The investigation of redox properties of palladium—zeolite catalysts

V. V. Kharlamov,* Kh. M. Minachev, L. P. Gulyaeva, and P. I. Slyunyaev

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Palladium catalysts based on A, X, Y, chabazite, erionite, mordenite, TsVM, and TsVK zeolites are studied by the methods of temperature-programmed reduction and hydrogen desorption. Palladium is shown to be located in zeolite pores in all catalysts except Pd/mordenite for which 24 % of the palladium is located on the external surface of the zeolite. The dispersity of the palladium on the zeolites is determined by the amount of H_2 evolved in the decomposition of the β-phase of PdH and by the value of the O/Pd ratio obtained by palladium oxidation in the 100 to 500 °C temperature range. According to the O/Pd ratio, the catalysts are divided into two groups: samples based on X, Y, chabazite, erionite, and mordenite (O/Pd = 0.4 to 0.7), and catalysts containing A, TsVM, and TsVK zeolites (O/Pd = 0.2 to 0.3). The catalysts of the first group are weakly active in the oxidative acetoxylation of propylene, while all of the catalysts of the second group except Pd/NaA are very active. The conclusion is drawn that the oxidation of palladium is not the limiting stage in the oxidative acetoxylation of propylene.

Key words: palladium, zeolites, allyl acetate, Pd oxidation, Pd reduction.

It has previously been shown[1,2] that active and selective Pd-containing catalysts based on zeolites can be prepared which are useful for the oxidative acetoxylation of propylene to allyl acetate.

$$C_3H_6 + AcOH + 1/2O_2 \rightarrow AcOC_3H_5 + H_2O$$

The activity of these catalysts depends substantially on the type and composition of the zeolite: it is not higher than $0.4 \cdot 10^{-3}$ mol (g Cat)$^{-1}$ h^{-1} for A, X, Y, chabazite, erionite, and mordenite zeolites, and increases to (3—7)$\cdot 10^{-3}$ mol (g Cat)$^{-1}$ h^{-1} for highly siliceous TsVM and TsVK zeolites.[3]

In addition to palladium on a zeolite, potassium acetate, which is a source of acetate ions for the reaction product, allyl acetate, is usually included in the composition of the catalyst. Different states of palladium in zeolites can be one possible reason for the different activities of Pd-zeolite catalysts in this reaction. In this connection, Pd-zeolite catalysts without potassium acetate are studied in this work by the methods of temperature-programmed reduction (TPR) and temperature-programmed hydrogen desorption (TPD H_2). The Pd distribution in the external surface and the cavities of zeolite crystals, the dispersity of metal, and the rate of its oxidation are also studied.

Experimental

Pd-zeolite catalysts were prepared by the known procedure.[3] Dried powdered samples were molded without a binder and crushed, and the 0.6—1.0 mm fraction was taken. Palladium content in the catalysts was determined by atomic adsorption spectroscopy (AAS).

TPR and TPD H_2 were carried out on a KL-1 flow-type catalytic installation (produced in the Designing Bureau of the Institute of Organic Chemistry, RAS) with a katharometer. A Pd-zeolite catalyst (0.15 g) was placed into a quartz reactor. The reactor was heated at a rate of 40 °C min^{-1}. TPR of a preoxidized catalyst sample was carried out with an Ar + 10 mol. % H_2 mixture. Argon was passed through the reactor when TPD H_2 spectra were recorded. Gases were passed through the reactor at a rate of 30 mL min^{-1}.

Argon and an argon—hydrogen mixture were purified from oxygen by passing them through columns filled with a copper catalyst and Mn/Al_2O_3. Gases were purified by a zeolite. The catalysts and adsorbents in the gas purification system were regenerated from time to time.

An initial sample of a catalyst was heated in the temperature-programmed regime to 500 °C in an argon flow in order to remove adsorbed water. Then the temperature was reduced to 100—500 °C and air was pressed through for 20 min. Finally the air was replaced with argon, the catalyst was cooled to −100 °C, TPR was carried out, the sample was cooled to −100 °C in the Ar + H_2 flow, and TPD was carried out.

Since in the samples studied the reduction of PdO takes place at 0 to 50 °C, the TPR method was also used to

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 642—648, April, 1995.

determine the amount of Pd located on the external surface of a zeolite and in its channels. With this purpose, a sample oxidized at 500 °C was cooled to room temperature, and water adsorption was carried out in an Ar flow. Water was adsorbed by dosing the carrier-gas saturated with H_2O vapor (saturator, 80 °C). The sample was kept at room temperature for not less than 30 min and cooled to −100 °C. The TPR was carried out by heating a catalyst to 50 °C. No water desorption occurs and only PdO located on the external surface is reduced. Then the thermodesorption of water was performed in an argon flow, the sample was cooled to −100 °C, and the TPR was performed again to reduce the PdO in the zeolite channels. For higher-siliceous zeolites ($SiO_2/Al_2O_3 \geq 30$), which are hydrophobic and in which water molecules do not fill the whole volume, water and *n*-hexane were adsorbed in turn, as in the case of TsVM-364 ($SiO_2/Al_2O_3 = 47$) and TsVK-2 ($SiO_2/Al_2O_3 = 68$) zeolites, or only *n*-hexane was adsorbed, as for TsVK-3 ($SiO_2/Al_2O_3 = 78$).

The stoichiometry of the reduction of palladium oxide on the surface of metal crystallites follows the reaction[4,5]

$$PdO + 3/2H_2 \rightarrow PdH + H_2O\ .$$

In the interior of the crystallites, the reduction of PdO is accompanied by the formation of the β-phase of palladium hydride in which the hydrogen content depends on the size of the metal crystallite.[5] In the experimental procedure used, the decomposition of the β-phase of PdH was registered at 50 to 70 °C, and in some cases the peak of hydrogen desorption partially overlapped the peak of hydrogen absorption as a result of PdO reduction. Therefore, in order to estimate the amount of reduced Pd, the surface area of the peak of desorbed hydrogen was subtracted from the surface area of the peak of absorbed H_2 and the reduction was assumed to occur according to the following equation

$$PdO + H_2 \rightarrow Pd + H_2O\ .$$

Results and Discussion

The TPR spectra of the Pd-zeolite catalysts oxidized at 500 °C are presented in Fig. 1. Two positive peaks in the −100 to 0 and −20 to 40 °C ranges and one negative peak at 50 to 70 °C are observed in all of the spectra. The peak in the −100 to 0 °C range relates to argon desorption from the intracrystalline cavities and channels of the zeolites, because it is observed in the spectra of both reduced Pd-zeolite catalysts and palladium-free zeolites. One specific feature of Pd/NaA catalysts is the absence of the peak of Ar desorption, probably due to weak adsorption of the latter at low temperatures.[6]

The peak in the −20 to 40 °C temperature range relates[7] to the reduction of the PdO phase. The temperature of its maximum ranges from 30 to 40 °C, which suggests that palladium interacts variously with the zeolite lattice.

The negative peak at 50 to 70 °C is likely to be related to hydrogen evolution in the decomposition of the β-phase of palladium hydride, which is known[4] to occur during the evacuation of the catalyst at room temperature.

The TPR spectra of the oxidized catalysts on which water, its mixture with *n*-hexane, or *n*-hexane were

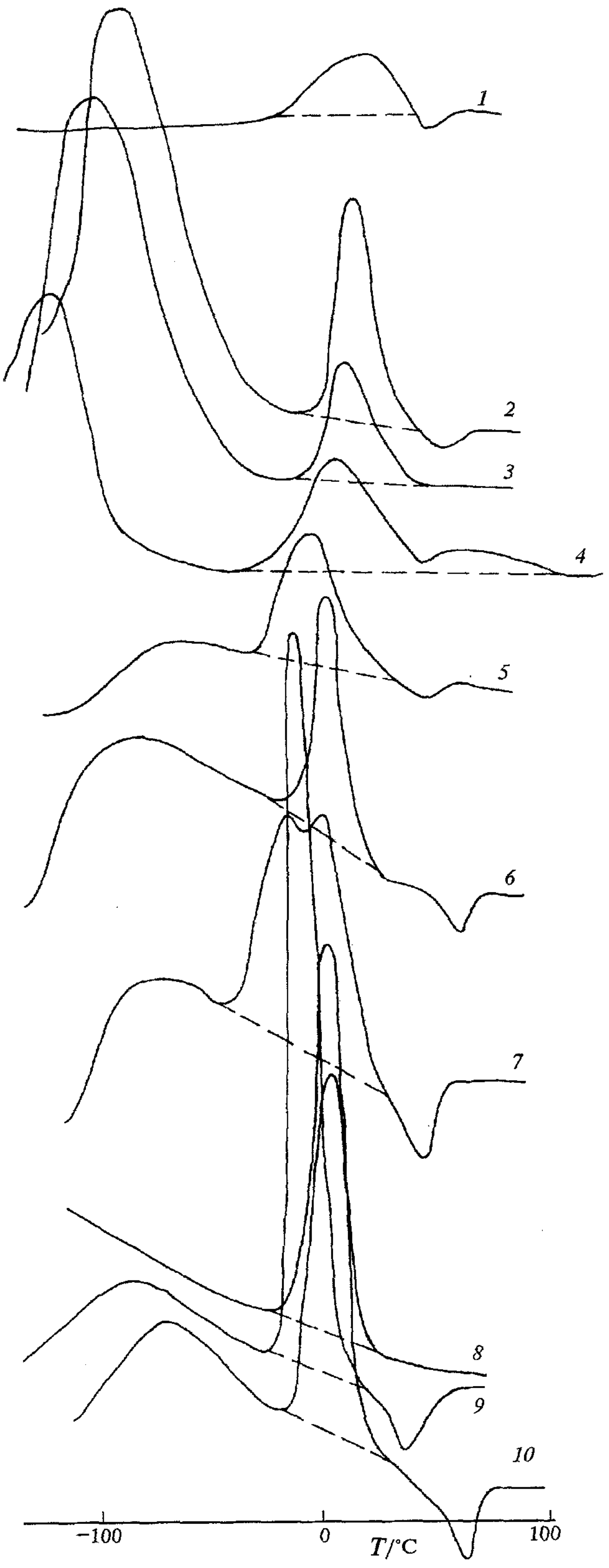

Fig. 1. TPR spectra of Pd-zeolite catalysts oxidized at 500 °C: 0.80 % Pd/NaA (*1*); 0.89 % Pd/NaX (*2*); 0.98 % Pd/NaY (*3*); 0.95 % Pd/chabazite (*4*); 1.30 % Pd/erionite (*5*); 0.89 % Pd/mordenite (*6*); 1.56 % Pd/TsVM-408 (*7*); 1.07 % Pd/TsVM-364 (*8*); 1.77 % Pd/TsVK-11 (*9*); 1.19 % Pd/TsVK-3 (*10*).

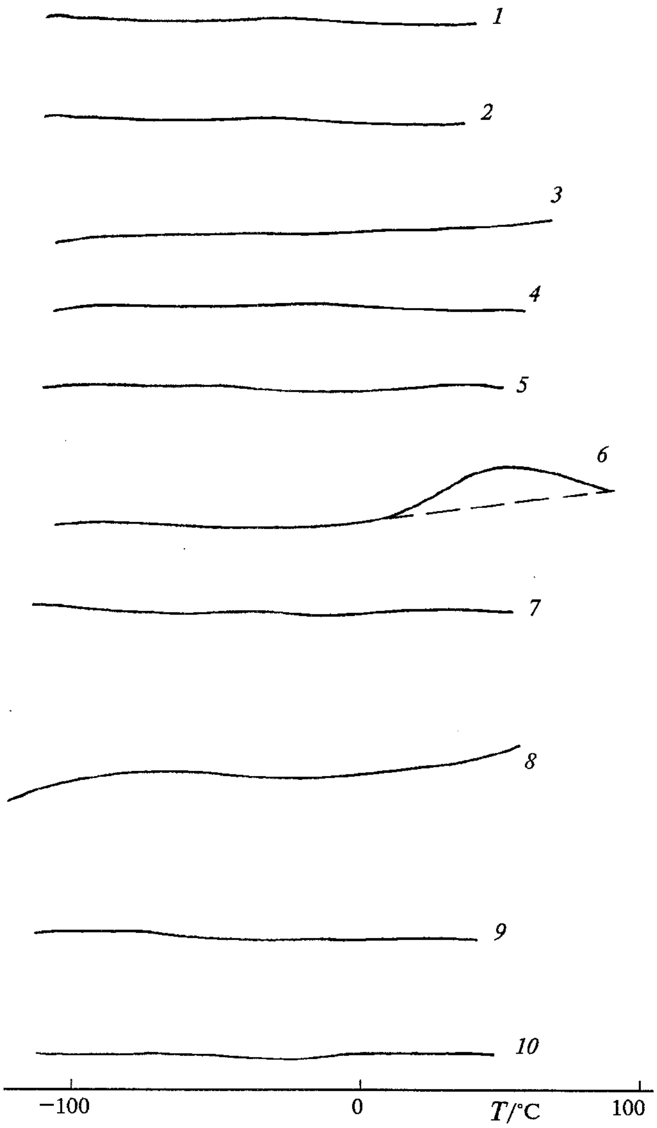

Fig. 2. TPR spectra of Pd-zeolite catalysts with adsorbed water (*1—7*), water and *n*-hexane (*8, 9*), and *n*-hexane (*10*). For the designation of the curves, see Fig. 1.

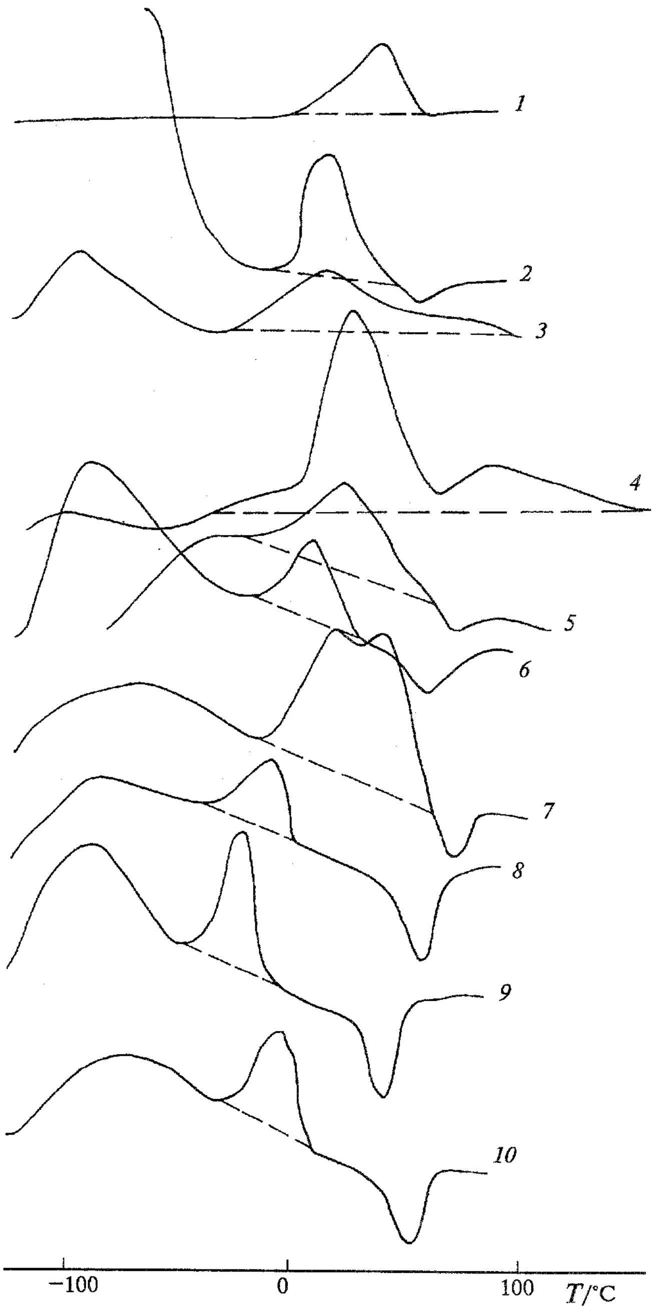

Fig. 3. TPR spectra of Pd-zeolite catalysts after thermodesorption of water (*1—7*), water and *n*-hexane mixture (*8, 9*), or *n*-hexane (*10*). For the designation of the curves, see Fig. 1.

adsorbed at ~20 °C are presented in Fig. 2. As can be seen, there are no peaks of Ar desorption, because the volumes of the zeolites are occupied by adsorbate molecules and hydrogen consumption for PdO reduction is observed only for Pd/mordenite. The ratio of the surface areas of the peaks corresponding to PdO reduction (see Figs. 1 and 2) is 0.24, *i.e.*, 24 % of Pd in the 0.89 % Pd/mordenite catalyst is on the external surface of the zeolite crystals. For the other catalysts, all of palladium is located inside the zeolite framework.

The TPR spectra of the catalysts after thermodesorption of H_2O or its mixture with *n*-hexane are presented in Fig. 3. They coincide qualitatively with the TPR spectra obtained without pre-treatment with water (see Fig. 1). The surface areas of the peaks in the TPR spectra of the catalysts based on TsVM-364, TsVK-11, and TsVK-3 zeolites after thermodesorption of n-C_6H_{14} or its mixture with H_2O are considerably smaller than those of the initial peaks (see Fig. 1). It is likely that PdO in these samples is partially reduced during the thermodesorption of *n*-hexane from the samples.

When the fraction of the metal on the external surface of the zeolite crystals is estimated by the method suggested, the question arises about the possible influence of adsorbed water on the reduction capability of PdO located on the external surface. To answer this question, a sample of 5 % Pd/NaY was prepared in which, according to the conditions of the preparation, most or all of palladium is located on the external surface of the zeolite crystals. The results of the study of this sample are presented in Fig. 4.

In the TPR spectrum of the sample with adsorbed H_2O, a small shift of the temperature maximum is observed for the peak of PdO reduction, while its surface area is nearly the same as that of the peak of the catalyst without adsorbed water. No PdO reduction is observed after desorption of H_2O, and only the peak of the desorption of the hydrogen formed in the decomposition of the β-phase of palladium hydride is in the spectrum. Therefore, in this catalyst sample, all of palladium is located on the external surface of the zeolite crystals, and adsorbed H_2O virtually does not affect PdO reduction.

Thus, in all of the Pd-zeolite catalysts studied except Pd/mordenite, all of the metal is located in the zeolite cavities and, hence, the difference in the activities of these catalysts in the oxidative acetoxylation of propylene is not related to different distributions of palladium in the samples.

The TPD H_2 spectra for the catalysts studied are presented in Fig. 5. No hydrogen desorption is observed in the 100 to 500 °C range. Signals appear only below 40 °C. The peak in the −20 to 10 °C temperature range is probably caused by the desorption of the hydrogen formed during the decomposition of the β-phase of palladium hydride. As can be seen from Fig. 5, the β-PdH phase decomposes during TPD H_2 at 60 to 70 °C below the temperature of the TPR experiments (see Fig. 1). This is caused by the fact that different gases pass through the catalysts: Ar for the TPD H_2 and Ar + 10 % H_2 for the TPR.

One more peak sometimes appears in the TPD H_2 spectra in the −80 to −50 °C temperature range. This peak can be associated with the desorption of argon from the zeolite micropores and desorption of the hydrogen physically adsorbed on palladium. One can qualitatively judge about the dispersity of palladium in the catalysts studied from the value of the peak of the hydride hydrogen. It has been shown[5] that the larger the palladium particles, the more hydrogen is located in the β-phase of PdH.

It can be seen from Fig. 5 that the values of the peaks of hydride hydrogen strongly differ for different zeolites. The smallest amount of hydrogen is evolved in β-PdH decomposition from the catalysts based on the NaX, NaY, and NaM zeolites. The H_{hydr}/Pd ratios for these catalysts are 0.18, 0.16, and 0.23, respectively. The maximum peak of hydride hydrogen is registered in the TPD spectrum of the catalyst based on TsVM-364

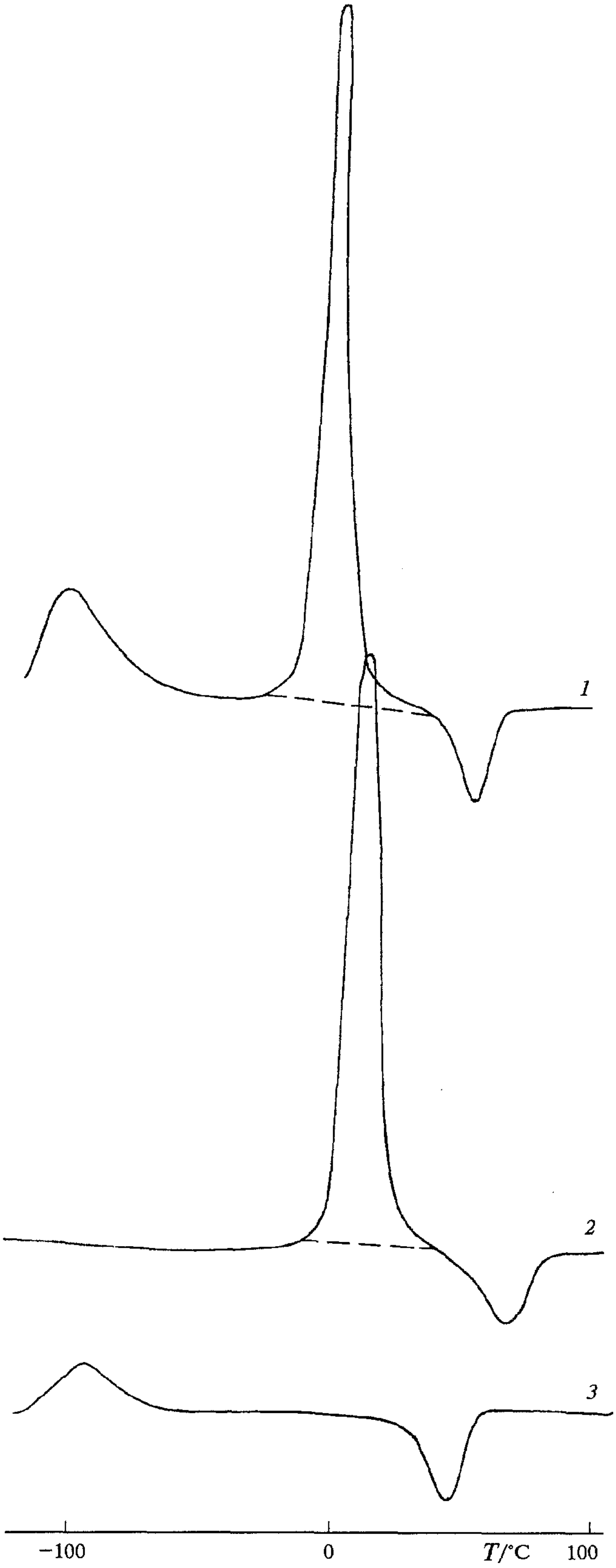

Fig. 4. TPR spectra of 5 % Pd/NaY catalyst: initial, preoxidized at 500 °C (*1*); oxidized with adsorbed H_2O (*2*); after desorption of H_2O (*3*).

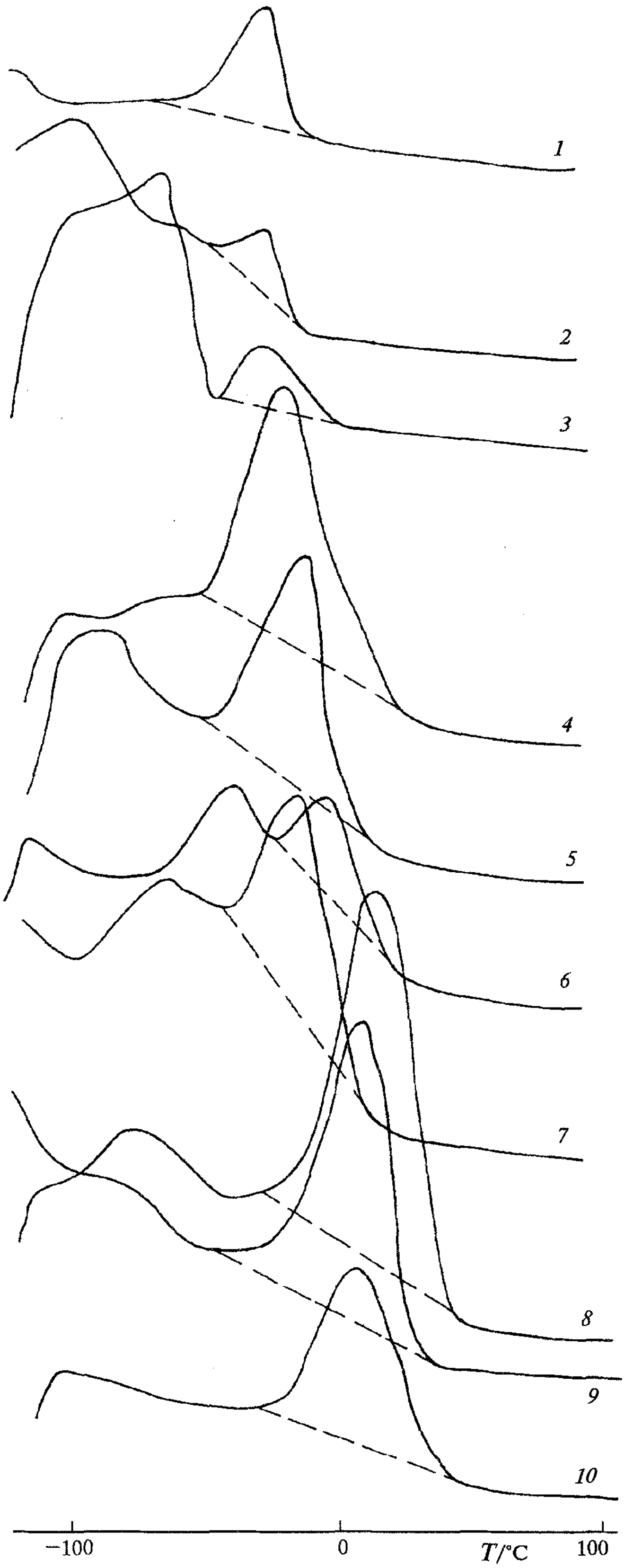

Fig. 5. TPD H_2 spectrum of reduced catalyst samples. Designation of curves is as in Fig. 1.

(H_{hydr}/Pd = 1.09). Therefore, the catalysts based on NaX, NaY, and NaM are characterized by the maximum dispersity of palladium, while the lowest dispersity is in the sample containing TsVM-364. The changes in the Pd dispersity and the catalyst activity are the opposite in the synthesis of allyl acetate: the lower the dispersity, the higher the activity.

The oxidation of the zeolite catalysts in a wide temperature range followed by TPR was studied in order to get a more exact estimation of the Pd dispersity. The surface area of the hydrogen absorption peak in the TPR spectrum usually increases with the temperature of the oxidation of the catalyst, while the temperature of the maximum of this peak and the temperature of the onset of catalyst reduction shift toward the high-temperature range.

The TPR spectra for the 200 to 500 °C range of the oxidation of the 0.8 % Pd/NaA catalyst are presented in Fig. 6 as an example. It can be seen that increasing the oxidation temperature results in a shift of the temperature of the peak maximum (or the temperature of PdO reduction) and in changes in the surface area and the shape of the peak. This is related to the fact that different amounts of metallic palladium, which is the catalyst of PdO reduction, remain unoxidized at different oxidation temperatures. Therefore, the content of Pd^0 atoms and the distances at which they are removed

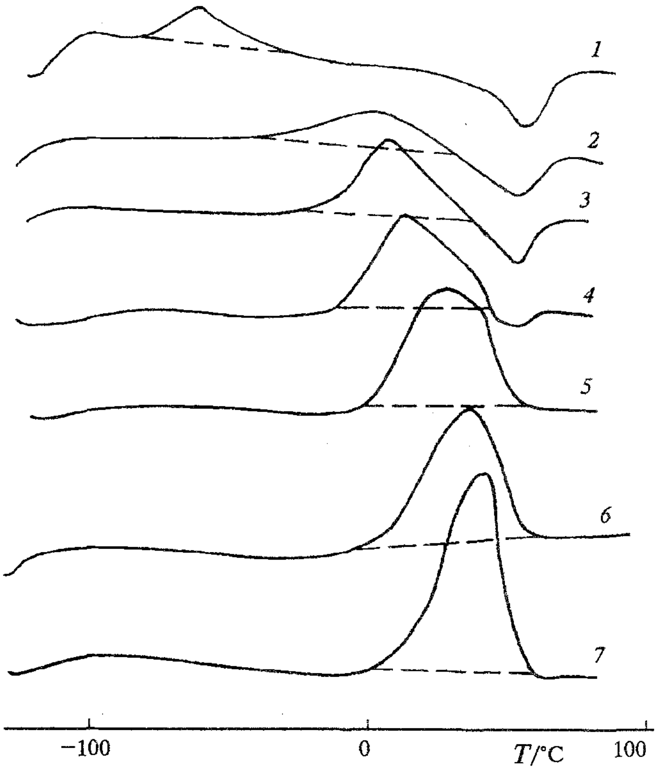

Fig. 6. Effect of the pre-oxidation temperature on the TPR spectrum of the 0.80 % Pd/NaA catalyst, T/°C: 200 (*1*); 250 (*2*); 300 (*3*); 350 (*4*); 400 (*5*); 450 (*6*); 500 (*7*).

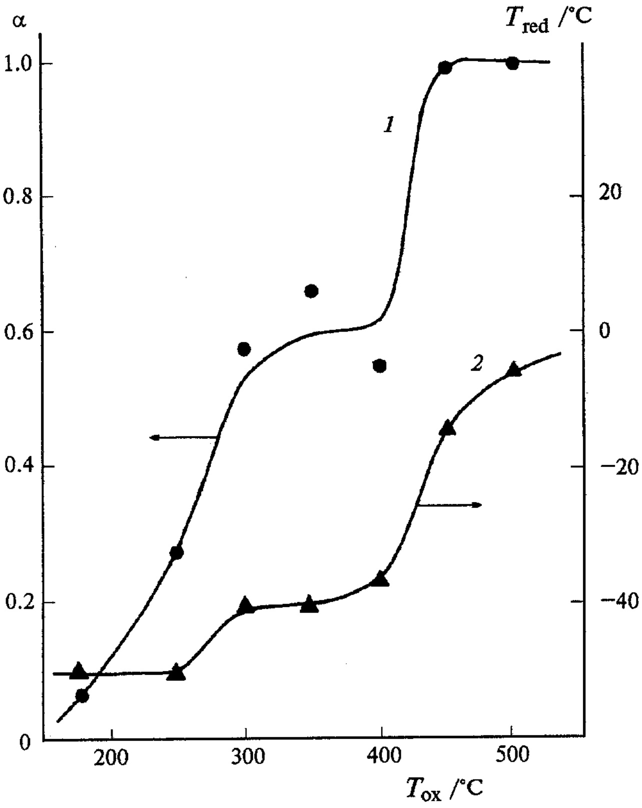

Fig. 7. Dependence of the extent of Pd oxidation (*1*) and the temperature of the beginning of the 0.89 % Pd/NaM catalyst reduction (*2*) on the temperature of sample oxidation.

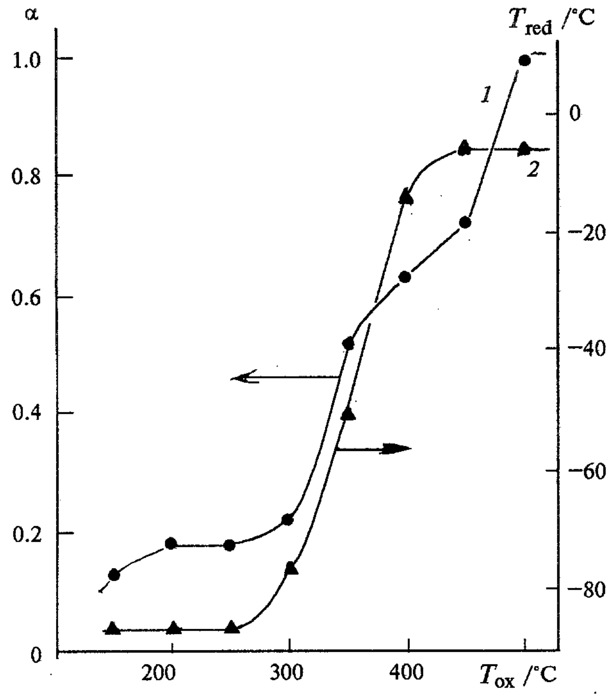

Fig. 8. Dependence of the extent of Pd oxidation (*1*) and the temperature of the beginning of the 1.19 % Pd/TsVK-3 catalyst reduction (*2*) on the temperature of sample oxidation.

from the PdO molecules have an effect on the reduction rate and the shape of the peak of hydrogen absorption.

The dependences of the extent of palladium oxidation and the temperature of the beginning of reduction on the temperature of the sample oxidation were plotted to estimate the dispersity of palladium in the zeolite catalysts. Typical plots are presented in Figs. 7 and 8. Plateaus, probably corresponding to the completion of the oxidation of the surface Pd atoms, usually exist in the curves of the temperature dependences of the extent of palladium oxidation. This is confirmed by a sharp increase in the temperature of the beginning of PdO reduction with a further increase in the temperature of catalyst oxidation. The temperature intervals of the plateaus differ for different Pd-zeolite catalysts. For example, for the sample of 0.89 % Pd/NaM (see Fig. 7) the plateau lies in the 300 to 400 °C temperature range, while for the 1.19 % Pd/TsVK-3 catalyst it lies between 200 and 300 °C. In addition, in the case of some catalysts, for example, the catalysts based on NaA and NaY, these plateaus are not very pronounced (they are only inflections), indicating that the Pd atoms in the interior of the metal crystallites begin to oxidize when the process on the surface is not completed. In these cases, the accuracy of the determination of the metal dispersity (O/Pd) decreases.

Since the values O/Pd and H_{hydr}/Pd characterize the dispersity of the metal in the catalyst, there is a correlation between them (Fig. 9). Curves I and II in Fig. 9 represent the calculated dependences for the cases when palladium crystallites exist on a planar surface or in large pores (when five sides of the cubic crystals are free for adsorption) and in narrow pores (when only two sides of the six can participate in adsorption). It follows from Fig. 9 that the experimental points lie mainly between the curves that characterize the two hypothetical cases mentioned above: "narrow" and "large" pores.

The data on the state of Pd in zeolite catalysts and their activities in the oxidative acetoxylation of propylene at 180 °C (see Ref. 3) are listed in Table 1. The catalysts whose dispersities of Pd estimated from the O/Pd value are 0.2 to 0.3 are active in the oxidative acetoxylation of propylene. The inactive 0.8 % Pd/NaA also enters into this group along with the catalysts based on highly siliceous zeolites probably because the reagent molecules cannot penetrate into the narrow pores of the zeolite.

We tried to estimate the rate of the oxidation of Pd in the catalysts by varying the duration of oxidation at 180 °C followed by TPR. It turns out that the surface area of the TPR peak corresponds to the oxidation of 10 to 13 % of the Pd atoms and remains constant when the

Table 1. Activity and state of palladium in Pd-zeolite catalysts of the oxidative acetoxylation of propylene

Zeolite	SiO_2/Al_2O_3	Pd content (wt. %) zeolite	Fraction of Pd on the external surface(%)	O/Pd	H_{hydr}/Pd	Activity, $A \cdot 10^3$ /mol (g Cat)$^{-1}$ h^{-1}
A	2.0	0.80	0	0.25	0.34	0
X	2.9	0.89	0	0.75	0.18	0
Y	4.8	0.98	0	0.50	0.16	0.35
Chabazite	5.0	0.95	0	0.40	0.70	0.44
Erionite	6.0	1.30	0	0.60	0.38	0.15
Mordenite	10.0	0.89	24.0	0.60	0.23	0.19
TsVM-408	29.6	1.56	0	0.17	0.34	7.33
TsVM-364	47.0	1.07	0	0.20	1.09	7.43
TsVK-11	68.0	1.77	0	0.30	0.41	5.52
TsVK-3	78.0	1.19	0	0.20	0.43	3.04

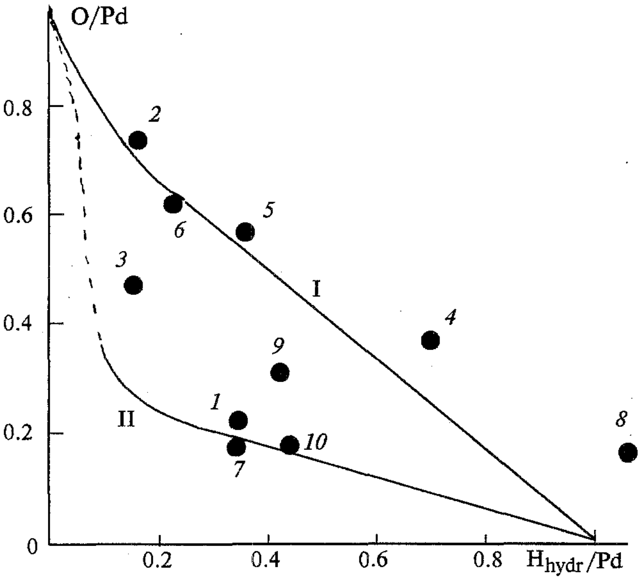

Fig. 9. Dependence of the O/Pd ratio on H_{hydr}/Pd obtained from the calculation of the model of "large" (I) and "narrow" (II) pores. The points correspond to experimental data, numeration of catalysts being as in Fig. 1.

duration of the oxidation of 0.8 % Pd/NaA is varied from 30 s to 10 min. This indicates that the rate of Pd oxidation in the zeolite catalysts is rather high and probably does not determine the overall rate of the oxidative acetoxylation of propylene. In order to answer more exactly the question about the slow stage of the reaction, one must take into account the possible promoting effect of the addition of AcOK, which is present in the catalyst under the conditions of real catalysis and was absent in the model systems studied in this work by the TPR method. We have recently shown that the values of the O/Pd ratio significantly differ for the catalysts 1.5 % Pd/TsVM and 1.5 % Pd/TsVM + 15 % AcOK. In the first case, this value is 0.48, while in the second case it increases[8] to ~4.0. It cannot be excluded that potassium acetate can also change the rate of palladium oxidation in the catalyst. Additional studies should be performed to answer these questions.

References

1. Kh. M. Minachev, O. M. Nefedov, V. V. Kharlamov, S. Yu. Panov, and S. F. Politanskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1490 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1191 (Engl. Transl.)].
2. Kh. M. Minachev, O. M. Nefedov, V. V. Kharlamov, S. Yu. Panov, A. M. Shkitov, and M. I. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2688 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **37**, 2409 (Engl. Transl.)].
3. Kh. M. Minachev and V. V. Kharlamov, *Proc. Intern. Symp. Zeolite Catalysis*, Siofok, Hungary, May 13—16, 1985, 497.
4. J. E. Benson, H. S. Hwang, and M. Boudart, *J. Catal.*, 1973, **30**, 146.
5. M. Boudart and H. S. Hwang, *J. Catal.*, 1975, **39**, 44.
6. D. Brek, *Tseolitovye molekulyarnye sita* [*Zeolite Molecular Sieves*], Mir, Moscow, 1976 (Russ.Transl.).
7. S. T. Homeyer and W. M. H. Sachtler, *J. Catal.*, 1989, **118**, 266.
8. Kh. M. Minachev, T. S. Starostina, V. V. Kharlamov, T. Romotovski, and I. Komorek, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1993, 1721 [*Russ. Chem. Bull.*, 1993, **42**, 1643 (Engl. Transl.)].

Received February 10, 1994;
in revised form November 15, 1994