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Platinum Nanoparticle Size Effect on Specific Catalytic Activity in *n*-Alkane Deep Oxidation: Dependence on the Chain Length of the Paraffin

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Abstract—The specific activity of 0.8% Pt/Al_2O_3 catalysts in the deep oxidation of C_1–C_6 *n*-alkanes increases with an increase in the Pt particle size from 1 to 3–4 nm. Further coarsening of the particles insignificantly changes the specific activity. The size effect was studied for a series of catalysts containing platinum nanoparticles 1 to 11 nm in diameter. The specific catalytic activity variation range depends on the size of the reacting hydrocarbon molecules. As the platinum particle size increases, the specific catalytic activity increases 3–4 times for the oxidation of CH_4 and C_2H_6 and by a factor of 20–30 for the oxidation of *n*-C_4H_{10} and *n*-C_6H_{14}.

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The deep oxidation of volatile organic compounds is among the main processes used in the catalytic treatment of exit gases from chemical plants and in automotive exhaust neutralizers [1]. As a rule, supported catalysts based on noble metals (first of all, platinum) are used in this reaction [2, 3]. Therefore, it is a challenging problem to reduce the cost and increase the efficiency of such catalytic systems. The worldwide tendency is towards lower concentrations of the noble metal in the catalyst, because its total amount is the main cost-determining factor. The efficiency of the catalyst should not decrease with a decrease in the amount of the active component. Such a contradictory problem can be solved through understanding the rules governing the catalytic performance of metal nanoparticles in the deep oxidation of organics.

The size of metal nanoparticles determines, to a considerable extent, their catalytic properties. On the one hand, the number of atoms accessible to the reactants increases with an increase in the degree of dispersion, and, hence, the efficiency of use of the metal increases. On the other hand, the probability of the formation of an active site consisting of several metal atoms arranged in a certain way on the surface decreases with a decrease in the metal particle size. These sites are necessary for structure-sensitive reactions to occur, and, therefore, the catalytic activity decreases with a decrease in the metal particle size.

The influence of the metal particle size on the total and specific catalytic activity in deep oxidation was studied by many authors. For example, it was found that the specific activity of platinum catalysts in propane oxidation decreases as the platinum particle size decreases from 5.9 to 1.9 nm [4]. The growth of the specific catalytic activity with an increase in the noble metal particle size was demonstrated in a number of works [5–7]. Pt/Al_2O_3 catalysts exhibit a substantial increase in the activity in *o*-xylene oxidation with an increase in the Pt particle size from 2 to 9 nm [8]. Similar results were obtained for the oxidation of benzene and cyclopentane on platinum catalysts [9, 10]. At the same time, it was found by investigation of the particle-size dependence of the specific catalytic activity of the Pt/Al_2O_3 catalyst in the deep oxidation of ethane and propane that the turnover frequency per surface atom changes insignificantly [11]. Thus, the data characterizing the influence of the platinum particle size on the total and specific catalytic activity remain contradictory. A comparison between experimental data obtained by independent authors suggests that the structural sensitivity of deep oxidation and the size effect of the platinum particles on the specific catalytic activity can be dependent on the structure (first of all, on the size) of the hydrocarbon molecule. It seems natural that the oxidation of large molecules proceeds more efficiently on larger platinum particles. A comparison between the specific catalytic activities of platinum particles of different sizes in the deep oxidation of hydrocarbons with different molecular sizes could clarify this problem. Unfortunately, at the moment such experimental data are lacking in the literature.

In view of the above, we undertook a systematic study of the dependence of the total and specific catalytic activity of Pt/Al_2O_3 catalysts in the deep oxidation of C_1–C_6 *n*-alkanes on the size of the platinum particles.

EXPERIMENTAL

Preparation of Catalysts

A series of monodisperse platinum catalysts on alumina with different sizes of supported platinum particles was examined. The starting γ-Al_2O_3 (Sasol TKA-432) was crushed, and the fraction with a granule size of 0.25–0.50 mm was taken and calcined at 500°C for 2 h (the BET specific surface area was ~215 $m^2 g^{-1}$). The support was treated with 20% acetic acid, dried in air at room temperature overnight and then in a drying box at 120°C for 4 h, and impregnated with a minor excess of an aqueous $H_2[Pt(OH)_6]$ solution acidified with nitric acid. The solutions used in the preparation of the catalysts differed in the $H_2[Pt(OH)_6]/HNO_3$ ratio, which predetermined both the degree of hydrolysis of $H_2[Pt(OH)_6]$ and the size of colloidal $[Pt(\mu\text{-}OH)_6]_{m2}$ particles formed in the solution. Changing the $H_2[Pt(OH)_6]/HNO_3$ ratio made it possible to control the colloidal platinum particle size in the solution in wide ranges and, finally, the degree of dispersion of platinum in the resulting catalysts (for details of catalyst preparation, see RF Patent no. 2352391). Excess solvent was removed at 50°C using a rotary evaporator under water-jet pumping. The resulting air-dry catalyst samples were dehydrated at 120°C for at least 4 h, heat-treated in air at 400–600°C in a muffle furnace, and reduced for 3 h at 350°C in a flowing nitrogen–hydrogen mixture containing 25% H_2. Next, the catalyst samples were cooled in an argon flow, placed in sealable containers, and stored in a vacuum desiccator. According to ICP-AES data, the platinum content of all catalyst samples was ~0.8 wt %.

Electron Microscopy

The average size of the active component particles on the catalyst surface and their size distribution were determined using high-resolution transmission electron microscopy (HRTEM) with a lattice resolution of 0.14 nm and an accelerating voltage of 200 kV (JEM-2010, Jeol Co., Japan). The samples to be examined were mounted on standard copper grids, which were placed in a holder and introduced into the electron microscope chamber. The Analysis iTEM v.5 program (Soft Imaging System GmbH, 2004) was used to determine the particle size and to study the particle size distribution. Histograms were constructed by measuring 200–700 particles per sample. The local energy dispersive X-ray microanalysis of the supported particles was carried out on an EDAX spectrometer (EDAX Co.) equipped with a Si(Li) detector with an energy resolution of 127 eV.

Chemisorption

The chemisorption characteristics of the samples were measured using an Autosorb-1-C-MS/TCD automated adsorption analyzer (Quantachrome Instruments, United States). The filled volume was determined by the volumetric helium method. The degree of dispersion of platinum (*D*) was determined by the irreversible chemisorption of hydrogen using the double isotherm method [12]: the first isotherm gave the total amount of adsorbed hydrogen, and the second isotherm, recorded after pumping at 150°C for 1 h, gave the amount of weakly adsorbed hydrogen. The amount of irreversibly adsorbed H_2 was calculated as the difference upon extrapolation to the zero pressure.

A sample (0.3–0.8 g) was placed in a quartz U-shaped flow reactor, dried in flowing helium at 120°C for 0.5 h, additionally reduced in flowing hydrogen at 300°C, and held at this temperature for 2 h. After reduction, the sample was pumped at the same temperature for 2 h and cooled to the isotherm temperature (40°C). The first isotherm was recorded under static conditions in the absolute pressure range from 2 to 560 Torr. After the first isotherm was obtained, the cell was pumped at the measurement temperature until the gas evolution from the sample was undetectable. The second isotherm was recorded at the same absolute pressures as the first isotherm.

Measurement of Catalytic Activity

The catalytic activity was measured in a quartz flow reactor (inner diameter of 7 mm) with a fixed catalyst bed. Gas mixtures were prepared by mixing a pure hydrocarbon (methane, ethane) or a hydrocarbon + nitrogen mixture (1% *n*-hexane in N_2, 10% *n*-butane in N_2) with air. The final hydrocarbon concentration in the gas mixture was 0.5–0.08 vol % (5000 ppm in terms of C_1). Oxidation was carried out at a GHSV of 60000 h^{-1}. The oxidation temperature interval was selected for each hydrocarbon so that the conversion changed from 0.3 to >20%. Measurements were taken three times per run to detect possible changes in the catalytic activity.

The reaction products were analyzed by gas chromatography using a flame ionization detector. In some experiments, the reaction products were analyzed with a GASMET-400 IR gas analyzer for determination of the CO/CO_2 ratio. In all cases, the CO_2 selectivity exceeded 95%.

Specific catalytic activity was calculated using the formula

$$W_{sp} = W/N_{Pt},$$

where W_{sp} is the number of hydrocarbon molecules converted on one surface Pt atom per second (s^{-1}), W is the oxidation rate calculated as the number of hydrocarbon molecules converted on 1 g of the catalyst per second (molecule $g^{-1} s^{-1}$), and N_{Pt} is the num-

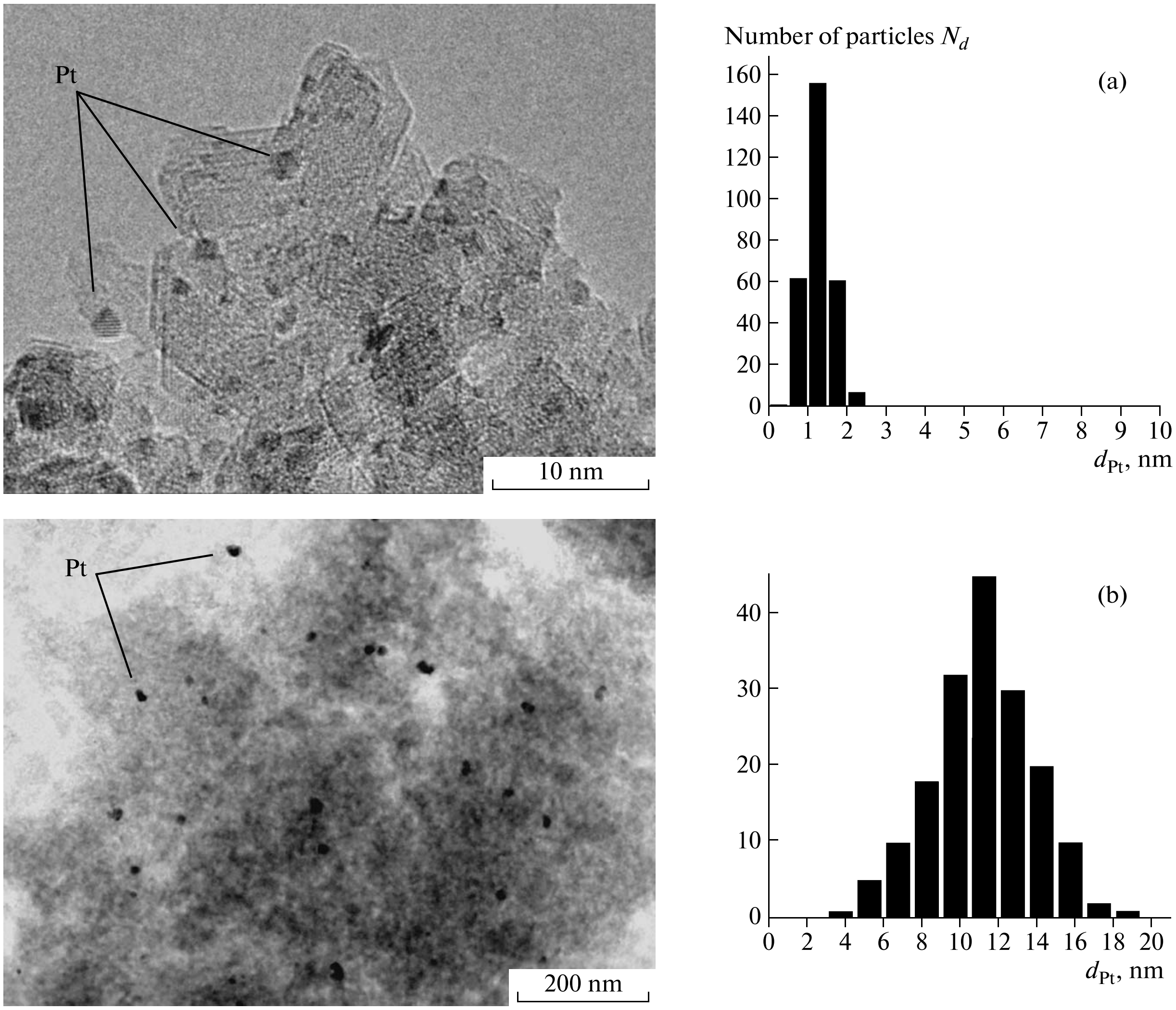

Fig. 1. Micrographs of the 0.8 wt % Pt/Al_2O_3 catalysts and the platinum particle size distribution histograms derived from microscopic data. The average Pt particle size is d_{Pt} = (a) 1 and (b) 11 nm.

ber of surface platinum atoms in 1 g of the catalyst according to hydrogen chemisorption data (atom/g).

RESULTS AND DISCUSSION

Particle Size of Platinum in the Catalysts

Figure 1 presents the micrographs of the most finely dispersed catalyst (Fig. 1a) and the sample with the largest Pt particles (Fig. 1b), as well as the platinum particle size distribution histograms derived from microscopic data. The finely dispersed catalyst contains platinum particles with an average size of about 1–1.5 nm. Clearly, the above-described preparation method affords Pt particles with a very narrow size distribution. Only a small number of platinum clusters are >2 nm in size. The center of the distribution histogram falls on an average particle size of ~1.25 nm. The particle size distribution is noticeably broader for the sample with the coarsest Pt particles. Nevertheless, the size of most of the platinum particles is between 6 and 16 nm, with the distribution maximum occurring at ~11.5 nm.

The platinum particle size data derived from chemisorption and HRTEM measurements are listed in Table 1. The data obtained by these two methods are in good agreement.

Temperature Dependence of the Conversion of Hydrocarbons with Different Molecular Sizes

The dependences of the conversion of C_1–C_6 alkanes on the reaction temperature are shown in Figs. 2a–2d. The conversion curves shift toward low temperatures as the carbon chain length increases. These results are consistent with the data of other authors according to which the rate of alkane oxidation increases with an increasing carbon chain length in the molecule [13, 14]. The oxidation rate increases because the rate-determining step is the breaking of the first C—H bond [15], which weakens as the length of the hydrocarbon molecule increases [16—18].

Note that a comparison between the conversion curves for catalysts containing platinum particles of different sizes suggests that the way the activity changes with an increase in the Pt particle size depends substantially on the reacting hydrocarbon. For instance, the Pt/Al_2O_3 catalyst containing particles with an average size of about 1 nm is the most active in the oxidation of CH_4 (Fig. 2a). The catalytic activity decreases systematically as the size of the supported Pt particles increases.

The catalyst containing platinum particles with an average size of ~1 nm shows the highest activity in ethane oxidation. However, a similar activity is observed for the catalysts containing Pt particles 2—3 nm in size.

Table 1. Average particle size d_{Pt} in the 0.8 wt % Pt/Al_2O_3 catalyst according to HRTEM and H_2 chemisorption data

Sample	d_{Pt} from HRTEM data, nm	Amount of surface Pt from H_2 chemisorption data, μmol/g	d_{Pt} from chemisorption data, nm
1 nm	1.3 ± 0.3	35.6	1.1
2 nm	2.2 ± 0.5	22.4	2.1
3 nm	2.9 ± 0.6	11.4	3.1
6 nm	6.5 ± 1.7	8.2	5.1
8 nm	8.3 ± 2.2	5.4	8.2
11 nm	11.5 ± 3.7	3.9	10.1

Essentially different dependences of activity on the platinum particle size are observed for the oxidation of *n*-butane (Fig. 2c) and *n*-hexane (Fig. 2d). For both hydrocarbons, the lowest reaction rate is observed for

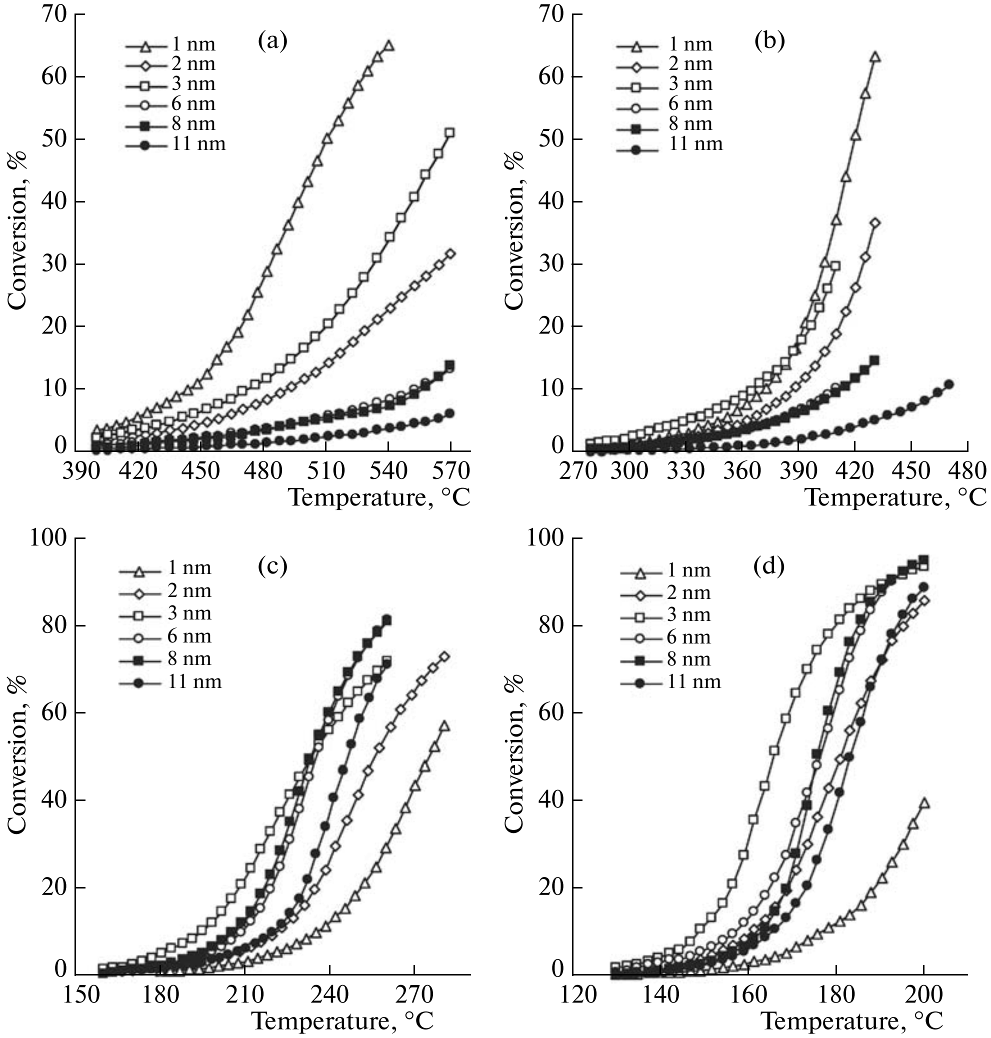

Fig. 2. Dependences of the conversion of C_1—C_6 *n*-alkanes on the temperature of oxidation on the 0.8 wt % Pt/Al_2O_3 catalysts containing Pt particles of different size: (a) CH_4, (b) C_2H_6, (c) *n*-C_4H_{10}, and (d) *n*-C_6H_{14}.

Table 2. Dependence of the specific catalytic activity of Pt/Al_2O_3 ($W_{sp} \times 10^2$, s^{-1}) on the platinum particle size in the deep oxidation of C_1–C_6 *n*-alkanes at different temperatures*

n-Alkane	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}
T_{react}, °C / d_{Pt}, nm	420	319	240	195	172
1	0.25	0.26	0.28	0.24	0.30
2	0.46	0.32	0.36	0.70	1.68
3	0.90	1.03	1.28	3.82	6.99
6	0.67	0.82	1.26	3.50	5.84
8	0.63	0.77	1.42	5.17	6.45
11	0.59	0.52	1.69	4.98	7.96

* The measurement temperature was chosen so as to obtain approximately equal W_{sp} values for the oxidation of all alkanes from C_1 to C_6 on the catalyst containing the platinum particles with d_{Pt} = 1 nm.

the catalyst with the smallest Pt particle size (1 nm), whereas the catalysts containing the medium-size (3–8 nm) platinum particles are the most active.

Dependence of the Specific Activity on the Platinum Particle Size

It is of interest to analyze how specific catalytic activity (SCA, or atomic activity), a fundamental characteristic of a catalyst, changes with the platinum particle size (SCA $= f(d_{Pt})$) in the oxidation of normal alkanes with different carbon chain lengths. When comparing SCA $= f(d_{Pt})$ relationships, one should take into account that the temperature intervals in which the reactions involving various hydrocarbons occur differ substantially (Fig. 2). For a correct comparison, the reaction temperature for each hydrocarbon was chosen so that the SCA of the catalyst with the smaller platinum particle size (1.2 nm) was about 0.025–0.030 s^{-1}. The SCA values for the other catalysts were determined at this temperature. The measurement of SCA under these conditions made it possible to perform measurements in the differential regime at hydrocarbon conversions not higher than 10–15%. The reaction temperatures and the SCA values are listed in Table 2. The plots of SCA versus the platinum particle size for the oxidation of C_1–C_6 *n*-alkanes are shown in Fig. 3. As can be seen from these plots, in all reactions the catalysts with the smallest platinum particle size (d_{Pt} = 1–2 nm) exhibit the lowest SCA. The SCA values increase as the particle size increases to 3–6 nm and remain almost invariable at d_{Pt} ~ 8–11 nm.

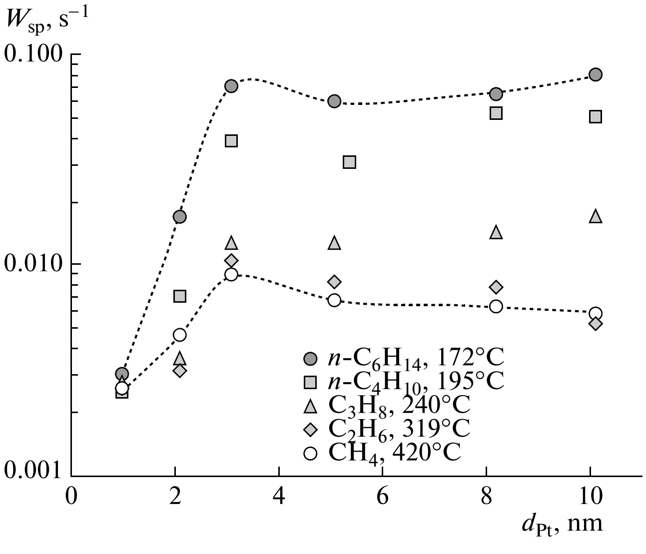

Fig. 3. Specific activity versus Pt particle size for the deep oxidation of C_1–C_6 *n*-alkanes on the 0.8 wt % Pt/Al_2O_3 catalysts.

The observed dependences of SCA on the platinum particle size are well consistent with the earlier data according to which SCA increases with a decrease in the degree of dispersion of the metal. It was found [19] that the SCA of Pt/Al_2O_3 in the total oxidation of n-C_5H_{12} increases by approximately one order of magnitude with an increase in the Pt particle size from 2.3 to 28 nm as a result of high-temperature calcination. The authors attributed the observed increase in the SCA to the acceleration of the hydrocarbon activation stage. Later, a similar effect was observed for Pd/Al_2O_3 catalysts [20]. The increase in SCA with an increase in the platinum particle size in supported Pt catalysts was also observed in the deep oxidation of propane [21].

The dependence of SCA on the platinum particle size established in the present work made it possible to explain some discrepancies in the literature data. For example, it was shown [11] that, in the deep oxidation of propane and ethane on Pt/Al_2O_3, SCA is independent of the platinum particle size. However, according to our data, a marked change in SCA in the oxidation of these hydrocarbons should be expected in the 1–3 nm range. In the cited work, the Pt particle size changed from 2.5 to 5 nm, which possibly explains the fact that no pronounced influence of the Pt particle size on the SCA was observed (see Fig. 3).

The following possible explanations for the high specific activity of the platinum particles with larger sizes in the oxidation reactions were suggested [22, 23]:

(1) The energy of bonding between oxygen and the surface of platinum particles decreases with an increase in their size, resulting in an increase in the reaction rate. This is due to the fact that the surface of large particles is dominated by crystallographic planes in which the platinum atoms are coordinatively less unsaturated (have larger coordination numbers).

(2) The larger platinum particles retain their metallic character, whereas the smaller particles oxidize readily and lose activity.

The observed regularities agree well with the results of thermodynamic analysis of the influence of the particle size of the active phase on the catalytic activity [24]. It was shown that the increase in the chemical potential of a nanoparticle with a decrease in its size (<10 nm) exerts a substantial effect on the adsorption equilibrium and, accordingly, on the rate of the overall catalytic process. For a high degree of filling with intermediates, one should expect a decrease in SCA with a decrease in the particle size. There was a kinetic analysis of the reaction rate versus particle size based on a thermodynamic approach [25]. It was shown that SCA increases with an increasing particle size. The functional dependence of SCA on the particle size (SCA = $f(d_{\mathrm{Pt}})$) can either asymptotically increase with an increase in the particle size to the values characteristic of the bulk metal or pass through a maximum.

In our opinion, our finding that the structural sensitivity of deep oxidation increases with an increase in the size of the molecule being oxidized is of greatest interest. A comparison of the dependences of SCA on the platinum particle size (Fig. 3) shows that the range in which SCA changes depends substantially on the carbon chain length of the *n*-alkane. In the oxidation of CH_4 or C_2H_6, SCA increases approximately 2–3 times as the Pt particle size changes from 1 to 11 nm. In propane oxidation, SCA increases approximately by a factor of 5–6, whereas in the oxidation of *n*-C_4H_{10} and *n*-C_6H_{14}, the specific activity increases 20 and 25 times, respectively. Thus, the structural sensitivity of the deep oxidation of *n*-alkanes increases with an increase in the size of the hydrocarbon molecule being oxidized.

Since the total activity of the catalyst is determined by the SCA value and the total platinum surface accessible to the reactants, the plots of the total activity versus the particle size are different for the oxidation of alkanes with different carbon chain lengths (Fig. 2) The catalysts with the maximum degree of dispersion of platinum (largest accessible platinum surface area) are most active in the oxidation of small molecules (CH_4 and C_2H_6) because the decrease in SCA with a decrease in the particle size is rather small. For the oxidation of larger molecules (*n*-C_4H_{10} and *n*-C_6H_{14}), the maximum activity (and, correspondingly, the lowest reaction onset temperature) is observed for the catalysts with the medium size of the metal particles (3–6 nm). There are two possible explanations for the observed effect.

The higher structural sensitivity of the deep oxidation of larger molecules can be due to the fact that a surface site consisting of a greater number of platinum atoms is required for the adsorption of a larger alkane molecule. Since the most probable rate-determining step of the overall process is the breaking of the first C–H bond in the adsorbed hydrocarbon, an increase in its surface concentration will inevitably increase the reaction rate. An increase in the relative concentration of adsorbed hydrocarbon can be expected on the larger platinum particles because of the higher probability of the formation of polyatomic adsorption sites. In turn, this will raise the SCA.

Another possible cause of the enhancement of the structural sensitivity of oxidation with an increase in the size of the oxidized molecule can be the temperature factor. As was shown above, the catalytic oxidation temperature decreases substantially with an increase in the molecular size. It can be assumed that the size effect is more pronounced at a lower reaction temperature. This is indicated by a thermodynamic analysis of the influence of the particle size of the active component on the adsorption equilibrium and on the rate of the catalytic process [24]. According to this analysis, the dependence of the reaction rate on the particle size becomes more pronounced as the temperature decreases. From the standpoint of the mechanism of the process, this can be due to the fact that the inhibition of the reaction by strongly bound oxygen is more pronounced at lower temperatures, as was demonstrated for propane oxidation under conditions of excess oxygen (lean mixtures) and deficient oxygen (rich mixtures) [26, 27].

CONCLUSIONS

Thus, it was established that the specific catalytic activity in the deep oxidation of *n*-alkanes on Pt/Al_2O_3 increases with an increase in the Pt particle size. The SCA variation range (size effect) depends on the length of the carbon chain of the alkane (size of the molecule). For small molecules (C_1–C_2) SCA changes by a factor of 3–4 times, whereas for the larger molecules of *n*-butane and *n*-hexane, SCA increases 20–30 times as the size of the platinum crystallites increases from 1 to 11 nm.

The catalysts with the maximum degree of dispersion of platinum (d_{Pt} = 1–2 nm) exhibit the highest total activity in the oxidation of small molecules. The catalysts consisting of larger Pt particles (3–6 nm) are most active in the oxidation of longer *n*-butane and *n*-hexane molecules, whereas the activity of the finer catalysts is substantially lower.

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