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OXIDATION KINETICS OF A COMMERCIAL DIESEL FUEL AND ITS FRACTION IN THE PRESENCE OF METAL-CONTAINING MULTI-WALLED CARBON NANOTUBE ADMIXTURES

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Abstract. This study is to evaluate the extent of aerobic oxidation of diesel fuel fractions in the presence of Fe-Co-containing multi-walled carbon nanotubes (Fe-Co@MWCNT). Fe-Co clusters located in the nanocarbon channels and outside actively catalyse the chain oxidation. Results suggest selecting efficient nanocatalytic systems for the oxidative conversion of multicomponent hydrocarbon feedstocks.

Keywords: petroleum hydrocarbons, diesel fuel fraction, metal-containing carbon nanotubes, aerobic oxidation, catalytic hydroperoxide, oxygen rate.

1. Introduction

Selective catalytic oxidation of hydrocarbons is one of the most promising routes to valuable organic oxygenated compounds[1]. Many of these chemical transformations have been developed into large-scale industrial catalytic processes and still have considerable reserves for modernization and improvement through the introduction of modern innovations[2–4]. Carbon nanocatalysis is one such means[5–7].

To date, considerable efforts have been made to develop various carbon-based catalytic systems, including amorphous carbon, carbon doped with heteroatoms and transition metals, carbon as an active catalytic support and carbon hybrids. Despite the development of many excellent catalysts, there remain several unresolved issues related to their activity, mechanism of action and technology for their rational industrial implementation.

In this work, iron- and cobalt-containing multi-walled carbon nanotubes were studied as promising catalytic couples for the synthesis of carboxylic acids by aerobic oxidation of hydrocarbons of the petroleum fraction. According to the stepwise scheme, the first kinetic regularities of the liquid phase aerobic oxidation of diesel fuel and its paraffin-naphthenic fractions have been studied.

It is obvious that selective oxidative transformations of petroleum hydrocarbons occupy an important place in the petrochemical synthesis and oil refining field for the production of various valuable oxygenated and related compounds[8–10]. This line of research has a rich history, sometimes associated with the development of synthetic naphthenic acid (SNA) production, which is achieved by catalytic aerobic oxidation of middle oil fraction hydrocarbons[11, 12]. In recent years, the use of carbon nanocatalysts has been successfully proposed for a number of advantageous patterns, where multi-walled carbon nanotubes (MWCNT) containing metal and metal compounds (being residues of CVD synthesis precursors) actively catalyse the aerobic oxidation of oil hydrocarbons[13].

Some works indicate that pristine CNTs reveal catalytic activity and accelerate the oxidation of hydrocarbons. Aerobic cumene oxidation in the presence of a commercial CNTs sample (Shen-zhen Nanotech Port Co. Ltd) was arranged to investigate the oxidation conversion measure[14]. The nanotube sample was pre-cleaned with hydrochloric acid, then washed with demineralized water and dried with hot air at T=110 °C for one day. The use of such prepared MWCNT for the oxidation of cumene at T=80 °C, an oxygen flow rate of FR=10 mL/min and the added amount of 10 g/L MWCNT resulted in a hydrocarbon conversion of 24.1 % and a selectivity of 88.4 % for the formation of cumene hydroperoxide. The authors are inclined to the radical mechanism of the

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process, since the addition of p-benzoquinone to the reaction system almost completely suppressed the oxidation process. The catalytic activity of MWCNTs was attributed to the initial formation of a MWCNT‴O_2 complex and further development of the chain process according to the generally accepted oxidation scheme[15].

A similar study was presented on the aerobic liquid phase oxidation of ethylbenzene and cyclohexane in the presence of CNTs, where a significant catalytic effect of CNTs was observed[16–18]. A high yield and selective oxidative conversion of ethylbenzene to acetophenone was found[16]. However, in contrast to the case of cumene oxidation, much more stringent process conditions were used. The reaction was carried out in an autoclave at T=155 °C, oxygen pressure p=1.5 MPa, reaction time t=4 hours, and the amount of nanotubes was w=20 g/L. The interaction between the radicals leading the oxidation chain and the graphene surface of carbon nanotubes promotes the accumulation of radicals in the active contact zone and thus significantly intensifies the catalytic processes of hydroperoxide decomposition with the resulting formation of alcohols and ketones.

Decorating CNTs with transition metals is one of the most efficient ways to increase the intrinsic oxidation catalytic activity of CNTs. In fact, there are a number of publications that have clearly demonstrated the promoting role of metals bonded or located in the channels of CNTs[19, 20]. This is therefore a very attractive area of research, which has already been described for the aerobic oxidation of aromatic hydrocarbons[21–24] and cyclic alkanes[25–28]. The next interesting related step is the enhanced oxidation catalytic activity of metals confined in CNT channels. The fundamentals state that the limited space of CNT channels causes specific electronic effects, creating a unique microenvironment that shifts the level of catalytic activity toward metals with higher binding energies[29]. The degree of catalytic activity depends on the nature of the metals and the diameter of the CNT. The proposed concept explains a variety of effects observed in experiments for various reactions quite well, including oxidation catalytic processes[29, 30].

General. Paraffin oxidation is a historical industrial process for the production of synthetic fatty acids by molecular oxygen in the presence of catalysts to be further processed to soaps, fats as well as to lubricating greases. Oxidation of a diesel oil mixture of hydrocarbons can produce valuable chemical base products in a similar process. However, this process is very complicated and requires specific oxidation catalysts of the highest selectivity. Therefore, we are focused on studying carbon nanocatalysts capacity, having the final target of developing a new process of petroleum carboxylic acids synthesis from multicomponent oil feedstock.

Thus, the testing catalytic activity of MWCNT containing transition metal (Co) located on the outer walls and those of (Fe) confined in the channels in the aerobic oxidation of diesel fuel and its paraffinic-naphthenic fractions was an objective of this investigation

2. Experimental

2.1. Materials

Commercial diesel fuel produced by the State Oil Company of the Republic of Azerbaijan (SOCAR) and the diesel dearomatized (paraffinic-naphthenic) fraction were used in the experiments.

The raw materials used for the CVD synthesis of MWCNT were propane (purity 98.7 %), diluent (argon, purity 99.9 %), precursor-catalyst – ferrocene (Sigma-Aldrich)

2.2. Methods of Synthesis and Preparation of Raw Materials

2.2.1. De-Aromatization Process for a Diesel Fuel

The removal of aromatic hydrocarbons from the diesel fraction (fuel) was carried out using oleum or concentrated sulphuric acid. The concentration of the sulphuric acid is an important point and significantly affects the overall interaction of the acid with the aromatic hydrocarbons. It is better to use 97–98 % sulphuric acid. The ratio of collected diesel fraction to sulphuric acid should be 1:3 (by volume). A 2 liter separatory funnel was used to carry out the process. The prepared required amounts of diesel fraction and sulphuric acid are placed in the separatory funnel and shaken for 15–20 minutes at room temperature.

The separatory funnel is then left for 30 minutes to allow the sulphonic acid derivatives formed to precipitate completely. Repeat up to 3 times at room temperature.

A 10 % KOH or NaOH solution is prepared beforehand. The alkaline treatment is used to neutralize the residual sulphuric acid and acid products formed after the first treatment. The dearomatized diesel fraction is washed several times with hot water and then drained.

The fractions are then placed in a litre beaker, heated to 70–80 °C, and the gumbrin powder is added and stirred. The gumbrin is very hygroscopic and actively absorbs moisture and settles quickly. The result of these procedures is a colourless and transparent finished paraffinic-naphthenic fraction.

It should be noted that the method of de-aromatization of middle oil fractions to remove aromatic hydrocarbons and obtain paraffin-naphthenic ones is widely used in our Institutes of oil profile and gives satisfactory results. Despite the mild conditions of the de-aromatization

procedure, a small content of unsaturated hydrocarbons – olefins, dienes and even triene is observed. Apparently, oleum – sulphuric acid as a strong oxidizing agent causes partial oxidation of saturated hydrocarbons with the formation of unsaturated analogues. This approach is described elsewhwere[11–13].

2.2.2. CVD Synthesis of Metal-Containing Multi-Walled Carbon Nanotubes (MWCNT)

MWCNTs were synthesized by chemical vapour deposition (CVD) using a home-built pyrolysis apparatus (Fig. 1).The raw material (propane, purity 98.7 %) and diluent (argon, purity 99.9 %) were fed into the gas conditioning unit, where their volumetric rate (ratio = = 1:20) was controlled by valves and flow meters. The gases were then passed through a mixer to the inlet of a quartz reactor. Before starting the synthesis, the catalyst precursor – ferrocene – was placed inside the reactor in a ceramic boat. The temperature in the first part of the reactor, where ferrocene vaporization took place, was maintained at 110 °C, while in the second part, where MWCNTs were directly formed, the temperature was 900 °C. Thus, the gas mixture in the first part of the reactor was mixed with ferrocene vapour and transferred to the second part of the reactor, where ferrocene decomposed under the influence of high temperature, forming catalytically active iron clusters on which the synthesis of carbon nanotubes was carried out. The resulting precipitate was deposited on the inner wall of the reactor. After 30 min of synthesis, the propane supply was stopped, the furnace was cooled, and the resulting product was removed from the reactor and weighed.

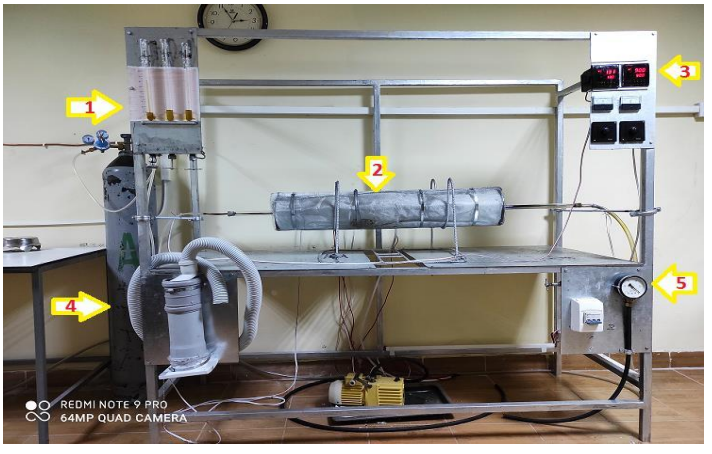

Fig. 1. Laboratory CVD unit for synthesis of MWCNT: 1 – gas treatment unit;
2 – two-section tubular reactor, blocks: 3 – temperature control unit; 4 – air supply; 5 – vacuum section

2.2.3. Preparation of Co-Fe-containing MWCNT

Thermal decomposition of cobalt nitrate $Co(NO_3)_2$ followed by reduction to Co, was used to deposit cobalt clusters on carbon nanotubes. For this purpose, the prepared Fe@MWCNT sample was treated with a measured volume of the aqueous salt solution to obtain a viscous suspension. The resulting suspension was then placed in a ceramic cup, incubated at 90 °C until the water was evaporated, and then it was calcined under an inert gas atmosphere (Ar) at 900 °C for 6–12 hours. The cobalt oxide (CoO), produced during the salt decomposition, was reduced with hydrogen to its final form as cobalt clusters.

2.3. Methods of analysis of materials involved in this study

The composition of the diesel fuel and that of the fraction was determined by gas chromatography-mass spectrometry on a GC-MS instrument, Agilent Technologies 7890B (GC) – 5977B (MSD), with identification of components in the mass range m/z = 30–550.

The structural and elemental composition of the obtained MWCNT samples was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and elemental analysis (EDX) (Figs. 2–4). The electronic microscopes, scanning JSM 6610-LV with EDX attachment and transmission JEM-1400 (both manufactured by JEOL, Ltd., Japan), were used.

2.4. Data on the hydrocarbon content in the diesel fractions

The key data on hydrocarbon content are selected and summarised in Tables 1 and 2[31, 32].

Table 1. Hydrocarbon components of the diesel fuel

No.	Aliphatic hydrocarbons	Content, wt. %
1	*n*-Paraffins	26.186
2	Monoalkyl-substituted aliphatic hydrocarbons	14.007
3	Dialkyl-substituted aliphatic hydrocarbons	2.856
4	Trialkyl-substituted aliphatic hydrocarbons	3.816
5	Tetraalkyl-substituted aliphatic hydrocarbons	8.874
∑	The total content of all aliphatic hydrocarbons	55.739
	Naphthenic hydrocarbons	
1	Unsubstituted naphthenic hydrocarbons	1.301
2	Monoalkyl-substituted naphthenic hydrocarbons	4.802
3	Dialkyl-substituted naphthenic hydrocarbons	3.284
4	Trialkyl-substituted naphthenic hydrocarbons	0.908
5	Tetraalkyl-substituted naphthenic hydrocarbons	1.110
6	Pentaalkylsubstituted naphthenic hydrocarbons	0.656
7	Hexaalkyl-substituted naphthenic hydrocarbons	0.724
∑	The total content of all naphthenic hydrocarbons	12.785
	Olefinic hydrocarbons	
1	Unsubstituted olefinic hydrocarbons	2.130
2	Monoalkyl-substituted olefinic hydrocarbons	2.910
∑	Total content of all olefinic hydrocarbons	5.040
	Aromatic hydrocarbons	
1	Unsubstituted aromatic hydrocarbons	0.009
2	Monoalkyl-substituted aromatic hydrocarbons	1.782
3	Dialkyl-substituted aromatic hydrocarbons	1.980
4	Trialkyl-substituted aromatic hydrocarbons	3.092
5	Tetraalkyl-substituted aromatic hydrocarbons	1.460
∑	The total content of aromatic hydrocarbons	8.323
	Naphthene-aromatic hydrocarbons	
1	Unsubstituted naphthenic-aromatic hydrocarbons	2.752
2	Monoalkyl-substituted naphthene-aromatic hydrocarbons	2.743
3	Dialkyl-substituted naphthene-aromatic hydrocarbons	2.233
4	Trialkyl-substituted naphthene-aromatic hydrocarbons	1.792
∑	The total content of naphthenic-aromatic hydrocarbons	9.520

Table 2. Hydrocarbon components of the diesel fuel paraffinic-naphthenic fraction

No.	Aliphatic hydrocarbons	Content, wt. %
1	*2*	3
1	*n*-Paraffins	31.214
2	Monoalkyl-substituted aliphatic hydrocarbons	15.123
3	Dialkyl-substituted aliphatic hydrocarbons	2.132
4	Trialkyl-substituted aliphatic hydrocarbons	3.418
5	Tetraalkyl-substituted aliphatic hydrocarbons	8.895
∑	The total content of all aliphatic hydrocarbons	60.782
	Naphthenic hydrocarbons	
1	*n*-Naphthenic hydrocarbons	1.646

Continuation of **Table 2**

1	*2*	3
2	Monoalkyl-substituted naphthenic hydrocarbons	11.729
3	Dialkyl-substituted naphthenic hydrocarbons	4.394
4	Trialkyl-substituted naphthenic hydrocarbons	2.221
5	Tetraalkyl-substituted naphthenic hydrocarbons	1.189
6	Pentaalkylsubstituted naphthenic hydrocarbons	1.058
7	Octaalkyl-substituted naphthenic hydrocarbons	0.618
∑	The total content of all naphthenic hydrocarbons	22.855
	Olefinic hydrocarbons	
1	Unsubstituted olefinic hydrocarbons	0.703
2	Monoalkyl-substituted olefinic hydrocarbons	2.540
3	Trialkyl-substituted olefinic hydrocarbons	0.068
∑	Total content of all olefinic hydrocarbons	3.311
∑	Total content of all other unsaturated hydrocarbons	0.938
	Naphthene-aromatic hydrocarbons	
1	Monoalkyl-substituted naphthene-aromatic hydrocarbons	0.288
∑	Total content of all naphthene-aromatic hydrocarbons	0.288

2.5. Morphology and elemental analysis of metallic carbon nanotubes

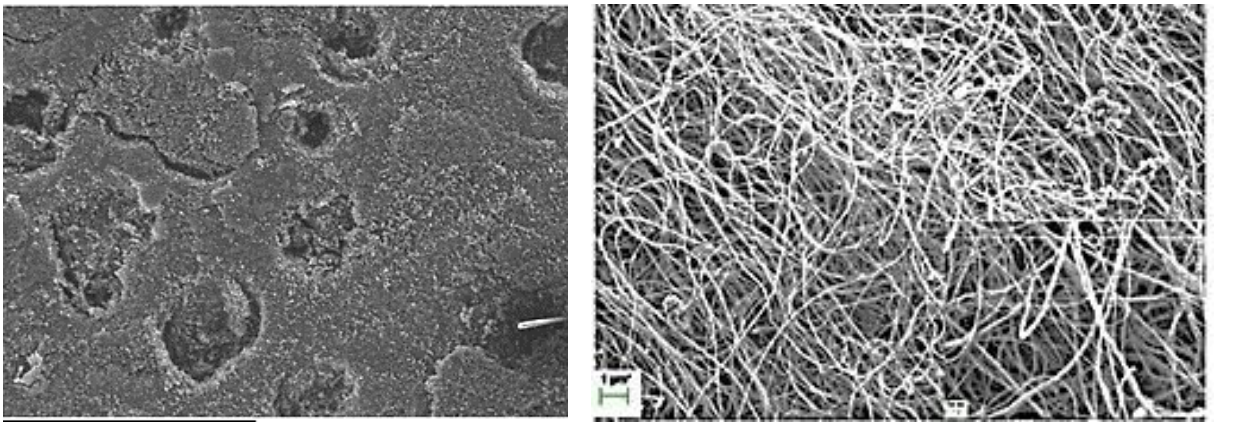

Fig. 2. SEM images of a Fe@MWCNT sample made at different resolutions

Element	Weight, %	Atomic, %
C	80.79	89.60
O	9.79	8.15
Fe	9.42	2.25
Total	100.00	

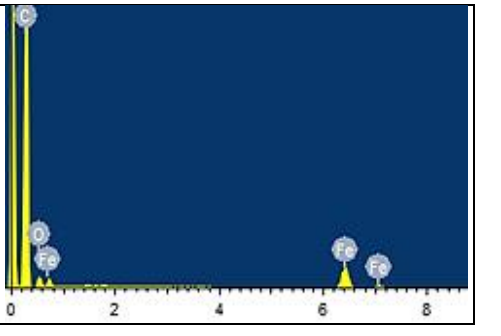

Fig. 3. Elemental analysis (EDX) data for Fe@MWCNT sample

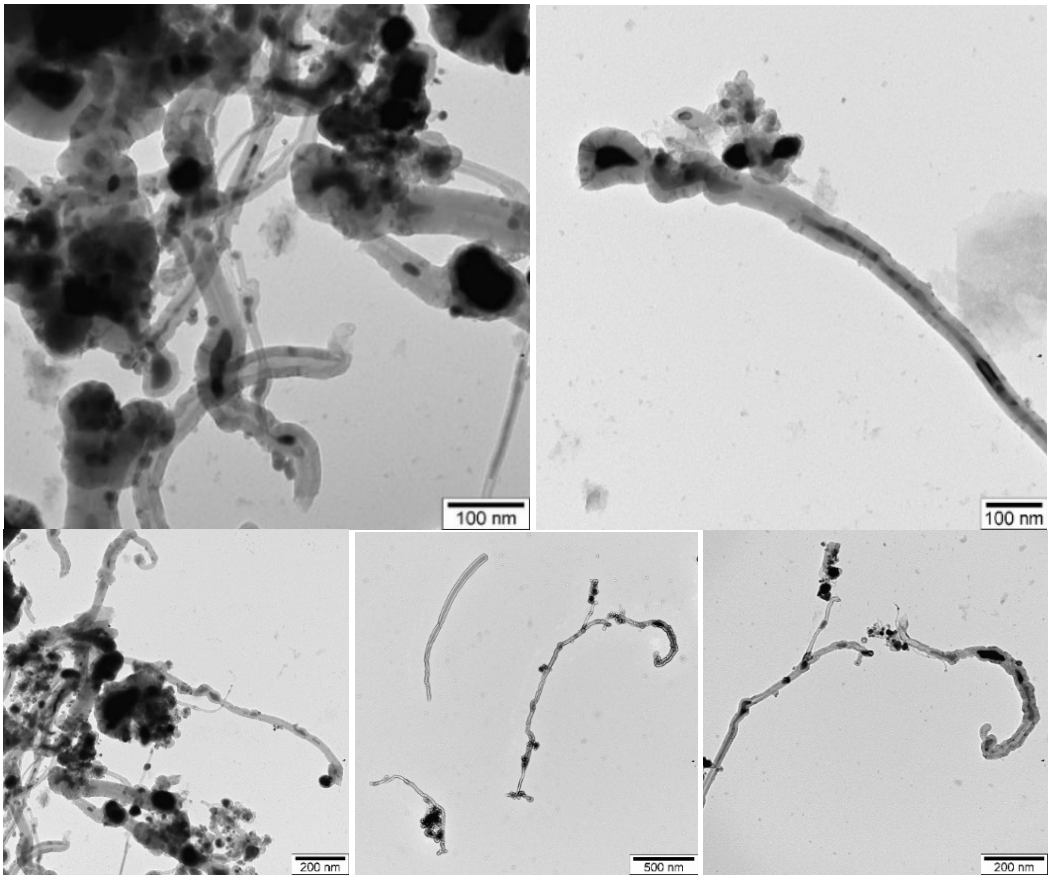

Fig. 4. TEM images of a Fe@MWCNT sample made at different resolutions

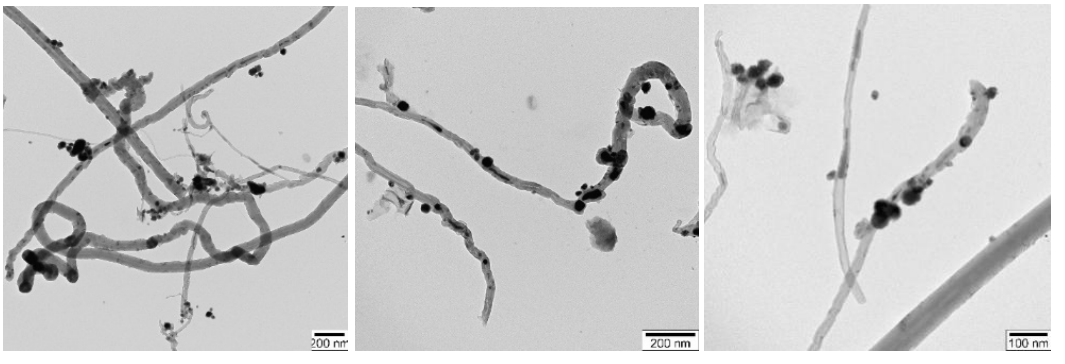

Fig. 5. TEM images of the Co-Fe@MWCNT sample

2.6. Oxygen uptake technique (kinetic measurements)

The aerobic oxidation of a sample of diesel fuel and a sample of the paraffin-naphthenic fraction was carried out in a barrel-shaped glass reactor with complete stirring of a liquid reactive mixture while shaking (Fig. 6). The liquid diesel and the fraction were oxidized in the kinetic range with full air-oxygen saturation of the reaction mixture.

The oxidation kinetic curves were graphically differentiated at different points to determine the progress of the chain reaction. The oxidation rate was determined by the tangent of the angle of slope of the graphical curves (or straight lines) of oxygen uptake: $-dO_2/dt = Wo_2$. The oxygen uptake rate 1 mm^3 O_2/min = 6.8×10^{-7}/V, mol $O_2/l\text{-}s$, where V is a reaction volume in cm^3. The average error of the measurements was about 5–7 %.

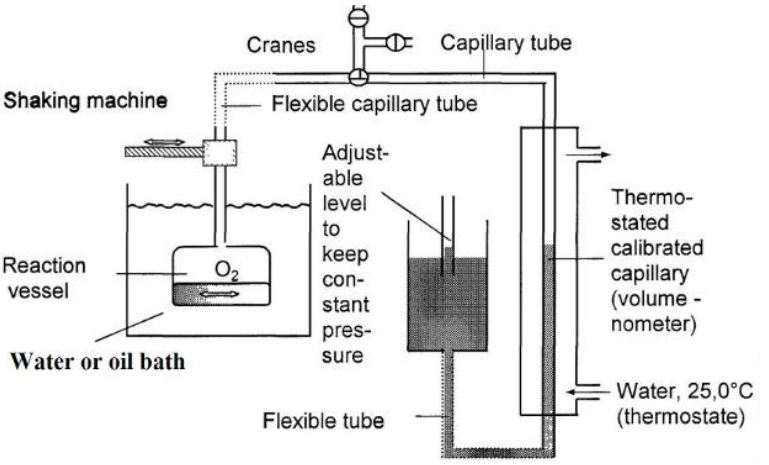

Fig. 6. Schematic representation of the laboratory unit for measuring the volume of gas consumed or evolved[33]

3. Results and Discussion

A profile of the kinetic curves for the air oxidation of the diesel fraction in the absence and presence of metal (M)-containing MWCNTs is shown in Fig. 7.

It can be seen that the oxidation proceeds with a clearly expressed long induction period for the non-catalytic reaction ($\tau = 43$ min). The introduction of the catalyst leads to a shortening of the induction period in the order of 20 (τ_1) and 10 min (τ_2) for the Fe@MWCNT and Co-Fe@MWCNT catalysts, respectively. The MWCNT additions with integrated metals (Fe, Co) promote the acceleration of oxygen consumption and the oxidation reaction proceeds in an autocatalytic mode. The observed catalytic effect can be explained in terms of a catalytic radical decomposition of hydroperoxides accumulated in the oxidation process (Scheme 1), which basically proves the mechanism proposed for such catalytic oxidation of hydrocarbons in our previous works[24–28]. It should be noted that under the experimental conditions, no oxygen uptake is observed during oxidation without a catalyst.

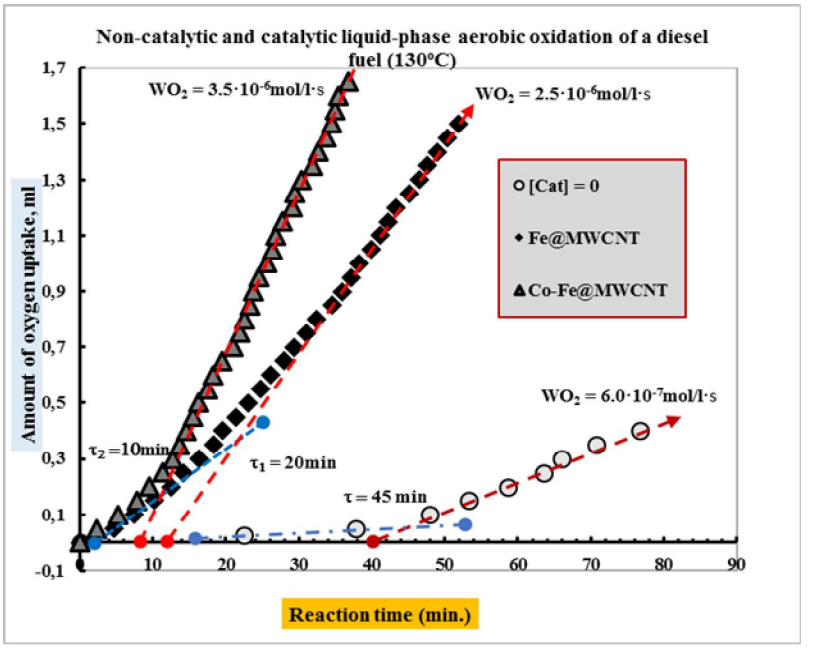

Fig. 7. Kinetic curves for the aerobic oxidation of a diesel fuel in the absence and presence of Fe (≈10 wt. %) and Co-Fe (≈ 20 wt. %)-containing MWCNT. Reaction volume – 10 mL, [M@MWCNT] = 3 g/L, 130 °C

Scheme 1. The presumptive reaction stages of petroleum hydrocarbons aerobic oxidation in the presence of metal-containing carbon nanotube catalysts (Wo_2 is the effective oxidation rate)

Chain initiation (formation of alkyl R• radicals, rate is W_o):

$$[R\text{-}H + M@MWCNT] \rightarrow R^{\bullet} + M@MWCNT \quad (1)$$

$$[H\text{-}R\text{-}R\text{-}H + M@MWCNT] \rightarrow$$
$$\rightarrow 2\,R^{\bullet} + M@\,MWCNT \quad (2)$$

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \quad (3)$$

$$2\,RH + O_2 \rightarrow 2\,R^{\bullet} + H_2O_2 \quad (4)$$

where RH – petroleum hydrocarbon, R•– carbon-centered radical, M – metal (Fe, Co).

Chain propagation and development (rate is W_d):

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad (5)$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \text{ (rate constant is } k_3) \quad (6)$$

The presence of a carbon nano-catalyst leads to decomposition of the intermediate catalytic complex [hydroperoxide···M@CNT] with formation of additional active radicals and reaction chain development:

$$ROOH + M@MWCNT \rightarrow$$
$$\rightarrow [ROOH * M@MWCNT * ROOH] \rightarrow$$
$$\rightarrow 2RO^{\bullet} + 2HO^{-} + M^{2+} \quad (7)$$

$$M^{2+} + ROOH \rightarrow RO^{\bullet} + {-}OH + M^{3+} \quad (8)$$

$$ROOH + M^{3+} \rightarrow M^{2+} + RO_2^{\bullet} + H^{+} \quad (9)$$

Chain termination (rate is W_t):

$$RO^{\bullet} + RO^{\bullet}/RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$$
$$\rightarrow \text{recombination products (rate constant is } k_6) \quad (10)$$

The general equations describing the scheme proposed may be presented as:

$$Wo_2 = (W_o + W_d)^{1/2}\, k_3 k_6^{-1/2} [RH] \quad (11)$$

$$\tau_n \propto W_o / W_d \quad (12)$$

The experiments carried out on the oxidation of the paraffinic-naphthenic fraction have shown that this process proceeds with a shorter induction period and at higher rates than the oxidation of diesel fuel (Fig. 8).

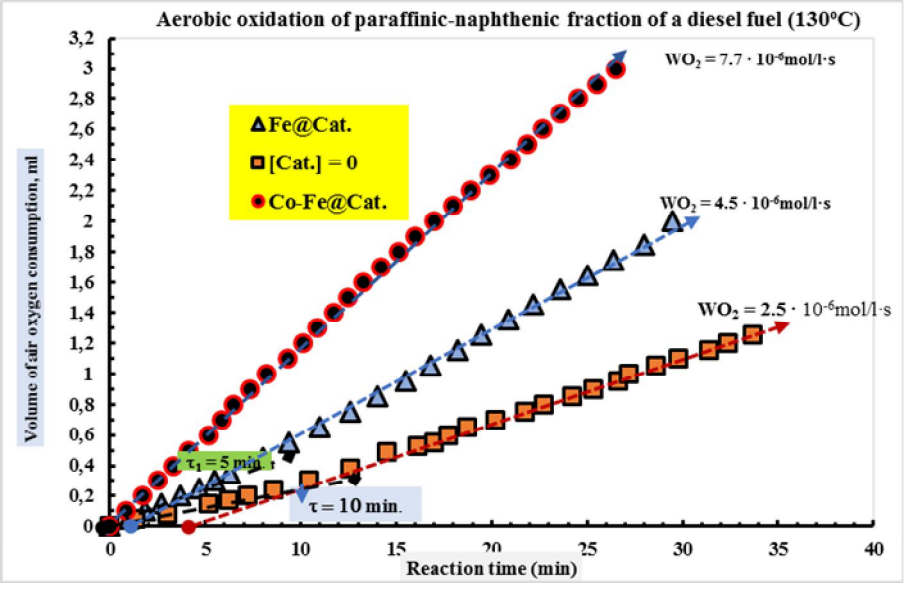

Fig. 8. Kinetic curves for the aerobic oxidation of a diesel fuel paraffinic-naphthenic fraction in the absence and presence of Fe (≈10 wt. %) and Co-Fe (≈ 20 wt. %)-containing MWCNT. Reaction volume – 10 mL, [M@MWCNT] = 3 g/L, 130 °C

The kinetic data obtained can be interpreted in terms of the component composition of the diesel fuel and the fraction. The paraffinic-naphthenic fraction does not contain aromatic hydrocarbons, which are known to be alkyl radical acceptors and therefore capable of inhibiting hydrocarbon oxidation chain processes[33, 34]. It should be emphasized that both objects are complex mixtures of hydrocarbons with representatives from all the basic homology series, and therefore, the oxidation rates measured are effective values that allow only a general estimation.

As a result of the CVD synthesis process, Fe atoms in α and γ crystal modifications and Fe carbides seem to be encapsulated by the hollow cylindrical carbon structures, so that they are located in the internal cavities of the final formed finished nanotubes (Fig. 4). In this respect, a growing number of experimental studies show that metal or metal oxide nanoparticles encapsulated inside CNTs exhibit different catalytic activity compared to the same metals deposited on the outer walls, with some reactions enhanced and others slowed down[30, 35, 36]. Different electronic structures and spatial confinement

exert stronger strains and deformations within the CNT channels that define and adjust the visible apparent catalytic activity[29].

It was found that Fe and its compounds encapsulated in MWCNTs significantly accelerate the aerobic oxidation of diesel fuel and its paraffin-naphthene fraction. The introduction of additional cobalt nanoclusters, located predominantly on the outside of the nanotubes (cf. Fig. 5), removes the existing diffusion limitations and leads to a measurable contribution to the catalytic activity of the oxidation process (cf. Figs. 7 and 8).

The aerobic oxidation of hydrocarbons and oil fractions has fractional order and mixed order kinetics, which is characteristic of this type of chain reactions. The order of the chain reactions can be rationalized using the steady state approximation for the concentration of reactive intermediates such as free radicals. Methodologically, this is quite a challenge, which we hope to address in our subsequent studies.

4. Conclusions

1. The extent of aerobic oxidation of diesel paraffin-naphthene fraction in the presence of Fe-Co-containing multi-walled carbon nanotubes has been evaluated.

2. The transition metals being in the nanotube channels, as well as on the surface and in the interchannel space, have been shown to act as efficient catalysts for the oxidative chain branching process.

3. A general scheme of the oil fraction catalytic aerobic oxidation is proposed and the kinetic equation of the effective reaction rate is presented.

4. Despite the different views on the mechanism of the hydrocarbons oxidation in the presence of carbon nanotubes available in the literature, this study proves the key role of metals being independently inside or outside of the nanotubes channels in the creation of high increscent catalytic activity.

5. Besides, in principle, this study provides new information on the synthesis of multi-walled fibrous carbon nanotubes, on the surface or inside of which transition metal ions of certain catalytic activity can be selectively impregnated.

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КІНЕТИКА ОКИСНЕННЯ КОМЕРЦІЙНОГО ДИЗЕЛЬНОГО ПАЛИВА ТА ЙОГО ФРАКЦІЇ У ПРИСУТНОСТІ МЕТАЛОВМІСНИХ СУМІШЕЙ БАГАТОСТІННИХ ВУГЛЕЦЕВИХ НАНОТРУБОК

Анотація. *Здійснено оцінювання ступеня аеробного окиснення фракцій дизельного палива в присутності Fe-Co-вмісних багатостінних вуглецевих нанотрубок (Fe-Co@MWCNT). Кластери Fe-Co, розташовані в нановуглецевих каналах і поза ними, активно каталізують ланцюгове окиснення. Отримані результати дають змогу підібрати ефективні нанокаталітичні системи для окиснювальної конверсії багатокомпонентної вуглеводневої сировини.*

Ключові слова: *нафтові вуглеводні, дизельна фракція палива, металовмісні вуглецеві нанотрубки, аеробне окиснення, каталітичний гідропероксид, швидкість доступу кисню.*