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Nanostructured metal films: Fabrication and catalytic properties

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Abstract

Thin nanostructured films consisting of monodispersive and amorphous Cu, Ni, or Pd nanoparticles were prepared by means of laser electrodispersion technique. These films were deposited on dielectric (thermally oxidized silicon) or semiconductor (naturally oxidized Si) supports, and the resulting particle surface density was closely controlled by the time of deposition. The nanoparticle size was 5 nm for Cu, 2.5 nm for Ni, and 2 nm for Pd. In all cases, the relative particle size dispersion was less than 10%. The most important common feature of the fabricated catalysts is their unusually high activity, which has been observed in several test reactions including chlorohydrocarbon conversions (Cu and Ni) and hydrogenation (Ni and Pd). The observed strong dependencies of the catalytic activity on the particle surface density and on the nature of the support clearly indicate that alongside with small particle size and their amorphous state, inter-particle interactions or particle interaction with the support play decisive role in determining the catalytic activity.

Keywords: Thin nanostructured films; Laser electrodispersion technique; Catalytic activity

1. Introduction

Recently the laser electrodispersion (LED) technique [1] has been applied for the deposition of monodisperse copper nanoparticles on a surface-oxidized silicon. The fabricated films were found to be highly active catalysts for the chlorohydrocarbon conversions [2,3]. These catalysts are several orders of magnitude superior in activity (10^4–10^5 product mol/Me mol h) than usual supported copper catalysts (10–100 product mol/Me mol h). An important feature of the catalytic behavior of these films in dichlorobutene isomerization and carbon tetrachloride reactions is that their activity depends strongly on the average distance between nanoparticles or on the particle density on a support. In all cases, the maximum of activity corresponded to the one-layer film consisting of closely packed ensembles of nanoparticles (Fig. 1). The similar data have been obtained previously for Cu- and Pd-polymer nanocomposites [4,5]. The catalytic activity of the ensembles of nanoparticles stabilized both on SiO_2 surface and in polymer matrix is many times higher compared to that for separated copper clusters and highly loaded films (Fig. 2). Other features of nanostructured films are the dependence of catalytic activity on a solvent polarity [2,3] as well as the correlation between their catalytic properties and conduction [4,5]. These results provided support for the view that the interaction between neighboring metal particles may be responsible for the unusual catalytic behavior of nanoparticle ensembles. It was suggested that starting from some threshold inter-particle distance, which entails a sharp change in the system conduction, metal particles become charged. Evidently, the appearance of charged particles can markedly affect the catalytic properties of the system because the chlorohydrocarbon reactions include electron transfer from the catalyst to the reactant molecule [6], and so they are sensitive to charge state of a catalyst. The experimental data are in good agreement with the theoretical estimates indicating that there is an optimum average inter-particle distance at which, due to electron tunneling between closely located particles, the amount of charged particles in one-layer film on dielectric support sharply grows, and

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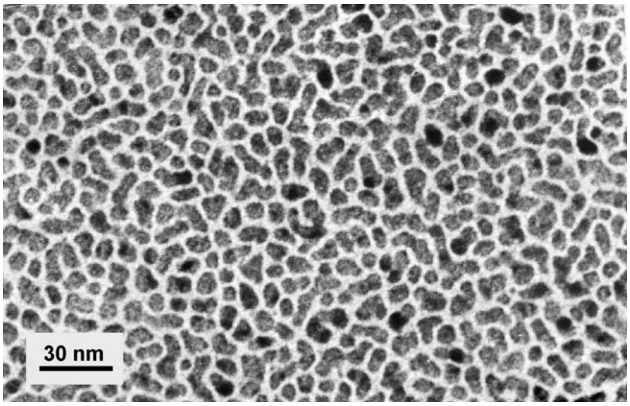

Fig. 1. TEM image of the nanostructured Cu film (deposition time $\tau = 5$ min, particle surface density $n = 4 \times 10^{12}$ cm^{-2}).

charging increases with the growth of both temperature and the dielectric permittivity of a solvent [7]. By this means, in addition to the well-known size effect, an average distance between metal particles determining a possibility of the interaction between nanoclusters may control catalytic properties of the nanoparticle system. This phenomenon named as a new type of size effect [8] opens up a new way for managing the catalytic properties of the nanostructured metal films.

The aim of this paper is to show the advantages of the laser electrodispersion technique for the fabrication of highly active nanostructured metal (Cu, Ni, Pd) films, and to establish common and specific features of their structures and catalytic behavior. The chlorohydrocarbon conversions (chloroolefin isomerization, CCl_4 addition to olefins and its interaction with decane) were taken as test reactions for a comparison of Cu and Ni films. The catalytic activities of Ni and Pd films were also tested in hydrogenation of olefins and aromatic hydrocarbons.

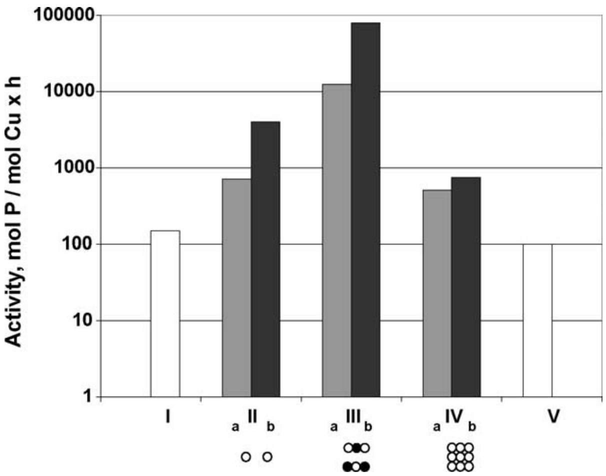

Fig. 2. Catalytic activities of different types of Cu catalysts in dichlorobutene isomerization (1) at 100 °C: (I) small clusters Cu_4L_4; (II) separated nanoparticles stabilized in polymer (a) and on oxidized silicon SiO_2/Si (b); (III) ensembles of nanoparicles; (IV) highly loaded films; (V) usual supported catalyst (1% Cu/silica gel).

2. Experimental

2.1. Laser electrodispersion technique

LED technique [1] has much in common with laser ablation of a metal target but the process parameters (laser pulse power, duration, etc.) are chosen in such a way that the liquid micron-size metal drops are first splashed out from the ablated target surface. Entering the laser torch, these drops become charged, and when their charge reaches the capillary instability threshold, they start to break up. The drop fission proceeds in a cascade way producing new generations of smaller drops, and it stops sharply when the size of secondary drops becomes uniformly small (few nanometer). At the trailing edge of laser pulse, liquid nanometer size droplets cool down at extremely high rate, which turns them into the amorphous solid state. As a result, amorphous metal nanoparticles of spherical shape and of very well-defined size (size distribution is less than 10%) are deposited onto a support surface under the electric field, which is applied to prevent the residual bigger particles from reaching the substrate.

2.2. Catalyst preparation

Cu, Ni, and Pd nanoparticles were deposited on Si supports by means of LED. The amount of the deposited metal, the particle surface density on the support, and consequently film structure were controlled by the deposition time τ. Two kinds of Si supports were used: (i) chemically polished (1 0 0) silicon wafers covered by thin natural oxide (Si) and (ii) intentially oxidized silicon wafers with thick thermal oxide layer on the surface (SiO_2/Si). The thickness of thermal oxide was about 0.5 μm, which ensures good electrical isolation of the deposited particles from the semiconductor substrate. Contrary to this, the thickness of natural oxide layer on Si support was small enough, ~4 nm, allowing electron tunneling between the deposited particles and the substrate.

Usual supported Cu (1 wt%) and Ni (2 wt%) catalysts for test studies were prepared by the impregnation of silica gel by copper or nickel nitrate followed by their reduction or with the use of metal-vapor-synthesis (MVS) [9]. Commercial catalyst 5% Pd/C (Nippon) was also taken for hydrogenation.

2.3. Catalyst characterization

Transmission electron microscopy (TEM) was used to study particle size distribution, structure, and arrangement in the deposited films. The amount of deposited metal was analyzed by means of atom-absorption method. The results were in a good agreement with estimations based on particle size and surface density determined by TEM. For example, the catalysts with the surface particle density $n = 10^{13}$ cm^{-2} contained $(7 \pm 2) \times 10^{-3}$ and $(5 \pm 2) \times 10^{-4}$ wt% of Cu and Ni, respectively.

Film structures were also characterized by measuring their conductance. The samples with a pair of lateral contacts to the granulated films were fabricated by using standard photolithography (the gap between the contacts was equal to 5 μm). The measured conductance was very low in the low-density films increasing sharply when the deposition time was increased up to certain threshold corresponding to the average inter-particle separation about 1 nm. In this case, electron can tunnel between the particles; it results in the measurable current in the film structure. Using the fabricated samples, temporal evolution of the lateral film conductance was measured for the films exposed in air. While the initial film conductance depends on the inter-particle separation (on the deposition time), the oxidation always resulted in the conductance reduction. Obviously this is related with the formation of oxide shells, which enlarge the tunnel barriers between the particles. It was found [10], however, that after a transition period film conductance stabilized at certain final value, at which it remained constant during long-term exposure in air (for at least several months). Measurements of temperature dependencies of the film conductivity indicate that the saturated conductivity is of tunnel type, which means that the cores of nanoparticles are still metallic, while the thickness and the composition of the oxide shells covering these grains remain constant. These results show that the fabricated structures are highly stable against oxidation in ambient atmosphere.

The mean size of the particles involved in the current transfer has been estimated by measuring temperature dependencies of the conductivity (in the range from 10 to 300 K). For the as-made Cu films deposited during 5 min, the temperature dependencies of conductivity were indicative for the presence of considerable spread in the particle sizes [11]. This should be attributed to the formation of particle aggregates (Fig. 1). Contrary to this, when these Cu films were well oxidized, the temperature dependence of the conductivity followed the activation law $\ln \sigma \propto 1/T$. The effective particle size extracted from the slope of this dependence gave the particle size equal to 5 nm, which coincides with TEM data. So, after the oxidation the particle ensembles become electrically disconnected, and they keep their individual characteristics even being densely packed. Similar data were obtained for Ni- and Pd-films.

2.4. Catalytic reactions

Chlorohydrocarbon reactions were carried out at 100–150 °C in sealed ampules with stirring as it was described [2,3]. Samples for reactions (2) and (3) were prepared in the absence of oxygen in vacuum unit.

1-Nonene hydrogenation was carried out at 20 °C at hydrogen pressure 20–40 bar in autoclave. Under these conditions hydrogen pressure does not affect the reaction rate.

Reagent volume was 0.2–0.5 ml (10^{-3} to 10^{-4} mol) in chlorohydrocarbon conversions and 5 ml (10^{-2} mol) in hydrogenation. Crashed metal films (usually 0.5–1 cm^2, 10^{-8} to 10^{-9} mol of metal) were used. In particular experiments, the size of film was increased up to 10 cm^2.

Chlorobenzene hydrogenation was carried out in the fixed-bed flow reactor with 0.5 cm^2 of Pd film at 150 °C at atmospheric pressure. The chlorobenzene flow rate was 30 ml/min.

The products were analyzed by means of gas chromatography. The catalytic activities were calculated from the moles of products converted per mole of metal in hour.

3. Results and discussion

3.1. Catalyst structures

When using LED the particle size, deposition rate, and film structure depend only on the metal. Silicon support does not affect these characteristics. According to TEM data, the nanoparticle size is 5 nm for Cu, 2.5 nm for Ni, and 2 nm for Pd. In all cases, the relative particle size dispersion is less than 10%. The time of deposition of completely filled one-layer coveridge was in the range from 3 s for Pd to 30 s for Ni and to 5 min for Cu. It has been found for Cu [2] that depending on the deposition time (τ) the film structure transforms from a composition of individual grains uniformly distributed over the surface ($\tau \leq 1$ min) to the system of islands ($\tau \approx 5$ min), each consisting of three to six closely packed but still individual particles (Fig. 1). With longer deposition ($\tau > 5$ min) highly loaded multi-layer granulated films were obtained. In distinction to Cu, Ni nanoparticles tend to assemble in chains consisting of several granules (Fig. 3). As shown in Fig. 4, Pd nanoparticles also form small aggregates of granules with the size of about 5 nm.

For Cu, Ni, and Pd films, the electron diffraction patterns obtained directly in TEM were of the form of non-structured hallo positioned at the center of the e-beam. This indicates that the particles are amorphous. However, after treating these films by intense e-beam, and probably, as a result of local structure heating, the initial diffraction patterns

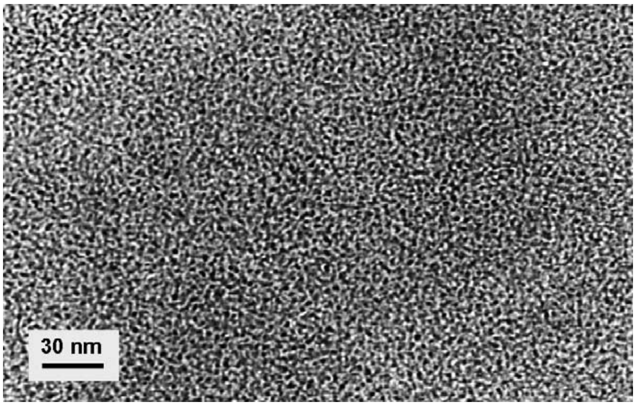

Fig. 3. TEM image of nanostructured Ni film ($\tau = 30$ s, $n = 10^{13}$ cm^{-2}).

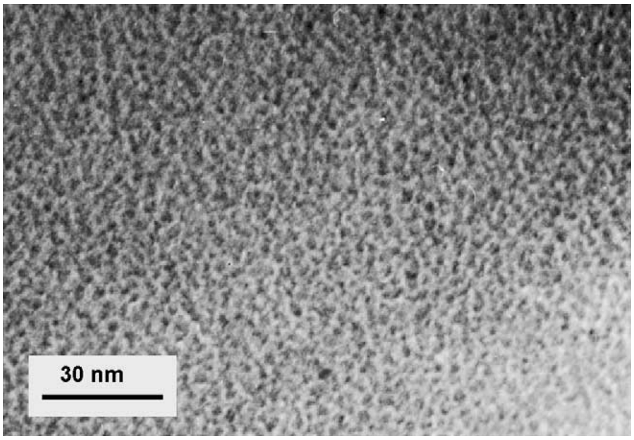

Fig. 4. TEM image of nanostructured Pd film ($\tau = 3$ s, $n = 10^{13}$ cm^{-2}).

transform into circles having the radii characteristic to the distance between crystallographic planes of the metal, i.e. the phase transition to the crystalline state takes place. Therefore, the nanoparticles in the fabricated films are amorphous and metastable. Because of amorphous structure particles did not coagulate even at extremely high particle surface density ($n > 10^{13}$ cm^{-2}), when neighboring metal grains, still persisting as individual particles, practically touch each other.

Another consequence of the particle amorphous state is the high oxidative stability. For example, the results of conductivity measurements [10] and XPS analysis [12] of Cu films keeping in ambient atmosphere during 2–3 months indicate that Cu nanoparticles are covered by thin Cu_2O shell with the average layer thickness less than 1 nm. Similar results were obtained for the structures composed of amorphous Ni and Pd particles in which the oxide formation was found even more decelerated.

4. Catalytic properties of nanostructured metal films

4.1. Cu and Ni films in reactions of chlorohydrocarbons

The catalytic behavior Cu and Ni films deposited on SiO_2/Si and Si supports was compared in the following reactions:

- dichlorobutene isomerization,

$$CH_2Cl{-}CHCl{-}CH{=}CH_2 \rightleftarrows CH_2ClCH{=}CHCH_2Cl; \quad (1)$$

- CCl_4 addition to 1-nonene,

$$CCl_4 + CH_3(CH_2)_5CH{=}CH_2 \rightarrow CH_3(CH_2)_5CHCl{-}CH_2(CCl_3); \quad (2)$$

- CCl_4 interaction with decane,

$$C_{10}H_{22} + CCl_4 \rightarrow C_{10}H_{21}Cl + CHCl_3. \quad (3)$$

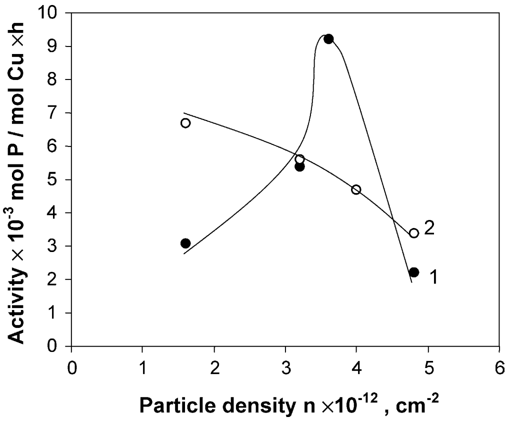

Fig. 5. Effect of particle surface density on the catalytic activity of Cu films deposited on a surface oxidized silicon SiO_2/Si (1) and a non-oxidized silicon Si (2) in dichlorobutene isomerization at 110 °C (3,4-dichlorobutene-1, 0.93 mol/l, solvent dichloroethane).

The most important feature of the Cu films deposited on the dielectric support (thermally oxidized silicon SiO_2/Si) is that the particle density dependencies of the catalytic activity in the reactions (1)–(3) pass through a maximum, which corresponds to ensembles of nanoparticles [2,3] as it was illustrated in Fig. 2. One example of such dependence in isomerization (1) is shown in Fig. 5. Our view that nanoparticle charging plays essential role in the catalysis is based on the fact that, according to the results of simulation [7,8], the number of charged particles is also maximum in densely packed one-layer films. In addition, the fact that the activity of the catalyst with the optimum particle density grows up with increasing a solvent polarity [2,3] correlates with the increase of the charge density. The reason why in the reactions involving the electron transfer the nanoparticle charge can influence the catalytic activity is that it is energy favorably for the molecule to get an electron from negatively charged particle and then to return it back to positively charged particle [7]. The time-averaged number of positively and negatively charged metal particles on dielectric supports is always equal (charge neutrality should hold).

Contrary to this, when Cu particles are deposited on the naturally oxidized Si support the catalytic activity in reaction (1) reduces with the increase of the particle surface density (Fig. 5). This may be caused by the interaction of the particles with the support. Indeed, in the presence of tunnel transparent surface oxide, the difference in the work functions of the support (Si) and metal (Cu) should result in Cu–Si charge exchange which will lead to the shift of the charge balance in the system of particles. Instead of bearing equal number of positively and negatively charged particles, as in case of dielectric support, one charge sign will dominate in the system of particles. In this situation, one-way for electron transfer (to or from the reagent molecule) becomes most probable while the opposite electron transmission is suppressed thus affecting the overall catalyst activity. One can further assume that the above shift of the charge balance is enhanced in higher density structures. It should be noted that the particle charging on the surface of semiconductor is quite complicated phenomenon, which has not been adequately studied yet.

Another example of unusual properties of the nanostructured films is the behavior of Ni films in the catalysis of reactions (1)–(3), in which traditional supported Ni catalysts (prepared by means of support impregnation and reduction or MVS) are much less active. But the activity of Ni films deposited by LED on both silicon and oxidized silicon supports was found to be close to that for Cu films. A comparison of catalytic activity of nanostructured Ni and Cu films with usual supported catalysts based on these metals is shown for reaction (1) in Fig. 6. The activity of Ni films in CCl_4 conversions is also unusually high and ranges up to 3×10^3 to 6×10^3 and 4×10^2 to 5×10^2 product mol/Ni mol h in reactions (2) and (3) at 130 and 150 °C, respectively. Supported Ni catalysts prepared by traditional methods are not active in CCl_4 reactions. The reason for high catalytic activity of nanostructured Ni films, in addition to small size and amorphous state of particles, may be their charging due to electron tunneling between nearby particles. As a result the catalytic behavior of Ni and Cu films becomes similar. Efficient activation energy of reaction (2) estimated from the initial rates at 120–150 °C is close to 50 kJ/mol for Cu and Ni films, this is below usual values 80–100 kJ/mol observed in CCl_4 addition for other types of catalysts [13,14].

The distinction between dependencies of catalytic activity on particle surface density was also observed for Ni particles deposited on Si and SiO_2/Si supports. As one can see in Fig. 7 for isomerization (1), the particle surface density does not affect the activity of Ni films on Si while the catalytic activity reduces when particle density increases for the films on SiO_2/Si. The most active films were obtained on SiO_2/Si with the shortest deposition time τ.

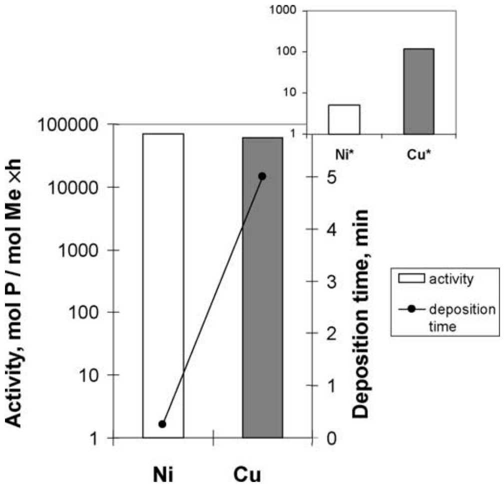

Fig. 6. Catalytic activity of nanostructured Cu and Ni films and usual supported catalysts (Cu*—1% Cu/silica gel, Ni*—2% Ni/silica gel; insert) in isomerization (1) at 110 °C.

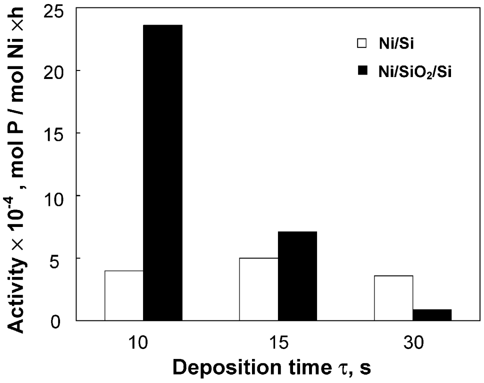

Fig. 7. Effect of deposition time τ (or surface particle density) on catalytic activity of Ni films deposited on SiO_2/Si and Si in isomerization (1) at 110 °C.

Another experimental result in support of our hypothesis is related to the catalytic behavior of Ni films in reaction (2) with a participation of the electron acceptor molecule—carbon tetrachloride. When n-type Si with electron conductivity has been used as a support, the activity of Ni films was two times higher compared to the films deposited on p-type Si with hole conductivity.

4.2. Ni and Pd films in hydrogenation

The catalytic activities of Ni and Pd nanostructured films were tested in the following reactions:

- hydrogenation of 1-nonene (Ni)

$$C_7H_{15}CH{=}CH_2 + H_2 \rightarrow C_7H_{15}CH_2CH_3; \qquad (4)$$

- hydrogenation of chlorobenzene (Pd)

$$2C_6H_5Cl + 5H_2 \rightarrow C_6H_{12} + C_6H_6 + 2HCl. \qquad (5)$$

Ni films deposited on both Si and SiO_2/Si supports were active in the reaction (4) even at 20 °C. The most active catalysts were obtained, however, with the use of Si support at low-surface covering. Fig. 8 demonstrates that the activity of Ni films on Si is many times higher compared to that for Ni films on SiO_2/Si and supported catalyst based on Pd. At the same time, usual supported Ni catalysts do not catalyze reaction (4) at room temperature. One should keep in mind that the size and the structure of individual Ni particles are independent on the particle density and on the type of the support, which is characteristic for the LED technique. Thus, traditional arguments explaining different catalytic activities by the variation of the particle size and structure are not consistent here. Therefore, we can conclude that the observed distinctions of the film activity are connected with inter-particle and support-particle interactions.

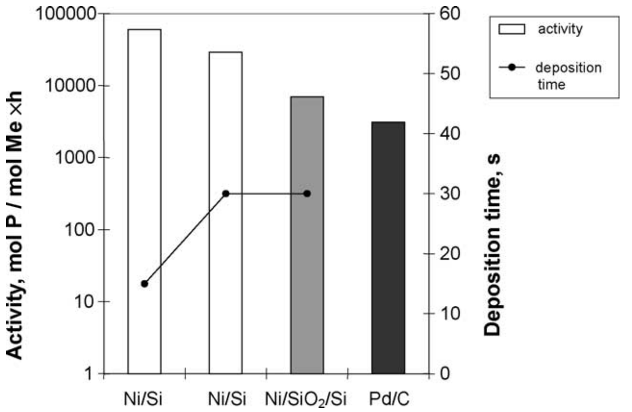

Fig. 8. Catalytic activity of nanostructured Ni films on SiO_2/Si and Si with different deposition time τ and usual supported catalyst (5% Pd/C, Nippon) in 1-nonene hydrogenation (4) at room temperature and pressure 40 bar.

Chlorobenzene hydrogenation (5) was realized at elevated temperatures over Pd films deposited on SiO_2/Si. The hydrogenation products are benzene and cyclohexane (1:2). For the Pd films deposited during $\tau = 8$ s, the 100% conversion was observed at 150 °C, while with $\tau = 5$ s only 30% conversion was obtained. The growth of catalytic activity with increase in τ is probably associated with the appearance of particle aggregates, which may be more active in catalysis than isolated particles. The activity of Pd films prepared by means of LED was at least 500 times higher than that of usual supported Pd catalyst observed in this reaction. Another distinguishing feature of the nanostructured Pd films is their high stability. The activity and selectivity of these films unchanged at least for several hours.

5. Conclusions

Laser electrodispersion technique has been applied to fabricate thin nanostructure films consisting of monodispersive and amorphous Cu, Ni, or Pd nanoparticles deposited on dielectric (thermally oxidized silicon) or semiconductor (naturally oxidized Si) supports. The most important common feature of the fabricated catalysts is their unusually high activity in the chlorohydrocarbon conversions (Cu and Ni) and hydrogenation (Ni and Pd). The strong dependencies of the activity on the particle surface density and on the nature of the support clearly indicate that alongside with small particle size and their amorphous state, inter-particle or particle-support interactions play decisive role in determining the catalytic activity. It is suggested that these interactions result in particle charging, and depending on the amount of charged particles and on the sign of the dominating charge, the catalyst activity can be either increased or decreased. The obtained results show new possibilities for controlling the activity of nanostructured metal catalysts by appropriate choosing the particle surface density and the type of the support. In this way, highly effective catalysts for conversion of hydrocarbons and halogen derivatives can be created.

Acknowledgements

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