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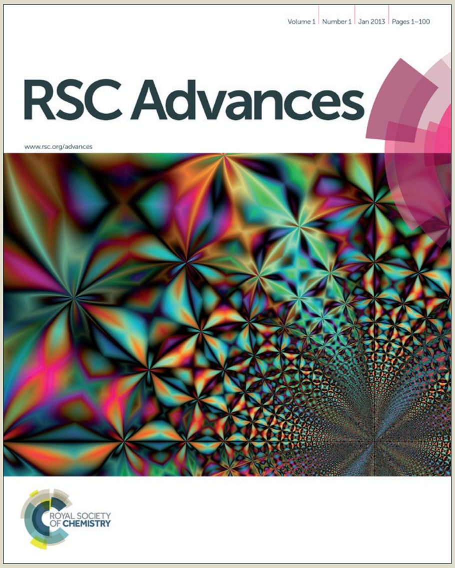

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PAPER

A Study of Oxidizing Centers in Carbon Nanotubes by Solid-state NMR

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Functionalized carbon nanotubes (CNTs) play an important role as catalyst in several oxidation reactions. Active centers, present in a catalyst, are mainly associated with oxidizing functional groups. Therefore, determining the concentration of oxidizing centers from various functional groups present on the surface of CNTs is very important, but it is yet to be achieved. In the present study, solid-state NMR SSNMR techniques were employed to study the adsorption behavior of trimethylphosphine (TMP) in CNTs using TMP as a probe molecule. The results show that TMP gets oxidized to TMPO (trimethylphosphine oxide). The concentration of oxidizing center was also selectively measured in the order of sub-mmol/g, employing SSNMR. The oxidizing centers comprise a very small portion among various functional groups present on the surface of CNTs. The concentration of oxidizing centers was found to be increased as the degree of functionalization of CNTs increased. Further studies are required to understand the exact structure of oxidizing centers present in CNTs.

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima et al. in 1991 [1], CNTs have attracted considerable interests for their special properties in mechanics [2,3], electrics [4-6], and optics [7-9], etc. CNTs also show great potential in the field of catalysis. The smooth and stable surface structure of perfect CNTs restricts them to be used for catalyzing chemical reactions directly. However, when it is functionalized by certain chemical methods (for example, oxidized by concentrated HNO_3 or H_2O_2), the sp^2 structure of carbons gets destroyed, and functional groups are created on the surface, thus making them ready to be used in a variety of chemical reactions. In recent years, more and more researchers have found that the functionalized CNTs as well as other nanostructured carbon materials (such as graphene or graphene oxide) can not only be used as supports to load catalysts of metal particles in the synthesis of ammonia [10,11], hydroformylation [12] and Fischer-Tropsch process [13], but also as metal-free catalysts for directly catalyzing the reactions such as oxidative dehydrogenation [14-17], oxidant of thiols and sulfides [18], oxidation of benzylic alcohols [19], oxidation of benzene to phenol [20], oxidation of various alcohols, and cis-stilbene [21], etc. In these oxidation processes, directly catalyzed by graphitized carbon materials, the graphite sheets act as framework, providing the mechanical stability and conductivity to the catalyst, while a certain oxygen-containing functional group provides active centers for oxidation process. The concentration of active centers for oxidation reaction is important in a catalytic process and necessary for the calculation of turnover of number (TON) or turnover of frequency (TOF) per active site, which is adopted to evaluate the activity and the efficiency of catalysts. However, it is always difficult to measure the concentration of active centers in a catalyst in a heterogeneous catalysis system, and in many cases, it is even difficult to identify the species that acts as active center. Therefore, determining the concentration of active centers present in a catalyst is very crucial. Furthermore, not all active centers are exposed on surface and accessible to reactant molecules. Some active centers may remain buried in the body of a catalyst; hence, they cannot catalyze substrate molecule in a real reaction system. In the case of metal-free carbon catalysts, the chemical structure of nanocarbon materials and the types of functional groups present on the graphite sheet are even more complicated. Different kinds of surface functional groups (such as hydroxyl, carbonyl, and carboxylic acid groups) may coexist in a catalyst since the synthesis or the surface modification procedure of nanocarbon catalysts always involves harsh physical or chemical processes, such as laser irradiation and oxidation by HNO_3, O_2, and O_3 [22,23]. Although the exact function of each surface species in an oxidation reaction is yet to be understood, it is generally recognized that oxidizing oxygen species remain closely related to active center and critical for catalyzing an oxidation reaction. X-ray photoelectron spectroscopy (XPS) and temperature programmed method have always been employed to quantitate functional groups. However, not all functional groups possess oxidizing ability among various species in carbon materials. Although functional groups, directly contributing

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in catalyzing oxidation reaction, only account for a very small fraction among the whole surface species, they attract maximum interests from scientists. Qi et al. have proposed a chemical titration method to quantify three types of oxygen functional groups on CNTs and determined carbonyl groups as the active sites in oxidative dehydrogenation (ODH) reaction of ethylbenzene [24]. However, developing spectroscopic methods that can selectively measure the accessible oxidizing centers from various functional groups in carbon materials is highly necessary.

Trimethylphosphine (TMP) has been used as a NMR probe molecule to characterize solid acids. It was first introduced by Lunsford et al. to study the acidity of zeolite [25-28]. TMP has some advantages which enables it to be used as a NMR probe molecule. First, it has a high gyro-magnetic ratio, which means a high NMR sensitivity. Second, the natural abundance of ^{31}P is nearly 100%, so the expensive isotope-enriched reagent for NMR is not needed. Third, it has a proper boiling point, and the process of adsorption onto solid sample is relatively easy. Besides, the P atom on TMP has a lone pair electron that makes it prone to oxidation. Realizing the advantages of the above properties, we developed TMP as a NMR probe molecule to detect the multi-walled carbon nanotubes (MWCNT) with different extent of functionalization and selectively measure accessible oxidizing centers on the surface among various other functional groups present in the CNTs.

Experimental section

Sample preparation

The multi-walled carbon nanotubes (MWCNT) were purchased from Chengdu Organic Chemicals Company Ltd. of Chinese Academy of Sciences. The outer diameter and the length of the MWCNTs are 8–15 nm, and ~50 µm, respectively.

The MWCNT samples were functionalized at different temperatures and for different hours. A typical procedure of functionalizing MWCNT is described as follows. To begin with, 3 g MWCNT was taken in a flask, and 150 ml concentrated HNO_3 was added to it. Next, the mixture was refluxed at 135 °C for 12 h in an oil bath, followed by dispersing the mixture in 1000 ml distilled water. The CNTs were precipitated out, and the supernatant was replaced with distilled water for three times. The mixture was then filtered until the pH of the filtrate became 7. The product was dried at 60 °C for 40 h and finally, was well ground; the sample was named as o-CNT.

The o-CNT sample was placed in a CAVERN apparatus to carry out the on-line treatment [29, 30]. The sample was first heated to 320 °C at a rate of 3 °C/min and purged with He for 30 min. Next, the sample was vacuumed at 10^{-2} Pa for 1 h, followed by cooling to room temperature (RT). At this stage, TMP was introduced, kept for 1 h at room temperature, and then the sample was degassed for 30 min to remove physical adsorbates from the surface. Finally, all the samples, prepared by the above method, were filled in-situ into an NMR rotor, sealed, and transferred to the spectrometer without exposure to air. In order to avoid oxidation and exposure to toxicity, the samples should be handled carefully, as mentioned above.

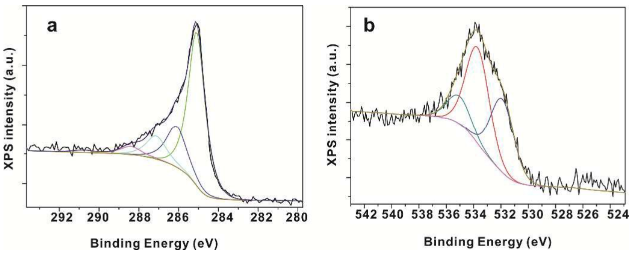

Fig. 1. Deconvoluted C_{1s} (a) and O_{1s} (b) XP spectra of the o-CNT sample.

Characterizations

X-ray photoelectron spectroscopy (XPS) experiments were performed on a Shimadzu Kratos spectrometer equipped with a Mg K_α X-ray radiation source. The step was 100 meV, and the dwell time was 298 ms. The Gaussian Lorentzian mixed function and Shirley background were used to deconvolute the spectra.

All NMR experiments were performed on a Varian Infinity-plus 400 spectrometer operating at a magnetic field strength of 9.4 T. The ^{31}P resonance frequency at this field strength was 161.9 MHz. A Chemagnetics 5 mm magic angle spinning (MAS) probe was employed to acquire all the spectra with a spinning rate of 4 kHz. The 90° pulse width for ^{31}P was 4.3 µs in ammonium dihydrogen phosphate or $NH_4H_2PO_4$ (ADP), while it was 6 µs in CNTs samples at the same power because of the shielding effect of CNTs. The recycle delay for ADP was 30 s. For TMP and TMPO adsorbed in CNT samples, the recycle delay was set as 0.5 s, longer than 5 times the ^{31}P T_1 which was measured as 0.07 s. In the static echo experiments, spectra were acquired using a standard Hahn-echo experiment of the form $\pi/2 - \tau - \pi - \tau -$ acquisition, where τ represents interpulse delay of 30 µs. The π/2 and π pulse widths were 6 and 12 µs, respectively. ^{31}P chemical shifts were referenced to NH_4H_2PO4 (0.8 ppm). The areas of ^{31}P peaks of TMP and TMPO (trimethylphosphine oxide) adsorbed in o-CNT samples were compared to avoid the susceptibility effect for the quantification.

Results and Discussion

XPS

To study the effect of concentrated HNO_3 on the functionalization of CNTs and the state of functional groups existing on the wall of CNTs, X-ray photoelectron spectroscopy (XPS) experiments were performed for the o-CNT sample (processed by concentrated HNO_3 at 135 °C for 12 h unless specified otherwise). Fig. 1a illustrates the C_{1s} XP spectra. Five peaks were discerned through deconvolution with binding energies at 285.1, 286.1, 287.1, 288.4, and 290.8 eV, respectively. There is general agreement in literature on the assignment of the peaks [31-35]. The peak at 285.1 eV corresponds to the graphite carbons of the CNTs, while the peak at 286.1 eV ascribes to carbons singly bound to oxygen in phenols and ethers. Carbons doubly bound to oxygen in ketones and quinones (i.e., C=O) appear at 287.1 eV. Carbons bound to two oxygen atoms in carboxyls, carboxylic anhydrides, and esters (i.e., -COO) are

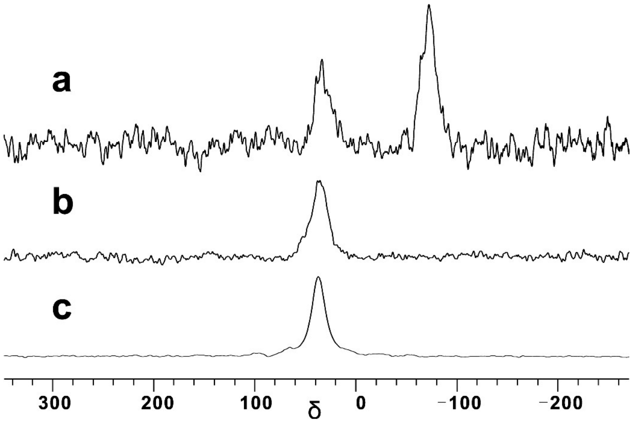

Fig. 2. ^{31}P MAS NMR spectra of (a) TMP adsorbed on o-CNT sample (b) TMP adsorbed on o-CNT sample after degassing (c) TMPO adsorbed on o-CNT sample. The numbers of scans were 384, 6640 and 11960 for spectrum (a), (b) and (c), respectively.

represented by the peak at 288.4 eV. The very weak signal at 290.8 eV (π-π* transition) is the shakeup line of carbon in aromatic compounds. The O_{1s} XP spectra of the o-CNT sample are shown in Fig. 1b. The deconvolution results in three peaks: the peak at 531.9 eV is assigned to oxygen doubly bound to carbon (i.e., O=C) in quinones, ketones, and aldehydes, while the peak at 533.7 eV is assigned to oxygen singly bound to carbon (i.e., O-C) in ethers and phenols. Oxygen atoms in esters, carboxyls, anhydrides, and pyrones, having both single and double bonds with carbon atoms, contribute to both above-mentioned peaks. The peak at 535.1 corresponds to H-O-H. Sensitivity factors of carbon and oxygen were set as 0.25 and 0.66 [36], respectively and the molar ratio of oxygen atoms to carbon atoms was found as 10.1:100 through comparing the total peak areas in each spectrum. As the content of hydrogen is normally very low in CNTs, the composition of o-CNT sample is often considered as carbon and oxygen, ignoring hydrogen atoms. Thus, we estimated the content of oxygen as *ca.* 7.4 mmol/g.

NMR

All the oxygen species present in CNTs were observed in XPS. To selectively measure the content of oxidizing functional groups among various oxygen species, solid state NMR (SSNMR) studies were performed employing reductive TMP as the probe molecule. Fig. 2a shows the ^{31}P MAS NMR spectrum of TMP adsorbed on o-CNT sample. There are two broad peaks, centered around 35 and -72 ppm, respectively, as evident from Fig. 2a. There are two possible assignments for the peak at -72 ppm. This peak may result either due to the physical adsorption of TMP in pores and channels of CNTs or the chemical absorption TMP by some groups, analogue to Lewis acids (similar as found in some solid acids). However, we found that the peak at -72 ppm disappeared after degassing the sample at room temperature for 30 min (Fig. 2b); therefore, the peak at -72 ppm can be assigned to the physically adsorbed TMP. However, we could hardly assign the peak at 35 ppm to any form of TMP based on the chemical shift region. The chemical shift of crystal trimethylphosphine oxide (TMPO) comes around 42 or 39 ppm [37,38]. TMP adsorbed on o-CNT may be oxidized to TMPO. To verify this presumption, TMPO was dissolved in dichloromethane and then adsorbed on the o-CNT sample; we observed only one peak around 38 ppm (Fig. 2c), the chemical shift very close to 35 ppm; hence, we assigned the peak at 35 ppm to TMPO, formed by the oxidization of TMP adsorbed on o-CNT.

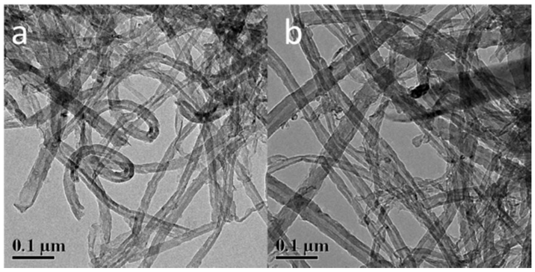

Fig. 3. TEM images of the (a) o-CNT and (b) o-CNT-1500 sample.

There could be three possible pathways for the oxidization of TMP adsorbed on o-CNT to TMPO. First, TMP might get oxidized because of oxygen exposure by careless manipulation during the adsorption step [39]. Second, TMP might get oxidized by metal oxide impurities introduced during the growth of CNTs. Third, TMP might get oxidized due to the oxygen-containing functional groups on the surface of o-CNT. In order to understand the correct mechanism of the oxidation of adsorbed TMP, we treated the sample in the following ways. First, every step of operation was checked carefully and repeated the experiment many times. The same results were obtained, and the first pathway was eventually ruled out. Next, the o-CNT sample was heated at 1500 °C under high vacuum in a special home-made oven; the processed sample was named as o-CNT-1500. All the functional groups and possible metal oxides were cleaned after such harsh process, but the frame of CNTs still remained intact [40]; TEM images corroborates the

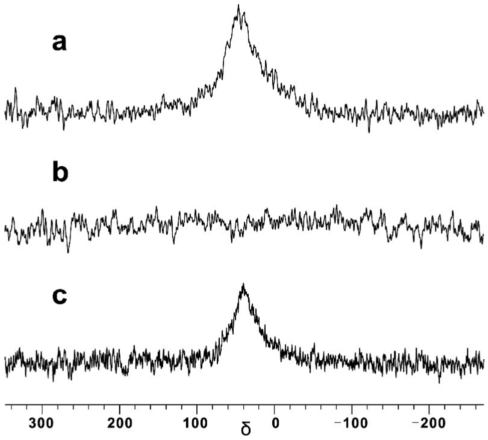

Fig. 4. ^{31}P static echo spectra of TMP adsorbed on (a) o-CNT sample (b) o-CNT-1500 sample (c) o-CNT-1500-HNO_3 sample after degassing. The number of scans for each of the spectra was 6640.

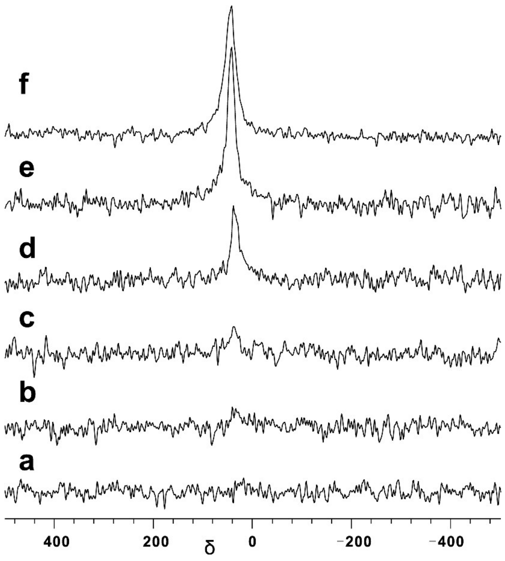

Fig. 5. ^{31}P MAS NMR spectra of TMP adsorbed on o-CNT samples processed by (a) HCl, RT, 2 h (b) concentrated HNO_3, RT, 0.5 h (c) concentrated HNO_3, 80 °C, 0.5 h (d) concentrated HNO_3, 110 °C, 0.5 h (e) concentrated HNO_3, 135 °C, 0.5 h (f) concentrated HNO_3, 135 °C, 12 h after degassing. The number of scans for each of the spectra was 11960.

experimental findings (Fig. 3). TMP was then adsorbed on o-CNT-1500, kept for 1 h, and finally, the sample was degassed at room temperature for 30 min to remove the physically adsorbed TMP. No ^{31}P signal was observed on the spectrum (Fig. 4b) [41]. Furthermore, the o-CNT-1500 sample was treated with concentrated HNO_3, and the functional groups were again created; the sample was named as o-CNT-1500-HNO_3. TMP was adsorbed on o-CNT-1500-HNO_3, kept for 1 h, and then the sample was degassed at room temperature for 30 min to remove the physically adsorbed TMP. The ^{31}P peak at 35 ppm appeared again with no significant difference compared to that of o-CNT (Fig. 4a and Fig. 4c). Therefore, the second pathway was also excluded, confirming third pathway through which the oxidation of adsorbed TMP occurred. While studying the acidity of the catalyst, Haw et al. also found that some amount of adsorbed TMP in sulfated zirconia got oxidized to TMPO [38]. Therefore, our findings are in agreement with the previous studies, and we confirm again that TMP gets oxidized by the functional oxygen groups on the surface of o-CNT. However, it is difficult to recognize the specific group that oxidizes TMP to TMPO because of the complex nature of o-CNT and the limitations of the widely used analysis methods [42]. Qualitatively comparing the O_{1s} XP spectra of o-CNT before and after TMP adsorption shows that the relative content of oxygen groups, bounded to carbon via single bond, decreases after TMP adsorption (Fig. S1, ESI†). Therefore, we cautiously speculate that TMP is possibly oxidized by the epoxide or peroxide groups on the surface of o-CNT; it is well known that TMP is readily oxidized by such groups. More proofs are needed to determine the structure of the oxidizing center accurately. However, it is certain that the oxidation of TMP is not the result of the laboratory technique rather it reflects the oxidizing properties of the surface. Hence, we employed TMP as a NMR probe molecule to study quantitatively the content of oxidizing centers on the surface of the functionalized CNTs.

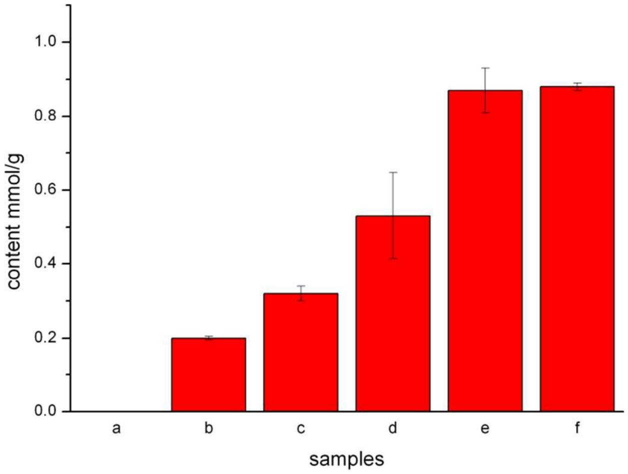

Fig. 6. The concentration of oxidizing centers in o-CNT samples processed by (a) HCl, RT, 2 h (b) concentrated HNO_3, RT, 0.5 h (c) concentrated HNO_3, 80 °C, 0.5 h (d) concentrated HNO_3, 110 °C, 0.5 h (e) concentrated HNO_3, 135 °C, 0.5 h (f) concentrated HNO_3, 135 °C, 12 h.

A series of functionalized CNTs with different extent of oxidization were prepared through controlling the experimental condition. The samples were saturated with TMP by excess TMP adsorption and degassed after 1 h at room temperature to remove the physically adsorbed TMP. Fig. 5 illustrates the ^{31}P MAS NMR spectra. No ^{31}P signal was detected when TMP was adsorbed in CNTs, processed by HCl (Fig. 5a). It is quite reasonable, because HCl is not an oxidizing agent; it can only clean the impurity of metal oxide in the CNTs but cannot create oxidizing centers on the CNTs. Fig.s 5b-5e show that the intensity of ^{31}P signal of TMPO grows as the extent of oxidization of CNTs samples increases in CNTs with adsorbed TMP, processed by concentrated HNO_3. It was found the content of oxidizing centers in the CNTs samples, as shown in Fig. 6. The data confirm again that there are no oxidizing centers in CNTs, processed by HCl. The concentrations of oxidizing center in CNTs samples, processed by concentrated HNO_3 at varying temperatures (room temperature, 80 °C, 110 °C, and 135 °C) for 0.5 h are 0.20 ± 0.005, 0.32 ± 0.020, 0.53 ± 0.120, and 0.87 ± 0.061 mmol/g, respectively. The CNTs samples, processed by concentrated HNO_3 at 135 °C for 12 h, have the highest oxidizing center concentration of 0.88 ± 0.010 mmol/g, which is far lower than the content of oxygen detected by XPS method (*ca*. 7.4 mmol/g). It means that only about 12% of all the oxygen atoms in the sample have the ability of oxidizing TMP to TMPO, if the difference in errors between the two methods is ignored.

Conclusions

Solid-state NMR techniques were employed to study the adsorption behavior of TMP adsorbed on functionalized CNTs. It was found that TMP was oxidized to TMPO during its adsorption on the surface of the functionalized CNTs. The results also show that the oxidizing centers originate from the functional oxygen groups on the surface of functionalized CNTs, thus reflecting the intrinsic oxidizing properties of the surface. In the present study, TMP was used as a NMR probe molecule for selective detection of oxidizing centers among various oxygen groups present on the surface of functionalized CNTs, and we found that the concentration of oxidizing center was of the order of sub-mmol/g, as measured. The oxidizing center comprises only a small portion of all the oxygen groups present on the surface of functionalized CNTs, as shown by XPS. The concentration of oxidizing center goes up with increase in the extent of oxidization of CNT samples by concentrated HNO_3. In the present study, we have also introduced a solid-state NMR method to measure oxidizing centers present in functionalized CNTs, a very important aspect in carbon catalysis. Considering the complex properties of the surface of functionalized CNTs, further studies will be needed to clearly understand the structure of oxidizing center.

Acknowledgements

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[41] Static echo spectra were used just because of a technical reason. It is always not easy to spin the rotor stably at magic angle when electroconductive or magnetic materials such as CNT were filled in the rotor. One should try several times in some cases, and our aim was to qualitatively check if there were TMPO signals in the spectra, hence static echo spectra were enough to illustrate this. To save time and reduce the risk of damaging the rotor, static echo spectra were adopted.

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