

Transformations of Hydrocarbons on Zeolites of Type Y

III. Hydrogenation of Unsaturated Hydrocarbons on Pd-, Pt-, and Ru-Containing Zeolites

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Received July 6, 1979; revised April 15, 1980

On the basis of ir and XPS data, measurements of magnetic susceptibility, and investigation of hydrogenation reaction rates of some unsaturated hydrocarbons, it has been established that electronic state and catalytic properties of the metal stabilized inside zeolite cavities are determined by the equilibrium position of interaction in the "reagent-metal-carrier" system. Position of this equilibrium depends on both electron-acceptive properties of the carrier surface and electron-donative properties of reagent molecules. It has been shown that the ratio of reaction rates of hydrogenation of hydrocarbons of different nature (factor of selectivity) is determined by the position of above-mentioned equilibrium too.

INTRODUCTION

At the present time metal-containing zeolites are widely used as catalysts for hydrotransformations of hydrocarbons and oil fractions. It has been shown (1-3) that specific catalytic properties of metals fixed in zeolites in high dispersion differ from those of the metals supported on nonacid carriers. This effect was associated with the existence of a strong interaction between metallic particles and electron-acceptive sites of zeolites. Previously we have shown (4) that specific catalytic activity of nickel fixed in zeolites in a high degree of dispersion is higher for olefin hydrogenation and lower for benzene hydrogenation as compared to that on other carriers. These differences were related to a discrepancy in the amounts of metallic surfaces which have been formed under conditions of chemi-

sorption measurements and catalytic experiments. This discrepancy was due to the instability of the reduced state of small metallic particles fixed inside zeolite cavities.

In this work we consider the results of investigation of electronic state and catalytic properties of palladium, platinum, and ruthenium introduced in decationated zeolites of type Y toward reactions of hydrogenation of *n*-hexene-1 and benzene in comparison with the catalytic action of these metals supported on other carriers and metal blacks.

EXPERIMENTAL

Platinum and palladium were introduced into zeolites by ion-exchange techniques described in Refs. (1-3). The NaY zeolite (GOZ VNII NP²) ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.5-4.8$)

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was used as a starting product. Decationated forms of zeolites of type Y were prepared by repeated treatment of the initial zeolite with ammonia buffer solution and intermediate calcination at 400°C between treatments. Platinum and palladium, supported on silica and alumina by impregnation of carriers with solutions of the corresponding chlorides, were used as catalysts of comparison. The Pt/SiO₂-2 catalyst was prepared by adsorption method using aqueous solutions of platinum aminocomplexes according to Ref. (5). Ruthenium-containing catalysts were prepared by impregnation of carriers with aqueous solution of ruthenium chloride.

Palladium- and platinum-containing catalysts were calcined in dry oxygen flow at 300–500°C. The all metal-containing catalysts were reduced with hydrogen at 150–500°C in the apparatus further used for investigations. Numbers in parentheses correspond to oxidation temperature (numerator) and reduction temperature (denominator).

The surface area of supported metals was determined from oxygen chemisorption data. Chemisorption measurements were carried out at room temperature using impulse chromatographic technique, special attention being paid to purification of all working gases. Drying was carried out with the help of alumina and zeolites up to the water condensation point not greater than –70°C. The electron microscopy method was used for the identification of metallic phases, localized on the external surface of zeolite crystals, and for the determination of their particle sizes.

The state of metals before and after reduction was examined using ir spectra of adsorbed CO and XPS methods. ir spectra were recorded at ambient temperature on a UR-10 spectrometer in the range from 1800 to 2300 cm⁻¹ with compensation of the gas phase. To record ir spectra, the samples under study were pressed into pellets with a surface density of about 13 mg/cm². The pressure of carbon monoxide in a cell was

changed in the range from 0.5 to 80 Torr; the pressure of unsaturated hydrocarbons ranged from 3 to 5 Torr. XPS spectra were recorded on a VG ESCA-3 electron spectrometer. These spectra were registered using AlK_α radiation ($E = 1486.6$ eV). The photoelectron lines correspond to Pd3d, Si2s, and Al2s levels. Position of the Pd3d line was determined relative to the Si2s line, the binding energy of the latter being taken equal to 154.0 eV.

Catalytic activity of all the samples was measured in a flow-circulating installation under gradientless steady conditions. Special attention was paid to purification of all hydrocarbons and gases from oxygen, water vapor, and sulfur compounds. Hydrogenation reactions were studied in the temperature range of 80–170°C. For comparison of activities of different metal-supported systems the following standard conditions were chosen: in *n*-hexene-1 hydrogenation reaction—temperature 150°C, olefin steady concentration 1.0 mmol/liter; in benzene hydrogenation reaction—temperature 127°C, benzene steady concentration 0.1 mmol/liter.

EXPERIMENTAL RESULTS

Investigation of the State of Metals in Zeolites

Metallic surface area in zeolites, calculated from the oxygen chemisorption value, depends on both acidity of the zeolite and pretreatment conditions. Oxygen chemisorption was insignificant (as in the case of palladium) or did not take place at all (as in the case of platinum) on the metal-containing acid zeolites pretreated in oxygen at 300°C and then in hydrogen at 300–500°C. The increase of preliminary oxidation temperature up to 500°C leads to the increase of oxygen chemisorption values independently of the temperature of subsequent reduction. In the latter case the platinum surface in acid zeolites, calculated from the oxygen chemisorption value, was approximately equal to the surface at two-dimensional distribution of the metal (280

these bands after high-temperature oxidation treatment and appearance of the bands at 2190 and 2215 cm^{-1} allows one to ascribe the latter bands to the Pd^{2+} -CO adsorption complex.

CO adsorption on palladium in zeolites pretreated under conditions (300/300) and (500/300) leads to practically identical ir spectra—the bands at 2100, 2120, and 2140 cm^{-1} , ascribed to Pd^{+2} -CO and Pd^{+1} -CO adsorption complexes.

CO adsorption on metallic palladium on alumina leads to the appearance in ir spectrum of two bands at 2085 and 1985 cm^{-1} . A shift of the band of CO adsorbed on metallic palladium in zeolites to a high-frequency region as compared to that for palladium on alumina is associated with a lowering of the electron-donative ability of palladium particles in the first case owing to their electron-deficient state (1, 2, 7).

Adsorption of benzene on palladium-containing zeolites at ambient temperature leads to the disappearance of all bands of adsorbed CO. The increase of CO pressure up to 80 Torr leads to the appearance of the band at 2080 cm^{-1} in the ir spectrum corresponding to Pd^0 -CO adsorption complexes. Evacuation at ambient temperature up to the residual pressure of 10^{-4} Torr with subsequent CO adsorption led to the appearance of the a band only at 2100 cm^{-1} in the ir spectrum corresponding to Pd^{+2} -CO adsorption complexes.

Study of Catalytic Activity.

In the stationary regime (under steady concentrations of unsaturated hydrocarbons less than 0.3 mmol/liter) the reaction order with respect to unsaturated hydrocarbons was independent of the carrier type, of the nature of metal and its content in the samples, and of the pretreatment conditions. In all cases the reaction order was about 0.5 for *n*-hexene-1 hydrogenation and near zero for benzene hydrogenation. The values of activation energy of investigated reactions were independent of the carrier type and pretreatment conditions of cata-

lysts too and were equal to 4.0 ± 0.5 and 8.0 ± 0.9 kcal/mole on palladium-containing catalysts, 6.5 ± 0.5 and 9.1 ± 0.6 kcal/mole on platinum-containing catalysts, 5.2 ± 0.1 and near zero kcal/mole on ruthenium-containing catalysts for *n*-hexene-1 and benzene hydrogenation reactions, respectively. The obtained results are in a good agreement with published ones (1, 8).

The catalytic activity of platinum and palladium in acid zeolites preoxidized at 300°C was the highest although the oxygen chemisorption on these samples was absent. Specific catalytic activity of supported metals (K_{sp}) independent on metallic surface area is shown in Fig. 3. It follows from the figure that average values of K_{sp} of metals in zeolites are either similar (as in case of ruthenium, or platinum and palladium after oxidation at 500°C) or exceed by a factor of 3–4 (as in case of nickel, and palladium after oxidation at 300°C) the average values of K_{sp} of metals supported on other carriers toward olefin hydrogenation reaction. At the same time K_{sp} of all these metals exceeds by a factor of 5–20 the corresponding average values for metals on other carriers toward benzene hydrogenation reaction. In this case K_{sp} of nickel in zeolites is an exception: it becomes lower approximately by a factor 2–3 than the corresponding average values for nickel on silica catalysts.

Relative activities of supported metals (K_{rel}) were estimated by relating the reaction rate under study to the reaction rate of *n*-hexene-1 hydrogenation under standard conditions. The values of K_{rel} of supported metals toward olefin and benzene hydrogenation reactions are presented in Tables 1 and 2, respectively.

K_{rel} of nickel in zeolites and in catalysts of comparison toward the reactions of propylene, cyclohexene, and styrene side olefin bond hydrogenation is equal to unity and dependent on neither metallic dispersion nor the carrier type (Table 1). K_{rel} of nickel in the reactions of hydrogenation of

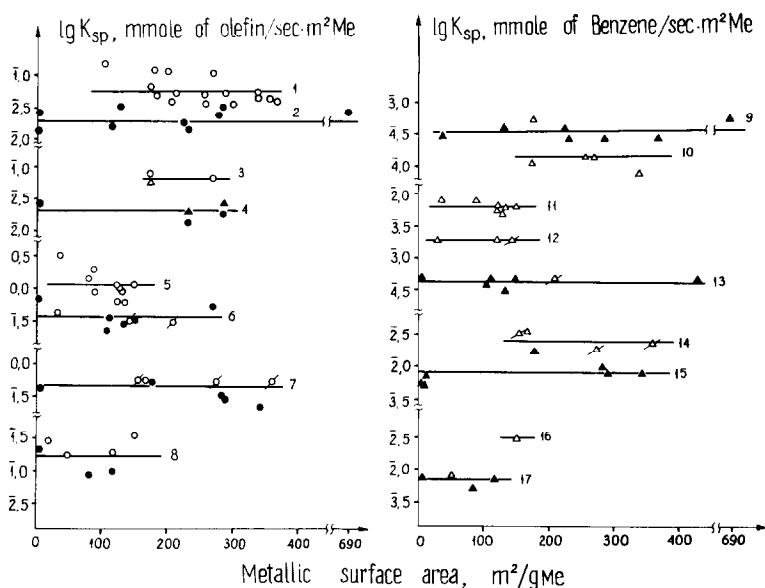


FIG. 3. Plots of specific catalytic activities of metals in zeolites (opened symbols) and catalysts of comparison (closed symbols points) toward olefin and benzene hydrogenation reactions versus metal surfaces. Crossed points correspond to metal-containing zeolites preoxidized at 500°C. *n*-Hexene-1 hydrogenation: (1, 2) Ni-systems; (5, 6) Pd-systems; (7) Pt-systems; (8) Ru-systems. Cyclohexene and styrene side bond hydrogenation: (3, 4) Ni-systems. Benzene hydrogenation: (9, 10) Ni-systems; (11, 12, 13) Pd-systems; (14, 15) Pt-systems; (16, 17) Ru-systems.

4-phenylbutene-1 olefin bond and complete styrene hydrogenation is lower than unity. In two latter cases K_{rel} of supported nickel is also independent of both metallic dispersion and the carrier type, but depends on the nature of converted unsaturated hydrocarbons.

K_{rel} of nickel in all zeolite-containing catalysts toward benzene hydrogenation reaction is lower than for nickel on silica samples (Table 2). Previously it was shown (4) that the difference increases with increases in the portion of the metal localized

inside zeolite cavities. K_{rel} of ruthenium toward the same reaction is practically independent of both metallic dispersion and the carrier type and is close to the value of K_{rel} of ruthenium black. K_{rel} of palladium in zeolites is almost an order of magnitude higher than that on comparison supports. K_{rel} of platinum supported on any carriers is higher than that for platinum black.

DISCUSSION

Metal Dispersion and Localization

For PdY samples preoxidized at 500°C

TABLE I

The Values of Relative Catalytic Activity (K_{rel}) of Supported Nickel toward Olefin Hydrogenation Reactions

Carrier	Propylene	Cyclohexene	Styrene olefin bond hydrogenation	4-Phenylbutene-1 olefin bond hydrogenation	Styrene complete hydrogenation
Metal black	—	0.78	—	—	—
Silica	0.6	0.6–1.0	0.8–1.5	0.3	1.6×10^{-3}
Zeolite NaY	0.6	0.6–1.2	0.9	0.2	1.4×10^{-3}

TABLE 2

The Values of Relative Catalytic Activity ($K_{rel} \times 10^3$) of Supported Metals toward Benzene Hydrogenation Reaction

Carrier	Nickel	Ruthenium	Palladium	Platinum
Metal black	4.8	73	0.8	12
Silica	20-22	64	—	25-33
Alumina	—	73	1-2	29-33
Zeolite NaY	—	51	2-3	37-58
Zeolite HY	1.3-4.8	84	6-10	24-37

and reduced in hydrogen at 150–500°C estimations of metal particle size, fulfilled by electron microscopy and chemisorption measurements, are in good agreements. Both methods indicate the formation of particles 20–40 Å in size. For acid platinum-containing zeolites there is no correlation between electron microscopic and chemisorption data. The value of the surface area estimated from the chemisorption data is close to that value at two-dimensional distribution of metallic platinum, while the electron microscopy method gives particles 20–30 Å in size.

After preoxidation at 300°C particles of both metals were not observed on the external surface of zeolite crystals. The Pd3d line in XPS spectra, which may characterize the palladium concentration on the ex-

ternal surface of zeolite crystals, was observed, but its intensity was substantially lower than after preoxidation at 500°C (Fig. 4). The latter two observations prove that both metals have stabilized mainly inside zeolite cavities after preoxidation of samples at 300°C. Simultaneously, namely, after this pretreatment condition, the oxygen chemisorption was insignificant on both platinum and palladium in acid zeolites.

From all the above it should be supposed that oxygen chemisorption on metallic platinum and palladium clusters in zeolites after pretreatment at (300/300) does not take place at all or occurs with a decreased stoichiometry.

State of Metals

Basing on the position of the ir band corresponding to the adsorption complexes of metallic palladium with carbon monoxide the conclusion may be made that palladium particles in zeolites are in electron-deficient state. It may be suggested that the state of platinum particles in acid zeolites after pretreatment at (300/300) should be electron-deficient too (3, 9).

Influence of Reaction Mixture Components

The disappearance in ir spectra of adsorbed CO of bands at 2100, 2120, and 2140

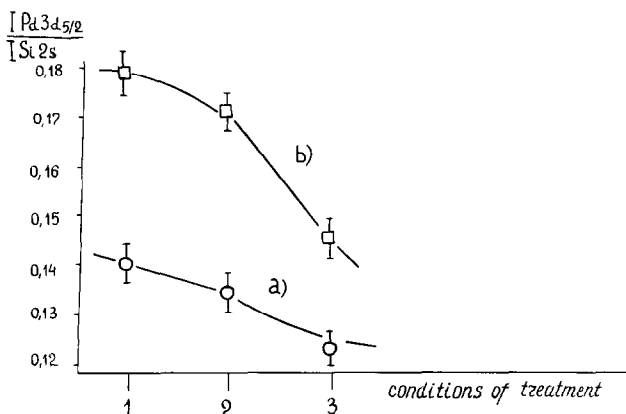
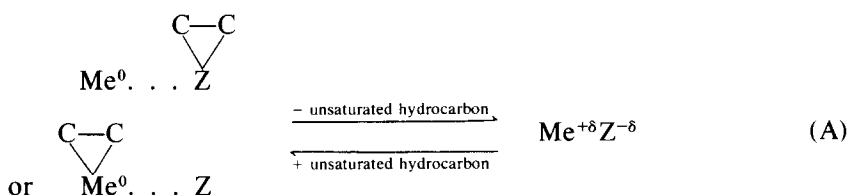


FIG. 4. Plot of relative intensity of Pd3d_{5/2} line in palladium-containing zeolites preoxidized at 300°C (a) and 500°C (b) versus the reduction conditions in spectrometer (see the legend for Fig. 1).

cm⁻¹ after additional adsorption of benzene permits the conclusion that "up-reduction" of all charged forms of palladium in zeolite, probably including Pd¹⁺, cations takes place (Fig. 2). This "up-reduction" process may proceed via two probable ways. First, complex formation through the charge transfer between electron-acceptive sites of the carrier and unsaturated hydrocarbon molecules is possible. The subsequent termination of interaction between metallic clusters and electron-acceptive sites will be resulted. Second, the disappearance of electron deficiency may be due to the

charge transfer between unsaturated hydrocarbon molecules and metallic clusters. Removal of adsorbed hydrocarbon under evacuation leads again to the formation of electron-deficient metallic clusters in zeolites (Fig. 2). Apparently in the case of a highly dispersed distribution of metal on a carrier with strong electron-acceptive sites the portion of metal in zero-valent state (Me⁰) is determined by Eq. (A). Position of the equilibrium in scheme (A) depends on both electron-acceptive properties of the carrier surface and electron-donative properties of reagent molecules.



If the above considerations of the instability of the reduced state of metallic clusters in zeolites are valid, one may conclude that the equilibrium (A) is displaced to the right side in the absence of reduction media. In this case the active component in zeolites is in the charged form and does not adsorb oxygen. Position of the equilibrium is displaced to the left side in the presence of the reduction media, i.e., the "up-reduction" process of the metal charged forms in zeolites occurs. Hence, metallic surface area values estimated from the oxygen chemisorption data should not correlate with the metallic surface in zeolites formed under reaction conditions.

Specific Catalytic Activity

Specific Catalytic activity (K_{sp}) of metals in zeolites toward investigated reactions exceeds K_{sp} of the same metals supported on other carriers. K_{sp} of nickel in zeolites toward benzene hydrogenation reaction is the only exception.

Taking into account the possible discrepancy between metallic surface areas,

formed in chemisorption and catalytic experiments, the supposition may be made that it only appears that the relation between K_{sp} of metals on different carriers experimentally obtained does not reflect the real situation.

Apparently, this phenomenon is not the case for metal particles fixed on the external surface of zeolite crystals. In fact, an increase of preoxidation temperature leads to an increase of metal portion on the external surface of zeolite crystals. As a result, K_{sp} values of metals in zeolites and in the catalysts of comparison become similar.

In this connection, the conclusions made earlier about variations of catalytic properties of palladium and platinum in zeolites as compared to those on nonacid carriers (1-3) require additional support.

Estimation of K_{sp} Value of Metals

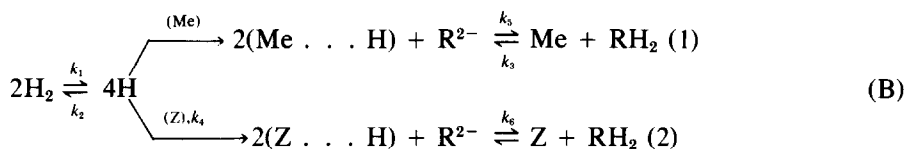
Estimation of K_{sp} value of metals ought to be more correct if the parameter, which characterizes the value of metallic surface area, was obtained under reduction condi-

tions. The reaction rate of *n*-hexene-1 hydrogenation (W_{hg}) may be used as such a parameter. It is known that this reaction is structure-insensitive. Hence, the value of K_{rel} , found as a relation of a rate of any hydrogenation reaction to W_{hg} , may be taken for a more correct estimation of K_{sp} .

The value of K_{rel} of supported nickel toward olefin hydrogenation reactions is independent of both the carrier type and metal dispersion (Table 1), the level of K_{rel} being determined by olefin reactivity only. K_{rel} of nickel in zeolites toward benzene hydrogenation reaction is much lower than that for nickel on silica samples (Table 2). This result may be associated with the displacement of the equilibrium (scheme A) to the right side in benzene-containing medium due to the comparatively lower electron-donative ability of benzene molecules. K_{rel} of ruthenium, fixed on the external surface of zeolite crystals, toward the benzene hydrogenation reaction is similar to that for metal supported on other carriers and ruthenium black. In fact, it is difficult to expect an influence of the zeolite carrier on the electronic state of relatively large metal particles localized outside zeolite cavities. K_{rel} of palladium in zeolites toward the same reaction is significantly higher than that of palladium on alumina and palladium black catalysts (Table 2), but K_{rel} of sup-

ported platinum is higher than that for platinum black almost independently of the carrier type.

In the latter two cases, higher values of K_{rel} toward benzene hydrogenation cannot be related to the electron-deficient state of metallic clusters, since the presence of a benzene atmosphere leads to displacement of the equilibrium (scheme A) to the left side. Hence, the most probable electronic state of metal is the zero-valent one (Me^0 , Fig. 2). If electron-deficient metal particles would be active in hydrogenation reactions, the change of the activation energy values and reaction orders as compared to those for metal black ought to be expected (10). However, such changes were not observed. The differences in the values of K_{rel} of supported metals cannot be related either to different metal dispersion in zeolites and on other carriers, since these differences are observed at similar values of W_{hg} in both cases. They also cannot be associated with the influence of electrostatic fields in zeolite cavities on reactivity of benzene molecules, as is suggested in Ref. (11), since, first, the effect is observed independently of the carrier type (as in the case of platinum) and second, the effect is independent of the size and the localization of particles of these metals in zeolites.



If proposals about hydrogen spillover (12) are valid, the exceeding of K_{rel} of palladium and platinum in zeolites toward the benzene hydrogenation reaction as compared to these values for metallic blacks and metals supported on other carriers may be connected with the appearance of additional hydrogenation surface. In this case, the benzene hydrogenation

reaction may be presented as a multistep process (scheme B), different stages of which can proceed on physically divided surfaces.

Transformation via route (2) may take place (i) if a carrier is pretreated under conditions leading to the formation of surface centers which can retain weakly active hydrogen; (ii) if high rates of active hydro-

gen formation and relatively low rates of its consumption on metal surface are observed, i.e., $(k_1-k_2) \gg (k_5-k_3)$. This may take place when the converted unsaturated compound has a fairly low reactivity.

In this connection the influence of hydrogen spillover on catalytic activity of metal-supported catalysts is more probable for hydrogenation reaction of benzene than of olefin. The activity of metals toward hydrogen dissociation reaction changes in the series: Pt > Pd > Ru > Ni (13). The differences in values of K_{rel} of metals supported on zeolites and other carriers are in agreement with this series. So far as this sequence must correspond to the increase of the rate constant of the first stage (k_1 , scheme B), it must correspond to the intensification of spillover effect under other equal conditions.

CONCLUSION

On the basis of the results obtained it is possible to conclude that the electronic state of metals in zeolites depends on both pretreatment conditions of the samples and on the position of the interaction equilibrium in the "reagent-metal-carrier" system. The latter depends on both electron-donative properties of reagent molecules and electron-acceptive properties of the carrier surface. The reversibility of this interaction leads to significant discrepancies in the values of surface areas which are catalytically active toward hydrogenation reactions and are estimated from the chemisorption data obtained in the absence of reaction medium components. So, the value of K_{sp} of metals estimated using gas chemisorption data cannot serve as a basis for conclusions about the peculiarities of the catalytic action of metals fixed in highly dispersed state inside zeolite cavities toward hydrogenation reactions.

Estimation of the peculiarities of the catalytic action of metals on different carriers is more correct when comparing the values of K_{rel} of metals defined as ratios of different reaction rates, since the value of K_{rel} of supported metal depends on the difference in the position of the interaction equilibrium in both "reagent(1)-metal-carrier" and "reagent(2)-metal-carrier" systems.

ACKNOWLEDGMENTS

The authors are thankful to P. A. Zhdan and A. A. Davydov for registration and interpretation of XPS and ir spectra.

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