ISSN: 2707-1146
e-ISSN: 2709-4189

https://doi.org/10.36719/2707-1146/47/17-22

Asmar Valiyeva
Western Caspian University
Doctor of Philosophy in Chemistry
esmer_elesgerli@mail.ru
Parviz Nadirov
Azerbaijan State Oil and Industry University
Doctor of Philosophy in Chemistry
parvizm1971@mail.ru
Jabrail Mirzai
Baku State University
Doctor of Chemical Sciences
mirzacabrayil@ gmail.com

Synthesis and Characterization of Nax/Ni Zeolite Nanocatalyst and Their Application in the Process of Oxidative Dehydrogenation Propanol

Abstract

Catalyst samples were synthesized by the method of impregnation on the basis of NaX zeolite and Ni metal and their activity was studied in the oxidation process of n-propanol in the temperature range of 423-723K. It has been established that the conversion rate of alcohol and the yield of reaction products on the modified samples increase significantly compared to the original NaX sample. According to the results of the research, it was found that if the reactions of intramolecular and intermolecular dehydration of alcohol predominate at relatively low temperatures, then the reactions of its partial and complete oxidation are accelerated at high temperatures. It was determined that the method of modifying the original NaX zeolite makes it possible to optimize the phase composition of the synthesized catalyst and the size of the active component, which allows to adjust the yield of the main reaction products and reduce the temperature limit of the reaction. As a result of the study, it was found that the average size of NiO particles included in the structure of NaX zeolite is 28314 nm. This suggests that the size of NiO particles in the zeolite structure is at the nanoparticle level.

Keywords: *catalysis, zeolite, alcohol, oxidation,nanotecnology*

Introduction

As is known zeolites have almost very weak oxiding and reducing properties when they contain an alkali metal cation as the primary exchange cation. However, highly active oxidation catalysts can be obtained by introducing transition metals into their crystal lattice in various ways**.** On the other hand, recently there has been great interest in processes involving nano-sized catalytic systems. The basis of the work carried out in this direction is the development of methods for the synthesis of catalytic systems with nanostructured particles, determination of their structure and morphology, and determination of methods that allow changing the basic properties of the catalyst (Henry, 2007, p. 354; Khalaji, 2013, p. 245).

Based on the above, it can be said that, the study of zeolites containing transition metals is of great importance and relevance both in terms of the theory of catalysis and the creation of new multifunctional catalytic systems and the development of new catalytic processes.

In practice, the conversion of alcohols can be carried out using various catalysts. The traditional catalysts for this process are zeolites. In case of application of zeolites in the mentioned process, the researcher has the opportunity to preselect the structure type and pore size of the catalyst, thereby directing the process in the desired direction. The conversion of alcohols, including low molecular weight dihydric alcohols such as ethanol, n-propanol, on zeolites, is generally a complex process consisting of several stages depending on the conditions. The study of the features of this process

is one of the pressing problems of the petrochemical industry complex today (Korobitsyna et al., 2008, p. 169).

Experimental part

Taking into account the above, the conversion of n-propanol in the presence of NaX-based zeolite catalysts containing Ni-transition metal has been extensively investigated. The mentioned catalysts were obtained using the impregnation method. For this, the nitrate salt solution of the given metal was soaked onto the original zeolite (NaX) and then the mass was dried at 1000C and then heated at 3000C until the salt was completely decomposed. In the end, the resulting mass was incandesced at a temperature of 5500C for twelve hours and catalyst samples were obtained. Thus, using the impregnation method, catalysts containing 1.0 %, 2.5 %, 5.0 %, 7.5 % and 10.0 % Ni-metal were synthesized. In order to prepare the synthesized catalysts for use in the process, they were first made into pill form and then crushed into 1-2 mm particles (Gaigneaux et al., 2002, p. 354; Purnomo, Salim & Hinode, 2012).

The study of the activity of the synthesized catalysts was carried out in the process of converting n-propanol in air oxygen environment. The process was carried out in a flow-through installation equipped with a tubular reactor in the temperature range of 423-773 K. The volume of the catalyst taken for the study was 5 ml, the feed rate of the initial reaction mixture into the reactor was 2400 h-1. Alcohol-air mixture was fed into the reactor in a ratio of 1:10. The chromatographic method was used for the analysis of the initial substances and reaction products (Qia et al., 2009: 13; Suryanarayan & Grant, 1998, p. 428).

X-ray phase analysis studies of catalyst samples containing different amounts of modifiers before and after the reactions were carried out on a RIGAKU SC-70 device at an angular velocity of 10 rev/min (40 kV, 15 mA) in the angular interval of 3-60^o in CuK-beams to study the phase state of the impregnated compounds. Decoding of diffractograms was performed using the ICDD, PDF-2 database (Min Kim et al., 2021, p. 162; Almashhadani et al., 2017, p. 428).

Thus, the NaX structure is an excellent starting point for the developing of the group of new zeotype catalysts where one of the most important materials is Na. Many efforts have been devoted to introduce intracrystalline mesoporosity into NaX structure in order to reduce the micropore environment restrictions, e.g. modified crystallization methods (Breck, Eversole & Milton, 1956; Weisz & Frilette, 1960, p. 382) templating and demetalation (Argauer & Landolt, 1972). In group of post-synthetic methods of modification of zeolitic materials one of the most effective and most economical seems to be desilication process. The desilication is identified with the process of selective extraction of silicon from the framework in the alkaline medium. The effectiveness of Si extraction from the framework depends on a number of parameters, including the value of Si/M ratio, framework topology, type and concentration of the desilication agent, temperature and time of process.

The results obtained and their discussion

The temperature dependence of the yield of the reaction products obtained from the conversion of N-propanol on NaX+Ni catalyst samples has been extensively studied. It has been established that the conversion of alcohol is observed starting from the temperature of 523K. The maximum alcohol conversion corresponds to the NaX (+5.0 % Ni) sample and is 70.0 % (723K). The maximum yield of carbonyl compounds (acrolein + propion aldehyde) corresponds to the above-mentioned catalyst sample and temperature and is 13.0 %. The maximum yield of propene also corresponds to the NaX sample (+5.0 % Ni) and is 22.3 % at a temperature of 623K. The maximum yield of carbon dioxide, which is a product of complete oxidation of alcohol, on the specified sample is 39.7 % (723K).

In the continuation of the research, X-ray phase and EPR analysis of Ni-containing catalyst samples used in the process of n-propanol oxidation was carried out before and after the process.

Figure 1 shows roentgenograms, of NaX samples containing 5.0 and 10.0 % Ni before and after the experiment.

ISSN: 2707-1146
e-ISSN: 2709-4189

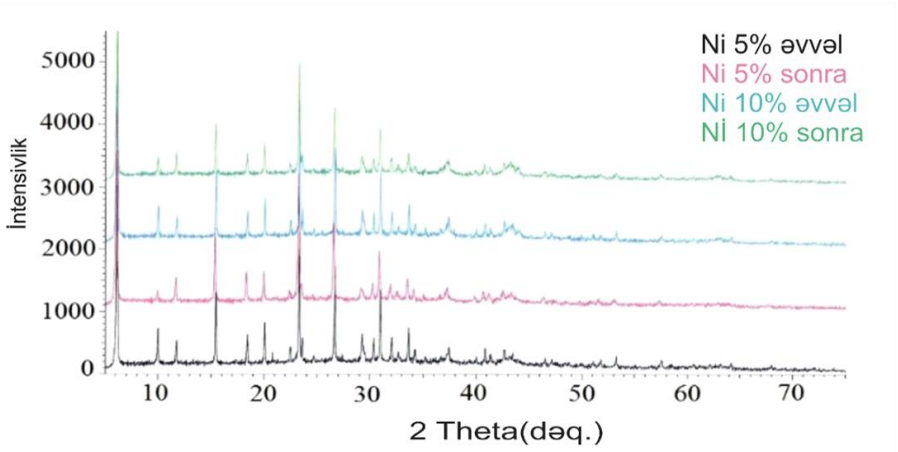


Figure 1. Radiographs of NaX (+5 % Ni), NaX (+10.0 % Ni) samples taken before and after the experiment

It was determined that the peaks of 2θ = 6.116, 10.002, 23.347, 26.669, 32.037° correspond to the standard pattern of primary NaX zeolite. The peaks of 2θ = 37.386 (111), 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 the NiO-nanoparticles have a high degree of crystallinity. This suggests that nickel (II) nitrate impregnated on the zeolite surface is completely decomposes into NiO nanoparticles when heated at 5500 C. Using the formula D = kλ / βcosθ, the average size of NiO crystals was determined. Here, λ is the wavelength of X-rays and is 1.54056 nm. β = FWHM and θ – diffraction angle is calculated based on the peak. And k is an empirical coefficient and is 0.9. As a result of the calculation, it was established that the average size of NiO particles included in the structure of NaX zeolite is 28314 nm. This suggests that the size of NiO particles in the zeolite structure is at the nanoparticle level.

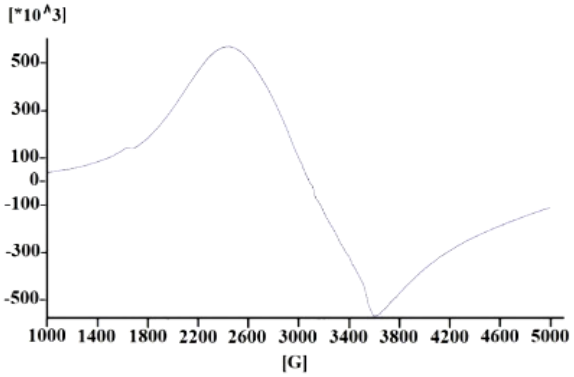
Table 1 shows the sizes (as a result of RF analysis) and values (as a result of EPR analysis) of magnetic resonance parameters of NiO particles formed in a pure state and on the surface of NaX zeolite. As can be seen from the table results, the size of NiO nanoparticles formed on the surface of NaX zeolite is smaller than the size of pure NiO crystallite.

Table 1.
Size and value of magnetic resonance parameters of NiO crystallite formed in pure state and on the surface of NaX zeolite

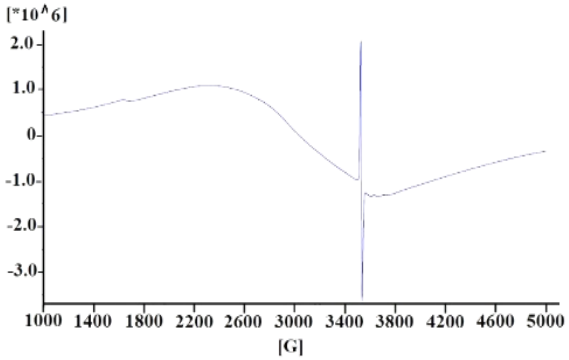
Parameters	Pure NiO crystallite	NiO/NaX
Nanoparticle size (nm)	32,65	28,31
g – factor value	1,92	2,1
EPR spectrum width, ΔHpp (mT)	72,5	66,9

Figure 2 shows the EPR spectra of NaX (+1.0 % Ni) and NaX (+5.0 % Ni) samples taken before the experiment and after 6 hours of operation during the n-propanol conversion process. It üas determined that the addition of even a small amount of metallic Ni (~1 %) to the original NaX zeolite causes a noticeable change in its ESR spectrum. Against the background of a broad signal created by a large magnetic field, a convex-shaped signal with a g-factor of 2.1 and a width ΔH = 19-20 mT is observed, which corresponds to nano-sized NiO particles.

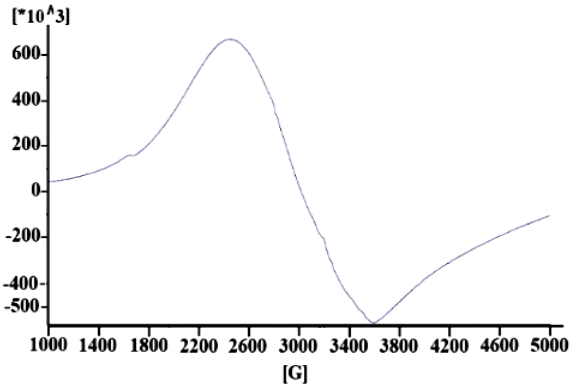
ISSN: 2707-1146
e-ISSN: 2709-4189



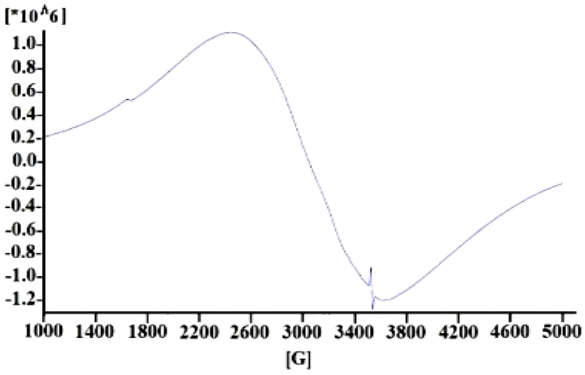
a) NaX (+1.0 % Ni), before the experiment



b) NaX(+1.0 % Ni), after the experiment



c) NaX (+5.0 % Ni), before the experiment



d) NaX (+5.0 % Ni), after the experiment

Figure 2. EPR spectra of NaX samples containing 1.0 % (a, b) and 5.0 % (c, d) Ni before the experiment and after 6 hours of operation in the n-propanol conversion process

It was found that when the mass amount of Ni included in the original zeolite increases up to 10.0 %, their EPR spectrum becomes complex and consists of many signals. For example, in the NaX (+5.0 % Ni) sample, the number of signals reaches six. Research has shown that the EPR spectrum of catalyst samples involved in the conversion of n-propanol undergoes a noticeable change within 6 hours. Based on the ESR spectra of the catalyst samples processed in the process, a certain amount of coke formation is observed on the surface of the catalyst. Thus, against the background of the broad signal, a narrow signal characterized by the parameters g=2.0026 and ΔH= 0.9 мТ is observed, which corresponds to coke residues with paramagnetic properties. It is assumed that the formation of coke on the surface of the catalyst creates the conditions for the reduction of nickel oxide to metallic nickel. Note that the EPR spectrum of the coked sample obtained after annealing in the presence of air at a temperature of 773 K is practically indistinguishable from the EPR spectrum of the initial catalyst sample. It is quite possible that the catalytically active centers of this reaction are nanosized particles of nickel oxide NiO, and the main participants in the redox stages of the process are Ni and NiO particles.

Catalyst samples processed for 6 hours in the n-propanol oxidation process were studied using the IR-spectroscopy method.

Figure 3 shows the IR spectra of the NaX (+2.5 % Ni) sample taken before and after processing in the mentioned process.

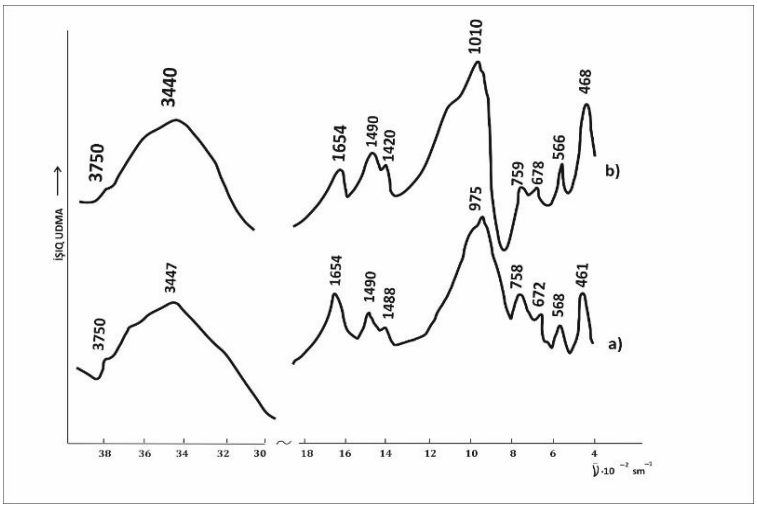


Figure 3. IR-spectra of NaX (+2.5 % Ni) catalyst before (a) and after (b) treatment in n-propanol conversion process

The comparison of the corresponding spectra shows that no significant changes of the spectral landscape occur in the vibrational regions of either the crystal lattice or water after the aforementioned catalytic process. Naturally, small shifts are observed in the maxima of some absorption bands. In addition, after the process there is an increase in the integral intensity of the absorption bands, observed at 1400-1500 cm-1 in the region of carboxylate structures (monodentant or bidentate).

Conclusion

In the process of oxidative dehydrogenation of N-propanol in the presence of nickel-containing NaX zeolite catalysts, in addition to the activity of the catalyst, its phase composition, active component distribution, magnetic and catalytic properties have also been widely studied. It has been shown that the amount of modifier in the catalyst allows to optimize its phase composition and the size of the active component, which allows to adjust the yield of the main products and reduce the reaction temperature. It has been shown that the inclusion of NiO nanoparticles in the composition of the zeolite leads to an increase in the activity of catalysts at high temperatures and significantly increases their stability. It was determined that the optimal amount of nickel in the catalyst is 5 % by mass. Thus, as a result of the process of oxidative dehydrogenation of propanol in the presence of the mentioned catalyst, the maximum yield of carbonyl compounds (acrolein + propion aldehyde) was 13.0 % (723K), and the maximum yield of carbon dioxide, which is the complete oxidation product of alcohol, was 39.7 % (723K), which is considered a fairly high result.

References

1. Henry, C. R. (2007). *Catalysis by nanoparticles. In Nanocatalysis.* Springer.
2. Khalaji, A. D. (2013). Preparation and characterization of NiO nanoparticles via solid-state thermal decomposition of nickel (II) Schiff base complexes [Ni (salophen)] and [Ni (Mesalophen)]. *Journal of Cluster Science*, 24(1), 209-215.
3. Korobitsyna, L. L., Velichkina, L. M., Vosmerikov, A. V., Radomskaya, V. I., Astapova, E. S., Ryabova, N. V., & Agapyatova, O. A. (2008). Ultra-high-silica ZSM-5 zeolites: Synthesis and properties. *Russian Journal of Inorganic Chemistry*, 53(2), 169.
4. Gaigneaux, E. M., De Vos, D. E., Jacobs, P. A., Martens, J. A., Ruiz, P., Poncelet, G., & Grange, P. (2002). *Scientific Bases for the Preparation of Heterogeneous Catalysts*. Elsevier.
5. Qiao, H., Wei, Z., Yang, H., Zhu, L., & Yan, X. (2009). Synthesis of pure Na–X and Na–A zeolite from bagasse fly ash. *Microporous and Mesoporous Materials*, 162, 6-13.
6. Purnomo, C. W., Salim, C., & Hinode, H. (2012). EPR (Electron Paramagnetic Resonance) spectroscopy of polycrystalline oxide systems. *Metal Oxide Catalysis*, 1-50.

7. Suryanarayana, C., Grant, N. J. N. Y. (1998). A Practical Approach Plenum Press. New York. Preparation and characterization of NiO nanoparticles by anodic arc plasma method. *Journal of Nanomaterials.*
8. Min, H. K., Kim, Y. W., Kim, C., Ibrahim, I. A. M., Han, J. W., Suh, Y. W., Jung, K. D., Park, M. B., Shin, C. H. (2022). Phase Transformation of ZrO2 by Si Incorporation and Catalytic Activity for Isopropyl Alcohol Dehydration and Dehydrogenation. *Chemical Engineering Journal*, 428. https://doi.org/10.1016/j.131766
9. Almashhadani, H., Samarasinghe, N., Fernando, S. (2017). Dehydration of n-propanol and methanol to produce etherified fuel additives. *AIMS Energy*, 5(2), 149-162.
10. Breck, D. W., Eversole, W. G., Milton, R. M. (1956). New synthetic crystalline zeolites. *Journal of the American Chemical Society*, 78, 2338-2339.
11. Breck, D. W., Eversole, W. G., Milton, R. M., Reed, T. B., Thomas, T. L. (1956). Physical and Inorganic Chemistry: Crystalline Zeolites. The Properties of a New Synthetic Zeolite. *Journal of the American Chemical Society*, 78, 5963-5972.
12. Weisz, P. B., Frilette, V. J. (1960). Intracrystalline and Molecular-Shape-Selective Catalysis by Zeolite Salts. *The Journal of Physical Chemistry*, 64, 382-382.
13. Argauer, R. J., Landolt, G. R. (1972). Crystalline zeolite ZSM-5 and method of preparing the same (U.S. 3702886 A).

Received: 22.05.2024
Revised: 10.07.2024
Accepted: 30.07.2024
Published: 20.08.2024