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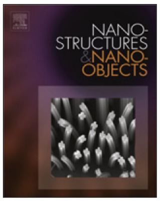

Assessing carbon or tungstates coverage of ZrO_2 nanoparticles supported on MWCNT *via* NO_x-TPD

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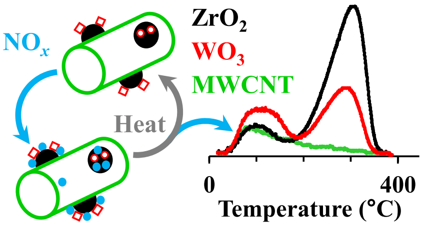
HIGHLIGHTS

- The coverage of ZrO_2 nanoparticles supported on MWCNT by C or WO_3 was assessed.
- Only NO_x-TPD could provide in-depth characterization of these complex nanomaterials.
- The size of the ZrO_2 nanoparticles estimated by TEM and NO_x-TPD were consistent.
- Monolayer coverage of ZrO_2 by WO_3 was nearly complete only when excess W was added.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-walled carbon nanotubes (MWCNT) promoted by oxides, that are far from trivial to characterize, have emerged as promising candidates in several fields such as biosensors and catalysis. In this study the coverage of ZrO_2 nanoparticles supported on MWCNT, by carbonaceous deposits or tungstates was investigated by NO_x temperature-programmed desorption (NO_x-TPD). ZrO_2 coverage by carbonaceous deposits was found to be about 30 %, whereas that by tungstates varied from 40 to 77 % depending on the W loading of the sample. The size of the ZrO_2 particles estimated by NO_x-TPD (∼2.3 nm) was found to be in excellent agreement with that determined by TEM. Remarkably, it was found that W interacted preferentially with the ZrO_2 nanoparticles for a W surface density of 1.9 W/nm^2_{ZrO2} (half monolayer coverage of the ZrO_2 nanoparticles by tungstates). Monolayer coverage of ZrO_2 by tungstates was nearly complete when introducing a W loading twice as high as that theoretically needed. These insights into the surface coverage of ZrO_2 by carbon or tungstates could not be obtained by any means other than NO_x-TPD, which makes it a unique method to provide advanced characterization of the surface of oxides supported on MWCNT, in particular, and carbon supports, to a broader general interest.

1. Introduction

Since the original discovery of carbon nanotubes (CNT) by Ijima in the early nineties [1] the properties of these materials have been extensively studied in various fields [2–5]. In the catalysis domain, CNT and multi-walled carbon nanotubes (MWCNT) have been suggested to be promising catalyst supports or promoters, in particular when modified with metals and/or oxides [6,7]. Regarding the modification of MWCNT by addition of ZrO_2, very few studies have been reported in the literature to our knowledge [8–20], although ZrO_2 has long been of interest in catalysis [21], in particular for acid-catalyzed reactions when promoted by sulfates [22] and tungstates (WO_x) [23–25]. Characterization

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of the ZrO_2-modified MWCNT materials has been carried out by electron microscopies [8–11,13,15,16,18–20,26] and XRD [8–13,15,16,18,20,26], as long as crystalline ZrO_2 particles are large enough for detection. From these studies it can be concluded that the size of the ZrO_2 particles were rather widespread [9–11] and higher than or equal to 10 nm in the majority of the synthesized samples [8,9,11,13,18,19]. Recently we proposed that narrowly distributed, highly dispersed, ZrO_2 nanoparticles (2–3 nm) could be obtained by grafting zirconium acetylacetonate ($Zr(acac)_4$) on MWCNT that were previously functionalized in nitric acid [14–17].

Although estimating the size of the ZrO_2 nanoparticles by XRD and TEM remains reliable, these physical methods are limited when interest lies in characterization of their surface, which is of fundamental importance when a catalytic application is considered. Recently, we have shown that the accessible surface of ZrO_2 in complex materials can be accurately estimated with the use of a novel chemisorption technique, namely the adsorption of nitrogen oxides ($NO_x = NO + NO_2$) at RT followed by their temperature-programmed desorption (NO_x-TPD) [27,28]. Thus, we have found it particularly interesting to characterize the size and accessible surface of ZrO_2 nanoparticles supported on MWCNT (ZrO_2/MWCNT) by this newly-developed technique.

The aforementioned ZrO_2/MWCNT composite has been further functionalized by adding W to make tungsten-promoted ZrO_2 nanoparticles supported on MWCNT (WO_3-ZrO_2/MWCNT). Due to their intrinsic acid properties, tungstated zirconias have attracted the attention of the catalysis community for about three decades [29]. Several studies have shown that the W surface density (W/nm^2), also reflecting the coverage of ZrO_2 by tungstates [30,31], is the critical parameter when determining performance of these catalysts in various catalytic reactions [25,29]. Consequently, much work has been devoted to determining the W surface density for which monolayer coverage of WO_x on a ZrO_2 support is achieved.

Physical probes such as Raman [24,31–33], Ion Scattering [34] and X-ray Photoelectron [35–39] spectroscopies have proven to be useful when characterizing bulk tungstated zirconias, however, there is inherent difficulty when using Raman spectroscopy to characterize lowly-loaded samples, such as the WO_3-ZrO_2/MWCNT samples described in this study. Furthermore, Ion Scattering and X-ray Photoelectron spectroscopies (ISS and XPS) are not readily available to all scientists characterizing these types of materials and this offers potential for new methods that are capable of characterizing these complex materials. The adsorption of chemical probes such as CO and CO_2 followed by FT-IR (CO [40]) or volumetric analysis (CO [34,40], CO_2 [31]) has also been used to characterize the coverage of ZrO_2 by tungstates. FT-IR becomes less favorable when a carbon support is introduced due to carbon absorbing the IR beam. In addition, the dependence of CO and CO_2 adsorption on the nature of the ZrO_2 polymorph being investigated [41] increases the uncertainty in methods relying on CO and CO_2 adsorption. For these reasons, the WO_3-ZrO_2/MWCNT samples in the current study were characterized by NO_x-TPD to determine the coverage of the ZrO_2 nanoparticles by tungstates. It is our understanding that NO_x-TPD can be performed by scientists everywhere and on tungstated zirconia samples of any composition, making it a sensitive and robust technique to determine the W surface density on ZrO_2 supports. To our knowledge, determination of the coverage of the ZrO_2 surface by tungstates in WO_3-ZrO_2/MWCNT materials has not been reported in the literature to date, whereas their use as substitutes of sulfated ZrO_2 materials, which are known to exhibit leaching issues in biomass processing applications [42–49], is of great interest.

2. Experimental

2.1. Catalyst preparation

The MWCNT used in this study were purchased from Cheap Tubes Inc. (>95% purity). These MWCNT (or pristine MWCNT, as described later) have an outer diameter of 10–20 nm, an inner diameter of 3–5 nm, and a length of 10–30 μm, as described by the supplier. The pristine MWCNT were functionalized by refluxing in nitric acid at ~120 °C for 2 h using ~69 wt % (15 M HNO_3) nitric acid (purchased from J.T. Baker). The mixture was then filtered and washed with 1000 mL of deionized water in five batches (5 × 200 mL) to remove excess acid and soluble oxidation products. The resulting material was then dried at 60 °C overnight in a thermostated oven and ground to a fine powder. These functionalized MWCNT were used as the starting material to prepare the ZrO_2/MWCNT composites.

Synthesis of ZrO_2/MWCNT was completed by grafting $Zr(acac)_4$ (98%, purchased from Sigma-Aldrich) onto functionalized MWCNT in refluxing toluene (300 mL) at ~111 °C for 3 h in a 500 mL round-bottom flask being purged with N_2 (ultrahigh purity, purchased from Airgas). The sample was filtered, washed three times with toluene, and dried overnight at 60 °C. A thermal treatment (annealing) was then performed in flowing He (ultrahigh purity, purchased from Airgas) at 450 °C for 2 h in a quartz reactor to decompose the acetylacetonate precursor and form ZrO_2 particles. Two batches of ZrO_2/MWCNT were prepared differing in the loading of ZrO_2 (8.1 and 6.8 wt %) and the starting functionalized MWCNT. From here on, these samples will be denoted as $ZrO_2(x)$/MWCNT, where x represents the ZrO_2 loading (wt %).

The ZrO_2(6.8)/MWCNT composite was then impregnated with aqueous solutions of ammonium metatungstate hydrate (99.99%, purchased from Sigma-Aldrich) prepared at various concentrations to achieve WO_3 loadings of 2.33, 4.57 and 8.74 wt %. The impregnated material was thermally treated again at 450 °C in flowing He for 2 h in order to form tungstated ZrO_2/MWCNT (WO_3-ZrO_2/MWCNT). The tungstated samples will be denoted as $WO_3(y)$-$ZrO_2(x)$/MWCNT, where y and x represent the loadings (wt %) of WO_3 and ZrO_2, respectively. Note that when ZrO_2/MWCNT of x wt % is tungstated, the wt % ZrO_2 is adjusted to $x' < x$ to account for the added WO_3, e.g., ZrO_2(6.8)/MWCNT becomes WO_3(2.3)-ZrO_2(6.6)/MWCNT.

2.2. Characterization techniques

The samples were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and NO_x-temperature-programmed desorption (NO_x-TPD).

Thermogravimetric Analysis (TGA). The final weight loadings of ZrO_2 and WO_3 were measured using TGA which was conducted on a Setaram Setsys 1750 instrument in flowing air (Ultra Zero grade, purchased from Airgas). During the measurement, the temperature was held at 200 °C for 30 min to remove adsorbed water and ramped to 1000 °C at a rate of 10 °C/min and then held at 1000 °C for 30 min. A second ramp on the oxidized sample was repeated to establish the baseline.

X-ray Diffraction Analysis (XRD). XRD patterns were collected using a Rigaku Miniflex 600 powder X-ray diffractometer with Cu Kα radiation at $\lambda = 0.154$ nm. XRD data was collected in the range $2\theta = 10$–$80°$ with a continuous scan mode at 0.5 °/min and counts recorded every 0.02°. The XRD patterns have been scaled to the MWCNT (002) diffraction peak to clearly depict differences in each sample.