

DUŠAN JOVANOVIĆ
BRANISLAV MARKOVIĆ
MIROSLAV STANKOVIĆ
LJILJANA ROŽIĆ
TATJANA NOVAKOVIĆ
ZORICA VUKOVIĆ
MIRJANA ANIĆ
SRDJAN PETROVIĆ

I.C.T.M., Department for
Catalysis and Chemical
Engineering, Belgrade

SCIENTIFIC PAPER

664.34+54-44:542.913+66.094.25

PARTIAL HYDROGENATION OF EDIBLE OILS—SYNTHESIS AND VERIFICATION OF THE NICKEL CATALYST

Developed in the late 1800s as a butter substitute, margarine is made with vegetable oils. Margarine was created by a scientist from Provence (France), Hippolyte Mege-Mouries, in response to an offer by the Emperor Louis Napoleon III. To formulate his entry, Mege-Mouries used margaric acid, a fatty acid component isolated in 1813 by Michael Chevreul and named because of the lustrous pearly drops that reminded him of the Greek word for pearl – margarites.

From this word, Mege-Mouries coined the name margarine for his invention that claimed the Emperor's prize. An American patent was granted in 1873 to Mege-Mouries who intended to expand his French margarine factory and production to the United States. While demand for margarine was strong in northern Europe ("Unilever" began manufacturing margarine in 1878) and the potential equally as promising in the U.S., Mege-Mouries's operations nevertheless failed and he died obscurely. In order for margarine to become solid, the oil must undergo a chemical transformation known as catalytic hydrogenation indicated as hydrogenated oils or partially hydrogenated oils.

During hydrogenation, extra hydrogen atoms are pumped into unsaturated fat, a process that creates trans fatty acids and converts the mixture into a saturated fat, thereby obliterating any benefits it had as a polyunsaturate. The catalytic hydrogenation of vegetable oils was introduced into the U.S. in 1910 and the "Crisco Company" went on sale in 1911. Just as the earlier cottonseed/tallow blends had been intended as replacement competition to lard, this new vegetable shortening was also marketed as a replacement for lard. In the 1930s, published texts on nutrition and dietetics included corn oil and peanut oil in lists of vegetable oils, and also referred to the commercial hydrogenation of cottonseed oil and its sale in the form of a solid fat. Until shortly before World War II, margarine were largely made of coconut oil, animal tallow, or lard – very little hydrogenation was required or used. Prior to World War II and depending on where one lived in Europe, much of the added fat or oil in food, other than animal, poultry, and dairy fats, came from small presses such as these used for flaxseed oil in Eastern Europe, the larger presses used for olive oil in the Mediterranean area, or

from hydrogenation plants in countries such as Holland or Denmark. As these hydrogenation plants were closed down during the war, the native populace consumed whatever animal and dairy fats were available. Beginning in the 1950s, the food industry capitalized on its ability to turn liquid oils, which were plentiful, but not sufficiently marketable, into solid fats for the budding fast food industry and for the expanding baking and snack food industry.

Animal tallow, fats and edible oils hydrogenation is a very important operation in the industrial process of producing vegetable tallow, vegetable fats, margarines and starting components for the cosmetic and chemical industry (emulgators, soaps, creams, pastes, etc.). The catalyst used in the industrial hydrogenation process is a nickel catalyst deposited on a silicate natural support (diatomite) or on a silicate support obtained from water glass [1–11]. The importance of obtaining a highly-active nickel hydrogenation catalyst is demonstrated by the fact that, even as early as 1976, a *Group for Catalysis* had been established at the European level, with the aim of standardizing the production of several exceptionally important strategic catalysts [12,13] within the EEC. One of those exceptionally important catalysts is EuroNi-1 catalyst, a Ni/SiO₂ hydrogenation catalyst with a nickel content of 25 wt %.

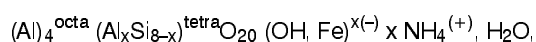
The goal of this study was to choose and activating a support using domestic ram materials and synthesize a nickel hydrogenation catalyst. The synthesis of a complex catalyst, such as this one, involves several phases: the preparation and activation of a suitable support; the synthesis of a catalysts precursor; reduction of the precursors, passivation and impregnation of the catalyst.

PREPARATION AND ACTIVATION OF A SUITABLE SUPPORT

Catalyst supports are very significant components of a catalyst. In addition to a series of other functions, supports contribute to a larger catalytic surface and,

Author address: D. Jovanović, Department for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Yugoslavia
E-mail: dusanmj@helix.chem.bg.ac.yu
Paper received: November 10, 2001
Paper accepted: March 5, 2002

therefore, to faster development of the target reaction, sometimes actively participating in it. There are numerous papers disclosing investigations of various materials that may be used as Ni-catalyst supports, some of which are just modifications of usual supports. So, for example, transition metals can not be directly inserted between graphite layers. It is, however, possible to insert the salts of such metals and after the reduction of these salts, to obtain a metal that is atomically dispersed between the graphite layers [14]. Some natural materials that may be used as catalyst supports, have also been studied. It is possible to use one type of silica [15] consisting of silica-aluminum-silica layers (21 layers) with a unit cell of the following composition:



where (x) is around 1.5.

In addition to the mentioned support of complex structure, other natural silica materials may be used as a catalyst support, for example sepiolite, palygorskite, bentonite and diatomite [9]. Sepiolite is a hydrated magnesium silicate of the phyllosilicates family within the group called sepiolite-palygorskite (or hormites) with channels in a network of dimensions 1.1 x 0.56 nm. It is a 2:1 type silicate the structural unit of which is formed by two tetrahedral sheets of silica and one octahedral sheet of magnesia. Palygorskite, is also formed by two tetrahedral layers of silica and one octahedral layer of magnesia (2:1) with channel dimensions of 0.9 x 0.53 nm. Bentonite is mainly formed by montmorillonite, a 2:1 phyllosilicate with an octahedral layer made of alumina. Diatomite is a biogenic rock the main constituent of which is amorphous silica as opale A.

Many other inorganic materials may also be used in obtaining a catalyst support: zeolites, titanium, magnesium and aluminum orthophosphates, as well as $AlPO_4 - Al_2O_3$ and $AlPO_4 - SiO_2$ systems [16]. Nickel catalysts on ion supports, NaF and CaF_2 [17] have also been synthesized by saturating a support with an aqueous solution of nickel nitrate which is, afterwards, exposed to UV light and treated with hydrogen. Several metal oxides (Cr_2O_3 , SiO_2 , ZrO_2 , CeO_2 , ZnO) have been used as supports for nickel catalysts [18-20].

Led by the main aim of this study, we chose a domestic raw material: diatomite from Baroševac, Kolubara Coal Basin [21-24], as a natural raw material for obtaining an adequate support for the synthesized Ni-catalyst. The crude and grounded diatomite was calcined and chemically treated in order to obtain an activated support vital for the synthesis of a Ni catalyst. Diatomite was subjected to a series of various mechanical and chemical processes and calcined at different temperatures, thus yielding supports of different characteristics [25-29].

Crude diatomite from Baroševac (the Kolubara Coal Basin - field B) with the following physico-chemical properties, was chosen: color (crude)

- grayish-brown; color (calcined at 800°C) from light yellowish to light pink; density (in block) - cca 1100 kg/m³; bulk mass - cca 700 kg/m³; granulation - 0-500 mm and humidity level (crude) - 45%-65%. The average chemical composition (dry substance, 105°C) is presented the Table 1.

Table 1. The average chemical composition of crude diatomite

Component	Mass Content (%)
SiO ₂	65.0 - 80.0
Al ₂ O ₃	4.5 - 12.5
Fe ₂ O ₃	0.5 - 2.5
CaO	0.5 - 4.0
MgO	0.2 - 2.5
S	0.05 - 0.5
Na ₂ O	tr. - 0.2
K ₂ O	0.1 - 0.8
FeO	0.05 - 1.3
TiO ₂	0.02 - 0.9
P ₂ O ₅	tr. - 0.05
MnO	tr. - 0.02
CO ₂	0.6 - 2.9
H ₂ O ⁺	0.01 - 7.2
H ₂ O ⁻	5.7 - 36.3
Loss by calcination at 1000°C	10.0 - 25.0

Chemical treatment was performed with hydrochloric acid and a conventional lab ceramic spherical grinder was used for grinding and a conventional lab furnace for calcination. The sample specific surfaces were measured by the B.E.T. method, while the real densities were measured with benzene by pycnometry. The granulometric composition of the samples was determined by a combined method ("pipette" with decantation method), while the DT and TG analysis were performed using a LINSEIS device (System 2000). The complete silicate analysis was done by a classical chemical procedure applicable in analyzing sediment rocks.

Crude diatomite is not suitable for direct mechanical treatment (grinding) due to its relatively high humidity level. A dry diatomite suitable for grinding was obtained by drying the smaller diatomite fractions (0-50mm) at 130°C under circulating air for 10 hours and after that it was ground in a ceramic laboratory grinder for 3 hours per charge. In order to determine the temperature of thermal treatment of the crude diatomite, DT/TG analysis was performed so the optimal temperature for the combustion of the organic substances and admixtures (Figure 1) could be defined.

Figure 1 shows that the exothermic process of carbon and organic impurities combustion starts at

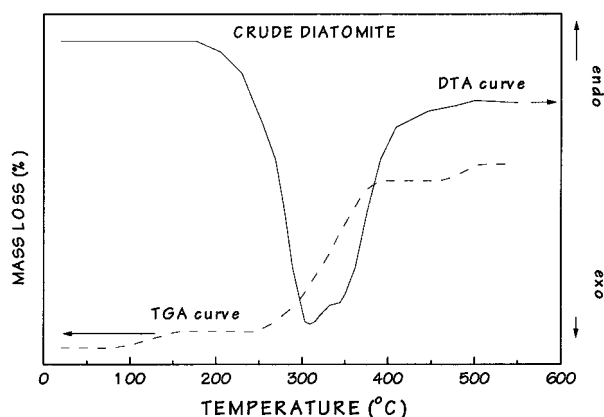


Figure 1. DT and TG curves of crude diatomite

about 180°C and ends at about 480°C. The diatomite sample was calcined at 800°C. The sample calcined at 300°C was gray, this color indicating the presence of non-calcined organic impurities. With increasing calcination temperature, the color of the calcined samples changed from light-gray to a shade of off-white-pink. The sample calcined at 600°C was a shade of pale-white-pink that remained the same even after treatment at 800°C. This result showed that the complete combustion of the present organic impurities had not occurred before a 600°C was reached. That is why the diatomite sample was calcined at 800°C during the of the support.

A 5% aqueous solution of HCl was added to the weighed quantity of diatomite. The mixture was heated to boiling with intensive stirring for 2 hours. A vessel containing the mixture was left to precipitate and the liquid was separated by decanting. After multiple rinsing with distilled water, the precipitate was filtered using a vacuum filter and then dried for at least 6 hours in a dryer at 150°C. The diatomite treated in this way was thermally treated at 800°C. The sample thermally treated at 800°C was white with a faintly visible shade of pale-pink due to the Fe₂O₃ residue with the following chemical composition: SiO₂ – 93.6%; Al₂O₃ – 4.3%; Fe₂O₃ – 0.6%; MgO – 0.7%; CaO – trace; Na₂O – 0.05% and K₂O – 0.6%, and with a real density of 1.92 g/cm³ and with a specific surface of 19.5 m²/g.

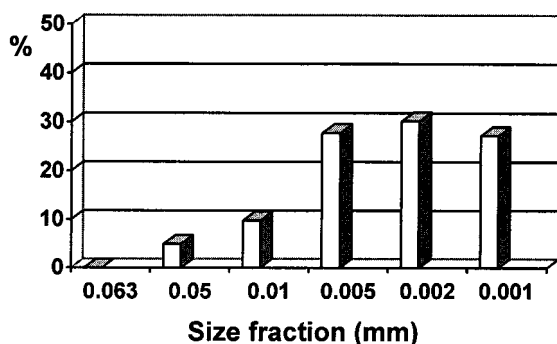


Figure 2. Histogram of the fractions distribution

Keeping in mind that the catalyst must also have a satisfactory filtering ability, granulometric analysis of the domestic activated diatomite support was performed – the obtained result is shown in Figure 2.

In diatomite, chemically treated and calcined at 800°C, there is almost the same percentage of particle fractions of 0.005 mm, 0.002 mm and 0.001 mm in size (about 30% each), while there is a considerably smaller percentage of the larger particle fractions (of 0.010 and 0.050 mm). Considering that the practical application of a hydrogenation catalyst means that one of the crucial catalyst properties must be its good filterability, the distribution of particle sizes of the activated diatomite support was found to be quite satisfactory.

SYNTHESIS OF THE PRECURSOR OF THE SUPPORTED NICKEL CATALYST AND EVALUATION OF THE PRECURSOR REDUCTION

A new nickel catalyst supported on a natural silicate – diatomite, for the selective hydrogenation of edible vegetable oils and fats (sunflower seed oil and soybean oil), was prepared by the precipitation method [30–37]. The choice and chemical preparation of the nickel catalyst support, the process of depositing nickel and a promoter on the support, as well as the process of activating them, are all of vital importance for obtaining a highly active hydrogenation catalyst. For the catalyst synthesis, nickel was chosen in the form of Ni(NO₃)₂ · 6H₂O with magnesium, serving as a promoter in the molar ratio Mg/Ni = 0.1. The alkaline precipitation agent was Na₂CO₃ in a concentration optimal for precipitation. Precipitation of the nickel ion and the promoter ion (Mg) by an alkaline agent, was performed at elevated temperature at strictly defined pH values. A support – an activated domestic diatomite was added to the reaction mixture in the form of an aqueous suspension of a concentration satisfying the molar ratios of SiO₂/Ni from 0.2 to 1.15. After drying, the homogenous mass was milled and ground for further homogenization. A dry and weighed amount of the finely powdered catalyst precursors were analyzed by thermogravimetry (LINSEIS System 2000) in hydrogen. The samples were heated at the following rates: 2°C/min; 5°C/min; 10°C/min and 20°C/min.

During the process of reducing all the samples, it was noticed that the fraction of decomposed solid (F) increased with nickel composition increase in the precursor mass (Figure 3) depending on the sample heating rate within a TG system. It was also noticed that the value of F is practically constant for each molar fraction of SiO₂/Ni, regardless of the change in heating rate during the reduction process.

The noted reactive effects occurring during the synthesis of the precursors were interpreted by IR spectroscopy. According to the IR data (Figure 4), the Ni/Mg-base carbonate is solely in the form of a carbonate complex of a unidentate, bidentate and a bypassed structure.

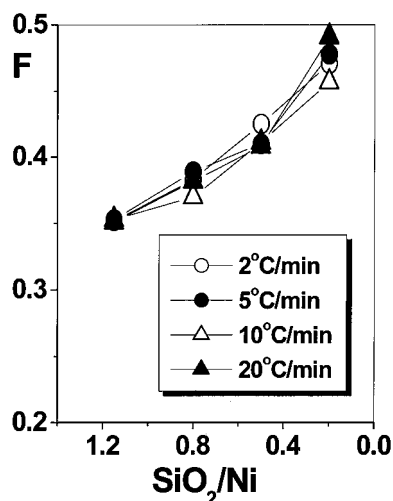
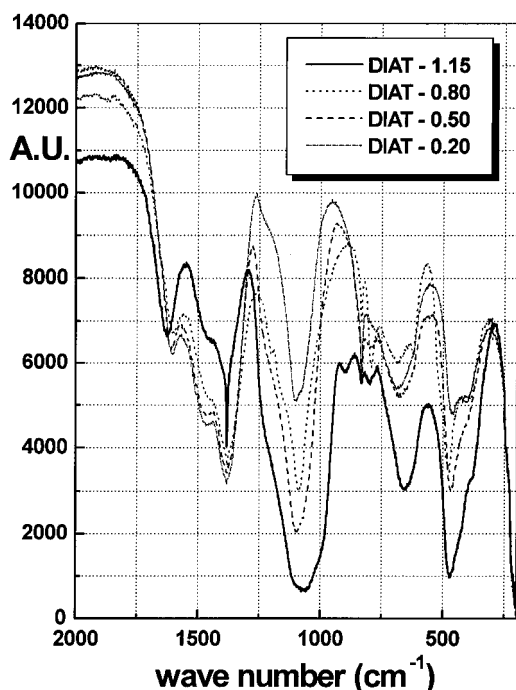
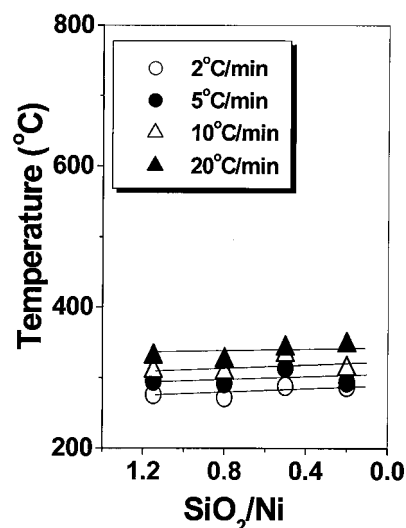
Figure 3. Fraction F vs. SiO_2/Ni 

Figure 4. IR Spectra of the synthesized catalyst precursors

In order to analyze the differences in the final reduction temperature, Figure 5 shows changes in the final reduction temperatures as a function of the molar fraction of SiO_2/Ni for all four heating rates. Figure 5 clearly shows that, in case the support is in diatomite form, there is no relevant change in the final temperature of the reduction process due to change in the molar fraction of SiO_2/Ni . A difference is noticed only due to the heating rate; so samples with the lowest heating rate have the lowest final temperature of the reduction process.

The use of thermogravimetric data to evaluate the kinetic parameters of solid-state reactions involving weight loss has been investigated by a number of researchers [38–41]. In the reaction $m \cdot M \rightarrow q \cdot Q + p \cdot P$,

Figure 5. Reduction end-point temperature vs. SiO_2/Ni

the rate of disappearance of M may be expressed by: $dF/dt = k(1 - F)^n$, where F is the fraction of M decomposed at time t , n is the order of the reaction, and k is the rate constant given by the expression: $k = Ae^{-E/RT}$; where A is the frequency factor and E is the activation energy of the reaction. For a linear heating rate of $v^\circ\text{C}/\text{min}$ ($v = dT/dt$), by combining the mentioned equations and for all the values of n except $n = 1$, after taking logs, the final equation becomes:

$$\log_{10} \left[-\log_{10} \frac{(1-F)}{T^2} \right] = \log_{10} \frac{A \cdot R}{F \cdot E} \left[1 - \frac{2 \cdot R \cdot T}{E} \right] - \frac{E}{2.303 \cdot R \cdot T} \quad (1)$$

Thus a plot of either $\log_{10} \left[\frac{1-(1-F)^{1-n}}{T^2(1-n)} \right]$ against $1/T$ or, when $n = 1$, $\log_{10} \left[\frac{-\log_{10} (1-F)}{T^2} \right]$ against $1/T$, should result in a straight line of the slope $-E/2.303 R$ for the correct value of n . Since there is theoretical justification for the orders of reaction of 0, 1/2, 2/3 and 1 in solid-state kinetics, it is possible to substitute these values into equation (1) to obtain the appropriate plots (Figure 6).

During the process of reduction it was noticed that the fraction of decomposed solid (F) increase with nickel composition increase in the precursor mass depending on the sample heating rate within a TG system. It was noticed that the value of F is practically constant for each molar fraction of SiO_2/Ni , regardless of the change in heating rate during the reduction process (Figures 3 and 5). From Figure 6 it may be seen that the activation energy of precursor reduction increases with decreasing heating rate (Figure 7) for a constant molar ratio of SiO_2/Ni . Also, it may be seen that the reduction process is complex and consists of two parts.

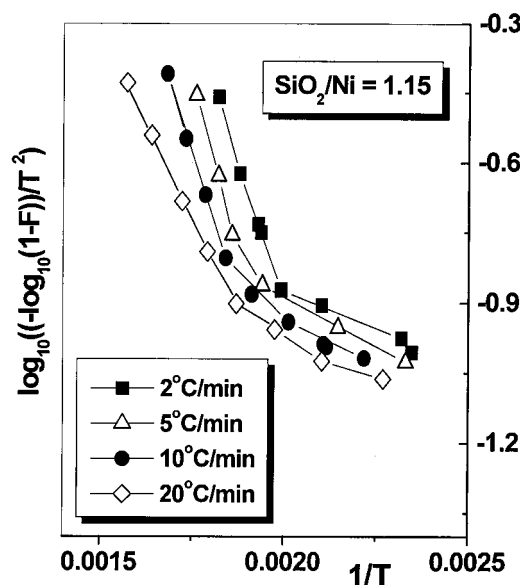


Figure 6. Arrhenius plots of the solid decomposed fractions (F) of the precursor SiO_2/Ni

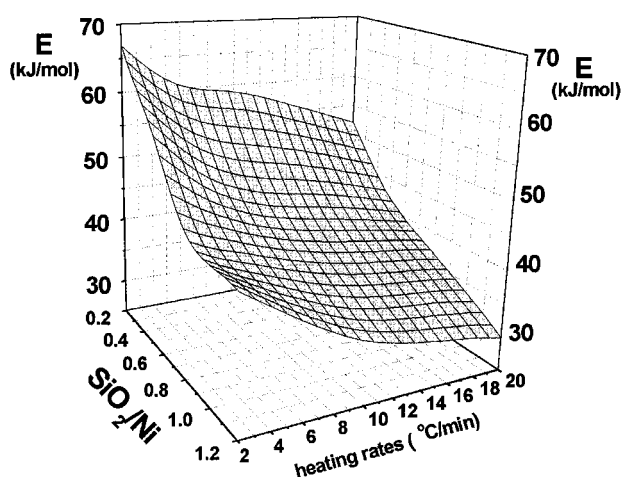


Figure 7. Activation energy (E) - SiO_2/Ni - heating rate diagram of the catalyst precursors

The reduction of Ni/Mg-base carbonate begins in the region of $1/T$ less than 0.002 ($n = 1$; equation (1)). This is indicative of the fact that the reduction is easier due to the lower heating rates and higher molar SiO_2/Ni ratio (Figure 7). According to the experimental results on the synthesized Ni-catalysts, the optimal experimental combination for a highly active hydrogenation catalyst is a molar SiO_2/Ni ratio of 1.15 and a heating rate of $2^\circ\text{C}/\text{min}$.

Based on the experimentally obtained results, it may be concluded that the reducibility of the Ni-hydrogenation catalyst precursor is greatly dependent on the molar SiO_2/Ni ratio and the heating rate. The obtained results demonstrate that the diatomite-based precursor with a molar SiO_2/Ni ratio equal to 1.15 is reduced at a considerably lower temperature ($\Delta T \approx 50^\circ\text{C}$) at a heating rate of $2^\circ\text{C}/\text{min}$,

than the precursors with the same molar SiO_2/Ni ratio, but at higher heating rates. The lower molar SiO_2/Ni ratio indicates a higher Ni concentration in the reaction and a higher concentration of Ni/Mg-base carbonate, which is the consequence of specific interactions occurring during the synthesis between the active components in the reaction system.

REDUCTION OF THE PRECURSOR AND PASSIVATION

Reduction of the precursor represents one of the most important operations in the course of synthesizing a catalyst. Depending on the quantity of initial precursor, the construction of the reactor, the heating rate during reduction, the hydrogen flow, the final reduction temperature, the duration of reduction and reduced mixture cooling, different catalytic activity are obtained. The reduction parameters were chosen in a manner appropriate for obtaining a catalyst with high hydrogenation activity. The catalyst precursor reduction parameters in a self-designed quartz reactor [25] were the following: reduction gas - H_2/N_2 (1:1) mixture; reduction gas flow: 10 lit/h; heating rate: $1.0^\circ\text{C}/\text{min}$; reduction temperature: 430°C ; reduction time: dependant on the precursor mass; and the cooling rate: equal to the heating rate. In order to reduce the exceptional pyrophority of the reduced nickel metal, it is necessary to partially passivate the nickel during the process, so that the handling of the reduced catalyst during its impregnation may be facilitated. Passivation was performed with a specially prepared mixture of 350 vpm O_2 in nitrogen at room temperature over a time necessary to reduce the catalyst pyrophority to a level desirable for preventing self-ignition of the reduced nickel.

Having achieved a satisfactory level of the catalyst passivity, impregnation of the active catalyst mass was initiated. Impregnation was performed with a highly hydrogenated fat (iodine value $I.V./ < 2.0$) inside a specially prepared container with intensive stirring at an elevated temperature. After completing the impregnation and pouring the mixture into molds and cooling the mixture, the final product - a nickel catalyst for fats and edible oils hydrogenation was obtained.

VERIFICATION OF THE SYNTHESIZED NICKEL CATALYST

Testing of the synthesized catalyst activity (the catalyst service name is: NICAT-2000) in the partial hydrogenation of edible oils (sunflower and soybean oils) was performed at an industrial level [42-55].

The industrial testing of the synthesized NICAT-2000 catalyst activity was performed in the Factory of Edible Oils and Fats, "VITAL" - Vrbas. Testing of the catalyst performance was conducted in a pilot plant and in an industrial reactor [the "scale-up" weight ratio was 1:1,000 - pilot plant sample (5 gr.) and

Table 2. Working conditions of the pilot and industrial reactor vessels in the process of oil hydrogenation

	pilot reactor	industrial reactor
type of reactor	D.D.VITAL	KRUPP-D404S
capacity [kg]	5.0	7,500
mass of the oil [kg]	5.0	5,000
H ₂ pressure (init.) [MPag]	0.08	0.05
H ₂ pressure (end) [MPag]	0.12	0.20
temperature (init.) [°C]	150	165
temperature (end) [°C]	167	195/200
catalyst [wt. %]	0.10	0.10
Ni [wt. %]	0.022	0.022
agitation [rpm]	720	400-405

industrial sample (5,000 gr.) under the conditions as presented in Table 2.

The soybean and sunflower oil used in the hydrogenation process had the following physico-chemical characteristics (Table 3).

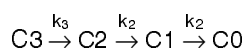
Table 3. Physico-chemical characteristics of soybean and sunflower oils

	soybean oil	sunflower oil
iodine value [g I ₂ /100g]	128	130
saponification value [mg KOH/g]	189	190
non-saponification residue [g/kg]	up to 15	up to 12
relative density [g/cm ³]	0.919 – 0.925	0.920 – 0.927
index of refraction [n _D ²⁰]	1.470 – 1.476	1.474 – 1.476
Fatty acid composition in mass %		
C16:0 – palmitic acid	10.12	6.51
C18:0 – stearic acid	4.13	3.92
C18:1 – oleic acid	21.15	21.26
C18:2 – linoleic acid	50.78	65.76
C18:3 – linolenic acid	7.23	0.18
C20:0 – arachidic acid	0.22	0.19

The iodine and saponification number values were determined by titration, the relative density measured with an aerometer at 20°C, while the refractive index at 20°C (and at 60°C) was determined with an Abbe refractometer. Only the last three figures of the refractive index following the values above 1.4, have been shown in the Figures 10 and 13. The gas-chromatography measurements of the fatty acid methyl esters in the examined oils and hydrogenated products were performed on a model HP5890, series Plus instrument (Hewlett Packard). The content of solid components (dilatometric number) at 20°C, 30°C and 35°C were

determined by the pulse-NMR method [56] on a BRUKER instrument; the hydrogenated product melting point was determined by the standard capillary method [57], while the total *trans*-fatty acids content in the hydrogenated product was measured by FTIR (Perkin Elmer, model 1725X) [58].

The soybean and sunflower oil hydrogenation process in a pilot plant and that of soybean oil in an industrial reactor, were monitored by taking and analyzing samples every 10 minutes from the pilot plant and after 30,40,75,85,95, 105 and 115 minutes from the industrial reactor, reaction. Although this hydrogenation reaction (soybean oil) includes a series of side (such as the geometrical and position isomerization reactions), the first approximation indicates that the basis of this mechanism is composed of a series of consecutive stages:



with C₃, C₂, C₁ and C₀ being the concentrations of linolenic, linoleic, oleic and stearic acids, and k₁, k₂ and k₃ being the corresponding rate constants. The rate constants k₁, k₂ and k₃ are, as previously emphasized, cumulative constants and, in the first approximation in order to apply a mathematical model, all the geometric and positional isomerization processes were neglected. The solution of a system of differential equations that determines the rate of the above process, may be explicitly expressed as a function of time (t) of all the system component concentrations:

$$C3 = A3 \cdot \exp(-k_3 \cdot t) \quad (2)$$

$$C2 = \left(A2 + A3 \frac{k_3}{k_3 - k_2} \right) \exp(-k_2 \cdot t) +$$

$$A3 \frac{k_3}{k_2 - k_3} \exp(-k_3 \cdot t) \quad (3)$$

$$C1 = \left[A1 + A2 \cdot \frac{k_2}{k_2 - k_1} + A3 \cdot \frac{k_2 \cdot k_3}{(k_2 - k_1)(k_3 - k_1)} \right] \exp(-k_1 t) +$$

$$\frac{k_2}{k_1 - k_2} \left(A2 + A3 \frac{k_3}{k_3 - k_2} \right) \exp(-k_2 t) +$$

$$A3 \frac{k_2 \cdot k_3}{(k_1 - k_3)(k_2 - k_3)} \exp(-k_3 t) \quad (4)$$

$$C0 = C3^{t=0} + C2^{t=0} + C1^{t=0} + C0^{t=0} - C3 - C2 - C1 \quad (5)$$

The relation (5) actually represents the law of mass preservation within this model. Since, based on relation (5), the system components are not all linearly independent, it is sufficient to find the equations (2-4) by integrating, with the fourth component being a linear combination of the first three. The chemical selectivity toward linolenic acid (C18:3) is designated as SLn and it represents the relation k₃/k₂, while the selectivity toward linoleic acid (C18:2) is designated as Slo, i.e. Slo = k₂/k₁. The rate constants were determined by a numeric minimization (Neadler-Mead method) of the square of

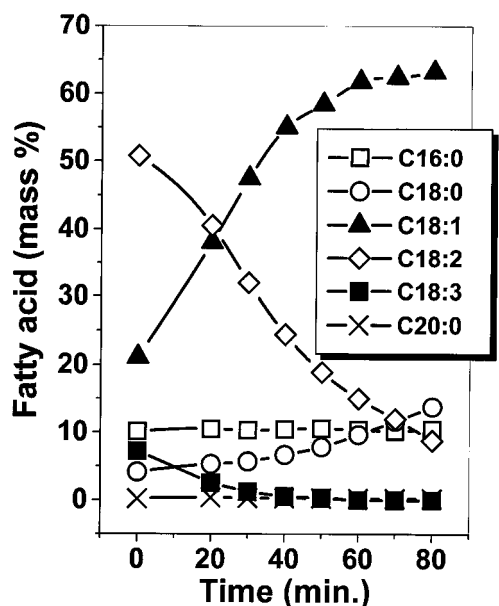


Figure 8. Fatty acids (FA) concentration vs. hydrogenation time (soybean oil)

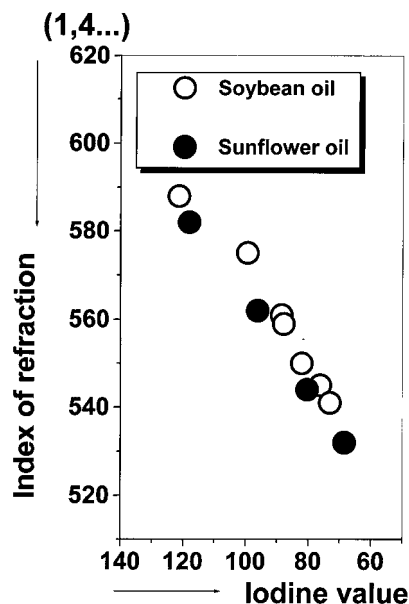


Figure 10. Index of refraction vs. iodine value

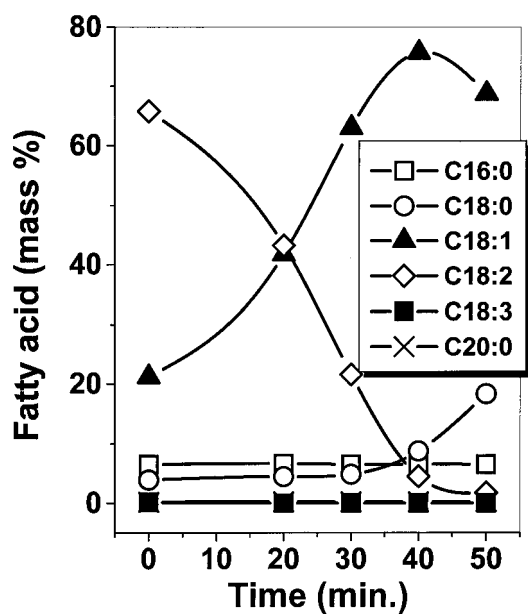


Figure 9. Fatty acids (FA) concentration vs. hydrogenation time (sunflower oil)

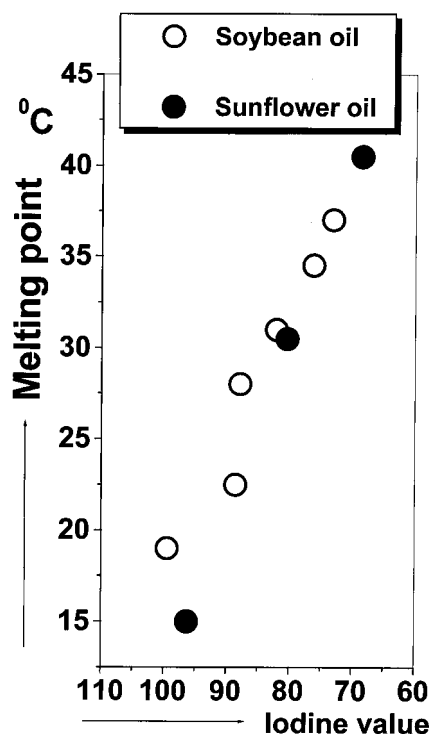


Figure 11. Melting point vs. iodine value

the deviation of the corresponding functions from the experimental values in three ways: by subsequent fitting.

The results of the fatty acids content changes as a function of time during soybean and sunflower oil hydrogenation in the pilot plant are presented in Figures 8 and 9; changes in the refraction index as a function of the iodine value change are given in Figure 10, while the changes in the melting point values as a function of the iodine number are presented in Figure 11 for both oil types. The final dilatation values for soybean and sunflower oils are: 37.04 (20°C), 16.25 (30°C) and 7.56

(35°C), i.e. 57.61 (20°C), 29.76 (30°C) and 15.50 (35°C), respectively.

Figures 8 and 9 clearly demonstrate that the hydrogenation process is moving in the targeted direction with the catalyst demonstrating good activity and selectivity (for soybean oil: SLn = 2.5; SLo = 59.4; for sunflower oil: SLn = 2.4; SLo = 67.1) in regard to mono- and poly-unsaturated fatty acids hydrogenation. In both experiments (Figure 10), a change in the

refractive index (n_D^{60}), i.e., its decrease with hydrogenation time, and a decrease in the hydrogenated product iodine value, were recorded.

Analogously, with the change in refractive index, an increase in the product melting point accompanied by a decline in the iodine number (Figure 11) takes place due to the hydrogenated product's change in fatty acids composition (which is also the consequence of the geometric and positional isometric occurrence in the C18:2, and even more in the C18:1 fatty acid [59]); the mono-unsaturated oleic fatty acid (C18:1) is dominant in both the *cis*- and *trans*-forms (55 *cis*- : 45 *trans*- at the end-point for both oil types) and in the stearic fatty acid (C18:0).

Applying the results obtained in the pilot plant, soybean oil hydrogenation (95% of the production of margarine in Yugoslavia originety from a partially hydrogenated soybean oil) was performed in an industrial reactor (KRUPP Co., type D404S) of an operating capacity of 5,000 kg, at the hydrator plant of the Factory of Edible Oils and Fats "VITAL" – Vrbas (the hydrogenation parameters given in Table 2). The results obtained are presented in Table 4, and the fatty acids composition changes (C18:3, C18:2, C18:1, C18:0) and the total *trans*- fatty acid content changes related to the iodine value are given in Figure 12.

Table 4. *Industrijal reactor vessel results (soybean oil)*

time of reaction. [min]	30	40	60	75	85	95	105	115
H ₂ pressure [MPag]	0.05	0.05	0.08	0.09	0.09	0.10	0.14	0.20
reaction temp. [°C]	190	195	195	195	195	195	190	195
iodine value [gJ ₂ /100g]	115.9	112.5	101.0	96.7	91.8	87.4	81.8	76.5
% solids [at 20°C]	0.54	1.19	2.97	5.16	8.57	15.41	23.84	36.25
% solids [at 30°C]	0.19	0.35	0.22	0.57	0.68	1.77	4.98	10.90
% solids [at 35°C]	0.36	0.27	0.18	0.07	0.36	0.15	0.64	3.59

The refractive index (n_D^{60}) and melting point changes – due to the iodine value change and the reaction duration are presented in Figures 13 and 14, while the selectivities are: SL_n = 2.7 and SL_o = 53.3.

CONCLUSION

The experimental results obtained at the pilot plant and industrial reactor level, have led to the following conclusions: the technology of activating diatomite with characteristics feasible for application in the synthesis of a nickel hydrogenation catalyst and the technology of

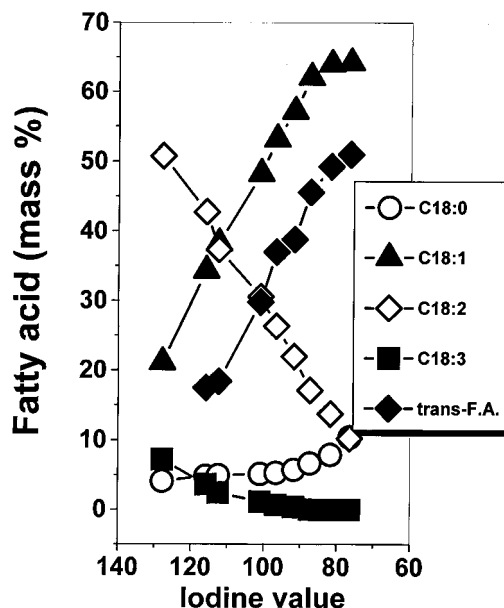


Figure 12. Fatty acids (FA) and total *trans*-FA concentration vs. iodine value for the soybean oil hydrogenation process (industrial reactor testing)

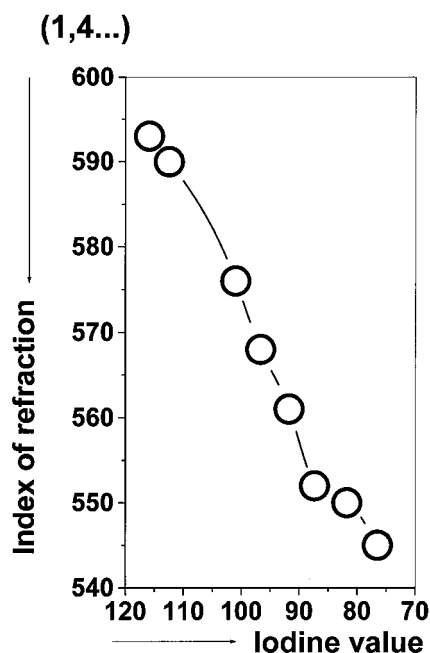


Figure 13. Index of refraction vs. iodine value for soybean oil hydrogenation process (industrial reactor testing)

the nickel hydrogenation catalyst synthesis, have been mastered. The performed synthesis of a "scale-up" catalyst has confirmed the high reproducibility of the synthesis methodology, as well as the good catalytic performances of the laboratory-level synthesized catalyst. The results obtained in the edible vegetable oils (soybean and sunflower oil) hydrogenation process, in a pilot plant and in an industrial 5-ton reactor, do indisputably demonstrate that the synthesized catalyst

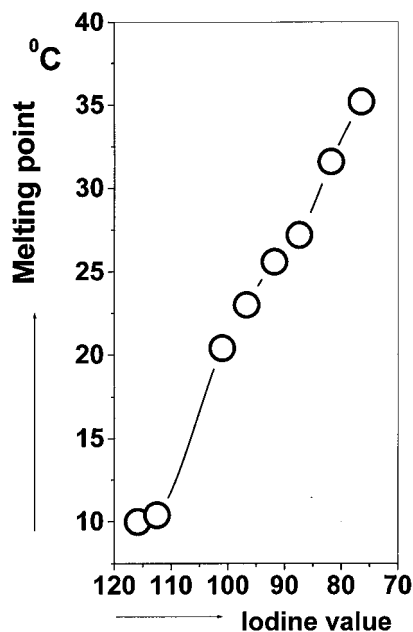


Figure 14. Melting point vs. iodine value for soybean oil hydrogenation (industrial reactor testing)

NICAT-2000 possesses all the properties of other modern catalysts of the same type. The parameters tested such as: the hydrogenation duration-related change of the fatty acids concentration; good selectivity of the catalyst; change in the refractive index and the hydrogenated mass melting point relative to the iodine value change; the change and content of total *trans*-fatty acids; dilatation changes; good filterability of the catalyst and a negative reaction to the residual nickel that may be present in the product after primary filtration, all indicate that the NICAT-2000 catalyst may be successfully applied in the food industry's vegetable oils hydrogenation processes.

For confirmation of all the above research results, the Factory of Edible Oils and Fats "VITAL" – Vrbas, has issued a certificate to the I.C.T.M. – Department for Catalysis and Chemical Engineering – Belgrade, verifying that the synthesized NICAT-2000 catalyst is successfully applicable in the industrial process of hydrogenating soybean oil, sunflower oil, palm oil and palm-kernels oil.

ACKNOWLEDGEMENTS

This work was supported by the Serbian Ministry of Science, Technologies and Development through the Project – Modification of Natural Silicates and Synthesis of New Hydrogenation Catalysts Supported on Natural Silicate materials (MHT.2.09.0022.B).

REFERENCES

- [1] C.L. Kibby, F.E. Massoth, H.E. Swift, *J. Catal.*, **42** (1976) 350
- [2] J.T. Richardson, R.J. Dubus, *J. Catal.*, **54** (1978) 207
- [3] G. Srinivasan, R.S. Murthy, K.M.V. Kumar, P.V. Kamat, *J. Chem. Tech. Biotechnol.*, **30** (1980) 217
- [4] G. Wendt, D. Hentschel, J. Finster, R. Schollner, *J. Chem. Soc., Faraday Trans. 1*, **79** (1983) 2013
- [5] Y. Nitta, T. Imanaka, S. Teranishi, *J. Catal.*, **96** (1985) 429
- [6] J.I. Ishiyama, Y. Kurokawa, T. Nakayama, S. Imaizumi, *Appl. Cat.*, **40** (1988) 139
- [7] S.M. Echeverria, *Appl. Cat.*, **66** (1990) 73
- [8] M.T. Rodrigo, S. Mendioroz, *J. Am. Oil. Chem. Soc.*, **69** (1992) 802
- [9] M.T. Rodrigo, L. Daza, S. Mendioroz, *Appl. Cat. A: General*, **88** (1992) 101
- [10] J.F. Ferreras, C. Pesquera, F. Gonzalez, I. Benito, C. Blanco, J. Renedo, *React. Kinet. Catal. Lett.*, **53** (1994) 1
- [11] Y. Kitayama, M. Muraoka, M. Takahashi, T. Kodama, H. Itoh, E. Takahashi, M. Okamura, *J. Am. Oil. Chem. Soc.*, **73** (1996) 1311
- [12] J.W.E. Coenen, *Appl. Cat.*, **54** (1989) 59
- [13] J.W.E. Coenen, *Appl. Catal.*, **54** (1989) 65
- [14] J.M. Lalancette, *U.S. Pat.*, 3, 847, 983 (1974)
- [15] W.T. Granquist, *U.S. Pat.*, 3, 847, 983 (1974)
- [16] K.G. Jome, P.N. Kuznetsov, D.M. Anufriev and V.N. Romanov, *Acta Phys. Chem. (Szeged)*, **24** (1978) 153
- [17] Yu. S. Mardashev and N.P. Karzhvina, *Zhur. Fiz. Kim.*, **51** (1977) 2631
- [18] D.V. Sokolski, T.M. Omarkulov, U. Suyunbaev, M.A. Abishev, V.A. Shoshenkova, V.M. Meekeev and K.Kh. Nurgozhaev, *Zh. Fiz. Khim.*, **56** (1982) 1773, *Russ. J.Phys. Chem.*, **56** (1982) 1075
- [19] V.T. Coon, T. Takeshita, W.E. Wallace and R.S. Craig, *J. Phys. Chem.*, **80** (1976) 1878
- [20] R. Kudlacek and J. Cabicar, *Collect. Czech. Chem. Commun.*, **43** (1978) 1818
- [21] Obradović, J. Hein, J. Đorđević: "Dijatomejska zemlja: Sastav i dijageneza", Kolubara Coal Basin, Serbia, Faculty of Mining and Geology and the US Geological Survey, California, 1992
- [22] V. Knežević, *Rudarstvo, geologija i metalurgija*, **19** (1968) 1509
- [23] V. Knežević: "Dijatomit (Diatomite)", *Proceed. of the 3rd Symp. on the Nonmetallic Miner. Deposits*, 229-237, Bled, 1983
- [24] V. Knežević, D. Randić, V. Grujičić, R. Radovanović: "Dijatomiti kolubarskog ugljenog basena i mogućnost njihove valorizacije kao nemetalne mineralne sirovine", *Geological Research in the Economy and Space Development of Belgrade*, Association of Engineers and Technicians of Belgrade, 313, Belgrade, 1984
- [25] D. Jovanović, A. Žujić, M. Stanković, N. Jovanović, B. Marković, T. Novaković: "Nickel Supported on Natural Silicate. Evaluation of Diatomite and Synthesis of the Catalyst", 7th Nordic Symposium on Catalysis, Turku/Abo, P46, 1996
- [26] R.P. Marinković-Nedučin, E. Kiš, O.D. Opačić, Lj.O. Vračar, D.M. Jovanović, Đ.L. Karlović, *Acta Periodica Technologica*, 29-30 (1998/1999) 143
- [27] D. Jovanović, S. Mitrovski, Ž. Jovanović: "Uticaj prirode nosača na redukciju prekursora niklovog hidrogenizacionog katalizatora". III Konferencija Društva fiziko hemičara Srbije, "Fizička hemija '96", Knjiga proširenih apstrakta, KN-19, p.135-136, Beograd, 1996
- [28] D. Jovanović, M. Stanković, B. Marković, I. Juranić: "Niklov hidrogenizacioni katalizator na nosaču od prirodnog silikata". III Konferencija Društva fiziko hemičara Srbije, "Fizička hemija '96", Knjiga proširenih apstrakta, KN-7, p.111-112, Beograd, 1996.
- [29] D. Jovanović, R. Radović, M. Dabović, I. Juranić, Lj. Mareš, M. Stanković, B. Marković, N. Jovanović, T. Novaković, D. Guzina: "Nickel Extraction from Spent Hydrogenation Catalysts and Synthesis of the New NICAT-2000 Catalyst" *EUROPACAT-III; Third European Congress on Catalysis*, Book of Abstracts, Vol. 2, p.676, Krakow (Poland), 1997
- [30] D. Jovanović, R. Radović, Lj. Mareš, M. Stanković, B. Marković *Catalysis Today*, **43** (1998) 21
- [31] D. Jovanović, M. Dabović, I. Juranić, M. Stanković, B. Marković, N. Jovanović: "Extraction of Nickel from the Spent Hydrogenation Catalysts and Synthesis of a New Catalyst" ("Ekstrakcija nikla iz istrošenih hidrogenizacionih katalizatora i sinteza novih") *Međunarodni skup "Stvaralaštvo kao uslov privrednog razvoja – od ideje do realizacije za bolji*

- kvalitet života", Knjiga radova/Proceedings: p. 8.61–68, Beograd, 1996
- [32] D. Jovanović, R. Radović, Lj. Mareš, M. Stanković, B. Marković: "New Nickel Hydrogenation Catalysts for Talow Hydrogenation and for Selective Hydrogenation of Sunflower Seed Oil", 15th Meeting of the North American Catalysis Society, P105, Chicago, USA, 1997
- [33] D. Jovanović, S. Mitrovski, M. Stanković, D. Guzina, Lj. Rožić, Ž. Jovanović: "Evaluation of the Precursor Reduction of Supported Nickel Catalyst" 4th International Conference on Fundamental and Applied Aspects of Physical Chemistry – Physical Chemistry '98, Proceedings, p. 240–242, Belgrade, 1998
- [34] D. Jovanović, Lj. Rožić, M. Stanković: "Reduction kinetics of nickel hydrogenation catalyst's precursor from thermogravimetric data", 5th International Conference on Fundamental and Applied Aspects of Physical Chemistry "PHYSICAL CHEMISTRY 2000", Proceedings, p. 166–168, Belgrade, 2000
- [35] D. Jovanović, A. Žujić, B. Marković, M. Stanković, N. Jovanović, T. Novaković: "Sinteza niklovog hidrogenizacionog katalizatora i provera njegove aktivnosti", 37. Savetovanje: Proizvodnja i prerada uljarica, Zbornik radova, str.169–178, Budva, 1996
- [36] D. Jovanović, U. Mioč, M. Dabović: "Hidrogenizacioni Ni katalizator. Prekursor: IC spektroskopska ispitivanja", III Konferencija Društva fiziko hemičara Srbije, "Fizička hemija '96", SP-20, p.89–90, Beograd, 1996.
- [37] M. Stanković, D. Jovanović, Lj. Rožić: "Sinteza i osobine prekursora Ni–hidrogenacionog katalizatora dobijenog taloženjem u sredini sa kontrolisanim pH", 40. Savetovanje: Proizvodnja i prerada uljarica, Zbornik radova, str. 321–326, Subotica, 1999
- [38] E.S. Freeman, B. Carroll, J. Phys. Chem., **62** (1958) 394
- [39] J. Bandrowski, C.R. Bickling, K.H. Yang, O.A. Hougen, Chem. Eng. Sci., **17** (1962) 379
- [40] N.W. Coats, J.P. Redfern, Nature, **201** (1964) 68
- [41] V.C.F. Holm, A. Clark, J. Catal., **11** (1968) 305
- [42] D. Jovanović, Ž. Čupić, M. Stanković, Lj. Rožić, B. Marković, J. Mol. Catal., A: Chemical, **159**, (2000) 353
- [43] D. Jovanović, Lj. Mareš, B. Marković, M. Stanković: "NICAT–2000 Catalyst in the Process of Soybean Oil Hydrogenation – Industrial Testing", 8th Nordic Symposium on Catalysis, p. 89–90, Oslo (Norway), 1998
- [44] D. Jovanović, Ž. Čupić: "Calculation of the Linolenic/Linoleic/Oleic Selectivity Ratios of the NICAT–2000 Hydrogenation Catalyst", 8th Nordic Symposium on Catalysis, p. 91–92, Oslo (Norway), 1998
- [45] D. Jovanović, Ž. Čupić, Lj. Mareš, M. Stanković, D. Guzina, Lj. Rožić, R. Kuč, B. Marković: "Selectivity Calculation of Soybean Oil Hydrogenation Process", 4th International Conference on Fundamental and Applied Aspects of Physical Chemistry–Physical Chemistry '98, p. 237–239, Belgrade, 1998
- [46] Ž. Čupić, D. Jovanović, Lj. Mareš, M. Stanković, Lj. Rožić, D. Guzina, Ž. Jovanović: "Isomerization During Partial Hydrogenation of Soybean Oil" 4th International Conference on Fundamental and Applied Aspects of Physical Chemistry–Physical Chemistry '98, p. 234–236, Belgrade, 1998
- [47] Ž. Čupić, D. Jovanović, Lj. Rožić: "Role of the catalyst in the isomerization reactions during soybean oil hydrogenation process", 5th International Conference on Fundamental and Applied Aspects of Physical Chemistry "PHYSICAL CHEMISTRY 2000", p. 169–171, 2000, Belgrade
- [48] D. Jovanović, Ž. Čupić, M. Stanković, B. Marković, Lj. Rožić, Acta Periodica Technologica, **31** (2000) 183
- [49] D. Jovanović, U. Mioč, V. Stamenković, R. Radović, M. Dabović, D. Guzina, Lj. Mareš, Z. Nedić: "Sadržaj trans masnih kiselina u margarinima – stepen trans izomerizacije pri upotrebi katalizatora NICAT–2000", 38. Savetovanje: Proizvodnja i prerada uljarica, str.255–264, Budva, 1997
- [50] D. Jovanović, R. Radović, Lj. Mareš, B. Marković, R. Kuč, M. Stanković, D. Guzina: "Industrijska provera katalizatora NICAT–2000 u procesu hidrogenizacije ulja", 38. Savetovanje: Proizvodnja i prerada uljarica, str.101–109, Budva, 1997
- [51] D. Jovanović, Ž. Čupić, Lj. Mareš, M. Stanković, D. Guzina, B. Marković, R. Kuč, Lj. Rožić: "Hidrogenizacija sojinog ulja – Selektivnost", 39. Savetovanje: Proizvodnja i prerada uljarica, str. 219–224, Budva, 1998
- [52] Ž. Čupić, D. Jovanović, D. Guzina, Lj. Mareš, M. Stanković, Lj. Rožić, B. Marković: "Optimizacija konstanti – geometrijske izomerizacije", 39. Savetovanje: Proizvodnja i prerada uljarica, str. 225–230, Budva, 1998
- [53] Ž. Čupić, D. Jovanović, M. Stanković, Lj. Mareš, D. Guzina, B. Marković, R. Kuč: "Soybean Oil Hydrogenation Process – Cis–trans Isomerization Rate Constants Optimization", 1st International Conference of the Chemical Societies of the South–East European Countries on Chemical Sciences and Industry, Vol. 1, PO 384, Halkidiki (Greece), 1998
- [54] D. Jovanović, Ž. Čupić, M. Stanković, Lj. Rožić, B. Marković: "The Influence of the Isomerization Reactions on the Soybean Oil Hydrogenation Process", EUROPCAT–IV; 4th European Congress on Catalysis, pp. 355, P/1/160, Rimini (Italy), 1999
- [55] Lj. Rožić, D. Jovanović, Ž. Čupić, M. Stanković, Procesna tehnika, **1** (2001) 188
- [56] Dilatometric Determinations of the Solid Fat Index, AOSC Tentative Method Cd 10–57
- [57] AOCs Official Method CC 3 – 25
- [58] A.R. Robert, J. Am. Oil. Chem. Soc., **46** (1969) 552
- [59] L.F. Albright, Chem. Eng., Sept. **11** (1967) 197

IZVOD

PARCIJALNO HIDROGENOVANJE JESTIVIH ULJA – SINTEZA I VERIFIKACIJA KATALIZATORA NA BAZI NIKLA

(Naučni rad)

Dušan Jovanović, Branislav Marković, Miroslav Stanković, Ljiljana Rožić, Tatjana Novaković, Zorica Vuković, Mirjana Anić, Srđan Petrović
IHTM, Centar za katalizu i hemijsko inženjerstvo, Beograd

Parcijalna hidrogenacija jestivih biljnih ulja je veoma važna operacija u industriji biljnih masti i ulja. Katalizator koji se uobičajeno upotrebljava u industrijskom procesu parcijalne hidrogenaciji biljnih ulja, je nikel nanešen na silikatni nosač. Izbor i hemijska sinteza niklovog katalizatora, postupak nanošenja nikla i promotora na nosač i aktivacija katalizatora su od vitalnog značaja za dobijanje visoko–aktivnog hidrogenacionog katalizatora. Niklov katalizator, nanešen na domaći prirodni silikat (dijatomska zemlja) sintetizovan je precipitacionom metodom sa Na_2CO_3 . Aktivnost sintetizovanog katalizatora je testirana na pilot postrojenju (5 kg) i u industrijskom reaktoru kapaciteta 5 tona. Dobijena aktivnost sintetizovanog katalizatora potvrđena je i na "scale–up" nivou sa faktorom 1000.

Ključne reči: Hidrogenacija • Katalizator • Sinteza •

Key words: Hydrogenation • Catalyst • Synthesis •