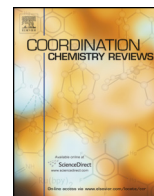




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Review

Coordination chemistry on carbon surfaces

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ABSTRACT

Immobilization of transition metal complexes with catalytic, electronic or luminescent properties onto solid supports is a theme of intense research. The relatively good knowledge of conventional oxide support (silica, alumina, zeolites) surface chemistry has already allowed the design, at the molecular level, of single site species and supported nanoparticles. However, carbon materials offer advantages over the oxide supports such as thermal and chemical stability, mechanical resistance, high surface area, optimum porosity and particularly a rich (but complex) surface chemistry. In the present exhaustive and comprehensive review article, we intend to give for the first time a complete overview of surface coordination chemistry and supramolecular coordination chemistry on carbon surfaces, including fullerenes, which have been developed mainly during the past few years (2007–2014).

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1. Introduction

Coordination and surface chemistry hardly influenced each other during their initial development, starting at the end of the 19th and in the early 20th century, respectively. Nevertheless,

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when decades later *modern surface science* investigations allowed for the detailed characterization of chemical bonding and reactions at metals, analogies between these disciplines became apparent, whence the term *surface coordination chemistry* came into practice [1]. Later on, the interfacial tethering of catalytically active metal complexes led to the conception of *surface organometallic chemistry*, bridging heterogeneous and homogeneous catalysis with the objective to tailor single-site catalysts and achieve novel reaction pathways [2]. More recently, the study at the atomic level of the interaction of metallic nanoparticles (NPs) with surfaces has merged, and is currently a critical issue for many applications of the nanotechnologies, including catalysis.

Immobilization of transition metal complexes with catalytic (or other) properties onto solid supports is a theme of intense research. The main objective of immobilization of homogeneous catalysts is to generate heterogeneous catalysts with improved catalytic properties when compared with homogeneous analogs. The activity and chemo- or enantioselectivity of the immobilized systems can be enhanced relatively to their free analogs due to two major key effects: the confinement concept and site isolation. Most reports on complex immobilization describe the use of organic polymers and porous inorganic materials, such as zeolites, mesoporous silicas and clays as metal complex supports. The polymers allow the use of an extended range of functional groups *via* straight organic synthesis for linking metal complexes [3]. Immobilization of catalysts on inorganic matrices has several important potential advantages over other approaches such as the use of organic polymer supports. The chemical stability of the inorganic supports is important, particularly with regard to oxidizing conditions. Their mechanical stability is often excellent, since the issue of swelling depending on solvent conditions can largely be avoided. Finally, inorganic supports have superior thermal stability. The relatively good knowledge of conventional oxide support (silica, alumina, zeolites) surface chemistry has already allowed the design, at the molecular level, of single site catalysts and supported NPs. For carbon materials however, a complex surface chemistry often imposes the use of empiric approaches for catalyst preparation. The carbon surface contains hetero-atoms (O, N, and H) in the form of surface functional groups (SFGs) by analogy to those appearing in organic compounds. The presence of these groups can affect the preparation of carbon-supported catalysts, as they induce an acid-base and/or hydrophilic character to the carbon surface. However, carbon materials offer advantages over the oxide supports such as thermal and chemical stability, mechanical resistance, high surface area, optimum porosity and particularly, several types of oxygen superficial groups that may be selectively maximized by thermal and chemical processes, which can be used as building blocks for the covalent attachment of transition metal complexes.

Some specific review articles and book chapters dealing with the immobilization of transition metal complexes on carbon surfaces have already been published, highlighting the interest on that subject, which covers other field than catalysis, such as sensors, and photoluminescent, photovoltaic, spintronic and nanoelectronic devices [4–9]. In the present exhaustive and comprehensive review article, we intend to give, for the first time, a complete overview of surface coordination chemistry and supramolecular surface coordination chemistry on carbon surfaces, including fullerenes, which have been developed mainly during the past few years (2007–2014). Surface coordination chemistry usually entails strong interactions with the surface, such as covalent bond formation, and takes place on an angstrom scale. These strong interactions will affect the properties of the coordination compounds or metallic cluster. Supramolecular coordination chemistry involves weaker interactions with the surface, such as hydrogen bonding, dispersion interactions, electron-donor/electron-acceptor interactions, and so on, and usually takes place on a nanometer scale.

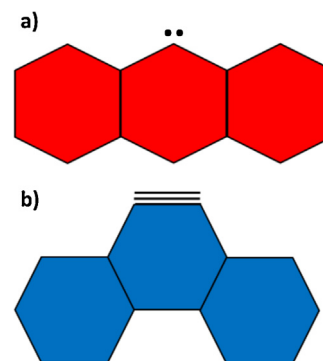


Fig. 1. Schematic of (a) zigzag and (b) armchair edge configurations.

These weak interactions will not significantly affect the properties of the coordination compounds or metallic cluster if no confinement effect arising from endohedral functionalization is involved. The endohedral functionalization of nanostructured carbon materials such as fullerenes or carbon nanotubes, which has been recently reviewed, is not within the scope of this review.

2. The surface chemistry of carbon materials

As for any materials, adsorption on carbon materials is related to their surface physical and chemical properties. Surface area and porosity are important physical properties that influence the quality, utility, and handling of carbon materials, which often must be carefully engineered to perform specific functions. Differences in the surface area and porosity of carbon materials, which otherwise may have the same physical dimensions; can greatly influence their adsorption performances. Therefore, it is critically important that these characteristics be accurately determined and controlled [10]. The surface chemistry of sp^2 carbon materials is governed by basal and edge carbon atoms [11,12], as well as by the presence of defects (*i.e.*, structural carbon vacancies, non-aromatic rings) [13]. These imperfections and defects along the edges of graphene layers are the most active sites owing to high densities of unpaired electrons. Indeed, the zigzag sites are carbene-like, and the armchair sites are carbyne-like (Fig. 1) [13]. Although, from the chemistry perspective it is not entirely correct to describe dangling bonds at zigzag edge as carbene, and the armchair edge as carbyne, this oversimplified description is generally accepted in the carbon community [11].

Heteroatoms, such as oxygen, hydrogen, nitrogen, and sulfur can be chemisorbed, leading to stable surface compounds, and resulting in a complex surface chemistry (see Section 2.2.1), if compared to classical oxides (Al_2O_3 , SiO_2 , TiO_2). Among the heteroatoms that can be voluntarily introduced, nitrogen has been particularly studied since it provides basicity to the surface [14–17]. If most of the adsorption sites for chemisorption on sp^2 and $sp^{2+\delta}$ carbon materials are on the basal planes (inner or outer surface in the case of carbon nanotubes, CNTs), the much higher activity of the heterogeneous groups can result in significant effects on the overall adsorption capacity. The exact mechanism by which the heterogeneous surface affects the adsorption is of great current interest. In that frame, computational approaches at the molecular scale can provide microscopic insight into adsorption behavior, complement and secure correct interpretation of experimental results, and are imperative to new material design.

2.1. Adsorption sites

2.1.1. Adsorption sites on sp^2 carbon materials

When considering adsorption on sp^2 carbon materials, the reactions may basically occur on two kinds of surfaces: prismatic

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