

SECOND INTERNATIONAL CONFERENCE
ON HIGHLY ORGANIZED CATALYTIC SYSTEMS
(MOSCOW, JUNE 14–17, 2004)

Unusual Catalytic Properties of Nanostructured Nickel Films Obtained by Laser Electrodispersion

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Received November 12, 2004

Abstract—Nanostructured nickel films deposited by laser electrodispersion onto a silicon (semiconducting) or thermally oxidized silicon (insulating) substrate show a remarkably high catalytic activity (of the order of 10^3 – 10^4 (mol product) (mol Ni)^{−1} h^{−1}) in the isomerization of chlorinated hydrocarbons and olefin hydrogenation. The special properties of the laser-deposited films are likely due to the small size (2.5 nm), developed surface, and amorphism of the nickel particles, as well as to highly active, charged particles appearing on the insulating substrate. The latter result from thermal fluctuations of electrons between closely spaced particles. In a film deposited on silicon covered with a natural oxide layer, a significant role is also played by charge redistribution between the substrate and metal particles.

DOI: 10.1134/S0023158406040203

The deposition of monodisperse metal clusters onto insulating substrates by the laser electrodispersion [1] has revealed some essential features of catalysis by nanostructured films. These features are manifested in a variety of reactions involving halogen derivatives and are the following: abnormally high catalytic activity, peaking dependences of the catalytic activity on the metal content and on the distance between nanoparticles, and a strong dependence of the reaction rate on the dielectric constant of the medium [2, 3]. These specific features were observed for metal–polymer composites [4, 5]. The totality of data obtained led us to recognize the important role of the specific charge states of nanoparticles in the electron exchange between the catalyst and the reactant. Charged particles appear in metal films at a certain surface coverage (or a certain surface density of particles) as a result of thermally stimulated tunnel electron transfer between closely spaced particles. The spontaneous charging of particles can markedly reduce the activation energy of the key step of a catalytic reaction that includes electron transfer [6]. Based on our results [2–6], we formulated the following statements, which are believed to be of importance for a correct description of catalysis by nanostructured films.

(1) Along with the dependence of catalytic activity on the nanoparticle size R , which is a well-known size effect, there is another kind of size effect, namely, the dependence of catalytic properties on the surface density of particles or on the mean interparticle distance L .

The effect of particle density comes into play once the threshold value of L is reached, when electron redistribution between neighboring particles is possible.

(2) If a significant electron redistribution between the catalyst and the reactant takes place in the transition state of the rate-determining step (i.e., if the reaction is sensitive to the charge occurring on the catalyst), then an increase in the surface density of particles and the related increase in the number of charged states in the ensembles of closely spaced particles will cause a dramatic enhancement of catalytic activity.

(3) Further raising the surface density of particles to an extent that L is below its optimum value causes the formation of extensive conducting aggregates of metal particles. The number of charged particles in the nanoparticle system decreases, and, accordingly, the catalytic activity falls.

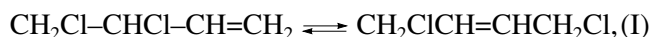
Obviously, along with particle size and particle distribution on the surface or in the bulk of the support, another significant factor in the formation of charge states and in catalytic activity is the nature of the metal and the support. The above density effects have been observed for copper nanoclusters fixed on supports and in matrices with pronounced insulating properties, namely, on the oxidized silicon surface [2, 3] and in the polymer matrix of poly-*para*-xylylene [4, 5].

The purpose of this study is to elucidate the specific features of the formation and kinetic behavior of nickel nanoparticles deposited by laser electrodispersion on

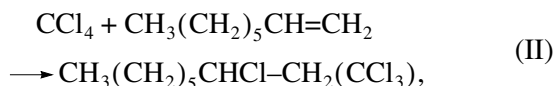
two types of silicon substrates, specifically, silicon covered with a thick film of SiO₂ obtained by thermal oxidation and unoxidized silicon. In the case of a thick, insulating SiO₂ film, Ni particles, which form a rather dense coverage on this film, can exchange electrons only among themselves. In the case of Ni particles on silicon covered with a thin (1- to 2-nm), tunneling film of natural oxide, a particle can gain a charge either by the interparticle tunneling of electrons or by tunneling electron transfer between this particle and the semiconductor bulk. Because of the difference between the work functions of Si and Ni, the substrate can exert a strong effect on the charge state of the metal nanoparticle system. If this is the case, the catalysts supported on these two types of substrates will have different properties.

Nanostructured Ni films were obtained by laser electrodispersion. A specific feature of this method is that a flow of nanoparticles with a fixed size results from the dispersion of metal in the laser plasma torch. These particles are initially in the liquid state. Leaving the plasma, they cool rapidly, so that the solid nanoparticles being deposited on a substrate are amorphous and are uniform in size and shape. Another essential feature of this method is that, at the instant the particles precipitate onto the substrate, their charge is nonzero, and this fact determines, to a considerable extent, the structure of the resulting coverage. Deposited metal particles undergo partial oxidation when in contact with air; however, complete oxidation is not observed even for copper particles [7]. These specific features of the nanostructured metal coatings obtained by laser electrodispersion impart unique catalytic properties to these coatings.

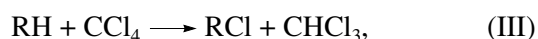
In this study, as in earlier studies on copper films [2–6], the catalytic properties of nickel films were evaluated for the following reactions: the allylic isomerization of 3,4-dichlorobutene-1 into *trans*-1,4-dichlorobutene-2,



the addition of carbon tetrachloride to the double bond of octene-1,



and the reaction between carbon tetrachloride and decane,



where R = C₁₀H₂₁.

The catalytic properties of the nickel films were compared to those of other catalysts in nonene-1 hydrogenation (reaction (IV)).

EXPERIMENTAL

Immobilized nickel nanoparticles were deposited by the laser electrodispersion method [1] onto polished, boron-doped, *p*-type Si(100) wafers. The wafers were either thermally oxidized or not heat-treated. The preliminary oxidation of Si wafers is described elsewhere [2]. The thickness of the thermal SiO₂ film was ~0.5 μm. The surface of untreated Si wafers was covered only with a natural oxide film no thicker than 1–2 nm. These two kinds of substrate are hereafter designated SiO₂/Si and Si. After films were deposited *in vacuo*, the substrates were stored in air.

An important advantage of laser electrodispersion as applied to the deposition of metal particles onto a substrate is that, according to earlier estimates, the weight fraction of metal in atomic form does not exceed 1% [1]. This is due to the marked difference between the specific energies of the melting and sublimation of nickel. Under real film formation conditions, the accumulation of individual atoms on the nanoparticle surface is energetically favorable, so the actual fraction of free atoms on the substrate is still smaller. This small proportion of atomic metal will not exert any significant effect on the rate of catalytic processes.

The mean size, size variance, and surface density of nanoparticles were determined by statistical processing of transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) images using low-density Ni films. The particle density on the substrate surface or the amount of deposited metal was varied in a wide range by varying the deposition time. The film thickness and, hence, the time needed for the deposition of one particle layer were determined by atomic force microscopy (AFM).

The amount of supported metal was also determined by atomic absorption spectrometry. For example, it was found by this method that, after a 30-s-long nickel deposition run (which results in a particle density of $1 \times 10^{13} \text{ cm}^{-2}$, lower than the density of a monolayer), the metal content of the film is $(5 \pm 2) \times 10^{-4} \text{ wt } \%$. Note that the large error in the atomic absorption analysis of the thin films is due to the very low metal content. Nevertheless, the analytical data are in satisfactory agreement with the estimate based on TEM particle size and density data under the assumption that each particle contains ~400 Ni atoms. It was found that the metal content of the film is proportional to the deposition time.

The oxidation resistance of the nanostructured Ni films was evaluated using a procedure reported in detail by Kozhevnikov et al. [7]: the longitudinal (in-plane) conductivity of the film was monitored while exposing the film to air. A test sample was a metal film deposited between chromium contact pads preliminarily fabricated on the SiO₂/Si substrate. Measurements were taken at room temperature.

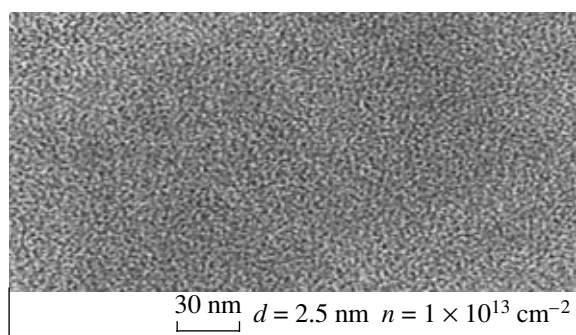


Fig. 1. TEM image of a nickel film with a particle density of $1 \times 10^{13} \text{ cm}^{-2}$ (deposition time 30 s).

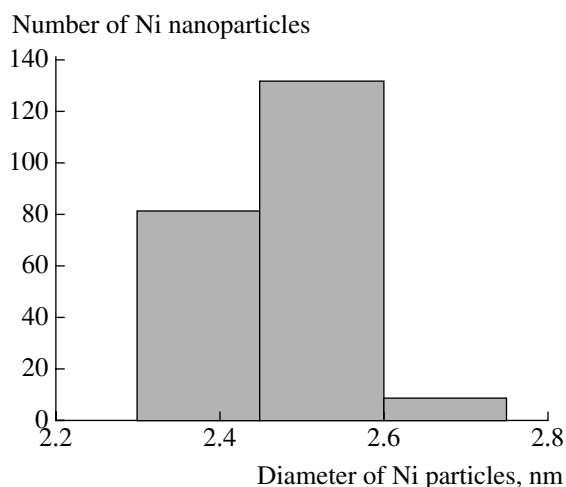


Fig. 2. Particle-size distribution in nickel films.

For comparison, we tested a commercial catalyst produced by Nippon (5 wt % Pd on graphite) and supported nickel catalysts prepared using two different procedures. A catalyst containing 2 wt % nickel (2% Ni/SiO₂) was obtained by the impregnation of silica gel (KSK-2) with nickel nitrate followed by reduction. The other nickel catalyst was prepared by metal vapor synthesis (Ni-MVS) using a procedure similar to that described in [8]. Nickel vapor and excess triethylamine were condensed on the surface of a glass reactor cooled to 80 K. The amine-to-metal ratio was varied between 100 : 1 and 1000 : 1 and had only a slight effect on the properties of the resulting particles. After condensation, the sample was warmed. The melting of the mixed condensate yielded a stable colloidal dispersion of the metal. According to TEM data, the dispersion was made up of 25- to 80-nm particles (which accounted for at least 90% of the metal) and the particle-size distribution peaked at 40 nm. The metal sol was transferred into a vessel containing a support (γ -Al₂O₃ with $S_{\text{sp}} = 140 \text{ m}^2/\text{g}$ or the macroporous silica gel KSK with $S_{\text{sp}} = 220 \text{ m}^2/\text{g}$). The resulting slurry was vigorously stirred

at room temperature for 4 h. The solution was decolorized because of the precipitation of the ultrafine metal particle onto the surface. Triethylamine was then removed *in vacuo*. The metal content of γ -Al₂O₃ and KSK was 0.3 and 1 wt %, respectively.

The reaction (I) and (III) conditions and product analysis are detailed elsewhere [2]. Nonene-1 (2–5 ml) was hydrogenated in an autoclave at room temperature and a hydrogen pressure of 10 to 40 atm. Kinetic control was ensured by vigorous stirring. The amount of metal in the reaction mixture was 10^{-8} – 10^{-10} mol. The activity of a catalyst in the conversion of chlorinated hydrocarbons was calculated as the ratio of product formed in 1 h to the amount of metal minus the catalytic activity of the substrate [2]. The yield of hydrogenation products in blank runs did not exceed 1%. Catalytic activity was determined with an accuracy of 15%.

RESULTS AND DISCUSSION

Structure of Nickel Films

Figure 1 visualizes the structure of a nickel film obtained by laser electrodispersion (deposition time 30 s). A statistical analysis of micrographs has demonstrated that the mean diameter of the nickel nanoparticles is $d = 2.5 \text{ nm}$ and the relative scatter of particles sizes is below 10% (Fig. 2). These data are in good agreement with STM data. Note that the size of the particles produced by laser electrodispersion depends only on the nature of the metal and is independent of the film deposition time. As compared to copper particles, whose mean size is $5 \pm 1 \text{ nm}$ [2], nickel particles are smaller and their size is scattered less widely. Using a transmission electron microscope, we obtained electron diffraction patterns for the nickel films. The absence of well-defined diffraction fringes is evidence that the nickel films, like copper films [7], consist of amorphous nanoparticles. As determined by AFM measurements of the Ni film thickness as a function of deposition time, the deposition time for a particle monolayer is approximately 80 s.

The size of nanoparticles and their surface distribution are the same for SiO₂/Si and Si substrates. Nanoparticles cover the surface rather uniformly, with a constant mean surface density n . However, even if the surface is incompletely covered, particles are aggregated into chains consisting of 15–20 ones (Fig. 1). The particle spacing in these aggregates is generally no wider than 2 nm. A similar situation is also observed for a shorter deposition time of 15 s. This uniform surface coverage is typical of nanostructured films prepared by laser electrodispersion and is due to Coulomb interaction between metal particles. The particles gain a charge in the laser plasma torch and retain it until deposition onto the substrate.

Because the nickel particles are small and capable of aggregation, the films are conducting even at short deposition times (15 s) and low surfaces coverages (~20%).

Their conductivity increases almost by 10 orders of magnitude as a particle monolayer is formed (Fig. 3). Since the tunneling transfer of electrons takes place in the films, the conductivity of a film depends very strongly on the particle size and on the interparticle gap condition. Therefore, measuring the evolution of the conductivity of a film being exposed to air provides a fine means of evaluating the oxidation rate of the particle surface. The oxidation of nickel nanoparticles in air proceeds at a very low rate, and it takes approximately 3 months for an invariable conductivity to be reached (Fig. 4). Thus, the nickel films obtained by laser electrodispersion are sufficiently stable for gaining reliable information concerning their catalytic activity.

Catalytic Properties of Nanostructured Nickel Films

Nanostructured nickel films on both SiO₂/Si and Si are active catalysts in all of the four test reactions (I)–(IV). Intercomparing the laser-deposited Ni films obtained under different conditions and comparing these films to other catalysts (Tables 1–3) shows that the catalytic activity of the nickel films in terms of product yield is extraordinarily high, exceeding the activity of conventional catalysts by 2–4 orders of magnitude. Reaction (III) and (IV) do not occur at all on the supported nickel catalysts 2% Ni/SiO₂ and Ni-MVS.

As is clear from the diagram presented in Fig. 5, the catalytic activity of the nickel films in the isomerization reaction (I) is similar to the activity of structured copper films [2, 3]. At the same time, the supported nickel catalysts prepared by conventional methods are much less active. This is also true for the reactions involving CCl₄ (reactions (II) and (III)). For example, the activity of the supported copper catalysts in reaction (II) is as low as ~10 (mol product) (mol Cu)^{–1} h^{–1} [2]. Moreover, the N-MVS catalysts are inactive under the same conditions. Therefore, of special interest is the fact that the catalytic activities of the nanostructures nickel and copper films are comparable. One reason why the laser-deposited nickel films are more active than their copper counterparts is that a nickel nanoparticle is approximately half as large as a copper nanoparticle. Apparently, the effect of nanoparticle interaction discussed above is

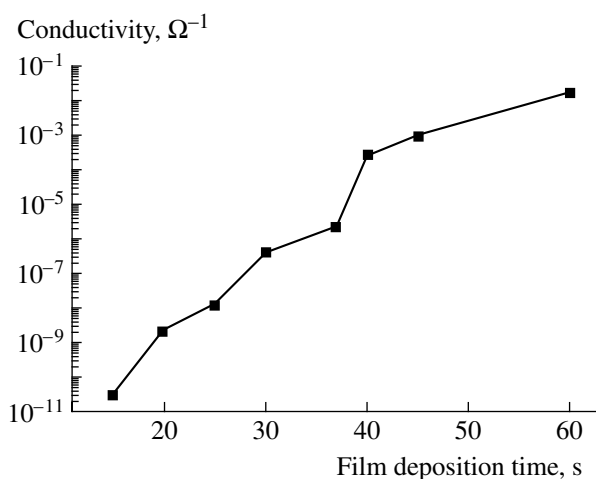


Fig. 3. Conductivity of a nickel film as a function of deposition time.

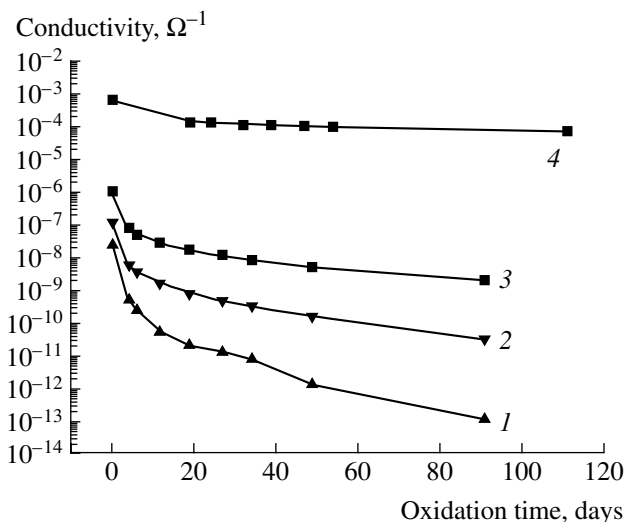


Fig. 4. Variation of the conductivity of nickel films exposed to air. The film deposition time is (1) 20, (2) 25, (3) 30, and (4) 40 s.

equally significant: this interaction dramatically enhances the catalytic activity of the nanostructured film by producing high-efficiency charged states. In the

Table 1. Catalytic properties of nickel films and 2% Ni/SiO₂ in 3,4-dichlorobutene-1 isomerization (reaction (I))

Catalyst	Deposition time, s	Amount of Ni, mol × 10 ⁹	1,4-Dichlorobutene-2 yield		Activity × 10 ^{–4} , (mol product) (mol Ni) ^{–1} h ^{–1}
			%	mol × 10 ⁴	
Ni/Si	15	1.23	14	1.29	5.0
	30	2.45	19	1.75	3.6
Ni/SiO ₂ /Si	15	1.23	19	1.75	7.1
	30	2.45	5	0.46	0.9
2% Ni/SiO ₂	–	9800	11	1.01	5 × 10 ^{–4}

Note: Reaction time, 2 h; 110°C; reactant concentration, 9.2 mol/l; reaction volume, 0.1 ml; catalyst weight, 0.03 g.

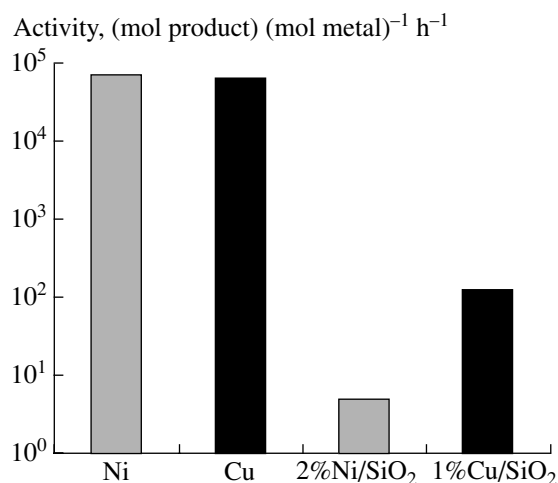


Fig. 5. Catalytic activity of copper and nickel films (surface density of particles, $(4-5) \times 10^{12} \text{ cm}^{-2}$; deposition time, 5 min and 15 s, respectively) and of the supported catalysts 1% Cu/SiO₂ and 2% Ni/SiO₂ in the isomerization reaction (I) at 110°C.

case of nickel nanoparticles, which are smaller and show a greater tendency to aggregation than copper nanoparticles, the particle interaction effect may be rather strong, particularly in Ni films on insulating substrates.

The effect of the substrate (SiO₂/Si or Si) on the catalytic properties of the nanostructured nickel films is most clearly manifested in the isomerization reaction (I). As the deposition time is lengthened from 15 to 30 s, the activity of the Ni/Si film decreases by a factor of 1.4 and the activity of the same film on SiO₂/Si decreases approximately by one order of magnitude, even though the size of individual particles in the film is unchanged (Table 1). In both systems, as the mean particle density increases, catalytic activity begins to fall at a surface coverage at which the film conductivity increases (Fig. 3), indicating an increase in the size of conducting aggregates. Once the aggregates have grown to the optimum size, the number of charged particles and catalytic activity start to decrease, as in the case of copper nanoparticles [2].

The fact that the catalytic activities of the films deposited on SiO₂/Si and Si depend differently on the surface density of particles will be understandable if it is taken into consideration that these substrates differ in terms of the charge state of supported particles. At a high particle density, a considerable proportion of particles on the insulating substrate SiO₂/Si are charged owing to the interparticle tunneling of electrons [3, 6]. The net balance of positive and negative charges is such that the system as a whole is electrically neutral. A different situation is observed for metal deposited on Si. As is mentioned above, the silicon surface under ordinary conditions is covered with a dense film of natural

Table 2. Catalytic properties of nickel films and 2% Ni/SiO₂ in the reactions between CCl₄ and octene-1 (reaction (II)) and between CCl₄ and decane (reaction (III))

Reaction	Catalyst	Reaction conditions		Catalyst weight, g	Amount of Ni, mol	Product yield		Activity, (mol product) (mol Ni) ⁻¹ h ⁻¹
		T, °C	time, h			%	mol × 10 ⁴	
(II)	Ni film	130	2	0.03	2.45×10^{-9}	26	0.31	6370
	2% Ni/SiO ₂	130	2	0.006	1.97×10^{-6}	7	0.08	2
(III)	Ni film	150	3	0.02	1.63×10^{-9}	6	0.20	410
	Ni film	150	3	0.03	2.45×10^{-9}	10	0.34	460

Note: Ni film deposition time, 30 s; [CCl₄] = 9.5 mol/l for reaction (II) and 6.9 mol/l for reaction (III); [C₈H₁₆] = 0.6 mol/l; [C₁₀H₂₂] = 1.7 mol/l; volume of each reactant, 0.2 ml.

Table 3. Catalytic properties of nickel films in nonene-1 hydrogenation (reaction (IV)) at room temperature

Catalyst	Deposition time, s	Catalyst weight, g	Amount of reactant, mol	H ₂ pressure, atm	Reaction time, h	Product yield, %	Activity × 10 ⁻⁴ , (mol product) (mol Ni) ⁻¹ h ⁻¹
Ni/Si	15	0.34	0.014	40	5	30	6.0
Ni/Si	30	0.36	0.014	40	10	57	2.8
		0.74	0.029	40	6	39	3.1
		0.77	0.012	20	6	88	2.8
		0.73	0.029	10	6	10	0.8
		0.07	0.014	40	10	3	0.7

oxide no thicker than 1–2 nm. The probability of an electron tunneling through this film is rather high, so tunneling electron transfer takes place both between particles and between a particle and the substrate. Since the semiconductor and the metal are characterized by different work functions, the electrical equilibrium in the system of particles is shifted. It can be assumed that it is due to this shift of charge equilibrium that identical structures supported on the insulating and semiconducting substrates show different behaviors.

The role of the conducting substrate in the other reactions examined is not so obvious. The catalytic activity of supported nickel particles in the initiation of the free-radical chain reactions involving CCl_4 (reactions (II) and (III)) depends only slightly on the nature of the substrate and on the surface coverage. The role of the Coulomb interaction between copper particles is also less pronounced in these reactions than in the isomerization of chlorinated olefins [2, 3]. However, the data presented in Table 2 clearly indicate that the structured nickel films on the silicon substrates are highly active in carbon tetrachloride conversion.

Another example illustrating the high activity of nanoparticles obtained by laser electrodeposition is olefin hydrogenation on the nickel films, which proceeds at a high rate even at room temperature (Table 3). The process rate and catalytic activity are independent of hydrogen pressure starting at 20 atm. The activity of the nickel film increases as the deposition time is shortened and is higher for the Si substrate than for oxidized silicon. As is clear from the diagram presented in Fig. 6, the activity of the films examined is higher than the activity of conventional Pd-based catalysts by more than one order of magnitude. No nonene hydrogenation products were detected for the other types of supported nickel catalysts. The high activity of the Ni/Si nanoparticles can be due to the above-noted charge redistribution between these particles and the substrate. In the case of a *p*-type silicon, small clusters on the substrate surface can have a low positive charge, favoring the hydrogenation reaction [9].

The catalytic activity of the nanostructured nickel films prepared by laser electrodispersion, as well as the activity of structurally organized copper films [2–6], generally exceeds the activity of catalysts prepared by conventional methods, including metal vapor synthesis. In some cases, the difference in activity is four orders of magnitude. Obviously, the factors causing this great difference include an ordinary size effect: depending on the type of catalyst, the size of nickel particles varies over an order of magnitude. At the same, the difference is too large to be accounted for by an ordinary size effect alone. It is very likely that a size effect of another kind is significant here: a short distance between small particles brings about specific charge states of the system of nanoparticles. Earlier calculations [6] suggest that the smaller the particle size, the better pronounced the role of charge states in reac-

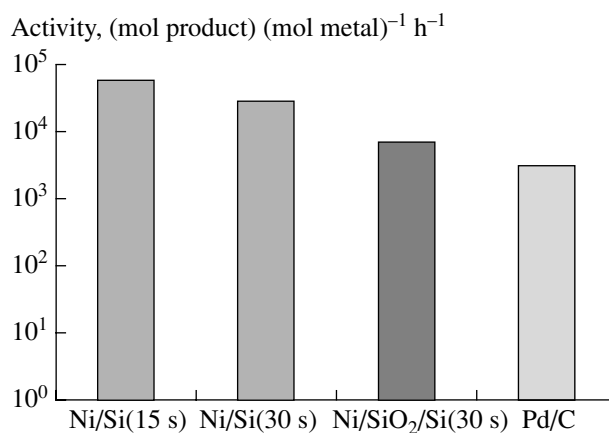


Fig. 6. Catalytic activity of nickel films (deposition time 15 and 30 s) and of the supported catalyst 5% Pd/C in nonene-1 hydrogenation at room temperature and hydrogen pressure of 40 atm.

tions that include electron transfer from the catalyst to the reactant. It is possibly due to this effect that the nanostructured nickel films examined here are comparable in catalytic activity with copper films, which are generally more active in conversions of chlorinated hydrocarbons involving an electron transfer step [9, 10].

The size effect in the mutual charging of closely spaced particles at optimum surface coverages is less likely for catalysts prepared by dispersion techniques producing particles randomly distributed on the surface [11]. The high activity of the nanoparticles formed by laser electrodispersion is likely due their small size, developed surface, and amorphous state. Another factor in their activity is that they are charged as a result of the thermally stimulated tunneling of electrons between particles or between a particle and the surface, an effect taking place in structured films with a high particle density. Further experimental and theoretical studies are necessary to answer the question as to the participation of conducting (semiconducting) substrates in the redistribution of electron density in ensembles of nanoparticles. However, it has already been demonstrated that conducting substrates that are in tunnel contact with a system of metal particles, along with insulating substrates, open up new opportunities for controlling the charge state of the metal and for designing catalysts with desired properties.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 02-03-32609), the RF Ministry of Science and Education (Physics of Solid-State Nanostructures Program), the Department of Physical Sciences of the Russian Academy of Sciences (Fundamental Research Program "New Materials and Structures"), and the International Science and Technology Center (grant no. 2955).

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