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INVESTIGATION OF THE COMPACTION PRODUCT ON A NICKEL/DIATOMACEOUS EARTH CATALYST

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The activity of the Ni/diatomaceous earth catalyst used in the process of obtaining acetone from isopropyl alcohol was studied in a laboratory setup over a wide temperature range (150–350°C) at atmospheric pressure. The analysis of raw materials and reaction products was carried out by the chromatographic method. In the process of isopropyl alcohol conversion on the Ni/diatomaceous earth catalyst surface, the formation of compaction products and the effect of oxygen and hydrogen on the catalyst surface were studied using a Mag-Ben setup equipped with a quartz-spring reactor. The formation of compaction products on the surface of the Ni/diatomaceous earth catalyst was determined by thermogravimetric and kinetic methods. The maximum amount of compaction products is formed at a temperature of 300°C and above on the Lewis sites. Thermogravimetric studies showed that the formation of compaction product on the surface of the Ni/diatomaceous earth catalyst is time and temperature dependent.

Keywords: compaction products, catalyst activity, conversion, thermogravimetric analysis, nickel/diatomaceous earth catalyst.

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Introduction

It is known that, as a rule, in some catalytic processes, the coke formed on the catalyst surface reduces the product yield and should be regenerated in order to restore its initial activity [1–7]. At the same time, the compaction products formed on the surface of the contact mass increase the rate of the process in some catalytic processes. It was found that in the process of catalytic cracking, coke accumulating on the catalyst surface has a negative effect on the yield of gasoline, oxidative dehydrogenation of alkyl aromatic hydrocarbons, and, on the contrary, has a positive effect on the yield of the product during the conversion of olefins into acids and ketones [8,9].

Earlier, the transformation of low-molecular alcohols into ketones on oxide and metal catalysts has been established. Recent studies have shown that ketones are produced with high yields from isopropyl and secondary butyl alcohols on industrial Ni-containing catalysts [10–13].

The main purpose of this work is to study the

compaction product on the Ni/ diatomaceous earth catalyst using kinetic and physicochemical methods.

Experimental

The activity of the Ni/diatomaceous earth catalyst used in the process of producing acetone from isopropyl alcohol was investigated in a laboratory setup in a wide temperature range (150–350°C) at atmospheric pressure. Thermal analysis of the samples was carried out on a Derivatograph Q 1050 instrument at atmospheric pressure at the rate of 10°C/min.

Analysis of raw materials and reaction products was carried out by chromatographic method using a chromatograph «CHROM-5» with a thermal ionization detector equipped with a column filled with a celite-22 sorbent impregnated with 17% polyethylene glycol.

The gaseous products obtained during the reaction were analyzed on a «CHROM-5» chromatograph equipped with a heat-conducting detector. An ester of n-fatty acids with diethylene glycol impregnated with Inse brick (INZ-600) was used as a sorbent.

In the process of isopropyl alcohol conversion

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on the Ni/diatomaceous earth catalyst surface, the formation of compaction products and the effect of oxygen and hydrogen on the catalyst surface were studied using a Mag-Ben setup equipped with a quartz-spring reactor in the temperature range of 200–300°C.

Results and discussion

As follows from previous researches, acetone, ether, water and H₂ are obtained from isopropyl alcohol during dehydrogenation in the temperature range 150–350°C on the investigated Ni/diatomaceous earth catalyst. As can be seen from Fig. 1, the optimum process temperature is 250°C, and the maximum acetone yield under these conditions is about 75%.

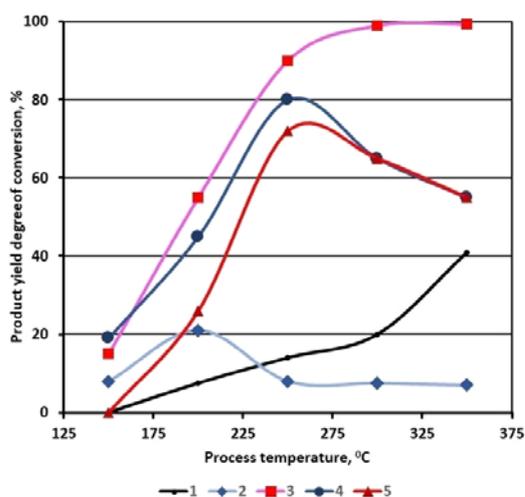


Fig. 1. Influence of temperature on the characteristics of the catalytic conversion of isopropanol in the presence of a Ni/diatomaceous earth catalyst: 1 – propylene yield; 2 – yield of diisopropyl ether; 3 – conversion of isopropanol; 4 – selectivity for ketones; and 5 – output of acetone

It is known that in many processes it takes from one second to several days to stabilize catalysts. The conversion of isopropyl alcohol to acetone on the studied catalyst also takes some time (Fig. 2).

It can be seen that at the initial stage of the process, the change in the acetone yield stabilizes or decreases over time, depending on the temperature. At the initial stage of the process, the reaction products formed on the catalyst surface have a definite effect on the catalyst activity.

It is assumed that the change in the acetone yield at 300°C is associated with the formation of a compaction product on the catalyst surface. Compaction products are formed mainly on active sites with high acidity, i.e. in the Lewis sites.

Thermogravimetric studies show that the formation of compaction product on the surface of the Ni/diatomaceous earth catalyst is time and

temperature dependent. As can be seen from Fig. 3, the maximum formation of the compaction product is observed at a temperature of 300°C. A stable state is observed after 40 minutes, 60 minutes, and 70 minutes at 300°C, 250°C, and 200°C, respectively.

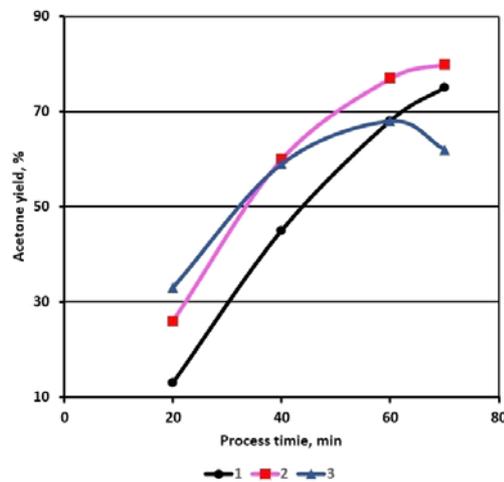


Fig. 2. Kinetic change in the yield of acetone at different temperatures: 1 – 200°C; 2 – 250°C; and 3 – 300°C

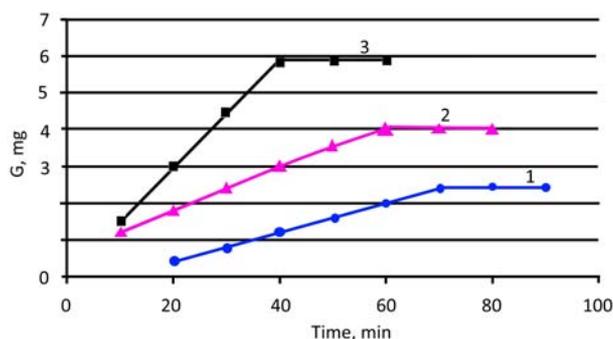


Fig. 3. Kinetic curves of compaction products collected on a Ni/diatomaceous earth catalyst during the conversion of isopropyl alcohol at different temperatures: 1 – 200°C; 2 – 250°C; and 3 – 300°C

Figure 4 shows the time dependence of the formation of a condensation product during the conversion of isopropyl alcohol in the temperature range of 250–300°C on a Ni/diatomaceous earth catalyst in an H₂ and O₂ atmosphere.

The commercial Ni/diatomaceous earth catalyst is known to be very sensitive to oxygen and it is believed that the Ni→NiO conversion occurs in the presence of oxygen.

On the basis of thermogravimetric studies, it was found that nickel, which is responsible for catalysis in H₂ in the temperature range of 250–300°C, passes from the oxide form to the metallic form, causing a

slight decrease in the catalyst mass, according to the following scheme:

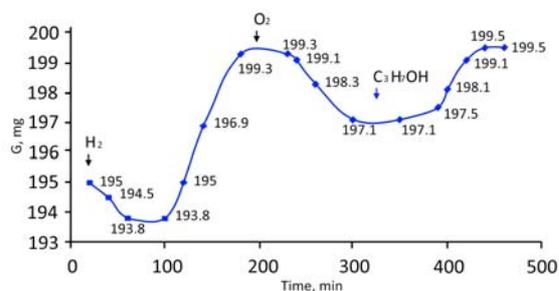


Fig. 4. Time dependence of the amount of compaction product as a result of the conversion of isopropyl alcohol on the surface of the Ni/diatomaceous earth catalyst in the presence of H₂ and O₂, respectively, at a temperature of 250–300°C. G_{cat}=195.5 mg. ↓H₂; ↓O₂; and ↓C₃H₇OH stand for the moment of supply of hydrogen, oxygen and alcohol, respectively

The catalyst mass increases again as a result of the formation of a condensation product in the presence of isopropyl alcohol. As can be seen from Fig. 4, the compaction product increases for 60 minutes and then reaches a steady state. The amount of product compacted in 60 minutes is 5.5 mg. Since the compaction product increases to a certain extent on the catalyst surface and then stabilizes, it can be assumed that the compaction product is adsorbed monomolecularly only on certain active sites, and the adsorption process does not occur after complete surface capture. In an oxygen atmosphere, a decrease in the catalyst mass occurs due to the combustion of compaction products on the surface.

The formation of a condensation product on the surface of the Ni/diatomaceous earth catalyst is confirmed by thermogravimetric analysis (TGA) (Fig. 5). Comparative results of thermogravimetric studies of the catalyst were carried out in the temperature range of 0–500°C in a nitrogen atmosphere before (1) and after (2) catalysis.

It is assumed that a significant decrease in weight in the temperature range of 50–150°C (5.65%) is associated with the evaporation of water molecules adsorbed on the surface of the primary catalyst sample. Thus, in the sample participating in the dehydrogenation process, this indicator is somewhat lower, which is associated with the evaporation of a certain part of the water remaining in the reaction medium.

As can be seen from Fig. 5, the results of TGA studies imply that a decrease in the initial mass of the

catalyst (by about 3% at 100°C) with increasing temperature is associated with the evaporation of hydrocarbon mixtures from the sample. At the same time, the broad peaks taken from the developed catalyst sample suggest the presence of compaction products of various natures on its surface.

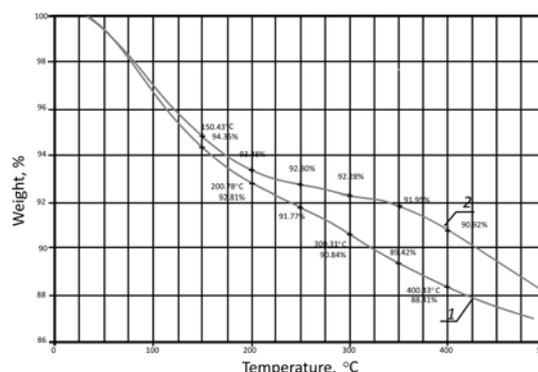


Fig. 5. TGA results of Ni/diatomaceous earth catalyst before (1) and after (2) catalysis

A decrease in the catalyst mass at temperatures above 400°C is associated with the decomposition of compaction products consisting of weakly condensed coke residues.

Summarizing conclusions

1. The formation of compaction products on the surface of the Ni/diatomaceous earth catalyst was established by thermogravimetric and kinetic methods. The maximum amount of compaction products is formed on Lewis sites at a temperature of 300°C.

2. Thermogravimetric studies showed that the formation of a compaction products on the surface of the Ni/diatomaceous earth catalyst is time and temperature dependent. The maximum formation of the compaction products is observed at a temperature of 300°C.

3. The formation of a condensation product on the surface of the Ni/diatomaceous earth catalyst was confirmed by thermogravimetric analysis. TGA studies allow assuming that the decrease in the initial mass of the catalyst with increasing temperature is associated with the evaporation of hydrocarbon mixtures from the sample.

REFERENCES

1. Selection of active modified zeolite catalyst and kinetics of the reaction of selective oxidative dehydrogenation of cyclohexane to cyclohexadiene 1,3 / Aliyev A., Shabanova Z., Najaf-Guliyev U., Melikova I. // *Mod. Res. Catal.* – 2015. – No. 4. – P.87-96.

2. *Okislitel'noe* degidrirovaniye naftenovykh uglevodorodov na metall-tseolitnykh katalizatorakh / Aliev A.M., Sabanova Z.A., Kerimov A.I., Nadzaf-Kuliev U.M. // *Kimya Problemleri*. – 2017. – No. 1. – P.26-38.

3. *Kolesnikov I.M.* Kataliz v gazoneftysnoi otrasli. – M.: Izdatel'stvo IC RGU Nefti i Gaza, 2012. – 471 p.

4. *Sakun A.N., As'an U.P., Litvinova S.M.* Nekotorye aspekty stabil'nosti novykh tseolitsoderzhashchikh katalizatorov izbiratel'nogo gidrokrekinga // *Khimiya i Tekhnologiya Topliv i Masel*. – 2001. – No. 2. – P.39.

5. *Introduction to zeolite science and practice* / Jacobs P.A., Flanigen E.M., Jansen J.C., Herman van Bekkum. – Amsterdam: Elsevier Science, 2001. – 1078 p.

6. *Katalizatory gidroochistki na osnove sul'fidov Co i Mo*, nanesennykh na mnogoslouinye uglevodnye nanotrubki / Vatutina U.V., Kazakov M.O., Kazakova M.A., et al. // *Proc. Int. Conf. «Perspective Materials with a Hierarchical Structure for New Technologies and Reliable Designs»*. X Int. Conf. «Chemistry of Oil and Gas». – Tomsk; 2018. – P.847.

7. *Halafova I.A., Alieva N.T., Abul-Fotuh T.M.* Intensifikatsiya protsessa kataliticheskogo krekinga // *Azerbaijan Chem. J.* – 2010. – No. 1. – P.161-165.

8. *Predpolagaemye puti prevrashcheniya vakuumnogo gazoila v usloviyakh okislitel'nogo kataliticheskogo krekinga (oksikrekinga)* / Gusejnova E.A., Mursalova L.A., Mamedhanova S.A., Dadaeva G.C., Adzhamov K.U. // *Kimya Problemleri*. – 2017. – No. 3. – P.283-290.

9. *Muller N., Jess A., Moos R.* Direct detection of coke deposits on fixed bed catalysts by electrical sensors // *Sens. Actuators B. Chem.* – 2010. – Vol.144. – No. 2. – P.437-442.

10. *Mehtieva N.T., Poladov F.M., Adzhamov A.K.* Kataliticheskoe prevrashchenie vtorichnogo butilovogo spirta na Ni-Cr katalizatore // *Proc. IV Republican Conference on Chemistry*. – Tbilisi, 2004. – P.75.

11. *Fiziko-khimicheskie svoistva poverkhnostei, modifitsirovannykh nanochastitsami metallov* / Sockaya N.V., Dolgih O.V., Kaskarov V.M., Len'sin A.S., Kotlarova E.A., Makarov S.V. // *Sorbtsionnye i Khromatograficheskie Protsessy*. – 2009. – Vol.9. – No. 5. – P.643-652.

12. *Issledovanie kislотно-osnovnykh svoistv poverkhnosti nanesennogo palladievogo katalizatora* / Filippov D.V., Ulitin M.V., Merkin A.A., Rvzanov M.A., Kravienko A.V. // *Izv. Vyssh. Uchebnykh Zaved. Ser. Khimiya i Khimicheskaya Tekhnologiya*. – 2011. – Vol.54. – No. 2. – P.60-63.

13. *Textural and structural analyses of industrial Raney nickel catalyst* / Rodella C.B., Kellermann G., Francisco M.S.P., Jordao M.H., Zanchet D. // *Ind. Eng. Chem. Res.* – 2008. – Vol.47. – No. 22. – P.8612-8618.

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ДОСЛІДЖЕННЯ ПРОДУКТУ УЩІЛЬНЕННЯ НА КАТАЛІЗАТОРІ НІКЕЛЬ/ДІАТОМІТ

Е.Т. Зейналов, Н.Т. Алієва, С.Г. Новрузова, О.Ю. Шмончева

Активність каталізатора Ni/діатоміт, який використовується в процесі одержання ацетону з ізопропілового спирту, досліджено на лабораторній установці в широкому діапазоні температур (150–350°C) при атмосферному тиску. Аналіз сировини та продуктів реакції проводили хроматографічним методом. У процесі конверсії ізопропілового спирту на поверхні каталізатора Ni/діатоміт досліджували утворення продуктів ущільнення та вплив кисню та водню на поверхню каталізатора на установці Mag-Ben з кварцово-пружинним реактором. Термогравіметричним і кінетичними методами визначали утворення продуктів ущільнення на поверхні каталізатора Ni/діатоміт. Максимальна кількість продуктів ущільнення утворюється при температурі 300°C і вище на центрах Льюїса. Термогравіметричні дослідження показали, що утворення продукту ущільнення на поверхні каталізатора Ni/діатоміт залежить від часу та температури.

Ключові слова: продукти ущільнення, активність каталізатора, конверсія, термогравіметричний аналіз, каталізатор нікель/діатоміт.

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REFERENCES

1. Aliyev A, Shabanova Z, Najaf-Guliyev U, Melikova I. Selection of active modified zeolite catalyst and kinetics of the reaction of selective oxidative dehydrogenation of cyclohexane to cyclohexadiene 1,3. *Mod Res Catal.* 2015; 4: 87-96. doi: 10.4236/mrc.2015.44011.

2. Aliev AM, Sabanova ZA, Kerimov AI, Nadzaf-Kuliev UM. Okislitel'noe degidrirovaniye naftenovykh uglevodorodov na metall-tseolitnykh katalizatorakh [Oxidative dehydrogenation of naphthenic hydrocarbons on metal-zeolite catalysts]. *Kimya Problemleri.* 2017; (1): 26-38. (in Russian).

3. Kolesnikov IM. *Kataliz v gazonefityanoi otrasli* [Catalysis in the oil and gas industry]. Moscow: Izdatel'stvo IC RGU Nefti i Gaza; 2012. 471 c. (in Russian).
4. Sakun AN, As'yan UP, Litvinova SM. Nekotorye aspekty stabil'nosti novykh tseolitsoderzhashchikh katalizatorov izbiratel'nogo gidrokrekinga [Some aspects of the stability of new zeolite-containing catalysts for selective hydrocracking]. *Khimiya i Tekhnologiya Topliv i Masel*. 2001; 2: 39. (in Russian).
5. Jacobs PA, Flanigen EM, Jansen JC, Herman van Bekkum. *Introduction to zeolite science and practice*. Amsterdam: Elsevier Science; 2001. 1078 p.
6. Vatutina UV, Kazakov MO, Kazakova MA. Katalizatory gidroochistki na osnove sul'fidov Co i Mo, nanesennykh na mnogoslainye uglerodnye nanotrubki [Hydrotreating catalysts based on Co and Mo sulfides supported on multiwalled carbon nanotubes]. In: *Proceedings of the International Conference «Perspective Materials with a Hierarchical Structure for New Technologies and Reliable Designs». X International Conference «Chemistry of Oil and Gas»*; Tomsk. 2018. p. 847. (in Russian). doi: 10.17223/9785946217408/593.
7. Halafova IA, Alieva NT, Abul-Fotuh TM. Intensifikatsiya protsessa kataliticheskogo krekinga [The effect of the magnetic field on catalytic cracking process]. *Azerbaijan Chem J*. 2010; (1); 161-165. (in Russian).
8. Gusejnova EA, Mursalova LA, Mamedhanova SA, Dadaeva GC, Adzamov KU. Predpolagaemye puti prevrashcheniya vakuumnogo gazoila v usloviyakh okislitel'nogo kataliticheskogo krekinga (oksikrekinga) [Prospective ways of converting vacuum gasoil in terms of oxidative catalytic cracking (oxycracking)]. *Kimya Problemleri*. 2017; (3): 283-290. (in Russian).
9. Muller N, Jess A, Moos R. Direct detection of coke deposits on fixed bed catalysts by electrical sensors. *Sens Actuators B Chem*. 2010; 144: 437-442. doi: 10.1016/j.snb.2009.03.008.
10. Mehtieva NT, Poladov FM, Adzamov AK. Kataliticheskoe prevrashchenie vtorichnogo butilovogo spirta na Ni-Cr katalizatore [Catalytic conversion of secondary butyl alcohol on a Ni-Cr catalyst]. In: *Proceedings of the IV Republican Conference on Chemistry*; Tbilisi. 2004. p. 75. (in Russian).
11. Sockaa NV, Dolgih OV, Kaskarov VM, Len'sin AS., Kotlarova EA, Makarov SV. Fiziko-khimicheskie svoystva poverkhnostei, modifitsirovannykh nanochastitsami metallov [Physical and chemical properties of surfaces modified with metal nanoparticles]. *Sorbtsionnye i Khromatograficheskie Protssy*. 2009; 9(5): 643-652. (in Russian).
12. Filippov DV, Ulitin MV, Merkin AA, Razanov MA, Kravchenko AV. Issledovanie kislotno-osnovnykh svoystv poverkhnosti nanesennogo palladievogo katalizatora [Investigation of the acid-base properties of the supported palladium catalyst surface]. *Izv Vyss Uchebnykh Zaved Seriya Khimiya Khimicheskaya Tekhnologiya*. 2011; 54(2): 60-63. (in Russian).
13. Rodella CB, Kellermann G, Francisco MSP, Jordao MH, Zanchet D. Textural and structural analyses of industrial Raney nickel catalyst. *Ind Eng Chem Res*. 2008; 47(22): 8612-8618. doi: 10.1021/ie800543t.