THE AEROBIC OXIDATION OF DECALIN AND TETRALIN WITH PRESENCE OF A METAL-CONTAINING CARBON NANOFIBERS

Aliyeva A. Z., Abbasov V. M., Aliyeva A. E., Nasibova G. G., Amirov F. A.

Abstract
The article describes the catalytic effects of metal-containing carbon nanofiber in reaction of aerobic oxidation of decalin.

Keywords: Decalin, tetralin, oxidation, naphthenic hydrocarbons, metal-containing carbon nanofiber, naphthenates

INTRODUCTION
The processes aerobic oxidation of hydrocarbons are important for science and practice. In the scientific aspect - it's broad avenues, bringing significant contribution to the understanding of the mechanism of natural and synthetic processes involving carbon and oxygen [1-4] in the application - is operating industrial processes, generating an important part of the global chemical products [5,6].

The catalysis oxidation of hydrocarbon – a major subsection of aerobic oxidation, widely reported in the literature [7-11]. Currently, researchers in this field not limited to the selection of new catalytic systems seen as the direction of development and use of non-traditional approaches, such as use of cavitation, magnetic, ultrasonic or microwave treatment techniques or solid catalysts for direct exposure to the reaction mixture during chemical transformation. Taking advantage of the scale factor has also become very fashionable in the aspect of application nanocatalysts. The article [12] was described catalytic effect of carbon nanofibers for oxidative dehydrogenation of ethylbenzene. Effect of particle size of cobalt supported on carbon nanofibers, on the Fischer-Tropsch reaction have been studied by the authors [13].

In synthesizing carbon nanofibers, carbon-containing gas molecules are decomposed at high temperature and carbon is deposited in the presence of transition metal catalysts on the substrate, on which there is a further growth of the fiber around the catalyst particles. The choice of this catalyst is interesting, since the combination of carbon and transition metals and, plus, the presence of nanoscale structures may lead to a good catalytic effect, on the theory. Decalin and tetralin are a hydrocarbon, modeling of composite components of diesel oil fractions, which are used to produce synthetic oil acids (SOA) [14-16].

The process of obtaining SOA is a core for our laboratory and therefore the results of the study presented for us is an optional value.

CHARACTERISTICS OF INITIAL RESEARCH FACILITIES, EQUIPMENT, METHODOLOGY FOR CONDUCTING EXPERIMENTS
In the work, the use of carbon nanofiber CNF of different structures and by containing metal, represented by the German company "FutureCarbon GmbH". Characteristics of the sample of the specification of the data sheet are shown in Table 1.
Table 1. Characteristics of carbon nanofibers CNF-PL, CNF-HB, CNF-SC

<table>
<thead>
<tr>
<th>Type of structure</th>
<th>Surface area (BET), m²/g</th>
<th>Metallic inclusions, %</th>
<th>middle diameter, nm</th>
<th>length, mkm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plates - CNF-PL</td>
<td>120</td>
<td>Fe ≤ 5%</td>
<td>100-250</td>
<td>1-5</td>
</tr>
<tr>
<td>Herringbone - CNF-HB</td>
<td>60</td>
<td>Ni ≤ 2%</td>
<td>200-600</td>
<td>5-50</td>
</tr>
</tbody>
</table>

Figure 1-3 shows microphotographs of the carbon nanofibers of different structure, obtained by transmission electron microscopy.

Figure 1. Structure and texture of iron-containing carbon nanofibers plate type CNF-PL (pictures SEM & TEM).

Figure 2. Structure and texture of nickel-containing carbon nanofibers herringbone type CNF-HB (pictures SEM & TEM).
The oxidation of decalin was carried out in the absence and presence of carbon nanofibers of different structure in a closed system gasometrical set Fig. 3 [17-20].

![Diagram](image)

**Figure 3.** Schematic diagram of measuring equipment used for oxygen uptake at constant pressure.

The reaction is carried out at temperatures of 100 °C and the oxygen pressure $P_{O_2} = 20$ kPa (air).

The reaction rate measured by the amount of absorbed oxygen.

For oxygen uptake rate of 1 mm$^3$/min have:

$$W_{O_2} = 1 \text{ mm}^3/\text{min} = 10^{-6} \frac{273}{298} \cdot \frac{1}{22.4} \cdot \frac{1}{60} \cdot \frac{1}{V} = 6.81 \cdot 10^{-10} \cdot \frac{1}{V} \text{ mol/l-s}$$

where $V$ - volume, in ml of the reaction mixture.

For $V = 0.01$ l (10 ml) of 1 mm$^3$/min = $6.81 \cdot 10^{-8}$ mol / l-s[20]

$W_{O_2}$ oxidation rate was determined from the kinetic dependence of the absorption of oxygen from the slope of graphic curves (or lines).
RESULTS AND DISCUSSION

Figure 4, 5 and table 2 shows the results of the kinetic experiments.

Table 2. The data on the kinetics of oxygen uptake in the aerobic oxidation of decalin and tetralin with catalyst presence of iron and nickel containing carbon nanofibers. [Cat.] = 20 q/l (~ 2%). $P_{O_2} = 20$ kPa (air)

<table>
<thead>
<tr>
<th>№</th>
<th>Amount of hydrocarbons, ml</th>
<th>Type of catalyst</th>
<th>Amount of catalyst, mg</th>
<th>Rate of oxidation $WO_2$, mm$^3$/min</th>
<th>Rate of oxidation $WO_2$, mol $O_2/(l\cdot sec)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Decalin -5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Tetralin - 5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>Tetralin – 5 /22/ Fe CNF-PL</td>
<td>100</td>
<td>11</td>
<td>7,5·10$^{-7}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Decalin - 5</td>
<td>Fe CNF-PL</td>
<td>100</td>
<td>3</td>
<td>2·10$^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>Decalin - 5</td>
<td>Ni CNF-HB</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>Decalin - 5</td>
<td>Ni CNF-HB</td>
<td>300</td>
<td>5,1</td>
<td>3,5·10$^{-7}$</td>
</tr>
</tbody>
</table>

Figure 4. Kinetic dependence $O_2$ uptake during the oxidation of decalin in the presence of Fe-CNF-PL, $T = 100 \, ^\circ C$, $P_{O_2} = 20$ kPa (air)
Following the results we have the following conclusions: 1) decalin and the tetralin is not oxidized at 100° C, and by catalytic presence of metal containing of carbon nanofibers the oxidation process significantly accelerated; 2) The oxidation of tetralin by iron containing carbon nanofibers process oxidation is much better than in decalin; 3) by catalytic presence of nickel containing carbon nanofibers reaction of oxidation in decalin is accelerated by increasing the amount of a catalyst; 4) considering the characteristics of the catalysts used (Table 1), it can be concluded that neither the structure nor the surface area and the diameter of the carbon nanofibers does not affect the oxidation process; 5) On the formation of hydroperoxides metal demonstrates the effect on the process, and in this case iron.

It is known that the temperature of the lower limit is 100 °C for decay of hydroperoxides in the aerobic oxidation of hydrocarbons [3,21,22]. As seen from these experiments (Tabl.2) at this temperature and other conditions of the experiment (closed system, the pressure of O₂ = 20 KPa) oxidation of tetralin and decalin occurs at an appreciable rate in the presence of Fe-CNF. Thus, it is believed that Fe-CNF catalysts exhibit high catalytic activity in the aerobic oxidation of hydrocarbon, and further, at more detailed study can be recommended as an active catalyst for these processes.

Infrared spectrum oxidate obtained by the oxidation of decalin in the presence of Fe-CNF-PL, T = 100° C, P₀₂ = 20 kPa (air) was removed on a spectrometer "Thermo Scientific" in the frequency range of 700-4000 sm⁻¹. Samples were analyzed in a cell with windows NaCl, thickness 0.052sm⁻¹. Spectrum is shown in Figure 6.
Figure 6. The IR spectrum of the reaction mixture obtained in the oxidation of decalin in the presence of iron-carbon nanofiber Fe-CNF-PL. T = 100 °C, PO₂ = 20 kPa (air), [Fe-CNF-PL] = 20 g/l (~ 2%).

The spectrum (Fig.6) of the absorption band in 3200-3500 cm⁻¹, corresponding to stretching vibrations of OH in the hydroxyl group. Absorption band 2510 cm⁻¹ corresponds to the carboxyl, 1720 cm⁻¹ - carbonyl, 995,1036,1111 cm⁻¹ - deformation vibrations of CH bond groups in the aromatic ring.

General scheme of the oxidation of decalin can be represented as[1]:

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The above mechanism of catalysis is caused by the oxidation of decalin and refers to electron transfer to redox catalysis. The high catalytic activity of the catalyst due to the fact that the atoms of transition metals may exist in different oxidation states which change does not require large expenditures of energy. As a result of electron transfer from the reagent to catalyst is easier than in the absence of a catalyst reducing the oxidant. When the one-electron transition produces free radicals and other active sites which are then involved in reaction. It appears that in this case decalin oxidation in the presence of carbon nanofibers containing different transition metals, the carbon support substantially facilitates electron transfer from metal. Scheme electron transfer in the oxidation process with the presence of a metal containing carbon nanofibers can be represented as follows:

\[ \text{RH} \rightarrow \text{ROOH} + \text{M}^{n+} \rightarrow \text{M}^{[n+1]+} + \text{RO}^\cdot + \text{OH}^\cdot \]

\[ \text{ROOH} + \text{M}^{[n+1]+} \rightarrow \text{M}^{n+} + \text{RO}_2^\cdot + \text{H}^\cdot \]

\[ \text{O}_2 \rightarrow \cdot\text{O}_2^\cdot \]

\[ \text{M}^{2+} \rightarrow \text{M}^{3+} \]

\[ \cdot\text{O}_2 + \text{RH} \rightarrow \text{products} \]

CONCLUSION

1. The low-temperature reaction (100 °C) aerobic oxidation of decalin and tetralin, catalyzed by metal-carbon nanofibers with different structures - platelet CNF-PL (content Fe = 5%) and herringbone - CNF-HB (content Ni = 2%) are done for the first time.

2. Determined that a different of structure of the nanofibers are not influencing the process and the emphasis on the catalytic effect of metals do

3. Shown that aerobic oxidation of the decalin and tetralin under the experimental conditions (temperature - 100 ° C, PO₂ - 20 kPa (air), the concentration of catalysts CNF-PL and CNF-HB = 20 - 60 g/l) reaction proceeds moderately. The result of the reaction indicates that the active centers do not participate in the linear chain termination.

The value of this work is to determine the catalytic properties of carbon nanofibers in the oxidation of hydrocarbons. The main interest - the study of the rate of absorption of oxygen in the oxidation of hydrocarbons with catalyst presence of carbon nanofibers.
References


