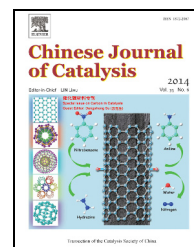


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## Minireview (Special Issue on Carbon in Catalysis)

## Catalysis: An old but new challenge for graphene-based materials

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## ABSTRACT

An assessment is offered regarding the progress made, and the remaining challenges, in the field of carbocatalysis. The fundamental principles that govern the preparation and performance of  $sp^2$ -hybridized carbon materials in heterogeneous catalysis have been known for decades, and the level of understanding of key issues – especially the importance of textural and ion-exchange properties (i.e., surface area, pore size distribution, and proton transfer) – remains quite satisfactory. The opportunities for novel catalytic materials – especially graphene nanosheets and carbon nanotubes – are tremendous, especially when it comes to taking advantage of their structural order, such that electron transfer can be both better understood and controlled to enhance catalytic activity and selectivity.

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## 1. Introduction

There exists much renewed interest in the catalytic applications of  $sp^2$ -hybridized (i.e., graphene-based) carbon materials. This is evidenced not only by the exponential growth of relevant publications – as of this writing, ISI's *Web of Science* lists 13,666 with titles containing 'carbon\*' and 'catalys\*' and 426 with titles containing 'graphene\*' and 'catalys\*' -- but also by the continued popularity of the biennial CarboCat conferences (most recently in Bressanone-Brixen, Italy, the next one in 2014 in Trondheim, Norway) and by the half-century-long tradition of catalysis-oriented symposia at annual international conferences on carbon (most recently, in 2013, in Rio de Janeiro, Brazil, the next one in 2014 in Jeju, Korea). Comprehensive [1,2] and updated reviews [3–10] on this subject, which cover both the science and the technology, are readily available, including a dedicated monograph [11]. So our purpose in the present contribution is to highlight and illustrate two fundamental issues related to both relevant processes and products: (1) In the development of new or improved processes, does

posterity take advantage of what is well known about existing processes? (2) In the development of novel products, do more recent studies recognize the relevance and comparative (dis)advantages of the more traditional products?

An example, randomly selected from a recent issue of the *Carbon* journal, will suffice to set the stage for such an approach. "Highly efficient supports" [12] for platinum fuel-cell catalysts (at loadings as high as 20 wt%) were recently prepared from graphene oxide (GO, obtained by exfoliation of natural graphite flakes) upon its treatment with ammonium sulfate and subsequent thermal treatment at 235 °C in argon. The authors did not quantify any of their surface properties; instead, they showed photographic evidence of their changes. Ultrasonication for 12 h produced a stable dispersion of the hydrophilic GO particles in water, as expected, which was lost due to precipitation upon thermal treatment (rGO) and recovered when thermal treatment was preceded by sulfonation (S-rGO); in the latter sample, the authors could not distinguish how much of the 1.4 mmol/g of titrated NaOH corresponded to sulfonate vs oxygen functionalities. The FTIR spectra did sug-

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gest, somewhat surprisingly (given the relatively low reduction temperature used), that there was “a simultaneous reduction of GO in the process of sulfonation”, even though the authors did not identify the most prominent  $1626\text{ cm}^{-1}$  band (due perhaps to “polarized C=C bond vibration near chemisorbed oxygen” [13]?). What is most puzzling, however, is the finding that “Pt [nanoparticles] are well dispersed on S-rGO ... with diameters in the 2.5 nm range” and also that “well dispersed Pt NPs are found on GO surfaces because of the presence of abundant functional groups”. The discussion offered by the authors is superficial on several scores, especially because they do not compare these results to the very abundant literature on carbon-supported Pt catalysts [1]. First, it is well known that the presence of acidic surface functionalities typically does *not* result in high catalyst dispersion when chloroplatinic acid is used, because of repulsion of  $\text{PtCl}_6^{2-}$  anions by the (typically) negatively charged carbon surface. (The authors did not report either the point of zero charge of their supports or the pH of their ethylene-glycol-containing suspension but, for example and as expected, Watkins et al. [14] reported that commercially available “sulfonate-functionalized carbon nanoparticles ... possess negatively charged sulfonate functional groups”.) Furthermore, even though sulfonated carbons have been the subject of much recent research [13,15–17], their surface chemical properties [18,19] have yet to be fully characterized and the presumed virtue of “sulfonic groups that can immobilize the Pt NPs and avoid their aggregation on S-rGO” remains to be confirmed and compared, say, to a similar role of CO-yielding oxygen functional groups [1,20]. Finally, the authors reported that the electrochemical surface area order was Pt/S-rGO ( $82.6\text{ m}^2/\text{g}$ ) > Pt/GO ( $61.8$ ) > Pt/rGO ( $55.6$ ) > Pt/C (Johnson-Matthey commercial catalyst,  $53.1$ ), which agreed with the electrocatalytic activity order (at 20 wt% Pt), Pt/S-rGO ( $12.6\text{ A/g}$ ) > Pt/GO ( $7.5$ ) > Pt/rGO ( $5.8$ ) > Pt/C ( $4.9$ ); it is puzzling, however, that they attribute it to “the optimized dispersion and size distribution of Pt NPs and the enhanced [triple phase boundary] by means of the function of  $-\text{SO}_3\text{H}$  groups grafted in rGO” (see section on proton transfer below).

It is somewhat disappointing that too many reports such as the one analyzed above, and even recent reviews dealing with carbon catalysis -- and there have been quite a few, mostly devoted to the virtues of ‘nanocarbons’ – have not been more comprehensive. Because the properties that are well known to be responsible for the “unparalleled flexibility in tailoring carbon’s properties to specific needs...” [1] – a phrase often quoted [5,13,21] but too often superficially invoked – have been clearly summarized more than a decade ago [1]: wide range of tailorable surface area and pore size distribution, surface charge ranging from quite positive (at relatively low suspension pH) to very much negative (at high pH), and inertness/reducibility/conductivity that can be adjusted by judicious selection or design of carbon crystallinity and surface functionality. Certainly the importance of physical surface (or textural) properties, as well as of those chemical surface properties that affect proton transfer, has been understood for several decades [1,6,10,11,18,22]. Whether this has resulted in successful recipes for the development of nanocarbon-based catalysts, espe-

cially taking into account the undoubtedly important but still insufficiently understood electron transfer, is discussed below. Given the existence of an almost overwhelming body of literature, the approach adopted here consists in analyzing the findings of illustrative publications mentioned in some of the recent reviews of carbon (i.e., graphene-based) materials in catalysis.

## 2. Importance of textural properties

In a review of ‘carbocatalysis’, among the virtues of graphene-based materials as catalysts in their own right, Dreyer et al. [7] remind the reader that “[h]igh surface area carbons are particularly useful ... because of their high ratio of catalytically active surface area to weight”. It is interesting that they mention carbon molecular sieves “with exceptionally high surface areas, reaching over  $3000\text{ m}^2\text{ g}^{-1}$  in some instances”, but not the much more ubiquitous activated carbons, whose tailoring of textural properties is a well documented science. While they clearly misrepresent the virtues of graphite (“[b]eyond its high surface area and unique chemical properties”), they leave the reader unnecessarily confused about the relative roles of surface ‘physics’ vs ‘chemistry’ in the utility of carbons in synthetic chemistry. The relevant issues have been well established for decades: the textural properties (surface area and pore size distribution) are more important when carbons are used as catalyst supports, especially at high catalyst loadings and for large adsorbing/reacting molecules. When carbons are used as catalysts, as evidenced by the effectiveness of materials with both very low ( $< 1\text{ m}^2/\text{g}$ ) and very high surface area ( $> 1000\text{ m}^2/\text{g}$ ), the proton- and/or electron-transfer properties are more important (see next sections).

The potentially genuine importance of textural properties has been invoked, for example, by suggesting [23] that carbon nanotubes (CNT) “show much higher catalyst loading efficiency” than carbon blacks (CB). These authors surmised, however, that “undesired bundling and incomplete functionalization normally only afford limited accessible area and defects” and thus went on to utilize graphene nanoribbons (GNR) which, presumably, “can display much larger surface area” than multiwall CNTs. Their reported order of electrocatalytic activity was indeed Pt/GNR ( $5.8\text{ A/m}^2$ ) > Pt/MWCNT ( $3.3$ ) > Pt/CB ( $2.4$ ), but they did not discuss the often very complex relationship between the catalytically active surface area and the support surface area, nor did they report measurements of total or accessible areas of their supports. In a similar and ambitiously titled study, Antolini [9] invokes similar arguments, acknowledges that in practice these surface area advantages may be nonexistent (“[s]urface area measurement of the reduced [graphene oxide] sheets via nitrogen gas a[d]sorption yielded a BET value of  $466\text{ m}^2/\text{g}$ ”) but insists that the “very high surface area of [graphene nanosheets] allows to load high amounts of catalysts maintaining a low metal particle size”. Clearly, claims of such advantages of graphenes, and to some extent of nanotubes as well, will remain largely hypothetical in the surprisingly frequent absence of even a rudimentary characterization of their textural properties.

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