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CONVERSION OF PROPANOL OVER THE NANOSTRUCTURED NiNaX ZEOLITE CATALYST

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Abstract. Catalyst samples were synthesized on the basis of NaX zeolite and Ni metal by absorption and their activity was studied in the process of oxidation of n-propanol in the temperature range 150-450 ^{0}C. It was found that the conversion rate of alcohols and the yield of reaction products on the modified samples increased significantly compared to the original NaX sample. Provided studies have shown that while intramolecular and intermolecular dehydration reactions of alcohol predominate at relatively low temperatures, complete oxidation reactions of alcohol accelerate at high temperatures. It was found that nano-sized NiO-particles, which contain active oxygen, play a key role in the synthesized samples as the active phase.

Keywords:. *Catalysis, zeolite, alcohol, oxidation.*

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1. Introduction

At present, low molecular weight alcohols, namely, ethanol, propyl and butyl alcohols, are promising basic raw materials for the production of various chemical compounds. Also, these alcohols are quite often used as additives in gasoline. For a long time, we have been conducting research on the conversion of low molecular weight alcohols into valuable chemical compounds. It is known that nickel-containing catalysts are quite often used for deep and partial oxidation of alcohols. In this regard, in this work, we studied the oxidation of propyl alcohol on a nickel catalyst supported on NaX zeolite. We used zeolite as a supporter, so it is available in large quantities in Azerbaijan.

2. The experimental part

Nickel oxide catalysts supported on zeolite were prepared by impregnation. For this purpose, a nickel nitrate solution was applied to NaX zeolite. The resulting sample was dried at 150°C and calcined at 250–300°C until complete decomposition of nickel nitrate. Then the resulting sample was calcined at 550°C for 10 hours (Gaigneaux *et al.*, 2002; Korobitsyna *et al.*, 2008; Henry, 2007; Purnomo *et al.*, 2012). In this way, zeolite NiNaX catalyst samples containing 1%, 2.5%, 5% and 10% nickel were obtained. The activity of the obtained catalysts was studied in the reaction of oxidation of n-propanol in the presence of atmospheric oxygen. The process was carried out in a flow unit equipped with a tubular reactor in the temperature range of 150-450°C. The reactor was loaded with 5 ml of catalyst with a grain size of 1-2 mm. The volumetric feed rate of the

initial reaction mixture was 2400 h^{-1}, and the alcohol:air ratio was 1:10. Analysis of the initial raw materials and reaction products was carried out by the chromatographic method. The amount of nickel in the catalyst samples was determined by atomic absorption on an IC3000 spectrometer manufactured by Thermo Scientific. The phase composition of the samples, the distribution of the active component in them, and their magnetic properties were studied using a D2 X-ray diffractometer (Bruker, Germany), XGT-7000 X-ray fluorescence microscope (Horiba, Japan) and EMX Micro (Bruker, Germany).

3. Results and their discussion

Propanol oxidation reaction products on the studied catalysts are propionaldehyde, propylene and carbon dioxide. Fig. 1 shows the dependence of the yield of products obtained from the conversion of n-propanol on NaX + Ni catalyst samples to the amount of nickel in the sample (T = 350°C).

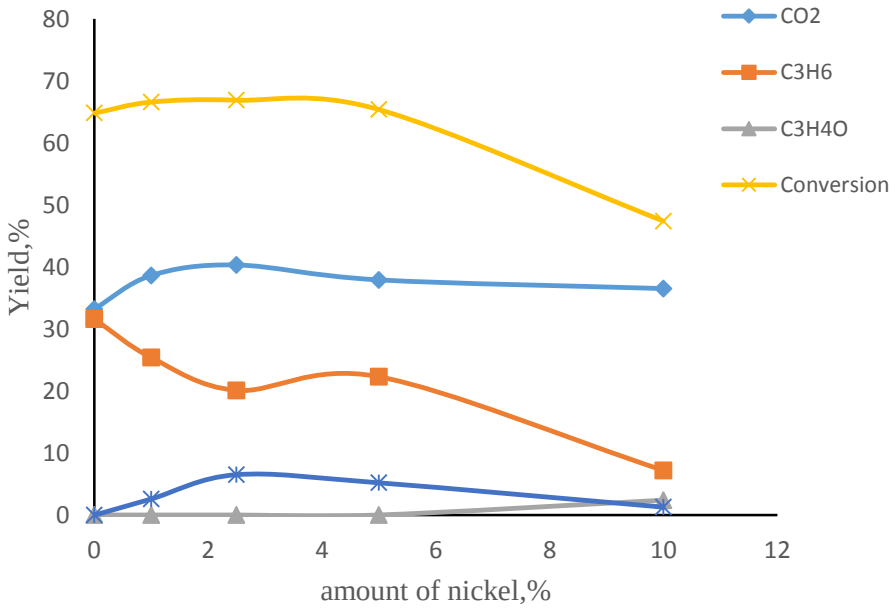

Figure 1. Dependence of the yield of n-propanol conversion reaction products on NaX + Ni catalyst samples on the amount of nickel in the sample: T = 350^0C

As can be seen from figure 1 with increasing of nickel amount the yield of propylene decreases, the yield of propionaldehyde passes throw maximum and the yield of carbon dioxide in initial slightly increases and then don't change. The conversion of n-propanol in initial don't change and then decreases.

Fig. 2 shows the influence of temperature on the yields of propanol oxidation products on NaX + 2.5% Ni catalysts.

As can be seen from Fig. 2 raising of reaction temperature leads to the increasing of propanol conversion until stable value equal 68%. With increasing of reaction temperature, the yields of propylene and propionaldehyde passes throw maximum.

In order to elucidate the dependence of the activity of the studied catalysts on their structural properties, X-ray phase analysis was carried out to determine the phase composition of the initial NaX zeolite and its Ni-modified samples. It has been established that the physicochemical features and catalytic activity of the catalyst

samples used in the study depend on the amount and size of the metal in it. On Fig. 3 shows X-ray diffraction patterns of the original zeolite NaX and its modified foms with metallic nickel.

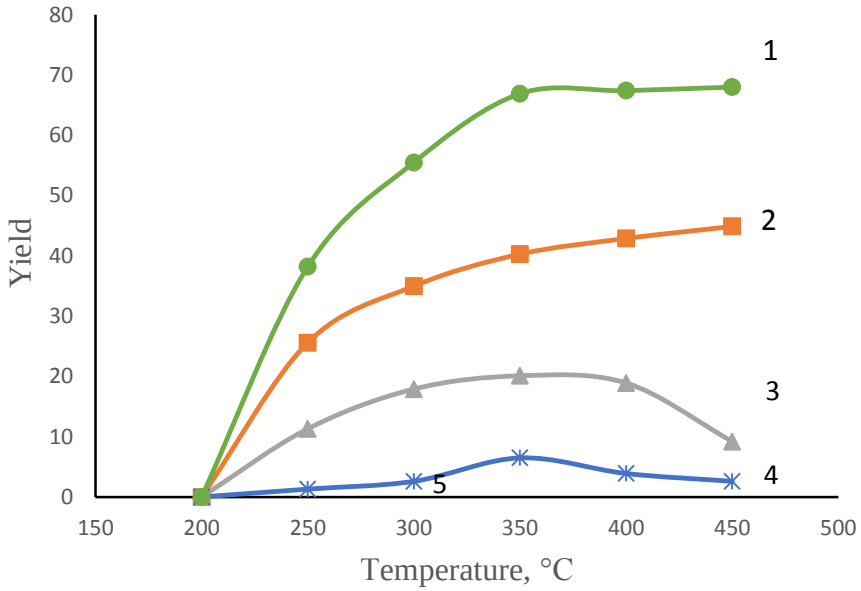

Figure 2. Temperature dependence of the yield of propanol conversion reaction products on a NaX + 2.5% Ni sample: 1. Conversion, 2. CO_2, 3. C_3H_6, 4. C_3H_6O

For the initial example, 2θ = 6.116; 10.002; 23.347; 26,669. Peak of 32.037° were obtained, which corresponds to the standard sample of X zeolite. 2θ = 37,386 (111); Peaks 43,478 (200) and 63,222∘ (220) prove the presence of NiO particles in NaX + Ni samples. The sharpness and intensity of these peaks suggest that NiO nanoparticles have a high degree of crystallinity (Khalaji, 2013; Qiao *et al.*, 2009). This suggests that nickel (II) nitrate absorbed on the surface of zeolite decomposes completely into NiO nanoparticles when heated to 5500 ° C. The average size of NiO crystals was determined using the formula D = kλ / βcosθ. λ is the wavelength of X-rays and is 1.54056 nm. β = FWHM and θ -diffraction angle is calculated on the basis of the peak. k is an empirical coefficient and is 0.9. As a result of the calculations, it was determined that the average size of NiO particles in the structure of NaX zeolite is 28,314 nm. This suggests that the size of NiO particles in the structure of zeolite is at the level of nanoparticles.

Fig. 4 shows the EPR spectra of the initial NaX sample, samples containing 1 and 5% Ni before processing, and 6 hours after processing.

Provided research has shown that even the addition of a small amount (1%) of nickel to the primary NaX structure causes a significant change in its EPR spectrum. Thus, the formation of a signal characterized by the parameters g = 2.1 and ΔH = 19-20 mT is observed, which belongs to nanoscale NiO particles. (Murphy, 2008; Suryanarayana & Grant, 1998).

It was found that as the amount of nickel included in the structure of the primary zeolite increases, the EPR spectrum becomes more complex. For example, the spectrum of a NiX + 5% Ni sample contains at least 6 signals (Fig. 4, d). As can be seen, there is a significant change in the spectrum of the samples processed in the process for 6 hours. This can be explained by the formation of coke on the surface of the treated catalyst

sample. Thus, it was determined that the narrow bands with the parameters g = 2.0026 and ΔH = 0.9 mT correspond to the paramagnetic coke residue. Note that after incinerating the coked sample at 500°C in the presence of air, the spectrum of the sample obtained is exactly equal to the spectrum of the original sample.

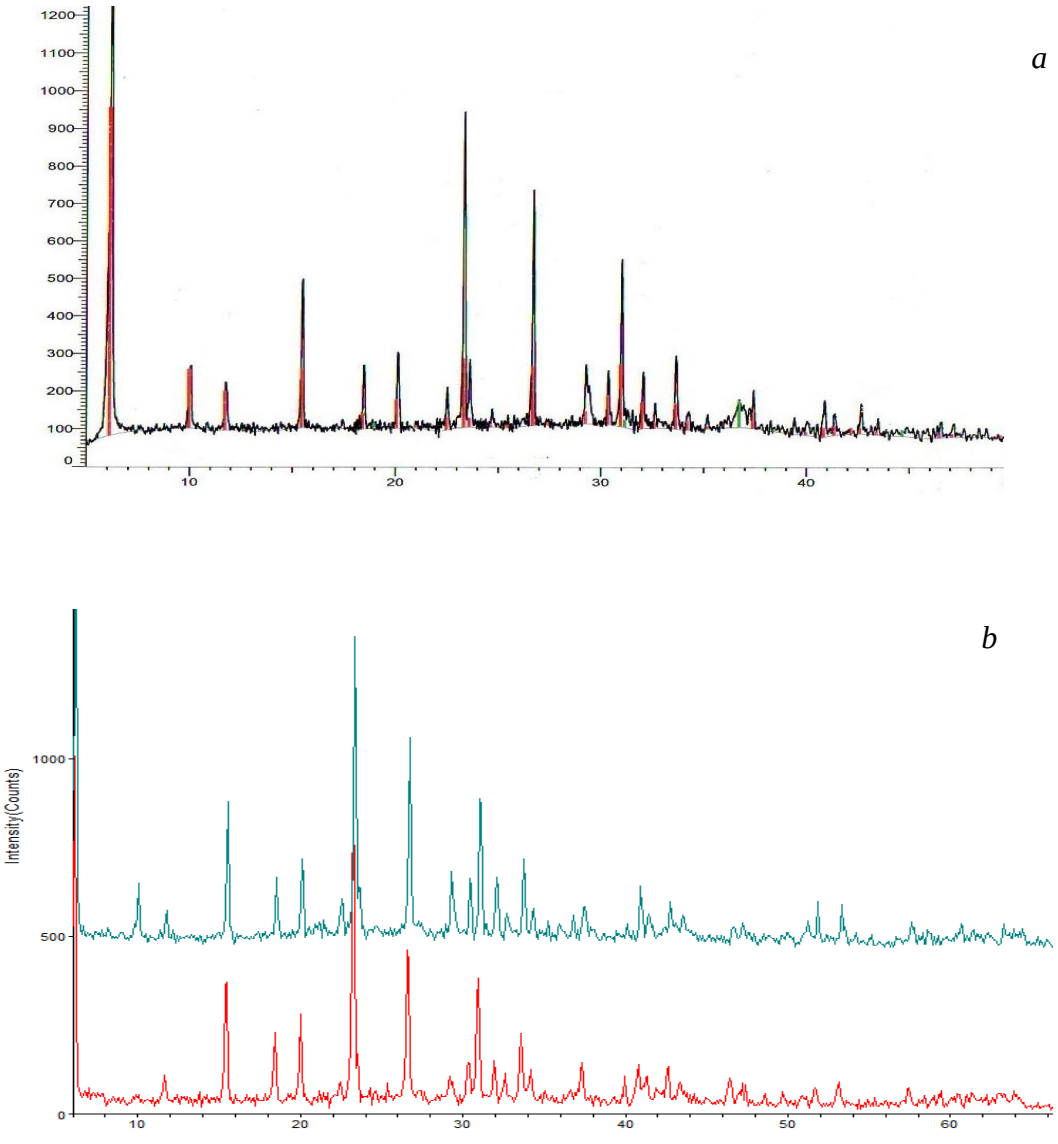

Figure 3. X-ray diffractograms of a) primary NaX zeolite and b) its modified forms with Ni metal before and after catalysis

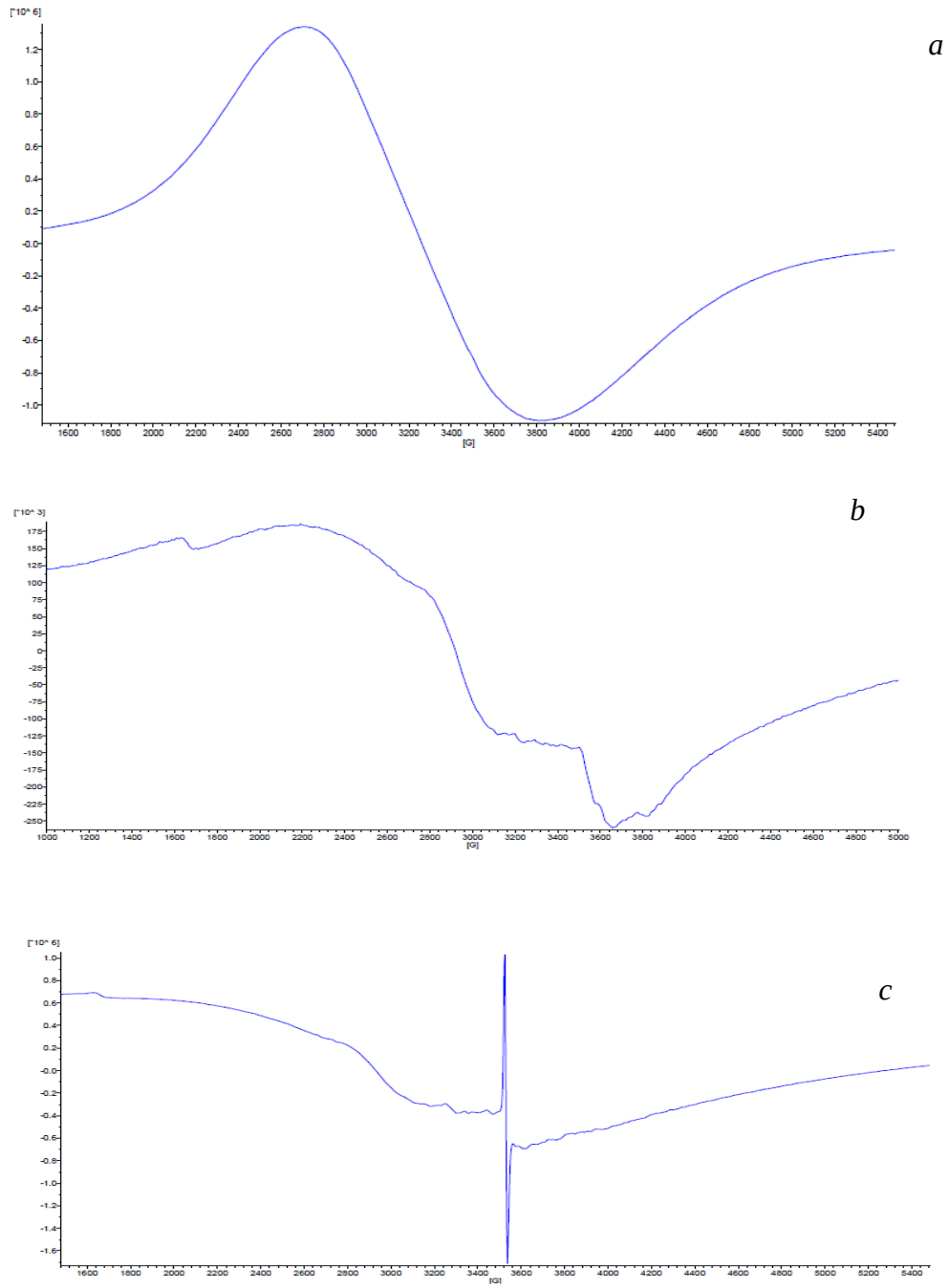

Figure 4. the EPR spectra of the initial NaX sample, samples containing 1 and 5% Ni before processing, and 6 hours after processing.
a) Primary NaX; b) NiX+5% Ni; c) NiX+5% Ni after catalysis

4. Conclusion

It is found that samples containing less than 5% nickel were found to be more active in this process. At the same time, it has been shown that during the decomposition of nickel (II) nitrate on the surface of zeolite NiO tends to dispersion is produced. It was found that the average size of NiO particles does not exceed 30 nm. This is much smaller than the size of NiO particles obtained from the decomposition of

free Ni (II) nitrate. This shows that the surface of zeolite plays an important role in the formation of a highly dispersed NiO phase. Based on the research, it was determined that depending on the conditions of modification of the original zeolite sample with Ni metal, it is possible to control the yield of the reaction product by optimizing the concentration and size of the active component (NiO) in the obtained catalyst sample.

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