



Carbon nanotubes catalysis in liquid-phase aerobic oxidation of hydrocarbons: Influence of nanotube impurities

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ABSTRACT

Pure carbon nanotubes (CNTs) have a high electron affinity and as such are able to actively absorb free radicals. This functional feature of CNTs leads to a linear chain breakage with the formation of inert spin adducts and effective inhibition of the oxidation process. However, there is a clear contradiction in this issue in the literature with the analysis of research results indicating that CNTs exhibit antioxidant activity mainly in polymeric materials, under conditions of diffusional restrictions for oxygen access. While, in the liquid-phase oxidation of hydrocarbons by CNTs (CNTs synthesised by the thermal catalytic pyrolysis of carbon-containing raw materials (CVD-process)), the CNTs enhance catalytic processes. In this study the aerobic liquid phase oxidation of cumene and initiated (by azobisisobutyronitrile) at low-temperature (333 K) in the presence of multi-walled carbon nanotubes (MWCNTs) obtained by thermal catalytic pyrolysis of cyclohexane (catalyst-ferrocene) has been undertaken. Kinetic analysis establishes that the catalysis of the oxidation process is associated with the presence of metal compounds in the structure of the MWCNTs. These metals are residues of metal catalysts remaining in the synthesis and in the process of pyrolysis. The metals are converted, as a rule, into metal carbides and are not easily removable by treatment with mineral acids. Thus, in the presence of metals in the composition of MWCNTs, interfering parallel reactions are observed with two processes running in parallel — $\text{MWCNTs} + \text{R}\bullet (\text{RO}_2\bullet) \rightarrow \bullet\text{MWCNTs-R} (\text{RO}_2)$ and $\text{ROOH} + \text{M} @ \text{MWCNTs} \rightarrow \text{RO}\bullet$ radicals ($\text{RO}_2\bullet$). The branching of the chain processes involving hydroperoxides suppresses the route of attachment of alkyl and peroxide radicals to the carbon cage structure of the nanotubes and the reaction proceeds in an autocatalytic mode. Contradictory conclusions regarding the effect of CNTs on the chain processes in the oxidation of organic substances (hydrocarbons, polymers) that exist in the literature are attributed to the lack of control over the presence and nature of the metal containing impurities in the CNTs.

1. Introduction

Carbon nanotubes (CNTs) are a relatively new class of materials, with a broad field of applications. In chemical processes CNTs can be effectively used in the reactions of cycloaddition, epoxidation, cross-combination, photocatalytic and electrochemical reactions. In these processes, CNTs act as carriers of the active phase of catalysts, where metal particles (Fe, Ni, Co, Pd, Pt, Ag, Au, etc.) and/or their oxides are either deposited on the surface of nanotubes or encapsulated inside their cavities [1–6].

Our research has focused on the behaviour of CNTs in the reactions of liquid-phase aerobic oxidation of hydrocarbons. We have previously shown that multi-walled carbon nanotubes (MWCNTs) containing metal (in our case the metals are, as a rule, residues of the catalyst synthesis) actively catalyse the aerobic oxidation of cumene [7] decalin [8] and hydrocarbons in the oil fraction [9,10].

MWCNTs have also been used in the catalytic liquid-phase oxidation of cumene with atmospheric oxygen in the presence of MWCNTs modified on the surface with silver nanocrystals by other authors [11]. The nanotubes were also used in the catalytic oxidation of phenol, nitrobenzene and aniline [12–14]. The field also contains reported aéro-

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bic selective liquid-phase oxidation of ethylbenzene to acetophenone, where the catalyst was a CNT filled with iron filaments (Fe @ CNTs) [15].

Significantly, in all the above processes, MWCNTs were acting as heterogeneous catalysts and can be used up to 5–6 times without any significant loss of catalytic activity.

Despite these investigations, the question of the mechanism of the catalytic action of CNTs themselves in oxidation processes is still not clear. In principle, the pure carbon framework of a CNT has a fairly high electron affinity (at about 3 eV) and is capable of actively attaching free radicals [16–19]. As the result of this activity, it has been repeatedly shown that CNTs inhibit chain oxidation processes by actively breaking off the oxidation chains with the formation of inert spin adducts [20–30]. It should be noted, that the antioxidant activity of CNTs was shown mainly for polymeric materials. At the same time, in a number of papers it was indicated that CNTs, on the contrary, possess catalytic activity and accelerate the processes of oxidation of hydrocarbons.

In one example, an industrially oriented process (Shen-zhen Nanotech Port Co. Ltd) nanotubes were used for the oxidation of cumene [31]. The CNTs material was preliminarily purified with hydrochloric acid, then washed with deionised water to pH = 6–7 and dried with hot air at 110 °C for 24 h. The use of such MWCNTs for the oxidation of cumene at 80 °C, an oxygen flow rate of 10 ml/min and the amount of MWCNTs added 10 g/l resulted in a hydrocarbon conversion of 24.1% and a selectivity of formation of cumene hydroperoxide of 88.4%. The addition of an acceptor of free radicals (namely, *p*-benzoquinone) to the reaction system almost completely retarded the oxidation process. The authors associate the catalytic activity of the MWCNTs with the initial formation of a complex of CNTs O₂ and further development of the reaction by a radical mechanism according to the following scheme:

Scheme 1

Chain origination

1. CNTs + O₂ → CNTs ... O₂
2. CNTs ... O₂ + RH → CNTs ... OH + R•

CNTs

3. ROOH → RO• + HO•
4. RO• + RH → ROH + R•

Chain propagation

5. R• + O₂ → ROO•
6. ROO• + RH → ROOH + R•
7. For Cumene: (C₆H₅)CO₂(CH₃)₂ → (C₆H₅)COCH₃ + CH₃•

Where: RH is a hydrocarbon; R•, RO•, ROO• is an alkyl, alkoxy and peroxide radical, respectively; ROOH is a hydroperoxide, ROH is an alcohol.

In another study [32], the authors describe the aerobic liquid-phase oxidation of ethylbenzene in the presence of CNTs obtained and processed similarly to those in the previously mentioned work [31]. In this case, a significant catalytic effect was observed from the use of CNTs. Here, the authors of the study conclude that the presence of CNTs makes it possible to oxidise ethylbenzene to acetophenone in the liquid phase with high selectivity. Unlike cumene oxidation, much more strict conditions of the process were used in this work - the reaction was carried out in a stainless-steel autoclave, in a solvent medium (CH₃CN) at a temperature of 155 °C and an oxygen pressure of 1.5 MPa, for 4 h with a concentration of CNTs to ethylbenzene of 20 g/l. Under these conditions, the ethylbenzene conversion was 35.6% and the acetophenone selectivity was 61.2%. It is interesting to note that for an un-purified CNTs sample, the conversion and selectivity indicators were found to be almost the same - 38.2 and 60.9%, respectively.

This shows that the CNTs purifying procedure with hydrochloric acid, undertaken to remove metallic impurities, has very little effect on the CNTs activity. As in the case of the oxidation of cumene, the addition of *p*-benzoquinone almost completely inhibits the oxidation of the ethylbenzene. This indicates the radical path of the process. The authors believe that the catalytic activity of CNTs is related to their ability to decompose phenylethyl hydroperoxide into free radicals and to promote the formation of acetophenone through π-π interactions between radical particles, peroxide and the graphene surface of CNTs. These new catalysts are offered as an effective alternative to cobalt-containing catalytic systems for the selective oxidation of ethylbenzene to acetophenone.

There is published work on the liquid-phase catalytic oxidation of cyclohexane in the presence of CNTs. It is shown that CNTs actively catalyse the oxidation of cyclohexane to cyclohexanone, cyclohexanol, and adipic acid. In this process it is possible to easily manipulate the selectivity of the formation of target products [33].

As an important step in creating a scientific basis for the use of catalytic systems based on nanocarbon structures, the authors of [34] considered the oxidation of cyclohexane in the presence of MWCNTs obtained by the pyrolysis of liquefied petroleum gas on a Fe – Mo/Al₂O₃ catalyst at 700 °C. Here they utilised single-walled CNTs (SWCNTs) obtained by the thermal-catalytic (Co, Mo) pyrolysis of ethanol on a quartz substrate at 800 °C. It should be noted that un-purified CNTs samples were used in the reactions. Cyclohexane was oxidized in an autoclave with a stirring speed of 1500 rpm, a temperature of 125 °C, an oxygen pressure of 1.5 MPa and the presence of a solvent (acetone). A reference compound (butanone) and CNTs in the amount of 0.5 g/l of hydrocarbon were also used. The authors of this study, using in situ spectral analysis and kinetic calculation methods according to the density functional theory, put forward a concept explaining the mechanism of the catalytic action of CNTs. They proposed that the reactions occur at the “liquid – surface of CNTs” interface and proceed incomparably more intensely than in the cell of the solvent. In this case, the radicals leading to the oxidation chain accumulate on the graphene layer of the CNTs and stimulate the flow of reactions with electron transfer, resulting in the production of an alcohol and a ketone.

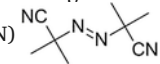
Carbon nanotubes also exhibit high catalytic activity and selectivity in the oxidation of α-pinene with a molecular acid [35]. In general, the oxidation of this bicyclic monoterpene proceeds, as a rule, in two main directions – epoxy-degradation and allylic oxidation. The presence of CNTs catalyses the first route, shifting the balance of the target products towards the formation of epoxy compounds. The activity of CNTs as a catalyst is considered by the authors as quite comparable with the activity of metal analogues. Based on the results of these studies, it is argued that catalytic systems based on CNTs are a good alternative to the well-known traditional oxidation catalysts based on metal-containing compounds [36,37]. Nevertheless, in evaluating the outcomes of the above articles [31–37], it is evident that none of them investigated the nature and content of metallic impurities originating from CNTs synthesis. Metal analysis has not been undertaken despite the fact that all the CNTs samples were obtained by the CVD method in the presence of various metal catalysts. In fact, the metal containing impurities, in the form of certain compounds, are practically an integral part of the raw CNTs samples. The subsequent processing of CNTs with mineral acids does not have a particular effect on the activity of the CNTs, and in some cases, the authors simply use un-purified samples of CNTs without any control and allowance of the metal impurity influence on the oxidation processes.

To clarify this issue, we have undertaken a study on the oxidation of cumene in the presence of CNTs obtained by thermal catalytic pyrolysis of cyclohexane. A simple kinetic approach was used, which made it possible to determine the effect of CNTs impurities.

2. Experimental

2.1. Chemicals and CNT preparation

In this work the following practical facilities and compounds were used:

1. Hydrocarbon - cumene (Alfa Aesar), purity of the reagent was 99%
2. Radical initiator - azobisisobutyronitrile (AIBN) 
3. Multi-walled carbon nanotubes (MWCNTs) were obtained by the CVD method during the thermal catalytic pyrolysis of cyclohexane in the presence of ferrocene. In the experiments, both, un-purified nanotubes (MWCNTs-c.) and purified nanotubes (treated for 12 h with hot concentrated hydrochloric acid in a flask with a reflux condenser (MWCNTs-pr.)) were used.

2.2. Oxygen adsorption technique (cumene)

The reaction of cumene oxidation was carried out in a reaction vessel with a volume of 30–40 ml. The vessel had the form of a closed cylinder with an exit through a thin section into the gasometric installation system, as shown in Fig. 1. The reaction rate was measured by the amount of absorbed oxygen in the air.

For the experiment, the reaction vessel was immersed in an ultra-thermostat and vibrated with a frequency of about 3–7 Hz to ensure saturation of the reaction mixture with oxygen. The reaction was carried out at a temperature of 333 K. 2–3 min after the vessel was immersed in the thermostat and the vessel was heated, the level of liquid in the burette was combined with the level in the tank and the measurements of the amount of absorbed oxygen were started. With an overpressure in the burette, when the gas evolution is observed, the three-way valve was again returned to its original position, the pressure was released, the liquid levels were combined, and the gas volume measurement procedure was repeated again. Distilled water was used as a thermostatic liquid for a burette and the temperature was 25 °C. The thermostat accuracy of the reaction vessel and burette was ± 0.05 °C.

The rate at which a fluid meniscus moves in the burette is proportional to the reaction rate. Oxygen absorption rate of $1 \text{ mm}^3/\text{min}$ is:

$$1 \text{ mm}^3 / \text{min} = 6.8 \cdot 10^{-7} / V, \text{ mol O}_2 / \text{l} \cdot \text{s},$$

where V is the volume of the reaction mixture in ml.

For the volume of the reaction mixture 10 ml, we have $1 \text{ mm}^3/\text{min} = 6.81 \times 10^{-8} \text{ mol O}_2 / \text{l} \cdot \text{s}$. The oxidation rate was determined from the tangent of the slope of the kinetic dependences of oxy-

gen absorption: $d\text{O}_2/dt = W\text{O}_2$. Each experiment was repeated three times, the error in determining the reaction rate was around 3–7%.

2.3. Multi-walled CNT's

The synthesis of MWCNTs was carried out in the laboratory of Scientific Instruments in Dresden GMBH, SCIDRE by pyrolysis of cyclohexane (CG) in the presence of ferrocene (FC) as a catalyst at 900 °C for 1 h, followed by chemical precipitation of the carbon from the gas phase. Synthesis precursors, taken in the FC/CG ratio = 20 mg/ml, were supplied to the reaction zone as an aerosol-assisted (AACVD) process [42].

The structure and composition of the MWCNTs was analysed by scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD).

The outer diameter of the nanotubes was, on average, 30–40 nm (Fig. 2).

At this stage our analytical assessment is based on a not so fully successive CNT purification and the evidence of metallic impurities as indicated by XRD. More detailed investigations into CNT's are in processes including variable preparative methodologies and the results will be published with detailed TEM and XPS analysis.

3. Results and discussion

The kinetic curves of oxygen absorption in the initiated oxidation of cumene in the presence of untreated and purified MWCNTs samples are shown in Fig. 3.

As can be seen from the kinetics, the oxidation reaction of cumene in the presence of as synthesised MWCNTs-c. is inhibited at the initial stages and proceeds with a certain induction period [Fig. 3 (2)]. After exiting the induction period, the reaction is catalysed and proceeds at rates exceeding the rate initiated by the oxidation of the control reaction [Fig. 3 (kinetics 1)]. Reactions with purified samples (MWCNT-pr.) proceed without any induction period and are actively catalysed by the addition of the nanotubes [Fig. 3 (kinetics 3–5)].

Fig. 4A and B shows the data for the XRD analysis of the MWCNTs-c. samples and MWCNTs-in its purified form.

From the XRD data it can be seen that in the as synthesised samples the crystalline phase of iron carbide Fe_7C_3 and iron in its α -form is present in significant amount. The treatment of MWCNTs with hot hydrochloric acid only leads to a different packing of the metal atoms in the crystal lattice with the formation of Fe_3C cohenite and γ -form iron. Thus, the purification of CNTs by treatment with hydrochloric acid, which is usually used for the purification of CNTs from impurities of iron-containing catalysts, does not have the desired purification effect. Iron and iron-containing compounds continue to be part of the MWCNTs and actively catalyse the oxidation of hydrocarbons, interacting with the hydroperoxides according to the well-known Haber – Weiss scheme, providing degenerate branching of the chains, accompanied by the formation of active radicals [43,44].

It is evident from the kinetic analysis of the oxidation of the hydrocarbons in the presence of MWCNTs-c. The initial inhibition process is observed as a consequence of the interaction of the carbon skeleton with free radicals up to a point where a critical concentration of hydroperoxides accumulates. Furthermore, the radical decomposition of the hydroperoxides, as catalysed by the iron compounds in MWCNTs-c., completely inhibits the antioxidant component of the process and the reaction proceeds in an autocatalytic mode. In the case of the use of MWCNTs-pr. samples, the catalytic action of Fe_3C and $\gamma\text{-Fe}$ plateaus the induction period at the onset of the reaction.

From the analysis of the literature and experimental data considered here, it can be concluded that CNTs free from any impurities can actively accept free alkyl $\text{R}\bullet$ radicals and considerably less active per-

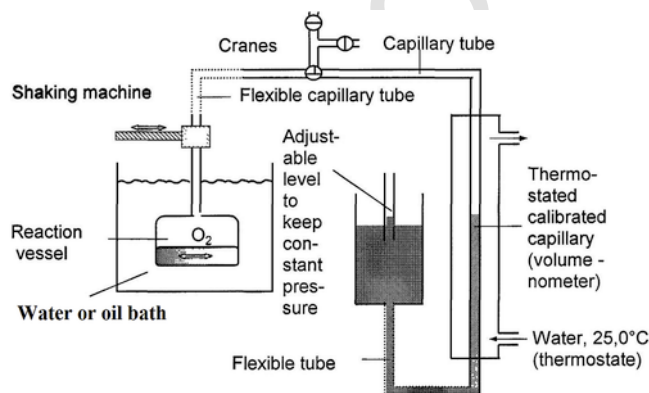


Fig. 1. Schematic representation of the laboratory setup for measuring the amount of gas absorbed or released [38–41].

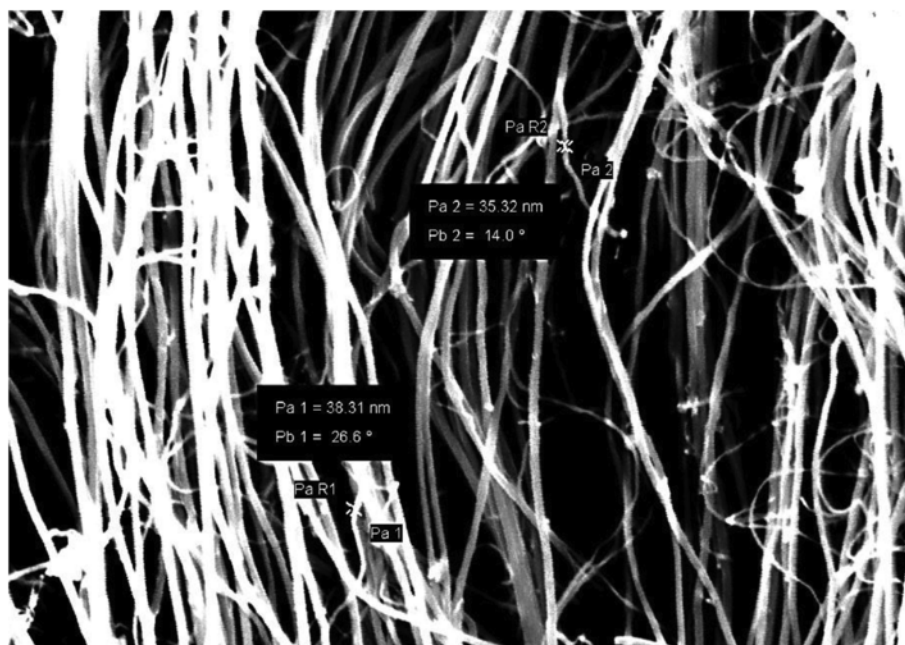


Fig. 2. A snapshot of the MWCNTs taken with a scanning electron microscope.

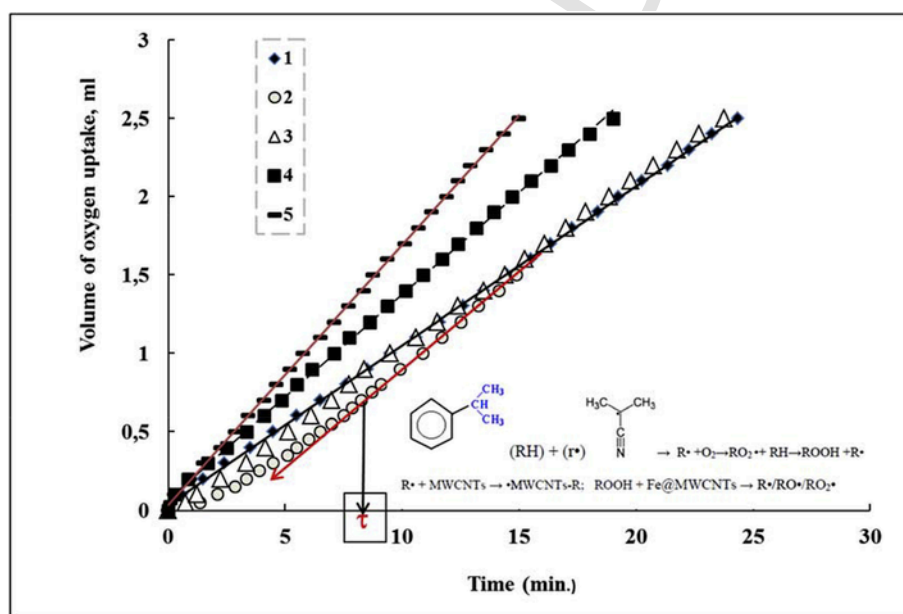


Fig. 3. Oxygen absorption kinetics in the initiated oxidation of cumene in the absence of (1) and the presence of as synthesised (2) and purified (3–5) MWCNTs. The volume of the reaction mixture is 10 ml, temperature 333K, oxygen pressure 20 KPa (air). The initiator is azobisisobutyronitrile (AIBN), the initiation rate $W_i = 6.8 \times 10^{-8} \text{ Ms}^{-1}$. Nanotube concentrations: [MWCNTs]: 1–0; 2–2 g/l; (MWCNT-c.); 3–0.5 g/l, 4–1 g/l, 5–2 g/l (MWCNTs-pr.).

oxide $\text{RO}_2\bullet$ radicals [18,45,46]. This conclusion is in good agreement with the data on other nanocarbon compounds — fullerenes C_{60} and C_{70} and graphene [23,26,47–53]. Graphene, as is known, has an electron affinity of 4.24 eV [54,55], which is much higher than the similar value for fullerenes and CNTs, and therefore, even when graphene is doped with variable valence metal salts, its catalytic properties are poor. For comparison, the oxidation reaction of naphthenic hydrocarbons from the diesel fraction 216–360 °C at 135–140 °C in a bubble reactor in the presence of the catalytic system MWCNTs + Mn naphthenate (0.1–0.2 wt.% for raw materials) leads to a record-high yield of synthetic naphthenic acids (SNA) $\geq 23\%$. On the other-hand, the use of graphene in identical conditions gives a yield of SNA of not more than 17% [9,56–60]. This conclusion is also supported by the fact that the

antioxidant activity of CNTs is well fixed mainly during thermo- and photo-oxidative aging of various polymer compositions, that is, under conditions of diffusional restrictions for oxygen access [61–64]. Under these conditions, the macro radicals are relatively long-lived. However, in the liquid phase with a sufficiently high oxygen pressure of 13.3–26.7 kPa, when the concentration of oxygen dissolved in a hydrocarbon is of the order of $\sim 10^{-3} \text{ M}$, the alkyl radicals $\text{R}\bullet$ almost instantaneously change into a peroxide by the reaction $\text{R}\bullet + \text{O}_2 \rightarrow \text{RO}_2\bullet$ [65,66]. At this stage, linear breakage of radicals on the carbon nanotubes almost disappears or proceeds at low rates. Thus, in the presence of metals in the composition of the CNTs, the reaction of CNTs + $\text{R}\bullet$ ($\text{RO}_2\bullet$) \rightarrow $\bullet\text{CNTs-R}$ (RO_2) cannot compete with the reaction $\text{ROOH} + \text{M} @ \text{CNTs} \rightarrow \text{radicals RO}\bullet$ ($\text{RO}_2\bullet$) and the oxidation process develops into a cat-

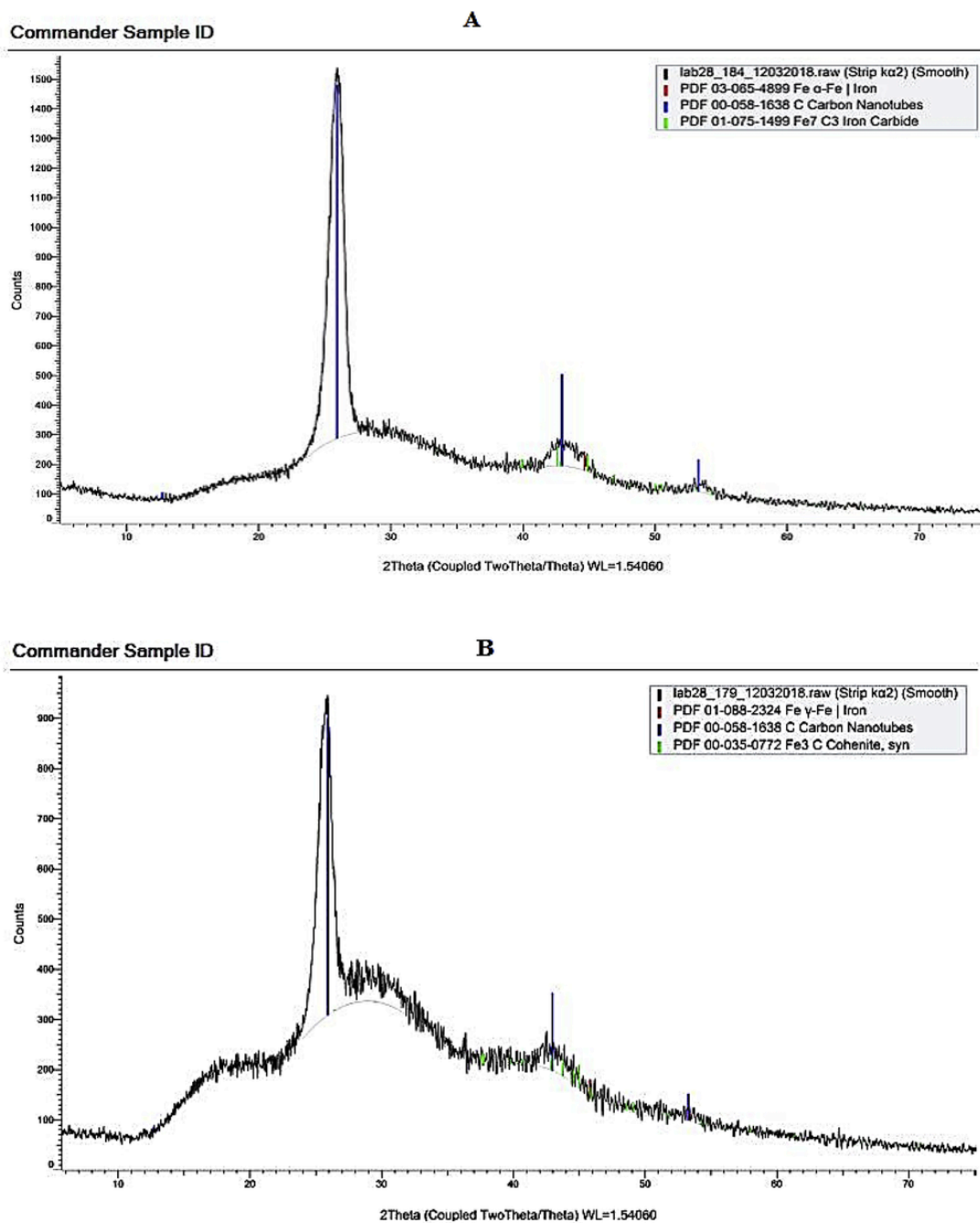


Fig. 4. XRD from as synthesised (A) and hydrochloride acid-purified (B) samples of multi-walled carbon nanotubes.

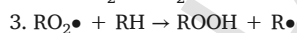
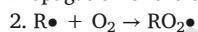
alytic mode.

Scheme 2

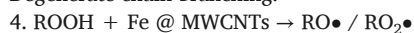
Chain origination:



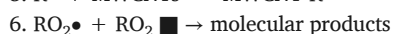
Propagation of the chain:



Degenerate chain branching:



Chain termination:



where $\text{R}\bullet$ ($\text{RO}_2\bullet$) are the radicals formed during the disintegration of the initiator, the other designations are indicated in Scheme 1.

* The conventional numbering of oxidation stages has been used [67,68].

4. Conclusions

1. Carbon nanotubes, obtained by chemical vapour deposition during the thermal catalytic pyrolysis of hydrocarbons in the presence of variable valence metal compounds, contain, as a rule, catalyst residues (impurities) — metals and metal carbides. The impurities catalyse the processes of chain liquid-phase aerobic oxidation of hydrocarbons by the radical decomposition of hydroperoxides.

- The effect of MWCNTs obtained by the thermal catalytic pyrolysis of cyclohexane in the presence of ferrocene as a catalyst on the kinetics of the oxidation processes (azobisisobutyronitrile) of cumene by atmospheric oxygen has been investigated. It has been established that the degenerate branching of the chain oxidation process suppresses the route of attachment of alkyl and peroxide radicals to the carbon cage of nanotubes inherent in pure CNTs, and the reaction proceeds in an autocatalytic mode.
- Using the example of cleaning CNTs containing Fe_7C_3 and iron in the α -form, it was found that cleaning CNTs from metal carbides by treatment with hydrochloric acid leads only to a different packing of the metal atoms in the crystal lattice (Fe_3C and γ -iron).
- A clearer and more effective reaction scheme for understanding the oxidation of hydrocarbons in the presence of CNTs as obtained by the CVD gas phase method during the thermal-catalytic pyrolysis of carbon-containing raw materials has been proposed.

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