanocarbons" and their assemblies.

Several phenomenological characteristics of CMs are used as the basis of a universal classification, namely, porosity, acidity in water, linear edge density, etc. [9]. A number of classifications are developed for some particular types of CMs, e.g. carbon fibers, graphites (implying all graphite-like materials), coals, etc., but most of these cannot be extended beyond their specific area. These classification schemes are very useful in technological applications, but in the majority of cases, they are not suitable for research. A very important step in organizing the terminology in carbon science was performed recently by the editorial board of Carbon journal [10]. However, their systematic organization concerns graphene-related terms only, which is not enough for clarity in terms usage.

So, unfortunately, there is only one structure-related classification of CMs – that derived from Franklin's idea of an ordering as non-graphitizable carbon. Meanwhile, other classifications involve only some particular types of CMs or are phenomenological approached.

4. Classification

Bearing in mind all of the above points, we would like to stress another approach in the classification of CMs, namely, by the origin of the precursor. One can note that the properties of a majority of CMs are history-dependent, with the exception of some rare cases, e.g., extremely graphitized (HOPG) samples (some characteristic examples are given in Fig. 1). Even materials with a seemingly ordered structure like CNTs are known to differ from batch to batch significantly. Differences in properties are often attributed to the presence of admixtures. However, unlike the chemistry of molecular compounds, in materials chemistry, this excuse has no sense since any component in

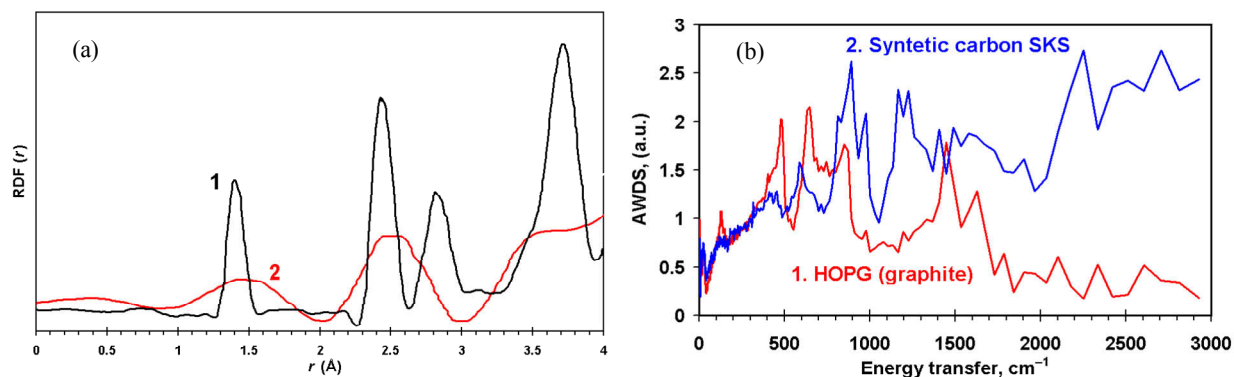


Fig. 1. Examples of structural differences between graphite and non-graphitic CMs. (a) Radial distribution function of graphite (1) [11] and carbon black (2) [12]; (b) Inelastic neutron scattering spectra of HOPG and SKS polymer-derived carbon [13].

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