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Effect of Controlled Deactivation on the Properties of a Supported Nickel Catalyst in the Reactions of Liquid-Phase Hydrogenation of Carbon–Carbon Multiple Bonds

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Abstract—The effect of controlled deactivation of Ni/SiO_2 catalysts in the reactions of liquid-phase reduction of the carbon–carbon double bond in maleic acid diethyl ester (MADE) molecule was examined. The influence of the total quantity of deposited metal and of the quantity of reduced metal on the structural and mechanical, as well as the catalytic properties of nickel deposited on silica gel was studied. The effect produced by the surface sulfidation on the catalytic properties of the active metal as dependent on the percentage of the nickel oxide deposited was demonstrated. Practical absence of the relative structure sensitivity of the supported catalysts was experimentally proved. The relative structure sensitivity of the catalyst was calculated as the fractal dimension of the surface of the Ni°/SiO_2 samples after one of the technological processes, related to that of the fresh nickel catalyst. The relative structure sensitivity of the catalyst surface as influenced by various hydrodynamic regimes, increased pressure, and nature of the solvent, as well as by adsorption of the reactants and the proceeding of the hydrogenation reactions and the deactivation process was considered. It was found that, during the synthesis process, the catalyst was saturated with hydrogen in the reactor, the reduction reaction of MADE proceeded, the catalyst was deactivation by the sulfide ion, and the catalyst surface underwent certain changes. Specifically, the surface roughness increased, and the sizes of the agglomerates and of the crystallites decreased. The influence of controlled partial deactivation of the nickel active sites by the sulfide ion on the activity of the supported catalysts was evaluated, and the ratios of the surface atoms of nickel, hydrogen, and sulfur in the catalytic systems possessing different activities were calculated. It was shown that, when the nickel catalyst surface was deactivated by the sulfide ions taken in a proportion of one sulfur atom per two surface nickel atoms, the activity of the catalyst was reduced by 90% and could not be subsequently restored.

Keywords: liquid-phase hydrogenation, maleic acid diethyl ester, modifying agents, skeletal and supported nickel catalyst, active metal, structure sensitivity effect of catalyst

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1. INTRODUCTION

The vast majority of large-scale production processes involving the hydrogenation stage are carried out today in the presence of transition metal-based heterogeneous catalysts. The main problems with the use of metal catalysts are the nearly complete absence of scientifically grounded approaches to the synthesis, as well as low selectivity, high sensitivity to the presence of catalytic poisons in the system, and scarce possibilities of regeneration [1–4]. The catalytic properties of metals are determined, above all, by their adsorption capacity with respect to the reaction participants, which, in turn, depends on the synthesis conditions and the process conditions chosen. The distribution of the catalytically active surface sites depending on the nature of catalysts, including those containing the promoting additives, is well covered in the literature [3, 5, 6]. At the same time, catalytic poisons produce a more significant effect on the activity of hydrogenation catalysts than any promoting additive [7].

The energy heterogeneity of the active metal surface is manifested in the formation of various adsorption forms of reactants which have different reactivities; in the case of hydrogenation reactions this concerns primarily hydrogen [8]. Earlier [9] it was suggested that the reactivity of adsorbed hydrogen be assessed by the method of regional rates, which treats the overall reaction rate as being numerically equal to the sum of the rates of substrate conversion at active sites of different types. The application of the method of regional rates to hydrogenation processes should involve matching the quantity of the adsorbed hydrogen and the experimental reaction rates. In this case, the experimental problem reduces to obtaining a set of catalysts of the same type, differing in the quantity of adsorbed hydrogen and in the catalytic activity, with the latter being determined specifically by the presence of accessible active surface sites. Solving this problem will allow predicting the activity, selectivity, and lifetime of transition metal-based catalysts employed in hydrogenation reactions.

For this very purpose, with the view of enhancing variability of the system, in order to increase the number of catalysts of the same type with different hydrogen contents, we used in this study a catalytic poison that blocked individual surface sites, thereby reducing the total adsorption capacity of the catalyst. Similar studies were carried out for a skeletal nickel catalyst [9, 10]. However, those studies had several disadvantages, including that in terms of a strong effect of adsorption-induced deformation [11], leading, in particular, to significant enhancement of activity due to particle size reduction and, consequently, to an increase in the specific surface area [12]. Such effects complicate analysis of the nature of deactivation, e.g., using the method proposed by Bartholomew [13] for assessing the selectivity of catalyst deactivation. In view of the above-said, we selected for this study a supported nickel catalyst for which the parameters of the supported particles lay in the nanoscale range and the support had a distribution maximum at 5 μm, so significant effect from adsorption-induced deformation was not expected.

As known [4, 7, 14], during the synthesis of a supported hydrogenation catalyst (in particular, a nickel-based catalyst) the metal is not fully reduced; the catalytic poison can be adsorbed on the reduced metal, on its compounds (oxide), and on the support proper. For taking into account the effect of the catalyst poison adsorption by catalyst components other than the active metal, we used in this study the catalyst with different quantities of the deposited and reduced nickel.

Herein, we evaluated the effect from partial deactivation of a supported nickel catalyst by the sulfide ion on the kinetics of hydrogenation of the carbon–carbon double bond through the example of maleic acid diethyl ester at a hydrogen overpressure, as well as on the structural and mechanical properties of a silica gel-supported nickel catalyst.

2. EXPERIMENTAL

2.1. Synthesis of Silica Gel-Supported Nickel Catalysts

We used catalysts with different percentages of deposited nickel. Silica gel L 5/40m served as a support. Average particle radius was 5 μm, and specific surface area, 355±5 m^2/g.

Supported nickel catalysts were prepared by nickel nitrate deposition on the support, which was followed by its decomposition and the stage of gas-phase reduction according to the following procedure.

A weighed portion of the support was placed in an aqueous solution of $Ni(NO_3)_2$ (7.5 g of support per 100 mL of solution) and kept under continuous stirring at a temperature of 303 K for 4 h until the adsorption equilibrium was achieved. Next, the support with the $Ni(NO_3)_2$ adsorbed on its surface was filtered off and calcined at 350°C in an argon atmosphere for 3 h until decomposition of nickel nitrate was complete. The resulting deposited nickel oxide was reduced with molecular hydrogen in the gas phase at a temperature of 450°C. The reduced catalyst was transferred to the liquid phase (water or aqueous solutions) in a hydrogen atmosphere, and this was followed by saturation with hydrogen in the liquid phase at 30°C. This technique affords nickel catalysts supported on different substrates with different catalyst loadings achieved by varying the concentration of the initial nickel nitrate solutions [13]. The temperature rising mode for the reduction of the deposited nickel oxide was selected in such a way as to ensure a minimal particle size of the resulting catalyst [13].

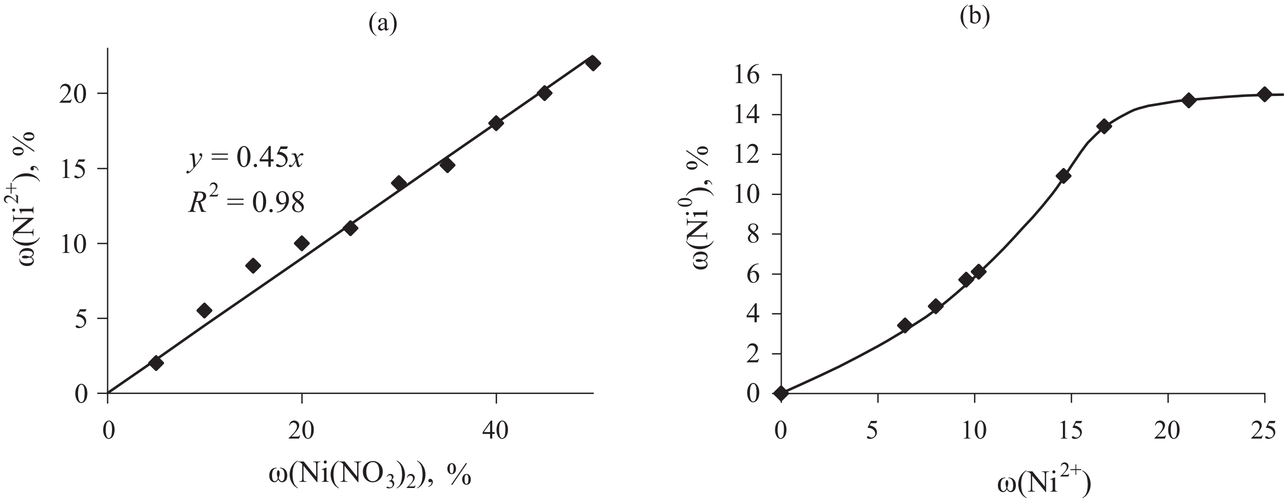

Fig. 1. Nickel deposition on the support: (a) deposited nickel oxide concentration as a function of nickel nitrate solution concentration and (b) active nickel concentration as a function of total quantity of the oxide deposited on silica gel during catalyst reduction in a stream of hydrogen. Reduction conditions: 298–723 K, temperature increase rate 4 K/min.

In this study, a series of silica gel-supported nickel catalysts with different metal loadings were synthesized. Figure 1 presents the plots of the concentration of deposited metal (a) versus the nickel nitrate solution concentration and of the concentration of active metal (b) resulted from reduction of the catalyst in the selected mode versus the total quantity of the deposited oxide.

2.2. *Conditions of Liquid-Phase Hydrogenation Reactions*

Hydrogenation was carried out by the static method, in a closed vessel under vigorous stirring of the liquid phase to avoid the effect of external mass transfer on the experimental results. The design of the liquid reactor enabled measuring the rate of the hydrogenation reaction based on the volume of the hydrogen absorbed during the reaction under vigorous stirring of the reaction mixture. Under the experimental conditions the stirring speed was 60 rps, and the temperature was 30°C. The hydrogen overpressure in the system was 0.8 MPa.

Maleic acid diethyl ester (MADE) was chosen as a compound to be hydrogenated, because, according to the literature [15, 16], the kinetic curves of the liquid-phase reduction of the molecules comprising a carbon–carbon double bond exhibit identical patterns, with the reaction proceeding in one step, without the formation of byproducts.

Water, which is as one of the best studied solvents, was used as a solvent.

Sodium sulfide was chosen as a deactivating agent, since sulfur compounds, in particular, those containing a sulfide ion, are the most-well characterized catalytic poisons able of significantly reducing the activity of hydrogenation catalysts [2, 11]. According to published data [2, 3, 11], the sulfur atoms blocking the active sites on the catalyst surface may provide an instrument for shifting the adsorption equilibrium between the individual forms of adsorbed hydrogen on the catalyst surface. This made sodium sulfide the best candidate for solving the problem set and for fine-tuning the catalytic activity of skeletal nickel within the framework of this problem.

2.3. *Evaluation of the Structural and Mechanical Characteristics of the Catalyst*

The particle size analysis for the obtained catalyst samples was carried out using an Analysette 22 Compact laser particle sizer (Fritsch).

The specific surface area was determined via low-temperature nitrogen adsorption/desorption experiments using a Sorbi MS device by the BET method.

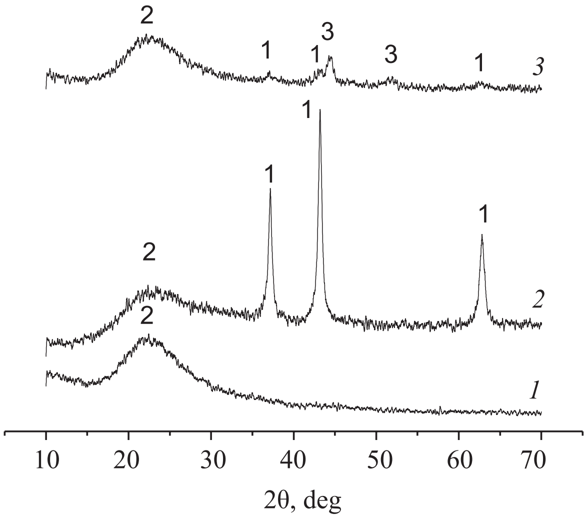

Fig. 2. X-ray diffraction patterns of the catalyst and its precursors: (*1*) pure silica gel, (*2*) 22 wt % deposited nickel (Ni_{tot} in the oxide form), and (*3*) reduced sample 2 to 14.7 wt % Ni°.

X-ray phase analysis (XPA) was performed on a Bruker D8 Advance diffractometer with CuK_α radiation ($\lambda = 0.15406$ nm). Phase identification by X-ray analysis was carried out using PDF-4 database and MINCRYST crystallographic database.

Micrographs were obtained using a TESCAN VEGA 3 scanning electron microscope. The SE images were used for analyzing the morphology of the catalyst particles, and the images obtained in BSE mode, for determining the size dispersion of the nickel agglomerates. For estimating the average size of the nickel agglomerate, measurements were taken from images of 200 particles.

2.4. Technique of Experimental Measurement of the Reduced Metal Quantity

The quantity of the reduced metal deposited on the support was determined as follows. The catalyst was reduced as described above (see 2.1). Further, immediately after reduction at a temperature of 450°C the entire system was saturated with argon without disassembling the reactor. After the system was saturated with argon, the gas flow rate was set at 20±5 cm^3/min. Next, temperature rising from 450°C to 600°C under continuous supply of argon to the system was started; gas was removed from the system through a water seal; the rate of temperature increase was 2°C/min. Upon reaching the temperature of 600°C the reactor was cooled to 25°C. Heating under argon afforded hydrogen desorption from the catalyst surface [17].

After cooling to 25°C the catalyst was transferred under a water layer into a resealable reactor with double-walled glass jacket for circulation of the coolant (water thermostated at 25°C). A burette system was connected to the reactor for measuring the volume of gas in the system, and argon supply to displace air from the system was turned on. After air was displaced from the system, the argon supply was turned off, the system was hermetically sealed, an HCl solution was introduced into the system without loss of sealing, stirring was switched on, and the quantity of the evolved gas was measured.

The mass of the catalyst used in the experiment was 1–5 g, the mass of distilled water, 50 g, and the volume of the HCl solution, 20 mL ($\rho = 1.2$ g/mL).

As known [18], in the reaction with hydrochloric acid only reduced nickel will give molecular hydrogen; in other cases no gaseous products will be formed under the actual conditions. Thus, based on the quantity of hydrogen evolved (data on the volume were normalized to standard conditions) the quantity of the reduced nickel could be calculated.

3. RESULTS AND DISCUSSION

In this study, the structural and mechanical properties of the synthesized catalyst samples were examined in relation to the nickel loading. Figure 2 presents examples of X-ray diffraction patterns of the catalysts and their precursors (reflection no. 1 NiO, no. 2 silica gel, and no. 3 Ni).

The X-ray diffraction data show that, as the concentration of the deposited nickel oxide increased from 4.7 to 23.2 wt %, the size of the coherent scattering regions (CSRs) increased from 7.0 to 18.0 nm, and the degree of crystallinity of the deposited oxide increased as well. It should be considered that the CSR size is typically smaller than the crystallite size, since it does not include the outer amorphisized crystallite layers [19, 20]. Upon the catalyst reduction with hydrogen under the conditions indicated, the characteristic peaks of nickel oxide became insignificant, and reflections corresponding to metallic nickel appeared.

As experimentally proven [4, 21], the activity of a nickel catalyst is determined by the structure of its surface containing crystallites with interplanar spacings of 5.6 Å; for skeletal nickel, peaks at 2θ = 54° and 43° correspond

Table 1. Synthesis conditions and structural and mechanical properties of the catalysts

Run no.	Mass of $Ni(NO_3)_2$ per gram of SiO_2 in solution	S_{sp}, m^2/g	Active metal quantity, %	Catalyst particle radius, μm	Crystallite size, nm	Interatomic distances, Å	Average sizes of nickel agglomerates, nm
1	6.7	264	14.7	5	17.7	7.4	146
2	4.3	317	10.9	5	15.5	6.8	127
3	2.2	362	3.4	5	10.0	5.5	116

to such crystallites; the crystallite size in this case is 130–160 Å. The X-ray diffraction patterns (see examples in Fig. 2) show that, in this study, the reduction of the NiO/SiO_2 samples resulted in conversion of 70% of the deposited oxide to metallic nickel having the structural properties characteristic of the active surface. Table 1 summarizes the main structural and mechanical properties of the catalyst samples and their synthesis conditions.

The present experimental results and published data [4, 7, 13] indicate that the catalytic activity of supported nickel catalysts exceeds several times that of a Raney-type skeletal nickel catalyst. For example, in the liquid-phase hydrogenation of MADE under similar conditions on supported nickel (active metal concentration 10%) the activity of supported nickel catalysts exceeded more than 5-fold that of skeletal nickel. Figure 3 shows the kinetic curves for the reaction of MADE reduction on supported nickel for different active metal quantities. The quantity of the hydrogenated compound corresponded to 200 cm^3 of hydrogen, which was sufficient for assessing the catalyst activity according to the technique of measuring the activity of catalytic systems [22].

The activity of the catalysts was calculated as the observed rates at degrees of conversion of 0.2. It varied in a complex, nonmonotonic manner, but nevertheless symbatically, with the quantity of deposited nickel. In turn, the latter and the sizes of the nickel crystallites and of the nickel agglomerates also varied symbatically with each other. The experimental kinetic data obtained in this study can be explained by a change in the accessible catalyst surface area because of pore blocking at high nickel concentrations, as well as by a shift of equilibrium for individual adsorption forms of the reactants, mainly of hydrogen. Also, enhanced crystallinity of the particles and the overall increase in the volume of nickel in a particle should lead to higher lability of the hydrogen adsorbed and absorbed by the metal [23]. Obviously [8, 9], this should also cause enhancement of catalyst activity.

The kinetic data indicate that the catalytic systems with different active metal loadings did not exhibit strictly symbatic variation of the observed activity parameters with the quantity of the deactivating agent added per gram of nickel. Moreover, it was shown previously for catalyst deactivation by sulfur [11] that, upon adding one sulfur atom per 8 surface nickel atoms, a skeletal nickel catalyst completely lost its activity. In our experiments, deactivation of the catalyst required a 3–5-fold increase in the Ni : S ratio on the catalyst surface. The sulfur adsorption was irreversible in both cases, which is partly attributable to sulfur adsorption on the nickel-free silica gel surface and on the unreduced nickel oxide. This was confirmed by selected experiments, but, nevertheless, the deposited nickel greatly surpassed the bulk catalysts

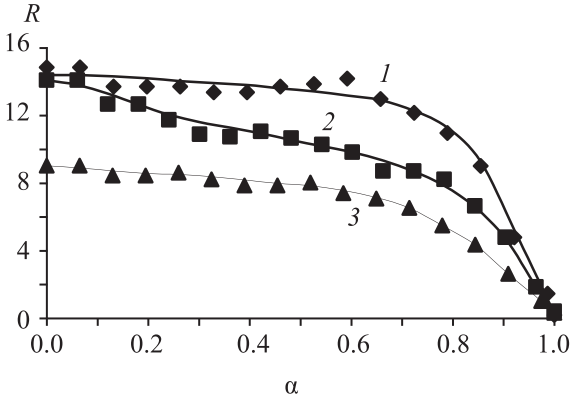

Fig. 3. Rate of hydrogen absorption in the reaction of MADE hydrogenation in water on the catalyst samples containing different quantities of the reduced metal. *R*, $cm^3(H_2)/s$ g(Ni) is the reaction rate, α, degree of conversion (*1*–*3*) quantity of reduced metal, %: (*1*) 14.7, (*2*) 10.9, and (*3*) 3.4. Hydrogenation conditions: $T = 30°C$; $m_{cat} = 2.177$ g; hydrogen overpressure 0.8 MPa.

Table 2. Activity of the catalysts in the reaction of reduction of the carbon–carbon double bond at conversion degrees of 0.2 in water at a temperature of 303 K and hydrogen overpressure of 0.8 MPa

Quantity of Na_2S added, mmol/g Ni	R_{obs}, $cm^3(H_2)/(min\ g(Ni))$	k_{obs} for MADE, s^{-1}	H_{ads}^{max} : S	Ni° : S	Fraction of sulfide-free active surface area, %
		Ni° 14,7 %/SiO_2			
0.00	15.31	590	1 : 0	1 : 0	100
0.21	14.24	449	1 : 0.6	1 : 0.11	89
0.42	8.01	252	1 : 1.2	1 : 0.22	78
0.63	4.93	155	1 : 1.8	1 : 0.33	67
0.84	2.61	82	1 : 2.4	1 : 0.44	56
		Ni° 10.9 %/SiO_2			
0.00	14.52	458	1 : 0	1 : 0	100
0.1	6.14	193	1 : 0.28	1 : 0.058	94.2
0.2	3.07	96	1 : 0.57	1 : 0.11	89
0.3	1.61	50	1 : 0.86	1 : 0.17	83
0.4	0.87	27	1 : 1.15	1 : 0.23	77
		Ni° 3.4 %/SiO_2			
0.00	6.2	346	1 : 0	1 : 0	100
0.5	5.29	167	1 : 1.43	1 : 0.73	27
1.0	3.33	105	1 : 2.87	1 : 1.46	0
1.5	1.58	49	1 : 4.31	1 : 2.2	0

in stability. The activity parameters of the partially deactivated Ni/SiO_2 and the corresponding atomic ratios in the catalytic system are listed in Table 2.

Table 2 presents the ratios of the metallic nickel atoms, sulfur atoms, and maximum hydrogen adsorption. According to different literature sources [24, 25], depending on the type of the single crystal faces, the nickel surface can contain from 1.14×10^{19} to 1.86×10^{19} atoms/m^2 (calculation was based on the average value). The maximum quantity of reactive hydrogen was determined using thermal analysis combined with mass spectrometric analysis, as well as by the method of adsorption calorimetry (see [26] for details of the procedure). Joint analysis of the catalyst activity and the fraction of the sulfide-free active metal surface area revealed easier deactivation of the catalyst at decreased nickel metal concentration on the catalyst surface. The Ni° : S atomic ratios in almost all the systems were less than unity, indirectly confirming the proceeding of sulfur adsorption on metallic nickel in a monomolecular layer. When the catalyst surface was deactivated with the sulfide ions occurring in the proportion of one sulfur atom per two nickel atoms, the catalyst activity decreased by 90% and was not subsequently restored.

Figure 4 shows the SE images of the surface of the nickel deposited on SiO_2 before reduction (a), after reduction (b), and after deactivation (c). The catalysts were dominated by particles of irregular polyhedral shapes with a sufficiently smooth surface, having 5 μm diameters.

Our experiments showed that, during the synthesis process, as a result of the preliminary catalyst saturation with hydrogen in the reactor, the proceeding of the MADE reduction reaction, and catalyst deactivation by the sulfide ion, the catalyst surface underwent certain changes. Specifically, the surface roughness increased, and the sizes of the agglomerates and of the crystallites decreased. However, by contrast to bulk nickel catalysts, the particle radius distribution functions changed noticeably (the distribution maximum shifted to particles with a smaller radius [13]); the particle radius distribution function of the catalyst samples changed negligibly in each stage of the catalyst synthesis procedure and during MADE hydrogenation, with the average size of the catalyst particles remaining equal to 5 μm. The results obtained were interpreted in the context of adsorption-induced deformation of bulk metal catalysts and nearly complete inertness of the support particles to the processes

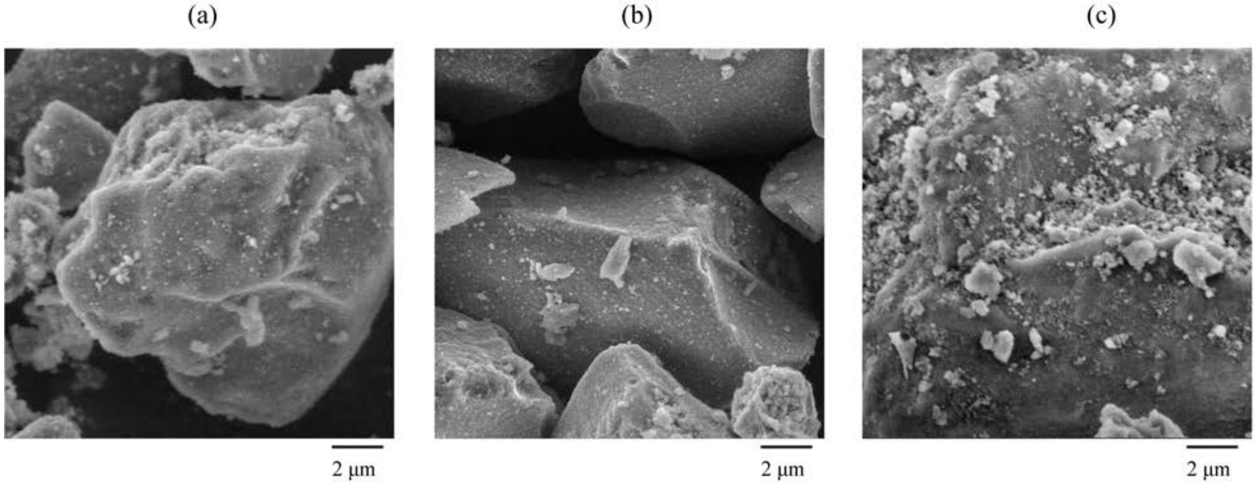

Fig. 4. SEM images of the catalyst samples: (a) NiO/SiO_2, (b)Ni/SiO_2, and (c) Ni/SiO_2 upon addition of 0.63 mmol (S^{2-})/g (Ni°) (in all the samples $\omega(Ni_{tot})$ = 22 wt %; in sample (b) ω(Ni°) = 14.7%; field of view 15.7 μm).

occurring during the synthesis and in the course of the hydrogenation reaction. The linear dimensions of the support particles changed negligibly, but the particle surface still underwent significant changes. Importantly, adsorption-induced deformation affected specifically nickel agglomerates, i.e., deformation was manifested exactly at sites, where the hydrogenation reaction took place. The effect of changes in the catalyst surface structure under the influence of different hydrodynamic regimes, increased pressure, specific nature of the solvent, adsorption of the reactants, proceeding of hydrogenation reactions, and the deactivation process can be called the relative structure sensitivity of the catalyst. The latter can be numerically expressed as the fractal dimension of the surface of the studied $Ni°/SiO_2$ samples after proceeding of one of the technological processes, related to the fractal dimension of the fresh catalyst. In practice, this effect consisting of a change in the structural and mechanical properties of transition metal-based catalyst surface under the process conditions adequately explains many of the kinetic regularities of liquid-phase hydrogenation reactions. A correlation between the numerical values of the relative structure sensitivity of the catalyst and the reaction conditions allows predicting the reaction rate and the shape of the kinetic curves.

A weakly pronounced change in the effect of relative structure sensitivity makes it possible, using the technique proposed in [3, 10, 11], to employ supported nickel catalysts for experimental determination of the reactivity of individual active surface sites and of the reactant molecules attached to such sites. This, in turn, will enable predicting the selectivity of nickel catalysts in the liquid-phase hydrogenation reactions.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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