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СХІДНОУКРАЇНСЬКИЙ НАЦІОНАЛЬНИЙ УНІВЕРСИТЕТ
імені ВОЛОДИМИРА ДАЛЯ**

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Полупан Ю.В., Полупан Є.В. ОДИН ІЗ СПОСОБІВ ДОСТУПУ ДО GOOGLE DRIVE БЕЗ ВИКОРИСТАННЯ АВТОРИЗАЦІЇ	99
Рейдемейстер А. Г., Шикунів А. А. ВЛИЯНИЕ ПАРАМЕТРОВ РЕССОРНОГО ПОДВЕШИВАНИЯ НА ДИНАМИЧЕСКУЮ НАГРУЖЕННОСТЬ ЛИТЫХ ДЕТАЛЕЙ ТЕЛЕЖЕК ГРУЗОВЫХ ВАГОНОВ	103
Шорохов М.М., Суворін О.В., Казаков В.В., Ожередова М.А. ВПЛИВ НАДЛИШКУ ОСАДЖУВАЧА НА ОЧИЩЕННЯ Cr ⁶⁺ ВМІСНИХ СТИЧНИХ ВОД ПРОМИСЛОВИХ ПІДПРИЄМСТВ	109
Philips T.C, Kudryavtsev S.A, Glikin I M, Korol D. SYNTHESIS OF DIISOPROPYL ETHER VIA CATALYTIC DEHYDRATION OF ISOPROPANOL USING THE TECHNOLOGY OF AEROSOL NANOCATALYSIS	113
Харламов П.О., Харламова О.М. КЕРУВАННЯ РОЗВИТКОМ МЕЗОЛОГІСТИЧНОЇ СИСТЕМИ РЕМОНТУ РУХОМОГО СКЛАДУ	120
Шапкін В.П., Парамонова Л.М., Мороз О.В., Бушуєв А.С. ВЛАСТИВОСТІ ГАЛОГЕНАНТРАХІНОНІВ В СИНТЕЗІ БІАРИЛІВ ДЛЯ ПОЛІЦИКЛІЧНИХ БАРВНИКІВ ТА ПІГМЕНТІВ	124
Шведчикова І.О., Шевченко О.І., Нікітченко І.В. АНАЛІЗ ПІДХОДІВ ДО УСУНЕННЯ МАГНІТНИХ ЗАВАД ПРИ ФЕРОЗОНДОВОМУ КОНТРОЛІ ОСЕЙ КОЛІСНИХ ПАР.....	130
Шевченко В.А. АЛГОРИТМ БЫСТРОЙ ОЦЕНКИ ПАРАМЕТРОВ СУДОВЫХ ЭЛЕКТРОЭНЕРГЕТИЧЕСКИХ СИСТЕМ	136

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SYNTHESIS OF DIISOPROPYL ETHER VIA CATALYTIC DEHYDRATION OF ISOPROPANOL USING THE TECHNOLOGY OF AEROSOL NANOCATALYSIS

Philips T.C, Kudryavtsev S.A, Glikin I M, Korol D

СИНТЕЗ ДІЗОПРОПІЛОВОГО ЕТЕРУ КАТАЛІТИЧНОЮ ДЕГІДРАТАЦІЄЮ ІЗОПРОПІЛОВОГО СПИРТУ ПО ТЕХНОЛОГІЇ АЕРОЗОЛЬНОГО НАНОКАТАЛІЗУ

Філіпс Т., Кудрявцев С.О., Глікiна І.М., Король Д.Р.

This paper proposes and describes a new method for the production of DIPE, using the technology of aerosol nanocatalysis on a vibrating fluidized bed. The catalyst used was NaX, which was later treated with ammonium nitrate, in order to increase its acidity and bridge the OH group, which in turn increased the bronsted acid sites. Parameters such as flowrate, temperature and mechanical chemical activation frequency of vibration were varied in order to ascertain the best conditions for the synthesis of DIPE through catalytic dehydration of isopropyl alcohol.

Keywords: aerosol nanocatalysis, vibrating bed, DIPE, bronsted acid sites, DIPE, NaX zeolite, mechanical chemical activation frequency.

1. Introduction.

Oxygenates are essential because they provide positive and distinguished compatible gasoline blending properties which include favourable octane rating, distillation temperatures that are low and ordinarily would not exist if they were not in production and application. Due to their extremely low reaction rate in the atmosphere, oxygenates decrease the long term toxicity of CO in the air, which invariably lowers smog and ozone formation.[1]

Experimentally oxygenates show that they substantially reduce primary particulate matter by as much as 25% to 30%. DIPE (Diisopropyl Ether) can be a potential oxygenate as it compares favourably with other ethers, that are obtained by etherification of isolefin with methanol in the case of Methyl Tert Butyl Ether (MTBE) or Ethyl Tert Butyl Ether (ETBE). DIPE can be seen to be more advantageous due to the much availability of olefin feedstock in the form of isopropylene, which is several times greater than the resources of isobutylene and isoamylenes. Consequently DIPE can be produced virtually in any refinery independent of external sources of alcohols, where water is used instead, and it compares favourably, due to its low toxicity, reduced emission and low cost of production.[2,6]

The synthesis of DIPE in this study is carried out by the catalytic dehydration of isopropanol over zeolite catalyst using aerosol nanocatalysis. Zeolites are much favourable because they operate at a higher temperature and it enables the production of DIPE via acidic catalytic dehydration of isopropanol. Due to the availability of both basic and acidic sites on NaX zeolite, it was necessary to enhance its acidic content by exchanging its sodium content with ammonium nitrate, in order to increase the bronsted acid site.[3]

The scientific foundation of catalytic dehydration of isopropanol to DIPE depends on the following factors, which are:

- High acidic content of the catalyst
- High pressure,
- Temperature and reaction time.

The principle of aerosol nanocatalysis is founded upon the following concepts:

- There is an exclusion from the catalytic process intra-diffusion stages;
- Synthesis in situ of superactive nanoparticles of a catalyst with a size of 8-100 nm;
- There is the absence of carriers in the catalytic system
- In situ implementation of continuous mechanochemical activation of the catalyst surface by a moving solid material;
- Equal accessibility for active surface reagents.

The foundations of AnC were developed by Soviet scientists under the leadership of Glikin M. in the Severodonetsk branch of the State Institute of Nitrogen Industry [4]. At the heart of AnC technology are mechanochemical effects arising from the constant mechanical action of the catalytically active substance. The catalyst system in AnC technology is a moving dispersing material. During the continuous movement of the dispersing material, there is a constant mechanochemical activation of the catalyst that occurs, which leads to a change in the thermodynamic potentials of the activated substance, creating surface

defects, and eventually leading to the grinding up to the nanoscale state [5].

The main goal of the study was to evaluate the main parameters of the catalytic dehydration of isopropyl under the conditions of aerosol nanocatalysis technology in a vibrating fluidized bed reactor.

- Implementation of the basic principles of AnC technology in a vibrating fluidized bed reactor, conducting experiments on the catalytic dehydration of isopropyl alcohol;

- Proof of the course of catalytic processes in a laboratory installation,

- The study of the influence of the intensity of mechanochemical activation on the efficiency of the process (selectivity, degree of conversion);

-The influence of bronsted acid sites/increased acidity on Zeolites and its influence on the dehydration of isopropyl alcohol.

-Detailed analysis of experimental data, selection of the most optimal variant of process parameters

2. Analysis of the current level of research in the field of AnC. The technology of Aerosol nanocatalysis is founded upon the mechanism of mechanochemical activation, which is used to improve the performance of the catalyst [8,9]. During mechanical interaction, the temperature rises at the points of contact and relaxation of the stress field [7, 9]. As a result of the moving and vibration of the catalyst bed, most of the work which would have been done against frictional forces manifests itself in the form of heat, which later influences the catalytic activity. On the surface layer, the temperature can instantaneously increase to 1300°K. Pulses of high energies lead to the sintering of nanoparticles. The time of existence of such temperature flares on an area of 10^{-7} - 10^{-9} m² is of the order of 10^{-4} s. Emerging freshly formed surfaces on the catalyst carry an electric charge. As a result, the destruction of reagents is likely on the surface layer. Under optimal conditions of the vibrating bed, defects are formed on the surface of the crystallites and the electronic properties of the surface change, which leads to an increase in the catalytic activity of the substances, the increase in catalytic activity is believed to be associated with crystal lattice distortions, rather than with an increase in surface area and this provides, new opportunities for controlling the kinetics of processes [8].

The implementation of catalytic processes in the conditions of AnC technology (without carrier) leads to a decrease in the amount of catalytically active substance (up to 10^6 times), and also removes mechanical and thermal limitations associated with the use of a carrier [16]. Under the conditions of this technology, it is possible to reduce the temperature range of the course of destructive transformations and increase the conversion of raw materials.

At the next stage of the development of AnC technology, it was suggested to carry out etherification studies in installations with a vibro-impact or vibrating layer, where the mechanochemical activation of the

catalyst is carried out by vertical reciprocal movements of the laboratory reactor and the catalytic system inside it [17]. The process was called Aerosol nanoCatalysis with Vibrating Bed (AnCVB). There is the expectation that the capacity of the reactor with the vibro-impact layer provides, new opportunities for controlling the kinetics of processes [17].

3. Experimental part.

AnC catalyst system consists of a catalytically active material powder with initial particle size of 200 microns and its dispersing solid material (mm) with a size of 1.0-1.2 mm. Both types of particles in the reactor are in constant motion. Such conditions allow the synthesis of nanoparticles of different size by mechanical action on the raw material dispersing catalyst particles [10]. In previous studies [11] with the aid of foreign scientists we were able to identify directly catalyst particle sizes during the reaction: 8-100 nm [12].

Previous work established that before the start of the experiment there should be starting materials for preparation of the catalyst system. A specific feature of AnC is the adhesion (type sorption) of the catalyst on the surface of the dispersing material [10]. It is necessary to ensure maximum adsorption of the catalyst particles in a reactor under conditions of vibration. This allows determining the amount of catalyst in the gas phase.

Before starting the experiment, the catalyst should be pre-adsorbed onto the surface of the dispersing material. Work is carried out as follows: for the experiment a certain amount of dispersing material (in laboratory experiments, is the glass bead with a diameter of 1.0-1.2 mm), which occupies about 50% of the reactor volume. Loading the material in an amount more than necessary into a glass flask. To this was introduced the catalyst powder, that was weighed on an analytical balance to the nearest 0.0001 g, in an amount exceeding the adsorption capacity of DM. The flask was covered and required a vigorous shaking performed at room temperature for 10 - 15 min. After shaking, the catalyst and the dispersing material are loaded into the vibrating reactor, and the reactor is operated at a vibration frequency to enable the total dispersion and heating of the catalyst on the dispersing material. Then, the catalyst system is discharged from the flask and sieved in order to separate the catalyst which was not adsorbed. The separated catalyst is weighed on an analytical balance. If the mass of the catalyst is less than the initial amount, a new measured catalyst is added to the glass beads in a flask, and then shook vigorously, and later loaded again unto the reactor which vibrates on a non definite MCA frequency for 1 hour. The process is repeated until; there is no change in mass

from the unloaded catalyst after heating in the reactor, in comparison with the 1st previously weighted catalyst after shaking in a flask. [13]

Previous studies have shown that in the absence of a catalyst in gas phase, as when it is excess, the reaction rate is minimal [13]. The catalyst powder is weighed and added to the reactor so as to create a constant concentration in the reaction volume. The reactor was checked for leaks before conduction of experiment [13].

Description of experimental setup: The process of synthesizing DIPE from catalytic dehydration of isopropanol using aerosol nanocatalysis technology was conducted in a laboratory setting, shown in Fig. 1 [17].

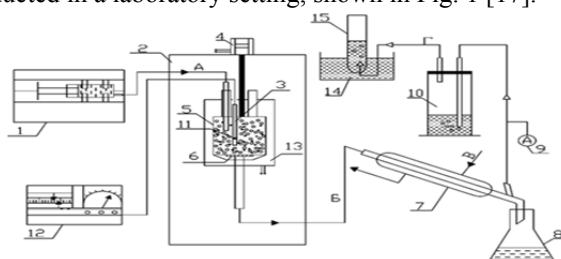


Fig. 1. Schematic diagram of the pilot unit: (1) - Syringe batcher; (2) - Thermal cabinet; (3) - Pocket of thermocouple; (4) - Vibrating device; (5) - Reactor; (6) - Metal-cloth filter; (7) - Water condenser; (8) - Receiver of liquid fraction; (9) - Sampling point; (10) - Gas washer; (11) - Thermocouple; (12) - Regulator for oscillation frequency and temperature; (13) - Heater; (14) - Water container; (15) - Gas receiver

The experiments were conducted on 2 different forms of catalyst, the normal NaX zeolite and the modified NaX (H-X) zeolite, using the same set of parameters, to analyse the difference in selectivity and conversion of IPA to DIPE and to analyse how the set principles of etherification influence the catalytic dehydration of isopropanol using the technology of aerosol nanocatalysis.

Before each reaction, the catalyst was preheated in situ for 2 hours at 150°C-300°C under nitrogen gas that was passed through the reactor through an aircompressor, after which isopropanol was fed into the reactor (5) by a syringe-batcher (1), which is located in the thermal cabinet (2), and it was then subjected to thermal treatment by heater (13). Etherification reactions took place inside the reactor. Experiments were conducted at temperatures: 140°C, 160°C, 180°C, 200°C, 220°C, 240°C, and at frequencies of 1.4 and 2.0 Hz. The temperature in the reaction zone was measured by a thermocouple (11), and sustained by a regulator (12). In order to keep the catalyst inside the reactor, a metal-cloth filter (6) was placed at the bottom of reactor, the liquid reaction products pass through a water-cooled condenser (7) and were then gathered in a flask for the liquid fraction (8). The etherification products were two fractions – liquid and gas. The non-condensed gases from the cracking process go through the sampling point (9), and were then sent to the gas

washer (10) where they bubble through the water layer. The gases were then directed into a gas container (15), and passed through container with water (14). The reactor moves upward and downward in a back-and-forth linear motion with the help of vibrating device (4). The oscillation frequency and temperature were set and controlled by a regulator (12).

The content of the gaseous products of the reaction were analytically determined by using calibrated gas chromatographs such as LHM-8, COLOR-500. and UNHPLC system, propylene (C_3H_6) was determined with an accuracy not less than 0.01 vol. %.

The products gotten from extractive distillation, were analysed with a UNHPLC chromatography apparatus.

The results gotten from the chromatograph indicated the presence of DIPE, IPA and water.

4. Materials and research results. The NaX zeolite used in this study was obtained from REAXIM Ukraine. It was in the form of 1.5mm extrudate. The Isopropyl alcohol was also purchased from REAXIM Ukraine. The NaX zeolite was treated with ammonium nitrate in order to increase its acidity.

The major goal of this research was to find out the possibility of synthesizing DIPE using the conditions of aerosol nanocatalysis on a vibrating fluidized bed, while adhering to the scientific principles of etherification, considering ACnVFB offers the following advantages, that are not common with other etherification reactions like:

- Strength and heat resistance of the catalyst;
- Use of a simple catalytic system;
- Creation of an optimum quasi-structure of the catalyst, controlling its concentration in the reaction zone;
- Mechanical activation of the catalyst in situ with changes in the surface properties of catalysis important for catalysis: adsorption, electrical conductivity, surface energy, electromagnetic effect, work function of an electron, etc.;
- Achievement (in terms of mass) of the aerosol activity of the catalyst is 10^4 - 10^5 times higher than that of the carriers;
- Possibility of catalyst regeneration by mechanical surface treatment in situ;
- Reducing the amount of catalyst used in the reactor by 10^5 - 10^6 times and bringing it to 4-10 g / m³ of the reaction volume. [16]

However synthesizing DIPE on a normal Na-X zeolite catalyst did not yield any result regardless of the variation in the operating parameters of aerosol nanocatalysis technology, the parameters being:

- Frequency of vibration
- Temperature
- Flow rate

Below are the results obtained from synthesis of DIPE using a non modified Na-X zeolite and modified H-X zeolite, with the variation of the above parameters

Table 1

For a flow rate of 0.03 ml/min and a frequency of =1.4Hz, using a normal Na-X zeolite

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	18	0.15	0.2	0	0
160	18	0.15	0.3	0	0
180	17.7	0.2	0.6	0	0
200	17.5	0.311	2.4	0	0
220	18	0.3275	3.57	0	0
240	18	0.4285	2.53	0	0

Table 2

For a flow rate of 0.03 ml/min and a frequency of =2.0Hz, using a normal Na-X zeolite

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	17.7	0.15	1.1	0	0
160	18.1	0.19	0.8	0	0
180	18.3	0.14	0.9	0	0
200	17.9	0.245	0.7	0	0
220	18.3	0.28	1.9	0	0
240	18.2	0.34	2.1	0	0

Table 3

For a flow rate of 0.1 ml/min and a frequency of =1.4Hz, using a normal Na-X Zeolite

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	18.2	0.15	0.4	0	0
160	18.2	0.15	0.6	0	0
180	18.3	0.2	2.1	0	0
200	18	0.3	1.92	0	0
220	17.9	0.305	3	0	0
240	18.1	0.4	0.4	0	0

Table 4

For a flow rate of 0.1 ml/min and a frequency of =2.0Hz, using a normal Na-X Zeolite

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	17.9	0.24	2.1	0	0
160	18.1	0.185	1.3	0	0
180	18.4	0.185	1.5	0	0
200	18.1	0.18	1.4	0	0
220	18.2	0.205	1.9	0	0
240	18.1	0.19	2.3	0	0

The following tables are results gotten based on an acidic modified zeolite based on variations of parameters as (1) Temperature (2) Frequency (3) Flow rate

Table 5

For a flow rate of 0.03 ml/min and a frequency of =1.4Hz, using modified Na-X zeolite (H-X Zeolite)

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	18.5	0.15	1.1	0	0
160	18	0.19	0.8	0	0
180	18.3	0.376	0.9	70.394	4.575
200	17.7	0.468	0.7	70.023	5.487
220	18	0.51	1	74.936	6.3
240	18	0.4	2	37.007	1.8

Table 6

For a flow rate of 0.03 ml/min and a frequency of =2.0Hz, using modified Na-X zeolite (H-X Zeolite)

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	18.6	0.15	1.1	0	0
160	18.3	0.19	0.8	0	0
180	18.1	0.41	1	68.667	4.7
200	17.56	0.594	1.12	73.016	6.84
220	18.2	0.645	1.3	78.101	8.19
240	18.1	0.45	3	18.327	0.9

Table 7

For a flow rate of 0.1 ml/min and a frequency of =1.4Hz, using modified Na-X zeolite (H-X Zeolite)

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	18.3	0.2	1.5	0	0
160	18.1	0.185	1.4	0	0
180	18.3	0.335	1	64.01	3.6
200	17.9	0.425	2.5	51.682	3.97
220	18.1	0.47	2.1	59.859	4.7
240	18.25	0.35	3	23.387	1.2

Table 8

For a flow rate of 0.1 ml/min and a frequency of =2.0Hz, using modified Na-X zeolite (H-X Zeolite)

T, °C	Liquid product(ml)	% Conversion IPA	Volume of H ₂ O (ml)	% Mass Selectivity DIPE	Volume of DIPE(ml)
140	18.3	0.145	0.9	0	0
160	18.2	0.185	0.7	0	0
180	18.1	0.385	1.2	60.559	3.6
200	18.4	0.5435	1.13	73.922	5.82
220	18.2	0.5875	2.1	68.521	6.74
240	18.3	0.5	4	10.9	0.6

These results show that synthesizing DIPE via aerosol nanocatalysis is possible, but there is also a re-emphasis on the importance of the role acidity plays in the production of DIPE, as it was seen based on the results, that DIPE could not be synthesized, if there is no high acidity, and also that pressure is not as important as the operating parameters that exist under the technology of aerosol nanocatalysis.

nanocatalysis is achievable based on the following four factors:

- The residence time of the reactant in the reactor
- High frequency of vibration of the reactor
- High acidic content of the catalyst
- Temperature

These four factors go in tandem; to achieve high DIPE selectivity. The residence time (flow rate) showed that, a decrease in flow rate of the reactants into the reactor, enabled the reactants to effectively interact with the catalyst, which resulted in the reactant having equal access to the sintered nanocatalyst. It was also observed that under the technology of aerosol nanocatalysis, the longer the residence time of the reactant in the vibrating reactor, the greater the synthesis of DIPE. The high catalytic activity is due to the result of the high pulses of energy that is introduced via the vibrating reactor, which leads to the formation of freshly formed electric charge on the surface of the catalyst. It is worth noting, that the destruction of reagents takes place on the surface of the catalytically charged catalyst. Under optimal conditions, defects are formed on the surface of the catalyst and the electronic properties of the surface change, which leads to an increase in the catalytic activity of the substances. In addition the catalytic system is a combination of a

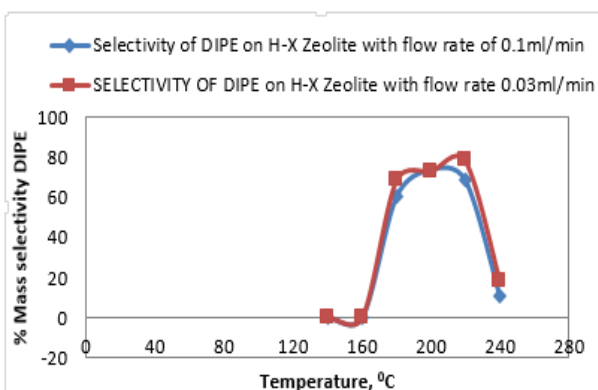


Fig. 2. Comparing the % mass DIPE selectivity of modified Na-X zeolite(H-X Zeolite) catalysts, using the same frequency of vibration=2.0Hz, but with different flow rates

Based on the following experiments, it was evidenced that synthesizing DIPE via aerosol

moving inert heat-resistant solid material and an aerosol of a catalytically active substance (without a carrier) in the reactor. The moving inert material carries out in-situ grinding of the initial catalytically active material, thereby ensuring mechanochemical synthesis of catalyst nanoparticles and constant activation of their surface, which in turn increases activity of the catalyst [7].

In other words, it can be said, that a high vibration frequency ensures a highly active catalytic system, which is believed to be associated with crystal lattice distortions, rather than with an increase in surface area [14]. Furthermore, a high frequency of vibration enabled the system always maintained its liquid phase, which is an important criterion in the synthesis of DIPE.

It was also noted that a synthesis of DIPE, has a favorable temperature range, because the selectivity of zeolite catalyst to DIPE ether, appears to have an optimum temperature [15], and it was noted using the modified Na-X zeolite (H-X Zeolite); that the optimum temperature to obtain DIPE was 220°C after which, the catalyst became more selective to propylene.

Conclusions

The conditions of aerosol nanocatalysis technology using a vibrating fluidized bed does not depend on an external pressure source, has been shown to be an effective option to synthesize DIPE, because the intensive mixing induced by the vibrating bed can create conditions for almost complete isothermocity, which is important for catalysis, also the effect of constant vibration ensures the reaction takes place in a liquid phase, which is essential for DIPE synthesis, but all these depends on the catalyst possessing sufficient amount of bronsted acid sites.

References

- G. Martini, U. Manfredi, JRC scientific and policy reports- Effect of oxygenates in gasoline on fuel consumption and emissions in 3 euro 4 passenger cars-2013
- Лавриненко Алексей Александрович "Получение диизопропилового эфира путем каталитической конденсации изопропанола на гетерополисоєдинєннях" *Москвой-2011*.
- Qiu, L., Murashov, V., White, M.A.: Zeolite 4A: heat capacity and thermodynamic properties. *Solid State Sci.* 2, 841–846 (2000)
- Tanaka, H., Fujii, A., Fujimoto, S., Tanaka, Y.: Microwave-assisted two-step process for the synthesis of a single-phase Na-A zeolite from coal fly ash. *Adv. Powder Technol.* 19, 83–94 (2008)
- Tanaka, H., Fujii, A.: Effect of stirring on the dissolution of coal fly ash and synthesis of pure-form Na-A and -X zeolites by two-step process. *Adv. Powder Technol.* 20, 473–479 (2009)
- M. A. Aramendia, V. Borau, C. Jiménez, J. M. Marinas, A. Porras, F. J. Urbano. Magnesium Oxides as Basic Catalysts for Organic Processes: Study of the Dehydrogenation–Dehydration of 2-Propanol. *J. Catal.* 161(1996) 829–838.
- Симіонеску К., Опрєа Кл. В. Механохімічний синтез // *Успєхи хімії*. – 1988, Т. VII. – Вип. 3. – С. 502–523.
- В.В. Молчанов, Р.А. Буянов. Механохімія каталізаторов // *Успєхи хімії*. – 2000, №69(5). – С.476–493
- Е.Г. Аввакумов. Механічні методи активації хімічних процесов: Новосібірськ, 1986. – 300 с.
- Kapustin V.M The oil refining industry of the USA and the former USSR / V.M Kapustin, SG Kukes, RG Bertolusini - Moscow "Chemistry", 1995. – 304 p [32] Patent No. 792682, 1958 (United Kingdom).
- Kashcheev A.S Catalytic cracking of a vacuum gasoil on the zeolite-containing catalyst (type Y) using technology of aerosol nanocatalysis / A.S Kashcheev, I.M Glikina, S.A Kudryavtsev, S.V Leonenko // IV International Conference of Students and Young Scientists Chemistry and Chemical Technology April 4-6, 2012. Collection of abstracts. Kyiv: The Ministry of Education, Youth and Sports of Ukraine National Technical University of Ukraine "Kyiv Polytechnic Institute" Chemical Engineering Department. - 2012. - p. 96.
- Крекінга мікросферическіє [відеозапись]/ KNT группа – http://kntgroup.ru/65/video_katalizatory_krekinga_mikrosfericheskie.
- S.A. Kudryavtsev. The process of hydrocarbon cracking to gasoline and olefins by aerosol nanocatalysis technology / S.A. Kudryavtsev, M.A. Glikin, I.M. Glikina // VIII Ukrainian-Polish Symposium «Theoretical and experimental studies of interfacial phenomena and their technological applications». – Odessa – 2004
- E80694518A2- Production of Isopropyl alcohol and Diisopropyl ether, Knifton John Frederick et al. 05/1996.
- Glikin M.A. Aerosolnij kataliz // *Teoreticheskie osnovy khimicheskoy tekhnologii* – 1996. Т. 30, № 4, P. 430–435.
- Glikina I.M. Osnovy tekhnologii aerosolnoji nanokatalitichnoji pererobky organichnykh spolkov u vibrozshizhenomu shari. // *Avtoreferat disertacii na zdobuttja naukovoogo stupenya kandidata technichnykh nauk*, Lviv. 2005. 20 p.
- Glikin M.A. Aerosolnyj nanokataliz. Izuchenije processa krekinga n-pentana do olefinov / Glikin M.A., Kudryavtsev S.A., Glikina I.M., Mamedov B.B. // *Khimichna promislovisť Ukrainy*. -2005. - №4. – P. 30–38.

Філіппс Т., Кудрявцев С.О., Глікїна І.М., Король Д.Р. Синтез діізопрілового етеру каталітичною дегідратацією ізопрілового спирту по технології аерозольного нанокаталізу

Анотація: В даній статті проведено порівняльний огляд можливостей технології аерозольного нанокаталізу в віброзрідженому шарі каталітичної системи та запропоновано застосування цієї технології в галузі синтезу кисневмісних сполук. Досліджувався процес дегідратації ізопрілового спирту із утворенням в якості основного продукту діізопрілового етеру. Проведено пошук оптимальних умов для активації каталізатора, в якості якого запропоновано застосувати натрієвий цеоліт, промотований нітратом амонію. Обробка цеоліту дозволила підвищити концентрацію Бренстедовських активних центрів та збільшила кислотність каталізатора. В якості змінних параметрів, що впливають на хімічну реакцію, варіювались температура та витрата сировини, а також специфічний для аерозольного нанокаталізу параметр – частота механохімічної активації каталізатору. Дослідження показали перспективність подальших досліджень в цьому напрямку.

Ключові слова: аерозольний нанокатализ, віброзріджений шар, діізопропиловий етер, Бренстедовські кислотні центри, цеолит NaX, механохімічна активація, частота.

Філліпс Т., Кудрявцев С.А., Гликіна І.М., Король Д.Р. Синтез диізопропилового ефіра каталитической дегидратацией изопропилового спирту по технологии аерозольного нанокатализа

В статье описан новый метод для получения диізопропилового ефіра с применением технологии, известной как аерозольный нанокатализ в виброожигженном слое каталитической системы. В процессе в качестве катализатора предложено применить цеолит NaX, промотированный нитратом аммония для увеличения кислотности и повышения содержания ОН групп. Это способствует увеличению числа Бренстедовских кислотных центров в цеолите. Для поиска оптимальных условий синтеза диізопропилового ефіра изменяли таких параметры, как температуру, расход сырья, и специфическую для аерозольного нанокатализа частоту механохимической активации катализатора. Оптимизации подвергалась химическая реакция дегидратации изопропилового спирта.

Ключевые слова: аерозольный нанокатализ, виброожигженный слой, диізопропиловый эфир,

Бренстедовые кислотные центры, цеолит NaX, механохимическая активация, частота.

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