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EFFECT OF Br-GRAFTED MULTI-WALLED CARBON NANOTUBES ON THE MODEL OXIDATIVE ENVIRONMENT

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Abstract. Two samples of brominated multi-walled carbon nanotubes [(Br)_n-MWCNTs] produced by the plasma-chemical technique were involved in the liquid-phase initiated oxidation of cumene. The powerful catalytic effect of (Br)_n-MWCNTs has been confirmed to recommend the substances for the use in oxidation of alkyl aromatic hydrocarbons as active additives. Obviously this phenomenon originates from the peculiarities of electronic configuration of (Br)_n-MWCNTs pattern. To elucidate a mechanism of the acceleration action of the functionalized CNTs the model experiment with a single-walled carbon nanotubes [(Br)_n-SWCNTs] at standard model conditions was conducted. There has been established that Br-groups are consumed during the reaction and (Br)_n-CNTs act in the model cumene oxidation as an additional source of free radicals and may be considered as a complementary initiator. The general scheme of oxidation has been proposed and additional initiation rates promoted by (Br)_n-MWCNTs have been calculated.

Keywords: multi-walled and single-walled carbon nanotubes, plasma-chemical technique, cumene, oxidation, catalyst, photoelectron spectroscopy, initiator.

1. Introduction

Functionalization of fullerenes, carbon nanotubes, nanofibers, nanoribbons, nanohorns, *etc.* is currently accepted as a crucial prerequisite for a broad scope of new applications since it enables to fine-tune the chemical properties of the material [1–6].

Among this variety the bromination of carbon materials may be considered as a promising approach for controlled coupling of a large variety of organic func-

tionalitys by nucleophilic substitution [7–9]. Literature, however, shows that graphitic materials, including the nanomaterials exhibit a low propensity to form covalent C–Br bonds. The planar aromatic system of a graphite (*sp*²) unit is highly stable towards an electron-seeking attack of bromine. Most reports deal with intercalation or adsorption into/onto graphitic layers. For instance, bromine intercalation/adsorption into/onto CNTs has been studied in the works [10–14]. Such intercalation or adsorption studies of CNTs were performed by a simple treatment in bromine water at room temperature or bromine vapour at elevated temperature for several hours [10, 11] or even weeks [13]. The treatment of graphite nanoplatelets (GNPs) by vapour-phase bromination, for instance, led to the intercalation of Br between the graphene layers [15]. There were indications for two types of C–Br bonds introduced simultaneously – ionic and covalent. The fraction of the ionic bond reached the highest value after 3 h bromine exposure. It has been found that the covalent bonds can be formed more readily with *sp*³-hybridized carbon atoms at the edges of the graphitic basal planes by the substitution of hydrogen terminations. Hence, GNPs with more *sp*³ carbon edge atoms are more susceptible to formation of covalent C–Br bonds [15].

In our recent work we have shown that the plasma-chemical bromination is well-suited for highly selective and effective covalent C–Br-functionalization of graphitic materials, including highly oriented pyrolytic graphite (HOPG), natural graphite (NG), MWCNTs and graphitized carbon fibres (GCFs) [9]. Elemental bromine vapor under low-pressure plasma conditions using a low-energetic inductively coupled radio-frequency plasma excitation in a fluidized-bed reactor allowed obtaining brominated MWCNTs that contain up to ca. 8 bromine

atoms per 100 C-atoms. In this process, the applied low-pressure conditions reduce bromine intercalation to negligible levels.

Moreover potential applications of the obtained $(\text{Br})_n\text{-MWCNTs}$ are presently under consideration. $(\text{Br})_n\text{-MWCNT}$ may deserve attention as halogenated flame retardants for polymer composites. Brominated CNTs appear also to be capable of reducing the anisotropy in the electrical conductivity in pristine samples [13]. C-Br sites on CNT are highly interesting approach to provide anchor groups for nucleophilic substitution reactions with various organic molecules [9].

Recently we have surprisingly discovered the catalytic influence of Br-containing CNTs [16, 17]. Continuing this scientific line which is full of many unknown sites, we have again studied the influence of other Br-containing multiwalled CNTs on the oxidation environment to get more convincing evidences.

2. Experimental

2.1. Objects

1. $(\text{Br})_n\text{-MWCNTs}$, $(\text{Br})_n\text{-SWCNTs}$ samples were obtained from MWCNTs "Baytubes C 150 P" (Bayer Material Science AG, Germany), SWCNTs "Elicarb" (Thomas Swan & Co. Ltd., UK) and bromoform (CHBr_3) by the plasma-chemical technique as described in details in the Ref. [9]. Percentage of the grafted bromine groups and other elements in $(\text{Br})_n\text{-MWCNT}$ patterns was found by X-ray photoelectron spectroscopy as: $(\text{Br})_n\text{-MWCNTs}$ (1), % C = 75.9, O = 3.1, N = 3.2, Br = 17.8; $(\text{Br})_n\text{-MWCNTs}$ (2), % C = 63.8, O = 1.5, Br = 34.7; $(\text{Br})_n\text{-SWCNTs}$, % C = 85.5, O = 9.1, Br = 5.4.

2. Cumene with 98% purity ("Aldrich") was a model hydrocarbon.

3. 2, 2'-Azobisisobutyronitrile (AIBN) was used as an initiator in the model oxidation. Before experiments the initiator was purified by recrystallization from benzene and ethanol.

2.2. Methods, Equipments and Procedures

The model cumene oxidation was carried out in the presence of different additions of $(\text{Br})_n\text{-MWCNTs}$ and $(\text{Br})_n\text{-SWCNTs}$ at the initiation rate $W_i = 6.8 \cdot 10^{-8} \text{ Ms}^{-1}$, $T = 333 \pm 0.02 \text{ K}$ and oxygen pressure $P_{\text{O}_2} = 20 \text{ kPa}$ (air). From existing experience – this condition is most suitable for the preliminary correct determination of activity of any involved additives [18, 19]. The volume of the reaction mixture was 10 cm^3 (298 K). In order to get the assigned initiation rate 10 mg of AIBN had to be added [18-20].

Rate constants for the cumene oxidation at 333 K are: chain propagation $k_3 = 1.75 \text{ M}^{-1}\text{s}^{-1}$, chain termination $k_6 = 1.84 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$, concentration of cumene $[\text{RH}] = 6.9 \text{ M}$ [18, 19, 21, 22].

The rate of oxidation was evaluated from the amount of oxygen consumed, which was measured volumetrically with the simple laboratory device shown schematically in Fig. 1. Oxidation rates (W_{O_2}) were assessed both from the slopes of the kinetic curves of oxygen consumption in the case of steady rate values and also by means of differentiating curves in the case of observed induction periods.

Correctness of the determined oxidation rate values was within the range of 3–7 %.

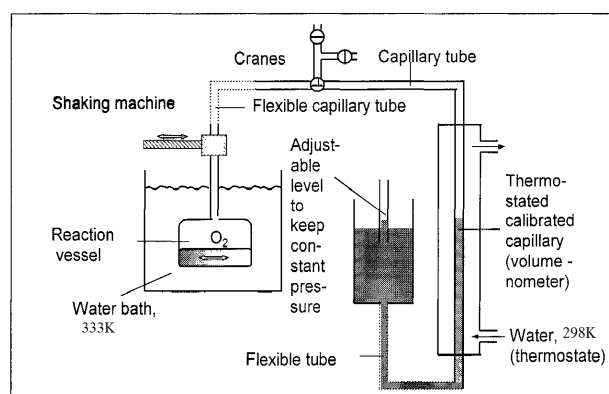


Fig. 1. Schematic diagram of measuring equipment used for oxygen uptake at constant pressure

3. Results and Discussion

Results of the model oxidation experiments are presented in Fig. 2.

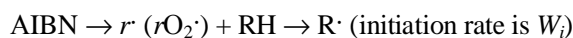
Oxidation line profiles in the presence of $(\text{Br})_n\text{-MWCNTs}$ display a strong accelerating activity of the additive under conditions of the model experiments while the virgin MWCNTs demonstrate the retarding action (Fig. 2 (line 2)). The latter result is in accordance with that of the obtained one in our previous works [24, 25]. The rate of blank oxidation (Fig. 2 (line 1)) is increased by several times when different $(\text{Br})_n\text{-MWCNTs}$ are added in the oxidation zone (Fig. 2 (lines 3-5)). More grafted Br-groups entail the increased oxidation rates. Presumably the oxidation rates can be increased as a result of supplemental formation of active radicals in the oxidizing system. The radicals can be generated either from the hydrocarbon (RH) as a result of the hydrogen abstraction by Br atoms (the activation energy $E_{act.}$ is very low, ca. $\sim 12.5\text{--}16.7 \text{ kJ/mol}$ [26]) or from the cumene

hydroperoxide (ROOH) radical decaying. In the first case (Br)_n-MWCNTs act as the initiator, in the second – as the catalyst of the hydroperoxide decomposition. As the oxidation rates were found to depend roughly linearly on square root of (Br)_n-MWCNTs concentration over the used range, *i.e.* $W_{O_2} \sim [(Br)_n\text{-MWCNTs}]^{1/2}$ we can suppose that (Br)_n-MWCNTs presumably act in the model oxidation system as a promoter of free radicals additional formation, *i.e.* operate as an initiator.

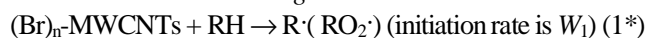
In order to check this idea and track the concentration of the grafted groups before and after the oxidative exposure a model experiment with SWCNTs was conducted for 1 h, at 333 K and $W_i = 6.8 \cdot 10^{-8} \text{ Ms}^{-1}$ followed by XPS analysis (executor is Mrs. Gundula Hidde). There was found that after the experiment the content of Br in the SWCNTs decreases from the initial 5.4 to 1.6 %, *i.e.* Br groups are substantially consumed during oxidation.

Thus the forwarded idea is almost supportive and the scheme of model reaction of cumene initiated oxidation at the presence of (Br)_n-MWCNTs may be represented as follows:

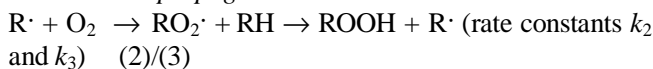
Chain initiation:



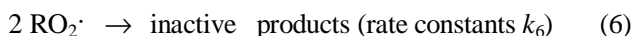
Additional radical generation:



Chain propagation:



Chain termination:



where $r \cdot (rO_2 \cdot)$ – radicals of the initiator;

(Br)_n-MWCNTs – brominated carbon nanotubes; RH – cumene, R \cdot and RO₂ \cdot – cumylalkyl and cumylperoxy radicals, respectively, ROOH – cumylhydroperoxide.

* here the generally accepted oxidation stage numbering is used [21, 23].

The reaction rate derived from this scheme is described by the following equation:

$$W_{O_2} = (W_i + W_1)^{1/2} k_3 k_6^{-1/2} [\text{RH}] \quad (1')$$

$$\text{or } W_{O_2}^2 = (W_i + W_1) k_3^2 k_6^{-1} [\text{RH}]^2 \quad (1'')$$

where W_{O_2} – oxidation rate in the presence of radical initiator (AIBN) and (Br)_n-MWCNTs; W_i – initiation rate promoted by AIBN; W_1 – additional initiation rate induced by the (Br)_n-MWCNTs; k_3 and k_6 rate constants of the cumene model oxidation chains propagation and termination, respectively; [RH] – assigned concentration of cumene.

From Eq. (1') the additional initiation rate promoted by (Br)_n-MWCNTs may be calculated as:

$$W_1 = W_{O_2}^2 k_6 / k_3^2 [\text{RH}]^2 - 6.8 \cdot 10^{-8} \quad (2')$$

Results of the calculation are given in Table 1.

Fig. 2. Kinetic dependences of oxygen uptake for cumene initiated oxidation in the absence (1) and presence of multi-walled carbon nanotubes MWCNTs (2) and (Br)_n-MWCNTs (3-5). Initiator is 2,2'-azobisisobutyronitrile (AIBN). Reaction mixture volume 10 ml, initiation rate $W_i = 6.8 \cdot 10^{-8} \text{ Ms}^{-1}$, temperature 333 K, oxygen pressure $P_{O_2} = 20 \text{ kPa}$ (air). Content of CNTs, g/l: MWCNTs 0 (line 1); 1.0 MWCNTs (line 2), (Br)_n-MWCNTs(1) (line 3); 2.0 (Br)_n-MWCNTs(1) (line 4) and (Br)_n-MWCNTs(2) (line 5)

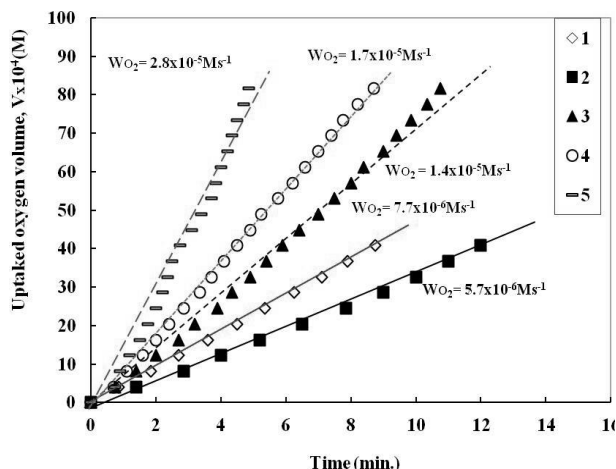


Table 1

Rates of initiation promoted by the Br-containing carbon nanotubes and commercial 2, 2'-azobisisobutyronitrile (AIBN) in the environment of cumene model oxidation. Reaction mixture volume 10 ml, temperature 333 K, oxygen pressure $P_{O_2} = 20 \text{ kPa}$ (air)

Additive/ Concentration in the oxidation environment	Rate of initiation, $W_{i(\text{AIBN})} \cdot 10^8, \text{ Ms}^{-1}$	Additional initiation rate, $W_1 \cdot 10^8, \text{ Ms}^{-1}$
$[(\text{Br})_n\text{-MWCNTs (1)}] = 1 \text{ g/l} = 2.2 \cdot 10^{-3} \text{ mol Br/l}$	–	18
$[(\text{Br})_n\text{-MWCNTs (1)}] = 2 \text{ g/l} = 4.5 \cdot 10^{-3} \text{ mol Br/l}$	–	30
$[(\text{Br})_n\text{-MWCNTs (2)}] = 2 \text{ g/l} = 8.7 \cdot 10^{-3} \text{ mol Br/l}$	–	92
2, 2'-Azobisisobutyronitrile (AIBN) = $6.1 \cdot 10^{-3} \text{ M}$	6.8	–

Thus, as it is seen from the obtained data the grafted Br-groups in CNTs generate in the model oxidation environment the initiation rates which much more exceed that of generated by the strong commercial radical initiator. It gives us a ground to recommend Br-containing CNTs as the active initiator of oxidation of alkyl aromatic hydrocarbons to be considered in science and for industrial purposes.

4. Conclusions

Multi-walled brominated carbon nanotubes (Br)_n-MWCNTs with different content of Br-groups accelerate the aerobic initiated (2, 2'-azobisisobutyronitrile (AIBN) oxidation of cumene. The linear dependence $W_{O_2} \sim [(Br)_n\text{-MWCNTs}]^{1/2}$ as well as the consuming Br-groups during oxidation have been established to consider (Br)_n-MWCNTs as the active radical initiator of the oxidation process. The oxidation rates are increased as a result of supplemental formation of active radicals in the oxidizing system, particularly due to the reaction $Br^\bullet + RH \rightarrow R^\bullet + HBr$.

The calculated magnitudes of additional initiation rates promoted by (Br)_n-MWCNTs exceed by several times, even by the order than that generated by the commercial AIBN.

The results obtained are considered as preliminary and require further thorough investigations.

Acknowledgements

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ВПЛИВ Вr-ПРИЩЕПЛЕНИХ БАГАТОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК НА МОДЕЛЬНЕ ОКИСНОВАЛЬНЕ СЕРЕДОВИЩЕ

Анотація. Досліджено два зразки броммісних багатошарових вуглецевих нанотрубок [(Br)_n-MWCNTs], отриманих плазмохімічним методом, в рідкофазному ініційованому окисненні кумолу. Підтверджено потужний каталітичний ефект [(Br)_n-MWCNTs] і рекомендовано використовувати їх як активні добавки при окисненні алкілароматичних вуглеводнів. Показано, що такий ефект викликаний особливостями електронної конфігурації [(Br)_n-MWCNTs]. Для з'ясування механізму прискореної дії функціоналізованих трубок проведено модельний експеримент з одношаровими вуглецевими нанотрубками [(Br)_n-SWCNTs] за стандартних умов. Встановлено, що Br-групи витрачаються під час реакції, а нанотрубки є додатковим джерелом вільних радикалів і можуть розглядатися як додатковий ініціатор. Запропоновано загальну схему окиснення та розраховані швидкості додаткового ініціювання.

Ключові слова: багатошарова і одношарова вуглецеві нанотрубки, плазмохімічна технологія, кумол, окиснення, каталізатор, фотоелектронна спектроскопія, ініціатор.