



# Synthesis and characterization of vanadium nanoparticles on activated carbon and their catalytic activity in thiophene hydrodesulphurization

Susana Pinto<sup>a,b</sup>, Lindora D'Ornelas<sup>b</sup>, Paulino Betancourt<sup>a,\*</sup>

<sup>a</sup> Centro de Catálisis, Petróleo y Petroquímica, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, AP, Caracas 40679, Venezuela

<sup>b</sup> Centro de Química Organometálica y Macromolecular, Facultad de Ciencias, Universidad Central de Venezuela, AP, Caracas 47778, Venezuela

## ARTICLE INFO

### Article history:

Received 23 August 2007

Received in revised form 18 February 2008

Accepted 21 February 2008

Available online 6 March 2008

### Keywords:

Nanoparticles

Vanadium carbide

V<sub>2</sub>O<sub>3</sub>

Hydrodesulphurization

## ABSTRACT

Vanadium nanoparticles (~7 nm) stabilized on activated carbon were synthesized by the reduction of VCl<sub>3</sub>·3THF with K[BET<sub>3</sub>H]. This material was characterized by inductive coupled plasma-atomic emission spectroscopy (ICP-AES), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analyses. The catalytic performance of the carbon-supported vanadium was studied using thiophene hydrodesulfurization (HDS) as model reaction at 300 °C and P = 1 atm. The catalytic activity of the vanadium carbide phase on the activated carbon carrier was more significant than that of the reference catalysts, alumina supported NiMoS. The method proposed for the synthesis of such a catalyst led to an excellent performance of the HDS process.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Over the last decade, petroleum refining industry has been facing important challenges because of the continuously decreasing permissible amount of emissions, such as SO<sub>x</sub>, NO<sub>x</sub> and aromatics from the combustion of fossil fuels. With the currently used technology, the quality of fuels prescribed by the new environmental regulations can be attained by the significant modifications of refining operations. This may include a considerable increase in the amount of the consumption of H<sub>2</sub> of the conventional catalyst (e.g. sulphide CoMo or NiMo), and the decrease of daily throughputs. At certain point, the additional cost of these modifications can be offset by novel catalysts. An ideal situation, which would require minimal modifications, involves the use of a novel multi-functional catalyst, which could replace conventional catalysts in the currently used reactors. In last decade, efforts have been made to develop such catalysts for hydroprocessing. Metal carbides have been identified as the potential catalysts for such applications. Interstitial carbides of early transition metals (groups IVB–VIB) are produced by dissolving carbon atoms into the metal lattices. These carbide materials have interesting physical and chemical properties, which combine the characteristic properties of three different classes of materials: covalent solids, ionic crystals, and transition metals. It

has been suggested that the introduction of carbon into the lattice of the early transition metals results in an increase of the lattice parameter. This leads to an increase in the d-electron density providing that the same number of levels is retained [1]. Then, after carburization, the early transition metals exhibit the noble metals-like behavior. Because of their small atomic radius, carbon can nest in the interstices of the lattice. Additionally, the research and development of transition metal nanoparticles has received a lot of attention in many areas of science. This interest is because nanosized particles show different physical and chemical properties to those of the same materials in the bulk [2,3]. The main reasons for these differences originate in the electronic properties and in the very high ratio between superficial atoms and total number of atoms in the particles found in these nanomaterials.

Inspired by these ideas, we designed a new method for preparing carbon-supported vanadium nanopowder by means of the reduction of the metal adduct VCl<sub>3</sub>·3THF with K[BET<sub>3</sub>H] at room temperature, obtaining a mixture of vanadium carbide and V<sub>2</sub>O<sub>3</sub>. This was well confirmed by our experimental results. Compared with conventional processes (high temperature), the reaction conditions are much simpler, and the as-obtained vanadium carbide nanopowder is the main phase and is well dispersed.

## 2. Experimental

All the reagents are commercially available and of analytical grades and used without further purification. All operations were carried out under argon atmosphere using Schlenk techniques [4].

\* Corresponding author. Tel.: +58 212 6051649; fax: +58 212 6051220.  
E-mail address: [pbetanco@strix.ciens.ucv.ve](mailto:pbetanco@strix.ciens.ucv.ve) (P. Betancourt).

## 2.1. Catalyst preparation

The vanadium nanoparticles were synthesized following the method established by Bönnemann [5]. A solution of  $K[BET_3H]$  (1 M, 4.6 ml, 4.6 mmol) in tetrahydrofurane (THF) was added dropwise to a suspension of  $VCl_3 \cdot 3THF$  (0.99 mmol) in THF at room temperature during 2 h. After 2 h of constant stirring at room temperature, a dark brown solution was obtained. The KCl formed during the reaction was removed by filtration. The dark solution obtained was added to an activated carbon/THF suspension. This suspension was stirred for at least 24 h, and then dried under vacuum during  $\sim 24$  h resulting in a black solid. Finally, the nanometric solid product was exposed to air. No changes in temperature were observed during synthesis process.

## 2.2. Characterization

### 2.2.1. Elemental analysis

Elemental analyses were performed by the Centro de Química Analítica-UCV, Venezuela. The characterization by ICP-AES of the obtained product show vanadium content of 0.64% in weight.

### 2.2.2. X-ray photoelectron spectroscopy studies

The XPS were recorded with a VG ESCALAB 220i-XL spectrometer equipped with Al source (Al  $K\alpha = 1486.6$  eV). The analyzer was operated in a constant pass energy mode ( $E_{pass} = 30$  eV) using the electromagnetic mode for the lens. Energy correction was performed by using the C1s level of carbon as a reference. The deconvolutions of the XPS spectra were carried out using a XPS Peak Fitting program Version 4.1.

### 2.2.3. X-ray diffraction measurements

XRD patterns of the samples were obtained using a Bruker D-8 Advance apparatus (Cu  $K\alpha$  radiation,  $\lambda = 0.154178$  nm, nickel filter) operating at 35 kV and 30 mA.

### 2.2.4. Transmission electron microscopy

The morphologies and structures of the obtained product were observed with a Hitachi H-800 high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The diameters were measured directly for particles shaped approximately circular.

### 2.2.5. Thiophene hydrodesulfurization

The catalyst was evaluated for the HDS of thiophene at 300 °C,  $P = 1$  atm. Before the reaction, the materials were activated in situ under  $H_2/H_2S$  flow for 1 h at 300 °C. A commercial HDS catalyst (NiMoS/Al<sub>2</sub>O<sub>3</sub>; 3.1%Ni and 15%Mo; SSA = 200 m<sup>2</sup> g<sup>-1</sup>) was used as reference catalyst.

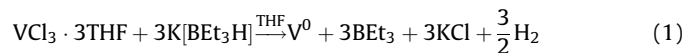
The products were analyzed by gas chromatography (Varian 3700, FID), and the reaction rate was calculated according to the equation  $R = FX/m$ , where  $R$  is the HDS rate (mmol g<sup>-1</sup> s<sup>-1</sup>),  $F$  the thiophene molar flow rate,  $X$  the thiophene conversion, and  $m$  is the catalyst mass.

## 3. Results and discussion

The crystallinity of the as-synthesized V/carbon sample was examined by X-ray diffraction (XRD). The XRD patterns of the sample, having a low metal concentration (0.64 wt.%) exhibit several peaks. The XRD pattern consists of peaks corresponding to V<sub>2</sub>O<sub>3</sub> (JCPDS 34-0187), VC<sub>1-x</sub> (JCPDS 73-0476) and poorly crystalline carbon. The characteristic peaks of the vanadium carbide were not apparent because is masked by the support phase. It is expected that only at high metal contents most peaks become clearly outlined. VC<sub>1-x</sub> belongs to space group  $Fm\bar{3}m$  with

a small amount of C vacancies, and the vacancies are randomly distributed in the VC<sub>1-x</sub> lattice [6]. The apparent carbon deficiency observed for the air exposed solid, could be a consequence of the presence of oxygen in the lattice [7].

The reactions between  $VCl_3$ ,  $K[BET_3H]$  and C may be written as follows:



The reaction between  $VCl_3$  and  $K[BET_3H]$  occurred first (Eq. (1)), and after started the reaction between  $V^0$  and C, so VC<sub>1-x</sub> was synthesized. As a result of the reaction, the large heat of formation of VC<sub>1-x</sub> might have accelerated the propagation of the reaction. Therefore, the reaction could be completed “easily”. When this system was exposed to air (molecular oxygen) probably a partial oxidation occurs, according to Eq. (3). Martínez-Mendez et al. [8] have proposed that due to the high reactivity of the THF stabilized metallic nanoparticles of titanium, vanadium and niobium with air, the surface analyses only showed the presence of the oxidized species.

X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental composition of the V/carbon nanocrystals, and can further provide evidence for the formation of vanadium carbide. The XPS spectrum for the vanadium/carbon systems exposed to air (Fig. 1) shows three different signals in the region for V2p<sub>3/2</sub> with binding energies at 516.6 eV, 515.3 eV and 513.4 eV (as shown in Fig. 1), indicate the V2p<sub>3/2</sub> species of VO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub> and V<sub>8</sub>C<sub>7</sub> (or V<sub>4</sub>C<sub>3</sub>), respectively [9]. The results agree well with the XPS spectrum of O1s energy region for vanadium carbide (not shown). The XPS spectrum of O1s energy region for vanadium carbide contains three peaks. The peaks at 532.9 eV and 531.7 eV are considered to be due to O<sup>-</sup> and OH<sup>-</sup>, respectively. These two kinds of oxygen species are mainly originated from air. The O1s peak with the binding energy of 530.3 eV is ascribed to V<sub>2</sub>O<sub>3</sub>. All assigned binding energies agree well with the literature values [9,10].

The TEM analysis (micrograph, diffraction pattern and histograms) for the V/carbon system is shown in Fig. 2. This material shows a homogeneous dispersion on the support and has a sphere-like morphology. The vanadium system shows nanoparticle sizes ranging from 2 nm to 24 nm and a mean size of 7 nm (Fig. 3).

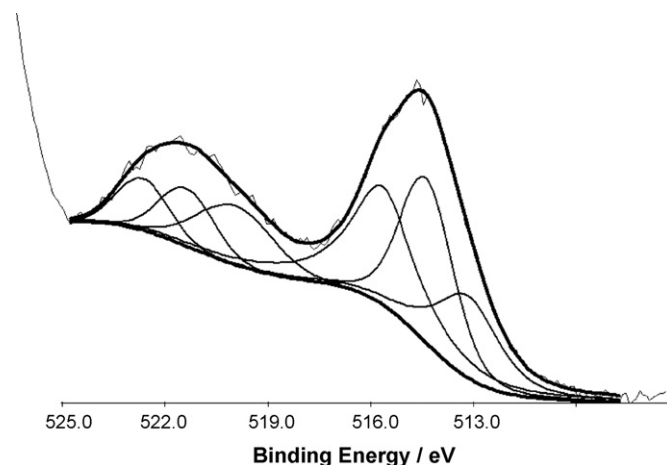


Fig. 1. XPS spectrum of V2p for the vanadium/carbon nanostructured system exposed to air.

Download English Version:

<https://daneshyari.com/en/article/5369431>

Download Persian Version:

<https://daneshyari.com/article/5369431>

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