JOURNAL OF CATALYSIS 57, 126–135 (1979)

The Peculiarity of the Catalytic Action of Nickel in Zeolites of Type Y in Hydrogenation Reactions

K. G. IONE, V. N. ROMANNIKOV, A. A. DAVYDOV, AND L. B. ORLOVA

Institute of Catalysis, Novosibirsk 90, USSR

Received January 12, 1978; revised May 30, 1978

The metal specific catalytic activity (K_{spec}) in hydrogenation of a series of unsaturated hydrocarbons: n-hexene-1, cyclohexene, the olefin bond in styrene, and 4-phenylbutene-1, as well as the aromatic ring in benzene, has been determined for a number of nickel–zeolite catalysts, nickel on silica and nickel black, with the surface of metallic nickel being varied from 4 to 690 m^2/g_{Ni}. It has been shown that K_{spec} for nickel in zeolites toward the hydrogenation of a simple olefin bond does not depend on its dispersion and only slightly differs from that for the catalysts of comparison. A decrease in oxygen specific chemisorption and specific activity in hydrogenation of the aromatic ring was observed with increasing nickel dispersion in zeolites. The latter fact was related to the specificity of atomic states in nickel clusters located in zeolite cavities.

According to Refs. (*1–3*), the electronic and catalytic properties of small metallic species fixed on the support may depend both on their dimensions and the acidity of the support.

Zeolites are peculiar supports incorporating large amounts of acid sites of different nature. Moreover, transition metals in a high dispersion degree (approaching the atomic one) may be fixed on zeolites (*4*). All of the above leads us to expect that the catalytic properties of metallic clusters on zeolites will show some peculiarities. In fact, a study of the catalytic properties of palladium introduced into the zeolite acid form (*5*) has shown that its specific catalytic activity toward benzene hydrogenation was higher than that of palladium on other nonacid carriers. This was considered to be due to the change in the metal atoms electron configuration as a result of interaction with the acid sites of zeolite framework (*5*). An increase in the specific activity of platinum on zeolites toward ethylene hydrogenation (*6*) also was explained by the change in the state of platinum atoms under the influence of the acidic zeolite support.

In Refs. (*7, 8*) it has been shown that nickel particles incorporated into zeolites of type Y do not catalyze hydrogenation of benzene. Specific activities of metallic nickel on zeolites of types A and X in the same reaction were similar, while nickel on Y zeolites was characterized by zero activity (*9*). However, in the latter case the samples containing metallic nickel in a coarsely dispersed form (the metal surface was 3–30 m^2/g_{Ni}) were studied. It is unlikely that at this dispersion the zeolite support may affect essentially the catalytic

0021-9517/79/040126-10$02.00/0

properties of the metal. Therefore, the absence of nickel activity in Y zeolites toward benzene hydrogenation detected in (*9*) cannot be accounted for by the influence of the zeolite surrounding.

In order to regulate the catalytic action of metal–zeolite catalysts in hydroconversions of hydrocarbons, it is necessary to study the hydrogenating properties of metals distributed in zeolites in a highly dispersed state.

With this aim, we have studied the catalytic properties of metallic nickel fixed on Y zeolites in comparison to its action on other nonacidic supports in hydrogenation of a series of unsaturated hydrocarbons. Infrared spectroscopy of adsorbed CO was used to study the state of nickel in zeolites.

EXPERIMENTAL

Nickel was introduced into zeolites of types NaY (GOZ VNII NP)[1] and HY by ion exchange by techniques described in (*10, 11*) ensuring the fixation of a large portion of nickel in the form of associated cations inside the zeolite cavities. Zeolites of type NaY and HY were treated with $0.1N$ solution of $Ni(NH_3)_6Cl_2$ at 20°C (to reach the 70–80% depth of exchange). Then zeolite crystals were washed with distilled water.

HY Zeolites were prepared by treating the NaY sample with $0.1N$ solution of $NH_4OH + NH_4Cl$ for 2–3 times. Between these procedures the sample was subjected to calcination at 400°C. Ni/SiO_2 with nickel surface 690 m^2/g_{Ni} was obtained according to procedure described in (*12*).

The samples were reduced under conditions ensuring the highest catalytic activity toward hexene-1 hydrogenation: reduction by hydrogen–hexene mixture (100°C, 2 hr) and then by hydrogen (350°C 2 hr). After reduction, physical and physicochemical properties of the samples were studied: nickel surface in zeolites was determined by measuring oxygen chemisorption at 20°C in a flow-chromatographic installation; the concentration of water vapors in all working gases corresponded to the water condensation point not greater than −65 to −70°C.

The dispersion of nickel fixed on the external surface of zeolite crystals was determined by means of statistical treatment of the electron-microscope pictures with an enlargement 20,000×. The smallest particle's size fixed at this treatment was 20 Å.

The study of the catalytic activity of all the catalysts was carried out in a gradientless flow-circulating installation; the time of reagent contact with a catalyst was about 0.1 sec. The samples were pressed into pellets and then crushed to obtain 0.1- to 0.16-mm fragments. The reaction mixture contained 1–5% of unsaturated hydrocarbons; the rest was hydrogen.

Prior to the reaction, all hydrocarbons were subjected to thorough purification from water and other impurities whose presence was controlled chromatographically and using the NMR spectra. The utilized gases (hydrogen, helium, oxygen) were dried by passing through the adsorber with NaA zeolite cooled to the temperature of liquid nitrogen.

The degree of nickel reduction was calculated from the value of the saturation magnetization using the Faraday balance at magnetic field 8000 Oe. Before sealing, the samples were subjected to heating under dry helium at 600°C for sintering of highly dispersed metal particles.

CO adsorption was carried out on the samples prereduced in the reactor according to the above-described technique, with further rereduction and evacuation in the cell. The temperature of both reduction and evacuation was 350°C. The spectra were recorded on a UR-10 spectrometer.

---

[1] Gorkovsky Experimental Plant of the All-Union Research Institute.

EXPERIMENTAL RESULTS

Determination of the Dispersion of the Metallic Phase. For all samples of nickel-containing zeolites under study the line intensity of the X-ray spectrum and the value of argon adsorption at 77°K were similar to the corresponding values of the initial zeolite NaY.

The electron-microscopic studies have shown that on the surface of nickel-containing zeolites, after their reduction, a new phase is detected identified as the phase of metallic nickel. The particle size was within 90–250 Å. It is probable that the other invisible portions of metal particles may be located inside zeolite cavities or have dimensions not larger than 15–20 Å in reduced state. It is known (*13*) that for coarsely dispersed nickel particles the stoichiometry of oxygen adsorption is equal to 1.7, while for finely dispersed particles it is equal to 1. Therefore, in the case of polydispersed distribution of metal particles, an error in the determination of its surface on the basis of oxygen adsorption and, hence, in the specific constant of the reaction rate (K_{spec}), may reach 1.7. For zeolites under study, the surface values were within 30–300 m^2/g nickel assuming an $O/Ni_{surface}$ ratio to be 1.7.

Study of the Catalytic Activity. Figure 1 shows the character of variations in the rate constant of olefin hydrogenation on NiNaY zeolite as a function of the reaction temperature. At 90–180°C the reaction order with respect to hydrocarbon was about 0.5 for all unsaturated hydrocarbons; the catalyst worked in the stationary regime. The reaction activation energies measured in this temperature region were almost independent of the catalyst's type and were determined only by the nature of unsaturated hydrocarbons.

TABLE 1

Chemical Composition of Nickel-Containing Catalysts

Catalyst	Ni wt%	Na wt%	Ni specific surface area (m^2/g Ni)	Extent of Ni reduction α
Ni/SiO_2-1	60	—	68	—
Ni/SiO_2-2	60	—	133	—
Ni/SiO_2-3	25	—	169	—
Ni/SiO_2-4	4.5	—	690	—
Ni/Cr_2O_3	40	—	164	—
NiY-1	5.0	1.9	103	0.27
NiY-2	4.0	0.9	106	—
NiY-3	4.5	1.2	118	0.30
NiY-4	5.0	1.0	121	0.70
NiY-5	4.1	0.2	126	0.40
NiY-6	3.9	0.7	152	0.52
NiY-7	5.0	0.5	153	—
NiY-8	2,5	3.4	159	0.30
NiY-9	3.5	0.5	170	—
NiY-10	5.0	0.5	177	—
NiY-11	4.8	0.6	177	0.82
NiY-12	4.5	1.8	200	—
NiY-13	5.0	0.5	200	—
NiY-14	3.5	0.5	212	—
NiY-15	4.3	1.7	218	0.83

Figure 2 gives the values of nickel specific catalytic activity in zeolites and the catalyst of comparison. The reaction rate constant was calculated relating the rate of hydrogenation to the all nickel content. The surface of nickel in zeolites was calculated at one of the extreme values of oxygen chemisorption stoichiometry being equal to 1.7 and the further assumption has been made that all nickel was in the reduced (elementary) state. An average arithmetic value of the specific rate constant of n-hexene-1 hydrogenation for nickel in zeolites accounts for 0.07 ± 0.05; it is twice as high for nickel on silica: 0.03 ± 0.006 $(mmol \cdot l)^{0.5}/sec \cdot m^2$ nickel. The values of K_{spec} of cyclohexene hydrogenation are 0.8 ± 0.01 and 0.017 ± 0.003 for nickel-containing zeolites and nickel on silica, respectively. For hydrogenation of a side bond in styrene, the corresponding values are 0.09 and 0.04 $(mmol \cdot l)^{0.5}/sec \cdot m^2$ nickel. In all three cases no distinct tendency in the change of the catalytic activity of nickel in zeolites with increasing its dispersion has been observed.

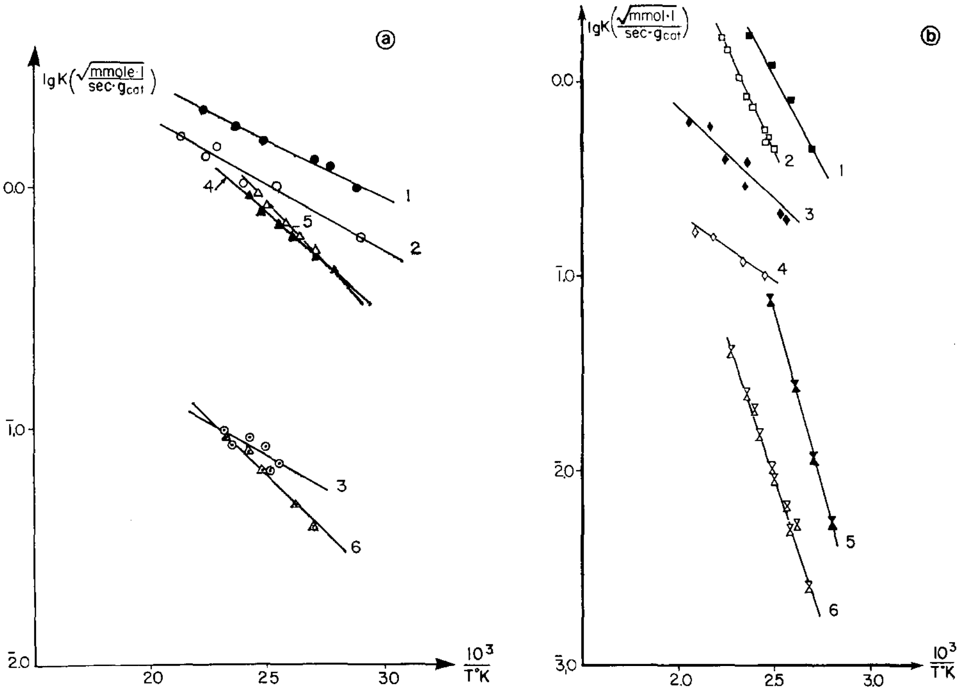


Fig. 1. Plot of the hydrogenation rate constant of unsaturated hydrocarbons versus reaction temperature for nickel-containing zeolite (10% wt Ni); nickel on silica (25% wt Ni), and nickel black. (a) Hydrogenation of n-hexene-1: 1, Ni/SiO$_2$; 2, NiNaY; 3, nickel black; hydrogenation of cyclohexane: 4, Ni/SiO$_2$; 5, NiNaY; 6, nickel black. (b) Hydrogenation of styrene olefin bond: 1, Ni/SiO$_2$; 2, NiNaY; hydrogenation of olefin bond of 4-phenylbutene-1: 3, Ni/SiO$_2$; 4, NiNaY; hydrogenation of benzene: 5, Ni/SiO$_2$; 6, NiNaY.

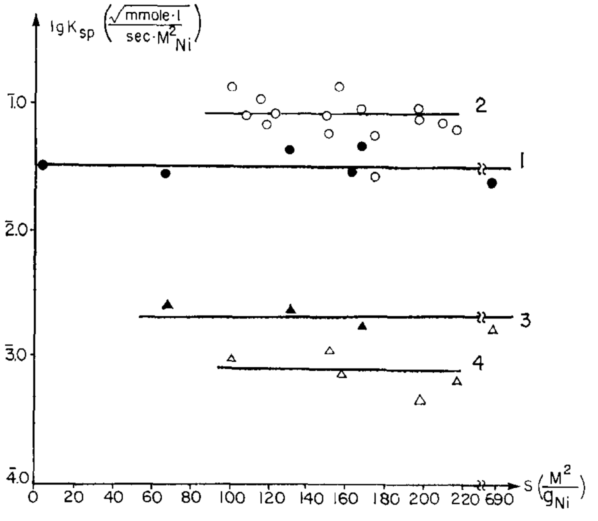


Fig. 2. Plot of the specific hydrogenation rate constant of unsaturated hydrocarbons versus nickel specific surface area determined from oxygen chemisorption (chemisorption stoichiometry 1.7). Hydrogenation of n-hexene, ±(150°C): 1, for nickel on silica and nickel black; 2, for nickel-containing zeolites; hydrogenation of benzene (127°C): 3, for nickel on silica; 4, for nickel-containing zeolites.

Different results have been obtained for benzene hydrogenation (Fig. 2). K_{spec} of benzene hydrogenation is equal to 0.75 $\times 10^{-3}$ for nickel in zeolites and 1.62 $\times 10^{-3}$ (mmole $1)^{0.5}$/sec m^2 Ni for nickel in catalysts of comparison. In both cases K_{spec} was independent of nickel surface value (like in hydrogenation of olefins). We should note very large dispersion of the values of K_{spec} for NiHY samples in hydrogenation of n-hexene-1. This fact indicates that the activity of catalysts depends not only on dispersion and metal concentration but also on some other factors.

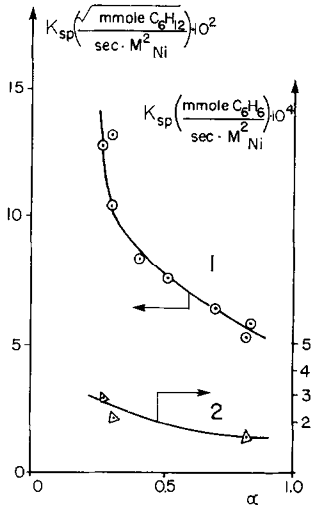


FIG. 3. Plot of K_{spec} for hexene (1) and benzene (2) hydrogenation on NiY versus the degree of reduction (α).

Figure 3 illustrates a strong dependence of K_{spec} in this reaction on the extent of nickel cation reduction in zeolites. This phenomenon is not quite clear since the extent of reduction must equally affect the apparent values of reaction rate constants and the surface of metallic nickel, i.e., K_{spec} must be independent on α. In benzene hydrogenation K_{spec} only slightly depends on α.

Since the O/Ni$_{surface}$ ratio is not known exactly we assume that the values of K_{spec} may be higher or lower than actual ones by the factor of 1.7.

The surface of the metal involved in hydrogenation may be estimated more accurately, using for its characteristic the process whose specific rate does not vary with the size of metal particles.

The hydrogenation of a double bond in linear olefins may be regarded as the structurally nonsensitive reaction (*3*, *14*). From the ratio of the rates of the processes under study or the oxygen adsorption value to the rate constant of such olefin hydrogenation, i.e., of n-hexene-1 per gram of Ni (value J), one may estimate the degree of structural sensitivity of the corresponding processes as compared to hydrogenation of n-hexene-1.

Values of J_{O_2} (ratio between the amount of adsorbed oxygen in mmole/g$_{Ni}$ and n-hexene-I hydrogenation constant) and J_b (ratio between the hydrogenation constant of benzene and n-hexene) are presented in Fig. 4a.

For the catalysts under consideration, Ni/SiO$_2$, Ni/Cr$_2$O$_3$, and nickel black, values J_{O_2} and J_b remain unchanged as the surface incorporated in the hydrogenation of n-hexene changes by 2.5 orders of magnitude. For nickel in zeolites different results have been obtained: Development of the metal surface by a factor of 2.6 in zeolites incorporated in n-hexene-1 hydrogenation results in the decrease of oxygen chemisorption value and benzene hydrogenation rate by a factor of 6 to 8. Similar J values for zeolite catalysts and catalysts of comparison have been obtained for samples with the smallest activity toward n-hexene-1 hydrogenation. Of special interest is the fact that in hydrogenation of cyclohexene and styrene side bond, J values are independent of both the carrier type and metallic phase dispersion (Fig. 4b).

ir Spectra of Adsorbed CO. It has been established that the character of ir spectra of CO adsorbed on nickel in zeolites depends on conditions of their pretreatment and on sodium concentration. Figure 5

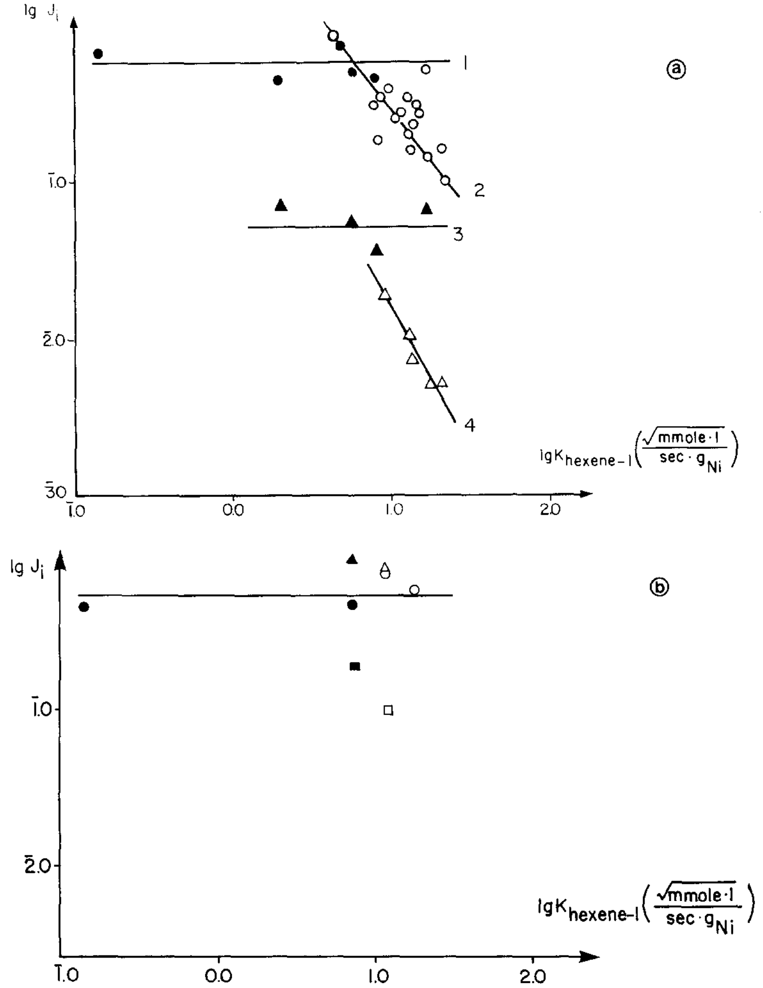


FIG. 4. Plot of oxygen specific chemisorption and hydrogenation rate constants of unsaturated hydrocarbons (J_i) versus hydrogenation rate constant of n-hexene-1 at 150°C. (a) oxygen chemisorption (J_{O_2}): 1, for nickel on silica[2] and nickel black; 2, for nickel-containing zeolites; hydrogenation of benzene (J_b) at 127°C: 3, for nickel on silica; 4, for nickel-containing zeolites. (b) hydrogenation of cyclohexene (J_i) at 127°C: ●, Ni/SiO$_2$ and nickel black; ○, NiNaY; hydrogenation of styrene olefin bond (J_i) at 150°C: ▲, Ni/SiO$_2$; △, NiNaY; hydrogenation of olefin bond of 4-phenylbutene-1, (J_i) at 150°C: ■, Ni/SiO$_2$; □, NiNaY.

shows that CO adsorption leads to the appearance of a band at 2220 cm^{-1} on nonreduced nickel in sodium-poor zeolite NiY-6 and additional bands at 2110 and 2145 cm^{-1} on the reduced one. In the spectrum of CO adsorbed on the reduced nickel in a sodium-rich zeolite NiY-15 two strong bands at 2010 and 2090 cm^{-1} and a very weak adsorption at 2145 and 2220 cm^{-1} are observed.

According to the interpretation of the spectra of adsorbed CO given in Ref. (*15*), we may ascribe the bands 2220 cm^{-1}, 2145, and 2020–2120 cm^{-1} to Ni^{2+}–CO, Ni^{1+}–CO, and Ni^{0}–CO complexes, respectively. Thus, in zeolites treated in the reducing media a portion of cations is not reduced and conserves a positive charge. This conclusion is supported by the magnetic data showing a partial reduction of nickel in the samples.

Figure 6 gives ir spectra of CO adsorbed on nickel in zeolite NiY-15 after introduction of hexene-1 (curve 3) and benzene (curve 2) into the cell. After admission of hexene-1 the band at 2220 cm^{-1} disappears and the intensity of the band at 2145 cm^{-1} drastically falls. The band 2110 cm^{-1} splits, giving the bands at 2110 and 2080 cm^{-1}. By contrast, adsorption of CO–benzene mixture results in the disappearance of the band 2145 cm^{-1} and in the decrease of the 2110-cm^{-1} band intensity. The 2220-cm^{-1} band remains unchanged. In both cases, evacuation of the zeolite and further admission of CO lead to the appearance of a spectrum characteristic of CO adsorbed on a freshly reduced nickel in NiY-15.

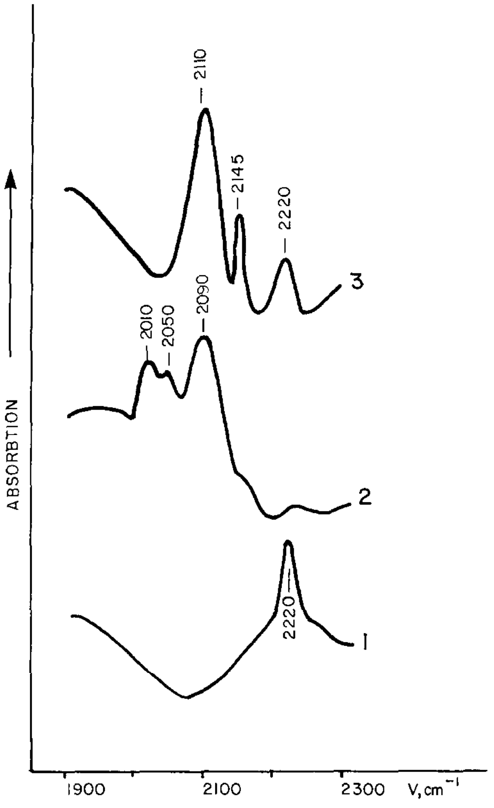


FIG. 5. The ir spectra of CO adsorbed at 20°C on: (1) nonreduced nickel in NiY-6; (2) reduced nickel in NiY-15; (3) reduced nickel in NiY-6.

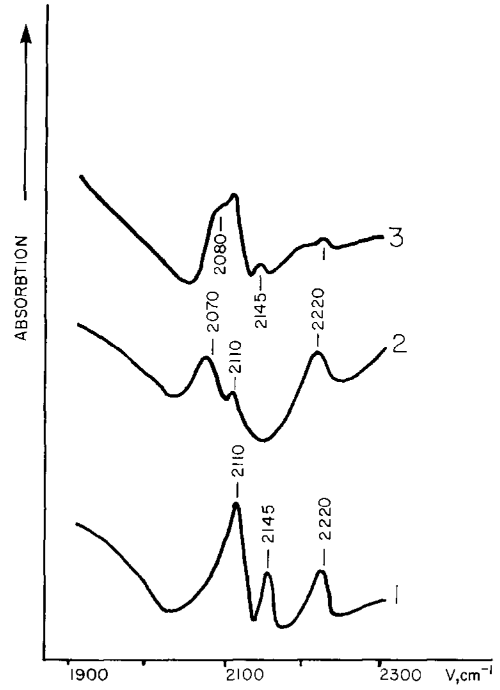


FIG. 6. The ir spectra of CO adsorbed on nickel in zeolite NiY-6 (1) after reduction; (2) after admission of benzene on prereduced nickel; (3) after admission of n-hexene-1 on prereduced nickel.

DISCUSSION

Considering the above results it must be admitted that conclusions about the influence of metallic nickel dispersion on K_{spec} may be different depending on the means of expression of the specific catalyst activity. K_{spec} values found from the ratio of the reaction rate constant to the metal surface determined from the oxygen chemisorption values are widely scattered. There is no distinct tendency of changing of K_{spec} with the decrease of the surface area of metallic species. There is some difference in the specific catalytic activity of nickel on zeolite and silica. The ratio between K_{spec} for zeolites and that for silica is 2–3 for hydrogenation of olefins and 0.2–0.4 for hydrogenation of benzene. The absolute values of these ratios depends on the taken stoichiometry of oxygen chemisorption on nickel in zeolites (1 or 1.7). However, the value of the specific oxygen chemisorption itself found as a relation of oxygen amount chemisorbed to the rate constant of n-hexene-1 hydrogenation (J_{O_2}) depends on both metal dispersion and the nature of the support (Figs. 4a and b).

For nickel in zeolites, J_{O_2} and J_b fall drastically with the increase of the hydrogenation surface. J coefficients were found to be constant only for reactions of hydrogenation of a simple olefin bond (in cyclohexene) and side bond (in styrene). For nickel on silica the values of oxygen specific chemisorption (J_{O_2}) and of J_b do not vary with increasing the surface involved in the hydrogenation of n-hexene-1.

The results obtained cannot be explained by the fact that under the given conditions the degree of reduction of nickel cations is different, since in calculations of relative values of K_{spec}, J_{O_2}, and J_b, α must be involved in the numerator and the denominator of the expression.

No decrease in the catalytic activity of nickel particles fixed on silica is observed with increasing their dispersion in the course of hydrogenation of the aromatic ring. Hence, there is no basis for ascription of the metal catalytic properties in zeolites only to the dispersion effect. It is not likely that the fall in J_b for nickel in zeolites is due to diffusional and steric restrictions. Our conclusion is supported by practical constancy of reaction orders and activation energies for all the cases. Moreover, a known fact of adsorption of benzene and its derivatives by zeolite Y indicates that such molecules may enter the zeolite cavities.

Since conflicting conclusions may be drawn from Figs. 2 and 4 it should be elucidated which of two processes, oxygen chemisorption or n-hexene-1 hydrogenation, may better characterize the real surface of nickel in zeolites involved in hydrogenation.

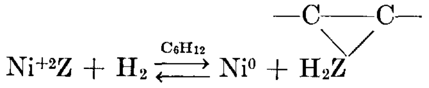
In zeolites, either evacuated or heated in oxygen, CO adsorption leads to the appearance of a band at 2220 cm^{-1} which points to the existence of Ni^{2+} cations in zeolites. The intensity of the band 2220 cm^{-1} and the value of α are in good agreement in reduced zeolites. For example, for NiY-15 ($\alpha = 83\%$) the intensity of the 2220-cm^{-1} band is very small; for NiY-6 and, especially for NiY-1 ($\alpha = 52\%$ and 27%, respectively) a strong absorption is observed in this region. Hence, after reduction, but in the absence of reducing agents, different portions of cations of two-valent nickel may exist in zeolites. Similar results have been previously published, e.g., in Ref. (*16*). In the presence of olefins, this band disappears even at room temperature. This may be due to CO displacement by hexene molecules according to the scheme:

$$Ni^{+2}\ldots CO \overset{C_6H_{12}}{\rightleftarrows} Ni^{+2}\ldots C_6H_{12} + CO \qquad (1)$$

or to the reduction of Ni^{2+} to the zero-valent state by olefin. The appearance of the bands at 2145 and 2110 cm^{-1} (*17*) indicate that the second assumption is more valid. The initial state of the catalyst may be reached by means of evacuation of hexene. It is likely that the reduced state of nickel in small metallic clusters inside zeolite cavities is unstable and the reaction of their reduction is reversible. Therefore, in the presence of the reaction medium, the nickel concentration in the lowest oxidation state is greater than that in the presence of the inert media. The factor determining equilibrium (2)

$$Ni^0 + Z \rightleftarrows Ni^{+2}\ldots Z^{-2} \qquad (2)$$

depends on the degree of interaction between the atoms of metallic cluster and electron-acceptor centers of the zeolite framework. Oxidation of metallic nickel under the influence of electron acceptor centers of the zeolite framework has no place only in two cases: (i) when nickel particles are outside the zeolite cavities or (ii) when an electron-acceptor center is blocked by a hexene-1 molecule:



$$\mathrm{Ni^{+2}Z + H_2 \overset{C_6H_{12}}{\rightleftarrows} Ni^0 + H_2}\overset{\overset{-\mathrm{C}-\!-\mathrm{C}-}{\diagdown\ \diagup}}{\mathrm{Z}} \qquad (3)$$

Only in the latter case is the cluster metallic state stabilized. Removal of hexene-1 and reducing media is accompanied by the shift of the equilibria (2) and (3) to the left.

According to the above results, benzene adsorption leads to the change only in Ni^{+1}–CO and Ni^0–CO complexes. This may be due to (a) Ni^{2+} stabilization in the centers inaccessible for benzene molecules (e.g., in cubooctahedral prisms) and (b) weaker benzene ability to electron-donor and reducing action as compared to olefins.

If the assumption about the reversible reduction is valid, after the removal of reducing agents a fixed portion of finely-dispersed nickel is converted to the cation state. This portion does not adsorb oxygen, does not possess ferromagnetic properties and does not participate in benzene hydrogenation. On the other hand, the same portion of nickel in the presence of reducing agents (hydrogen + olefin) is in the reduced state. Therefore, the former three characteristics must not be in agreement with the quality of the nickel metallic phase formed under olefin hydrogenation conditions.

This discrepancy must increase with increasing nickel concentration inside zeolite cavities. Taking this into account, correction for the degree of cation reduction (α) is needed for calculating the specific surface area but not for calculating K of olefin hydrogenation per gram of metallic nickel. After this correction, values of K_{spec} and $J_{\mathrm{O_2}}$ become equal to their values for Ni/SiO_2.

CONCLUSION

On the basis of our results and the data published earlier (*7, 8, 16, 19*) we may draw some conclusions about the influence of the zeolite surrounding on the state and the catalytic activity of nickel components in zeolite in the course of hydrogenation reactions.

In zeolites treated with reducing media three types of nickel localization may be distinguished: (a) 20–500 Å particles outside zeolite crystals on their external surface. At low temperatures of reduction, the formation of this phase takes place due to the reduction of the hydroxide phase, which inevitably appears during the ion exchange procedure if no special precautions have been taken to prevent hydrolysis of the salt (*20*). The formation of this phase is also due (but to a lesser degree) to diffusion of nickel atoms from zeolite cavities onto the surface; (b) small metallic clusters, retained inside zeolites and formed as a result of reduction of cation associates of the Me–O–Me type (*20*); (c) Ni^{2+} cations, localized in the crystallographic centers such as S_I, S_{II}, etc., where cations are coordinated only by oxygen atoms of zeolite framework. Reduction of these cations with hydrogen takes place at about 450°C and higher temperatures (*11*). Reduction process is accompanied by the diffusion of nickel atoms toward external surface of zeolite crystals. The quantitative distribution of nickel between states a, b, and c depends on conditions of the ion exchange and on the temperature of reduction.

There is no evidence indicating that the behavior of metallic species outside zeolite crystals differs from that of the metal supported on other carriers. The ratio O/Ni_{surface} for this nickel portion may be 1.7. In reactions of hydrogenation of unsaturated compounds, the specific activity of these particles should not differ from the corresponding values for nickel on other supports.

The peculiarities of the behavior of the nickel portion fixed inside zeolite cavities are due to the unstable valent state of metal atoms in small clusters. The low-charged, zero-valent state of metal atoms in this cluster is possible only in the presence of reducing medium and molecules which "neutralize" acidic sites of zeolite structures, e.g., olefins. In the absence of such a medium, atoms of the metallic cluster are oxidized as a result of interaction with acidic sites of the zeolite framework. Therefore, the apparent degree of Ni-cation reduction, the value of the metal surface on zeolites determined on the basis of oxygen chemisorption, for the latter case, must not be in agreement with the real metal surface acting in olefin hydrogenation reaction.

Owing to this, the conclusion should be made cautiously concerning the fact that hydrogenation specific constants for nickel on zeolites are larger than those for nickel on nonacid supports. Estimation of the metallic phase dispersion in zeolites from the constant of olefin hydrogenation is more correct than from the value of gas chemisorption. The low activity of small nickel clusters toward benzene hydrogenation may be due to the fact that benzene molecules do not stabilize the cluster metallic state in zeolites.

REFERENCES

1. Anderson, I. R., "Structure of Metallic Catalysts," Academic Press, New York, 1975.

2. Ruckenstein, E., *J. Catal.*, **26**, 70 (1972).

3. Slinkin, A. A., "Structura i Kataliticheskie Svoistva Geterogennykh Katalizatorov," p. 51. Sb. Itogi Nauki, Ser. Khim., Moscow, 1971.

4. Breck, D., "Zeolitovye Molekulyarnye Sita," pp. 515, 534. Mir, Moscow, 1976.

5. Figueras, F., Gomez, R., and Primet, M., *Advan. in Chem. Ser.* **121**, 480 (1973).

6. Dalla-Betta, R. A., and Boudart, M., *in* "Proc. of the 5th Intern. Congress on Catalysis, 1973." Vol. 2, No. 96, p. 1329.

7. Selenina, M., and Wencke, R., *Z. Anorg, Allg. Chem.* **380**, 2, 190 (1972).

8. Romanovski, W., *Z. Przem. Chem.* **47**, 741 (1968).

9. Penchev, V., and Minchev, Kh., *Izvestia OKHN Bulg. Akademiya Nauk*, **6**, No. 2, 403 (1973); Penchev, V., Davidova, N., Kanazirev, V., Minchev, H., and Neinska, Y., *Advan. in Chem. Ser.* **121**, 461 (1973).

10. Ione, K. G., and Bobrov, N. N., Vostrikova, L. A., Shinkarenko, V. G., *React. Kinet. Catal. Lett.* **1**, No. 2, 223 (1974).

11. Ione, K. G., Shinkarenko, V. G., Klueva, N. V., Orlova, L. B., and Nosyreva, G. N., *Izv. Akad. Nauk SSSR, Ser. Khim.* **8**, 1729 (1975).

12. Yermakov, Yu. I., Kuznetsov, B. N., Karakchiev, L. G., and Derbeneva, S. S., *Kinet. Katal.* **14**, 709 (1973).

13. Borisova, M. S., Kuznetsov, B. N., Dzis'ko, V. A., Kulikov, V. I., and Noskova, S. P., *Kinet. Katal.* **16**, 1028 (1975).

14. Dzis'ko, V. A., *Usp. Khim.* **43**, 977 (1974).

15. Bobrov, N. N., Davydov, A. A., and Ione, K. G., *Kinet. Katal.* **16**, 1272 (1975); Davydov, A. A., Bobrov, N. N., and Lokhov, Yu. A., *in* "Conf. on The Use of Zeolites in Catalysis, USSR, 1st, sep., prep., Novosibirsk, 1976."

16. Richardson, J. T., *J. Catal.* **21**, 112 (1971).

17. Orlova, L. V., Lokhov, Yu. A., Ione, K. G., and Davydov, A. A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, in press.

18. Rickert, L., *Ber. Bunsenges Phys. Chem.* **73**, 331 (1969).

19. Ione, K. G., The influence of carrier nature on catalytic activity of metals in hydrogenation reactions *in* "Proceedings of Soviet Conference on Supported Catalysts for Hydrocarbon Transformation, Novosibirsk, 1978"

20. Ione, K. G., *Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **2**, No. 4, 78 (1976).