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Effect of promotion of nickel sulfide catalyst with silver on kinetics of decarbonilation of stearic acid

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The kinetics of liquid-phase decarbonylation of stearic acid in *n*-dodecane on γ-Al_2O_3 supported nickel sulfide catalyst promoted with silver was experimentally studied at 350 °C. The parameters of the reaction steps were determined and a structural kinetic model was developed. The model was compared with an earlier developed kinetic model for the unpromoted catalyst. It was suggested that an increased reaction selectivity in the presence of silver promoted catalyst was caused by a change in the composition of the adsorption complexes formed by the active sites of the catalyst. This change in the composition of the complexes is probably associated with an increase in the average size of the surface active particles of the catalyst.

Key words: decarbonylation, stearic acid, higher olefins, reaction kinetics, kinetic model, catalyst promotion, inhibition, heterogeneous catalysis.

The scale of production of higher olefins with an even number of carbon atoms by oligomerization of ethylene is very high. The reason is that these olefins are key raw materials for surfactants,[1] which are the bases of synthetic detergents, synthetic grease oils and additives to them,[2] high-temperature heat carriers, as well as for a number of other petrochemical products. As a rule, higher olefins are part of narrow, for example C_{14}—C_{16}, or wider fractions. Unfortunately, due to some features in distribution of ethylene oligomerization products upon the length of carbon chain, C_{16}—C_{22} fraction is formed in insufficient quantities and cannot fully meet the industrial needs in these compounds.[3] Industrial synthesis of individual higher olefins with an odd number of carbon atoms is not implemented.

Another source for the production of higher olefins is processing of renewable resources which have either vegetable or animal origin.[3] This enables one to obtain valuable materials by hydrolysis (glycerin and fatty acids, mainly stearic (St) and oleic acids). Nickel sulfide supported catalysts emerged as effective systems for selective decarbonylation of acids to linear olefins C_{17} in a hydrogen medium.[3—5] The catalysts show reduced activity in the side reaction of hydrogenation of olefins and a property to effectively inhibit oligomerization.[6,7]

Promoting such catalysts with silver significantly increases the selectivity towards olefins and little increase in St conversion occurs; however, the reasons of the promoting effect are still unclear.[3,5]

In the present work, an attempt is made to use structural kinetic modeling to explain the effect of silver addition on the selectivity of the nickel sulfide catalyst in St conversion to heptadecenes (Hde).

Experimental

Reagents, solvents and materials. Nickel sulphate ($NiSO_4 \cdot 7H_2O$, special purity grade, USSR state standart GOST 4465-74, 99.5%), silver nitrate ($AgNO_3$, Fluka, 99%), sodium hydroxide (special purity grade, USSR state standart GOST 4328-77, 98.0%), sulfuric acid (reagent grade, 94%), dodecane (high purity grade, Himmed, Russia, 99%), tridecane (high purity grade), chloroform (reagent grade), ethyl alcohol (rectificate 96%), strearic acid (analytical grade, USSR state standart GOST 9419-78, 99.2%), hydrogen (A, 99.99%), nitrogen (special purity grade, 1 grade, 99.999%), and carbon monoxide (high purity grade, 99.8%) were used. As a support, γ-Al_2O_3 (Dneprodzerginsk, USSR state standart GOST 8136-85, AOA-1, extrudate, specific surface area determined by BET is 254 $m^2 g^{-1}$) was applied. All reactants and solvents were used as received.

Catalyst synthesis The method and conditions used to prepare the nickel sulfide catalyst, to promote it with silver, and to reduce by hydrogen were described earlier.[5] The size of the catalyst granules was 0.08—0.2 mm, the molar ratio of Ag : Ni was 0.87 at Ni content of 3.08%.

It was previously shown[5] that the addition of silver increased the average size of surface catalytic particles from 4.7 to 11.9 nm. At the same time, the peaks typical of metallic silver were found in the XRD patterns, while relatively small amounts of NiS and Ni_3S_2 sulfides were identified. Hence, it can be assumed that nickel and silver do not directly interact with each other, although, the catalytic data[5] showed that they were not spatially separated. The absence of reflections from metallic nickel in difractograms can be explained by the small size of nickel crystallites and their low concentration.

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Table 1. Planned conditions for the kinetic experiments on decarbonylation of St in the presence of silver promoted nickel sulfide catalyst supported on γ-alumina oxide at 350 °C

Series	$P(H_2)^a$	$C(St)^a$	$C(Ni)^{a,b}$	t/min	Note
1	15	0.6	0.02	0, 30, 60, 120	—
2	10	0.6	0.02	0, 60	—
3	7	0.6	0.02	0, 60	—
4	5	0.6	0.02	0, 60	—
5	15	1.2	0.02	0, 60	—
6	15	0.6	0.04	0, 30	—
7	10	0.6	0.02	0, 60	$P(CO) = 5$
8	7	0.6	0.02	0, 60	$C(H_2O) = 1.1$

[a] Concentrations (mol L^{-1}) and gas pressures (atm.) are calculated at room temperature.

[b] Calculated concentration of the catalyst based on nickel content.

Methods for kinetic experiments. Methods of conducting kinetic experiments, as well as the experiments indicating the kinetic mode of the reaction, are described in our earlier publication.[6] A 50 mL autoclave (Autoclave Engineers Inc.) with a stirrer and low-inertia heating with Wood's alloy was used as a reactor.

Planning kinetic experiments. One of the main goals of experiment planning is to obtain maximum information about the influence of input factors on output indicators (for example, the concentration of the substrate on the selectivity of the reaction) with the minimum number of experiments. Each series in Table 1 contains the planned values of the initial concentrations or pressures of the reactants, as well as the sampling time for analyzes. We used four various initial hydrogen pressure levels $P(H_2)$, two carbon monoxide pressure values $P(CO)$, and two initial concentrations of St C(St), water $C(H_2O)$, and catalyst C(Ni) (for Ni).

The level of factors in this plan is set by a researcher. However, the plan was not drawn up according to the rules of classical experiment planning, since mathematical models of the kinetics of chemical reactions are not linear in parameters. Moreover, unlike the classical one, this plan is not required to be performed exactly, *i.e.*, the values of factors, for example, the initial hydrogen pressure or the reaction time, may be somewhat different from those recommended by the plan. Based on our earlier studies[6,7] we can conclude that the proposed plan is sufficient to establish the structure and calculate the parameters of the kinetic model of the given reaction.

In experiments, in which the reaction time was taken as 0 min, the autoclave was heated to the operating temperature for 15 min, then rapidly cooled to ~20 °C, and the reaction mixture including the gas phase products was analyzed.

It is assumed that the results of the analysis of such a mixture can be taken as the initial concentrations of the reactants. In this case, the contribution of the chemical transformation into the non-isothermal mode by heating the reaction mixture to the operating temperature is excluded. In other experiments, after reaching the specified temperature, the reaction was allowed to proceed for a specified time, after which the reactor was rapidly cooled to ~20 °C and the products were analyzed.

Analysis of the reaction products. The techniques used for the analysis were described in detail earlier.[6,7] The concentration of unreacted St was determined by acid-base titration with a color indicator in a mixture of chloroform and ethanol. Gas-liquid chromatography with an internal standard (tridecan) was used to measure the concentrations of heptadecenes (Hde), heptadecane (Hd), and St, with St being methylated in the reaction mixture. The amount of H_2, CO, CO_2, N_2, and trace amounts of methane were determined by adsorption chromatography with an absolute calibration using pure gases. Chromato-mass spectrometry and NMR spectroscopy were used to analyze the products with minor concentration, for example, heptadecyl stearate (Es) and diheptadecyl ketone (Kn). The values of the concentrations of the main components of the reaction mixture, calculated from the analytical results are shown in Table 2.

Construction and analysis of the kinetic model. Methods and algorithms for data processing, the choice of an adequate kinetic model, as well as the analysis of the single-valuedness and error in determining its parameters are set out in our earlier publications.[6—10] The mathematical model is a system of ordinary differential equations with the values of starting concentrations as initial conditions (the Cauchy problem). The search for an adequate kinetic model was carried out according to the classical scheme of hypothesis suggestion and testing. The considered hypotheses included only structural models. Hypothesis forma-

Table 2. Measured consentrations (mol L^{-1}) of the components of St decarbonylation (the results of calculation by the kinetic model are in brackets)*

Series	t/min	C(St)	C(Hde)	C(CO)	C(Hd)	$C(CO_2)$
1	30	0.295 (0.296)	0.207 (0.217)	0.301 (0.260)	0.031 (0.024)	0.010 (0.011)
	60	0.229 (0.219)	0.214 (0.246)	0.319 (0.329)	0.044 (0.044)	0.015 (0.014)
	90	0.193 (0.170)	0.244 (0.250)	0.422 (0.372)	0.068 (0.063)	0.016 (0.015)
	120	0.121 (0.135)	0.268 (0.244)	0.471 (0.403)	0.079 (0.079)	0.018 (0.017)
2	60	0.330 (0.293)	0.172 (0.189)	0.256 (0.275)	0.024 (0.031)	0.015 (0.015)
3	60	0.360 (0.327)	0.122 (0.136)	0.210 (0.217)	0.020 (0.022)	0.016 (0.017)
4	60	0.316 (0.325)	0.145 (0.108)	0.179 (0.170)	0.023 (0.020)	0.028 (0.026)
5	60	0.551 (0.540)	0.258 (0.258)	0.526 (0.431)	0.052 (0.053)	0.036 (0.035)
6	30	0.236 (0.202)	0.232 (0.261)	0.349 (0.335)	0.032 (0.040)	0.006 (0.006)
7	60	0.339 (0.305)	0.162 (0.155)	1.300 (1.374)	0.021 (0.020)	0.016 (0.018)
8	60	0.451 (0.478)	0.085 (0.099)	0.155 (0.146)	0.014 (0.012)	0.018 (0.019)

* The concentrations are determined concerning the volume liquid phase under the conditions of the kinetic experiments; Hde are heptadecenes, Hd is heptadecane.

tion was based on the Langmuir mechanism with the following assumptions:

1) an active site can adsorb more than one molecule,

2) the vapor-gas portion of the system (CO, CO_2, H_2O, H_2, N_2) was considered as an ideal gas,

3) the solubility of gases and vapors follows the Henrys law.

The first assumption, in contrast to the classical theory of Langmuir adsorption, creates a large number of possible compositions of adsorption complexes, and a change in the composition of at least one adsorption complex generates a new hypothesis. The same applies to other details of the mechanism scheme, for example, the kinetic order of single steps. The suggested hypotheses were tested by the generally accepted least squares method. The weighted sum of squares of the deviations of reactant concentrations, which were calculated by the model from the values obtained experimentally, was used as an objective function.[10] As *g* weight, we used the inverse square of the error in determining the corresponding concentration $g = 1/\varepsilon^2$.

The objective function was minimized by the configuration method, one of the direct search methods that does not assume the need to calculate the derivatives of the objective function from the desired parameters. The initial approximations for the rate constants and equilibria were formed according to known recommendations.[10] For reliability, the minimization of the objective function was performed using several initial approximations. When a hypothesis did not provide an adequate description of the experimental data by the model it was rejected using the Fisher adequacy criterion. In total, over 100 hypotheses were considered. If more than one hypothesis turned out to be adequate, the simplest hypothesis was chosen.

The mean square relative error of the description of the experimentally determined concentrations by the mathematical model was ± 5%, which is close to the reproducibility of measurements. The characteristics of this model, *i.e.*, the stoichiometric and kinetic equations of the stages, the values of the equilibrium constants of adsorption, and the rate constants of single steps, as well as interpretation are given in the next section.

Results and Discussion

In our previous publication[6] we described the main transformations of St over the unpromoted nickel-sulfide catalyst:

decarbonylation of St

$$\mathrm{St} \longrightarrow \mathrm{Hde} + \mathrm{CO} + \mathrm{H_2O}, \qquad (1)$$

hydrogenation of Hde

$$\mathrm{Hde} + \mathrm{H_2} \rightleftarrows \mathrm{Hd}, \qquad (2)$$

decarboxylation of St

$$\mathrm{St} \longrightarrow \mathrm{Hd} + \mathrm{CO_2}, \qquad (3)$$

formation of anhydride of steric acid (An)

$$2\ \mathrm{St} \rightleftarrows \mathrm{An} + \mathrm{H_2O}, \qquad (4)$$

formation of heptadecyl stearate (Es)

$$\mathrm{St} + \mathrm{Hde} \rightleftarrows \mathrm{Es}, \qquad (5)$$

decarboxylation of An to diheptadecyl ketone (Kn)

$$\mathrm{An} \longrightarrow \mathrm{Kn} + \mathrm{CO_2}, \qquad (6)$$

water gas shift reaction

$$\mathrm{CO} + \mathrm{H_2O} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2}, \qquad (7)$$

dimerization of Hde

$$2\ \mathrm{Hde} \longrightarrow \mathrm{Dime}. \qquad (8)$$

The characteristics of the active phase of silver promoted nickel sulfide catalyst, as well as the effect of the Ag : Ni ratio on the reaction parameters were disclosed earlier.[5] The characteristics refer to the size, shape, structure, and composition of the supported catalytic particles. It was found that the main routes of St transformations in the presence of the promoted catalyst were the same as those in the presence of the unmodified catalyst, although the addition of silver increased St conversion by a factor of 1.4. Even more important parameter for the assessment of the efficiency of the catalyst for decarbonylation was a 12% increase in selectivity towards olefin. In addition, in the presence of silver promoted nickel sulfide catalysts, the rates for St decarboxylation (3) and water gas shift reaction (7) were lower, hence little CO_2 was formed and its fraction in the selective transformation of St was only 2—7%.

In order to understand the nature of the promoting effect of silver, the kinetic models of the decarbonylation of stearic acid over unpromoted and silver promoted catalysts can be compared.

As structural kinetic modeling for silver promoted nickel sulfide catalyst shows, the adsorption complexes of the reactants with the active sites Z are formed by the following equations:

$$\mathrm{Z} + \mathrm{St} + 3\ \mathrm{H_2} = \mathrm{Z(St)(H_2)_3}, \qquad (\mathrm{I})$$

$$\mathrm{Z} + \mathrm{St} + 2\ \mathrm{H_2O} = \mathrm{Z(St)(H_2O)_2}, \qquad (\mathrm{II})$$

$$\mathrm{Z} + \mathrm{Hde} + \mathrm{St} + \mathrm{H_2O} + \mathrm{H_2} = \mathrm{Z(Hde)(St)(H_2O)(H_2)}, \qquad (\mathrm{III})$$

$$\mathrm{Z} + \mathrm{H_2O} + \mathrm{H_2} = \mathrm{Z(H_2O)(H_2)}, \qquad (\mathrm{IV})$$

$$\mathrm{Z} + 2\ \mathrm{CO} + \mathrm{H_2} = \mathrm{Z(CO)_2(H_2)}, \qquad (\mathrm{V})$$

$$\mathrm{Z} + 2\ \mathrm{H_2} + \mathrm{H_2O} = \mathrm{Z(H_2)_2(H_2O)}. \qquad (\mathrm{VI})$$

With roman numbers we denoted both the numbers of the steps of adsorption and the corresponding adsorption complexes. There appeared to be six, rather than eight steps, as assumes the kinetic model for the nickel sulfide catalyst, and certain differences were observed in the composition of these complexes. Thus, according to the kinetic model for the promoted catalyst, the adsorption complex I formed in the St decarbonylation step contains an additional hydrogen molecule. Besides, the adsorption complex VI, which participates in Hde hydrogenation, includes a water molecule. The corresponding values of the adsorption equilibrium constants obtained using a numerical kinetic model are presented below.

Equation	K
(I)	$8.24 \cdot 10^2$
(II)	$3.01 \cdot 10^4$
(III)	$7.93 \cdot 10^3$
(IV)	$1.24 \cdot 10^7$
(V)	$3.73 \cdot 10^5$
(VI)	$5.03 \cdot 10^5$

High values of the constants correspond to the almost complete coverage of the catalytic active sites with reactant molecules, so that the number of unoccupied active sites is less than one per 10^7 sites. Based on the ratio of the adsorption equilibrium constants, one can conclude that the concentration of adsorption complexes with $Z(St)(H_2)_3$ composition, which are intermediate in decarbonylation, is four orders higher than the concentration of unoccupied active sites. However, the major part of the active sites is combined in with the $Z(H_2O)(H_2)$ complex.

Table 3 shows the kinetic equations of selected stages, as well as the values of the rate constants and equilibrium constants. The equations of the main stages include the concentration of adsorption complexes.

Hydrogenation of heptadecenes proceeds in parallel by two mechanisms: 2 (1) is Langmuir mechanism, which proceeds *via* decomposition of the adsorption complex III; 2 (2) is Ili—Riedel mechanism which involves the interaction of the olefin with the adsorption complex VI. At the same time, the kinetic equations of the main stages of St deoxygenation, expressed using concentration of reagents, are as follows:

decarbonylation

$$w_1 = k_1 K_{\mathrm{I}} C(\mathrm{St}) C(\mathrm{H_2})^3 C(\mathrm{Ni})/\mathrm{Den},$$

hydrogenation

$$w_2 = [k_{2(1)} K_{\mathrm{III}} C(\mathrm{Hde}) C(\mathrm{St}) C(\mathrm{H_2O}) C(\mathrm{H_2}) C(\mathrm{Ni}) + \\ + k_{2(2)} C(\mathrm{Hde}) K_{\mathrm{VI}} C(\mathrm{H_2})^2 C(\mathrm{H_2O}) C(\mathrm{Ni})]/\mathrm{Den},$$

oligomerization

$$w_8 = k_8 C(\mathrm{Hde})[C(\mathrm{H_2}) C(\mathrm{Ni})]^{-0.5},$$

where k_j is rate constant of the step j, K_i is the equilibrium constant of adsorption i,

$$\mathrm{Den} = 1 + K_{\mathrm{I}} C(\mathrm{St}) C(\mathrm{H_2})^3 + K_{\mathrm{II}} C(\mathrm{St}) C(\mathrm{H_2O})^2 + \\ + K_{\mathrm{III}} C(\mathrm{St}) C(\mathrm{Hde}) C(\mathrm{H_2O}) C(\mathrm{H_2}) + K_{\mathrm{IV}} C(\mathrm{H_2O}) C(\mathrm{H_2}) + \\ + K_{\mathrm{V}} C(\mathrm{CO})^2 C(\mathrm{H_2}) + K_{\mathrm{VI}} C(\mathrm{H_2})^2 C(\mathrm{H_2O}).$$

The total concentration of active sites is conventionally taken to be equal to C(Ni). The difference between the reactions occurring over the unpromoted and promoted catalysts is mainly governed by the difference in the compositions of the adsorption complexes I and VI.

It is known[8—10] that the problem of calculating the values for the parameters of a mathematical model often has many solutions. Therefore, the same calculated concentration values for the reactants can correspond to a multitude sets of rate constants and equilibrium constants. This ambiguity can be accounted for by numerous reasons. Among these are the stationary state of the system or the quasi-equilibrium of adsorption before the decomposition of the adsorption complex, as described in detail earlier.[8] In this case, not all the parameters of the model,

Table 3. Kinetic equations and the values of the rate constants and equilibrium constants of the stages*

Step	Kinetic equation	k	K
1	$w_1 = k_1 C(\mathrm{I})$	$1.56 \cdot 10^3$	—
2 (1)	$w_{2(1)} = k_{2(1)} C(\mathrm{III})\{1 - C(\mathrm{H_2}) C(\mathrm{Hd})/[K_2 C(\mathrm{Hde})]\}$	$3.66 \cdot 10^2$	$3.78 \cdot 10^0$
2 (2)	$w_{2(2)} = k_{2(2)} C(\mathrm{Hde}) C(\mathrm{VI})\{1 - C(\mathrm{H_2}) C(\mathrm{Hd})/[K_2 C(\mathrm{Hde})]\}$	$5.28 \cdot 10^0$	$3.78 \cdot 10^0$
3	$w_3 = k_3 C(\mathrm{II})$	$4.35 \cdot 10^1$	—
4	$w_4 = k_4 [C(\mathrm{St})^2 - C(\mathrm{An}) C(\mathrm{H_2O})/K_4]$	$1.59 \cdot 10^{-3}$	$1.72 \cdot 10^{-5}$
5	$w_5 = k_5 [C(\mathrm{St}) C(\mathrm{Hde}) - C(\mathrm{Es})/K_5]$	$1.91 \cdot 10^{-3}$	$2.51 \cdot 10^0$
6	$w_6 = k_6 C(\mathrm{An})$	$1.93 \cdot 10^1$	—
7	Contribution of water gas shift reaction is insignificant	~0	1.30
8	$w_8 = k_8 \mathrm{C}(\mathrm{Hde})[C(\mathrm{Ni}) C(\mathrm{H_2})]^{-0.5}$	$1.22 \cdot 10^{-4}$	—

* Concentrations of liquid and gaseous compounds are represented in mol L^{-1}, time is in min, catalyst loading (C(Ni)) is present in moles of Ni per 1 L of liquid phase, the values of the rate constants and equilibrium constants are represented in accordance with the numerical kinetic model and their dimensions correspond to the kinetic equations.

Table 4. Unambiguosly estimated parameters and parametric functions (complexes) of kinetic models, their values and errors of calculations

Line	Parametric function	Numerical value	Logarithmic calculation error (±)
a	$K_{IV}/(K_{VI}k_{2(2)})$	$4.67 \cdot 10^0$	0.08
b	$k_1K_I/(K_{VI}k_{2(2)})$	$4.84 \cdot 10^{-1}$	0.08
c	k_4	$1.59 \cdot 10^{-3}$	0.05
d	$k_3K_{II}/(K_{VI}k_{2(2)})$	$4.93 \cdot 10^{-1}$	0.10
e	k_8	$1.22 \cdot 10^{-4}$	0.11
f	k_6K_4	$3.32 \cdot 10^{-4}$	0.12
g	$k_{2(1)}K_{III}/(K_{VI}k_{2(2)})$	$1.09 \cdot 10^0$	0.14
h	k_5	$1.91 \cdot 10^{-3}$	0.24
i	$K_V/(K_{VI}k_{2(2)})$	$1.40 \cdot 10^{-1}$	0.46
j	K_2	$3.78 \cdot 10^0$	0.46
k	K_5	$2.51 \cdot 10^0$	0.68

but only some packages of parameters, the nonlinear parametric functions (NPF), can be unambiguously determined (calculated and represented in the form of "mean ± error"). If the parameter value is calculated unambiguously, such an estimate is referred to as "unmixed".[8—10] Table 4 represents six uniquely estimated NPFs of our kinetic model, their corresponding values (lines *a*, *b*, *d*, *f*, *g*, *i*) and "unmixed" estimates of the sought for parameters of the kinetic model (lines *c*, *e*, *h*, *j*, *k*).

The unambiguously estimated nonlinear parametric functions ("packages", lines *a*, *b*, *d*, *f*, *g*, *i* in Table 4) include the products of adsorption equilibrium constants and the rate constants of the decomposition of the corresponding adsorption complexes, as well as the ratio of adsorption equilibrium constants. Evidently, the NPFs include several parameters of the model, between unknown values of which a functional relationship exists. The inevitability of the appearance of such NPFs is associated, firstly, with the construction of a kinetic model based on the Langmuir mechanism which includes the assumption of a quasi-equilibrium of the adsorption steps. Secondly, a very small fraction of unoccupied catalytic sites must be taken into account. It is in the last case when the contribution of occupied sites is governed by the ratios of the adsorption equilibrium constants rather than by the values of these constants. Therefore, a direct comparison of the values of model parameters for unpromoted and silver promoted catalysts is not informative and, as a result, inadvisable.

An unambiguously determined NPF (line *f* in Table 4) corresponds to the case of a quasi-equilibrium shifted to the left (formation of stearic anhydride), which is well-known in formal chemical kinetics, followed by the decomposition of its product (decarboxylation of the anhydride to diheptadecyl ketone). An attempt to substitute steps 4 and 6 by a single common step, made in elaborating the hypothesis, did not result in an adequate model. Hence, without the assumption of anhydride of St as an intermediate, the kinetics of an admixture Kn formation cannot be adequately described.

As it was found earlier, an unusual behavior of nickel sulfide catalysts involves an increase in heptadecene selectivity with increasing hydrogen pressure.[3—7] This is associated with the known ability of metal hydrides, including nickel and silver, to inhibit the chain polymerization/oligomerization of olefins, in particular, the radical-chain (thermal) polymerization.[3—7] This feature of hydride behavior is consistent with the empirical kinetic equation of the corresponding step 8 (see Table 3), which contains negative orders of 0.5 for the catalyst and hydrogen concentrations.

In the group of nickel sulfide catalysts for decarbonylation of fatty acids, an unusual tendency is observed: the loss of heptadecenes due to a secondary hydrogenation with heptadecane formation decreases with increasing hydrogen pressure. This was typical of the undoped catalyst; however, this effect is even more pronounced in the presence of a silver promoted catalyst. Kinetic modeling provides a rational explanation for this fact. As follows from the composition of the adsorption complex I (see the scheme presented above), the target decarbonylation step (1) is sharply accelerated and up to the third order of magnitude with increasing pressure of hydrogen, which is not consumed at this step. The reason is that with increasing pressure of hydrogen the quasi-equilibrium concentration of the above mentioned complex involved in decarbonylation increases. In agreement with the composition of the corresponding adsorption complexes III and VI, an increase in the rate of secondary hydrogenation steps 2 (1) and 2 (2) is less strong. Thus, an increase in hydrogen pressure does not only inhibit the side reaction of oligomerization of target heptadecenes,[3—7] but also increases the rate of formation of the target heptadecenes relative to their consequent hydrogenation. The total effect becomes apparent in an increase in olefin selectivity with increasing hydrogen pressure.

Now we can try to explain why the contribution of the side reaction of hydrogenation of olefins over a silver-promoted catalyst is not as high as found with an unpromoted system. As can be seen in the diagram reflecting the results of kinetic modeling, adsorption complex I contains an additional hydrogen molecule as compared to the complex formed in the presence of the unpromoted catalyst. Incorporation of hydrogen in the adsorption complexes formed by the active sites of the catalyst may indicate that in the absence of hydrogen the activity of these sites in decarbonylation is low or not evident. It is possible that hydrogen bonding disorders the structure of the active sites and thus contributes into an enhancement of the catalytic activity.

Silver and nickel in silver promoted nickel sulfide catalyst are found in supported particles of different nature, the average size of which is 11.9±2.8 nm, and the smallest particle size found is 8 nm.[5] Since the catalytic activities of unpromoted and silver promoted nickel sulfide catalysts are close, it is logical to assume that active sites are located on nickel-containing particles. In the unpromoted nickel sulphide catalyst, the average size of these particles is 4.3±1.8 nm, hence, the size of more than 90% of particles is less than 8 nm.[4] Therefore, a plausible explanation of the difference in the composition of the formed adsorption complexes is that in the silver promoted nickel sulfide catalyst the sites are located on particles characterized by a larger size than in an unpromoted catalyst. Similar findings for other catalysts were described in the previously published review.[11]

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