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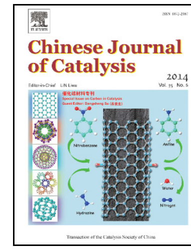

Perspective (Special Issue on Carbon in Catalysis)

Carbon-based catalysts: Opening new scenario to develop next-generation nano-engineered catalytic materials

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This essay analyses some of the recent development in nanocarbons (carbon materials having a defined and controlled nano-scale dimension and functional properties which strongly depend on their nano-scale features and architecture), with reference to their use as advanced catalytic materials. It is remarked how their features open new possibilities for catalysis and that they represent a new class of catalytic materials. Although carbon is used from long time in catalysis as support and electrocatalytic applications, nanocarbons offer unconventional ways for their utilization and to address some of the new challenges deriving from moving to a more sustainable future. This essay comments how nanocarbons are a key element to develop next-generation catalytic materials, but remarking that this goal requires overcoming some of the actual limits in current research. Some aspects are discussed to give a glimpse on new directions and needs for R&D to progress in this direction.

Keywords: Nano-carbon; Catalysis on carbon; Nanostructured carbon-based material; Carbon hierarchy; Nano-engineering of the carbon materials

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1. Introduction

Carbon is an old and new catalytic material [1–5]. Active carbons (AC) are used commercially in many catalytic formulations, particularly for hydrogenation catalysts, for the excellent properties of dispersion of metal particles (particularly based on noble metals) and absence (or limited) presence of sites, which may catalyse side reactions [6–8]. The different adsorption properties of carbon materials with respect to other type of supports, metal oxides for example, are another relevant element determining they large industrial use, particularly in selective hydrogenation reactions. There are many attracting properties in ACs:

- The high surface area, together with the possibility of tuning the porosity;
- The robustness and chemical inertness, apart in high-temperature reactions in the presence of oxygen;
- The flexible tuning of the surface properties, by changing for example the graphitic character (which is related to both electronic and heat conductivity) or the presence of surface groups induced by post- or pre-treatment, which allow to change various properties, between which the degree of hydro-philicity or -phobicity and the interaction with the supported catalytic nanoparticle;
- The low cost of production, between the cheaper of catalytic support materials.

However, carbon can be considered also as a new catalytic material. A large range of new nanocarbon materials have been recently developed recently [1–5,9–18], from the more known graphene, carbon nanotubes (CNTs) and fullerene (and their derivatives) to a large range of other type of sometime fancy nanostructures: nano-fibers, -coils, -diamond, -horns, -onion, etc. Here the term nanocarbon [1] indicates carbon materials having from zero- to tri-dimensional character, but characterized from an ordered structure at nano-scale dimension and from functional properties significantly depending on nano-scale characteristics [19,20]. These materials are specifically synthetized, while AC is mainly deriving from natural sources, although a series of treatments are necessary to obtain the necessary characteristics.

Nanocarbon (or alternatively nano-structured carbon) definition includes various types of carbon-based nanomaterials, from zero-dimensional such as carbon dots (we may classify here also fullerenes) to tri-dimensional ordered mesoporous carbon materials. We include in these definitions also carbon nano-composites with metal ions, metal-oxide, metals and quantum dots used in various applications as advanced elec-

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trodes for energy conversion and storage, as well as other applications such as catalysis. These carbon/inorganic nano-hybrids are at the frontier of research for the development of advanced devices for sustainable energy, including artificial leaves [3,18,21–29]. Of growing interest, also the area of nanocarbon-nanocarbon hybrids, for example functionalized fullerenes linked to CNTs, in order to develop multifunctional superstructures, of particular relevance for example in the field of devices for solar light conversion or sensors [30–33].

2. Outlook and economic perspectives

Nanocarbons can be considered between the first nanotech materials with significant commercial use and mass-production, although the closing of production of some large manufacturers evidences how this field needs to establish on more solid bases. Bayer stopped to produce CNTs-commercial name Baytubes. Several other companies are facing growing difficulties and they are reshaping the market addressed; Nanocyl, for example, is moving to the specialized area of CNT-based coatings for naval applications. The research "excitement" about some of the classes of nanocarbons (graphene, in particular) has to be view from a longer term and correct industrial perspective. Even if discovered more than twenty years ago, CNTs still find problems in large-scale applications, although their cost of production decreased of two–three orders of magnitude. Thus, cost was not the only aspect determining their industrial use, as often indicated. The global CNTs industry is one of the largest in the area of nanotech materials, with about 700 million US$ in 2010 (over 90% of which related to multi-walled carbon nanotubes-MWCNTs; production capacity was about 2500 metric tons [34]), but can be considered still small with respect to market for chemicals and materials. The outlooks are of expansion to more specialized uses, from electronic industry to that of materials for energy storage devices and photovoltaic cells [34], rather than to traditional area of plastics and composites, which still cover about 70% of the market.

This has clearly consequences on the use of CNTs in catalysis, because this market (in term of cost value of the product) is closer to commodities than to that of specialized products. We suggest that the scenario of evolution of the market in the future will seen the use of nanocarbon materials more oriented to high-tech applications rather than to large-scale applications (plastics and composite), the opposite of what supposed few years ago. In fact, the cost of processing these nanocarbons (for CNTs it is not only the cost of production, but of further treatment to realize an effective dispersion within the polymeric mass) still is not favourable (in terms of cost-effectiveness) with respect to alternatives. R&D will be thus more oriented to the preparation of specific nanocarbon materials for dedicated high-value productions rather than for large-scale productions. Thus, the decreasing trend observed in prices for CNTs will be probably inverted, driving to higher costs all the field of nanocarbon materials.

This will impact the use of nanocarbons in the preparation of novel catalysts. We have to remark that still no commercial catalysts are based on nanocarbons, if not for minor niche applications. Although many papers claim the superior performances of nanocarbon-based catalysts, in general it was not proven the effective superior performances with respect to state-of-the-art (commercial) catalysts. The comparison is often not made with the appropriate benchmark catalysts and/or right experimental conditions (for example, high conversion). Even when comparison reveals better properties (which necessarily are not of reactivity only, they may allow reduced mass transfer limitation or better heat transfer, for example), the cost-effectiveness has to be considered. Although it is often not easy to estimate the possible cost and decrease during commercialization stage, a rule of thumb is that only a significant benefit (in terms of potential market) will push the industrialization of new material (nanocarbon), even more critical in this case due to the concerns regarding health effects of nanomaterials and the absence of clear legislation regarding their use.

We believe that the use of nanocarbons for preparing advanced catalytic materials will grown in the future and become a key element of the panorama for advanced catalysts, but there are some necessary conditions to enable this possibility:

- Research in the use of nanocarbons materials has to move to applications where there is the need of significant improvement in the performances for relatively large scale catalytic processes, which justify the development of new catalysts and the investment necessary for its commercial introduction; often still research is more focused on the synthesis of nanocarbon rather than their use, and reactivity is often a side aspect rather than the core of investigation.
- It is necessary to use the peculiar properties of these catalytic materials to address novel pathways of reactions, which (i) reduce the number of steps in catalytic synthesis, the formation of byproducts and the environmental impact, (ii) enhance the selectivity and reduce the costs of downstream processing (separation, purification, environmental cleaning), (iii) reduce energy consumption and enable the use of alternative (more sustainable) raw materials. Although researchers often claim these aspects, they are not often proven and limited effort in literature can be seen to discover game-changer catalytic applications of nanocarbon materials.
- The number of novel syntheses and type of nanocarbon materials has exponentially grown and more slowly is increasing also the understanding of their characteristics, including reactivity. It is necessary to turn approach, and develop a theory of catalysis by nanocarbon materials allowing to define which type of properties are specifically requested to improve the behaviour in a specific catalytic reaction. Then synthetize the nanocarbon having these characteristics.
- It is necessary to put more attention on the reproducibility of the performances, especially at nanoscale level, in moving to large-scale applications. Still many factors are uncontrolled.

These aspects will be further commented later.