

Influence of the activation method on the activity of the nickel catalyst

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Abstract: The results of a comparative analysis of the influence of the activation method on the catalytic properties of a nickel diatomaceous earth catalyst during the conversion of isopropyl alcohol to acetone are presented. Studies of the activity of the catalyst in the reaction of gas-phase dehydrogenation of isopropyl alcohol were carried out on a flow-type laboratory installation at a temperature of 150–350°C. The mechanical activation of the nickel diatomaceous earth catalyst was carried out in a planetary mill. Traditional activation included pre-heat treatment of nickel diatomaceous earth catalyst in an atmosphere of O₂ and H₂ at 250°C; IR radiation was carried out using an incandescent lamp. It is shown that the nature of the activator determines the features of the formed surface nickel complexes. The activity of samples of the nickel diatomaceous earth catalyst subjected to activation by thermal reduction and thermal oxidation, as well as IR irradiation, testified to the low efficiency of these methods. A comparison of the activity of industrial nickel diatomaceous earth catalyst samples subjected to different activation methods showed that processing of samples by thermal reduction and thermal oxidation slightly increases the yield of acetone. In contrast, the original catalyst's IR irradiation and mechanical activation decreased its activity. Thus, thermal reduction and oxidation methods are promising for further research to increase the industrial nickel diatomaceous earth catalyst activity in dehydrogenating isopropyl alcohol into acetone.

Keywords: nickel catalyst; activation; activity; dehydration.

1. Introduction

Nickel-based catalysts are widely used in industrial catalysis. Despite the number of publications on this topic, many works are dedicated to their study, not decreasing¹⁻³. Nickel catalysts are active catalysts for various hydrocarbon conversion reactions and are widely used in industry⁴⁻⁶.

Earlier, we showed that the industrial nickel diatomaceous earth catalyst effectively dehydrates aliphatic alcohols to the corresponding ketones⁷⁻¹⁰. The correlations between catalytic activity and the catalyst's electronic, magnetic, and morphological properties were established.

However, studies have shown that the commercial nickel diatomaceous earth catalyst exhibits insufficiently high activity and selectivity in the reaction of dehydrogenation of isopropyl alcohol to acetone. In this regard, in recent years, we have conducted studies on increasing the activity of industrial nickel diatomaceous earth catalysts by pre-activation. According to literature data and the development of several new original methods of pre-activation of metal-containing catalysts, traditional processes continue to be studied^{11,12}.

To increase the activity of industrial nickel diatomaceous earth catalyst, we used various activation methods, both classical and new methods of pre-activation. In the present work, data from the comparative analysis of the effectiveness of the application of some activation methods used on the catalytic properties of the industrial nickel-diatomaceous earth catalyst in the process of dehydrogenation of isopropyl alcohol to acetone, namely mechanical activation, thermal treatment in a stream of air and hydrogen and IR irradiation, are considered.

2. Experimental

During the experiments, nickel diatomaceous earth catalyst samples were used as 4x4 mm tablets taken from an industrial batch (TU 38.101396-89E).

The activity of the investigated catalysts was studied on a flow through installation with a tubular reactor in the temperature range of 100–350°C. 5 ml of the examined catalyst with a grain size of 1.0–2.0 mm was loaded into the reactor, and its activity in the isopropyl alcohol conversion reaction was studied. A mixture of isopropyl alcohol with steam and nitrogen with isopropyl alcohol: water: nitrogen ratio of 1: 4: 5

was passed through the catalyst loaded into the reactor. The space velocity of the feed mixture was 600 h^{-1} . Carbon dioxide was determined on a chromatograph with a thermal conductivity detector and a 3-meter-long column filled with liquid paraffin deposited on a sorbent Celite. Ethanol and its conversion products were determined on a chromatograph with a flame ionization detector on a 3 m long column filled with specially treated Polysorb-1 sorbent.

The mechanical activation of the nickel-kieselguhr catalyst was carried out in an MP/0.5 planetary mill with steel balls 5–10 mm in diameter at a drum rotation frequency of 10 s^{-1} and a drum volume of 200 cm^3 .

Conventional activation included pre-heat treatment of the nickel diatomaceous earth catalyst in an atmosphere of O_2 and H_2 at 250°C . Then, the

activation medium was applied to the catalyst's surface at a 20 ml/min rate for 2 hours.

IR irradiation was carried out using an incandescent lamp, a glass flask with an internal mirror coating, where a tungsten spiral is placed. IR activation was carried out at room temperature for 2 h.

3. Results and Discussion

A study of the dehydrogenation reaction of isopropyl alcohol over an industrial nickel-diatomaceous earth catalyst showed that the primary product of the reaction is acetone. Propylene is obtained as a byproduct in small amounts. The research results on the activity of industrial nickel over a diatomaceous earth catalyst in the dehydrogenation reaction of isopropyl alcohol at 250°C are presented in Table 1. As can be seen from Table 1, the yield of acetone at 250°C is 58.4 % with a selectivity of 85%, and the total conversion of isopropyl alcohol is 68.7%.

Table 1. Conversion of isopropyl alcohol over industrial nickel on diatomaceous earth catalyst. $T=250^\circ\text{C}$.

Sample	Process indicators		
	Acetone yield, % (vol.)	Acetone selectivity, %	Alcohol conversion, % (vol.)
Ni/diatomaceous earth	58,4	85,0	68.7

Under the catalysis conditions, the nickel diatomaceous earth catalyst is in a reducing medium containing hydrogen formed during the reaction. Its effect on the catalytic process consists not only in changing the equilibrium composition of the gas phase but also of the degree of oxidation of the metal, the formation of the active nickel phase, and its catalytic properties.

According to our previous studies, during alcohol dehydrogenation, a homogeneous nickel phase is formed on the surface of a nickel diatom catalyst, which exhibits a spinel structure: a closed cubic lattice of oxygen ions in the tetrahedral and octahedral voids,

in which the nickel ions. Under the influence of the reaction medium, the reduced metallic nickel is introduced into the crystal lattice of nickel oxide, deforming it, and making it more favorable for the dehydrogenation reaction. On the other hand, any preliminary physicochemical treatment of the catalyst will inevitably change the composition, properties, and mechanism of the formation of surface complexes. In this regard, a series of catalysts was studied to study the features of the active phase formed on the surface of the catalyst under conditions of different pre-activation of the nickel diatomaceous earth catalyst (Table 2).

Table 2. Activation conditions.

Sample No.	Method of catalyst activation	Activation conditions	Activation duration
1	Thermal reduction	In H_2 atmosphere, 523 K	2 h
2	Thermal oxidation	In an O_2 atmosphere, 523 K	2 h
3	IR irradiation	In air atmosphere, 295 K	2 h
4	Mechanical activation	In air atmosphere, 295 K	90 sec

A comparative analysis of the process's quantitative indicators (conversion, acetone yield, and selectivity) indicated a significant effect of the activation method (Figure 1). It is important to note that the

dehydrogenation of alcohol to acetone occurred in all samples but with some particularities. It was found that the activity of the studied samples decreased in the series:

reduction in H₂ atmosphere Sample 1 > oxidation in O₂ atmosphere Sample 2 > mechanical activation Sample 4 > IR irradiation Sample 3

A comparison of the activated samples showed that in the first case (sample 1), presumably hydrogen and participation in the reduction of surface nickel oxide was also physically adsorbed on the catalyst surface. A high yield of acetone is associated with this: the

reaction proceeds simultaneously along two routes: through the surface decomposition of alcohol and its interaction from the gas phase with the available adsorbed hydrogen.

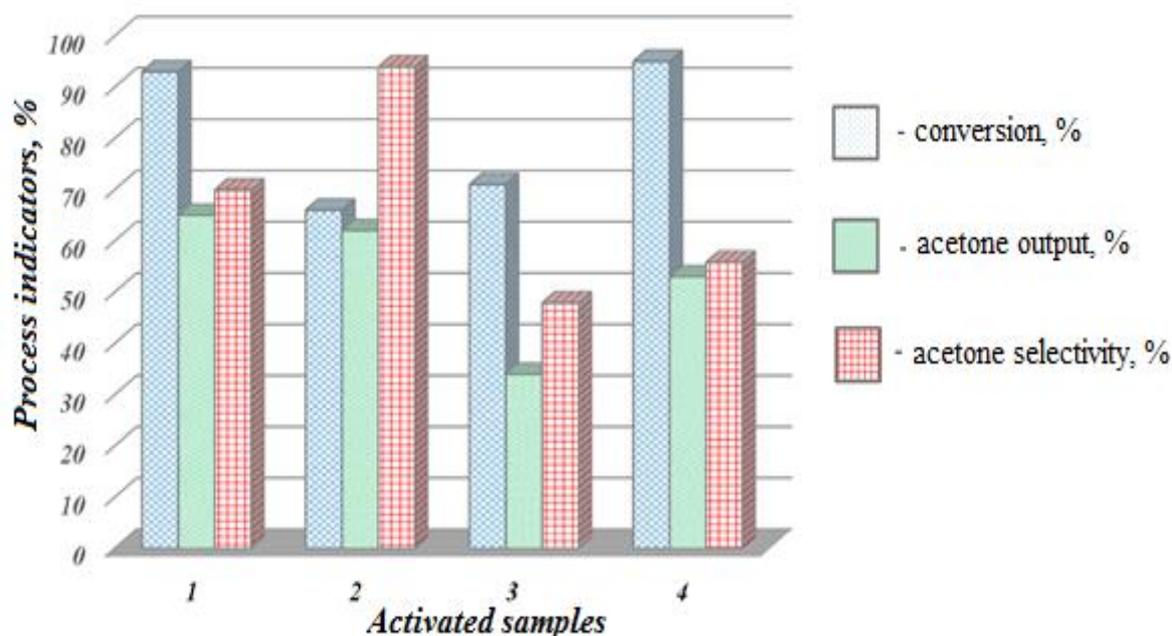


Figure 1. Comparative analysis of activated samples of nickel diatomaceous earth catalyst. (1-4 are the numbers of activated samples, see Table 1)

The lower yield of acetone in the presence of sample 2 can be explained by the fact that the supplied oxygen partially fills the surface, forming a more or less thermally unstable surface compound, which is retained by nonspecific van der Waals adsorption. It is likely that the formation of a surface form of adsorbed oxygen prevents the selective reduction of nickel ions and is responsible for the relatively low activity of the catalyst.

It is known that during the mechanical processing of solids, the accumulation of point defects, dislocations, amorphous regions on the surface and in the volume, an increase in the area of intergranular areas, vital loosening, the formation of new surfaces, as well as the activation of chemical bonds, and other changes occur.

The conducted studies showed that no noticeable change in the color scale of the catalyst (initially having an intense black color) was observed during mechanical activation.

The absence of visible signs of a phase transition does not exclude the possibility of amorphization of the system and partial reduction of nickel, which is in good agreement with the data available in the

literature, according to which the formation of cobalt metal accompanies the mechanical treatment of the cobalt-iron precursor.

The lowest activity was characteristic of sample 3 subjected to IR irradiation. The yield of acetone was 34%, 19, 28 and 31%, respectively, lower than that obtained with the mechanically activated sample, as well as in H₂ and O₂ atmospheres. It should be noted that the degree of conversion of alcohol, in this case, reached 71%. Having a good penetrating ability, infrared radiation, however, did not contribute to the change in the valence state of nickel, its photoreduction, and the formation of the active phase.

A more detailed study of the activation mechanism was continued using such a convenient factor from the point of view of characterizing the catalyst's operational properties as the process's duration (Figure 2).

When considering the experimental results, specific induction periods attract attention. With a change in the process's duration, the acetone release dynamics for all four samples become stable after passing through a certain minimum.

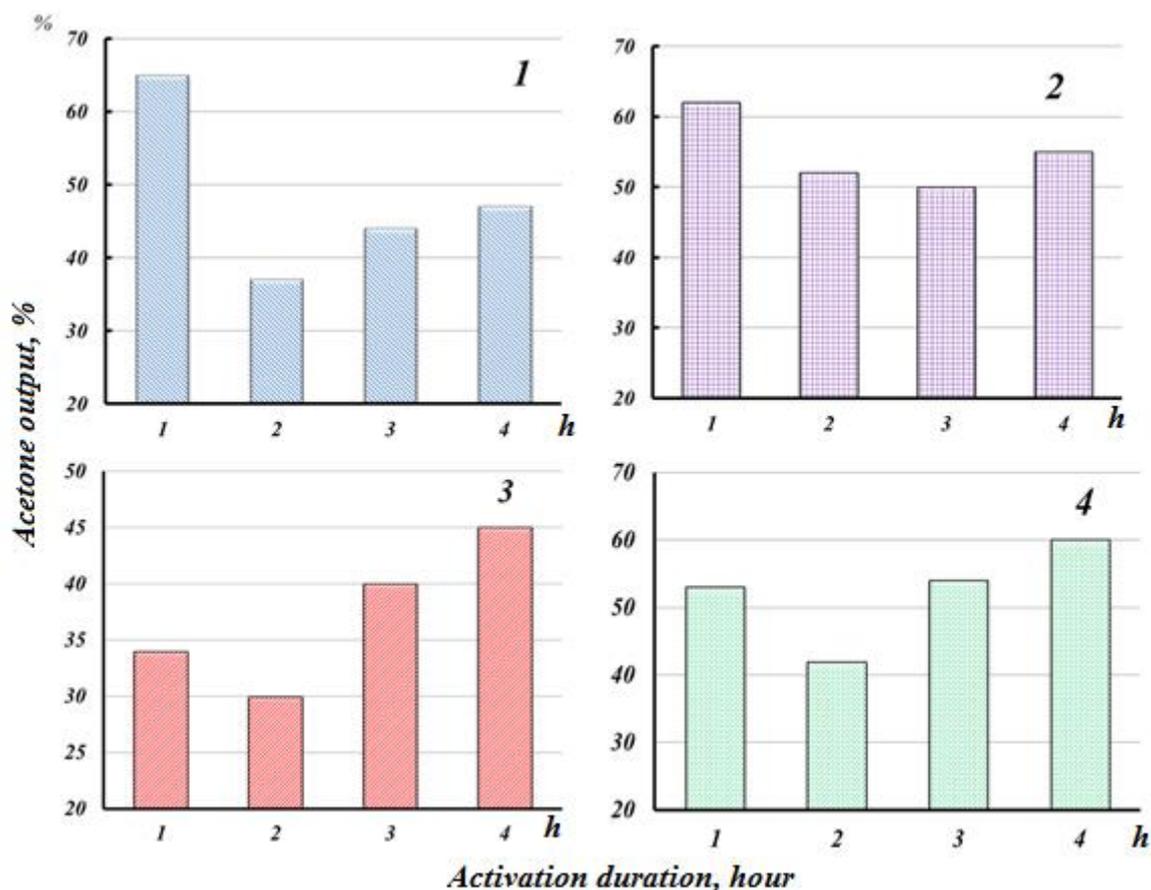


Figure 2. The dynamics of the output of acetone on the duration of the process in the presence of activated samples: 1 – thermal recovery; 2 – thermal oxidation; 3 – IR irradiation; 4 – mechanical activation

In the initial phase of the process, the sample subjected to thermal reduction shows high activity for the target product, which is probably associated with adsorbed hydrogen. For the same reason, in the second hour of work, its initial indicators decrease sharply and do not reach the previous indicators again. The repeated supply of hydrogen may increase activity in the short term.

In contrast to the thermally reduced catalyst, the catalytic activity of the oxidized sample, although slightly inferior to the latter, does not change so sharply during the process. Part of the adsorbed oxygen (not passing into the chemisorbed state) may be directly involved in forming surface nickel complexes, precursors of active centers.

The data obtained with the participation of an IR-activated sample show that their catalytic activity is significantly lower than that of the reduced samples in the O_2 and H_2 atmospheres. At the same time, it should be noted that after 8 hours of catalyst operation, the acetone yield indicators for IR- and H_2 -activated samples become almost the same, which indicates that at this stage, the influence of the activation method is practically exhausted.

The activity of the mechanically activated sample over time is comparable to the action of one of the best samples, thermally oxidized (sample 2). This is because mechanoactivation, as well as the presence of

oxygen, induces activity. However, two interesting facts should be noted: the presence of an induction period, in this case, is limited to 2 hours (against 3 hours in the presence of O_2), after which the catalyst begins to exhibit higher activity than the initial one. And the second effect of mechanoactivation is significantly greater stability of catalytic properties (action is maintained throughout the experiment) than in other methods. Probably, the mechanical activation of the nickel diatomaceous earth catalyst promotes the accumulation of energy in crystals in the form of defects or other changes in the solid, which make it possible to reduce the activation energy of the subsequent chemical transformation of the substance and improve the steric conditions for the process. In addition, as noted above, the possibility of increasing the ratio of deeply reduced nickel in the surface layer will affect the Ni/Ni₂O₃/NiO ratio.

In turn, this will increase the formation rate of active surface intermediates "reagent-catalyst" and, in general, acceleration the reaction of isopropyl alcohol conversion into acetone.

4. Conclusion

A comparison of the activity of industrial nickel diatomaceous earth catalyst samples subjected to different activation methods showed that processing of samples by thermal reduction and thermal

oxidation slightly increases the yield of acetone. In contrast, the original catalyst's IR irradiation and mechanical activation decreased its activity. Thus, thermal reduction and oxidation methods are promising for further research to increase the industrial nickel diatomaceous earth catalyst activity in dehydrogenating isopropyl alcohol into acetone.

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