



## Short communication

# Hydrodeoxygenation of guaiacol: Tuning the selectivity to cyclohexene by introducing Ni nanoparticles inside carbon nanotubes



A.B. Dongil<sup>a</sup>, L. Pastor-Pérez<sup>b</sup>, A. Sepúlveda-Escribano<sup>b</sup>, R. García<sup>a</sup>, N. Escalona<sup>c,d,\*</sup>

<sup>a</sup> Universidad de Concepción, Facultad de Ciencias Químicas, Casilla 160C, Concepción, Chile

<sup>b</sup> Laboratorio de Materiales Avanzados, Instituto Universitario de Materiales de Alicante, Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

<sup>c</sup> Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, Macul, Santiago, Chile

<sup>d</sup> Facultad de Químicas, Pontificia Universidad Católica de Chile, Chile

## HIGHLIGHTS

- Catalysts comprising Ni supported on carbon nanotubes were studied for guaiacol conversion.
- The location of the Ni nanoparticles can be controlled via the synthesis method.
- Ni nanoparticles located inside the nanotubes favor the formation of cyclohexene.
- Ni nanoparticles located outside the nanotubes favor the formation of cyclohexane.

## ARTICLE INFO

## Article history:

Received 21 October 2015

Received in revised form 30 December 2015

Accepted 2 January 2016

Available online 8 January 2016

## Keywords:

Carbon nanotubes  
Hydrodeoxygenation  
Guaiacol  
Ni

## ABSTRACT

Ni nanoparticles have been selectively loaded inside or outside commercial carbon nanotubes by the wet impregnation method, and their catalytic performance on the conversion of guaiacol in batch reactor at 5 MPa and 573 K has been studied. Different characterization techniques were used to investigate the effect of confinement in nanotubes. The catalysts showed different selectivity to cyclohexene compared to cyclohexane was enhanced when the nanoparticles were loaded inside. This result was attributed to the different adsorption mode of the molecule inside the nanotubes.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Catalytic studies focusing on hydrodeoxygenation (HDO) of 2-methoxyphenol (guaiacol), representative of the methoxy phenols found in bio-oil derived from wood, provide insights into catalyst optimization for lignin valorization technologies. Sulfide catalysts have long been studied; however, other alternatives such as monometallic and bimetallic catalysts supported over ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, zeolites or carbon nanostructures have been explored due to the fast deactivation of sulfides [1–6]. A cheaper alternative which has proven to offer good catalytic performance is Ni-based catalysts [7–13]. It has also been found that the support plays an important role in the product distribution [14]. In this sense,

carbon nanotubes (CNT) offer further opportunities due to their special electronic properties, accessibility of the active phase, chemical stability in aggressive media and inert surface which, in turns, normally requires the oxidation of the surface to obtain a high dispersion of the active phase. The selective loading of metal nanoparticles inside CNT has been increasingly explored due to the possibility of improving their catalytic performance. It has been reported that the metal-support interactions are different when the nanoparticles are located inside the nanotubes, leading to different structural and chemical properties compared to the nanoparticles deposited on the external surface [15–17]. Moreover, different adsorption modes, changes in the diffusion of the molecules along with steric constraints may be responsible for different reaction mechanisms [18–20]. These properties might be more pronounced when the internal diameter is smaller than 10 nm [21]. However, loading the nanoparticles inside smaller tubes is more complicated, and the wet impregnation assisted by

\* Corresponding author at: Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, Macul, Santiago, Chile. Tel.: +56 2 23544927.

E-mail address: [neescalona@ing.puc.cl](mailto:neescalona@ing.puc.cl) (N. Escalona).

**Table 1**  
Textural properties of supports and catalysts and Ni particle size in the catalysts.

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$V_{\text{meso}}$ (cm <sup>3</sup> /g)	$V_t$ (cm <sup>3</sup> /g)	dp-TEM (nm)
CNT	300	0.01	1.76	1.77	–
CNTm	375	0.02	0.42	0.44	–
Ni/CNT	241	0.01	1.07	1.08	6.1
Ni/CNTm	314	0.01	0.41	0.42	6.5

ultrasound over previously cut CNT has been one of the most applied synthesis methods [22].

Therefore, the focus of this work was to explore the distinctive catalytic behavior of Ni nanoparticles located inside and outside the surface of commercial carbon nanotubes on the selectivity and conversion of guaiacol.

## 2. Experimental

### 2.1. Catalysts preparation and characterization

Commercial carbon nanotube Nanocyl 3100 (>95% purity) was used as starting material (CNT). Their characterization by thermogravimetry, XPS spectra has been included in the supporting information Fig. S1. A portion of the parent CNT was submitted to ball milling treatment in a planetary stainless steel Spex 800 rpm for 1 h and labeled as CNTm. Two catalysts were prepared by wet impregnation using the proper amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.9%, Sigma–Aldrich) to obtain 15 wt.% Ni. The Ni/CNT catalyst was prepared with an ethanolic solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.025 mol/l); after stirring the resulting slurry for 12 h, the solvent was removed under vacuum at 333 K. The Ni/CNTm catalyst was prepared with an ethanolic solution of the metal precursor; the slurry was sonicated for 1 h in order to favor the diffusion of the Ni precursor inside the nanotubes [23] and then the same procedure as that for Ni/CNT was followed. Finally, the materials were treated at 723 K for 5 h under flowing Ar (50 mL/min). The materials were characterized by N<sub>2</sub> adsorption at 77 K, X-ray powder diffraction, TEM images, H<sub>2</sub>-TPR profiles, CO-chemisorption and X-ray photoelectron spectroscopy (XPS). More details of the technical characterization are described elsewhere [7,24].

### 2.2. Hydrodeoxygenation reaction

HDO of guaiacol was carried out in an autoclave reactor operating in the batch mode at 573 K and 5 MPa employing 200 mg of catalyst, previously reduced at 623 K for 4 h under H<sub>2</sub> as employed in previous works [7,24]. The samples were analyzed on a Perkin Elmer CG (autosystem XL), with a semi-capillary column CPSIL-5CB. The specific rate for the total conversion of guaiacol was deduced from the plot of the initial slope of conversion as a function of time, and expressed in mol g<sup>-1</sup> s<sup>-1</sup>. The deoxygenation (HDO) rate was calculated from the conversion of guaiacol to O-free compounds (benzene, cyclohexane, cyclohexene, and analogous compounds). Reaction blank tests were performed with the bare supports and no activity was observed during the 4 h reaction time. Additional experimental details can be found elsewhere [24,25].

## 3. Results

### 3.1. Characterization

The N<sub>2</sub> adsorption/desorption isotherms at 77 K of CNT and CNTm supports are shown in Fig. S2 and the textural properties

are summarized in the Table 1. The BET surface area was 300 m<sup>2</sup>/g and 375 m<sup>2</sup>/g for CNT and CNTm supports respectively. The higher value obtained for the sample CNTm seems to indicate that the treatment has effectively opened some of the tubes, thus increasing the available surface area. This is agreement with a new hysteresis loop observed at medium relative pressure for CNTm support which is associated with the mesoporosity originated by the inner hollow cavity of open-ended open some of the tubes. The marked decrease of the pore volume for CNTm can be explained by the larger proportion of agglomerated nanotubes compared to CNT as shown in the representative TEM image in the supplementary information Fig. S4b. The surface area of the catalysts is also included in Table 1, and the values show a decrease which is approximately proportional to the 15 wt.% Ni loaded in comparison to the parent supports, and the same happens with the pore volumes.

The XRD patterns of the supports are reported in Fig. S3. They both show the characteristic diffraction of the (002) plane of graphite at  $2\theta = 26^\circ$  slightly shifted to higher angles due to the curvature of the layers [26]. No changes were observed on the profile of the sample CNTm compared to CNT, this confirming that the treatment did not significantly affect the CNT structure.

Representative TEM images of the catalysts are shown in Fig. 1. The morphology of the CNT consists of long straight graphitic walls with barely any defects or amorphous carbon on the surface. Moreover, the images in Fig. S4, shows that most of the tubes of sample CNT were closed. The images of catalysts in Fig. 1b and d show two representative areas where the Ni nanoparticles were found in open-ends tubes for Ni/CNTm catalyst, Fig. 1d, and on the external surface for Ni/CNT catalyst, Fig. 1b. As long as the particle size is concerned, it can be observed that nanoparticles are homogeneously distributed on the supports with a narrow particle size distribution for both catalysts. TEM images of the catalysts were used to estimate the average particle size reported in Table 1 in agreement to previous findings [27].

Fig. 2 shows the evolution of H<sub>2</sub> consumption as a function of temperature for the prepared catalysts in H<sub>2</sub>-TPR. They both show two main peaks, the first one appearing at 591 and 473 K for Ni/CNT and Ni/CNTm catalysts, respectively. The contribution at higher temperatures appeared as a broad band with maxima at 780–790 K. Reduction of bulk NiO has been reported at 638 K; however, when it is supported the reduction temperature may vary depending on the size of the nanoparticles and on the interaction with the support, with a reduction temperature in the range 423–873 K [15,27,28]. For CNT supports, the possibility of nanoparticles being located inside the nanotube has also been considered as a cause for different reduction temperature [25,26]. The images obtained by microscopy suggested that a proportion of nanoparticles in Ni/CNTm catalyst are located inside, and this would explain the lower temperature at which the reduction of NiO was observed. Apparently, the metal–oxygen bond is more easily reduced by H<sub>2</sub> when the metal oxide is located inside the CNT. The inner cavity of the CNT support is more electron deficient than the outer surface, this leading to a stronger interaction between the inner surface of support and the oxygen in the metal oxide which weakens the strength of the metal–oxygen bond [29].

Download English Version:

<https://daneshyari.com/en/article/205214>

Download Persian Version:

<https://daneshyari.com/article/205214>

[Daneshyari.com](https://daneshyari.com)