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Influence of nanosizing on hydrogen electrosorption properties of rhodium based nanoparticles/carbon composites

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Composites made of ultra-small Rh hydride nanoparticles (NP) with controlled average sizes of 1.3, 1.9 and 2.3 nm dispersed in high surface area graphite powders were synthesized. The hydrogen electrosorption properties of the Rh nanohydride that is stable under ambient conditions were characterized by cyclic voltammetry under various scan rates in the hydrogen potential domain with the help of a cavity microelectrode. During the first cycles, an evolution of the voltammograms, characterized by an isopotential point, is observed that corresponds to a surface conversion of RhH_x into Rh, the core of the NP remaining in the hydride phase. After stabilization, the voltammograms exhibit the classical hydrogen electrosoprtion peaks of Rh, but a shift to positive potentials indicates that H is more weakly bounded to the surface as the NP size decreases. The onset of the HER follows the same trend. Interestingly, it is observed that the quantity of electrosorbed hydrogen strongly increases when downsizing the NPs, with the H/Rh ratio reaching 0.47 ± 0.11 for NPs with an average size of 1.3 nm. This enhancement cannot be explained just by the increase in surface area by NP downsizing. It may arise from the creation of new multi-fold adsorption surface and sub-surface sites due to the presence of many corner and edge atoms in ultra-small NPs with strong surface curvature.

1. Introduction

Composites materials made of nanoparticles (NPs) dispersed in a porous carbon and particularly Rh/carbon composites are commonly used as electrocatalysts for oxidation or reduction reactions in fuel cells or in environmental applications, for example ethanol oxidation [1,2], borohydride oxidation [3,4] or nitrate reduction [5].

Various synthetic methods are reported for obtaining such Rh/carbon materials. A colloidal suspension of NPs can be synthesized by reduction with $NaBH_4$ in the presence of PVP (poly(vinyl-pyrrolidone)) and then mixed with the carbon powder [1]. NPs can also be synthesized directly in the carbon host in presence of reducing and stabilizing reagents [2,4] or by a polyol method [3]. We have recently developed an alternative route to elaborate size-controlled Pd NPs [6,7]. It consists in impregnating the carbon powder with the metal salt in aqueous solution followed by reduction during heating under a hydrogen flow. In a recent work, we applied the same synthetic approach to produce Rh hydride (RhH_x) NPs supported on a high surface area graphitic carbon [8]. The NP size is controlled by the reduction temperature. A series of composites with RhH_x was synthesized with average NP sizes ranging from 1.3 to 3.0 nm. This study revealed that NPs below 2.3 nm can be synthesized as metallic Rh which forms a hydride phase (RhH_x) at room temperature and H_2 pressure below 0.1 MPa, in contrast to bulk Rh that can be hydrogenated only at 4 GPa. Above 2.3 nm, NPs only form solid solutions with H under the same conditions (0.1 MPa, RT). This evidences a nanoscale effect that drastically changes the H sorption thermodynamics of Rh. In addition, it was also observed that once formed, the hydride phase is stable at room temperature, a complete dehydrogenation only occurring under thermal treatment around 175 °C in vacuum.

Hydrogen electrosorption at Rh electrode surfaces has been studied for a long time, either on bulk Rh (mono or polycrystalline) or on Rh films [9–16]. To our knowledge, only a few recent works have addressed the electrochemical properties of Rh NPs (supported or not) towards hydrogen sorption as well as oxygen sorption [1,4,5,10,17,18]. Surprisingly, in none of these works, the amount of adsorbed H per Rh as a function of the particle size has been investigated.

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The ability of our synthetic route to elaborate RhH_x NPs with well-defined and controlled size below 10 nm offers a suitable mean to investigate, for the first time to our knowledge, the effect of nanosizing on hydrogen/oxygen electrosorption of RhH_x. In the light of our recent results on the enhanced hydrogen ad/absorption in ultra-small Rh NPs under ambient conditions [8], electrochemical studies have been carried out to complement our previous solid/gas experiments. In the present article, composite powders containing RhH_x NPs with different and well controlled sizes were synthesized and characterized. Electrochemical analyses were carried out using the Cavity MicroElectrode (CME) [6,19]. Cyclic voltammetry studies in the hydrogen potential domain (in acidic medium) have been performed to characterize for the first time the hydrogen electrosorption properties of RhH_x and their evolution as a function of the NP size.

2. Experimental

Composites of RhH_x NPs in carbon were synthesized *via* the following chemical procedure. The high surface area carbon powder HSAG500 from Imerys Graphite & Carbon (hereafter designated as C) was impregnated with an aqueous rhodium chloride ($RhCl_3$) solution under magnetic stirring. The mixture was then dried at 60 °C in an oven for one night and treated under Ar/H_2 flow at different temperatures to reduce Rh(+III) to Rh(0), which further reacts with H_2 gas to form RhH_x NPs as detailed in [8]. We have shown previously that the average size of RhH_x-based nanoparticles can be controlled by the applied reducing temperature [8]. A series of composites with RhH_x-based NPs were synthesized with average sizes of 1.3, 1.9 and 2.3 nm (175, 200 and 250 °C, respectively). The final amount of metal is 10 wt.% over the total mass of the composite. The composites will be labelled RhH_x-*s*/C, where *s* stands for the average NP size (diameter) in nm and *x* as the hydrogen content in the initial hydride phase. A compound consisting of pure non hydrogenated Rh powder was synthetized as a reference material by reducing a rhodium chloride ($RhCl_3$) aqueous solution by $NaBH_4$ in the absence of C. This Rh powder (designated as Rh_p hereafter) was not mixed with carbon but used directly for the electrochemical studies.

Scanning electron microscopy (SEM) images were obtained with a Merlin FEG microscope from Zeiss. Microstructural observations were performed by Transmission Electron Microscopy (TEM) with a 200 kV FEG TEM (FEI Tecnai F20 equipped with a Gatan energy Imaging Filter, resolution 0.24 nm). The mean NP size has been determined by statistical analyses of several TEM images using the software ImageJ.

Electrochemical measurements were carried out in a classical 3-electrode cell using an Autolab PGSTAT 30 potentiostat. The working electrode was a homemade cavity microelectrode (CME). The CME is fabricated with a Pt wire as described in details elsewhere [19,20]. The cavity of the CME (diameter 50 μm, depth 90 μm) was filled up with the powder materials using the electrode as a pestle. The same CME was used for all experiments, the cavity being unloaded by washing with an ultrasonic cleaner in distilled water for 5 minutes. In addition, a macroelectrode with a well-known amount of RhH_x-1.9/C has been prepared for quantitative analysis, by mixing the composite powder (95 wt%) and Teflon (5 wt%) and pressing the obtained film (11 mg) on a stainless steel grid of 1 cm^2 under 3 tons. The grid was then fixed on a gold wire as current collector. The counter electrode was a Pt wire and the reference electrode was a calomel electrode saturated with KCl (SCE). In the text, the potentials refer to the Reversible Hydrogen Electrode (RHE). The electrolyte was a 0.5 mol L^{-1} H_2SO_4 solution that was deoxygenated by bubbling argon gas. Before each voltammetric experiments, a pre-treatment to remove surface oxide layer was applied consisting to impose a controlled potential of 0.25 V/RHE for 30 s. The peak charges and intensities were determined according to the method described by Biegler et al. [21].

3. Results

3.1. Electron microscopy characterization.

The prepared materials have been characterized by electron microscopy. Fig. 1 shows a SEM image of the pure Rh powder (A) and TEM images of the RhH_x-*s*/C composites synthesized by reduction of $RhCl_3$ in Ar/H_2 at 175 (B), 200 (C) and 250 °C (D).

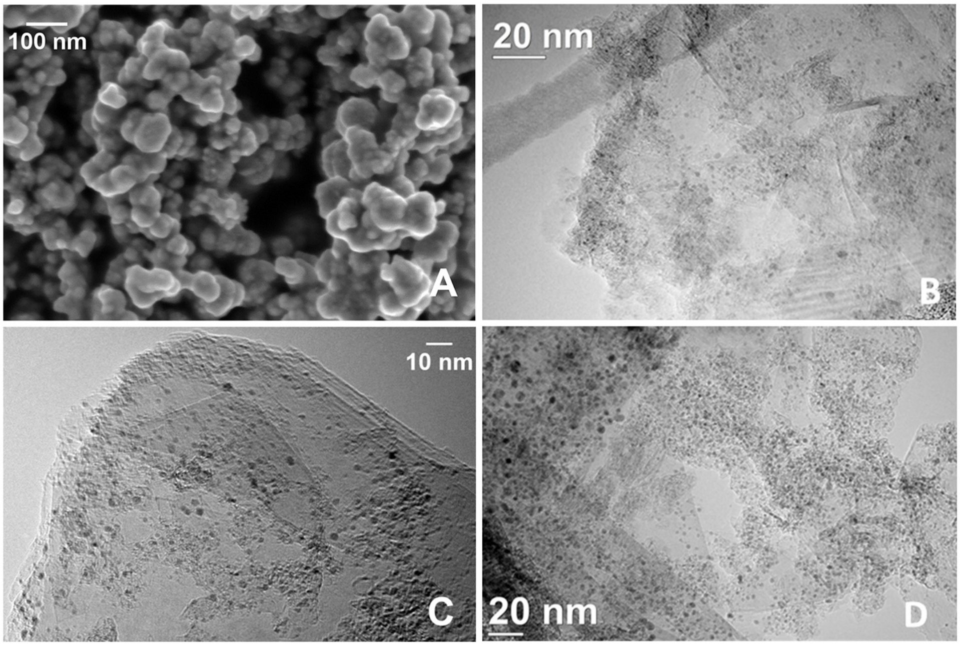

Fig. 1. SEM image of Rh_p (A) and TEM images of the three RhH_x-*s*/C composites synthesized at 175 (B), 200 (C) and 250 °C (D).