

Understanding Ru/CNT interactions: A rational design of Ru nanocatalysts

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ABSTRACT

A comprehensive experimental and theoretical study of the surface chemistry of multi-walled carbon nanotubes (CNTs) and its effect on the deposition of ruthenium nanoparticles is reported. It is shown that the oxidation of CNTs by nitric acid creates various oxygen surface functional groups (SFGs) on the CNT external surface which is a critical step for the 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 stability of Ru nanoparticles, modeled by a Ru₁₃ 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 shown that, after a high-temperature treatment performed 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.

Keywords: Carbon nanotubes, Ruthenium, Nanoparticles, Surface chemistry

1 INTRODUCTION

Carbon materials such as activated carbons, carbon blacks, and graphitic materials are widely-used as support for metal nanoparticles in catalysis, because of their high surface area, their stability and relative inertness, and potentially high electronic conductivity [1]. Under the influence of the support, the properties of supported metal nanoparticles are different from that of isolated ones, 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 nanoparticles 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]. 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 by analogy to those appearing in organic compounds. Thus, the question concerning whether these groups affect the final metallic dispersion in a positive way due to their reactivity, or in a negative way (due to sintering of the metal nanoparticles (NPs) and loss of dispersion) as a consequence of their decomposition during catalyst pretreatments remains open to discussion. The possibility of specific interactions between the graphene surface defects and metal NPs and/or metallic precursors is an important subject in catalyst preparation. It has been shown that the presence or absence of SFGs can directly affect the catalytic behavior of the active phase [5,6]. Using carbon nanotubes as a model support, we report in this work a detailed study based on experimental data combined with density functional theory calculations of the nature of the ruthenium-carbon interface in Ru/CNT catalysts prepared from neutral Ru(0) organometallic precursors [7].

2 RESULTS AND DISCUSSION

CNT and Ru/CNT characterization

Detailed characterization of CNT_p (purified) and CNT_o (oxidized) as well as the mechanism of CNT nitric acid oxidation has been reported elsewhere [8]. The main effects of HNO₃ oxidation are as follows: (i) a slight increase in the Raman I_D/I_G ratio, usually attributed to the presence of disordered carbon in CNT samples, the quantity of which decreases upon oxidation, (ii) an increase in the BET surface area and pore volume due to CNT tip opening, and (iii) the introduction of acidic carboxylic SFGs (among others), as shown by a change in point of zero charge (PZC) value and the value of the TPD CO/CO₂ ratio (Table 1).

Sample	Raman (I _D /I _G)	BET (m ² g ⁻¹)	PZC	CO/CO ₂
CNT _p	1.5	134	7.6	1.5
CNT _o	1.6	172	3.5	1.7

Table 1. Textural and chemical characterization of the purified and functionalized CNTs.

A series of Ru/CNT catalysts were prepared on both **CNTp** and **CNTo** from two ruthenium organometallic precursors ([Ru(COD)(COT)] (**Ru1**), and [Ru₃(CO)₁₂] (**Ru2**). The Ru/CNTo samples have been further heat-treated under argon at 973 or 1173 K in order to evaluate the influence of oxygen surface group removal on metal particle size and surface chemistry. The excess solvent impregnation method led to different Ru loading depending on the precursor used, higher loading being obtained when starting from the **Ru2** cluster (2.7 vs. 1.3 wt.%). Higher loadings were also obtained on **CNTo** compare to **CNTp**, suggesting the implication of oxygen SFGs in the grafting process. The Ru crystallite diameter was smaller when starting from the **Ru1** than with the **Ru2** precursor (*ca.* 1.5 and 4 nm, respectively). This could be explained by a higher reactivity of **Ru1** during the grafting procedure (faster nucleation rate), and/or by the fact that we used two precursors of different nuclearity (3 Ru atoms are grafted for each molecule of **Ru2**, compared to only 1 for **Ru1**). We also investigated the influence of Ru location on their size and thermal stability. For **Ru1**, we found that the ruthenium nanoparticles located inside (NP_{in}) **CNTo** are significantly smaller than the NP_{out} (NP_{in} size is 1.1 nm, whereas NP_{out} is 1.5 nm). As far as the thermal stability is concerned, NP_{in} is more sensitive to sintering than the NP_{out}, indicating a difference in stability of the adsorption sites or nanoparticle diffusion. However, and even for Ru1/CNTo1173 sample, the mean NP_{in} size remains smaller than the mean NP_{out} size, due to template effect of CNT cavity preventing sintering.

XRD patterns of the reduced Ru-based samples (reduction temperature 573 K) show peaks at $2\theta \approx 26^\circ$ that corresponds to the (002) plane of CNTs, and reflections of metallic ruthenium, which are consistent with an exclusive hexagonal geometry and establish the presence of Ru⁰.

The TPD-MS profiles of the supported catalysts provides valuable information on the influence of oxygen SFGs on ruthenium grafting (Fig. 1). Two main phenomena are observed: (i) the CO₂ evolution profile is much more affected by ruthenium deposition than the CO one, and (ii) the high-temperature treatment (Ru_x/CNTo1173 sample) contributes to a significant decrease in the oxygen SFG-releasing CO upon decomposition, except for the epoxy groups (peak at 870-880 K). As far as CO₂ evolution is concerned (Fig. 1a), ruthenium deposition on the **CNTo** surface leads to the disappearance of most of the carboxylic acid (peak at 565 K), anhydride (peak at 735 K), and lactone groups (peak at 950 K). Ruthenium deposition induces the formation of new CO₂ releasing groups at 640 and 742 K for **Ru1** and **Ru2**, respectively. The fact that (i) two very narrow peaks, characteristic of a catalytic decomposition, are observed in the CO₂ evolution profile for Ru1/CNTo and Ru2/CNTo and (ii) that their position depends on the nature of the ruthenium precursor (different particle sizes), supports the fact that these new groups are associated with ruthenium. TPD-MS profiles of Ru_x/CNTo1173 sample show that, even if on those samples

most of the oxygen SFGs have been removed by the heat treatment, a surface reconstruction reaction is still occurring. This reaction produces groups that evolve CO₂ upon decomposition but in lower amounts and at higher temperatures. For CO evolution (Fig. 1b), an increase in the intensity of the peak at 870-880 K was noticed, attributed to epoxy groups, upon Ru deposition. Interestingly, epoxy groups are still present on the samples heat treated at 1173 K, suggesting their reformation during the surface reconstruction reaction.

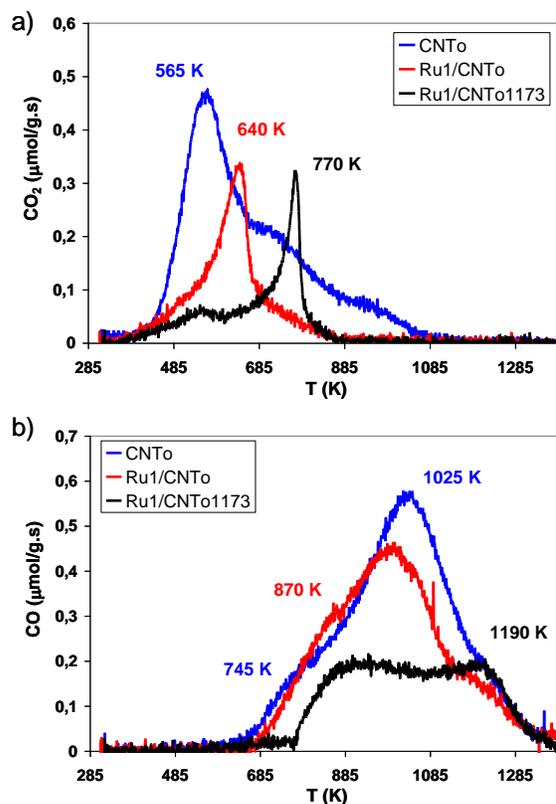


Figure 1. TPD-MS profiles of the carbon-supported ruthenium samples, (a) CO₂, and (b) CO evolution.

All these data suggest that the surface reconstruction should involve the following: (i) the ruthenium NPs, (ii) surface carbon atoms, and (iii) a source of oxygen. The mechanism of this reaction has been investigated by DFT (see last section). Concerning the source of oxygen, it can be either (i) oxygen SFGs that have not been decomposed, (ii) new oxygen SFGs that could have formed upon air exposure of the reduced catalysts, or (iii) oxygen arising from a thin RuO_x layer that can form upon air exposure of the reduced NPs. This surface reconstruction reaction, which leads to the formation of an Ru-acetato interface, and of epoxy SFGs occurs either at room temperature, during the air exposure of the reduced samples, or during the TPD experiment under He.

Hence, the catalyst characterization provided two important pieces of information, concerning the nature of

the metal-support interaction. First, **Ru1** reacts with anhydride, lactone and carboxylic groups to form a species grafted to the surface, probably through an acetato surface ligand. Upon reduction at 573 K, the acetato surface ligand decomposes and Ru nanoparticles are produced. Upon air exposure, the ruthenium surface is oxidized and a surface reconstruction reaction occurs that involves Ru, oxygen (probably from RuO_x), and reactive surface carbon atoms to produce a new acetato surface ligand for the nanoparticles, and epoxy surface functional groups. Second, the fact that CNTs present a low edge/basal plane ratio contributes to catalyst stability.

Reactivity of Ru precursors with anthracene derivatives

In order to better understand the anchoring mechanism of the ruthenium precursor on the CNT surface, the reactivity of **Ru1** and **Ru2** toward anthracene and several oxygenated anthracene derivatives as analogues to the CNT surface was investigated. In a screw cap NMR tube, the ruthenium precursor was dissolved in acetone-d₆ and an excess of anthracene (2 eq.) was added to the yellow solution. As expected, the ruthenium complexes did not react with the aromatic rings. As CNTs contain several oxygenated SFGs, we performed the same experiment with several oxygenated anthracene derivatives (9-anthracenecarboxylic acid, 9-anthracenecarboxaldehyde, and 9-anthracenol). None of these species reacted with [Ru₃(CO)₁₂]. The aldehyde and the alcohol derivatives did not react with [Ru(COD)(COT)], even after long periods of reaction (up to 60 h at 318 K). On the other hand, the carboxylic acid derivative induced the formation of a yellow precipitate in the NMR tube after heating 20 h at 318 K. The ¹H NMR spectrum showed the formation of a yellow ruthenium complex (Fig. 2) and the structure was confirmed by single crystal XRD.

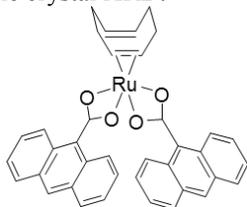


Figure 2. [Ru(9-anthracenecarboxylate)₂(COD)]

DFT study on the adsorption mode of Ru nanoparticles on the carbon support

DFT calculations were performed in order to further understand the metal anchoring and surface reconstruction mechanisms. Since after HNO₃ treatment -COOH groups are present, we also performed calculations with a graphene monolayer presenting one or two -COOH groups, named Gr-Carb1 and Gr-Carb2, respectively, and a monolayer presenting a di-vacancy, decorated by one or two carboxylic groups (Gr-DV-Carb1, Gr-DV-Carb2).

The presence of carboxylic groups at the CNT surface clearly influenced the adsorption modes of the nanoparticles. The interaction between Ru nanoparticles and the pristine support was found to be already strong; the

situation was even more favorable as soon as structural defects were involved. The most stable adsorption mode appeared to be the Ru₁₃ in interaction with a double vacancy (DV) decorated by 2 carboxylic groups, with a complex grafting mode (Fig. 3 top).

Surface reconstruction reaction upon re-oxidation due to air exposure

Re-oxidation process has been investigated, assuming that after heat treatment, most of the oxygenated SFGs have been removed from the carbon honeycomb structure. We have also assumed that the oxygen source, involved in the formation of epoxy and carboxylate groups, is O₂ molecules. Due to the presence in excess of O₂, we further hypothesize that small NPs will be completely oxidized; while large ones will probably be coated by a thin RuO_x film. This has been verified by a series of calculations, where we have checked that a freestanding Ru₁₃ NP can easily absorb up to 30 O atoms, a number slightly in excess in comparison with the standard stoichiometric RuO₂ case. It is a thermodynamically favorable configuration since the adsorption energy per O atom is still -167 kJ/mol.

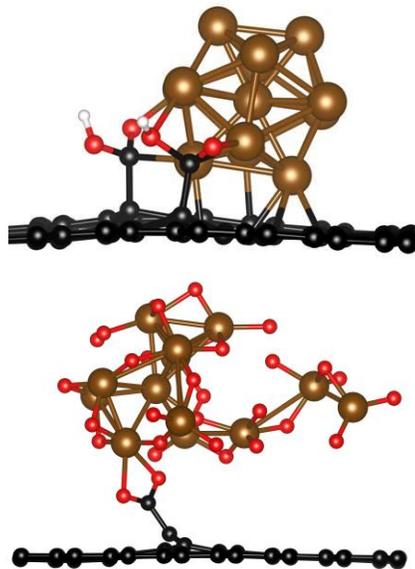


Figure 3. (top) Side-view of Ru₁₃ adsorbed on Gr-DV-Carb2; (bottom) Stable carboxylate group at the interface

Assuming that the source of the new oxygen SFGs is atomic O present at the RuO_x-graphene interface, we have investigated possible pathways of O-release on the graphene layer, mainly by hopping processes, involving one or two O atoms from the oxidized nanocluster to the graphene monolayer with and without defect. Considering that the process is thermodynamically driven, if one assumes that it happens at room temperature, it means that the final state, *i.e.* oxygen atoms chemically bound to one or more C atoms of the support and possibly to Ru atoms too, has to be lower in energy than the initial state, with the concerned O atom in interaction with Ru atoms.

From the theoretical data, in the scenario of sidewall re-oxidation, there is a need of atomic O accumulation at the oxidized Ru-surface-CNT sidewall interface, to favor the atomic O transfer to the support. These transfers have low energy barriers and are thermodynamically driven. Additionally, in the case of a pristine substrate, we have provided theoretical evidences that the formation of a carboxylate group is even possible at the interface. It appears that this interfacial functional group is more stable than a surfacic carboxylate group, in good agreement with experimental data (Fig. 3 bottom). Indeed, due to their deep location at the interface, the interfacial carboxylates have a shorter C–C bond 1.48 Å compared to 1.58–1.63 Å, and which we obtained in the case of SFGs. A possible reason for this stronger binding is the more sp^2 pronounced character of the basal C that allows for a larger delocalization of charge coming from the two O atoms.

3 CONCLUSIONS

The anchoring of ruthenium nanoparticles in/on carbon nanotubes was investigated from an experimental and theoretical point of view. Surface groups such as carboxylic acids, carboxylic anhydrides and lactones were found to act as anchoring centers for the Ru precursor, presumably as surface acetato ligands. Upon heating at high temperature (1173 K) to remove these surface groups, Ru/CNT materials can react with oxygen from air, *via* a surface reconstruction reaction, which produces a new acetato Ru-acetato interface through an epoxy group. The thermal stability of the newly formed -COORu surface groups was higher than that of the initial -COOH groups, allowing for the preparation of extremely stable and very small Ru nanoparticles (< 2 nm).

4 EXPERIMENTAL

The carbon nanotubes 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 with HCl at room temperature (CNTp) and functionalized with HNO₃ solution under reflux (CNTo). The ruthenium catalysts (3 wt.%) were prepared by excess solvent impregnation on CNTp and CNTo, using two different Ru(0) precursors, [Ru(COD)(COT)] (Ru1), and [Ru₃(CO)₁₂] (Ru2). Given the reactivity of Ru1 precursor, the impregnation was carried out in a Schlenk tube under argon atmosphere. As for Ru2 precursor, the same suspension was agitated for 12 h in air at room temperature. The catalysts were subsequently dried at 393 K overnight, and reduced in flowing H₂/Ar mixture (80:20 in volume) at 573 K for 2 h.

In a typical experiment to check the reactivity of [Ru(COD)(COT)] toward anthracene derivatives, to a 15 mM solution of [Ru(COD)(COT)] (3.4 mg, 0.011 mmol) in acetone-d₆ (0.7 mL), 2 equivalents of an anthracene derivative were added. The solution was introduced into a screw cap NMR tube, and a NMR spectrum was recorded at room temperature. The solution was heated at 318 K for 17

h and a second NMR spectrum was recorded at room temperature (9-anthracenecarboxylic acid: 4.7 mg; 9-anthracenecarboxaldehyde: 4.4 mg; 9-anthracenol: 4.1 mg; and anthracene: 3.8 mg).

The surface chemistry and morphology of the materials was characterized by analytical techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), temperature programmed desorption (TPD) and point of zero charge (pH_{PZC}) measurements.

DFT calculations were carried out using the Vienna *ab initio* simulation package VASP. The code uses the full-potential projector augmented wave (PAW) framework. In order to model the interaction between the nanotubes' sidewalls and the grafted Ru nanoparticles we have used a (7x7) primitive cell of graphene, presenting (or not) a di-vacancy of 555-777 type and functionalized (or not) by carboxylic groups, and a nanocluster of Ru consisting of 13 atoms. A kinetic-energy cutoff of 400 eV was found to be sufficient to achieve a total energy convergence within several meV considering a k-point sampling with a (3x3x1) grid. During geometry optimization runs, all the atoms were fully relaxed until forces on individual atoms were smaller than 0.02 eV/Å. The adsorption energy that describes the interaction between Ru₁₃ and the graphene layer is defined as: $E_{\text{ads}} = E_{\text{Ru@Graph}} - E_{\text{Ru}} - E_{\text{Graph}}$, where $E_{\text{Ru@Graph}}$ stands for the total energy of the composite system, while E_{Ru} is the total energy of the ideal icosahedral structure, or the energy of the oxidized aggregate and E_{Graph} is the total energy of the graphene layer substrate, be it pristine or presenting a di-vacancy, be it decorated by carboxylic groups or not. Geometries were produced thanks to the 3D visualization program VESTA.

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