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PECULIARITIES OF THE AEROBIC OXIDATION OF OIL HYDROCARBONS CATALYZED BY CARBON NANOCOMPOUNDS

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Results of the catalytic oxidation of naphthenic hydrocarbons of the diesel cut in the presence of fullerenes C_{60} and C_{70} , single- and multi-walled carbon nanotubes, containing Co and covalently grafted Br-groups have been considered. Efficiency of a catalytic activity of the nanocarbons considerably exceeds that for the most active transition metal salt (Mn naphthenate) and leads to considerable higher yield and selectivity of synthetic naphthenic acids. The carbon nanocatalysts are estimated as the most advanced and suited for oxidation of hydrocarbons to be used in the industrial scale.

Keywords: oil hydrocarbons, oxidation, fullerenes, carbon nanotubes, manganese naphthenate, catalytic activity, synthetic naphthenic acids

Introduction

Synthetic naphthenic acids (SNA) production reached by the direct aerobic oxidation of naphthenic hydrocarbons blend of a petroleum diesel cut has been an accented subject of comprehensive explorations for last decades [1, 2]. This scientific direction launched by the scientific school of Academician B.K.Zeynalov then was developed by his successors. They were clearly understanding that the oil system subjected to the oxidation is very mutable and changeable, the reaction is going spontaneously and unamenable to control, selectivity is reduced because of lower yields and high conversions. Maximum yield of SNA was 16% that gives the same selectivity even at 100% of a naphthenate concentrate conversion. This is fairly low rates and task of investigators was to find special balanced conditions of the process to get higher output.

There was difficult to undertake something to shift temperature range to change the balance between SNA and oxynaphthenic acids (OSNA) unless use biomimetic catalytic system. As for a catalytic system used, the all efforts to do it with conventional hydroperoxide decomposers like salts of transition metals - Mn, Fe, Co, Ni, Cr, Cu, Ti naphthenates, stearates, acetates, palmitates and oths. to make

the industrial process economically sounded did not give any positive results. Optimal temperature was fixed as before at the range 403-413K. Other reserve is a rate of air passed through the reaction mixture - used one within 100-300 l per hour was found in vitro and accepted as providing the kinetic state of the reaction proceeding.

Novel horizons was recently discovered when we became to use carbon nanocompound-containing transition metals and Br-grafted functionality. It has brought really noteworthy results. Surprisingly there was revealed that selectivity and yield of the process towards SNA increase at the same conversion degree while those for OSNA is substantially sunk.

Experimental procedures

Naphthenate hydrocarbons isolated from a diesel cut of Azerbaijan oils industrial blend boiled up at 493-613K were subjected to the oxidation in the presence of carbon nanocompounds - fullerenes C_{60} and C_{70} , carbon nanotubes, containing Co (1.5-2 wt. %) - CoCNT-MW (producer is Future Carbon GmbH, Germany) and brominated multiwalled $(Br)_n$ -MWCNT and single-walled $(Br)_n$ -SWCNT carbon nanotubes produced by plasma-chemical technique in the BAM (Bundesanstalt für Materialforschung und-

prüfung: Federal Institute for Materials Research and Testing, Berlin, Germany).

Characteristics of the oil stock are presented in table 1.

Oxidation of the oil stock, containing inclusions of carbon nanocompounds was conducted in glass laboratory setup. Schematic view of the flow reactor for the oxidation experiments is shown in the figure 1.

Table 1

Physico-chemical features of the diesel cut of Azerbaijan (Baku) crude oils blend

Fraction (boiling/freezing points range, T°C)	Hydrocarbons content, wt.%			MW (molec. weight)	ρ_4^{20} , g/cm ³ (density)	d_4^{20} (refraction index)
	Aromatic	Paraffinic	Naphthenic			
crude [216-360/ (-35°C)]	16 -18	20-22	60-62	247	0.8555	1.4695
naphthenic [(220-350/ (-52)°C)]	0.6-0.8	6 -8	90-92	235	0.8330	1.4620

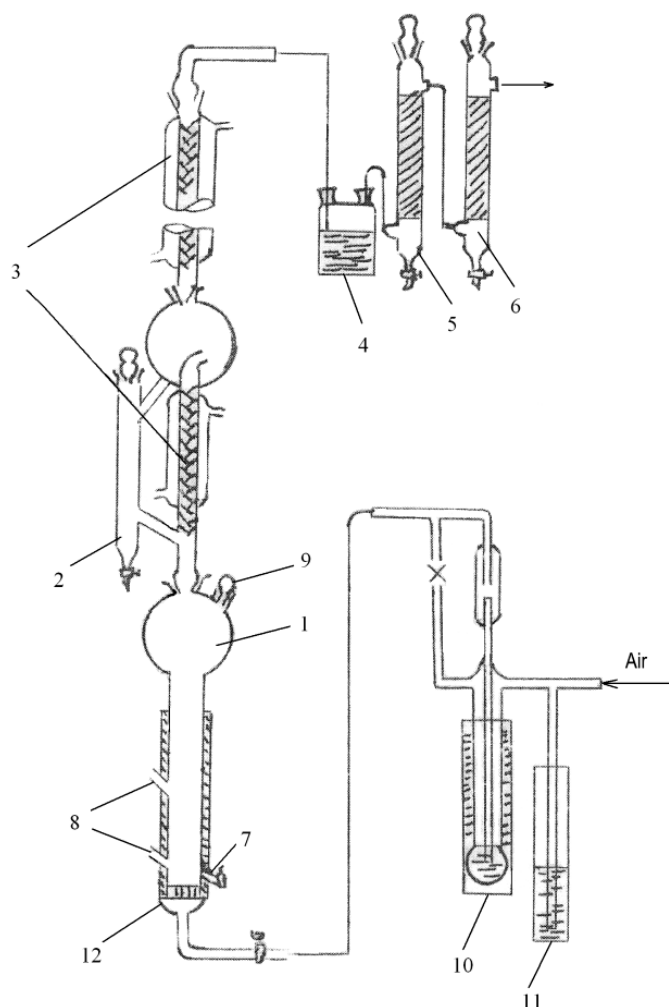


Fig. 1. Schematic representation of laboratory glass reactor for oxidation of liquid hydrocarbons.

1 – upper reaction zone of bubbling liquid hydrocarbons; 2- water trap; 3, 4 – condensers; 4-6 – absorbents; 7 – bibcock for sampling and draining; 8 – holders for contact thermometer and temperature indicator; 9- hole for a stock feeding; 10-11 – devices for air cleaning and air stream regulation; 12 – filter glass

Criteria of the oxidative conversion of oil hydrocarbons were values of acid number (A.N.) of a reacting mixture (oxidate) and yields SNA and OSNA. The acidic components (SNA + OSNA) were isolated from an oxidate by the alkali (NaOH or KOH) treatment followed by reverse recovering SNA + OSNA with the acidizing (the mineral acids). Next step was the separation of SPA from OSPA and unsaponifiables by light benzene or petroleum ether processing.

Results and discussions

The oxidation results obtained are accumulated in table 2 [3-8].

The data obtained are convincing evidence of the advantage of carbon nanocatalysts in regard to the salt of transition metal. Much lesser amounts of the nanocompounds lead to

higher SNA yields and selectivity than those for the conventional industrial catalysts. It should be also specially noted that results are impressive since the heterogeneous catalysis capability are compared with that for homogeneous catalysis with manganese naphthenate.

We forward several explanation of the observed effect: 1. No doubt that this phenomenon originates from the peculiarities of electronic configuration of a structure of carbon nanocompounds 2. Carbon nanocompounds may serve as an active support providing faster transfer of electron from metal to substrate 3. Moreover, a plausible mechanism of the catalytic activity may be connected with formation of reactive oxygen species.

The effects of catalytic activity may be schematically illustrated in the figure 2.

Table 2

Rates for the catalytic aerobic oxidation of the petroleum fraction 493-613K hydrocarbons.

Amount of the taken oil stock is 128 g (150 ml), reaction temperature 140°C, speed of air stream = 100-120 l/hour. A.N.-acid number. MnNapht. – Mn(II) salt of indigenous naphthenic acids

Catalyst type	Catalyst amount, mas. %	Reaction time, h.	A.N. (oxidate) mgKOH/g	Yield of acids, %	
				SNA	OSNA
C ₆₀ /C ₇₀ + MnNapht.[3, 4]	0.01 + 0.4	6	60	19	4
C ₆₀ /C ₇₀ + MnNapht. (dried) [4]	0.01 + 0.4	3	53	21-24	-
MnNapht.[1]	1.5	5.0- 5.5	50-60	13.3 - 16	10-12
CoCNT-MW [3, 5, 6]	0.01	6	58	20	1.3
CoCNT-MW [3, 5, 6]	0.1	6.5	55	19	1.5
(Br) _n -SWCNT [7]	0.16	6	60	25	3.0
(Br) _n -MWCNT [8]	0.16	6	75	30	5.0-7.0

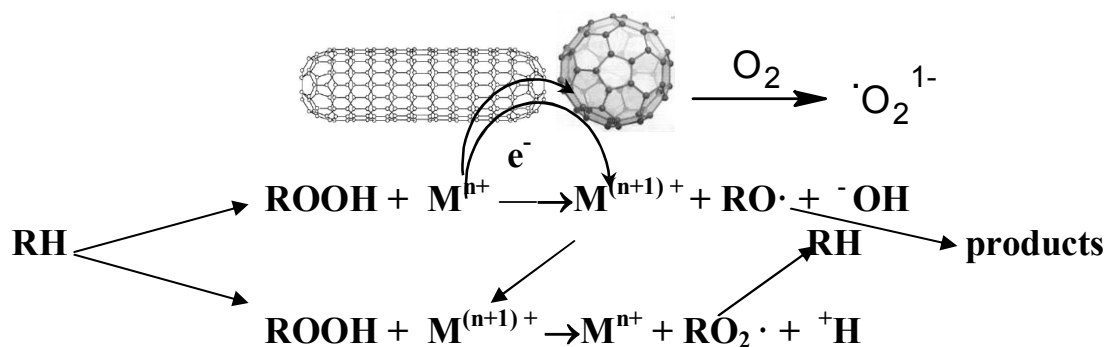


Fig. 2. Catalytic action stage of the oxidation of hydrocarbons

The literature confirmative data is [9]: interactions of the transition metal atoms with carbon nanotube walls are investigated using a tight-binding molecular dynamics method that allows for spin unrestricted geometry optimization. Comparison with the results for bonding on graphite indicates major differences in bonding sites, magnetic moments and the direction of charge transfer. The significant values of magnetic moments obtained for the metal atoms on nanotube walls is consistent with the recent experimental findings.

Conclusions

Metal- and Br- containing carbon nanocompounds are utmost active and selective catalytic systems for oxidation of hydrocarbons and have considerable advantages over salts of transition metals. These nanocompounds are catalysts of the future. Currently their using is restricted due to relatively high cost.

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REFERENCES

1. Зейналов Б.К. Синтетические нафтеневые кислоты. Баку: ЭЛМ, 1996, 252с.
2. Mal'kovskii P.A., Zainullov M.R., Minkhairov M.F., Gaifullin A.A. & Solodova N.L. Oxidation of naphthenic hydrocarbons of senomanian condensate // Petroleum Chemistry, 2003, v.43, N.1, p. 46-49.
3. Aliyeva A.Z., Zeynalov E.B., Ibragimov Kh.D., Nuriyev L.G., Seidov N.M. Synthesis of carbon nanostructures and their application as catalysts for oxidation of petroleum hydrocarbons // Processes of Petrochemistry and Oil Refining 12, 2011, v. 4, N.48, p. 220-227.
4. Zeynalov E.B., Agayev B.K., Nuriyev L.H., Iskenderova S.A., Sadiyeva N.F., Aliyeva A.Z. A new metal-containing catalytic systems in reactions of oil hydrocarbons oxidation and obtaining esters on the basis of synthetic petroleum acids // Processes of Petrochemistry and Oil Refining 11, 2010, v.1, N.41, p.12-17.
5. Алиева А.З., Нуриев Л.Г., Зейналов Э.Б. Получение синтетических нефтяных кислот каталитическим окислением нафтенового концентрата с участием нанотрубок // Азербайджанское нефтяное хозяйство, 2009, № 10, с. 47-50.
6. Зейналов Э.Б., Алиева А.З., Нуриев Л.Г., Ибрагимов Х.Д., Ищенко Н.Я. Многостенные углеродные нанотрубки, содержащие металл в качестве катализатора // Нефтегазовые технологии, 2011, № 6, с.69-72.
7. Zeynalov E.B., Friedrich J., Meyer-Plath A., Hidde G., Nuriyev L., Aliyeva A., Cherepnova Yu. Plasma-chemically brominated single-walled carbon nanotubes as novel catalysts for oil hydrocarbons aerobic oxidation // Applied Catalysis A: General 454, p. 115-118 (15 March 2013).
8. Zeynalov E.B., Friedrich J.F., Hidde G., Ibrahimov H.J., Nasibova G.G. Brominated carbon nanotubes as effective catalysts for petroleum hydrocarbons aerobic oxidation // Erdöl Erdgas Kohle, 2012, v. 3, p. 45- 48.
9. Menon M., Andriotis A.N., Froudakis G.E. Curvature dependence of the metal catalyst atom interaction with carbon nanotubes walls // Chem. Phys.Lett. 2000, v. 320 (5-6), p. 425-434.

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NANOKARBON BİRLƏŞMƏLƏRİ İLƏ KATALİZ OLUNAN NEFT KARBOHİDROGENLƏRİNİN AEROBİK OKSİDLƏŞMƏ XÜSUSİYYƏTLƏRİ

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C₆₀, C₇₀ fullerənləri, kobalt və funksional Br qrupları saxlayan tək- və çoxlaylı karbon nanoboruları iştirakında dizel fraksiyasının naften karbohidrogenlərinin katalitik oksidləşmə proseslərinin nəticələri təhlil edilmişdir. Müəyyən edilmişdir ki, nanokarbon katalizatorları təsir effektivinə görə keçid metallarının ən aktiv duzlarını (Mn naftenat) əhəmiyyətli dərəcədə üstələyir və onlar daha yüksək çıxım və selektivliklə sintetik naften turşularının alınmasına gətirib çıxarır.

Təsvir edilmiş nanokarbon katalizatorları sənaye oksidləşmə prosesləri üçün ən perspektiv katalitik sistemlər kimi qiymətləndirilir.

Açar sözlər: neft karbohidrogenləri, oksidləşmə, fullerənlər, carbon nanoboruları, manqan naftenat, katalitik aktivlik, sintetik naften turşuları

ОСОБЕННОСТИ АЭРОБНОГО ОКИСЛЕНИЯ НЕФТЯНЫХ УГЛЕВОДОРОДОВ, КАТАЛИЗИРУЕМОГО УГЛЕРОДНЫМИ НАНОСОЕДИНЕНИЯМИ

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Рассмотрены, результаты каталитического окисления нафтеновых углеводородов дизельной фракции в присутствии фуллеренов C₆₀, C₇₀, одностенных и многостенных углеродных нанотрубок, содержащих кобальт и Br-функциональные группы. Установлено, что наноуглеродные катализаторы значительно превосходят по эффективности действия самые активные соли переходных металлов (нафтенат Mn) и приводят к получению синтетических нафтеновых кислот с высоким выходом и селективностью. По результатам работ углеродные наносоединения оцениваются как наиболее перспективные катализаторы окисления углеводородов и рекомендуются для реализации в промышленном масштабе.

Ключевые слова: нефтяные углеводороды, окисление, фуллерены, углеродные нанотрубки, нафтенат марганца, каталитическая активность, синтетические нафтеновые кислоты