

Effect of Thermal Activation of Supported Catalysts Pt/MeO_x, Where MO_x = Al₂O₃, CeO₂, La₂O₃, and ZrO₂, for Complete Oxidation

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Received May 30, 2001

Abstract—A sharp increase in the atomic catalytic activity (ACA) of supported platinum catalysts in the model reaction of *n*-pentane complete oxidation is found on going from the preliminary calcination temperature of 500–600°C to a temperature of 700°C. ACA increases by an order of magnitude for the Pt/γ-Al₂O₃ system, ~3 times for Pt/ZrO₂, and ~1.5 times for Pt/CeO₂. The per-gram activities of all catalysts decrease because of a decrease in the dispersion of supported platinum with an increase in the temperature of preliminary calcination.

INTRODUCTION

The thermal activation effect, which consists in a sharp increase in the atomic (specific) catalytic activity upon calcination at elevated temperatures, has been found and studied for the MnO_x/Al₂O₃ and MnO_x/ZrO₂ oxide systems [1–5]. This effect is due to the initial interaction (at relatively low temperatures) between the components of the catalytic system and often produces new phases or solid solutions, which decompose upon high-temperature treatment or reduction. The above effect was seen over many catalysts including platinum-based ones. It was shown in [6, 7] by the X-ray radial atom distribution method that in aluminum–platinum catalysts modified with rare-earth metal oxides [6], mixed compounds are formed in the subsurface support layer, for example, a solid solution of Pt⁴⁺ in cerium aluminate, which decomposes to evolve into disperse platinum upon calcination in air at ~720°C or reduction with hydrogen at 500°C. As a result, disperse platinum is formed and strongly interacts with the support and is therefore resistant to sintering. The atomic catalytic activity of this platinum is lowered compared to platinum supported on unmodified γ-Al₂O₃. At the same time, the thermal treatment of platinum supported on pure γ-Al₂O₃ oxide at temperatures >750°C significantly enhances the specific catalytic activity per 1 m² of platinum in the complete oxidation of *n*-butane, which is due to a change in the Pt^{+/Pt⁰} ratio on the surface of the platinum crystals, as was assumed in [8]. It was pointed out in [9] that the activity of ionic Pt in hydrocarbon complete oxidation is substantially lower than that of metallic platinum. This was confirmed in [10] by the fact that the activity of Pt/γ-Al₂O₃ was maximal when Pt was only partially oxidized. When the

starting samples are thermally treated in air at temperatures ≥600°C, the surface Pt “oxide” structures become unstable and decompose, whereas disperse “ionic” Pt, which was previously stabilized on the support defects and interacted with the support, is reduced to form metallic Pt crystallites. Hence, the Pt^{+/Pt⁰} ratio in the samples decreases; that is, the number of Pt⁰-containing sites on which hydrocarbon molecules can adsorb dissociatively increases [10].

An increase in the atomic catalytic activity of platinum in aluminum–platinum catalysts for complete oxidation with an increase in the calcination temperature was reported in other papers. It was found in [8, 9, 11] by XRD and electron microscopy that an increase in *T*_{cal} of aluminum–platinum catalysts from 500 to 1000°C results in the polymorphic transformation of the support Al₂O₃ (γ → (δ, θ) → α) and strong Pt sintering, whereas both the starting and calcined aluminum–platinum catalysts are polydispersed. The morphology of the supported platinum crystallites also changes dramatically with an increase in the calcination temperature. Thermal treatment in air at 750–980°C results in the transformation of initially almost spherical small particles of platinum into large crystals with a regular shape and clear faceting. An increase in the size of the supported metal crystallites with an increase in the temperature of preliminary treatment leads to a decrease in the donor–acceptor interaction with the support. This results in the enhancement of the electron density on the surface atoms of the supported metal and, hence, the catalytic activity [12, 13]. It was shown in these papers that the strength of the Pt–O_{ads} bond in the calcined samples does not change with *T*_{cal}.

although the size and shape of the Pt crystallites change essentially due to sintering.

The effect of the atomic catalytic activity enhancement with an increase in the preliminary calcination temperature prompted us to study the thermal activation of the Pt/MO_x system, where MO_x = Al₂O₃, CeO₂, La₂O₃, and ZrO₂.

EXPERIMENTAL

Catalyst preparation. Supports Al₂O₃, La₂O₃, CeO₂, and ZrO₂ in the form of rods were prepared by the extrusion of nitric acid-peptized hydroxides preliminarily precipitated with ammonia from the corresponding metals (analytical grade) followed by drying at $T = 120^\circ\text{C}$ and calcination at $T = 500^\circ\text{C}$ for 4 h (600°C for La₂O₃). A fraction of 0.5–1.0 mm was chosen for subsequent platinum deposition.

Catalysts were prepared by the impregnation of the above fraction of the ZrO₂ and La₂O₃ supports with an acetone solution of platinum carbonyl followed by acetone evaporation in an argon flow and drying the samples at 100°C for 1 h; in the case of the CeO₂ and Al₂O₃ supports, the catalysts were prepared by platinum carbonyl chemisorption. Thermal treatment was carried out in a muffle oven by calcination in air at 500, 600, and 700°C for 2 h.

The phase composition of the supports and catalysts was studied by X-ray phase analysis (a DRON-3 instrument, CoK_α irradiation with a β filter behind the a sample and in front of a counter). Diffraction patterns were obtained by powder diffractometry according to the Bregg–Brentano method.

Chemical analysis of the catalysts for platinum was performed according to a known procedure [14].

The catalytic activity of the samples was tested in *n*-pentane complete oxidation in a flow-circulation setup under gradientless conditions in the kinetic regime at 300°C. The catalyst loading was ~1.5 g. The starting gas mixture contained *n*-pentane (0.1 vol %) and air (99.9 vol %). The gas flow rate through the reactor with a sample was varied in the range 10–60 l/h to obtain 50% conversion of the reactant. The circulation rate was ~800 l/h. The reaction mixture was analyzed before and after the reactor on an LKhM-8 MD chromatograph (ionization-flame detector, 3 mm × 2 m stainless steel column packed with Polisorb-1). The reaction was monitored by the change in concentration of unreacted *n*-pentane at the reactor outlet. No peaks, except for that of *n*-pentane, were found.

The atomic catalytic activity (ACA) of the samples was calculated using the following formulas:

$$W_{\text{ACA}} = W_{\text{sp}}/N_{\text{Pt}},$$

where W_{ACA} is the atomic catalytic activity ($\text{cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$); W_{sp} is the specific catalytic activity calculated per 1 g of the catalyst ($\text{cm}^3 \text{ g}^{-1} \text{ s}^{-1}$); N_{Pt} is the

number of surface platinum atoms in 1 g of the catalyst (atom/g).

The N_{Pt} value was calculated according to the formula

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

where C_{Pt} is the platinum concentration in the catalyst (wt %), D_{Pt} is the dispersion of supported platinum, N_{A} is the Avogadro number, and M_{Pt} is the platinum atomic weight.

Supported platinum dispersion (D) was estimated by H₂–O₂ titration in an all-sealed glass setup according to a known procedure [15] (except for CeO₂ samples) including the following main stages:

- (1) Drying the sample loaded into the reactor in a vacuum at 120°C for 2 h;
- (2) Reduction of the sample at 500°C with a gradual increase in temperature in the reactor with hydrogen circulation and freezing out the reaction products at $T = -196^\circ\text{C}$ for 1 h;
- (3) Blank titration with oxygen at room temperature for 20 min;
- (4) Hydrogen chemisorption at 150°C for 30 min; and
- (5) Titration of adsorbed hydrogen with a specified oxygen volume.

The specific surface area of the samples was measured on a Sorpty-1750 instrument using the BET method from nitrogen adsorption at $p = 135$ torr and $T = 77$ K.

RESULTS AND DISCUSSION

X-Ray phase analysis showed that

(1) The Pt/γ-Al₂O₃ sample is a two-phase system consisting of metallic platinum crystals and the γ-Al₂O₃ phase.

(2) The Pt/ZrO₂ sample consists of three crystalline phases: metallic platinum crystals, monoclinic ZrO₂, and tetragonal-lattice ZrO₂. The monoclinic structure prevails in all three samples calcined at 500, 600, and 700°C, and the relative amount of the tetragonal phase decreases with an increase in the calcination temperature, whereas that of the monoclinic phase increases.

(3) The Pt/CeO₂ sample consists of two phases: metallic platinum and CeO₂.

(4) The Pt/La₂O₃ sample is a two-phase system consisting of metallic platinum crystals and La(OH)₃ formed during slow cooling of the sample in air. The relative concentration of La(OH)₃ in the support declines with an increase in the calcination temperature, which is accompanied by the appearance of a new phase, lanthanum carbonate La₂O₃. Nevertheless, we preserved the designation Pt/La₂CO₃ for this sample.

The total specific surface areas of the supports determined by the BET method were (m^2/g): γ-Al₂O₃, 201; ZrO₂, 39; CeO₂, 52; and La₂O₃, 24.

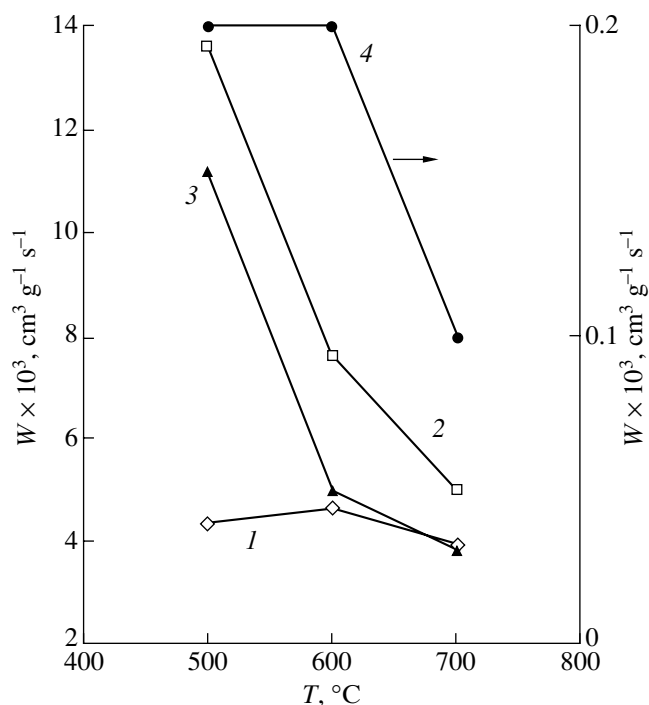


Fig. 1. The activity of 1 g of the catalyst (1 wt % Pt) in *n*-pentane complete oxidation at 300°C as a function of the temperature of preliminary calcination over the samples: (1) Pt/γ-Al₂O₃, (2) Pt/ZrO₂, (3) Pt/CeO₂, and (4) Pt/La₂O₃.

Figure 1 shows that the per-gram activity of supported platinum in the Pt/CeO₂ catalyst drops with an increase in the calcination temperature. The above activity of the Pt/ZrO₂ catalyst also drops and is maximal in its absolute value among all the samples calcined at 500°C. The activity of the Pt/γ-Al₂O₃ sample after calcinations at 500–600°C remains practically constant within the accuracy of the experiment and decreases after calcination at $T_{\text{cal}} = 700^\circ\text{C}$. Pt/La₂O₃ has the lowest activity, and its variation shown in Fig. 1 is within the experimental error.

Thus, W_{sp} of all catalysts decreases with an increase in the preliminary calcination temperature due to a decrease in the platinum dispersion (see table).

As can be seen from the table and Fig. 2, the atomic catalytic activity of the Pt/γ-Al₂O₃ samples calcined at 700°C is higher than that of the samples calcined at 500 and 600°C by approximately an order of magnitude. A similar dependence is seen for the supported Pt/ZrO₂ catalyst. However, the sample calcined at 700°C was ~3 times more active than that calcined at 500°C. For Pt/La₂O₃, no clear dependence follows from the above data because of the poor activity and possible experimental error. However, it can be qualitatively concluded that the atomic catalytic activity of platinum decreases upon the calcination of this sample at 600–700°C.

When H₂–O₂ titration was used to measure the platinum dispersion in the Pt/CeO₂ catalyst, we failed to

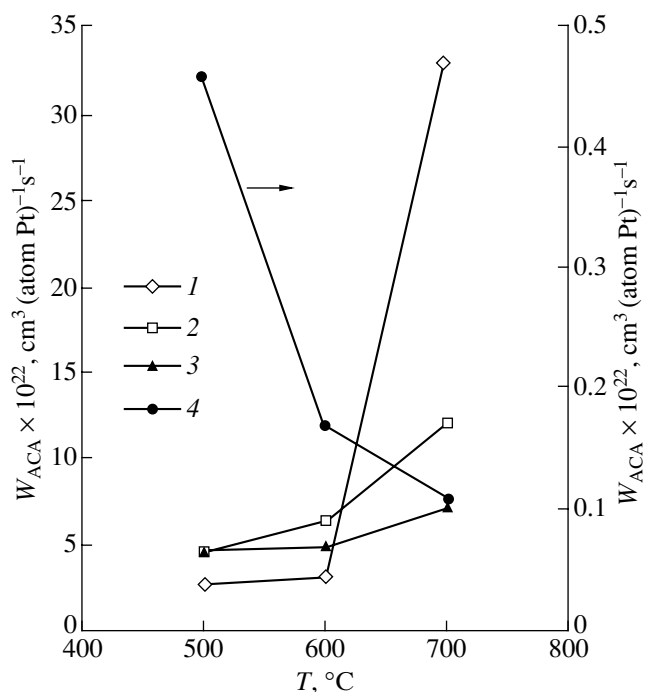


Fig. 2. The atomic catalytic activity of supported platinum catalysts in *n*-pentane complete oxidation at 300°C as a function of the temperature of preliminary calcination for the samples: (1) Pt/γ-Al₂O₃, (2) Pt/ZrO₂, (3) Pt/CeO₂, and (4) Pt/La₂O₃.

determine the atomic catalytic activity because of the abnormally high O₂ consumption. This fact is due to the oxidation of the surface CeO₂ layer preliminarily reduced with hydrogen. To estimate the platinum dispersion in Pt/CeO₂ catalysts, we developed a procedure based on CO adsorption at room temperature on the surface of preliminarily treated samples. The pretreatment of samples included drying in a vacuum, reduction at 350°C for 2 h in the reactor with hydrogen circulation, freezing out the reaction products at $T = -196^\circ\text{C}$, and blank titration with oxygen at room temperature followed by hydrogen chemisorption at 150°C for 30 min. Then, H₂ is desorbed from the catalyst surface by evacuation at 350°C for 1–1.5 h and cooled to room temperature in a vacuum. The study was carried out in the same setup that was used for H₂–O₂ titration. The atomic catalytic activity of the Pt/CeO₂ samples calcined at 700°C was ~1.5 times higher than the activities of samples calcined at 500 and 600°C. The experimental error including the error in the determination of the catalytic activity and chemisorption measurements was ~20%.

To compare the catalytic properties of samples, two main assumptions were used in the calculation of the atomic catalytic activity:

(1) All the surface atoms are active (common suggestion);

Characteristics of the catalysts calcined at various temperatures

Sample	$T_{\text{cal}}, ^\circ\text{C}$	$C_{\text{Pt}}, \text{wt } \%$	$S_{\text{sp}}, \text{m}^2/\text{g}$	$W \times 10^3, \text{cm}^3 \text{g}^{-1} \text{s}^{-1}$	$W \times 10^3, \text{cm}^3 \text{g}^{-1} \text{s}^{-1}$ per 1% Pt	D	$W_{\text{ACA}} \times 10^{22},$ $\text{cm}^3 (\text{atom Pt})^{-1} \text{s}^{-1}$
Pt/Al ₂ O ₃	500	0.97	237	4.2	4.3	0.49	2.8
Pt/Al ₂ O ₃	600	0.97	185	4.5	4.6	0.47	3.2
Pt/Al ₂ O ₃	700	0.97	180	3.8	3.9	0.04	33
Pt/ZrO ₂	500	0.84	57	11.4	13.6	0.94	4.7
Pt/ZrO ₂	600	1.1	16	8.4	7.6	0.39	6.4
Pt/ZrO ₂	700	1.4	15	7.0	5.0	0.14	12
Pt/CeO ₂	500	0.6	48	6.7	11.2	0.76	4.8
Pt/CeO ₂	600	0.6	45	3.0	5.0	0.33	4.9
Pt/CeO ₂	700	0.6	32	2.3	3.8	0.17	7.2
Pt/La ₂ O ₃	500	1.0	24	0.2	0.2	0.14	0.46
Pt/La ₂ O ₃	600	1.0	22	0.2	0.2	0.37	0.17
Pt/La ₂ O ₃	700	1.0	28	0.1	0.1	0.29	0.11

(2) The number of the surface Pt atoms change insignificantly on going from an oxidative to a reductive medium [8, 9, 16].

As can be seen from the data above, the thermal activation effect was found for the Pt/Al₂O₃, Pt/ZrO₂, and Pt/CeO₂ catalysts. Note that the platinum dispersion in the Pt/La₂O₃ sample passes through a maximum with an increase in the calcination temperature, whereas the platinum dispersion in other systems decreases. This behavior of Pt/La₂O₃ during calcination was not studied in detail due to the instability of the support composition in air.

To summarize, this work showed that the effect of a sharp increase in the atomic catalytic activity of supported platinum catalysts takes place in the following systems (in order of decreasing effect): Pt/ γ -Al₂O₃, Pt/ZrO₂, and Pt/CeO₂. The per-gram activity of all the samples decreases regularly with an increase in the calcination temperature.

As was mentioned above, the strength of the Pt–O_{ads} bond in the calcined Pt/ γ -Al₂O₃ and Pt–Ce(La,Zr)/ γ -Al₂O₃ samples does not change with an increase in T_{cal} despite a significant increase in the size and shape of the Pt crystallites upon sintering [12, 13]. This means that the strength of the oxygen bond in these samples does not determine a change in the platinum specific catalytic activity per 1 m² in hydrocarbon complete oxidation upon the calcination of the catalysts at elevated temperatures. Hence, an increase in SCA Pt or atomic catalytic activity (ACA Pt) of the calcined samples, that is, the appearance of the thermal activation effect, is due to the acceleration of the hydrocarbon activation stage, that is, a change in the number and/or nature of the chemisorption and activation sites.

We have no data on the bond strength for chemisorbed oxygen or hydrocarbon with a surface of platinum supported on pure oxides ZrO₂, CeO₂, and La₂O₃.

Similarly to platinum supported on γ -Al₂O₃ modified with the above oxides, one can suggest that the thermal activation effect is due to the acceleration of the hydrogen activation stage.

ACKNOWLEDGMENTS

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

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