Effect of Pt nanoparticle size on the specific catalytic activity of Pt/SiO_2 and Pt/TiO_2 in the total oxidation of methane and *n*-butane

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The dependence of the specific catalytic activity (A_{sp}) of the catalysts Pt/SiO_2 and Pt/TiO_2 in the total oxidation of CH_4 and n-C_4H_{10} on the Pt nanoparticle size (in the range from 1 to 4 nm) was studied. The specific catalytic activity increases with an increase in the platinum nanoparticle size, indicating that the total oxidation is a structure-sensitive reaction. The structure sensitivity depends on the size of an oxidized molecule: it increases sharply on going from CH_4 to n-C_4H_{10}. The support also exerts a considerable effect on the A_{sp} value: in the oxidation of both CH_4 and C_4H_{10} the specific catalytic activity for the catalysts Pt/TiO_2 is 3—4 times that for Pt/SiO_2.

Key words: catalysts Pt/SiO_2 and Pt/TiO_2, Pt nanoparticles, size effect, specific activity, total oxidation of methane and *n*-butane.

The effect of metal nanoparticle size on its catalytic activity is one of fundamental challenges of heterogeneous catalysis.[1] For metallic catalysts, changing the metal nanoparticle size (R_M) can dramatically change the specific catalytic activity (A_{sp}), depending on the reaction type.[2,3] Therefore, elucidation of the dependence of the specific catalytic activity on the nanoparticle size $A_{sp} = f(R_M)$ is of considerable interest for both understanding the mechanisms of catalytic reactions and determining the efficiency of the operation with the catalyst.

The concept of structure sensitivity of catalytic reactions is widely used for interpretation of data on the effect of metal nanoparticle size on A_{sp}.[4,5] In spite of intensive studies of the dependence of A_{sp} on the metal nanoparticle size, the problem of assignment of catalytic reactions to structure-sensitive or structure-insensitive reactions remains unclear for many reaction classes. One of these classes include reactions of total oxidation of volatile organic compounds. The data of structure sensitivity of total oxidation reactions are rather contradictory, although these reactions are widely used in many industrial processes.[6,7] For example, it was shown that methane oxidation[8,9] on the Pt catalysts can be assigned to structure-insensitive, because the specific catalytic activity is almost independent of the Pt nanoparticle size. Similar conclusion was drawn in the study of A_{sp} of the catalyst Pt/Al_2O_3 in the total oxidation of ethane and propane.[10] At the same time, it was shown[11,12] that A_{sp} tends to increase with increasing size of the noble metal particles.

The detailed study[13,14] of the dependence of A_{sp} on the Pt nanoparticle size (1—10 nm) in the oxidation of n-alkanes C_1—C_6 clarified, to some extent, the problem about structure sensitivity. It was shown that the structure sensitivity increased with an increase in the size of a molecule of the oxidized substance. In addition, we were able to show that the maximum change in A_{sp} occurs with the variation of the Pt nanoparticle size in the range between 1 and 4 nm, whereas in the range 4 to 10 nm the reaction of total oxidation of hydrocarbons can be considered as structure-insensitive.

However, these relationships were obtained only for the catalysts Pt/Al_2O_3 and, hence, it remained unclear whether they can be extended to the platinum catalysts prepared using supports of other types.

In the present work, we attempted to reveal how does the change in the Pt nanoparticle size affect the specific catalytic activity in the total oxidation of CH_4 and n-C_4H_{10}. In addition, it seemed interesting to evaluate the effect of the support on the specific catalytic activity by comparing the activity of the Pt catalysts containing platinum nanoparticles of equal size but deposited on supports of different nature (SiO_2 and TiO_2).

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Experimental

A series of monodispersed platinum catalysts on titania (S_{sp} = 65 m^2 g^{-1}) and silica (S_{sp} = 120 m^2 g^{-1}) was used. The supports were impregnated with aqueous solutions of platinum nitrate. After stirring the formed suspension (1 h), solvent excess was distilled off on a rotary evaporator at 50 °C. Thus prepared air-dried samples of the catalysts were dehydrated at 120 °C (≥4 h) and then subjected to high-temperature thermal treatment in air at 400—600 °C in a muffle furnace and reduction in a flow of a nitrogen—hydrogen mixture with the H_2 content 25% (3 h). Then the catalyst was cooled in an argon flow, poured into a sealed container, and stored in a vacuum desiccator. According to the data of inductively coupled plasma atomic emission spectroscopy (Baird), the platinum content in all catalyst samples was about 0.8 wt.%.

Electron microscopy. The Pt particle size distribution on the catalyst surface and their average size were determined by high-resolution transmission electron microscopy (JEM-2010, Jeol Co., Japan). The lattice resolution was 0.14 nm at an accelerating voltage of 200 kV. The samples for studies were fixed on standard copper grids, which were placed in a holder and introduced into the chamber of an electron microscope. The Analysis,iTEM v.5 program (Soft Imaging System Gmbh, 2004) was used to determine the particle size and the particle size distribution. Between of 200 and 700 particles were counted for each sample to plot a histogram.

Chemisorption measurements. The chemisorption characteristics of the samples under study were determined using an Autosorb-1-C-MS/TCD automated adsorption analyzer (Quantachrome Instruments, USA). The filling volume was determined by the helium volumetric method. The dispersity of platinum (D) was determined by irreversible hydrogen chemisorption using the double isotherm method, assuming that the number of atoms of chemisorbed hydrogen corresponds to the number of surface Pt atoms.[15]

For the Pt/TiO_2 catalyst, it was impossible to determine the specific surface area because of the effect of strong metal—support interaction (SMSI) on the chemisorption of hydrogen.[16]

Measurement of the catalytic activity. The catalytic activity was measured in a flow-type, fixed-bed quartz reactor (inner diameter 7 mm). Gas mixtures were prepared by mixing neat hydrocarbons (methane, *n*-butane) with air. The hydrocarbon concentration in a gas mixture was 5000 ppm based on C_1. Oxidation was carried out at a flow rate of 60 000 h^{-1} in the temperature range that was selected for each hydrocarbon in such a way that the conversion was changed from 0.3 to >20%. Measurements were carried out three times during an experiment to monitor a possible change in the catalyst activity. Reaction products were analyzed by gas chromatography. In particular experiments, the composition of reaction products was analyzed with a GASMET-400 IR gas analyzer to determine the ratio CO/CO_2. In all cases, the selectivity of CO_2 formation exceeded 95%. The specific catalytic activity was calculated by the formula

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

where A_{sp} is the number of hydrocarbon molecules converted on one surface Pt atom within 1 s; W is the oxidation rate calculated as the number of hydrocarbon molecules converted on 1 g of the catalyst within 1 s; and N_{Pt} is the number of surface platinum atoms in 1 g of the catalyst. For the Pt/SiO_2 catalysts, this value was determined by the hydrogen chemisorption data (Table 1). For the Pt/TiO_2 catalysts, the number of surface platinum atoms were calculated by the data of electron microscopy using the known procedure.[17]

Table 1. Average size of the Pt particles (R_{Pt}^{av}) according to the data of electron microscopy (HREM) and chemisorption of H_2 (CM)

Sample*	R_{Pt}^{av}/nm		N_{Pt}**/μmol g^{-1}
	HREM	CM	
Pt(1)/TiO_2	1.1±0.2	—	—
Pt(2)/TiO_2	2.0±0.5	—	—
Pt(2)/SiO_2	1.9±0.5	21.4	2.1
Pt(4)/SiO_2	3.9±1.3	10.2	4.9

* The figure in parentheses corresponds to the average size of platinum nanoparticles in the sample (nm).

** N_{Pt} is the amount of accessible Pt according to the data of chemisorption of H_2.

In order to estimate the contribution of parent supports to the overall conversion, their catalytic activity was determined in particular experiments. It was established that this contribution can be neglected, because the conversion of CH_4 and n-C_4H_{10} on the parent supports did not exceed 1—2% in the temperature ranges where methane and butane conversion on the Pt-containing catalysts reached 100%.

Results and Discussion

Dispersion of platinum in the catalysts. Figure 1 shows the microscopic images of the Pt/TiO_2 and Pt/SiO_2 catalysts containing platinum nanoparticles of similar average size (~2 nm) and the histograms of the platinum nanoparticle size distribution obtained on the basis of electron microscopic data. The center of the distribution histograms for the both catalysts falls on the particles with an average size of ~2 nm. Only a small number of platinum clusters have the size exceeding 2 nm. For Pt/SiO_2 the platinum particle size distribution is somewhat broader. Nevertheless, in both the Pt/SiO_2 and Pt/TiO_2 samples only an insignificant part of the platinum clusters has sizes exceeding 3 nm. The data presented suggest that the method used for preparation provides the supported Pt clusters with a very narrow size distribution.

The data for all prepared samples obtained by electron microscopy are summarized in Table 1. The results of chemisorption measurements of the area of accessible platinum surface in the Pt/SiO_2 samples and the average sizes of metallic particles calculated from these data are also presented in Table 1. The Pt particle size was calculated according to the known procedure.[17] The data of the both methods are well consistent.

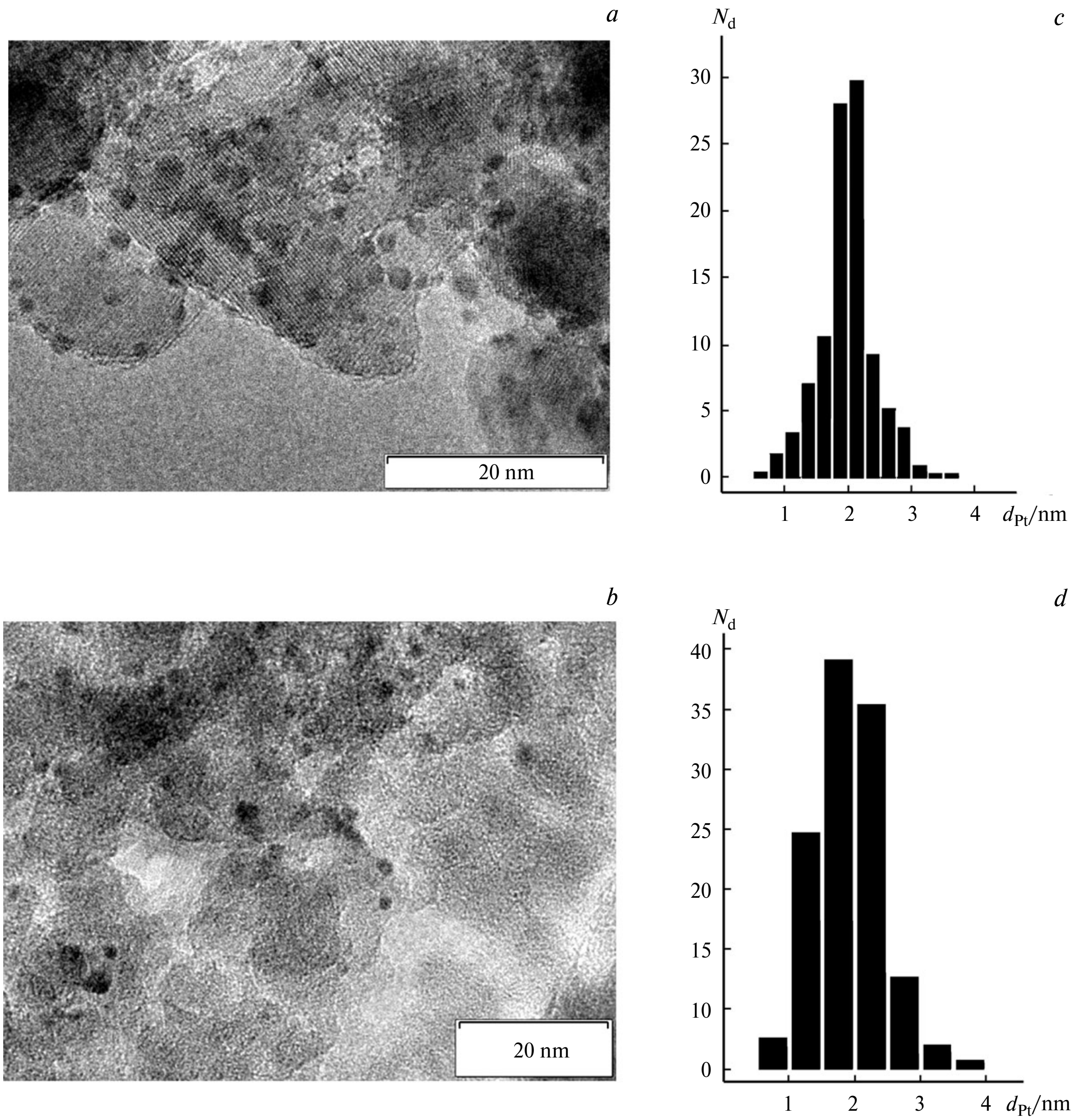

Fig. 1. Microscopic images of the catalysts (*a*, *b*) and the histograms of platinum particle size distribution (*c*, *d*) in the catalysts Pt(2)/TiO_2 (*a*, *c*) and Pt(2)/SiO_2 (*b*, *d*). N_d is the number of particles.

Temperature dependences of the conversion and A_{sp} in the oxidation of CH_4. *Effect of the support.* The temperature dependences of the conversion of methane and *n*-butane in total oxidation on the catalysts Pt/TiO_2 and Pt/SiO_2 are shown in Fig. 2. The oxidation of CH_4 (see Fig. 2, *a*) occurs in the 250 to 600 °C temperature range, depending on the catalyst nature. Methane conversion on the catalysts Pt/TiO_2 begins at temperatures 250—300 °C, whereas on the catalysts Pt/SiO_2 is starts at temperatures 350—400 °C. The comparison of the temperatures of the 50% conversion of hydrocarbon (T_{50}) on the catalysts Pt(2)/TiO_2 and Pt(2)/SiO_2 containing platinum nanoparticles of equal size ($d_{Pt} \approx 2$ nm) shows that on Pt(2)/TiO_2 the T_{50} value is by ~90 °C lower than that on Pt/SiO_2. Thus, the TiO_2-supported Pt catalysts possess substantially higher activity than Pt/SiO_2. The comparison of the A_{sp} values for Pt/TiO_2 and Pt/SiO_2 (Table 2) shows that in terms of the specific catalytic activity the TiO_2-supported Pt catalysts is approximately three times more active than Pt/SiO_2.

Effect of the Pt nanoparticle size. In order to estimate how the catalyst activity depends on the Pt nanoparticle size, we can compare the temperature dependence of the methane conversion for the catalysts containing platinum particles of

Table 2. Specific catalytic activity (A_{sp}) of the Pt/SiO$_2$ and Pt/TiO$_2$ samples in the total oxidation of CH$_4$ and n-C$_4$H$_{10}$ and the apparent activation energies (E_a) of the reactions

Sample	CH$_4$ (400 °C)*		n-C$_4$H$_{10}$ (200 °C)*	
	$A_{sp} \cdot 10^2$ /s^{-1}	E_a /kJ mol^{-1}	$A_{sp} \cdot 10^2$ /s^{-1}	E_a /kJ mol^{-1}
Pt(1)/TiO$_2$	3.2	51.4±1.8	0.6	75.2±2.6
Pt(2)/TiO$_2$	3.4	50.8±2.0	1.9	88.9±2.2
Pt(2)/SiO$_2$	1.0	74.3± 1.9	0.5	74.6±2.8
Pt(4)/SiO$_2$	1.1	78.2±2.3	1.8	88.6±2.7

* Temperature of measurement of the specific catalytic activity.

different size (Fig. 2). The activity of the Pt(1)/TiO$_2$ catalyst ($d_{Pt} \approx$ 1 nm) is noticeably higher than that of Pt(2)/TiO$_2$ ($d_{Pt} \approx$ 2 nm). For the Pt/SiO$_2$ catalysts, the activity also increases with a decrease in the platinum nanoparticle size: Pt(2)/SiO$_2$ ($d_{Pt} \approx$ 2 nm) is more active than Pt(4)/SiO$_2$ ($d_{Pt} \approx$ 4 nm). These results indicate that in CH$_4$ oxidation an increase in the Pt dispersity results in an increase in the overall catalytic activity of both Pt/TiO$_2$ and Pt/SiO$_2$.

Let us consider the influence of the Pt nanoparticle size on the specific catalytic activity, *i.e.*, on the activity of one surface atom in the Pt/TiO$_2$ and Pt/SiO$_2$ samples. The temperature dependences of A_{sp} are presented as the Arrhenius plots in Fig. 3. The A_{sp} values are listed in Table 2 along with the activation energies of CH$_4$ oxidation calculated from the Arrhenius plots.

The comparison of the temperature dependences of A_{sp} for Pt/TiO$_2$ shows that the catalysts containing platinum nanoparticles 1 and 2 nm in size (Pt(1)/TiO$_2$ and Pt(2)/TiO$_2$, respectively) have almost equal values of the specific catalytic activity. At 400 °C this value is ~(3.2—3.4)$\cdot 10^{-2}$ s^{-1} (see Table 2). The temperature dependences of the specific catalytic activity (see Fig. 3) are also almost identical for the catalysts Pt(2)/SiO$_2$ ($d_{Pt} \approx$ 2 nm) and Pt(4)/SiO$_2$ ($d_{Pt} \approx$ 4 nm). For the both catalysts, the A_{sp} value at 400 °C is approximately equal to (1.0—1.1)$\cdot 10^{-2}$ s^{-1} (see Table 2). The data obtained

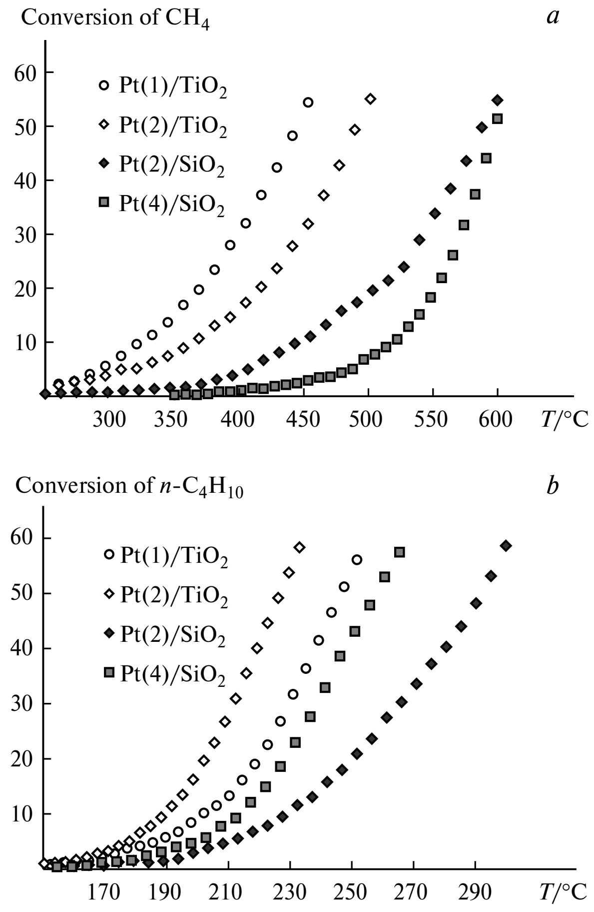

Fig. 2. Temperature dependences of the conversion of methane (*a*) and n-butane (*b*) on the catalysts 0.8% Pt/SiO$_2$ and 0.8%Pt/TiO$_2$ containing Pt nanoparticles of various size indicated in parentheses.

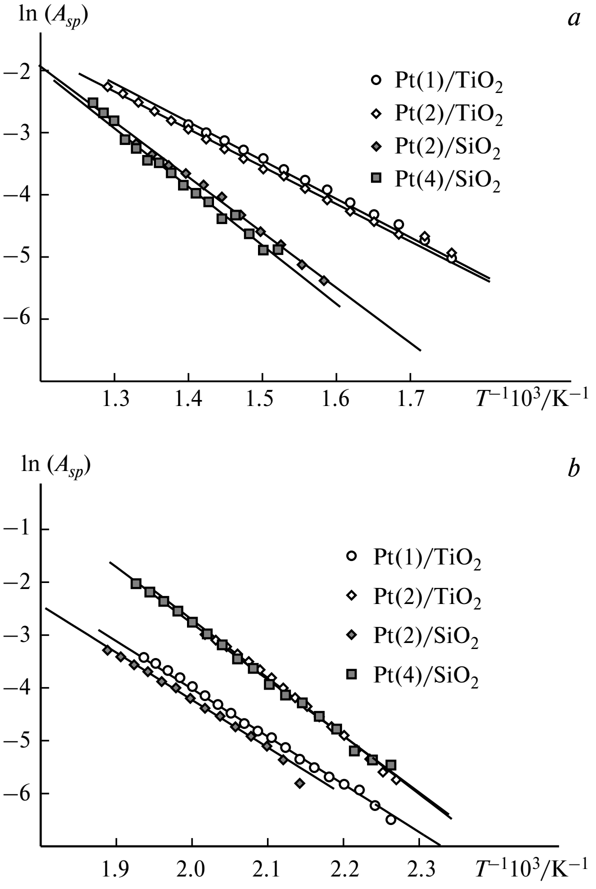

Fig. 3. Temperature dependences of A_{sp} in the Arrhenius coordinates for the total oxidation of methane (*a*) and n-butane (*b*) on the catalysts 0.8% Pt/SiO$_2$ and 0.8%Pt/TiO$_2$ containing Pt nanoparticles of various size.

indicate low structure sensitivity of the reaction of CH_4 oxidation.

The E_a values are ~51 kJ mol^{-1} for Pt/TiO_2 and ~74—78 kJ mol^{-1} for Pt/SiO_2, which corresponds to the literature data.[18,19]

Temperature dependences of the conversion and A_{sp} in the oxidation of n-C_4H_{10}. *Effect of the support.* n-Butane is oxidized (Fig. 2, *b*) at a substantially lower temperature (150—300 °C) than methane, which is due to a higher reactivity of an n-C_4H_{10} molecule.[20] The same values of n-C_4H_{10} conversion are achieved in the catalysts Pt/TiO_2 at lower temperatures than on the Pt/SiO_2 samples. On the catalyst $Pt(2)/TiO_2$ ($d_{Pt} \approx 2$ nm) the temperature of the 50% conversion of n-C_4H_{10} (T_{50}) is 225 °C. On the $Pt(2)/SiO_2$ samples containing the Pt nanoparticles of the same size T_{50} is ~255 °C. The A_{sp} value for $Pt(2)/TiO_2$ is almost fourfold higher than that for $Pt(2)/SiO_2$: $1.9 \cdot 10^{-2}$ and $0.5 \cdot 10^{-2}$ s^{-1}, respectively (see Table 2). The data obtained show that the catalysts supported on titania are more active, as well as in the oxidation of methane.

Effect of the Pt nanoparticle size. The comparison of the temperature dependences of the conversion of n-butane on the catalysts $Pt(1)/TiO_2$ ($d_{Pt} \approx 1$ nm) and $Pt(2)/TiO_2$ ($d_{Pt} \approx 2$ nm) shows that the activity of Pt/TiO_2 increases with an increase in the Pt nanoparticle size despite a decrease in the surface area of Pt accessible for the reaction. A similar dependence is observed for Pt/SiO_2 catalysts. The conversion of n-butane on $Pt(4)/SiO_2$ ($d_{Pt} \approx 4$ nm) proceeds at temperatures 50—60 °C lower than those on $Pt(2)/SiO_2$ ($d_{Pt} \approx 2$ nm). Thus, unlike the oxidation of CH_4, in the oxidation of n-butane the catalysts with a larger size of Pt particles possess higher activity.

The temperature dependences of the specific catalytic activity (A_{sp}) are presented in the Arrhenius coordinates in Fig. 3, *b*. The A_{sp} values at 200 °C are listed in Table 2. For the $Pt(2)/TiO_2$ catalyst ($d_{Pt} \approx 2$ nm), the specific activity is substantially higher than that for $Pt(1)/TiO_2$ ($d_{Pt} \approx 1$ nm). At 200 °C on the $Pt(1)/TiO_2$ sample with a smaller nanoparticle size, A_{sp} is about $0.6 \cdot 10^{-2}$ s^{-1} (see Table 2). On the $Pt(2)/TiO_2$ sample with the Pt nanoparticle size about 2 nm, A_{sp} reaches $1.9 \cdot 10^{-2}$ s^{-1}. A similar tendency is also observed for Pt/SiO_2. With an increase in the Pt nanoparticle size from 2 nm ($Pt(2)/SiO_2$) to 4 nm ($Pt(2)/SiO_2$), the specific catalytic activity increases from $0.5 \cdot 10^{-2}$ to $1.8 \cdot 10^{-2}$ s^{-1} (see Table 2).

Thus, the specific catalytic activity in n-butane oxidation increases 3.5—4 times with an increase in the Pt nanoparticle size (see Table 2). Such a substantial increase in A_{sp} occurring with an increase in the platinum nanoparticle size results in the difference in the overall catalytic activity. In particular, the catalysts containing the larger Pt nanoparticles show an enhanced overall activity in the oxidation of n-butane compared to the samples with higher Pt dispersion (see Fig. 2, *b*). The regularities observed in changing A_{sp} on the studied catalysts indicate significant structure sensitivity of n-butane oxidation.

So, the degree of structure sensitivity of the total oxidation reaction increases on going from methane to n-butane. As a result, the activity (both specific and overall) of the catalysts containing larger platinum nanoparticles increases. This effect is observed for both Pt/SiO_2 and Pt/TiO_2. In addition, the data presented in Figs 2 and 3 indicate a substantial effect of the support on the activity of the metallic catalysts. The catalysts supported on titania exhibit the higher activity in the oxidation of both CH_4 and n-C_4H_{10}.

The increase in the structure sensitivity in the total oxidation reaction observed on going from small to larger molecules agrees well with our previous results[13] on studying the structure sensitivity of the total oxidation of n-alkanes C_1—C_6 on the catalyst Pt/Al_2O_3. It was shown that for n-butane oxidation the A_{sp} value increases threefold with an increase in the Pt nanoparticle size from 1 to 2 nm. The A_{sp} value increases fivefold on going from the nanoparticle 2 nm in size to the nanoparticle 3—6 nm in size.[13] Approximately the same range of changing A_{sp} was established in the present work (see Table 2) for the catalysts Pt/SiO_2 and Pt/TiO_2. Almost no increase in A_{sp} occurs with an increase in the Pt nanoparticle size for the oxidation of CH_4. The comparison of the data obtained on the catalysts Pt/SiO_2, Pt/TiO_2, and Pt/Al_2O_3 suggests that the effect of increased structure sensitivity observed in the total oxidation reaction on going from methane to n-alkanes C_4 is independent of the support nature and is mainly determined by the Pt particle size.

The following probable reasons for increasing A_{sp} with an increase in the platinum particle size can be proposed. According to the modern concepts,[20,21] the oxidation of alkanes on the Pt catalysts includes the following main steps:

$$O_2 \longleftrightarrow 2\,O_{ads}, \tag{1}$$

$$C_xH_y \longleftrightarrow C_xH_{y,ads}, \tag{2}$$

$$2\,C_xH_{y,ads} + O_{ads} \longrightarrow C_xH_{y-1,ads} + H_2O, \tag{3}$$

$$C_xH_{y-1,ads} + [2x + (y-1)/2]\,O_{ads} \longrightarrow$$

$$\longrightarrow xCO_2 + (y-1)/2\,H_2O. \tag{4}$$

An oxygen molecule is dissociatively chemisorbed in step (1). An alkane molecule is adsorbed in parallel step (2). The step determining the overall reaction rate is the interaction of an adsorbed alkane molecule $C_xH_{y,ads}$ with a chemisorbed oxygen atom O_{ads} resulting in the formation of the highly reactive alkyl radical $C_xH_{y-1,ads}$ (step 3). In the subsequent steps described by the overall equation (4), the alkyl radical is rapidly consecutively oxidized to carbon oxides and water. The Pt surface is mainly covered with O_{ads}, because the energy of oxygen adsorption (step 1) is much higher than the adsorption energy of relatively inert alkane molecule (step 2). As a result, the metal surface is blocked for alkane adsorption. It was shown in many studies that the rate of alkane oxidation decreases with an increase in the partial oxygen pressure because the surface is blocked with strongly bonded O_{ads} particles.[22,23]

The considerable increase in A_{sp} with an increase in the platinum particle size in the oxidation of n-C_4H_{10} can be due to a decreased blocking of the surface with strongly bonded chemisorbed oxygen O_{ads} (step 1). The reason for this phenomenon is a decrease in the degree of deficiency of the Pt nanoparticle surface with an increase in their size, resulting in a decrease in the energy of oxygen adsorption.

This effect is insignificant in the oxidation of CH_4, because the reaction occurs at temperatures 150—200 °C higher than those of n-C_4H_{10} oxidation. With the reaction temperature rise, the blocking of the surface with chemisorbed oxygen decreases due to its reciprocal desorption. Therefore, A_{sp} changes insignificantly with a change in the Pt nanoparticle size. Validity of this explanation is also confirmed by the results of thermodynamic analysis of the size effect of nanoparticles of the active component on the adsorption equilibrium and the rate of the catalytic process.[24] It was shown[24] that the dependence of the reaction rate on the nanoparticle size became less pronounced with an increase in the temperature of the catalytic process.

Another possible reason for an increase in the structure sensitivity of the reaction on going from methane to butane can be due to the fact that a multiatomic surface site consisting of a greater number of platinum atoms is required for the adsorption of a larger alkane molecule (step 2). An increase in the relative concentration of adsorbed hydrocarbon can be expected on larger platinum particles, since the probability of formation of multiatomic adsorption sites increases, resulting, in turn, in an increase in A_{sp}.

As for the higher activity of the Pt/TiO_2 catalysts compared to Pt/SiO_2, the most probable reason is a higher acidity of the TiO_2 surface. Available literature data indicate a considerable effect of this factor on both the specific and overall activity of the catalysts of total oxidation. The activity of Pt/Al_2O_3 in the oxidation of C_3H_8 increases substantially when the alumina surface is sulfated.[25,26] It was assumed that an increase in the reaction rate is associated with the formation of acid sites (stable sulfate groups) at the metal/support interface in Pt/Al_2O_3. These sites enhance the chemisorption of propane (step 2), thus increasing the observed specific catalytic activity of Pt. The independent study of the activity of the Pt catalysts supported on MgO, Al_2O_3, and SiO_2—Al_2O_3 also showed that the rate of propane oxidation increases with an increase in the acidity of the support.[27,28] It was proved by EXAFS spectroscopy *in situ* that the resistance of platinum to oxidation on more acidic supports increases when the reaction is carried out in a large oxygen excess.[29] A larger amount of metallic Pt in the catalysts deposited on an acidic support results in a higher activity.

Thus, it was found in the present study that the structure sensitivity of the Pt catalysts in total oxidation increases on going from CH_4 to n-C_4H_{10}. As a result, the activity of the Pt catalysts in the oxidation of n-C_4H_{10} increases with an increase in the Pt nanoparticle size from 1 to 4 nm for both the Pt/TiO_2 and Pt/SiO_2 catalysts.

The support determines, to a considerably extent, the activity of the platinum catalysts in the reactions under study. Both the specific and overall catalytic activities of the Pt/TiO_2 samples are 3—4 times higher than the activity of the Pt/SiO_2 catalysts.

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