Microporous and Mesoporous Materials 139 (2011) 164–172

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Hybrid Rh catalysts prepared with carbon nanotubes of different inner diameter

L.J. Lemus-Yegres [1], M. Pérez-Cadenas [2], M.C. Román-Martínez *, C. Salinas-Martínez de Lecea

Departamento de Química Inorgánica, Universidad de Alicante, Apdo. 99, Alicante 03080, Spain

ARTICLE INFO

Article history:
Received 21 June 2010
Received in revised form 20 October 2010
Accepted 20 October 2010
Available online 26 October 2010

Keywords:
Carbon nanotubes
Inner diameter
Hybrid catalysts
Confinement
Hydrogenation

ABSTRACT

Hybrid catalysts have been prepared by the immobilization of a Rh diamine complex on four multiwall carbon nanotubes of different inner diameter (average inner diameter ranging from 4 to 10 nm). The complex has been tethered to the support by the reaction of the $-Si(OCH_3)_3$ functionality in the rhodium complex with phenol type –OH groups on the support surface, that have been created by oxidation with air. The hybrid catalysts have been tested in the hydrogenation of cyclohexene and carvone. In general terms, the obtained hybrid catalysts are more active than the Rh complex in homogeneous phase and they are recyclable. It has been found that the nanotubes dimensions have an influence in the catalytic properties. In the case of the thinner nanotubes (inner Ø ~ 4 nm) the support has not a positive effect while the catalysts prepared with nanotubes of inner diameter around 7 nm give the best results.

1. Introduction

The problems of separation and reutilization of homogeneous catalysts have lead to turn the attention to hybrid catalysts, those conformed by a homogeneous catalyst (usually a metal complex) immobilized on a solid material [1].

Carbon nanotubes have interesting properties for their application as catalysts support. They have a regular porous structure, without microporosity, high stability in many reaction media and their surface (inner and outer) can be functionalized by different treatments. The active species supported on carbon nanotubes can, eventually, be located inside the tubular cavity and, in this case, the carbon nanotubes supported catalysts can be considered to act as nano-reactors.

Recently, very good results have been obtained using carbon nanotubes and nanofibres for the immobilization of metal complexes [2–5]. This kind of supports has given better results than the traditional activated carbon [4]. The catalytic activity of the complex is noticeably exalted upon immobilization in carbon nanotubes and nanofibres and it has been related with the location of the complex in the support porosity, in particular in the inner cavity of the tubular structures. As indicated by Li et al. [6], for a reaction taking place in a stereo space, such as a pore, layer or cavity, the effect of the space on the reaction can be defined as a confinement effect. Derouane has studied it in detail, particularly in the case of zeolites [7], and he has concluded that it is very difficult to quantify. For catalytic applications, apart of the existence of a constrained environment, it has to be taken into account that there must be clearance around the immobilized complex for the catalytic cycle (coordination, transformation and dissociation of the product) to take place. It means that, likely, certain dimensions of the location room would give an optimum confinement situation and it depends on the catalytic system (metal complex, reactants and products, basically).

The present work deals with the preparation of hybrid catalysts using carbon nanotubes of different inner diameters as support with the objective of analyzing the effect of the nanotubes dimensions in the catalytic properties of the immobilized complex. The Rh complex used is $[Rh(COD)NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3]^+BF_4^-$, where COD is cyclooctadiene. It is a Rh(I) tetracoordinated complex, in which the bidentate amine ligand contains a trimethoxysilane group. The largest dimension of this rhodium complex, named here Rh(NN)Si, is estimated to be about 1.5 nm. The anchoring procedure is intended to be the creation of a siloxane type bond between the metal complex and the support. Such a bond would be the result of the reaction of the $-Si(OCH_3)_3$ functionality with phenol type –OH groups on the support surface produced by air oxidation [8]. This type of bonding, frequently reported for the immobilization of metal complexes on SiO_2, zeolites and silicates [9,10], has been recently applied by our research group [2–4] for the tethering of metal complexes to the surface of carbon materials. The proposed model for the mentioned anchorage is shown in Scheme 1.

---

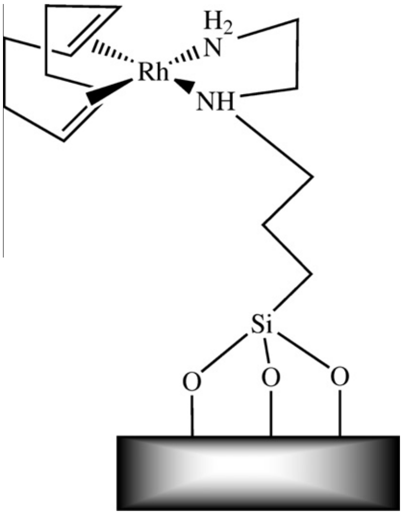
* Corresponding author. Tel.: +34 965903975; fax: +34 965903454.

E-mail addresses: lily@topsoe.dk (L.J. Lemus-Yegres), mariaperez@ccia.uned.es (M. Pérez-Cadenas), mcroman@ua.es (M.C. Román-Martínez), c.salinas@ua.es (C. Salinas-Martínez de Lecea).

[1] Present address: Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs, Lyngby, Denmark.

[2] Present address: UNED, Facultad de Ciencias, Dpto. de Química Inorgánica y Química Técnica, Paseo Senda del Rey No. 9 CP: 28040, Madrid, Spain.

1387-1811/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2010.10.034



Scheme 1. Proposed model for the anchored Rh complex.

In the present work, the prepared hybrid catalysts have been tested in the hydrogenation of two substrates: cyclohexene and carvone.

2. Experimental

2.1. Supports

Four different multiwall carbon nanotubes were used in the study. The origin of the samples and the treatments used are presented below (the number added to the general name NT has been given after the average inner diameter of the sample determined as indicated later in the text):

Carbon nanotubes NT4: Sample NT4 was synthesized at the Center de Recherche sur la Matière Divisée (CNRS-University of Orléans, France) by acetylene decomposition at 873 K on Co particles of a solid solution $Co_xMg_{1-x}O$ [11]. The as-received sample was submitted to an activation treatment with KOH with the purpose of removing amorphous carbon and opening the nanotubes [12]. The weight ratio KOH:NT4 was 3:1, the heat treatment was performed at 873 K for 1 h (heating rate 5 K/min) in a horizontal furnace under N_2 flow (40 ml/min). After cooling down to room temperature, the sample was washed five times with HCl 5 M and with distilled water to neutral pH, and then it was dried overnight at 373 K. The ash content of this sample is reduced from 9.3 wt.% to 4.5 wt.% through this treatment.

Carbon nanotubes NT5: They are commercial nanotubes from Columbian Chemical Company produced by CVD. The original sample has 0.6 wt.% ash content (Fe) and was used as received.

Carbon nanotubes NT7: Sample NT7 (named NT in Refs. [2–4]) was produced by CVD using an iron catalyst at the Institute National Polytechnique de Toulouse (INPT) [13]. The sample was submitted to acid purification treatments (H_2SO_4 and HCl) and the remaining ash content is 0.8 wt.%.

Carbon nanotubes NT10: Sample NT10 was prepared by CVD using a Fe catalyst at the Centre for Applied Energy Research (CAER) in Kentucky (USA) [14]. The original sample was treated with HCl solution (37%) and the ash content was reduced from 9.4 to 4.7 wt.%.

In order to create phenol-type surface oxygen groups, the nanotubes were submitted to a heat treatment in synthetic air flow (80% N_2, 20% O_2, 40 mL/min) for 3 h at 623 K, except sample NT7 that was oxidized at 773 K for 1 h at the INPT.

Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2010 microscope working in the acceleration range of 100–200 kV. The line resolution is 0.14 nm and the point resolution is 0.25 nm.

Raman spectroscopy measurements were carried out using a dispersive spectrometer LabRam (Jobin-Ivon) equipped with a confocal microscope, three laser lines (514, 632 y 785 nm) and a CCD detector. The obtained spectra are the average of 10 runs.

The textural properties of the original and treated carbon materials were analysed by means of N_2 adsorption isotherms at 77 K, which were carried out using the automatic volumetric apparatus Autosorb-6B from Quantachrome. The samples, approximately 0.1 g, were previously degassed at 523 K during 4 h.

To analyse the supports surface chemistry, temperature programmed desorption (TPD) experiments were done. Samples, approximately 5 mg, were heated at 20 K/min up to 1200 K, in a He flow of 100 mL/min. The gases evolved were analysed with a mass spectrometer, Balzers MSC 200 Thermostar.

2.2. Hybrid catalysts

The complex $[Rh(COD)NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3]^+BF_4^-$, where COD is cyclooctadiene, was synthesized according to the method described previously [2]. The complex name is abbreviated here as Rh(NN)Si.

The procedure to prepare the hybrid catalysts was as follows, a solution of complex Rh(NN)Si (20 mg, 0.038 mmol) in methanol (60 mL) was brought in contact with 200 mg of the oxidized carbon material and maintained under reflux for 16 h. Afterwards, the catalysts was filtered and washed with methanol in Soxhlet for 24 h. The hybrid catalysts are named adding –Rh to the name of the support.

To determine the metal content, 50 mg of the catalyst were digested with 10 mL H_2SO_4 (98%) and 5 mL HNO_3 (65%). The suspension was heated at 573 K (under reflux) until a clear solution was obtained (about 24 h). After solvent evaporation, 1 mL HNO_3 (65%) and 3 mL HCl (37%) were added. The obtained solution was transferred into a 10 mL calibrated flask and the volume completed with deionised water. The solution was then analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using Perkin Elmer Optima 3000 and 4300 equipments.

X-ray photoelectron spectroscopy (XPS) measurements were carried out in a VG-Microtech Multilab spectrometer, using MgKα (1253.6 eV) radiation from a double anode with an energy flow of 50 eV. The chamber was hold at 5×10^{-10} mbar. C1s transition was adjusted at 284.6 eV.

2.3. Catalytic activity measurements

The hydrogenation of cyclohexene and carvone was carried out in a stainless steel 40 mL Parr reactor at 333 K, using 30 mg of the hybrid catalyst and 10 mL of a 5v/v% methanol solution of the substrate. Hydrogen pressure and substrate to catalyst molar ratio (S:C) were, respectively, 10 bar and 5000:1 for cyclohexene hydrogenation, and 20 bar and 3000:1 for carvone hydrogenation. The sequence of reactions involved in carvone hydrogenation is presented in Scheme 2. The hemicetal of carvomenthone can be produced by the interaction of the substrate with the solvent.

Analysis of reaction products was performed at the end of each experiment using a HP6890 Series II chromatograph, with a HP-1 Methyl Siloxane capillary column, 30 m × 250 μm × 0.25 μm and a FID detector.

In all cases the amount of product formed corresponds to the amount of consumed substrate (in mol). This allows discarding the substrate adsorption on the catalyst surface.