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IMPACT OF AS-PREPARED AND PURIFIED MULTI-WALLED CARBON NANOTUBES ON THE LIQUID-PHASE AEROBIC OXIDATION OF HYDROCARBONS

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Abstract. The article presents simple kinetic approaches to study the effect of multi-walled carbon nanotubes (MWCNTs) additives on the aerobic oxidation of hydrocarbons and to propose real acceptable mechanisms of the process. The aerobic liquid phase low-temperature oxidation of ethylbenzene conducted in the presence of multi-walled carbon nanotubes has been used as a model pattern. Kinetic analysis established the catalytic action associated with the presence of the iron compounds in inner channels of MWCNTs. These compounds are identified as ferric carbides provoking decomposition of the ethylbenzene hydroperoxide and thereby suppressing the competitive route of alky-peroxide radicals addition to the nanocarbon cage. Thus the reaction finally proceeds in the autocatalytic mode.Contradictory conclusions on the effect of CNTs on the oxidation chain processes existing in the literature are associated with the lack of control over nature and content of metal impurities in channels of nanotubes.

Keywords: carbon nanotubes, CVD process, electron affinity, chain aerobic oxidation ofhydrocarbons, rate of oxygen uptake, oxidation chains linear breakage, chain ramification, oxidation catalysis.

1. Introduction

Carbon nanotubes (CNTs) relate to new promising class of materials, with a broad field of various applications. In direction to chemical processes, then CNTs can be effectively used in the reactions of cycloaddition, epoxidation, cross-combination, photocatalytic and electrochemical reactions. In these processes, CNTs act as carriers or 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 catalytic pyrolytic synthesis) actively catalyse the aerobic oxidation of cumene [7], decaline [8] and hydrocarbons in the oil fraction [9, 10].

MWCNTs have also been used in the catalytic liquid-phase oxidation of cumene with the 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 aerobic 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 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 a catalytic activity and accelerate the processes of hydrocarbons oxidation.

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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 383 K for 24 h. The use of such MWCNTs for the oxidation of cumene at 353 K, 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 cumenehydroperoxide formation 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 ... O_2 and further development of the reaction by a radical mechanism according to the following scheme:

$$\text{Chain initiation}\quad \text{CNTs} + O_2 \rightarrow \text{CNTs} \ldots O_2 \qquad (1)$$

$$\text{CNTs} \ldots O_2 + \text{RH} \rightarrow \text{CNTs} \ldots \text{OH} + \text{R}\bullet \qquad (2)$$

$$\text{ROOH} \xrightarrow{\text{CNTs}} \text{RO}\bullet + \text{HO}\bullet \qquad (3)$$

$$\text{RO}\bullet + \text{RH} \rightarrow \text{ROH} + \text{R}\bullet \qquad (4)$$

$$\text{Chain propagation}\quad \text{R}\bullet + O_2 \rightarrow \text{ROO}\bullet \qquad (5)$$

$$\text{ROO}\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}\bullet \qquad (6)$$

$$\text{RO}\bullet \rightarrow (C_6C_5)\ COCH_3 + CH_3\bullet \qquad (7)$$

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

Scheme 1

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 (CH_3CN) at a temperature of 428 K 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 unpurified CNTs sample, the conversion and selectivity indicators turned out to be almost the same – 38.2 % and 60.9 %, respectively. This shows that the CNTs purifying procedure with hydrochloric acid, used 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 phenylethylhydroperoxide into free radicals and to promote the formation of acetophenone through *π*-*π* interactions between radical particles, peroxide and the graphene surface of CNTs. New catalysts are offered as an effective alternative to cobalt-containing catalytic systems for the selective oxidation of ethylbenzene to acetophenone.

There is a 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/Al_2O_3 catalyst at 973 K. Here they utilised single-walled CNTs (SWCNTs) obtained by the thermal-catalytic (Co, Mo) pyrolysis of ethanol on a quartz substrate at 1073 K. 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 398 K, 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" phase 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 an electron transfer, resulting in the production of an alcohol and a ketone.

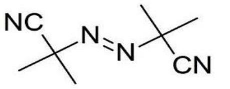
Carbon nanotubes also exhibit high catalytic activity and selectivity in the oxidation of *α*-pinene with a molecular acid [35]. In general, the oxidation of this bicyclic monoterpene proceeds, as a rule, in two main directions – epoxy-degradation and allylic oxidation. The presence of CNTs catalyses 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 investigated the nature and content of metallic inclusions in the CNTs. This is regardless of the fact that all the CNTs samples were obtained by the CVD method in the presence of various metal catalysts. The metal remnants, 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 confirm this issue, we have undertaken a study on the oxidation of ethylbenzene in the presence of CNTs obtained by a thermal catalytic pyrolysis of cyclohexane. It is continuation of our previous investigation [38] when we used cumene as a reference hydrocarbon. Now we involve the hydrocarbon with the secondary functional carbon atom to utilize the same simple kinetic approach making possible to determine the regularities of the effect of additives of various CNTs on the course of this standard model reaction and suggest a real acceptable process for the mechanism of oxidation.

2. Experimental

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

Hydrocarbon − ethylbenzene (Alfa Aesar), the degree of purity of the reagent was 99 %.



Radical initiator − azobisisobutyronitrile (AIBN).

Multi-walled carbon nanotubes (MWCNTs) were obtained by the method of deposition of chemical vapour during the thermal catalytic pyrolysis of cyclohexane in the presence of ferrocene. In the experiments, crude, unpurified nanotubes (MWCNTs-c.) and samples were treated for 12 h with a hot concentrated hydrochloric acid in a flask with a reflux condenser (MWCNTs-pr.).

The reaction of ethylbenzene oxidation was carried out in a 30–40 ml reaction vessel. 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 experiments, the reaction vessel was immersed in an ultra-thermostat and shaken with a frequency of about 3-7 cycles per second to ensure saturation of the reaction mixture with oxygen. The reaction was carried out at a temperature of 333 K. After the vessel was immersed in the thermostat and heated for 2–3 min, 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 298 K. The thermostat accuracy of the reaction vessel and burette was ±0.05 K.

The rate at which a fluid meniscus moves in the burette is proportional to the reaction rate. Oxygen absorption rate is: 1 $mm^3/min = 6.8\cdot10^{-7} / V$, mol $O_2/l\cdot s$, where V is the volume of the reaction mixture, ml.

For the reaction mixture volume of 10 ml, we have 1 $mm^3/min = 6.81\cdot10^{-8}$ mol $O_2/l\cdot s$. The oxidation rate was determined from the tangent of the slope of the kinetic dependences of oxygen absorption: $dO_2/dt = WO_2$. Each experiment was carried out three times, the error in determining the reaction rate was around 3–7 %.

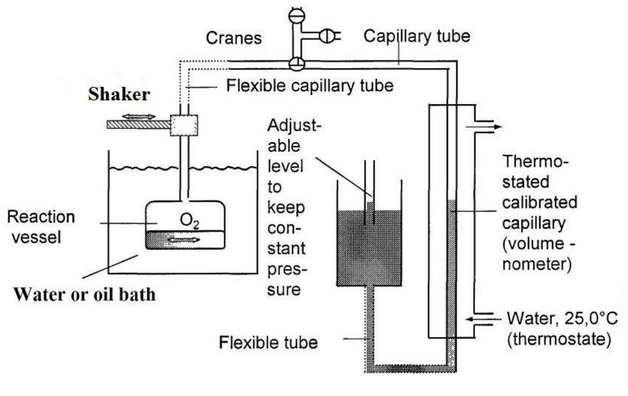


Fig. 1. Schematic representation of a laboratory setup for measuring the amount of gas absorbed or released [39-42]

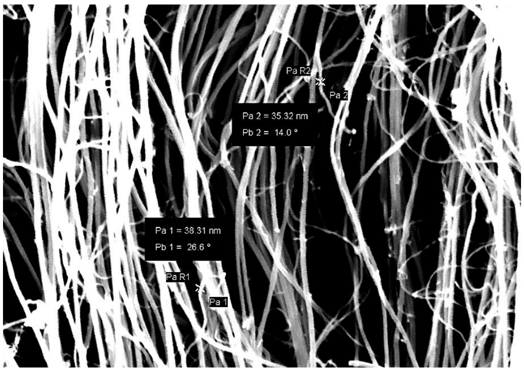


Fig. 2. A snapshot of the MWCNTs taken with a scanning electron microscope

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 1173 K 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 (AACVD process) [43].

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 30–40 nm on the average (Fig. 2).

3. Results and Discussion

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

As can be seen from the curves, the oxidation reaction of ethylbenzene in the presence of crude MWCNTs-c. is inhibited at the initial stages and proceeds with a certain induction period [Fig. 3, *line* 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, *line* 1). Reactions with purified samples (MWCNT-pr.) proceed without any induction period and are actively catalysed by the addition of the nanotubes (Fig. 3, *lines* 3, 4).

Figures 4a and 4b show the data for the X-ray structural analysis of the MWCNTs-c. samples and MWCNTs-in its purified form.

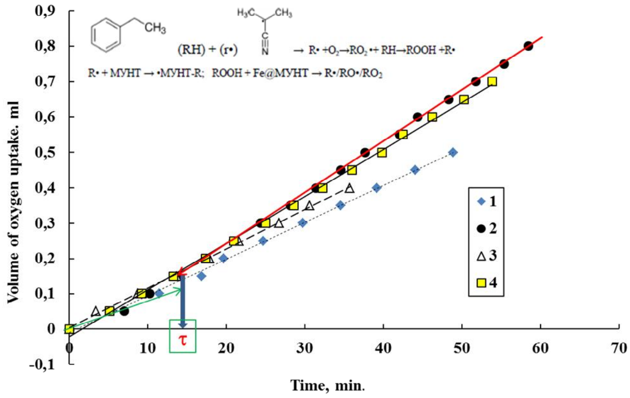


Fig. 3. Kinetic dependences of oxygen absorption in the initiated oxidation of ethylbenzene in the absence (1) and presence of crude (2) and purified (3-5) samples of multi-walled carbon nanotubes (MWCNTs).
The volume of the reaction mixture is 10 ml, temperature is 333 K, oxygen pressure is 20 kPa (air). The initiator is azobisisobutyronitrile (AIBN), the initiation rate $W_i = 6.8 \cdot 10^{-8}$ $M \cdot s^{-1}$. [MWCNTs]: 0 (1) and 1 g/l MWCNT-c. (2); 0.5 and 1 g/l MWCNTs-pr

From the XRD data it can be seen that in the untreated samples the crystalline phase of iron carbide Fe_7C_3 and iron in its α-form is present in a significant amount. The treatment of MWCNTs with a 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 [44, 45].

It seems that in the oxidation of hydrocarbons in the presence of MWCNTs-c. the inhibition in the initial part is observed as a result of the interaction of the carbon skeleton with radicals until a certain concentration of hydroperoxides accumulates. Further, the radical decomposition of hydroperoxides, catalysed by iron compounds in MWCNTs-c., completely suppresses the inhibiting component of the process and the reaction proceeds in an autocatalytic mode. In the case of the use of MWCNTs-pr. samples, the induction period is obfuscated by the catalytic action of Fe_3C and γ-Fe almost from the very beginning 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 R• radicals and considerably less active peroxide RO_2• radicals [18, 46, 47]. This conclusion is in good agreement with the data on other nanocarbon compounds − fullerenes C_{60} and C_{70} and graphene [23, 24, 26, 48-53]. 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 489–633 K at 408–413 K 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) ≥ 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 macroradicals are relatively longlived. However, in the liquid phase with a sufficiently high oxygen pressure of 13.3–26.7 kPa, when the concentration of oxygen dissolved in an hydrocarbon is of the order of ~10^{-3} M, the alkyl radicals R• almost instantaneously change into a peroxide by the reaction R• + $O_2 \rightarrow RO_2$• [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 + R• (RO_2•) → •CNTs-R(RO_2) cannot compete with the reaction ROOH + M@CNTs → radicals RO• (RO_2•) and the oxidation process develops into a catalytic mode.

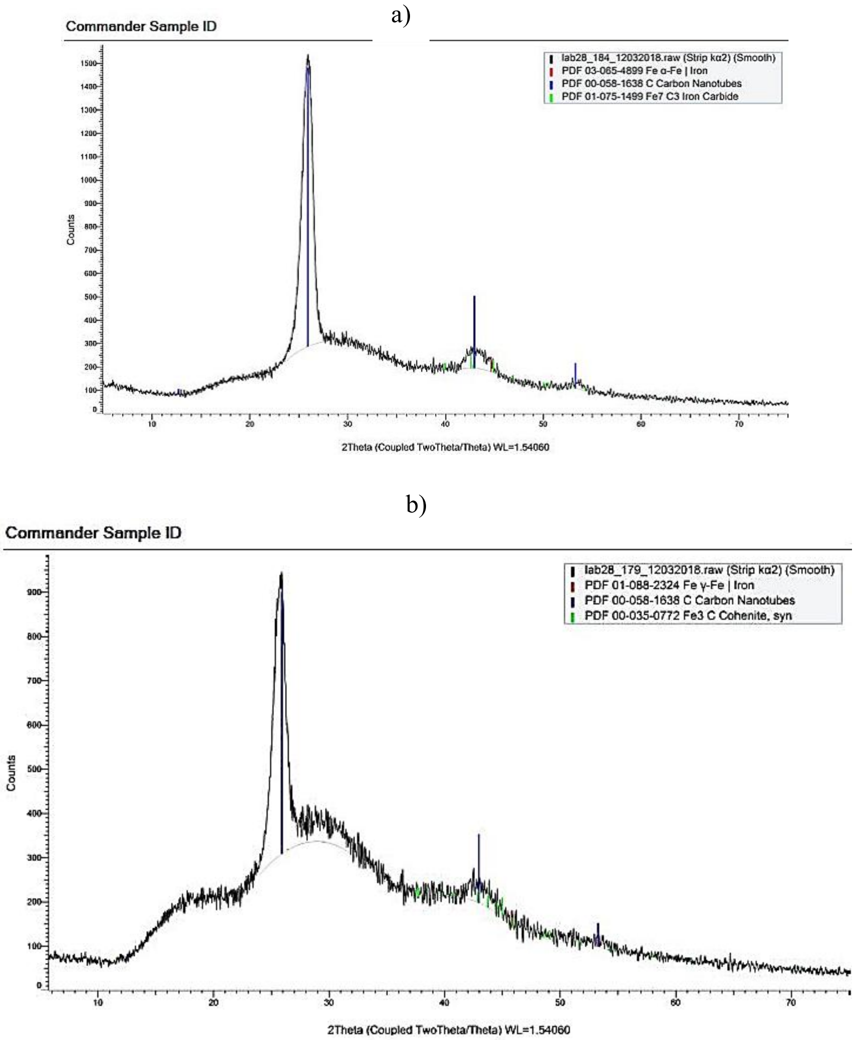


Fig. 4. Spectra of X-ray analysis of crude (a) and hydrochloride acid-purified (b) samples of multi-walled carbon nanotubes

Chain origination: AIBN $\xrightarrow{\perp}$ (T°C) r• (RO_2•) + RH → RH + R• (W_i initiation rate) (8)
Propagation of the chain: R• + $O_2 \rightarrow RO_2$• (9)
RO_2• + RH → ROOH + R• (10)
Degenerate chain branching: ROOH + Fe@MWCNTs → RO• / RO_2• (11)
Chain termination: R• + MWCNTs → •MWCNT-R (12)
RO_2• + RO_2• → molecular products (13)

where r• (rO_2•) 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 [65, 67].

Scheme 2

4. Conclusions

Carbon nanotubes, obtained by a chemical vapor deposition during the thermal catalytic pyrolysis of hydrocarbons in the presence of variable valence metal compounds, contain, as a rule, catalyst residues − metals and metal-like 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 ethylbenzene 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 the cleaned CNTs containing Fe_7C_3 and iron in the α-form, it was found that refinement of CNTs from metal carbides by the treatment with hydrochloric acid leads only to a different packing of the metal atoms in the crystal lattice (Fe_3C and γ-iron), which, as a rule, contains more carbon atoms.

A real scheme for the oxidation of hydrocarbons in the presence of CNTs obtained by the method of deposition from the gas phase during the thermal-catalytic pyrolysis of carbon-containing raw materials has been proposed.

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ВПЛИВ ПОПЕРЕДНЬО ПРИГОТОВЛЕНИХ І ОЧИЩЕНИХ БАГАТОСТІННИХ ВУГЛЕЦЕВИХ НАНОТРУБОК НА РІДКОФАЗНЕ АЕРОБНЕ ОКИСНЕННЯ ВУГЛЕВОДНІВ

Анотація. *Представлені прості кінетичні підходи до вивчення впливу багатостінних вуглецевих нанотрубок (MWCNT) на аеробне окиснення вуглеводнів та запропоновано реальні прийнятні механізми процесу. Як модель використано аеробне рідкофазне низькотемпературне окиснення етилбензену у присутності багатостінних вуглецевих нанотрубок. За допомогою кінетичного аналізу визначено, що каталітична дія пов'язана з наявністю сполук заліза у внутрішніх каналах MWCNT. Ці сполуки ідентифіковані як карбіди заліза, що провокують розкладання етилбензенгідропероксиду і тим самим пригнічують конкурентне додавання алкілпероксидних радикалів до клітин нановуглецю. Встановлено, що реакція протікає в автокаталітичному режимі. Показано, що суперечливі висновки щодо впливу вуглецевих нанотрубок на ланцюговий оксидаційний процес, які існують у літературі, пов'язані з відсутністю контролю над природою та вмістом металевих домішок у каналах нанотрубок.*

Ключові слова: *вуглецеві нанотрубки, CVD-процес, спорідненість до електронів, ланцюгове аеробне окиснення вуглеводнів, швидкість поглинання кисню, лінійний розрив ланцюгів окиснення, розгалуження ланцюга.*