ASOIU
Azerbaijan State Oil and Industry University

AJCN, Vol .7, No.2 , 2025, pp.33-40
https://doi.org/10.32010/AJCN04022025-31

ACCUMULATION OF ORGANOMETALLIC COMPOUNDS ON THE ZCC SURFACE UNDER CONDITIONS OF CATALYTIC OXYCRACKING

[1]Elvira Guseinova 0000-0003-0297-1516
Department of "Petrochemical technology and industrial ecology"
Professor, doctor of chemical sciences, ASOIU
elvira_huseynova@mail.ru
[2]Samira Safarova. 0000-0003-4663-5557
Research Institute "Geotechnological Problems of Oil, Gas and Chemistry
PhD student
ssafarova22@gmail.com
[3]Maya Abdullayeva 0000-0002-1380-1216
Department of "Petrochemical technology and industrial ecology"
Associate professor, ASOIU
mayaabdullayeva@hotmail.com
[3]Gakhraman Hasanov 0000-0001-9272-6084
[4]Research Institute "Geotechnological Problems of Oil, Gas and Chemistry"
Professor, doctor of technical sciences
gaman51@mail.ru

Abstract:*The paper presents the results of studying the accumulation of organometallic compounds on the surface of a zeolite-containing catalyst (ZCC) during the catalytic oxycracking of heavy hydrocarbon raw materials. The aim of the study was to determine the nature and degree of accumulation of trace elements that can affect the activity and stability of the catalyst. The experiments were carried out at a temperature of 500 °C, an oxygen concentration of 1 %, a contact time of 1.2-2 s, and a process duration of 900 s. The elemental composition of the catalyst surface before and after catalysis was studied by energy-dispersive microanalysis (EDM). It is established that during the process, the accumulation of trace elements Fe, Ni, Cr, and Ca occurs on the surface of the catalyst Ca, due to their migration from the raw material. As the contact time increases, the Fe content increases to 2.3%, Cr to 0.1%, Ni to 0.04%, and Ca to 0.02 %. The obtained values are significantly lower than the known critical levels at which the active sites of the catalyst are deactivated. This allows us to conclude that the accumulation of metals on the surface of ZCCs is not the main reason for the decrease in its activity during catalytic oxycracking, and decontamination is associated with other factors that require further study.*

Keywords: catalytic oxycracking, zeolite-containing catalyst, organometallic compounds, energy dispersion analysis, iron, nickel, chromium, calcium, catalyst deactivation.

INTRODUCTION

Heterogeneous catalysts allow efficient use of scarce raw materials, both renewable (for example, biomass, polymer waste and household waste) and non-renewable (for example, crude oil, coal and natural gas), in a variety of hydrocarbon and carbohydrate conversion processes. Although the popular definition of catalysts suggests that they are not used in the chemical reaction itself, this does not mean that the catalysts have eternal life. Unfortunately, in fact, various chemical and physical processes most often lead to deactivation of solid catalysts. Examples of such processes are loss of function due to sintering and poisoning of metal, as well as structural degradation processes such as dealuminization of zeolite and destruction of the zeolite framework [1-5]. Another example of catalyst deactivation is the formation of carbon deposits that clog the pores of the catalyst or otherwise prevent access to the catalytic centers. Thus, catalyst decontamination is an important area of both academic and industrial research. The mechanisms of deactivation of new or industrial catalysts are studied both *in in situ* and *operando*. The fact that catalysts are usually deactivated over time makes it difficult to determine the appropriate time in the life of the catalyst to determine activity (or speed (TOF)).

One of the urgent problems of developing the concept of catalytic oxycracking in the presence of ZCC is understanding the dynamics of its activity and selectivity. It is reliably proved that the process parameters have different effects on its selectivity and conversion of VG. In our previous works [6-8], based on the study of the parameters of the catalytic oxycracking process in the presence of ZCCs of the system, it was shown that the temperature and degree of oxidation equally strongly determine the conversion of raw materials and the distribution of products, while the temperature and contact time show the opposite effect. Similar to traditional catalytic cracking (CC), the key parameters are the process temperature and the contact time of raw materials with the catalyst, but their action is multidirectional.

The effect of temperature can be illustrated as follows:

– at 450 °C, the conversion rate reached 54.7 %, the yield of liquid target products was 29.6 %, and that of gaseous products was 16.1 %,
– when the temperature was increased to 500 ° C, the degree of transformation increased to 69.4 %, the yield of light fractions increased to 38.6 %, gas — to 17.3 %, and compaction products (CP) - to 13.2 %. This indicates a simultaneous acceleration of primary and secondary reactions,
– at 550 °C, the conversion reached a maximum of 71.8 %, but the yield of light fractions decreased (to 21.4 %, which is 8% and 17% less than at 500 °C and 450 °C). Gaseous products increased more than twofold due tore-cracking, while coking decreased from 13.2 % to 12.1 %.

In the course of studies on the effect of the duration of the OCC process, the maximum gas yield (35.1 %) was observed after 300 s, and for target liquid fractions I and II - after 600-900 s (up to 38.5–38.6 %). With a further increase in the duration to 1800-2700 s, the conversion decreased to 56.5-55.1 %, which is explained by the accumulation of products of oxidative compaction and blocking of the active centers of the catalyst.

The study of the effect of the oxidation state allowed us to establish that with 0.5% oxygen, the conversion was minimal (36.0 %) at lowcoking, at 1% the conversion increased to 69.0 %, and the total yield of light fractions reached 38.6 %, which is 15.6% higher than with OTC, and only 1.4 % lower than with at 2 %, the conversion was maximal (74.0 %), but the yield of light fractions dropped to 19.7 %. The amount of gas and products of oxidative compaction increased almost exponentially. The unsteady nature of the catalytic oxycracking process was also noted due to the oscillatory deactivation of the catalyst, which is followed by a period of activity.

The marked decrease in the activity of the catalyst can occur due to the formation of coke on the surface, which blocks the active centers. In addition, decontamination can be caused by agglomeration of metals, the action of catalytic poisons entering the system, changes in the texture and phase composition under the influence of high temperatures. When decontaminated with compaction products or temporary poisons, the activity can be restored by performing appropriate procedures, while in other cases, decontamination is irreversible and requires periodic replacement of the catalyst with a fresh one.

EXPERIMENTAL PART

In the course of the study, 2 types of spent catalyst samples were selected: after catalysis - participation in OCC, and after participation in CC. They were granules with a diameter of 1-2 mm, differed in dark color, and contained individual granules from dark gray to black.

Catalytic experiments were performed in a flow-through installation at atmospheric pressure. A steam-drop mixture of raw materials and oxygen was passed at a linear rate of 1 ml / min through a quartz glass reactor with a diameter of 2 c mind a length of 8 cm, into which 5 cm^3 of the corresponding zeolite was preloaded in the form of granules with a diameter of 1-2 mm. Before feeding the reaction mixture, the catalyst was calcined in a dried air current at 500°C for 2 hours, then the reactor was brought to the required temperature of the experiment in the He current and kept for 10 minutes. The temperature in the reactor was 500°C. In the case of OCC, the oxidation state of raw materials was 1%, and the contact time, equal to the ratio of the catalyst volume (cm^3) to the flow rate of the raw mixture (cm^3/s), was 1.7 s. In the case of CC, all parameters remained unchanged except for the presence of an oxidizer.

The elemental composition was determined by energy-dispersion microanalysis (EDM) on a JEOL JSM-6610 LV electron microscope equipped with a set-top box.

RESULTS AND DISCUSSION

The spent catalyst samples were pellets with a diameter of 1-2 mm. They were characterized by a dark color, and contained individual granules from dark gray to black. The samples that took part in the OCC under mild conditions had a brownish-brown color. This section presents analytical data on the accumulation of organometallic compounds on the ZCC surface.

As is known, the composition of oil includes many metals, including alkaline and alkaline earth (Li, Na, K, Ba, Ca, Sr, Mg), metals of the copper subgroup (Cu, Ag, Au), zinc subgroups (Zn, Cd, Hg), boron subgroups (B, Al, Ga, In, Tl), vanadium subgroups (V, Nb, Ta), many metals of variable valence (Ni, Fe, Mo, Co, W, Cr, Mn, Sn, etc.), as well as typical nonmetals (Si, P, As, Cl, Br, I etc.).

The negligible concentrations of these elements do not allow, given the current state of analytical technology, to isolate and identify the substances in which they are included. It is generally accepted that the elements contained in micro-quantities in oil can be found in it in the form of fine aqueous solutions of salts, fine suspensions of mineral rocks, as well as in the form of complex or molecular compounds chemically related to organic substances. The latter, according to V.F.Kamyanov, are divided into: organoelement compounds, i.e. containing a carbon-element bond; salts of metals substituting for a proton in acidic functional groups; chelates, i.e. intramolecular complexes of metals; complexes of several homogeneous or mixed ligands; complexes with heteroatoms or a π-system of polyaromatic asphaltene structures [9].

In the 70s, research on the composition and physicochemical characteristics of

ISNN: print 2663-7006; online 2709-2666

trace elements was intensified in all oil regions of our country – Azerbaijan, D. I. Zulfugarli [10-12]. He summarized the extensive data on the content and distribution of trace elements in oil and sedimentary rocks, organisms and reservoir waters published in the world literature before 1957, including the results of original studies of Azerbaijan's inorganic objects obtained by the author himself.

A great deal of work on the study of trace elements in the oils of offshore fields of Azerbaijan, accompanying and seawater, and the establishment of the relationship of trace elements in them was carried out by Corresponding Member of the National Academy of Sciences of Azerbaijan, Doctor of Chemical Sciences F.Samedova [13]. It was found that the dominant elements in the studied oils are Mn, Mo, Fe (content 91.54-221.7, 313.3-624.4 and 49.7-373.4 g/t, respectively). The studied oils are young and slightly metamorphosed, they are located at depths of 100-4235 m and, apparently, in this connection, they are characterized by a high content of manganese. Compared to the ancient oils of the Mesozoic deposits of the CIS countries, the studied oils of Azerbaijan contain 2-3 orders of magnitude less zinc (0.001-0.007 wt %). According to data from [14], vanadium in the form of pentoxide is contained in oils $4\cdot10^{-5}$-$5\cdot10^{-5}$ %, traces of nickel in the form of oxide.

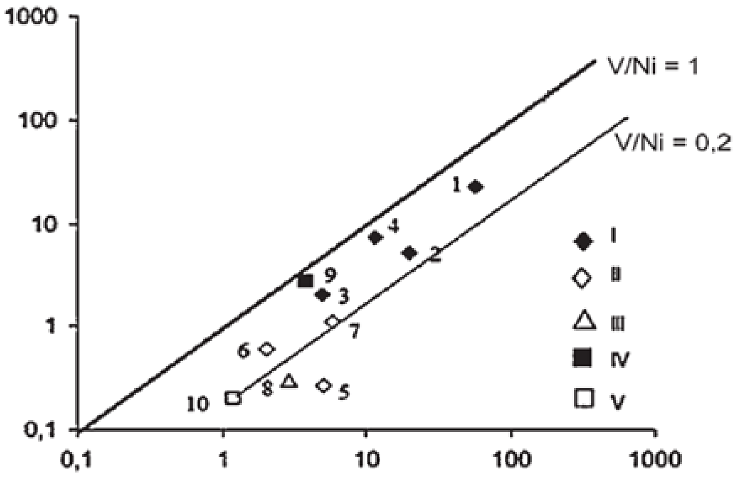

Fig. 1. The ratio of vanadium and nickel in oils generated by OM of rocks of various lithophage. Facies oils: marine: I – deep – water, II-shallow-water; continental: III-lacustrine, IV-coal-bearing with a high content of resinite, V-coal-bearing with a high content of leuptinite. Regions: 1-California; 2-Belarus; 3-Sakhalin; 4-Japan; 5-Azerbaijan; 6-Georgia; 7-Ciscaucasia; 8-China; 9 – Western Siberia (Cenomanian); 10 – New Zealand

According to [15], Azerbaijani oils belong to immature oils of the early generation of the nickel metallogeny, are depleted in ME and formed in immature source rocks. The distribution of Ni in oil fractions confirms its primacy, its association with nitrogenous ligands, and explains the nickel specialization of immature fluids. The transition from fluids generated by OM of marine origin to oils from continental OM (fig.1) results in a decrease in the V and Ni contents. Oil is concentrated in the V/Ni ratio field below unity. Characteristic indicators for Azerbaijani oils are $\sum(V+Ni) \leq 10$, vanadylporphyrin $\sum V_pVp = 1.7$, nickel Ni porphyrin $Ni_p = 3$ g / t; concentration series, metallogeny - Ni > Fe (V) > V (Fe) Nickel, Ni, Fe, Cu, Pb, Zn, Br, Co, V, As, Au, Ce; Physical and chemical properties-p = 0.850, S (sulfur content,%) = 0.5, C+A (sum of resins and asphaltenes,%) = 12; Type of oil in terms of ME concentration - Depleted (primary).

Table 1

Distribution of metals in fractions

Fraction, °C	Content, 10^{-6} wt%						
	V	Ni	Cu	Fe	Mg	Mn	Ca
250-350	0.007	-	0,30	0,49	0,17	0.003	0.02
350-450	0.025	0.006	10.57	2,54	1,54	0.006	0.35
>450	57.04	24.08	9.12	3.43	4.86	0.009	1.94

As can be seen from the data presented in the table 1, metals in terms of their content in high-boiling fractions are arranged in a row: for the 250-350°C fraction: Fe > Cu > Mg > Ca > V > Ni, Mn; for the 350-450°C fraction: Cu > Fe > Mg > Ca > V > Mn > Ni; for fractions >450°C: V > Ni > Cu > Mg > Fe > Ca > Mn.

The presented results indicate that trace elements in fractions above 350°C can be divided into two groups: vanadium, nickel (as the main ones) and those that are an order of magnitude lower – copper, iron, magnesium and calcium.

It is known that during the processing of heavy raw materials, nickel, iron, copper, cobalt and vanadium compounds poison and destroy the catalyst. Metals are deposited on the cracking catalyst and increase the formation of hydrogen and coke. Since the formation of hydrogen and / or coke usually has a negative effect on the production of target products, both hydrogen and coke are undesirable products of the cracking process. In addition, metals are not removed during the catalyst regeneration process. According to the effectiveness of reducing the activity of ZCCs, they can be arranged in a row: Pb < Cr < Fe<V< Mo < Cu < Co <Ni.

Taking into account the well-known fact that the presence of metals of the first group leads to a decrease in the catalytic activity of ZCCs under cracking conditions, it was of undoubted interest to find out how much the decrease in activity, deactivation of ZCCs under catalytic oxycracking conditions is associated with this factor. Taking into account that in the course of our research, we found that the minimum conversion value was recorded during OCC under conditions of 500°C, 1%, a process duration of 900 s, and a contact time of 2 s, the elemental composition of the spent sample was studied under these conditions. The initial ZCC and post-catalysis ZCCs were also studied as controls under conditions of 500°C, 1%, and a process duration of 900 s, but a contact time of 1.2 s.

The results of our EDM analysis are presented in the form of a graphical relationship (fig 2). It shows the dynamics of both aluminum, silicon, and oxygen, its modifier chlorine, as well as natural aluminum silicate impurities in the form of iron and titanium, and those that appear on the surface of the catalyst after participation in the

ISNN: print 2663-7006; online 2709-2666

process of chromium, nickel and calcium. As can be seen from these data, an increase in the contact time from 1.2 to 2 s leads to an increase in the iron content by 0.78-2.29%, chromium by 0.1% by weight, nickel by 0.04% by weight, and calcium by 0.02% by weight. The presence of chlorine on spent catalysts was not observed, which indicates its entrainment during the process.

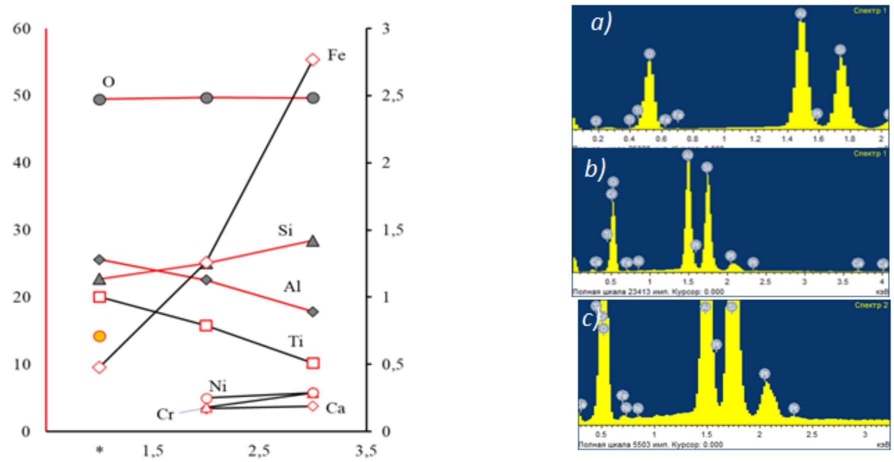

Fig. 2. Dependence of the trace element content and EDM spectra of ZCC samples on the contacttime: a-initial, before catalysis; b – contact time 1.7 s; c – contact time 2 s; * - initial ZCC, before catalysis

Relative to nickel, it enters the raw material in the form of metal porphyrins, etc. complexes. During the cracking process, they are destroyed and Ni is deposited on the surface of the catalyst. Probably, under the conditions of oxidative cracking in the regeneration zone, Ni passes into NiO, interacts with oxygen, and then is reduced again by hydrocarbons in the reactor. As a result, the catalyst is enriched with active Ni^{2+}/Ni^{o} centers, which are not acidic centers of zeolite, but work as dehydrating/dehydrogenating centers of oxidative dehydrogenation. The same can be said about iron. Although it is less active in the dehydrogenation reaction than nickel, its presence nevertheless leads to an increase in the gas and gas yield. Here you should pay attention to one nuance – iron, unlike nickel, chromium, is present in the composition of the initial ZCC (before catalysis). This indicates that its initial concentration is related to the substances used in the preparation of the catalyst. The subsequent increase in its concentration (excluding its ingress due to abrasive wear of the surface of the iron reactor, etc.) is associated exclusively with ingress from raw materials. The increase in conversion in the presence of nickel- ZCC was noted earlier [6,7]. The presence of chromium and calcium is secondary to the activity of cracking catalysts.

At the same time, based on the values known in the literature, at which the critical content of nickel is 2000-3000 ppm, which is 3 times higher than that observed at the contact time of 2 s of the OCC sample, and for iron its "activity" is more than 4 times lower than that of nickel, the obtained values allow us to exclude the fact that accumulation of metals on the surface of the OCC catalyst as the most likely cause of its deactivation.

CONCLUSION

Thus, the energy dispersion microanalysis of the surface of the zeolite-containing catalyst (ZCC) after participation in the catalytic oxycracking process revealed the accumulation of trace elements Fe, Ni, Cr and Ca. It was found that an increase in the contact time of the raw material with the catalyst from 1.2 s to 2 s leads to an increase in the content of Fe (up to 2.3%), Cr (up to 0.1%), Ni (up to 0.04%) and Ca (up to 0.02%) on the surface of the ZCC. The data obtained indicate the dependence of the degree of metal enrichment on the duration of the interaction of the raw material with the catalyst, which confirms their migration from the feedstock. A comparison of the obtained metal concentrations with the literature data showed that their level is significantly lower than the critical limits at which deactivation of the catalyst surface is observed. This eliminates the accumulation of metals as the main cause of ZCC deactivation during catalytic oxycracking.

REFERENCES

1. Rosyadi, I., Suyitno, S., Arifin, Z., Sutardi, T. Novel approaches to zeolite deactivation mitigation and regeneration in biomass gasification. Journal of Thermal Engineering. 2025, Vol.11(5), pp. 1552-1584
2. Ihli J, Jacob RR, Holler M, Guizar-Sicairos M, Diaz A, Da Silva JC, et al. A three-dimensional view of structural changes caused by deactivation of fluid catalytic cracking catalysts. Nat Commun. 2017, Vol.8(1), 809 p
3. Liu P, Chen Z, Li X, Chen W, Li Y, Sun T, et al. Enhanced degradation of VOCs from biomass gas-ification catalyzed by Ni/HZSM-5 series catalyst. J Environ Manage 2023, 345 p
4. Morales–Leal FJ, Ancheyta J, Torres–Mancera P, Alonso F. Experimental methodologies to perform accelerated deactivation studies of hydrotreating catalysts. Fuel. 2023, Vol.332, 12607 p
5. Das S, Pérez-Ramírez J, Gong J, Dewangan N, Hidajat K, Gates BC, et al. Core–shell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO_2. Chem Soc Re. 2020 , Vol.49, pp. 2937-3000
6. Guseinova, E.A., Rasulov, S.R. Hydrocarbon Group Composition of the Liquid Products of the Catalytic Oxycracking of Vacuum Gas Oil. Chem Technol Fuels Oils. 2025, Vol. 61, pp. 631 - 634
7. Guseinova, E.A., Rasulov, S.R. Catalytic Oxycracking of Vacuum Gas Oil. Chem Technol Fuels Oils. 2024, Vol.60, pp. 239–243

ISNN: print 2663-7006; online 2709-2666

8. Guseinova, E.A., Adzhamov, K.Y., Mursalova, L.A. et al. Formation kinetics of hydrocarbon compounds in the vacuum gas oil oxycracking process. Reac Kinet Mech Cat. 2020, Vol.131, pp. 57–74
9. Heteroatomic components of oils: a monograph V. F. Kamyanov. Novosibirsk: Siberian Branch, 1983, 236 p
10. Babayev F.R., Martynova G.S., Nanadzhanova R.G. Microelement indication oil of Azerbaijan READINGS OF A.I. BULATOV Materials of I International scientific and practical conference (on March 31). 2017, pp. 97-101
11. Zulfugarli D. I. Copper in the oil of Azerbaijan. -Dokl.AN Az.SSR. 1949, Vol. 5, Sh 12, pp. 492-497
12. Zulfugarli D. I. On the presence of nickel in the oil of Azerbaijan. -Dokl. AN Az. SSR, 1950, Vol. 6, №. 3, pp. 117-123
13. Samedova F. I. Oil of Azerbaijan. Baku, ElmPubl., 2011, 412 p.
14. Masagutov P. M. Alumosilicate catalysts and changes in properties in the cracking of petroleum products. M., Chemistry. 1975, 272 p
15. Punanova S.A. Trace elements in naphthides in oil and gas basins. Doklady Earth Sciences. 2019. Vol. 488. №. 2. pp. 1207-1210