= CHEMICAL KINETICS AND CATALYSIS =

Revealing the Influence of Silver in Ni–Ag Catalysts on the Selectivity of Higher Olefin Synthesis from Stearic Acid¹

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Abstract—Results on the conversion of stearic acid to olefins over Ni–Ag/ γ -Al₂O₃ catalysts are presented. XANES and EXAFS experiments in situ and DFT calculations were applied to reveal the structure of active sites therein. It is shown that the introduction of Ag to Ni catalysts leads to an increase in the olefin yield. After a reduction in hydrogen (350°C, 3 h) alumina-supported nanoparticles of nickel sulfides and metallic Ag are formed. The role of metal hydrides formed during the reaction is extensively discussed.

Keywords: silver, nickel, higher olefins, stearic acid, heterogeneous catalysis, structure-activity relationships, renewable resources

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While prices for fossil hydrocarbon sources are going down there is still a considerable interest for renewables [1]. This implies a continuing interest in the production of chemicals from renewable sources including the conversion of fatty acids and their esters to higher olefins. Esters of glycerol and fatty acids are predominant components of vegetable oils and fats. Deoxygenation of these compounds is one of the ways to produce more valuable chemicals. The process of deoxygenation can be accomplished via three basic directions: hydrodeoxygenation, decarboxylation and decarbonylation [2, 3]. The former two lead to a diesel-type fraction composed mostly of saturated hydrocarbons while the decarbonylation route affords unsaturated products. Higher olefins comprise a significant part of these products and can be used as sources for the production of lubricants, industrial detergents, surfactants, plasticizers [4–6].

The highest yield of hydrocarbons in the deoxygenation of fatty acids is reached when Pd and Ni-based catalysts are used. These catalysts are stable in the hydrogen atmosphere but mostly give rise to saturated hydrocarbons [7–16]. Some efforts were put forth to enhance the selectivity of Ni-based catalysts by doping them with agents reducing activity towards olefin hydrogenation [17]. It is also observed that silver can be used as a promoter for catalysts in some similar processes for production of different organic compounds including olefins [18, 19].

In this study, it is found that the decarbonylation of stearic acid over Ni-based catalysts yields mostly C_{17} olefins. Meanwhile, the selectivity for these olefins increases significantly when silver is added as a dopant. This work is devoted to the in-depth examination of this fact in order to reveal reasons for such a selectivity increase upon silver doping.

EXPERIMENTAL

Materials, Reagents, and Solvents

The following compounds were used: nickel sulfate (NiSO₄·7H₂O, GOST 4465-74, 99.5%), silver nitrate (AgNO₃, Fluka, 99%), dodecane (C₁₂H₂₆, Russia, Khimmed, 99%), stearic acid (Russia, Mosreaktiv Ltd., 99.2%). γ -Alumina (γ -Al₂O₃, Dneprodzer-zhynsk, GOST 8136-85 AOA-1, extruded, surface area >200 m²/g) was used as a support.

Catalyst Preparation

The Ni catalyst 1 was prepared as following: the support was crushed and the fraction with a particle size of 0.08-0.2 mm was selected. For the preparation of 10 g of the catalyst 9.7 g of Al₂O₃ were dried at 200°C and put into the container for impregnation. 1.554 g of

¹ The article was translated by the authors.

nickel sulfate were dissolved in 10 mL of distilled water and then added to Al_2O_3 under stirring. The product was dried in air at 80–90°C for 3 h and then at 120–130°C for 3 h. The resulted catalyst contained 3.24% Ni.

The Ag catalyst **2** was prepared via the same procedure as the catalyst **1**, but silver nitrate was used instead of nickel sulfate. 0.500 g of silver nitrate was dissolved in 8 mL of distilled water and the solution was added to $5.0 \text{ g of } \text{Al}_2\text{O}_3$. The further procedure was the same as for the catalyst **1**. The content of Ag was 6.33% Ag.

For the preparation of the Ni–Ag catalyst **3**, the preprepared catalyst **1** was used as a precursor. 5.0 g of the catalyst **1** was impregnated by a solution of 0.408 g of silver nitrate in 6 mL of distilled water. The product was dried via the procedure described above. The metal content in the catalyst was 3.08% Ni and 4.97% Ag.

Catalytic Experiments and Product Analysis

Catalytic experiments were carried out in an autoclave (50 mL) with a stirrer (Autoclave Engineers, US). A glass beaker preventing the contact of the reaction mixture with the walls was placed in the autoclave. The catalyst was loaded (0.50-0.55 g) in it and reduced under a hydrogen flow (4-6 L/h) for 3 h at a pressure of 10 atm and temperature of 350°C. Hydrogen from the reactor exit passed through 10% water solution of lead nitrate to check for the formation of black lead sulfide (qualitative test for the H₂S presence). Afterwards, the autoclave was cooled to room temperature and dodecane (6.5-7 g) was loaded into the autoclave without opening it through a special feeder line. Dodecane covered the catalyst and protected it from oxidation in air. Then, the autoclave was opened and stearic acid (2 g) was added.

Next, the autoclave was closed again. The reactor was twice filled with hydrogen up to 15 atm and then the pressure was released down to 1 atm. Afterwards, the reactor was filled again with hydrogen up to 15 atm, the reaction proceeded at 350° C, hydrogen pressure 5–15 atm and intense stirring (1000–1100 rpm) for 1 or 2 h. After completion of the experiment, the reactor was fast cooled and gas probes were sampled for analyses. Then, the reactor was again heated to 60–70°C, the autoclave was opened, the glass beaker with products was weighted and liquid probes sampled for analyses. Each experiment was repeated 2–3 times to check for reproducibility.

The amount of unreacted stearic acid was measured by the titration method. Reaction products dissolved in 1:1 ethanol—chloroform mixture were titrated with 0.1 mol/L solution of NaOH in ethanol. The amount of hydrocarbons produced in the reaction was analyzed by the gas—liquid chromatography (GLC). The product contained unreacted stearic acid. Therefore, the methylation step was performed first. The methylation of the product was performed according to GOST R 51486-99 in the following sequence. The melted product (2.0 g) was put into a three-neck flask. Then, 7 mL of 1 M H_2SO_4 solution in methanol was added.

The mixture was refluxed for 1 h at a temperature $65-70^{\circ}$ C and cooled down to a room temperature. After, 12.5 mL of distilled water was added. The flask content was carefully transferred to a separatory funnel and extracted 3 times with heptane (total volume 10 mL). The extract was weighed, washed 3 times with distilled water (15 mL each portion) until complete removal of acid (control by a pH indicator paper) and dried with anhydrous sodium sulfate. Tridecane (the internal standard) was added to an aliquot of the extract for a GLC analysis. GLC was carried out on a Crystal-2000M chromatograph (FID, quartz column HP-ultra-2 with 50 m length, 0.2 mm inner diameter, and 5% phenylsiloxane in polymethylsiloxane as absorbent). The analysis was conducted at a detector temperature of 250°C and an evaporator temperature of 270°C. The column temperature was programmed to be constant at 60°C for 5 min, then increased at a rate of 10°C/min from 60 to 250°C, and then again kept constant at 250°C for 20 min.

The identification of heptadecenes was conducted using a GC-MS apparatus (Agilent Technology 6890N, USA, electron ionization detector 5973, 70 eV). For the separation, an HP-1 column was used (length 30 m) at an evaporator temperature of 250°C, gas carrier speed of 1 mL/min. The following temperature program was implemented: constant at 50°C for 5 min, then increased at a rate of 15°C/min from 60 to 250°C, and then kept constant at 250°C for 5 min. The mass-spectroscopy analysis of heavy products was conducted on a Finnigan MAT Incos 50 spectrometer with the direct inlet of the sample to ion source (electron impact 70 eV, source temperature 240°C, the sample heating rate was 10°C/min from 50 to 280°C).

The analysis of gas products was carried out on an LKhM-80 chromatograph (Russia), equipped with TCD. The following columns were used: column 1 (analysis of H₂, CH₄, O₂, N₂, and CO) with Zeolite 5A (fraction 0.14–0.40 mm)–the steel column 3 m × 3 mm (Ar, 30 mL/min, 100°C, detector current 100 mA), column 2 (analysis of CO₂) with Porapak Q (80–120 mesh fraction)–the steel column 2 m × 2 mm (Ar, 30 mL/min, column temperature 25°C 100°C, detector current 100 mA). The quantitative composition of the gas was determined by the absolute calibration method.

Catalyst Characterization

The metal content in the catalysts was determined by X-ray fluorescence analysis carried out on a wavelength-dispersive spectrometer Spectroscan-LF. The range of elements determined was from Ca to U, the instrumental error was 0.5%.

X-ray diffraction patterns of the catalysts were obtained at the "Structural Materials Science" station (Kurchatov synchrotron radiation source, NRC "Kurchatov Institute," Moscow, Russia) [20]. Measurements were performed in the transmission geometry (Bragg–Brentano) using a two-dimensional detector ImagingPlate (FujiFilm) with the wavelength of the incident radiation $\lambda = 0.68886$ Å (Zr absorption *K*-edge). The sample-to-detector distance was 200 mm, the average exposure time was 15 min. The primary processing of two-dimensional diffraction patterns was performed using the Fit2D software [21]. Polycrystalline silicon (NIST SRM 640c) was used for the calibration. JCPDS database was used for the phase identification [22].

XANES and EXAFS measurements were also performed at the "Structural Material Science" station. X-ray absorption spectra at the Ni and Ag K-edges were obtained in the transmission geometry using two ionization chambers. They were filled with appropriate air-argon mixtures to provide optimum absorption of 20 and 80% for I_0 and I_p respectively. Si(111) and Si(220) channel-cut crystals were used for the monochromatization of the incident radiation. Higher harmonics rejection was made by a slight detuning of the upper crystal with a piezo-drive within intrinsic elasticity limits. EXAFS calculations and fits were performed using the IFEFFIT and LARCH software packages [23, 24]. Additionally, a series of X-ray absorption spectra at the Ni K-edge were measured in situ in a reductive atmosphere (5% $H_2/95\%$ He, the gas flow rate of 400 mL/min) upon heating and subsequent cooling.

The Ag K-edge XAFS spectra as well as diffraction patterns were measured only before and after the hightemperature treatment. EXAFS two-sphere fits (Ni–O, Ni–S) were made simultaneously on the whole set of data with a minimization of the average r-factor (the sum of r-factors for each EXAFS fit divided by their number). Backscattering phases and amplitudes were calculated with FEFF8.5L program [25]. The amplitude factor S_0^2 was obtained from the fit of the NiO standard and then fixed for the whole dataset. In the first approximation Debye-Waller temperature factors σ^2 were assumed to change linearly with T in our temperature range (300-800 K), only two linear coefficients were fitted for each sphere. Energy shifts ΔE were assumed the same for each sphere. Coordination numbers and distances were the only fully independent variables. The fit was performed for k^2 and k^3 -weighted chi (k) functions in a 2-10 Å⁻¹ range of photoelectron wave-vectors k and 1.3–3.0 Å in *R*-space. The average *r*-factor in the end of the fit was 6.7%.

Transmission electron microscopy of the Ni–Ag catalyst reduced in hydrogen (3 h at 350°C) was performed on a LEO 912 ABOMEGA microscope at an accelerating voltage of 100 kV.

Quantum Modeling

All calculations were performed in the framework of the density functional theory (DFT) using the Priroda program [26]. The relativistic effects have been taken into account with the scalar-relativistic approach (the Dirac-Coulomb-Breit hamiltonian). The exchange-correlation functional PBE and L11 all electron basis set were employed [27, 28]. For systems with open electron shells, the spin-polarized calculations were performed. The geometries of the structures were optimized without any symmetry constraint. The types of found stationary points (transition state or minima) were characterized by an analysis of the normal vibrational frequencies. In order to check the correspondence of the found transition states to the local minima, calculations of the intrinsic reaction coordinate were performed.

An electrically neutral 13-core Ag cluster with an icosahedral structure was chosen as a model of the active site. The relative free energy (ΔG_{623}) of the cluster in the electronic state with a multiplicity (*M*) equal to 4 was only 0.2 kcal/mol higher compared to the most preferred state with M = 6.

RESULTS AND DISCUSSION

As it has been already mentioned above, nickel catalysts typically promote the deoxygenation of stearic acid into paraffins $C_{17}H_{36}$. We have found that alumina-supported nickel catalysts prepared in the proposed by us way give rise to a mixture of higher olefins C_{17} , while the introduction of silver into the nickel catalyst significantly increases the yield of olefins under identical reaction conditions (Table 1).

The olefin selectivity and yield depend on the silver-to-nickel ratio and hydrogen pressure (Table 2). The catalyst with the Ag/Ni ratio equal to 0.87 demonstrates the highest figures.

To understand the effect of silver on the selectivity of the process we have studied the most active and selective Ni–Ag catalyst (Table 1, catalyst 3) with various techniques for study of local structure.

Three major crystalline phases discovered in the initial catalyst **3**. XRD analysis has shown that after impregnation and drying the catalyst contains aluminum oxide with a spinel structure (γ -Al₂O₃), boehmite AlO(OH) and silver sulfate (Fig. 1). Most probably, boehmite has been formed partly by the hydrothermal treatment of alumina during the drying stage of the preparation. No nickel-containing phases e.g., nickel nitrate or oxide is observed. Thus, nickel is probably

Characteristic	1 Ni/Al ₂ O ₃	2 Ag/Al ₂ O ₃	3 NiAg/Al ₂ O ₃	1 + 2 mixture
Conversion of stearic acid, %	78.5	64.4	85.6	66.1
S (hydrocarbons), mol %	58.9	43.9	71.7	55.5
S (heptadecanes), mol $%$	16.1	12.7	16.7	12.1
S (octadecanes), mol %	0.2	0.0	0.2	0.0
S (heptadecenes), mol $%$	42.6	31.2	54.8	43.4
Yield (heptadecenes), mol %	33.4	20.1	46.9	28.7
<i>c</i> , mmol	Ni 0.276	Ag 0.276	Ni 0.262 Ag 0.230	Ni 0.276 Ag 0.239

Table 1. Catalytic tests of the Ni $-Ag/\gamma$ -Al₂O₃ catalysts in the deoxygenation of stearic acid (2 h, 350°C, 15 atm H₂, dodecane solvent, 0.5 g of catalyst loaded)

The last column shows data for a mechanical mixture of two catalysts (Ni/ γ -Al₂O₃ and Ag/ γ -Al₂O₃). Molar ratio was the same as in the bimetallic catalyst (Ag/Ni \approx 0.87); *c*—amount of metal in the loaded catalyst.

present in a surface chemisorbed phase with a general formula $Ni_xAl_2O_{3+x}$.

It should also be noted that in the initial catalyst nickel and silver occur in different spatially separated phases. There is a clear evidence of silver sulfate in the catalyst: corresponding peaks at ca. 13° , 14° , 20° , 22° , and 27° of 2θ are observed in the diffraction pattern (Fig. 1, interplanar distances in Å: 2.91, 2.81, 1.98, 1.87, 1.45). This indicates that the impregnation of nickel sulfate on boehmite with an aqueous solution of silver nitrate results in the exchange reaction between two salts.

After the reduction in hydrogen, the catalyst color changes from pale green to black. The reason for that is probably the formation of silver nanoparticles, which is confirmed by diffraction data. The diffraction

Table 2. Catalytic activity (*a*), selectivity (*S*), and yield (*y*) in the olefin production vs. Ag/Ni ratio in the catalyst (catalyst $3, 350^{\circ}$ C) and vs. hydrogen pressure

Ag/Ni (15 atm H ₂ , 2 h)	<i>S</i> , %	у, %	$a, \mu mol$ $g^{-1} s^{-1}$
0	42.6	33.4	0.653
0.29	46.4	35.0	0.684
0.59	48.0	37.6	0.734
0.87	54.8	46.9	0.916
1.17	44.2	33.1	0.647
Pressure H ₂ , atm			
(Ag/Ni = 0.87, 1 h)			
5	40.4 (13.0)	12.3 (4.0)	0.479
7	38.2 (11.5)	11.7 (3.5)	0.457
10	58.7 (14.2)	16.9 (4.1)	0.660
15	72.9 (16.3)	26.6 (5.9)	1.040

The activity expressed as an olefin formation rate referred to the weight of the catalyst in a reaction unit volume.

pattern shows broad peaks at 17° , 19° , 28° , 32° , and 34° of 2θ (Fig. 1, interplanar distances in Å: 2.37, 2.05, 1.45, 1.24, 1.19, correspondingly). Same color changes can be referred to the formation of metallic nickel, nickel sulfide or oxide. During the heating, the boehmite phase disappears. The state of nickel in the sample is difficult to be determined solely from diffraction data, because there are no reflections that can be assigned to either nickel oxide or metallic nickel.

A deeper understanding of the ongoing transformations one can obtain by an analysis of X-ray absorption spectroscopy data (Figs. 2–4). The oxygen environment of Ni in the initial sample is octahedral (the coordination number is close to 6). This can correspond to a surface phase of nickel oxide. Alternatively, the initial disordered structure can transform in the inverted spinel phase. In this phase, one-half of nickel occupies octahedral sites and the other half occupies tetrahedral sites [29].

During the reduction of the initial sample with hydrogen, the first visible changes are observed in the phase composition at the temperature above 200– 250°C. A decrease in the intensity of the white line in XANES spectra and the corresponding reduction of the Ni–O contribution in EXAFS Fourier transforms take place (Figs. 2, 3). There is no evidence of emergence of metallic nickel or Ni–Ag alloy. Instead, the formation of a disordered nickel sulfide phase occurs. XANES spectra correspond to nickel sulphide and also EXAFS spectra show distinct Ni–S contribution (Fig. 3). Ni or Ni-based alloy phases can be present but only in trace concentrations.

During the reduction in hydrogen the Ni–O coordination number (CN) decreases from 6 to ca. 2, while CN (Ni–S) increases from 0 to 2. Ni–O distance for cubic NiO is 2.09 Å. In our catalyst this distance is only slightly lower. Thus, EXAFS data confirm that in the initial catalyst Ni atoms have mostly octahedral coordination. Ni–S contribution appears only after 2-3 h of reduction (200–250°C) and slowly increases



Fig. 1. Azimuthally integrated diffraction pictures for the initial catalyst **3** (*1*) and the reduced catalyst **3** (*2*), $\lambda = 0.68886$ Å (Zr absorption *K*-edge).

with time and temperature. The CN = 2 for the sulphide sphere after reduction indicates that Ni is not fully sulphided. There are almost equal amounts of oxygen and sulfur atoms in the nearest coordination of Ni. If NiS_x particles are formed, they should somehow be connected with the oxide support. Thus, the oxygen CN must not be 0. It should be mentioned that for technical limitation of in situ XAS experiment we couldn't achieve 15 atm pressure of H₂. At higher hvdrogen pressures we could observe more Ni-S contribution or an appearance of metallic nickel. However, TEM and XRD results give evidence that no metallic nickel phase is observed. Thus, the formation of nickel sulfide phase is undoubtful. Ni-S distance in the catalyst is smaller than in hexagonal NiS (2.24 vs. 2.39 Å). This fact can be explained with the size effect. The smaller the size of NiS_x particles the smaller the Ni-S distance they have. A small increase in the Ni-S distance during the experiment can be explained with the growth of NiS_x particles.

The presence of isosbestic points in XANES spectra (app. 8350, 8360, 8390, 8410 eV) can indicate that only two species contribute to XANES (Fig. 2). PCA analysis confirmed that there are only two components. Therefore, a simple linear combination fit can be done.

Ag *K*-edge EXAFS data (Fig. 4) are in a full accord with the XRD data. The initial catalyst **3** is characterized by an oxygen environment of Ag atoms, and the formation of metallic silver nanoparticles starts at temperatures above $200-250^{\circ}$ C during the reduction. There is no evidence of silver alloying with nickel. Thus, the reduced catalyst **3** contains nickel in a sulfide phase and silver is present as metal nanoparticles. Direct interactions between Ni and Ag are observed neither in the initial nor in reduced catalysts. These observations are consistent with the results of trans-



Fig. 2. Ni *K*-edge XANES spectra of the catalyst **3** during the reduction in hydrogen (from bottom to top). Nickel oxide spectrum is shown as a reference at the bottom of the figure.

mission electron microscopy. The average particle size is 11.9 ± 2.8 nm and the metal particles are essentially spherical. The selected-area electron diffraction mode makes it possible to identify the following phases:

• metallic Ag (interplanar distances in Å: 2.317, 2.078, 1.441, 1.188, 1.004, 0.917, JCPDS Card no. 04-0783);

• Ni₃S₂ (interplanar distances in Å: 2.317, 2.078, 1.379, 1.210, 1.188, 0.917, 0.900, JCPDS Card no. 44-1418);

• NiS (interplanar distances in Å: 2.317, 1.948, 1.441, 1.379, 1.188, 0.917, JCPDS Card no. 47-1739).

There is also an evidence of the H_2S presence during reduction. This fact with XRD, EXAFS, TEM data give a reason to assume that synthesized catalysts contain nickel sulfide system that play a main role in the selective olefin formation.

It has been already mentioned earlier that the introduction of Ag into the Ni catalyst results in an increased selectivity towards formation of olefins. To



Fig. 3. Fourier-transformed EXAFS functions (Ni *K*-edge) of the catalyst **3** during the reduction in hydrogen (from bottom to top).

explain this fact, we have analyzed our own and literature data. First of all, our catalysts as well as other catalysts lead to the deoxygenation of stearic acid via the decarbonylation route [30, 31]:

$$C_{17}H_{35}COOH = C_{17}H_{34} + CO + H_2O$$

The decarboxylation is kinetically problematic and, therefore, do not take place [30]. In addition, the gaseous products contain only traces of CO_2 (molar ratio CO_2 to CO is 0.03–0.06 for the each catalyst under study). Besides, the main decarbonylation reaction competes with a side reaction of olefin hydrogenation to paraffins:

$$C_{17}H_{34} + H_2 = C_{17}H_{36}$$

This reaction degrades the yield of desired products. However, in our experiments, if we assume that paraffins are produced by the hydrogenation of olefins, the total selectivity of hydrocarbons appears to be notably less than 100% (Table 1). This indicates that olefins participate in other transformations besides hydrogenation. The most probable transformation can be an oligomerization of $C_{17}H_{34}$ olefins [32]:

$$nC_{17}H_{34} = (C_{17}H_{34})_n$$

Mass-spectrometry study confirms the formation of oligomers in the reaction. In particular, a distinct high-mass peak of 761 a.m.u. is clearly observed. We attribute this peak to ester of stearic acid and heptadecene dimer ($C_{34}H_{68}$). Therefore, at least the dimerization of heptadecenes takes place at reaction conditions. On the other hand, one can expect an increase in the rate of olefin hydrogenation at higher hydrogen pressure, which should also decrease the olefin yield. But quite opposite an increased olefin yield from ~12 mol % at 7 atm H₂ to ~27 mol % at 15 atm H₂ is observed for the catalyst **3** (Table 2).

It is known that sulfate ions can be reduced by hydrogen to H₂S in the presence of metals, what probably occurs in our case and gives rise to nickel sulfides, in particular, Ni_3S_2 . This sulfide can be further reduced with hydrogen to metallic nickel [33]. But there is no evidence of metallic nickel neither in XANES/EXAFS nor in XRD data, probably due to its very low concentration and high dispersion. Ag compounds can react with hydrogen with the formation of Ag–H bonds [34, 35]. Our calculations show that the interaction of molecular hydrogen with Ag₁₃ icosahedral particles (within the active complex model), is energetically favorable and $\Delta H_{623} = -2.9$ kcal/mol. After the adsorption of a hydrogen molecule, the H-H bond length does not change and remains identical to that in the free molecule (0.79 Å).

The cleavage of the H–H bond in the chemisorbed H_2 molecule leads to the formation of μ_3 -coordinated H atoms on Ag clusters. This may indicate that the homolytic dissociation of the H–H bond is preferred. This stage proceeds with a low activation barrier (9.9

and 21.9 kcal/mol for ΔE_0^{\neq} and ΔG_{623}^{\neq} , respectively) and results in a decrease in the free energy of the system from 7.5 to 3.8 kcal/mol (relative to the sum of energies for isolated Ag₁₃ and H₂). Besides the fact that the dissociation of hydrogen leads to a decrease in the Gibbs energy of the system, it is still higher than the energy for individual species (a silver cluster and a hydrogen molecule). This may indicate that the reaction equilibrium between molecular hydrogen and silver is shifted to the reagents side.

A profile of Gibbs free energy changes (calculated for experiment temperature 623 K) for the interaction of silver nanoparticles with molecular hydrogen is shown in Fig. 5. It demonstrates that the dissociation of H–H bond results in Ag–H bond formation. These fragments are able to interact with two radicals in the following way:

$$2(*C_{3}H_{7}) + Ag_{n}(H)_{2} = 2C_{3}H_{8} + Ag_{n}.$$

Figure 5 also shows changes in the Gibbs free energy for the subsequent reaction of Ag hydride with two isopropyl radicals. This reaction can be regarded as a model one for the description of the chain termination



Fig. 4. Fourier-transformed EXAFS functions (Ag *K*-edge) of the catalyst 3 before the reduction (*1*) and after the reduction in hydrogen (*2*).



Fig. 5. Free energy profile (relative to the energy of non-interacting reagents) for dissociation stages of H_2 (in a doublet spin state) and hydrogenation stages of isopropyl radical on the surface of Ag_{13} (in a triplet state for $[Ag_{13}H_2 + *CH(CH_3)_2]$ and in a quartet state for $[Ag_{13}H + *CH(CH_3)_2]$).

in the thermally activated oligomerization of olefin radicals promoted by Ag hydrides. It is evident that Ag_{13} can assist the dissociation of molecular hydrogen into atomic hydrogen. Afterwards the hydrogen atom is transferred from the silver nanoparticle to the radical giving rise to a stable RH molecule. Herein, the activation barrier of the H atom transfer to the radical is lower than the barrier for the H₂ dissociation on the surface of silver nanoparticles and is equal to 19.6 and

13.9 kcal/mol (ΔG_{623}^{\neq}) for the interaction of the H atoms with the first and the second *C₃H₇ radicals, respectively.

It is known that metal hydrides are efficient catalysts for terminating radical chain reactions [36]. Our own quantum-chemical calculations show that silver hydrides can probably also inhibit such reactions including thermal oligomerization. The concentration of silver hydrides along with nickel hydrides increases with an increase in hydrogen pressure. This probably explains the experimental dependence of the olefin yield on the hydrogen pressure. Consequently, the introduction of silver into the nickel catalyst can lead to the formation of hydrides increasing their total concentration. This increases the olefins yield (Table 1) due to the inhibition of the oligomerization processes. Probably, growth and termination stages of the chain oligomerization reaction occur directly at the surface of the catalyst without transport to the liquid phase. In this case, nickel active sites catalyze the decarbonylation of $C_{17}H_{34}COOH$ into olefins and silver hydride sites are responsible for the suppression of oligomerization. These two types of active sites should be relatively close to each other. This condition is satisfied in the catalysts described taking into account the fact that a mere mechanical mixture of silver and nickel catalysts catalyze decarbonylation with a substantially lower olefin yield than bimetallic silver-nickel catalysts deliberately prepared on the same support (Table 1).

CONCLUSIONS

In the presence of Ni catalysts, fatty acids and esters usually deoxygenate to paraffins. Presented studies have shown that nickel catalysts prepared in a proposed by us way are active towards decarbonylation, for example, of stearic acid with the formation of C₁₇ olefins. The introduction of Ag to Ni catalysts leads to an increase in the olefin vield. In this study, Ni-Ag catalysts have been examined by various techniques, e.g., X-ray diffraction (XRD) and X-ray absorption spectroscopy (XANES and EXAFS) in situ using synchrotron radiation, transmission electron microscopy, etc. The results show that the increased selectivity of the Ni catalysts after the addition of Ag is not associated with the formation of new active sites, containing both Ag and Ni. There is a clear evidence of the exchange reaction between precursor salts (nickel sulfate and silver nitrate) with the formation of silver sulfate and, probably, nickel nitrate.

After reduction in hydrogen (350°C, 3 h) nanoparticles containing nickel sulfides (NiS and Ni_3S_2) and metallic Ag are formed on the surface of the alumina support. The average size of these particles is $11.9 \pm$ 2.8 nm. Metallic Ni particles cannot be reliably detected, possibly due to their very small size and low concentration. No direct contact between Ag and Ni is observed while the results of the catalytic experiments indicate that these centers should be relatively close to each other. It is suggested that nickel and silver active sites have different functions. The former catalyze the decarbonylation of stearic acid to olefins. They are low active in hydrogenation of olefins, thus they do not substantially reduce olefin yield. The quantum chemical modeling shows that under the reaction conditions Ag sites tend to form hydrides. The same can be with Ni sites [37]. These hydrogenated sites are able to scavenge the radicals generated by the thermal oligomerization. Thus, side reactions, which lead to a selectivity decrease, are suppressed. In other words, hydrogen molecules activated on the surface of silver nanoparticles are prone to dissociation. The hydrogen atoms react with organic radicals and terminate the radical chain side-reaction generating molecular products. This phenomenon can be called the negative catalysis of the radical side-reactions of C_{17} olefin oligomerization.

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