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Palladium decoration of hybrid carbon nanotubes/charcoal composite and its catalytic behavior in the hydrogenation of *trans*-cinnamaldehyde

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ABSTRACT

In the present study, we addressed the palladium (Pd) decoration of multiwalled carbon nanotube (CNT)/activated carbon (AC) hybrid composites (MWCNT/AC), and examined the catalytic behavior of the composites in the hydrogenation of *trans*-cinnamaldehyde. The MWCNT/AC composites were prepared by growing CNT network on the surface of AC granules, using the chemical vapor deposition method. XPS analysis revealed that the MWCNT/AC and COOH–MWCNT/AC composites and isolated AC adsorbed Pd at different oxidation states when dipped into a Pd^0 microemulsion: isolated AC and the COOH–MWCNT/AC composite adsorbed Pd nanoparticles at di- and tetravalent states ($Pd^{2+/4+}$), while the MWCNT/AC composite adsorbed Pd nanoparticles at zero and tetravalent states (Pd^0/Pd^{4+}). The MWCNT/AC composite may thereby have hierarchical Pd adsorption properties dependent on the MWCNT network type grown onto the AC surface. Regarding the catalytic performance, the ($Pd^{0/4+}$)-MWCNT/AC catalyst displayed higher selectivity to hydrocinnamaldehyde formation (95.9%) when compared with the ($Pd^{2+/4+}$)-AC and ($Pd^{2+/4+}$)-COOH–MWCNT/AC catalysts (72.1% and 91.4% selectivity, respectively). The catalytic performance of the ($Pd^{0/4+}$)-MWCNT/AC catalyst with 2.8 wt% of Pd loading was also superior than the catalytic performance of commercial catalysts with 5 and 10 wt% of Pd loading and other Pd/CNTs catalysts reported in the literature.

1. Introduction

Most of the current industrial chemical processes involve at least one catalyzed step [1]. The heterogeneous catalysts are used in numerous reactions of oxidation [2], hydrogenation [3], hydrogenolysis [4], coupling [5], and cracking of alkanes [6], among others. Chemists have used various types of transition metals, especially noble metals such as Rh, Ru, Pt, and Pd, as catalytic sites due to their high reactivity and selectivity [7].

In recent years, several research groups have sought the development of new catalytic supports. Carbon nanotubes (CNTs) are materials with unique physical and chemical properties [8–10] that have provided excellent catalyst supports [11–16]. CNTs can be functionalized with many chemical species, including metal catalysts [17,18]. The resulting metal/CNTs composites find application in the selective hydrogenation of *trans*-cinnamaldehyde (CMA) [19–22] and in other types of reactions [23,24]. The advantages of the use of CNTs as catalyst supports are: (1) they are thermally stable in both oxidizing and reducing media; (2) they display high thermal conductivity, which enables rapid temperature homogenization throughout the structure of the catalytic bed and avoids catalyst sintering at higher temperatures; (3) they adsorb the metal nanoparticle, thereby preventing catalyst mobility or release during the reaction; (4) they can modify the electronic structure of the metal nanoparticle [25–31].

CNTs and carbon nanostructures like graphene can be combined with nanoparticles and/or micrometric materials to produce hybrid and hierarchical composites, free-standing carbon electrodes, and micro/nanostructured granular materials. These products share the potential technological applications envisaged for CNTs [32–41]. Several types of CNTs and micrometric substrates can be used to

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prepare the aforementioned kind of hybrid composite, which may be submitted to different chemical and thermal treatments, in particular when the micrometric substrate is a carbonaceous material. CNTs growth conditions control the architecture of CNTs network on the surface of other materials. Micrometric aggregates of CNTs are relatively friendly to the aqueous environment [42].

To date, it is still unclear how palladium (Pd) adsorbs onto multiwalled CNTs/charcoal composite (MWCNT/AC) and whether it has catalytic properties in this kind of composite. In the present study, we assessed whether the MWCNT/AC matrix has catalytic potential for Pd catalysis – particularly in the case of *trans*-cinnamaldehyde (CMA) hydrogenation reaction – and how Pd nanoparticles in a microemulsion adsorb onto this kind of composite.

2. Experimental

2.1. Materials

n-Heptane and the surfactant Brij® 30, purchased from Sigma–Aldrich and Acros Organics, respectively, were used to prepare the catalysts. Activated carbon (AC) was provided by Alpha Carbo Industrial (particle size = 325 mesh). The chemicals used in the catalytic tests – *trans*-cinnamaldehyde (98%), 1,4-dioxane, and the commercial catalysts 5% Pd/C and 10% Pd/C – were acquired from Sigma–Aldrich.

2.2. Instrumentation

The metal content of the catalysts was determined by atomic absorption on a Perkin Elmer Analyst 800 spectrometer. The microscopic analyses were performed using a Carl Zeiss EVO-50 scanning electron microscope and a JEOL JEM-100cx II 485 transmission electron microscope. BET experiments were carried out using a Quantachrome NOVA 1200 BET Surface Area Analyzer system. The X-ray photoelectron spectra (XPS) of the samples were recorded on a concentric hemispherical analyzer (CHA), in ultra-high vacuum (UHV) with a base pressure below 10^{-9} Torr, by employing an Al-Kα unmonochromatised source (1486.7 eV) operating at 10 kV, and a constant pass energy of 58.5 eV for survey scans, as well as for detailed scans. All binding energy values were charge-corrected to the adventitious C (1s) signal, which was set at 285.1 eV.

Formation of reaction products was monitored using a gas chromatograph (GC 2014, Shimadzu), equipped with FID detector and a RTX-1 fused silica capillary column (30 m length × 0.25 mm i.d., 0.25 μm film thickness), operating at temperatures in the range of 100–130 °C. The identification of the formed products was made by comparison with the retention time of standard samples.

2.3. Preparation of the composite

Considering that the growth conditions and geometry of the chemical vapor deposition reactor affect the yield of CNTs, the studied samples were prepared using exactly the same type of reactor and growth parameters described by Montoro et al. [43]. The micro/nanostructured MWCNT/AC was prepared by growing CNTs network on the substrate (AC), using ethanol chemical vapor deposition and Mn/Co catalysts, which provide tubes with low concentration of defects [43]. The CNT concentration in the CNT/AC (40 wt%) was determined with the aid of an analytical balance and an atomic absorption spectrometer. The concentrated nitric acid method (reflux at 50 °C, 8 h) was employed to functionalize MWCNT with the COOH group. Before decoration with Pd, the MWCNT/AC samples were treated with concentrated HCl to extract the Mn/Co catalyst.

2.4. Preparation of Pd catalysts

The incorporation of metallic Pd nanoparticles into MWCNT/AC, AC, and COOH–MWCNT/AC was carried out by reverse microemulsion of water in oil and surfactant. First, the microemulsions were prepared by adding a 0.10 mol L^{-1} aqueous solution (5.2 g) of the metal precursor ($PdCl_2$ in 0.1 M HCl) to a mixture of *n*-heptane (28.3 g) and Brij® 30 (10.0 g), under stirring at 40 °C. The overall composition of the prepared microemulsion was (wt): H_2O 12%, Brij® 30 or polyethyleneglycol-dodecylether 23%, and *n*-heptane 65%. To reduce the Pd salt, a 2.00 mol L^{-1} aqueous solution (5.2 g) of $NaBH_4$ was rapidly added to the emulsion, and the mixture was kept under stirring for 30 min at 40 °C; this procedure yielded a black Pd^0 microemulsion.

Next, an appropriate amount of MWCNT/AC, COOH–MWCNT, or AC was added to the same volume of the microemulsion prepared above, and the mixture was stirred for 1 h. In the specific case of Pd incorporation into MWCNT/AC, it was possible to modulate Pd loading efficiency by changing the time of dipping in the Pd microemulsion. The resulting Pd catalysts were filtered through 0.22 μm PVDF membranes (Merck-Millipore), rinsed thoroughly with ethanol, and dried for 24 h, at 100 °C.

2.5. Characterization of Pd catalysts

The growth of MWCNTs over AC and the morphology of the resulting composites were characterized using scanning electron microscopy. To examine the deposition of Pd particles on the surface of CNTs, the prepared catalysts were analyzed by TEM. To prepare the TEM grids, the Pd–MWCNT/AC composite samples were milled to extract the tubes from CA. The amount of Pd (wt%) in the prepared hybrid composite was determined by atomic absorption spectroscopy. The specific surface areas of Pd/AC, Pd–COOH–MWCNT/AC, and Pd–MWCNT/AC, determined from BET N_2 isotherms, were 190, 172, and 168 $m^2\,g^{-1}$, respectively.

The quantitative evaluation of each peak of XPS was obtained by dividing the integrated peak area (PA) by the atomic sensitivity factor

[ASF (Pd 5/2) = 2.7, ASF (C 1s) = 0.25] [44], after subtracting the background signal by a smooth polynomial function [45,46]. Core level analyses followed the deconvolution of spectra by means of Voigt functions for singlets (C 1s) and doublets (Pd 3d) component. During the fitting, constant width and shape for the doublet peaks of Pd^0, Pd^{2+} and Pd^{4+} were used for all the samples. The branching ratio was kept at the statistical value.

2.6. Catalytic hydrogenation of trans-cinnamaldehyde (CMA)

The hydrogenation of CMA was carried out in a 150 mL stainless steel reactor equipped with a magnetic agitator. The reaction temperature was controlled with a thermostatic water bath. The catalysts were activated under hydrogen atmosphere before each reaction, as follows: 30 mg of catalyst were suspended in 6.0 mL of anhydrous 1,4-dioxane; the vessel was purged three times and pressurized with hydrogen to 1 MPa; the reaction mixture was stirred under hydrogen atmosphere for 2 h, at 70 °C; the reactor was cooled to room temperature.

To initiate the hydrogenation reaction, 300 mg of CMA were added to the catalytic suspension. After the reaction was completed, the reaction mixture was filtered through Celite® to remove the catalyst. The filtrate was analyzed by gas chromatography to determine the starting material conversion rate and the proportion of products formed. Conversion of CMA and selectivity to hydrocinnamaldehyde (HCMA), hydrocinnamic alcohol (HCMO), and cinnamic alcohol (CMO), were calculated using the following expressions: