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Understanding the surface chemistry of carbon nanotubes: Toward a rational design of Ru nanocatalysts

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ABSTRACT

A comprehensive experimental and theoretical study of the surface chemistry of ruthenium nanoparticles supported on/in multi-walled carbon nanotubes (CNTs) is reported that could pave the way to the rational design of metal–carbon nanocomposites. It is shown that the oxidation of CNTs by nitric acid that creates various oxygen surface functional groups (SFGs) on the CNT external surface is a crucial step for metal grafting. In particular, it is demonstrated that carboxylic acid, carboxylic anhydride, and lactone groups act as anchoring centers for the Ru precursor, presumably as surface acetato ligands. The HNO_3 treatment that also allows CNT opening contributes to the endohedral Ru deposition. The stability of Ru nanoparticles, modeled by a Ru_{13} cluster, on different adsorption sites follows the order: Gr-DV-$(COOH)_2$ > Gr-DV > Gr (where DV is a double vacancy and Gr the graphene surface). It is evidenced that, after a high-temperature treatment performed in order to remove the SFGs, the Ru/CNT material can react with oxygen from air *via* a surface reconstruction reaction, which reforms a stable Ru-acetato interface. The mechanism of this reaction has been investigated by DFT. These Ru/CNT catalysts are extremely stable, keeping a mean particle size <2 nm, even after heating at 973 K under a hydrogen atmosphere.

1. Introduction

Metal nanoparticles (NPs) exhibit size-dependent physical, chemical, and electrical properties that differ significantly from the bulk materials, due to the large fraction of surface atoms and the quantum confinement effect. The application of these nanostructures in areas such as heterogeneous catalysis, sensors, and microelectronics reflects their economic importance. Metal NPs deposited on a support are particularly suitable for catalysis applications. Carbon materials such as activated carbons, carbon blacks, and graphitic materials are widely used as support for metal NPs in fine chemistry catalysis and electrocatalysis [1], because of their high surface area, their stability and relative inertness, and potentially high electronic conductivity. Under the influence of the support, the properties of supported metal NPs are different from that of isolated NPs and strongly dependent not only on the particle size and surface composition, but also on the surface morphology and nature of metal–support interactions [2]. Understanding and developing catalysts with supported NPs requires comprehensive experimental and theoretical studies of their thermal, structural, and dynamic properties [3]. The impact of (molecular) surface chemistry on all these properties should therefore be taken into consideration for the rational design of supported catalysts [4,5].

The relatively good knowledge of conventional oxide support (silica, alumina, zeolites) surface chemistry has already allowed the design, at the molecular level, of supported NPs and single-site catalysts [6]. For carbon materials, however, a complex surface chemistry often imposes the use of empiric approaches for catalyst preparation. The carbon surface contains heteroatoms (O, N, and H) in the form of surface functional groups (SFGs) by analogy to those appearing in organic compounds [7]. 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. Thus, even if it has been demonstrated since many years that oxygen SFGs play a crucial role in the wetting of carbon supports and can affect dispersion or sintering of the metal particles [8,9], it is still a matter of debate whether they also function as anchoring sites for NPs [10]. Fig. 1 shows the various oxygen-containing functionalities present on a carbonaceous surface, together with the products resulting from their thermal decomposition under an inert atmosphere [11]. It has been experimentally shown that the more acidic groups, such as the carboxylic ones, decrease the hydrophobic character of the carbon surface and positively

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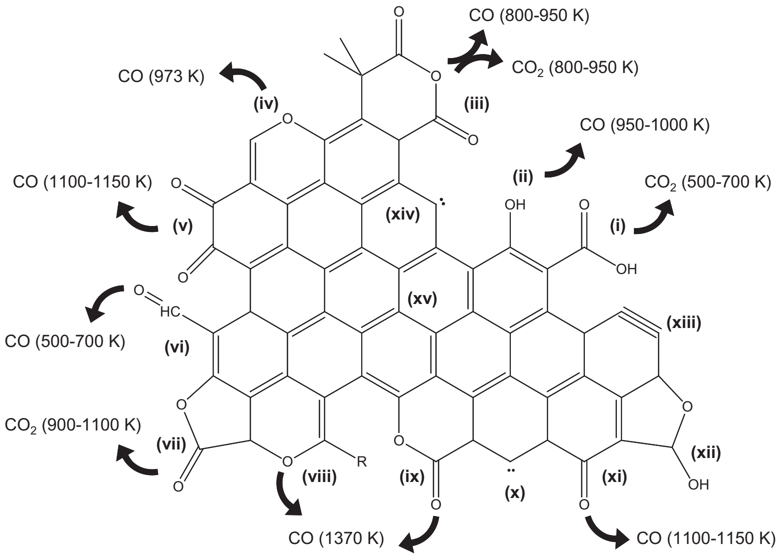

Fig. 1. Oxygen SFGs, and specific sites generally present on carbon surface: (i) carboxylic acid, (ii), phenol, (iii) carboxylic anhydride, (iv) ether, (v) quinone, (vi) aldehyde, (vii) lactone, (viii) chromene, (ix) pyrone, (x) carbene like species, (xi) carbonyl, (xii) lactol, (xiii) carbyne like species at armchair sites, (xiv) carbene like species at zigzag sites, and (xv) p electron density on carbon basal plane. The arrows show the decomposition product(s), from TPD deconvolution spectra (adapted from Ref. [11]).

impact the metal dispersion, providing anchoring sites for exchange of cationic metallic precursors [8,9]. On the other hand, the less acidic and thermally more stable SFGs, such as the carbonyls, favor the interaction between the metal particle and the carbon surface, thus minimizing sintering [8,9]. However, it is often omitted that the thermal stability of the carboxylic groups is limited to temperatures close to 673 K, and such temperatures are often used for the decomposition and/or reduction in the metallic phase.

Thus, the question concerning whether these oxygen SFGs affect the final metallic dispersion in a positive way due to their reactivity, or in a negative way (sintering of the metal NPs and loss of dispersion) as a consequence of their decomposition during catalyst pretreatments [12] remains open to discussion [13]. Moreover, in many cases, it is difficult to draw unequivocal conclusions, since the introduction or removal of oxygen SFGs can also lead to a difference in pore structure of the carbon support, in addition to the possibility of influencing the particle size. Indeed, micropores in the carbon support might be beneficial for metal dispersion. In that respect, the use of mesoporous carbon support, such as multiwalled carbon nanotubes (CNTs), the porosity of which being unchanged by heat treatment at $T < 1273$ K, could allow a better control of catalyst preparation [14]. Furthermore, the possibility of specific interactions between the graphene surface defects and metal NPs and/or metallic precursors is an important subject in catalyst preparation. Finally, it has also been shown that the presence or absence of SFGs can also directly affect the catalytic behavior of the active phase [15–18]. We are particularly interested in carbon-supported ruthenium catalysts, the catalytic performances of which have already been evaluated in Fischer–Tropsch synthesis, ammonia synthesis/decomposition, hydrogenation, and liquid-phase oxidation reactions [1].

In this work, we report a detailed study on the nature of the ruthenium–carbon interface in Ru/CNT catalysts prepared from neutral Ru(0) organometallic precursors. Experimental data combined with density functional theory (DFT) calculations allowed to conclude that both Ru precursor and NPs are anchored on the external surface *via* the carboxylic surface groups, presumably *via* surface acetato ligands. Additionally, it is demonstrated that after a high-temperature treatment, performed to assist oxygen SFG removal, a surface reconstruction reaction occurs involving oxygen atoms present on the ruthenium NP surface and the carbon atoms remaining after oxygen SFG removal.

2. Experimental section

2.1. General methods

All reactions were carried out under argon atmosphere using standard Schlenk techniques or in an MBraun glove box. Solvents were purified by standard methods or by a MBraun SPS-800 solvent purification system. [Ru(COD)(COT)] was purchased from Nanomeps, Toulouse, 9-anthracenecarboxylic acid from Avocado, [$Ru_3(CO)_{12}$], 9-anthracenecarboxaldehyde, 9-anthracenol, and anthracene from Sigma–Aldrich.

2.2. Synthesis

2.2.1. Carbon nanotubes and supported catalysts

The CNTs were produced by chemical vapor deposition of ethylene in the presence of hydrogen on iron catalysts supported on hydroxyapatite. The as-produced samples were purified by HCl washing during 12 h at room temperature, then filtered, washed with deionized water repeatedly until neutrality of the rinsing waters, and dried for 3 days in an oven at 393 K to produce CNT_p. The CNT surface was then modified by a concentrated nitric acid solution under reflux for 4 h (CNT_o). The nanotubes were again filtered, washed with distilled water, and dried in an oven for 3 days at 393 K.

The ruthenium catalysts were prepared by excess solvent impregnation on two kind of supports consisting of purified (CNT_p) and HNO_3 oxidized (CNT_o) CNTs, using two different Ru(0) precursors, [Ru(COD)(COT)], (1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium (**Ru1**), and [$Ru_3(CO)_{12}$] (**Ru2**). Given the reactivity of **Ru1** precursor, the metal impregnation was carried out in a Schlenk tube under argon atmosphere with 1 g CNTs and 50 mL of pentane (stirred 2 days at 318 K, under reflux). As for **Ru2** precursor, the same suspension was agitated for 12 h in air at room temperature. The impregnated samples were filtered and washed thoroughly with the pentane and dried at 393 K in an oven overnight. The catalysts were subsequently reduced in flowing H_2/Ar mixture (80:20 in volume) at 573 K for 2 h.

2.2.2. [Ru(COD)(COT)] reactivity toward anthracene derivatives

In a typical experiment, to a 15 mM solution of [Ru(COD)(COT)] (3.4 mg, 0.011 mmol) in acetone-d_6 (0.7 mL), 2 equivalents of an