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Impregnating ionic Pt species on vanadium oxide nanotubes

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ABSTRACT

Vanadium oxide nanotubes (VNT) have drawn increasing attention as vanadium compounds may be used in a wide range of applications. In this contribution, VNT was synthesized by a hydrothermal treatment from V_2O_5 using hexadecylamine as template. XRD, FTIR, SEM, TEM/HRTEM and TG analyses were used to investigate their chemical stability and suitability to adsorb platinum ionic species without damaging the nanostructure. It was shown that the nanostructures are open-ended multiwalled nanotubes, formed by 13–16 layered walls, with inner diameter of 30–50 nm and outer diameter of 150–200 nm. The impregnation of Pt was found to be feasible but their structure and morphology are sensitive to the pH of the impregnation media.

1. Introduction

Nanotubes of transition metal oxides are interesting nanostructures as they may present a number of oxidation states with different redox-active properties. Vanadium oxide nanotubes (VNT) have drawn increasing attention as vanadium compounds may be used in a wide range of catalytic and electrochemical applications [1]. It has indeed been reported that the mixed valent vanadium oxide nanotubes exhibit distinct optical [2] and electrochemical properties [1], which may be changed by controlling some characteristics such as the interlayer distance during preparation [3]. It is possible since the layered structure of V_2O_5 allows the synthesis of different phases with various organic or metal cations intercalated between the VO_x layers. Some authors have indeed reported on the exchange of protonated organic templates with nonhydrolyzing salts of Cd, Mn, Zn, Co, Cu, Ni and Mg [4–7]. These cations are rather small, leading to a decrease of the distance between the layers and an improvement in the thermal stability of such nanostructures. Nevertheless, the ability of vanadium oxide nanotubes to accommodate larger ions, such as some noble metal ionic species, has rarely been investigated. This knowledge is rather critical if these nanomaterials are taken to design bifunctional noble metal-based nanostructured catalysts, where both metallic and redox-active sites are demanded. Undoubtedly, the development of nanostructured catalysts supported on tube-shaped nanomaterials represents a step forward in exploiting the remarkable physico-chemical properties provided by the nanoscale, taking advantage of their unique characteristics due to their shape-specific and quantum size effects [8].

This contribution examines the VNT chemical stability and its flexibility to allow topochemical reactions with ionic Pt species under the usual conditions applied for heterogeneous catalysts preparation without damaging the nanostructure.

2. Experimental

VNT was synthesized from a suspension of V_2O_5 and hexadecylamine, with a molar ratio 1:1, prepared in distilled water and allowed to hydrolyze under vigorous stirring for 48 h [9]. The composite was hydrothermally treated at 180 °C for 7 days in a Teflon-lined autoclave with a stainless steel shell, which was allowed to naturally cool down to room temperature. The resulting material was extensively washed with ethanol and hexane and dried at 80 °C for about 10 h. All chemicals were used without further purification.

The chemical and structural stabilities were investigated by suspending the as-synthesized sample in aqueous solutions with different pH, adjusted with HCl and NH_4OH, for 4 h. They were then washed and dried overnight at 100 °C. All samples were carefully weighted before and after each experiment in order to detect any dissolution under these pH conditions.

The nanotubes were also impregnated with aqueous solutions of H_2PtCl_6 and $(NH_3)_4Pt(NO_3)_2$ with the appropriate concentrations to obtain a nominal Pt load of about 1 wt.%. The initial pH values of both impregnation solutions were 3.1 and 5.7, respectively. After 4 h of vigorous stirring, the excess solution was removed by filtration and the powders were washed and dried overnight at 100 °C. All samples were labeled following their

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composition or the pH value at which it was treated. For instance, VNT1 stands for a VNT treated with an aqueous solution at pH 1.

X-ray powder diffraction (XRD) was performed using a Rigaku Miniflex diffractometer with Cu Kα radiation, operating at 40 mV. The measurements were carried out with 2θ ranging from 1° to 60°, with a scanning rate of 0.01 s^{-1}.

The nanostructures were imaged with a JEOL JSM-5800 LV SEM, equipped with a secondary electron detector. The TEM/HRTEM analyses were carried out using a Tecnai 20 FEI microscope operating at 200 kV and the elemental analyses were performed with a EDAX Energy Dispersive Spectrometry (EDS) system. All measurements were performed using Axion Vision 4.0 software.

Infrared spectra were collected in a Nicolet Magna 560 spectrometer. The samples were pressed with KBr (3 wt.%) and the measurements were taken from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

Thermal analyses were conducted in both air and nitrogen flow at a heating rate of 20 °C/min from room temperature to 650 °C in a SDT-Q600 TA Instruments equipment.

3. Results and discussion

The X-ray diffraction pattern of the as-synthesized material (Fig. 1) features the low-angle reflection peaks ($2\theta < 15°$) typical of well-ordered layered structures, corresponding to the 0 0 *l* reflections. Peaks with lower intensity at higher Bragg angles are also detected (not shown) and are regarded to the *h k* 0 reflections of the two dimensional vanadium structures within the layers. The interlayer distance calculated from the *d* values of the 0 0 1 reflection peak was determined to be 3.26 nm, which is in line with the values reported in the literature for a similar synthesis procedure [10]. This distance is also consistent with the length of the hexadecylamine chain (d_{calc} ($C_{16}H_{33}NH_2$) = 3.3 nm) [11] used as structure-directing agent in this work, evidencing that the intercalated long chain alkylamine lays perpendicular to the oxide layers as suggested elsewhere [8,9,11].

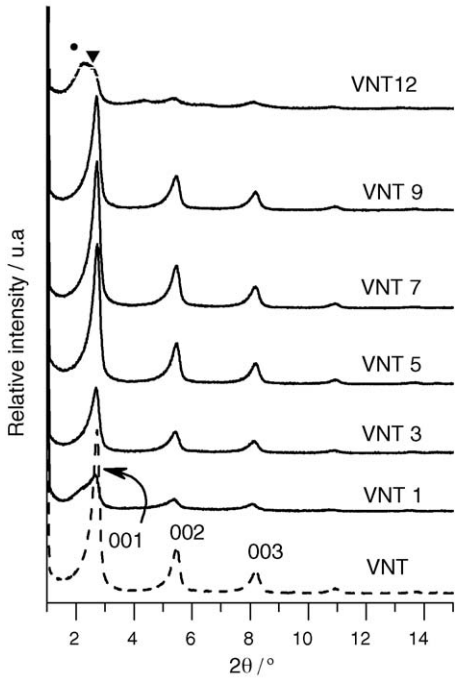

Fig. 1. XRD patterns of as-synthesized vanadium oxide nanotubes (VNT) and after exposure to aqueous solutions at different pH (VNT1–12).

It should be noted that no reflection corresponding to crystalline vanadium pentoxide used as starting material could be detected. Indeed, the XRD patterns (Fig. 1) and SEM investigations (Fig. 2a) indicated that the synthesized material consists mainly of well-developed tubes. It can also be observed by SEM images that the nanotubes are grown in bundles. The TEM and high-resolution TEM (HRTEM) analyses of the vanadium oxide nanotubes are depicted in Fig. 2b and c. It is shown that the nanostructures are open-ended multiwalled nanotubes (indicated by arrows in Fig. 2b), formed by 13–16 layered walls, with inner diameter of 30–50 nm and outer diameter of 150–200 nm. The dark fringes represent the VO_x layers while the bright parts reveal the interlayer. The measured average interlayer distances were around 3.5 nm, quite consistent with the estimated values obtained by XRD; however, it should be mentioned that it varied along the nanotube length. All these features are dependent on the preparation conditions, particularly the template molecule, its concentration and time of hydrothermal treatment as reported elsewhere [9,10,12].

A series of experiments was designed and carefully performed in order to evaluate the chemical stability of the nanotubes as well as their flexibility to allow exchange reactions with large ionic noble metal species without damaging the nanostructure.

The possibility of extracting the structure-directing agent was tested firstly by dispersing the vanadium oxide nanotubes in an aqueous media under a wide range of pH media, simulating thus the conditions for the noble metal adsorption step used for catalyst preparation. After 4 h of vigorous stirring, the powders were centrifuged, dried at 100 °C and characterized by XRD, SEM, TEM/HRTEM, FTIR and TGA/DTA analyses in order to assess any structural and morphological changes.

The 0 0 *l* peaks in the XRD patterns for these samples are also depicted in Fig. 1 and show that the layered structure was retained in all cases. However, two peaks at 0 0 1 may be envisaged for both VNT1 and VNT12 (marked in Fig. 1) and allow the identification of two kinds of layered distances (VNT1 – d_1 = 4.03 nm; d_2 = 3.28 nm; VNT12 – d_1 = 3.89 nm; d_2 = 3.37 nm). As a matter of fact, a close analysis of the diffractograms of these two samples revealed that two peaks are detected at all 0 0 *l* reflections. The larger interlayer spacings may be attributed to the insertion of water molecules (VNT1) and NH_4^+ ions (VNT12) between the VO_x layers along with the pre-existing hexadecylamine. Indeed, FTIR spectra indicated that the alkylamine is still intercalated between the layers even after exposing the nanotubes at any of the tested conditions as the characteristic stretching (2956, 2918 and 2849 cm^{-1}) and bending (1468 cm^{-1}) modes of C–H vibration in the amine were detected. Furthermore, the TGA curves (not shown) revealed that while the weight loss is around 46–48% for the samples treated in a pH range of 3–9, it increased to 58% for those samples submitted to more severe pH conditions (VNT1 and VNT12). As the weight loss is primarily associated with the decomposition of the hexadecylamine, these results corroborate the suggestion of water or NH^{4+} insertion into the nanostructure.

As regarding the structure of the vanadium layers, the IR spectra also presented strong absorptions at 486 and 571 cm^{-1}, related to symmetric and asymmetric stretching vibrations of V–O–V, and at 996 cm^{-1} assigned to the V=O bond from the vanadyl groups [13]. Nevertheless, it is worth noting the appearance of another absorption band in the V–O vibration region (Fig. 3) of the VNT1 and VNT12 spectra. By the absorption frequencies (643 cm^{-1}), it seems clear that these vibrations arise from different V–O bonds in the VO_x layers. These findings suggest that the structure of vanadium layers is somehow rearranged in aggressive acidic or basic media.

In a pretty good agreement with all those reported results, electron microscopy studies showed that the nanotubular shape

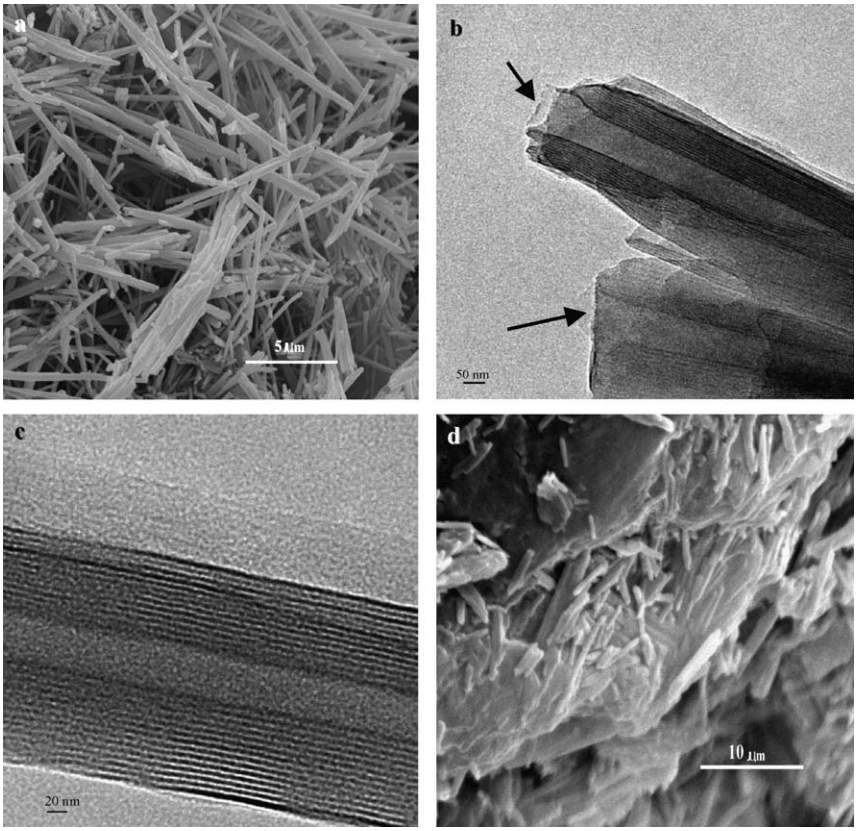

Fig. 2. SEM (a); TEM (b) and HRTEM (c) images of as-synthesized vanadium oxide nanotubes (VNT); SEM image of a VNT exposed to aqueous solution at pH 12 (d). In the TEM/HRTEM images, the dark lines depict the VO_x layers and the bright ones the alkylamine template.

was in no way damaged by aqueous solutions with pH values of 3–9 and, as a consequence, the morphology resembles that of the as-synthesized nanotubes depicted in Fig. 2a–c. Conversely, extreme low or high pH conditions seem to modify the VNT morphology leading to a poorly-defined tube-shaped material as presented in Fig. 2d. It should be stressed that this image is quite representative of both VNT1 and VNT12 samples as the same effect was observed under those conditions.

All changes observed for VNT1 and VNT12 might be caused by a partial dissolution of the as-synthesized VNT once it is suspended in the corresponding aqueous solution. Indeed, by determining the weight of the samples recovered after the treatments it could be

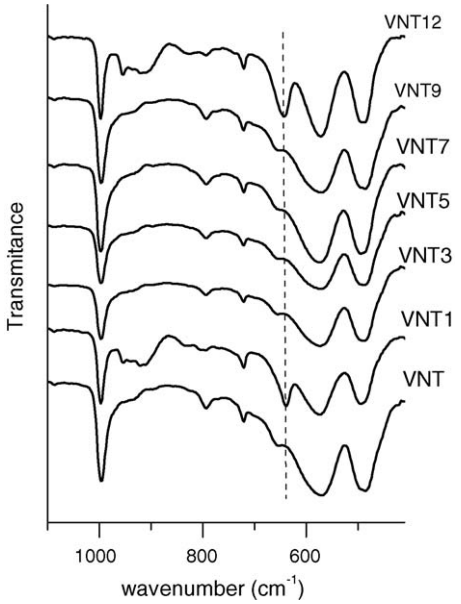

Fig. 3. FTIR spectra in the V–O vibration region of the studied vanadium oxide nanotubes.

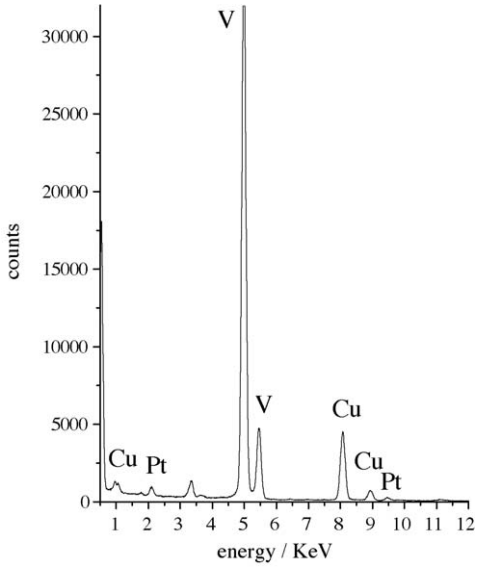

Fig. 4. Typical energy dispersive X-ray spectrum (EDS/TEM) of the studied vanadium oxide nanotubes.

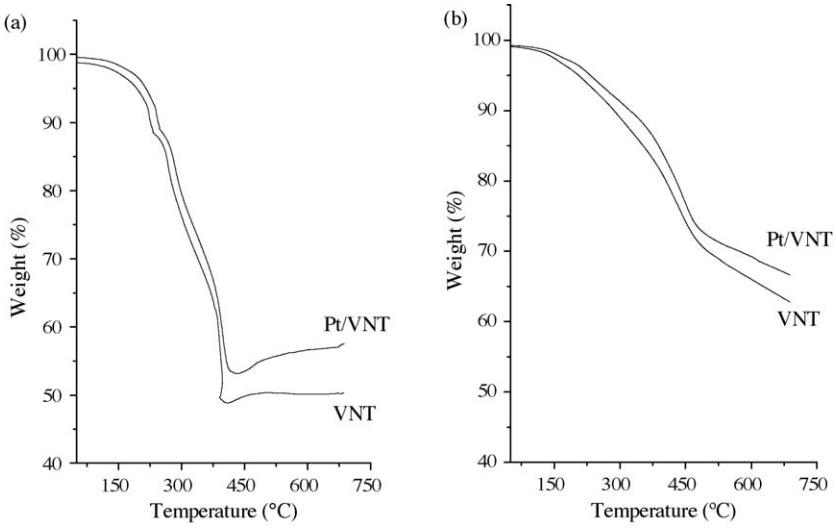

Fig. 5. TG profiles of VNT and Pt/VNT samples under air (a) and nitrogen (b) flow.

verified that a weight loss did occur when the pH of the aqueous solution was adjusted to either 1 (weight loss of 44%) or 12 (weight loss of 59%).

Platinum impregnation was carried out with both anionic and cationic metal precursors within the pH range established based on the above-discussed results, avoiding thus any strong structural modification or dissolution due to the metal solutions themselves. The metal introduction was confirmed by collecting the energy dispersion X-ray spectra of different regions of all samples during TEM analyses. A typical spectrum is depicted in Fig. 4 to illustrate the quality of the results.

Similar XRD patterns were recorded and it was found no significant difference in the interlayer distances compared to the genuine ones as determined by the 0 0 1 planes. Distances of 3.31 and 3.20 nm were determined for the samples impregnated with H_2PtCl_6 and $(NH_3)_4Pt(NO_3)_2$, respectively. It seems that neither anionic nor cationic Pt species are inserted between the vanadium layers under these impregnation conditions. Accordingly, the IR spectra of such impregnated samples (not shown) exhibited all absorption vibrations previously identified for the as-synthesized nanotubes, confirming that the alkylamine molecules are still intercalated into the vanadium nanostructure. These findings therefore provide evidence that no ionic exchange reaction or extraction of dodecylamine take place upon impregnation, which may thus be associated with an ordinary electrostatic adsorption of such ionic species in solution. Finally, by analyzing the higher Bragg angle region corresponding to $h\,k\,0$ reflections, it was seen that no evident damage was caused to the vanadium layer either.

After platinum impregnation higher weight losses were determined by TG analyses, which is consistent with the decomposition of adsorbed platinum complexes along with the alkylamine up to 400 °C. An increase of mass was observed above this temperature for the analyses carried out under air (Fig. 5a), which may be ascribed to the oxidation of vanadium from the collapsed layers into vanadium oxide (V_2O_5) as well as the formation of platinum oxide from the previously adsorbed ionic species. It could indeed be observed that the mass increased more significantly for the impregnated nanotubes samples. Fig. 5b is presented to contrast the TG profiles obtained under inert conditions (nitrogen flow) instead.

The images obtained by examining both impregnated samples by SEM and TEM/HRTEM are quite similar to those earlier presented in Fig. 2, and indicate that the tubular morphology is well preserved in all adsorption experiments.

4. Conclusions

It is feasible to impregnate vanadium oxide nanotubes with chlorine and chlorine-free platinum salts by controlling the noble metal adsorption conditions. Attention should be drawn to the pH of the impregnation media as both the structure and morphology of the nanotubes were shown to be sensitive to strong acidic and basic aqueous solutions.

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