Microporous and Mesoporous Materials 225 (2016) 378–384

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Enhancement of the hydrogenation activity of a Pd-tridecilamine (TDA) complex by confinement in carbon nanotubes

I. Such-Basáñez [a, *, 1], M.C. Román-Martínez [a], P. Serp [b]

[a] Department of Inorganic Chemistry and Materials Institute, University of Alicante, Spain
[b] Laboratoire de Chimie de Coordination, CNRS-Université Toulouse, France

ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
8 January 2016
Accepted 11 January 2016
Available online 18 January 2016

Keywords:
Palladium
Hybrid catalyst
Carbon nanotube
Hydrogenation
Confinement

ABSTRACT

An active hydrogenation Pd complex has been immobilised by impregnation on CNTs submitted to several treatments that lead to important differences in their surface chemistry and in the proportion of tubes with both ends open. Most of the hybrid catalysts are more active than the complex in homogeneous phase, but the support properties have an important impact in the catalytic activity. In general, the more developed the surface chemistry, the lower the activity. However, when CNTs are open at both ends, the Pd complex can enter the tubular cavity and an important enhancement of the catalytic activity due to a confinement effect is observed.

1. Introduction

Homogeneous catalysts have played an important role in all areas of fine chemistry production as they are well known to be very active and selective under mild reaction conditions, an important factor to be taken into account when dealing with expensive organic substrates [1]. However, contrarily to heterogeneous catalysts, homogeneous catalysts lack the ability to be easily recovered from the reaction medium. It would therefore be desirable to obtain a homogeneous catalyst immobilised on a solid support that could combine both, the high activity and selectivity of homogenous catalysts and the easiness of recovery of heterogeneous catalysts. Such system is often referred to as a hybrid catalyst, and it might give rise to other interesting properties such as activity or selectivity enhancements due to the particular combination of metal complex and support. Researchers in this area of knowledge often seek this sort of synergistic effects.

Preparation of hybrid catalysts has been now thoroughly studied, as it is apparent from the literature [2–9]. A great variety of metal complexes and ligands, active and selective in a plethora of important reactions, have been immobilised on many different supports such as silica, zeolites, mesoporous ordered materials (MOMs), clays, polymers and carbon materials. Different anchorage methods have been explored mainly attending to the stability of the immobilisation. From this point of view, formation of a covalent bond between the homogeneous catalyst and the support has been the most used approach to this problem but other methods such as electrostatic or dispersive interactions cannot be overlooked. For example, a Pd complex with alkyl amine ligands was immobilised on active carbon materials by means of dispersive interactions by Díaz-Auñón et al., showing that this procedure leads to stable and active hydrogenation catalysts [10].

Researchers have paid attention to the use of carbon nanotubes (CNTs) as catalyst support from the time of their discovery [11]. In particular, the characteristic shape factor of this material inspires its use as a drug delivery carrier [12] or, more related to catalysis, as a nanoreactor [13]. There are many examples of their use as catalyst support for the immobilisation of either homogeneous catalysts [8,11,14] or metal nanoparticles in the hollow cavity of nanotubes [15–18]. Previous work in our group showed that, in many cases, hybrid catalysts based on CNTs are more active than analogous catalysts prepared with other carbon materials and this has been attributed to the confinement of the active species in the inner cavity of the nanotube [19–24]. Other researchers have also

---

* Corresponding author.

E-mail addresses: ion.such@ua.es (I. Such-Basáñez), mcroman@ua.es (M.C. Román-Martínez), Philippe.Serp@ensiacet.fr (P. Serp).

[1] Present address: Technical Research Services. University of Alicante Spain. Ap. 99 03080 - Alicante Spain.

http://dx.doi.org/10.1016/j.micromeso.2016.01.011
1387-1811/© 2016 Elsevier Inc. All rights reserved.

reported such effects when using metal-complex species [14,18,25,26]. The present work deals with the immobilisation of an active hydrogenation model catalyst on CNTs submitted to different treatments. Conditions to obtain stable immobilised catalysts by means of dispersive interactions on nanotubes will be discussed. In the course of this research an effect of the oxygen content of the support on the activity of hydrogenation catalysts was found and will also be analysed in this paper.

2. Experimental

2.1. Synthesis of complex *trans*-$[PdCl_2(NH_2{-}(CH_2)_{12}{-}CH_3)_2]$ (PdTDA)

Preparation of *trans* square-planar PdTDA complex was described elsewhere [10] and can be summarized as follows: 100 mg (0.56 mmol) of $PdCl_2$ were added to a 50 mL toluene solution of 228 mg (1.1 mmol) of $NH_2{-}(CH_2)_{12}{-}CH_3$ (TDA), and the resulting suspension was heated to 338 K under flowing Ar for 4 h. The obtained yellow solution was evaporated and the product was purified by column chromatography (Acros 0.200–0.500 mm; $CHCl_3$:CH_3OH 6:1), obtaining a yellow solid that was characterised by elemental analysis (Micro TruSpec LECO CHNS), ^1H and ^{13}C NMR (Bruker AV300), FTIR (Bruker IF66/S) and FT-Raman (Bruker RFS/100) spectroscopies. Characterisation shows that the expected complex has been prepared.

EA: C: 54.50% (54.21%); N: 4.54% (4.86%); H: 10.22% (10.15%).

^1H–NMR (300 MHz): t 0.89 ppm (6H, $C\boldsymbol{H_3}$); b 1.26 ppm (36H, internal $C\boldsymbol{H_2}$); b 1.31 ppm (4H CH_2CH_3); m 1.66 ppm (4H $C\boldsymbol{H_2}CH_2NH_2$), m 2.74 ppm (4H, $C\boldsymbol{H_2}NH_2$), b 2.78 ppm (4H, $N\boldsymbol{H_2}$).

^{13}C–NMR (300 MHz): 14.1 ppm (CH_3); 22.7 ppm ($\boldsymbol{C}H_2CH_3$); 26.5 ppm ($\boldsymbol{C}H_2CH_2CH_2NH_2$); 7 signals between 29.1 and 29.7 ppm (internal $\boldsymbol{C}H_2$); 31.5 ppm ($\boldsymbol{C}H_2CH_2CH_3$); 31.9 ppm ($\boldsymbol{C}H_2CH_2NH_2$); 45.2 ppm ($\boldsymbol{C}H_2NH_2$).

FTIR: 3250 cm^{-1}, d weak (N–H coordinated to Pd). The low number of multiple bands in the spectrum suggests *trans* symmetry [27].

Raman: 3250 cm^{-1}, d weak (N–H coordinated to Pd); 288.5 cm^{-1}, s, medium, (Pd–N with contribution of Pd–Cl [28]).

2.2. Preparation and characterisation of supports

Multiwall carbon nanotubes (MWCNT) were prepared at the Laboratoire de Chimie de Coordination (CNRS-Université Toulouse) using a metal growth technique over Fe particles [29], followed by a purification treatment with H_2SO_4 solution. The sample named NT, was characterised by TEM, revealing that the MWCNT present external diameters between 8 and 21 nm and inner diameters between 4 and 12 nm, which means that they have between 7 and 16 walls. Characterisation by gas adsorption techniques suggests that sample NT has one of its ends capped by the metal particle and a carbon shell, while the other end is open [21].

Sample NT was submitted to different treatments, which are schematically shown in Fig. 1. Such treatments were: ball milling for 200 min (sample NTBM), air oxidation at 773 K for 1 h (sample NTOx) and HNO_3 oxidation at room temperature (HNO_3 70%, 14 h) (sample NTN). Sample NTOx was further treated with HCl 5 M (20 mL/g) at room temperature for 24 h in order to remove remaining metal impurities. Demineralised sample was named NTOxD. Sample NTN was treated with NaOH 0.25 M (20 mL/g, 10 h, washing until pH 7) to develop sodium compensated anionic hydroxylate groups on its surface. This sample was named NTN-ONa.

Ash content of CNT supports was measured by burning 1 g of sample in a muffle furnace at 1173 K in air and determining the remaining weight.

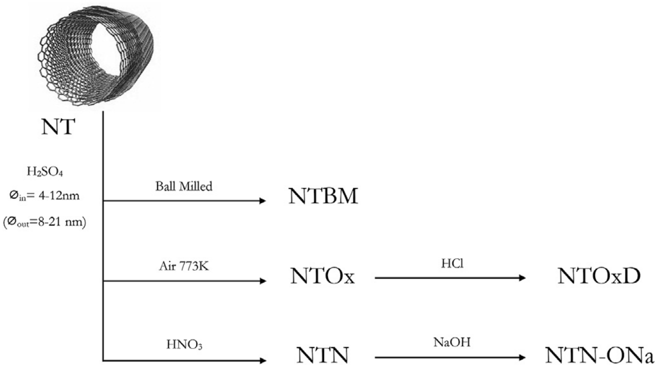

Fig. 1. Preparation of supports.

Surface texture was characterised by gas adsorption isotherms (N_2 at 77 K and CO_2 at 273 K) measured in a Quantachrome Autosorb 6B instrument. Textural parameters were calculated according to the procedure proposed by Rodríguez-Reinoso et al. [30]. Surface area was assessed from the N_2 adsorption isotherm by the BET method (S_{BET}). The total volume of micropores (V_{μ}) and the volume of micropores with diameters narrower than 0.7 nm ($V_{n\mu}$) were determined by applying the Dubinin-Radushkevich equation to the N_2 and CO_2 adsorption data, respectively. The difference $V_{\mu} - V_{n\mu}$ is taken to be the volume of micropores with diameters between 0.7 and 2 nm ($V_{s\mu}$). Finally, the volume of N_2 adsorbed by the sample between $p/p^0 = 0.2$ and $p/p^0 = 0.7$ is used to calculate the volume of pores with diameters between 2 and 7.5 nm (V_{meso}).

Surface chemistry was assessed by X-Ray photoelectron spectroscopy (XPS) measured in a VG-Microtech Multilab 3000 using Mg Kα radiation with detector in constant energy mode at 50 eV, and temperature programmed desorption (TPD) performed in a simultaneous TGA-DSC SDT 2960 coupled to a Pfeiffer ThermoStar mass spectrometer.

2.3. Preparation and characterisation of hybrid catalysts

Most catalysts were prepared by the incipient wetness impregnation method as follows: 16.2 mg of the PdTDA complex were dissolved in 7 mL of toluene and slowly added over 1 g of the nanotubes support (amounts to obtain 0.30 wt.% Pd); samples were left to dry overnight at RT and then vacuum dried at 333 K for 12 h. This preparation led to catalysts PdTDA/NT, PdTDA/NTBM, PdTDA/NTOx, PdTDA/NTOxD and PdTDA/NTN.

Searching for a more stable immobilisation of the catalyst supported on NTN-ONa, a different procedure was used: 1 g of support was suspended in a 20 mL methanol solution containing 16.2 mg of PdTDA, the mixture was stirred for 20 h at RT and then, the catalyst was filtered and thoroughly washed with methanol and toluene in order to remove ionic and weakly bound species. In this case, a more stable immobilisation by means of substitution of chloride ligands of the original complex by anionic moieties at the support's surface [29,31] is pursued. Fig. 2 shows the design strategy for the preparation of catalyst NTN-O-PdTDA.

Pd content was measured by ICP-AES. The experimental method used to extract Pd from the catalyst was described elsewhere [32].

Catalysts were characterised by X-Ray photoelectron spectroscopy (VG-Microtech Multilab 3000) using Mg Kα radiation with detector in constant energy mode at 50 eV.

Sample NTN-O-PdTDA was also characterised by X-ray fluorescence in a Philips Magix Pro PW2400 spectrometer.