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Assessing Carbon or Tungstates Coverage of ZrO\textsubscript{2} Nanoparticles Supported on MWCNT via NO\textsubscript{x}-TPD

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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$^2$ZrO$_2$ (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.

Keywords: Multi-walled Carbon Nanotubes (MWCNT); Tungstated-zirconia; NO$_x$-TPD; TEM; XPS
1. Introduction

Since the original discovery of carbon nanotubes (CNT) by Iijima 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 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 synthetized 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 of particular interest 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 [31,32-34], Ion Scattering [35] and X-ray Photoelectron [36-40] 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 [41]) or volumetric analysis (CO [35,41], 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 [42] 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[43-50], 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 ZrO₂ particles. Two batches of ZrO₂/MWCNT were prepared differing in the loading of ZrO₂ (8.1 and 6.8 wt %) and the starting functionalized MWCNT. From here on, these samples will be denoted as ZrO₂(\(x\))/MWCNT, where \(x\) represents the ZrO₂ loading (wt %).

The ZrO₂(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 WO₃ 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 ZrO₂/MWCNT (WO₃-ZrO₂/MWCNT). The tungstated samples will be denoted as WO₃(\(y\))-ZrO₂(\(x\))/MWCNT, where \(y\) and \(x\) represent the loadings (wt %) of WO₃ and ZrO₂, respectively. Note that when ZrO₂/MWCNT of \(x\) wt% is tungstated, the wt% ZrO₂ is adjusted to \(x' < x\) to account for the added WO₃, e.g., ZrO₂(6.8)/MWCNT becomes WO₃(2.3)-ZrO₂(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 NOₓ-temperature-programmed desorption (NOₓ-TPD).

Thermogravimetric Analysis (TGA). The final weight loadings of ZrO₂ and WO₃ 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 λ = 0.154 nm. XRD data was collected in the range 2θ = 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.

**Transmission Electron Microscopy (TEM).** Bright field TEM was performed at the Plate-forme of Institut des Matériaux de Paris Centre using a JEOL 2010 microscope operating at 200 kV with a LaB₆ filament and equipped with an Orius CCD camera (Gatan). The TEM samples were prepared by dropping ethanol suspensions of the materials on a copper grid. The ZrO₂ particle-size distributions were estimated by counting from 497 to 1133 particles.

**X-ray Photoelectron Spectroscopy (XPS).** XP spectra were collected on an Omicron Argus X-ray photoelectron spectrometer, using a monochromated Al Kα (hν = 1486.6 eV) radiation source having a 300 W electron beam. Photoelectrons emitted from the sample were analyzed at a takeoff angle of 45° under ultra-high vacuum conditions (1 x 10⁻⁸ Pa). XP spectra were collected at a pass energy of 20 eV with 0.1 eV steps. After data collection, the binding energies were referenced to the C 1s line (284.5 eV). The peak areas were determined after subtraction of a Shirley background and the atomic ratio calculations were performed after normalization using Scofield factors. Spectrum processing was carried out using the Casa XPS software package and Origin 7.1 (Origin Lab Corporation).

**NOₓ Temperature-Programmed Desorption (NOₓ-TPD).** The NOₓ-TPD experiments were carried out in a U-shape quartz reactor (15 mm i.d.). The samples were held on a plug of quartz wool and the temperature was controlled by a Eurotherm 2408 temperature controller using a K-type thermocouple. Reactant gases, used as received, were fed from independent gas cylinders (purchased from Air Liquide) by means of mass flow controllers (Brooks...
5850TR) with a total flow rate of 230 mL\textsubscript{NTP}/min. Due to the presence of the MWCNT support, and its known sensitivity to oxidation at high temperature in the presence of O\textsubscript{2} [9], the pretreatment and desorption feeds were modified compared to those used in our earlier studies [27,28]. O\textsubscript{2} was removed from these feeds and replaced with He to maintain identical flow rates. It was verified on a bulk ZrO\textsubscript{2} sample tested earlier (ZrO\textsubscript{2}-600 fa [27]), that replacing the O\textsubscript{2}-He pretreatment and desorption feeds with He did not alter the desorption profiles (not shown) or the amount of NO\textsubscript{x} desorbed (475.5 µmol/g compared to 445.5 µmol/g [27]). Prior to the NO\textsubscript{x}-TPD experiments, the MWCNT samples (~0.15 g) were annealed in situ in He at 500 °C (3 °C/min) for 2 h with a flow rate of 100 mL\textsubscript{NTP}/min. Following the in-situ annealing, the sample was exposed to the adsorption mixture which consisted of 400 ppm NO\textsubscript{x} (mainly NO with some NO\textsubscript{2}) in He. The reactor outlet was continuously monitored by a chemiluminescence NO\textsubscript{x} analyzer (Thermo Environmental Instruments 42C-HL) that allowed the simultaneous detection of both NO and NO\textsubscript{2}. The samples were exposed to the adsorption mixture at RT until the outlet NO\textsubscript{x} readout was equivalent to the inlet NO\textsubscript{x} readout. This latter parameter was set to ensure that each sample was saturated under the present experimental conditions. The time after which no change was observed in the gas phase NO\textsubscript{x} concentration was strongly dependent on the W surface density of the samples. It has been clearly demonstrated that the nature of formed ad-NO\textsubscript{x} species on such materials is affected to a significant extent by the presence of O\textsubscript{2} in the NO-containing mixture [51]. As the presence of ppm levels of O\textsubscript{2} could not be excluded, NO\textsubscript{x} adsorption was thus carried out in the presence of a large excess of O\textsubscript{2} (8 %). Before the NO\textsubscript{x}-TPD experiments, the samples were flushed in He at RT to remove weakly chemisorbed species until the NO and NO\textsubscript{2} concentrations detected at the outlet of the reactor were found to be negligible. NO\textsubscript{x}-TPD experiments were carried out from RT to about 400 °C at a heating rate of 3 °C/min under a flow of 230 mL\textsubscript{NTP}/min of He. After each NO\textsubscript{x}-TPD experiment, the NO\textsubscript{x} analyzer was calibrated with a
NO/He standard mixture containing 933 ppm of NO. As reported earlier \cite{27,52,53}, it should be noted that NO\textsubscript{x} chemisorption does not occur on WO\textsubscript{3} species. The reactor outflow was also analyzed periodically using a µ-GC (Agilent Technologies, CP4900) equipped with a 5A molecular sieve column (80 °C, 150 kPa He, 200 ms injection time, 30 s backflush time) and a poraplot Q column (60 °C, 150 kPa He, 200 ms injection time). Under the NO\textsubscript{x}-TPD conditions, the only detected product was CO\textsubscript{2} at ppm levels on the second column. The NO\textsubscript{x} and CO\textsubscript{2} amounts were deduced from the integration of the corresponding TPD profiles. For the ZrO\textsubscript{2}-containing materials, the amount of NO\textsubscript{x} released per g of ZrO\textsubscript{2} was obtained by correcting the amount of NO\textsubscript{x} released per g of sample for the amount of WO\textsubscript{3} and/or the background contribution of the MWCNT support.

3. Results and Discussion

3.1. MWCNT supports

TEM images show the MWCNT diameter’s range from 9 to 24 nm and wall thicknesses of 5 ± 2 nm (Fig. 1a), consistent with the specifications indicated by the provider. Prior to studying the WO\textsubscript{3}-ZrO\textsubscript{2}/MWCNT materials, the corresponding MWCNT supports were submitted to NO\textsubscript{x}-TPD experiments. As indicated in Fig. 2, which displays the NO\textsubscript{x} and CO\textsubscript{2} profiles recorded in the course of a NO\textsubscript{x}-TPD experiment carried out on the functionalized MWCNT support used for the preparation of ZrO\textsubscript{2}(8.1)/MWCNT, the carbon support releases measurable amounts of NO\textsubscript{x} from 50 to 400 °C with a maximum at 80 °C. The NO\textsubscript{x} species are mainly released as NO except at low temperatures for which NO\textsubscript{2} is the dominant species. The production of CO\textsubscript{2} increased monotonously as the temperature increased. From a quantitative point of view, the amounts of NO\textsubscript{x} released and CO\textsubscript{2} produced were found to be 58 and 41 μmol/g\textsubscript{MWCNT}, respectively.
Two successive \( \text{NO}_x \)-TPD experiments, with intermediate annealing at 500 °C for 2 h under He, were also performed on the functionalized MWCNT support used for the preparation of \( \text{ZrO}_2(6.8)/\text{MWCNT} \). The NO, and CO\(_2\) profiles (not shown) were found to be similar to those reported in Fig. 2. The amounts of NO released and CO\(_2\) produced in these successive experiments were found to be reproducible (70 ± 4 µmol NO\(_x\)/g\(_{\text{MWCNT}}\) and 54 ± 0 µmol CO\(_2\)/g\(_{\text{MWCNT}}\)) and slightly higher than those obtained on the first batch of functionalized MWCNT investigated in this work (Table 1).

### 3.2. \( \text{ZrO}_2(8.1)/\text{MWCNT} \)

In agreement with our earlier studies \([15,16]\), TEM images show that the outer surface of the MWCNT becomes uniformly decorated with ZrO\(_2\) nanoparticles after grafting with Zr(acac)\(_4\) and annealing in He (\( \text{ZrO}_2(8.1)/\text{MWCNT} \), Fig. 1b). The ZrO\(_2\) particle size distribution of this sample was found to be rather narrow (Fig. 1c) and the average ZrO\(_2\) particle size was estimated to be 2.1 nm. This average size is consistent with our earlier work in which it was found that sintering of the ZrO\(_2\) particles only occurred for highly-loaded samples and when thermally treated at high annealing temperatures \([15]\). The lower ZrO\(_2\) particle density observed in Fig. 1b compared to those observed earlier \([15]\) is also consistent with the lower ZrO\(_2\) loading used in the present study. Fig. 1d,e indicate that the particle size was hardly affected after four successive \( \text{NO}_x \)-TPD experiments, as the average particle size was estimated to be 2.3 nm for this particular sample. In these \( \text{NO}_x \)-TPD experiments the annealing temperature never exceeded 500 °C and this result is in agreement with the finding that limited sintering of the ZrO\(_2\) particles supported on MWCNT was previously reported for annealing temperatures lower than or equal to 550 °C \([15]\).

Four \( \text{NO}_x \)-TPD experiments were performed successively on \( \text{ZrO}_2(8.1)/\text{MWCNT} \) (Fig. 3). Prior to each \( \text{NO}_x \)-TPD experiment, the sample was annealed in He for 2 h at 500 °C
following the original pretreatment procedure (100 mL/min He, 3 °C/min ramping rate). It must be highlighted however that this pretreatment was slightly modified after the third NO\textsubscript{x}-TPD experiment as we anticipated that it would be of interest to monitor the CO\textsubscript{2} production in the course of the annealing treatment. For this purpose, the He flow rate was changed from 100 to 230 mL/min at 150 °C and the annealing treatment was performed under these particular conditions from 150 to 500 °C before carrying out the fourth NO\textsubscript{x}-TPD experiment.

Fig. 3a shows that the NO\textsubscript{x}-TPD profiles obtained for ZrO\textsubscript{2}(8.1)/MWCNT are significantly different from that obtained on MWCNT (Fig. 2). The NO\textsubscript{x} contribution near 85 °C is of slightly higher intensity and an intense NO contribution is observed close to 290 °C on ZrO\textsubscript{2}(8.1)/MWCNT when compared to blank MWCNT (Fig. 2). The NO\textsubscript{x}-TPD profiles, corrected for the contribution of the MWCNT support (not shown), are found to be qualitatively consistent with that found on bulk ZrO\textsubscript{2} with low and high NO\textsubscript{x} temperature desorption peaks [27]. Fig. 3a-d show an increase in the formation of NO\textsubscript{2} in the low-temperature desorption peak and a change in the shape of the NO\textsubscript{x} peak as the number of successive NO\textsubscript{x}-TPD experiments increases, in particular for the third and the fourth NO\textsubscript{x}-TPD experiments (Fig. 3c,d). This change is clearly illustrated in Fig. 4a in which an increase in the intensity of the low temperature NO\textsubscript{x} desorption peak can be easily observed for temperatures higher than 85 °C. Let us note that the shape of the low-temperature NO\textsubscript{x} desorption peak recorded in the third and the fourth NO\textsubscript{x}-TPD experiment (Fig. 4a) is closer to that reported earlier on bulk ZrO\textsubscript{2} [27] than those recorded in the two first NO\textsubscript{x}-TPD experiments. The main difference between bulk ZrO\textsubscript{2} and ZrO\textsubscript{2}(8.1)/MWCNT is related to the nature of the NO\textsubscript{x} species released. Whereas NO\textsubscript{2} was found to primarily be released from bulk ZrO\textsubscript{2} [27], NO was almost exclusively released from ZrO\textsubscript{2}(8.1)/MWCNT (Fig. 3). Before discussing this difference, it is interesting to note that an intense CO\textsubscript{2} contribution was observed in parallel with the NO contribution at 290 °C (Fig. 3) and that this CO\textsubscript{2} contribution
was only recorded in the NO\textsubscript{x}-TPD experiments. Pretreatment of ZrO\textsubscript{2}(8.1)/MWCNT under He only showed the presence of a CO\textsubscript{2} background from 150 to 500 °C (Fig. 4b, black trace). The nature of the NO\textsubscript{x} adsorbed species (NO\textsuperscript{+}, NO\textsubscript{2}\textsuperscript{−}, N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O\textsubscript{4}, NO\textsubscript{3}\textsuperscript{−}) at the origin of the NO\textsubscript{x} released at low temperatures on bulk ZrO\textsubscript{2} remains complex [54], whereas those responsible for the release of NO\textsubscript{2} at high temperatures have been attributed unequivocally to nitrates (NO\textsubscript{3}\textsuperscript{−}) [54-57]. The observed release of NO at high temperatures, instead of NO\textsubscript{2} as expected from the experiments carried out on bulk ZrO\textsubscript{2} [27] can thus be attributed to the reduction of NO\textsubscript{2} to NO assisted by the concomitant oxidation of the MWCNT support (y NO\textsubscript{2} + *CO\textsubscript{x} = y NO + CO\textsubscript{2}, where x + y = 2 and *C designates a carbon atom from MWCNT), in agreement with the conclusions drawn in the field of automotive exhaust soot oxidation [58-59]. Such an attribution is supported by the much greater CO\textsubscript{2} production observed for ZrO\textsubscript{2}(8.1)-MWCNT (Fig. 4b) compared to MWCNT (Fig. 2).

Of much more interest is the evolution of the amounts of NO\textsubscript{x} released and CO\textsubscript{2} produced in the successive NO\textsubscript{x}-TPD experiments reported in Fig. 3 and Fig. 4. Overall, an increase in the amounts of NO\textsubscript{x} released and CO\textsubscript{2} produced was observed from 220 to 286 μmol NO\textsubscript{x}/g\textsubscript{sample} and from 164 to 210 μmol CO\textsubscript{2}/g\textsubscript{sample}, respectively, as the number of NO\textsubscript{x}-TPD experiment increased (Table 1). It must be emphasized that the increase in the amounts of NO\textsubscript{x} released and CO\textsubscript{2} produced in the NO\textsubscript{x}-TPD experiments were found to be more pronounced for the third experiment and seemed to stabilize after 3 consecutive NO\textsubscript{x}-TPD experiments (Table 1). By correcting the amount of NO\textsubscript{x} released per g of sample for the contribution of the MWCNT support (58 μmol NO\textsubscript{x}/g\textsubscript{MWCNT}), the amount of NO\textsubscript{x} released per g of ZrO\textsubscript{2} was deduced to increase from 2063 to about 2834 μmol NO\textsubscript{x}/g\textsubscript{ZrO\textsubscript{2}} as the number of successive NO\textsubscript{x}-TPD cycles increased (Table 1). Given that the NO\textsubscript{x} surface density on ZrO\textsubscript{2} was determined to be 6 μmol NO\textsubscript{x}/m\textsuperscript{2}ZrO\textsubscript{2} [27,28], the accessible surface of the ZrO\textsubscript{2}
nanoparticles of ZrO$_2$(8.1)/MWCNT was determined to increase from 344 to about 470 m$^2$/g$_{ZrO_2}$ as the number of successive NO$_x$-TPD cycles increased (Table 1). This indicates that the accessible surface of the ZrO$_2$ nanoparticles increased after three successive NO$_x$-TPD experiments and then stabilized. By considering spherical ZrO$_2$ nanoparticles and a ZrO$_2$ density of 5.8 x 10$^6$ g/m$^3$, the size of the corresponding particles was estimated to decrease from 3.0 to 2.2 nm as the number of successive NO$_x$-TPD increased (Table 1). TEM showed that the size of the ZrO$_2$ particles was hardly affected by successive NO$_x$-TPD experiments and remained close to 2.2 nm (Table 1, Fig. 1b-e). The apparent decrease in the size of the ZrO$_2$ particles estimated from the NO$_x$-TPD data can be assigned to the occupation of the NO$_x$ adsorption sites on the ZrO$_2$ particles by carbonaceous deposits that were progressively oxidized by NO$_2$ in the course of the successive NO$_x$-TPD experiments. The surface coverage of the ZrO$_2$ particles by these carbonaceous deposits is estimated to be about 30 %. It should be noted that the source of the carbonaceous deposits is likely the acetylacetonate decomposition of the zirconium precursor, not the MWCNT. From the fact that after four cycles the catalyst continues to produce significant quantities of CO$_2$ (Fig. 3d), it can be concluded that most of the CO$_2$ produced in the successive NO$_x$-TPD experiments (Fig. 3) is a result of oxidation of the MWCNT support by NO$_2$ released from the ZrO$_2$ particles, as discussed previously. This series of NO$_x$-TPD experiments was duplicated on a second aliquot of ZrO$_2$(8.1)/MWCNT and the results obtained were found to be fairly reproducible with the NO$_x$-TPD data reported in Fig. 3 and Table 1. Finally, it is of particular interest to highlight that the size of the ZrO$_2$ particles, freed of their initial C deposits, in ZrO$_2$(8.1)/MWCNT estimated by NO$_x$-TPD was found to be in remarkable agreement with the size of the ZrO$_2$ particles estimated by TEM (3$^{rd}$ and 4$^{th}$ NO$_x$-TPD, Table 1, 2.2 nm).
3.3. ZrO$_2$(6.8)/MWCNT

TEM indicates the ZrO$_2$(6.8)/MWCNT and ZrO$_2$(8.1)/MWCNT samples contain ZrO$_2$ particles of similar size (Fig. 1f,g, ~2.2 nm). In addition, the NO$_x$ and CO$_2$ profiles recorded in the three successive NO$_x$-TPD experiments (Fig. 5) were found to be similar to those reported for ZrO$_2$(8.1)/MWCNT (Fig. 3). In contrast to what was observed on ZrO$_2$(8.1)/MWCNT (section 3.2.), the successive NO$_x$-TPD experiments performed on ZrO$_2$(6.8)/MWCNT were found to be reproducible, as indicated by the amounts of NO$_x$ released and CO$_2$ formed in these experiments, 257 ± 6 µmol NO$_x$/g and 192 ± 5 µmol CO$_2$/g (Table 1), respectively. The size of the ZrO$_2$ particles of ZrO$_2$(6.8)/MWCNT was estimated to be ca. 2.2 nm from the NO$_x$-TPD data, thus in excellent agreement with the size of the ZrO$_2$ particles determined by TEM (Table 1). Considering all of the above, these results strongly suggest the absence of carbonaceous deposits on the ZrO$_2$ particles of ZrO$_2$(6.8)/MWCNT. Two successive NO$_x$-TPD experiments were performed on a second aliquot of ZrO$_2$(6.8)/MWCNT and confirmed the absence of carbonaceous deposits on this particular sample. The reason for the presence of carbonaceous deposits on ZrO$_2$(8.1)/MWCNT and their absence on ZrO$_2$(6.8)/MWCNT remains unclear at present. One explanation could stand in the change of the annealing reactor for ZrO$_2$(6.8)/MWCNT, which may have resulted in differences in the annealing procedure. The measurements performed on the ZrO$_2$/MWCNT samples in the present study therefore provide further evidence to the robustness and the sensitivity of the NO$_x$-TPD method. The absence of carbonaceous deposits on ZrO$_2$(6.8)/MWCNT led us to select this sample as the starting material for the preparation of the tungstated samples studied below.

3.4. WO$_3$-ZrO$_2$/MWCNT

Fig. 6 shows XRD patterns for nitric acid treated MWCNT, ZrO$_2$(6.8)/MWCNT and ZrO$_2$(6.8)/MWCNT impregnated with three different W loadings. At such a low loading of
ZrO$_2$, comparison of the blank MWCNT and ZrO$_2$(6.8)/MWCNT diffraction patterns only shows subtle differences in the 2$\Theta$ = 15 – 60° range. The most noticeable deviation between ZrO$_2$(6.8)/MWCNT and the blank MWCNT is between 28 – 38° and is likely due to the presence of small ZrO$_2$ particles. After addition of W to the ZrO$_2$(6.8)/MWCNT material, more signal is detected between 28 – 38° and a shoulder appears at 24° that grows with increasing W loading. WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT and WO$_3$(4.6)-ZrO$_2$(6.5)/MWCNT, which contain W loadings lower than that required to achieve a monolayer coverage of ZrO$_2$ by the tungstates, have very similar diffraction patterns although twice as much W is present in the latter sample. The additional signal in both samples when compared to ZrO$_2$(6.8)/MWCNT, is most likely a result of diffuse but coherent diffraction from the tungstates. WO$_3$(8.7)-ZrO$_2$(6.2)/MWCNT contains above the required amount of W to achieve a monolayer of tungstates and the XRD pattern exhibits a strong shoulder on the MWCNTs diffraction peak at 24° and a peak at 34° that is most likely due to diffraction from WO$_3$ domains (JCPDS 43-1035), in agreement with the corresponding contributions observed on a WO$_3$(8.0)/MWCNT sample (not shown) that was synthesized and treated thermally under similar conditions as those described for WO$_3$(y)-ZrO$_2$(x)/MWCNT (section 2.1.).

Among the tungstated samples, only WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT was investigated by TEM (Fig. 1h,i). This sample exhibited WO$_3$-ZrO$_2$ particles of about 2.4 nm, thus of a size comparable to that of the ZrO$_2$ particles present on the parent ZrO$_2$(6.8)/MWCNT composite (Table 1). Characterization methods such as XRD and TEM did not prove to be extraordinarily useful when investigating these complex materials therefore XPS and NO$_x$-TPD were explored.

XPS measurements found the binding energies of Zr 3d5/2 and W 4f7/2 to be 182.5±0.1 and 35.7±0.1 eV, respectively, which is in good agreement with the presence of Zr$^{4+}$ (zirconia) [40] and W$^{6+}$ (tungstates) [37,38,40] species in the samples. Fig. 7 shows the
The evolution of the W/Zr atomic ratio determined by XPS as a function of the bulk W/Zr atomic ratio estimated from the ZrO$_2$ and WO$_3$ weight loadings of the tungstated samples. It is observed that the W/Zr atomic ratio determined by XPS does not vary linearly (Fig. 7, dotted line) with the known W/Zr atomic ratio of the samples investigated in this study. One explanation to account for this result is that W does not deposit in a highly dispersed state in the series of samples investigated, as is the case for bulk tungstated zirconias for comparable W surface densities, i.e., for W surface densities greater than or equal to that required to achieve monolayer coverage of ZrO$_2$ by tungstates [36-40]. In the case of the WO$_3$-ZrO$_2$/MWCNT materials, tungstates may also deposit onto the MWCNT support as WO$_3$ nanoparticles with diameters larger than the escape depth of excited electrons from the W 4f transition (~2.63 nm [39]). This would contribute to the deviation of W/Zr atomic ratio measured by XPS from linearity (Fig. 7) despite that monolayer coverage of the ZrO$_2$ nanoparticles by the tungstates was not achieved. The material complexity therefore makes the use of XPS as a means to probe the coverage of the ZrO$_2$ nanoparticles by tungstates difficult. In contrast to bulk tungstated zirconias, these XPS data cannot be taken as direct evidence of monolayer coverage of the ZrO$_2$ nanoparticles by tungstates. To our knowledge, the only method capable of demonstrating monolayer coverage of ZrO$_2$ by tungstates is NO$_x$-TPD.

As observed for ZrO$_2$(6.8)/MWCNT, the two successive NO$_x$-TPD experiments performed for each tungstated zirconia composite were found to be reproducible (Table 1). Fig. 8 only shows the NO$_x$ and CO$_2$ profiles recorded in the first NO$_x$-TPD experiment for each tungstated zirconia composite as the second cycle is nearly identical. As expected from our earlier investigation on bulk tungstated zirconias [27,28] the amount of NO$_x$ released was found to decrease on the introduction of increasing quantities of tungstates (Fig. 9a and Table 2). In parallel, the amount of CO$_2$ produced was also found to be lower on tungstate
incorporation (Fig. 9b and Table 1). The fact that the amounts of NO$_x$ released, decreased on the introduction of increasing quantities of tungstates indicates that the tungstates interact with the ZrO$_2$ nanoparticles. The tungstate coverage, defined as the fraction of ZrO$_2$ covered by tungstates, is estimated with the NO$_x$-TPD data and found to be 40.2, 64.6 and 77.3 % (Table 2) for WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT, WO$_3$(4.6)-ZrO$_2$(6.5)/MWCNT and WO$_3$(8.7)-ZrO$_2$(6.2)/MWCNT, respectively.

The theoretical W surface density of the tungstated zirconia composites can be estimated on the basis of their ZrO$_2$ and WO$_3$ loadings and considering that the size of the spherical ZrO$_2$ particles of the ZrO$_2$(6.8)/MWCNT parent material is 2.2 nm (Fig. 1f,g, Table 1). The method used to determine such a theoretical W density will be detailed for WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT. The specific surface area of spherical ZrO$_2$ particles with a diameter of 2.2 nm is about 470 m$^2$/g (Table 1). Hence, 1 g of WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT contains 31.2 m$^2$ of ZrO$_2$ and 100.5 µmol of WO$_3$. The W surface density, which is the ratio of the number of atoms of W to the specific surface of ZrO$_2$ [28] is therefore deduced to be 1.9 W/nm$^2$ ZrO$_2$. Applying this method to the two other tungstated zirconia composites resulted in theoretical W surface densities of 3.9 and 7.8 W/nm$^2$ ZrO$_2$ for WO$_3$(4.6)-ZrO$_2$(6.5)/MWCNT and WO$_3$(8.7)-ZrO$_2$(6.2)/MWCNT, respectively.

From the difference between the amount of NO$_x$ released from the ZrO$_2$(6.8)/MWCNT parent material and those released on the tungstated zirconia composites, and the fact that it was found that the addition of 1 W atom prevented the adsorption of 0.77 NO$_x$ molecule in our earlier investigation on bulk tungstated zirconia materials [28], the amount of W interacting with ZrO$_2$ can be estimated and the corresponding W surface density deduced. This resulted in W surface densities of 1.9, 3.0 and 3.6 W/nm$^2$ ZrO$_2$ (Table 2) for WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT, WO$_3$(4.6)-ZrO$_2$(6.5)/MWCNT and WO$_3$(8.7)-ZrO$_2$(6.2)/MWCNT, respectively. It is remarkable that the W surface density determined by means of the NO$_x$-
TPD method agrees perfectly with that predicted theoretically for WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT (1.9 W/nm$^2$ZrO$_2$, Table 2). This indicates that W interacted preferentially with the ZrO$_2$ particles in this sample. In contrast, the W density was found to be lower than that corresponding to monolayer coverage (4.1 W/nm$^2$ZrO$_2$ [28]) for the more highly-loaded tungstated samples (Table 2). The fact that the high temperature NO$_x$ desorption peak did not vanish even for the most highly-loaded sample (Fig. 9a) suggests that excess tungsten interacted with MWCNT rather than ZrO$_2$ and started to form tridimensional WO$_3$ crystallites in agreement with the XRD data (Fig. 6). Finally, it can be concluded that monolayer coverage of ZrO$_2$ by W on the studied tungstated zirconia composites is almost complete when introducing W loadings twice as high as that theoretically needed.

5. Conclusions

In this study, the coverage of ZrO$_2$ nanoparticles supported on MWCNT by carbonaceous deposits or tungstates was investigated. For this purpose, the materials were characterized by NO$_x$-TPD and these results were combined with XRD, XPS and TEM analyses. It was found that carbon deposition may occur on the ZrO$_2$ nanoparticles in the course of the synthesis process. These carbonaceous deposits, which covered approximately 30 % of the ZrO$_2$ surface, can be removed by successive NO$_x$-TPD experiments, most likely via oxidation by NO$_2$ released from ZrO$_2$. The size of the ZrO$_2$ particles estimated by NO$_x$-TPD on ZrO$_2$/MWCNT free of carbonaceous deposits and on a carbon-free ZrO$_2$/MWCNT material were found to be in excellent agreement with that determined by TEM. Incorporation of increasing quantities of W on carbon-free ZrO$_2$ nanoparticles supported on MWCNT revealed that tungstate coverage of ZrO$_2$ increased from 40 to 77 % and that W interaction with the ZrO$_2$ nanoparticles decreased as the amount of W added increased. Remarkably, it was found that W interacted preferentially with the ZrO$_2$ nanoparticles for a W surface
density of 1.9 W/nm$^2_{ZrO_2}$ (half monolayer coverage of the ZrO$_2$ nanoparticles by tungstates). It was also found that monolayer coverage of ZrO$_2$ by tungstates on the studied tungstated zirconia composites was nearly complete when introducing W loadings twice as high as that theoretically needed. To our knowledge, 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.

Acknowledgments

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References


Table 1. Summary of the NO$_x$-TPD and TEM data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NO$_x$-TPD run</th>
<th>CO$_2$</th>
<th>NO$_x$ released</th>
<th>Accessible ZrO$_2$ surface$^a$</th>
<th>ZrO$_2$ crystallite size (nm)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>µmol/g</td>
<td>µmol/g</td>
<td>m$^2$/g</td>
<td>m$^2$/g$_{ZrO_2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>MWCNT</td>
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<td>41</td>
<td>58</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>ZrO$_2$(8.1)/MWCNT</td>
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<td>164</td>
<td>220</td>
<td>2063</td>
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<td>236</td>
<td>2252</td>
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<td>991</td>
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<td>99</td>
<td>640</td>
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<td>55</td>
<td>96</td>
<td>579</td>
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$^a$Values estimated by considering a NO$_x$ surface density of 6 µmol/m$^2$$_{ZrO_2}$ [27,28]

$^b$Values estimated by considering spherical particles and a ZrO$_2$ density of 5.8 x 10$^6$ g/m$^3$
Table 2. Tungstate coverage and W surface density of the WO$_3$(y)-ZrO$_2$(x)/MWCNT samples estimated from NO$_x$-TPD data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tungstate coverage (%)</th>
<th>NO$_x$ released µmol NO$_x$/g ZrO$_2$</th>
<th>W density (W/nm$^2$ZrO$_2$)</th>
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</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZrO$_2$(6.8)/MWCNT</td>
<td>-</td>
<td>2821</td>
<td>-</td>
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<td>WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT</td>
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<td>1687</td>
<td>1.9</td>
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<td>WO$_3$(4.6)-ZrO$_2$(6.5)/MWCNT</td>
<td>64.6</td>
<td>998</td>
<td>3.9</td>
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<td>WO$_3$(8.7)-ZrO$_2$(6.2)/MWCNT</td>
<td>77.3</td>
<td>640</td>
<td>7.8</td>
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</table>

$^a$ calculated on the basis of the loadings of ZrO$_2$ and WO$_3$ in the samples, and considering a mean ZrO$_2$ particle size of 2.2 nm (470 m$^2$/g ZrO$_2$, Table 1)

$^b$ based on the amount of NO$_x$ released from the ZrO$_2$(6.8)/MWCNT parent sample and those released on the tungstated zirconia composites, and considering that the addition of 1 W atom prevented the adsorption of 0.77 NO$_x$ molecules [28]
Figure Captions

**Fig. 1.** TEM micrographs and particle size distributions of (a) MWCNT, (b) and (c) as-prepared ZrO$_2$(8.1)/MWCNT, (d) and (e) ZrO$_2$(8.1)/MWCNT submitted to 4 successive NO$_x$-TPD experiments, (f) and (g) ZrO$_2$(6.8)/MWCNT submitted to 3 successive NO$_x$-TPD experiments, (h) and (i) WO$_3$(2.3)-ZrO$_2$(6.6)/MWCNT submitted to 2 successive NO$_x$-TPD experiments. The scale bar is 10 nm in each micrograph.

**Fig. 2.** NO$_x$ (magenta), NO$_2$ (red), NO (blue) and CO$_2$ (green) profiles obtained on 0.1399 g of MWCNT, after annealing the sample at 500 °C for 2 h in 100 mL$_{NTP}$/min of He and RT exposure to 230 mL$_{NTP}$/min of NO$_x$(400 ppm)-O$_2$(8%)-He for about 160 min followed by temperature-programmed desorption from RT to 420 °C (3 °C/min) in 230 mL$_{NTP}$/min of He. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

**Fig. 3.** NO$_x$ and CO$_2$ profiles obtained in successive NO$_x$-TPD experiments (a) 1$^{st}$ NO$_x$-TPD, (b) 2$^{nd}$ NO$_x$-TPD, (c) 3$^{rd}$ NO$_x$-TPD, (d) 4$^{th}$ NO$_x$-TPD on 0.1515 g of ZrO$_2$(8.1)/MWCNT, after annealing of the sample at 500 °C for 2 h in 100 mL$_{NTP}$/min of He and RT exposure to 230 mL$_{NTP}$/min of NO(400 ppm)-O$_2$(8%)-He for about 190 min followed by temperature-programmed desorption from RT to 370 °C (3 °C/min) in 230 mL$_{NTP}$/min of He. It must be noted that the He flow during the annealing step between the 3$^{rd}$ and the 4$^{th}$ NO$_x$-TPD was set to 230 mL$_{NTP}$/min at 150 °C. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)
Fig. 4. (a) NO\textsubscript{x} and (b) CO\textsubscript{2} profiles obtained in successive NO\textsubscript{x}-TPD experiments: 1\textsuperscript{st} NO\textsubscript{x}-TPD (blue), 2\textsuperscript{nd} NO\textsubscript{x}-TPD (red), 3\textsuperscript{rd} NO\textsubscript{x}-TPD (magenta), 4\textsuperscript{th} NO\textsubscript{x}-TPD (green) on 0.1515 g of ZrO\textsubscript{2}(8.1)/MWCNT, after annealing of the sample at 500 °C for 2 h in 100 mL\textsubscript{NTP}/min of He and RT exposure to 230 mL/min of NO(400 ppm)-O\textsubscript{2}(8%)-He for about 190 min followed by temperature-programmed desorption from RT to 370 °C (3 °C/min) in 230 mL\textsubscript{NTP}/min of He. Please note that the He flow during the annealing step between the 3\textsuperscript{rd} and the 4\textsuperscript{th} NO\textsubscript{x}-TPD was set to 230 mL\textsubscript{NTP}/min at 150 °C and the corresponding CO\textsubscript{2} trace was recorded (black). (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

Fig. 5. NO\textsubscript{x} and CO\textsubscript{2} profiles obtained in successive NO\textsubscript{x}-TPD experiments (a) 1\textsuperscript{st} NO\textsubscript{x}-TPD, (b) 2\textsuperscript{nd} NO\textsubscript{x}-TPD, (c) 3\textsuperscript{rd} NO\textsubscript{x}-TPD on 0.1155 g of ZrO\textsubscript{2}(6.8)/MWCNT, after annealing of the sample at 500 °C for 2 h in 100 mL\textsubscript{NTP}/min of He and RT exposure to 230 mL\textsubscript{NTP}/min of NO(400 ppm)-O\textsubscript{2}(8%)-He for about 180 min followed by temperature-programmed desorption from RT to 380 °C (3 °C/min) in 230 mL\textsubscript{NTP}/min of He. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

Fig. 6. XRD data for MWCNT (green), ZrO\textsubscript{2}(6.8)/MWCNT (black), WO\textsubscript{3}(2.3)-ZrO\textsubscript{2}(6.6)/MWCNT (red), WO\textsubscript{3}(4.6)-ZrO\textsubscript{2}(6.5)/MWCNT (purple) and WO\textsubscript{3}(8.7)-ZrO\textsubscript{2}(6.2)/MWCNT (blue) annealed at 450 °C, vertical lines in inset represent WO\textsubscript{3} (solid, 23.2, 29.2 and 33.3°) and ZrO\textsubscript{2} (dashed, 30.1 and 34.9°). All spectra are scaled to the intensity of the (002) diffraction of MWCNT, equivalent to referencing to the same amount of MWCNT. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)
Fig. 7. W/Zr atomic ratio determined by XPS as a function of the nominal W/Zr atomic ratio for the WO\(_3\)(y)-ZrO\(_2\)(x)/MWCNT samples.

Fig. 8. NO\(_x\) and CO\(_2\) profiles obtained in the 1\(^{st}\) NO\(_x\)-TPD experiment on (a) WO\(_3\)(2.3)-ZrO\(_2\)(6.6)/MWCNT, (b) WO\(_3\)(4.6)-ZrO\(_2\)(6.5)/MWCNT, (c) WO\(_3\)(8.7)-ZrO\(_2\)(6.2)/MWCNT, after annealing of the sample at 500 °C for 2 h in 100 mL\(_{\text{NTP}}\)/min of He and RT exposure to 230 mL\(_{\text{NTP}}\)/min of NO(400 ppm)-O\(_2\)(8%)-He for about 180 min followed by temperature-programmed desorption from RT to 380 °C (3 °C/min) in 230 mL\(_{\text{NTP}}\)/min of He. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

Fig. 9. (a) NO\(_x\) and (b) CO\(_2\) profiles obtained in the 1\(^{st}\) NO\(_x\)-TPD experiment on ZrO\(_2\)(6.8)/MWCNT (black), WO\(_3\)(2.3)-ZrO\(_2\)(6.6)/MWCNT (red), WO\(_3\)(4.6)-ZrO\(_2\)(6.5)/MWCNT (purple), WO\(_3\)(8.7)-ZrO\(_2\)(6.2)/MWCNT (blue) and MWCNT (green) after annealing of the sample at 500 °C for 2 h in 100 mL\(_{\text{NTP}}\)/min of He and RT exposure to 230 mL\(_{\text{NTP}}\)/min of NO(400 ppm)-O\(_2\)(8%)-He for about 180 min followed by temperature-programmed desorption from RT to 380 °C (3 °C/min) in 230 mL\(_{\text{NTP}}\)/min of He. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)
Fig. 1 (continued)
Fig. 1

\[
\frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} = 2.4 \text{ nm}
\]
Fig. 2
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.
Fig. 9.