

The Effect of Support Nature and the Temperature of Preliminary Calcination on the Atomic Catalytic Activity of Supported Palladium Catalysts for the Complete Oxidation of Hydrocarbons

D. P. Chzhu*, P. G. Tsyrul'nikov*, G. N. Kryukova**, V. F. Borbat***,
E. N. Kudrya*, M. D. Smolikov*, and A. V. Bubnov*

* Boreskov Institute of Catalysis (Omsk Branch), Siberian Division, Russian Academy of Sciences, Omsk, 644053 Russia

** Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

*** Omsk State University, Omsk, 644077 Russia

Received September 20, 2002

Abstract—It is shown that for palladium catalysts supported on various supports, there is no effect of thermal activation consisting of an increase in the turnover number (TON) of palladium with an increase in the temperature of sample calcination from 500 to 700°C, as was observed in the case of similar supported platinum catalysts; for two palladium–alumina catalysts calcined at 500°C and differing in the concentration of palladium and dispersity, the TON of low-dispersity palladium is substantially higher than the TON of high-dispersity palladium; all other conditions being the same, the TON of supported palladium is determined by the support nature.

INTRODUCTION

Hydrocarbon oxidation processes over supported platinum and palladium catalysts have been discussed in a huge number of papers. However, as follows from the published data, there is no common opinion regarding the relationships between the structural and surface changes of the catalysts in the course of preliminary treatment and a reaction and changes in the catalyst activity.

One of the important characteristics of platinum and palladium catalysts that determines whether a reaction is structure-sensitive is the turnover number (TON), which is the activity per one surface atom of a supported metal.

In several recent publications, the relationships between the TON, the state of the active component and the size of the metal particles on the catalyst surface were studied for hydrocarbon oxidation reactions. Briot *et al.* [1, 2] showed that the catalytic combustion of methane on platinum and palladium catalysts supported on alumina is structure-sensitive, because the TON increases with an increase in the size of the particles. An analogous conclusion was drawn for the catalytic oxidation of propylene [3] and *n*-heptane [4] over the same catalytic systems. Hicks *et al.* [5, 6] studied the behavior of supported platinum and palladium in the reaction of methane oxidation at 300°C. On both metals, the reaction was also structure-sensitive. Cullis and Willat [7] found for methane oxidation that the TON

does not depend on the size of the metal particles, whereas Baldwin and Burch [8] reported a change in the TON but without any relation to the particle size.

Earlier we established that the effect of a drastic increase in the TON after catalyst calcination in air at 600–700°C, which has been called the effect of thermal activation, reveals itself over the supported catalysts Pt/MO_x (where MO_x is Al₂O₃, CeO₂, La₂O₃, and ZrO₂) in the complete oxidation of *n*-pentane [9]. One might expect that this phenomenon is only characteristic of platinum catalysts. In this connection, the goal of the study was to search for ways to change the TON of supported palladium in model reactions of the complete oxidation of methane and *n*-pentane after thermal treatment of the samples in air at elevated temperatures, and finding the relationships between the TON and the size of the metal particles.

EXPERIMENTAL

Catalyst preparation. Support materials Al₂O₃, ZrO₂, and CeO₂, formed as chips, were prepared by extrusion of hydroxides peptized with nitric acid; hydroxides were preliminarily precipitated with ammonia from the nitrates of the corresponding metals (analytical purity grade) with further drying at 120°C and calcination at 500°C for 4 h. To prepare another support, ZrO₂ was calcined at 750°C for 4 h.

The support (0.3 mol) CeO₂–(0.7 mol) ZrO₂ and supports based on modified alumina (Al₂O₃–CeO₂, Al₂O₃–ZrO₂, and Al₂O₃–La₂O₃) in the form of chips

were prepared by the extrusion of hydroxides preliminarily coprecipitated with ammonia from the nitrates of the corresponding metals (analytical purity grade) and peptized with nitric acid. They were dried at 120°C and calcined at 500°C for 4 h. The 0.5–1.0 mm fraction was used to further support the palladium.

Palladium catalysts were obtained by the impregnation of the same fraction of ZrO₂ and CeO₂–ZrO₂ with the solution of palladium nitrate. The samples based on CeO₂ and γ -Al₂O₃ were prepared by chemisorption from the solution of palladium nitrate at room temperature. For the modified supports Al₂O₃–CeO₂ (7.2 wt % CeO₂), Al₂O₃–ZrO₂ (4.9 wt % ZrO₂), and Al₂O₃–La₂O₃ (7.2 wt % La₂O₃), palladium catalysts were obtained by chemisorption from the solution of palladium nitrate at room temperature. The samples were then dried at 120°C for 1 h. Thermal treatment of the samples was carried out in a muffle furnace by calcination in air at 500, 600, and 700°C for 2 h.

The phase composition of the support and palladium catalysts were studied by XRD (on a DRON-3 instrument using MoK α irradiation with a β -filter after the sample before a counter (for Pd/Al₂O₃, Pd/CeO₂, and Pd/La₂O₃) and CuK α irradiation with a β -filter after the sample before a counter (for Pd/ZrO₂, Pd/Al₂O₃–CeO₂, and Pd/Al₂O₃–ZrO₂)). Samples were analyzed by the Bregg–Brentano method of powder diffractometry.

Electron microscopic imaging of the samples was carried out using a transmission electron microscope JEM-2010 (resolution, 0.14 nm; accelerating voltage, 200 kV). The samples were prepared for study by supporting from an alcohol suspension on an ultrasound dispersant UZDN-3.

Chemical analysis of catalysts for determining the palladium concentration was carried out according to the known technique [10].

The catalytic activity of the samples was determined in the kinetics-controlled regime using a flow-circulation setup under gradientless conditions in the model reactions of methane and *n*-pentane oxidation. The catalyst loading was ~1.5 g. In the case of CH₄ oxidation, the initial gas mixture consisted of methane (0.5 vol %) and air (99.5 vol %). In the case of *n*-pentane oxidation, the initial mixture consisted of *n*-pentane (0.1 vol %) and air (99.9 vol %). The rate of the gaseous mixture flow through the reactor with a sample was varied from 10 to 60 l/h. The circulation rate was ~800 l/h. Analysis of the reaction mixture before and after the reactor was carried out using an LKhM-8 MD chromatograph with a flame-ionization detector and a stainless steel 3 mm $\times$ 2 m column packed with Polisorb-1. The reaction was controlled by changes in the concentration of unreacted methane (or *n*-pentane) at the reactor inlet. No other peaks except for the peak of methane (or *n*-pentane) were observed. The TON of the samples was compared at 500°C (in the case of methane oxida-

tion) or 300°C (in the case of *n*-pentane oxidation) at 50% conversion, which corresponded to a concentration of methane of 0.25 vol % or *n*-pentane of 0.05 vol %.

The TONs of the samples were calculated using the following formulas:

$$W_{\text{TON}} = W/N_{\text{Pd}}, \quad (1)$$

where W_{TON} is the turnover number (ncm³ CH₄ atom⁻¹ s⁻¹ or ncm³ C₅H₁₂ atom⁻¹ s⁻¹), W is the activity per 1 g of the catalyst (ncm³ CH₄ g⁻¹ s⁻¹ or ncm³ C₅H₁₂ g⁻¹ s⁻¹); and N_{Pd} is the number of surface palladium atoms per 1 g of the catalyst (atom/g),

$$N_{\text{Pd}} = (0.01 C_{\text{Pd}} D_{\text{Pd}} N_{\text{A}})/M_{\text{Pd}}, \quad (2)$$

where C_{Pd} is the concentration of palladium in the catalyst (wt %), D_{Pd} is the dispersity of supported palladium, N_{A} is Avogadro's number, and M_{Pd} is the molar weight of palladium.

The experimental error, including the error in determining the catalytic activity and chemisorption measurements, was ~20%.

The dispersity of supported palladium (D_{Pd}) was determined using H₂–O₂ titration in the all-soldered glass setup using the known technique [11] (except for the samples that had CeO₂ in their composition). The determination of dispersity included the following main steps:

- (1) Drying the sample charged into the reactor at a low pressure and 120°C for 2 h;
- (2) Sample reduction at 500°C (with a continuous increase in the temperature from room temperature) in the reactor with hydrogen circulation and freezing (at $T = -196^\circ\text{C}$) the reaction products for 1 h and further vacuuming;
- (3) "Blank" titration with oxygen at room temperature for 20 min without checking the result with further vacuuming;
- (4) Hydrogen chemisorption at 150°C for 30 min; and
- (5) Titration of adsorbed hydrogen by a certain volume of oxygen.

The dispersity of catalyst supported on CeO₂ or on modified Al₂O₃ was determined by CO adsorption at room temperature on the surface of samples preliminarily prepared in the same setups where H₂–O₂ titration was carried out. The method for determining the dispersity included the following steps:

- (1) Drying the samples charged into the reactor at a low pressure (10⁻² Torr) and 120°C for 2 h;
- (2) Sample reduction at 350°C for 2 h (with a continuous temperature increase from room temperature) in the reactor with hydrogen circulation and freezing

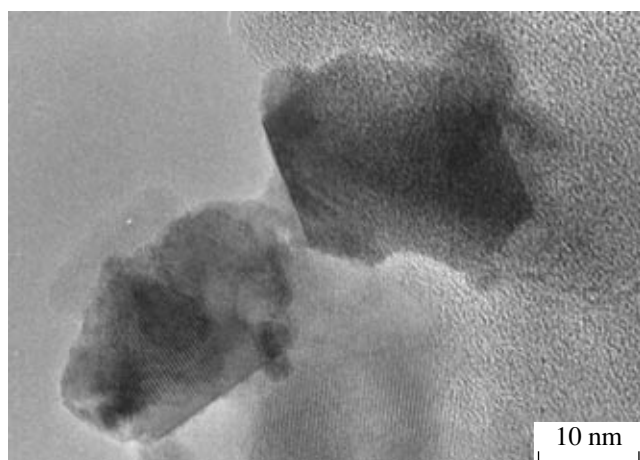


Fig. 1. Microscopic image of the freshly prepared sample 2%Pd/Al₂O₃-CeO₂, which was preliminarily calcined in air at 500°C (2500000 magnification).

(at $T = -196^{\circ}\text{C}$) the reaction products and further vacuuming to 10^{-2} Torr;

(3) “Blank” titration with oxygen at room temperature (without documenting the result) for 20 min and further vacuuming);

(4) Hydrogen chemisorption at 150°C (for platinum catalysts) or at room temperature (for palladium catalysts) for 30 min;

(5) H₂ desorption from the catalyst surface (10^{-2} Torr) with an increase in temperature from 150 to 350°C for 1–1.5 h;

(6) Cooling to room temperature at a low pressure; and

(7) CO chemisorption on the sample prepared.

The total BET surface area of the samples was measured using a Sorpt-1750 instrument from single-point nitrogen adsorption at $P = 135$ Torr and $T = 77$ K.

RESULTS AND DISCUSSION

The XRD analysis of the samples showed that

1. The Pd/ γ -Al₂O₃ samples (with palladium concentrations of 1 and 2 wt %) after preliminary calcination at 500 and 700°C are a two-phase system consisting of palladium metal crystals and the phase of γ -Al₂O₃. However, for the sample Pd/ γ -Al₂O₃ (1 wt % Pd) calcined at 600°C, a new PdO phase appears in addition to the two phases mentioned above, although the corresponding peak is poorly resolved.

2. The Pd/ZrO₂ sample (T_{calcin} ZrO₂, 500°C) consists of three crystalline phases: metallic palladium, ZrO₂ with monoclinic and tetragonal structures. In the sample calcined at 500°C, the monoclinic structure dominates over the tetragonal one. With an increase in the calcination temperature to 700°C, the intensity of the peak of tetragonal phase in the XRD pattern remains the same, whereas that of the monoclinic phase

increases. These data suggest that a portion of the zirconia is initially in an amorphous state and crystallizes to form the monoclinic modification with an increase in the temperature of calcination.

In the Pd/ZrO₂ sample (T_{calcin} ZrO₂, 750°C) calcined at 500 and 700°C, the above three crystalline phases are also present, but zirconia is basically monoclinic because it was preliminarily calcined at 750°C.

3. The Pd/CeO₂ sample after calcination in air at 500 and 700°C consists of two phases: metallic palladium crystals and the CeO₂ phase.

4. The Pd/Al₂O₃-CeO₂ sample calcined at 500 and 700°C consists of three phases: metallic palladium crystals, the γ -Al₂O₃ phase, and the CeO₂ with a coherent scattering region (CSR) $d \sim 35\text{--}40$ Å.

5. The Pd/Al₂O₃-ZrO₂ sample after calcination at 500°C contains the phases of γ -Al₂O₃ and PdO. After calcination in air at 700°C, the cubic ZrO₂ phase (CSR $d \sim 80$ Å) and palladium crystals also appear.

Electron microscopic images of modified palladium-aluminum samples 2% Pd/Al₂O₃-CeO₂ are shown in Figs. 1–3. The initial freshly prepared sample calcined at 500°C in air but not studied in the oxidation reaction (Fig. 1) is characterized by an average size of supported palladium particles of ~ 10 nm, although some particles are elongated. The high-resolution image (Fig. 1) shows that the particles have cuttings and their internal structure is well ordered. Figure 2 shows the same sample calcined in air at 500°C and tested in methane oxidation. Upon the reaction the size of the supported particles insignificantly increases (up to 15 nm). These are still isolated particles with well cutting (Fig. 2a). It is likely that alumina particles interact with ceria particles, which reveals itself in the form of a characteristic regular contrast on high-resolution images of the support (Fig. 2b). The interaction of alumina and ceria and the formation of aluminum phases were noted in [12]. After calcination in air at 600°C, particles are sintered to form a size of 40 nm, but there are some particles with a size of 10 nm (Fig. 3b, where palladium crystallites are shown as dark spots). Sintering was disordered with the formation of noncoherent boundaries between particles, where the structure of the material is strongly distorted (Fig. 3a). Isolated particles with a size of 10 nm have a well-ordered internal structure and are characterized by regular cutting (Fig. 3b).

Thus, as follows from the electron microscopic data, with an increase in the calcination temperature of the Pd/Al₂O₃-CeO₂ samples to 600°C, the formation of noncoherent boundaries between sintered palladium crystallites takes place. This phenomenon can be associated with the fact that in the course of sintering the CeO₂ fragments migrate together with the palladium crystallites with which they interact.

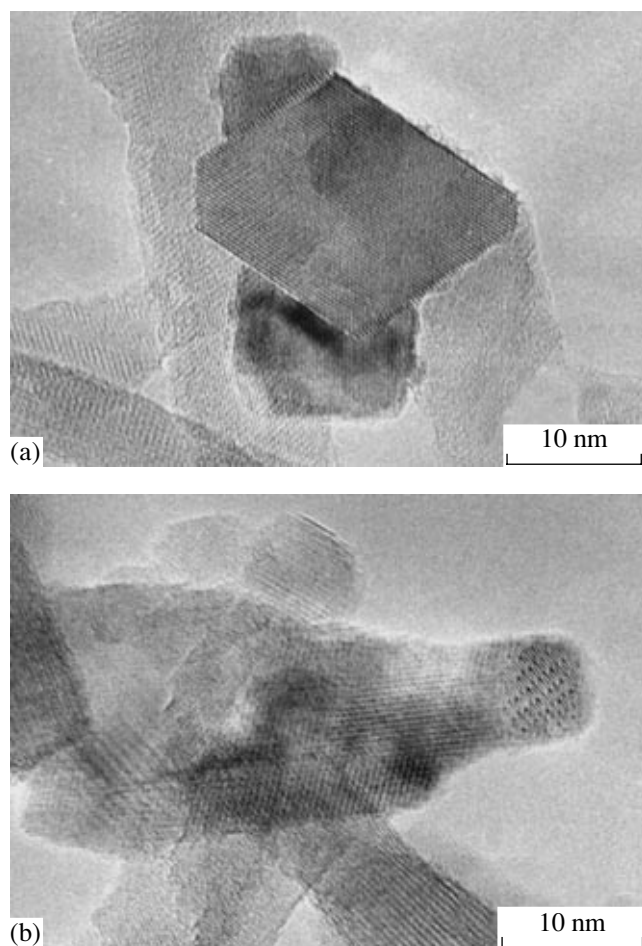


Fig. 2. Microscopic image of (a) the sample 2% Pd/Al₂O₃–CeO₂, tested in the complete oxidation of methane (2500000 magnification) and (b) the support.

The total BET specific surface area for the supports was (m²/g): γ -Al₂O₃, 201; ZrO₂, 39; CeO₂, 52.

Catalytic Activity of the Samples

The specific catalytic activity of the samples (based on 1 g of the catalyst) for the process of the complete oxidation of methane. The characteristics of the 2% Pd catalysts supported on γ -Al₂O₃, ZrO₂ (T_{calcin} 500 and 750°C), and CeO₂, as well as CeO₂ (0.3 mol)–ZrO₂ (0.7 mol) and calcined at two different temperatures in air (500 and 700°C), are shown in Table 1. As follows from these data, the most active systems are supported palladium–aluminum catalysts, whose catalytic activity changes insignificantly with an increase in the temperature of calcination in air. The Pd/ZrO₂ samples are also rather active in this reaction, and their activity is close to that of Pd/Al₂O₃. Note that an increase in the calcination temperature of the support ZrO₂ from 500 to 750°C leads to an increase in the catalytic activity by a factor of ~1.5. As in the case of aluminum–palladium catalysts, the catalytic activity of 1 g

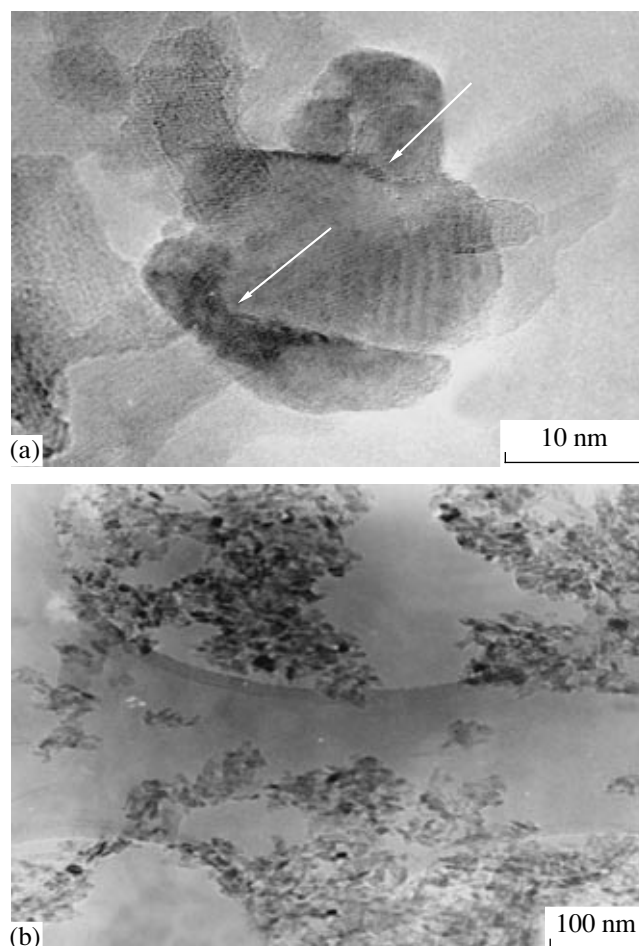


Fig. 3. Microscopic image of the sample 2% Pd/Al₂O₃–CeO₂ calcined at 600°C and tested in the reaction of the complete oxidation of methane ((a) 2500000 magnification, (b) 200000 magnification). Arrows show the regions of the formation of noncoherent boundaries of the particles, where the structure of the material is strongly distorted.

of the sample somewhat decreases with an increase in T_{calcin} in air from 500 to 700°C. Palladium catalysts based on CeO₂ and CeO₂–ZrO₂ have about the same catalytic activity in methane oxidation; their activity is an order of magnitude lower than for the catalysts supported on Al₂O₃ and ZrO₂. With an increase in the temperature of preliminary calcination from 500 to 700°C, the catalytic activity of these samples nearly halves.

For 1% Pd/ γ -Al₂O₃ (Table 1), the catalytic activity in the complete oxidation of methane decreases by a factor of ~1.5 with an increase in the calcination temperature from 500 to 700°C and becomes much lower (~2–3 times lower) than the activity of the corresponding 2% sample.

Thus, in methane oxidation, the activity per 1 g decreases with an increase in the calcination temperature from 500 to 700°C for all supported palladium catalysts. However, the apparent decrease in the activity with an increase in the calcination temperature for var-

Table 1. Characteristics of supported palladium catalysts for the complete oxidation of CH₄ calcined at various temperatures

No.	Sample	$T_{\text{calc}}, ^\circ\text{C}$	Pd concentration, wt %	$S_{\text{sp}}, \text{m}^2/\text{g}$	D_{Pd}	$W(\text{CH}_4) \times 10^3, \text{ncm}^3 \text{g}^{-1} \text{s}^{-1}$	$W_{\text{AKA}}(\text{CH}_4) \times 10^{22}, \text{ncm}^3 (\text{atom Pd})^{-1} \text{s}^{-1}$
1	Pd/Al ₂ O ₃	500	1	244	0.24	69	51
2	"	600		198	0.16	51	56
3	"	700		183	0.13	48	65
4	Pd/Al ₂ O ₃	500	2	203	0.11	158	132
5	"	700		168	0.09	140	140
6	Pd/ZrO ₂ (T_{calc} ZrO ₂ = 500°C)	500	2	—	0.10	100	91
7	"	700		—	0.06	71	104
8	Pd/ZrO ₂ (T_{calc} ZrO ₂ = 750°C)	500	2	44	0.06	148	218
9	"	700		44	0.05	128	225
10	Pd/CeO ₂	500	2	49	0.29	12	3.6
11	"	700		35	0.13	6	4
12	Pd/CeO ₂ (0.3)/ZrO ₂ (0.7)	500	2	49	0.18	18	9
13	"	700		17	0.05	4	7

ious samples differs. This is due to the fact that the activity is proportional to the dispersity of the supported metal, and a decrease in the dispersity for all studied samples that are thermally treated under the same conditions differs. Therefore, a decrease in the activity also differs.

The dynamics of the activity of platinum and palladium supported on alumina were studied in methane combustion at 200–600°C [1, 2]. The authors of those papers established that the Pd/Al₂O₃ sample treated at 600°C in a methane–oxygen–nitrogen mixture for 14 h is much more active (based on 1 g of the catalyst) than the same sample calcined at 500°C in a flow of argon and reduced by hydrogen. They also observed a decrease in the dispersity of the catalyst “aged” under the conditions of the reaction medium by a factor of ~2 compared to the sample reduced in hydrogen. Note that samples aged in the absence of methane (i.e., in an oxygen–nitrogen mixture) at 600°C did not result in an increase in the catalytic activity. Analogous results were obtained for the platinum–alumina sample. These observations led the authors of [1, 2] to conclude that the presence of both reactants (methane and oxygen) is a necessary condition for an increase in the catalyst activity. In our case, all samples were calcined in air and the activity per 1 g of the catalyst naturally decreases with a decrease in the dispersity. This difference can be explained by the fact that an increase in the size of the palladium particles in the atmosphere of the reaction medium is accompanied by the formation of

the active metal state as follows from [6]. For the species formed after sample calcination in air under the reaction conditions, some time is required for their transition into the active state. A similar phenomenon of the increase in the reaction rate of methane oxidation per 1 g of the catalyst in the course of the reaction has been observed for the systems Pd/Al₂O₃, Pd/ZrO₂, and Pd/SiO₂–Al₂O₃ calcined in air at 500–850°C [13]. To observe a noticeable increase in the reaction rate of methane oxidation with time, several tens of hours are needed. In our case the experimental times were much shorter.

Specific catalytic activity of the samples (per 1 g of the catalyst) for the process of complete *n*-pentane oxidation. Modification of alumina-supported palladium catalysts (~1 wt % Pd) by La₂O₃ and CeO₂ leads to some decrease in the activity compared to Pd/Al₂O₃, although the dependences of activity on the temperature of preliminary calcination are similar. In the case of alumina modification by zirconia, the activity per 1 g of the catalyst remains practically the same as for the nonmodified sample after preliminary calcination at various temperatures. The catalytic activity of Pd/Al₂O₃ passes through a slight maximum after preliminary calcination at 600°C, which is also characteristic to some degree of the Pd/Al₂O₃–La₂O₃ and Pd/Al₂O₃–ZrO₂ systems (Table 2).

The results obtained suggest that modifying the palladium–alumina catalysts by ZrO₂ does not lead to a substantial change in their activity toward the complete

Table 2. Characteristics of supported palladium–aluminum catalysts for the complete oxidation of n -C₅H₁₂ calcined at various temperatures

No.	Sample	T_{calcin} , °C	Pd concentration, wt %	S_{sp} , m ² /g	Modifier, wt %	D_{Pd}	$w \times 10^3$ (C ₅ H ₁₂), ncm ³ g ⁻¹ s ⁻¹	$W \times 10^{22}$ (C ₅ H ₁₂), ncm ³ (atom Pd) ⁻¹ s ⁻¹
1	Pd/Al ₂ O ₃	500	1.0	244	–	0.24	2.9	2.1
2	"	600	1.0	198		0.16	4.5	4.9
3	"	700	1.0	183		0.13	3.5	4.7
4	Pd/Al ₂ O ₃ –ZrO ₂	500	1.16	201	4.9	0.27	4.0	2.3
5	"	600	1.16	180		0.23	4.5	3.0
6	"	700	1.16	165		0.21	3.5	2.5
7	Pd/Al ₂ O ₃ –CeO ₂	500	1.1	201	7.2	0.28	2.1	1.2
8	"	600	1.1	210		0.24	1.9	1.3
9	"	700	1.1	185		0.22	2.0	1.4
10	"	750	1.1	176		0.21	1.6	1.2
11	Pd/Al ₂ O ₃ –La ₂ O ₃	500	1.1	181	7.2	0.24	2.5	1.7
12	"	600	1.1	186		0.21	3.0	2.3
13	"	700	1.1	157		0.19	2.5	2.1

oxidation of n -pentane. The addition of CeO₂ and La₂O₃ to the Pd/Al₂O₃ system leads to some decrease in the activity of the catalyst in this reaction compared to the nonmodified sample. Note that modification by the cited rare-earth element oxides and ZrO₂ leads to the stabilization of the values of the specific catalytic activity of the samples calcined in air at various temperatures.

Turnover Number

The TON of the samples in the complete oxidation of methane. The dependence of the TON of the nonmodified supported palladium samples (1 and 2 wt % Pd) on the temperature of their preliminary calcination (500 and 700°C) is described in Table 1. In the case of the systems Pd/Al₂O₃, Pd/ZrO₂ (T_{calcin} (ZrO₂) = 500°C), and Pd/ZrO₂ (T_{calcin} (ZrO₂) = 750°C) containing 2% Pd, an increase in the calcination temperature from 500 to 700°C leads to an insignificant increase in the TON despite a substantial decrease in the dispersity. For the Pd/CeO₂ system, the dispersity almost halves with an increase in the calcination temperature, but the TON increases insignificantly as well. In the case of the system Pd/CeO₂ (0.3 mol)–ZrO₂ (0.7 mol), a small decrease in the TON with an increase in the calcination temperature is observed. In general, for the catalysts mentioned above and the conditions of their preliminary treatment in the reaction of complete oxidation of

methane, we observed the fulfillment of Boreskov's rule of constant specific catalytic (TON in our case).

The TON of the samples in the reaction of complete oxidation of n -pentane. Table 2 shows the dependences of TON in n -pentane oxidation over palladium–alumina catalysts modified by ZrO₂, CeO₂, and La₂O₃, on the temperature of their preliminary calcination in air. It can be seen from the preliminary data that the addition of rare-earth element oxides and ZrO₂ to Pd/Al₂O₃ significantly stabilizes the dispersity of the supported palladium; its value insignificantly decreases upon preliminary calcination of the catalysts at 700°C. For the nonmodified sample, the dispersity almost halves. In the case of palladium–alumina catalysts modified by ZrO₂, CeO₂, and La₂O₃, the TON slightly changes in the whole calcination temperature range 500–700°C. For the nonmodified 1% palladium–aluminum catalyst, the TON increases 2.5 times when T_{calcin} is increased from 500 to 600°C but then remains the same when T_{calcin} is increased from 600 to 700°C.

Analogous results were obtained in [14]: the stabilization of the TON values for platinum–aluminum catalysts modified by the same rare-earth element oxides and ZrO₂ after the thermal treatment of samples in air.

Note a trend toward a decrease in the TON in the series: the nonmodified palladium–alumina catalyst, modified by zirconia, and modified by rare-earth element oxides. As in [14], this can be explained by the strengthened interaction between a modifier and the

particles of supported platinum, which, on the one hand, leads to the stabilization of the high dispersity and, on the other hand, to a decrease in the TON because of the enhanced deficiency of electron density on the surface palladium atoms.

The same but more pronounced trend is seen for palladium catalysts supported on pure modifying oxides in the reaction of the complete oxidation of methane (Table 1), with the exception of palladium supported on monoclinic ZrO_2 for which the TON is the highest.

Thus, for methane oxidation, the TON decreases in the series: $(\text{Pd}/\text{ZrO}_2, T_{\text{calcin}} = 750^\circ\text{C}) \rightarrow (\text{Pd}/\text{Al}_2\text{O}_3) \rightarrow (\text{Pd}/\text{ZrO}_2, T_{\text{calcin}} = 500^\circ\text{C}) \rightarrow (\text{Pd}/\text{CeO}_2)$ (2 wt % Pd).

For the 1 wt % palladium–alumina catalyst modified by rare-earth element oxides and ZrO_2 , the TON in the complete oxidation of *n*-pentane decreases in the series: $(\text{Pd}/\text{Al}_2\text{O}_3) \rightarrow (\text{Pd}/\text{Al}_2\text{O}_3\text{--}\text{ZrO}_2) \rightarrow (\text{Pd}/\text{Al}_2\text{O}_3\text{--}\text{La}_2\text{O}_3) \rightarrow (\text{Pd}/\text{Al}_2\text{O}_3\text{--}\text{CeO}_2)$.

A similar dependence of the TON on the nature of the modifier for platinum–alumina catalyst in the reaction of complete oxidation of *n*-butane was reported in [14].

As mentioned above, an increase in the TON in the reaction of the complete oxidation of hydrocarbons with an increase in the metal particles size was noted by many researchers. This was observed not only in the case of the aging of platinum–alumina and palladium–alumina samples in the reaction mixture at high temperatures [1, 2] but also upon sample calcination in air at 500–(850°C) 900°C (for platinum and palladium supported on Al_2O_3 , ZrO_2 , and $\text{SiO}_2\text{--}\text{Al}_2\text{O}_3$) [6, 13]. For the systems $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/ZrO_2 , an increase in the TON was also noted with an increase in the reaction time [5].

It is quite possible that an increase in the TON (and the specific catalytic activity) could be due to the removal of admixtures from the catalysts during their calcination in air or in the course of catalyst aging in the reaction medium. Thus, it was shown in [15] that, when the palladium catalyst supported on the lanthanum oxide is prepared from H_2PdCl_4 , the catalyst activity increases for about 10 h in the reaction of *n*-butane oxidation until it becomes constant due to the removal of the chloride ions that stabilize the palladium in the oxidized electron-deficient inactive state.

The addition of a modifier stabilizes the dispersity of palladium in the studied range of calcination temperatures (500–700°C), and this fact suggests that there is an effect of dispersity on the TON of supported palladium. On the other hand, a change in the dispersity with an increase in the calcination temperature for the non-modified palladium–alumina catalyst creates uncertainties in the interpretation of the relationship between the TON and dispersity because at elevated temperatures, the processes of particle sintering and their restructuring may occur: for instance, a decrease in the fraction of a cluster and monatomic states of palladium on the support surface, a change in the structure of

defects in palladium crystallites, etc. [16]. We compared palladium–alumina catalysts calcined at the same temperature, but with different dispersities, obtained by varying the concentration of palladium in the catalysts.

It was found (Table 1) that for 1 and 2% palladium–alumina catalysts calcined at 500°C, an increase in the concentration of palladium from 1 to 2 wt % leads to an increase in the average size of particles by a factor of 2.2, and the TON decreases by a factor of 2.6. Proceeding from these data, we conclude that an increase in the size of the supported palladium particles leads to an increase in the TON. The explanation for such an effect of particles size on the TON can be a hypothesis of a decrease in the acceptor effect of the support on the crystallites of supported palladium with an increase in their size. On the other hand, the smaller the crystallites, the more pronounced the acceptor effect of support leading to the deficiency in the electron density on Pd(Pt) atoms, that is, to an increase in the oxidation state. At the same time, according to [17], the activation of hydrocarbon molecules is determined by the concentration of the electron density on the active sites to be transferred to the antibonding orbital of the C–H bond.

An analysis of the data in Table 1 shows that, the concentration of palladium being the same and the dispersities being close, the TON is largely determined by the nature of the supporting oxide; the stronger the metal–support interaction the lower the TON.

Considerable changes are observed after calcination at 600°C (Fig. 3a). As mentioned above, noncoherent boundaries are formed by sintered species, which point to the strong distortion in the particle structure, whereas isolated particles are well ordered and cut. It is probable that due to the strong interaction, the fragments of the modifying oxide move together with the palladium particles interacting with them at an elevated temperature, and do not allow the palladium particles to sinter. This explains the existence of noncoherent boundaries between sintered particles. The existence of such structural barriers stabilizes the dispersity of supported palladium and its activity.

Thus, in this work we showed that, for palladium catalysts supported on various oxides, the effect of thermal activation (an increase in the TON of palladium with an increase in the calcination temperature of the samples from 500 to 700°C) is not observed in contrast to supported platinum catalysts [9]. A comparison of two palladium–alumina catalysts calcined at 500°C, differing in the concentration of palladium and its dispersity shows that the TON of palladium is much higher for palladium with a lower dispersity. All other conditions being the same, the TON of supported palladium is determined by the support nature.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 99-03-32135a).

REFERENCES

1. Briot, P., Auroux, A., Jones, D., and Primer, M., *Appl. Catal.*, 1990, vol. 59, p. 141.
2. Briot, P. and Primet, M., *Appl. Catal.*, 1991, vol. 68, p. 301.
3. Carballo, L.M. and Wolf, E.E., *J. Catal.*, 1978, vol. 53, p. 366.
4. Völter, J., Lietz, G., Spindler, H., and Lieske, L., *J. Catal.*, 1987, vol. 104, p. 375.
5. Hicks, R., Qi, H., Young, M.L., and Lee, R.G., *J. Catal.*, 1990, vol. 122, p. 280.
6. Hicks, R., Qi, H., Young, M.L., and Lee, R.G., *J. Catal.*, 1990, vol. 122, p. 295.
7. Cullis, C.F. and Willat, B.M., *J. Catal.*, 1983, vol. 83, p. 267.
8. Baldwin, T.R. and Burch, R., *Catal. Lett.*, 1990, vol. 6, p. 131.
9. Chzhu, D.P., Tsyrl'nikov, P.G., Kudrya, E.N., Smol'nikov, M.D., Borbat, V.F., and Bubnov, A.V., *Kinet. Katal.*, 2002, vol. 43, no. 3, p. 410.
10. Ginsburg, S.I., Gladyshevskaya, K.A., Ezerskaya, N.A., *et al.*, *Rukovodstvo po khimicheskomu analizu platinykh metallov i zolota* (Handbook on Chemical Analysis of Platinum Metals and Gold), Moscow: Nauka, 1965, p. 159.
11. Karnaukhov, A.P., *Sibirskie chteniya po katalizu* (Siberian Lectures on Catalysis), Novosibirsk, 1979, part 1, p. 136.
12. Drozdov, V.A., Tsyrl'nikov, P.G., Popovskii, V.V., *et al.*, *React. Kinet. Catal. Lett.*, 1985, vol. 27, no. 2, p. 425.
13. Ribeiro, F.H., Chow, M., and Dalla Betta, R.A., *J. Catal.*, 1994, vol. 146, p. 537.
14. Drozdov, V.A., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Institute of Catalysis, 1987.
15. Starostina, T.G., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Institute of Catalysis, 1987.
16. Chen, J.J. and Ruckenstein, E., *J. Phys. Chem.*, 1981, vol. 85, p. 1606.
17. Golodets, G.I., *React. Kinet. Catal. Lett.*, 1981, vol. 17, nos. 1–2, p. 97.