

Effects of the Modification of Reforming Alumina–Platinum Catalysts with Zirconium

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Abstract—The effects of the modification of supported platinum as a constituent of reforming Pt/Al₂O₃ and Pt–Re/Al₂O₃ catalysts by introducing zirconium, which was obtained from various starting compounds, into the composition of the support were studied. These effects were most pronounced if difficult-to-hydrolyze compounds served as a source of zirconium. It was found that zirconium affected the metal–support interaction strength, which is responsible for the formation of the most strongly adsorbed hydrogen species (over the temperature range of 300–500°C). This suggests a change in the electronic state of platinum under the action of zirconium. Platinum sites became more regular; as a result of this, the reaction rate parameters of heptane conversion changed.

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INTRODUCTION

Reforming is one of the most important basic oil-refining processes; it largely determines the technological and economic level of this branch of industry. In turn, the technology depends on the quality of a catalyst [1, 2]. Thus, it is clear that, in economically developed countries, attention is focused on the improvement of reforming catalysts. Current concepts of the structure of platinum catalysts are based on the results of studies in which an important role of new platinum species in the catalysis of hydrocarbon conversions was found [3–8].

A reforming catalyst consists of a support and an active component. Thermally stable alumina (as a rule, its γ -modification) with a highly developed surface usually serves as a support. The active components are platinum (0.25–0.35 wt %), chlorine, and promoters (Re, Sn, Ge, etc.). The detection of surface platinum ionic species Pt^σ [8] as surface platinum(II) complexes incorporated into the near-surface layers of alumina because of the effect of strong interactions with the support should be considered as one of the most important results obtained in previous years. An increase in the Lewis acidity of the support facilitates platinum stabilization in the state Pt^σ; this acidity can be increased by modifying the support with the oxides of difficult-to-reduce metals, such as Zr and La [9, 10]. The effects of strong interactions with the support are responsible for the appearance of a charge on Pt atoms, and they facilitate their high thermal stability.

These states exhibit a number of advantages over dispersed platinum metal Pt⁰; the most important of these advantages is that the activity of Pt atoms in

alkane aromatization reactions is higher by one order of magnitude [7, 11, 12]. However, the catalytic properties of Pt^σ are not a constant; they can considerably vary depending on the nature of the ligand environment of the central atom of platinum. Previously, it was found that halogens, S, Se, Te, Sn, Ge, etc., belong to the elements that can affect Pt^σ [7, 13].

The aim of this work was to study the effects of the modification of platinum with zirconium in reforming platinum and platinum–rhenium catalysts.

EXPERIMENTAL

Continuous cold and batch precipitation pseudoboehmite from ZAO Promyshlennye Katalizatory (Ryazan, Russia) was used to prepare the support [14]. The concentrations of iron and sodium trace impurities in the pseudoboehmite were lower than 0.01 wt %. The supports were prepared by the plastification of AlOOH with a solution of acetic acid (the molar ratio was CH₃COOH/Al₂O₃ = 0.02) with continuous stirring. Then, the mass was shaped into extrudates 1.5 mm in diameter, dried at 120°C, and calcined at 600°C. The specific surface area of the resulting samples was 250–270 m²/g; the pore volume was 0.65 cm³/g; and the effective pore radius was 5.0 nm. Zirconium compounds as solutions in acetic acid were introduced at the stage of plastification.

0.25% Pt (or 0.25% Pt together with 0.3% Re) mixed with dilute solutions of hydrochloric and acetic acids was applied to the calcined support. The samples dried at 120°C were calcined at 520°C in a flow of dry air and then reduced in hydrogen at 500°C.

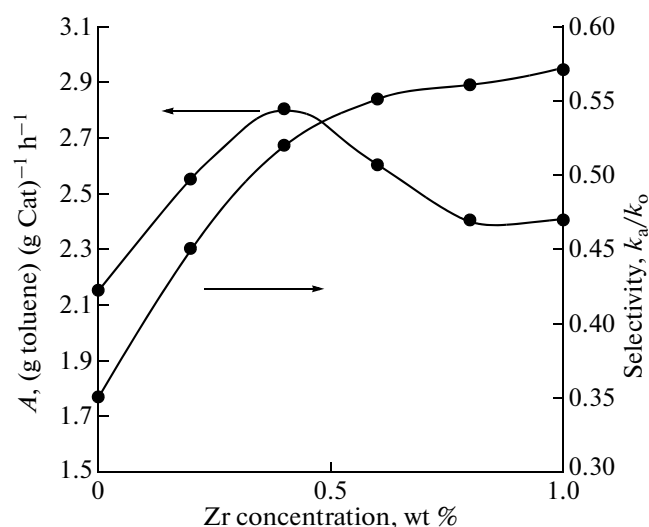


Fig. 1. Dependence of the activity and selectivity of the Pt-Re/Al₂O₃ catalyst in the reforming of *n*-heptane on the zirconium content of the support.

The dispersity of the metal and the amounts of ionic (Pt⁺) and metallic (Pt⁰) platinum were evaluated using a previously developed adsorption method [15–18].

The acidic properties of Al₂O₃ and catalyst samples were studied by the IR spectroscopy of adsorbed CO [19, 20] on a Shimadzu 8300 Fourier transform IR spectrometer (resolution, 4 cm⁻¹; number of accumulated spectra, 50). The samples were milled and pressed into pellets with no binder; thereafter, they were evacuated in the IR cell for 2 h at 500°C to a residual pressure of 10⁻⁴ Torr. The adsorption of CO was performed at the liquid-nitrogen temperature (–196°C) in a pressure range from 0.1 to 10 Torr. The spectra were measured over the range of 1200–4000 cm⁻¹. The detection limit of Lewis acid sites (LASs) was 0.2 μmol/g. The concentration of sites was calculated from the integral intensity of absorption

bands corresponding to LASs ($\nu_{\text{CO}} = 2170\text{--}2240\text{ cm}^{-1}$). The accuracy of quantitative measurements was $\pm 25\%$.

The catalysts were tested in *n*-heptane reforming, which was performed in an isothermal plug-flow reactor at an elevated pressure of hydrogen [21]. Based on the results of the tests, the rate constants of the main reactions of *n*-C₇—aromatization (k_a) and cracking (k_{cr})—were calculated. The apparent activation energy of the target reaction and the selectivity of aromatization $S = k_a/k_o$, where k_o is the overall rate constant of *n*-C₇ conversion, were calculated from the temperature dependence of the rate constants. The catalyst activity (A) in the target reaction was evaluated by the specific productivity for toluene at 490°C (averaged value over the temperature range of 460–520°C). The deactivation constant k_d , which characterizes the stability of the catalyst, was calculated by monitoring changes in the specific productivity in the course of long-term tests at 520°C.

RESULTS AND DISCUSSION

Figure 1 shows the activities and selectivities of Pt-Re catalysts containing from 0 to 1.0 wt % zirconium. As the zirconium content of the support was increased, the selectivity of aromatization increased from 0.35 to 0.57, whereas the activity passed through a maximum in the Zr concentration range of 0.3–0.6 wt %.

The effects of the modification of supported platinum as a constituent of Pt and Pt-Re catalysts on Zr-containing supports were analogous (Table 1). In the Pt-Zr/Al₂O₃ system, modification resulted in an increase in the activity from 2.2 to 2.4 (g toluene) $^{-1}$ h $^{-1}$, in the selectivity from 0.52 to 0.59, and in the stability (k_d) from 0.78 to 0.89. Note that the activation energy of the aromatization reaction noticeably decreased from 127 to 97 kJ/mol. In the Pt-Re system, the kinetic parameters changed even more considerably: the activity, selectivity, and stability of the catalyst significantly increased, whereas the

Table 1. Results of the catalytic tests of samples in the reforming of *n*-heptane

Characteristic	Pt/Al ₂ O ₃	Pt-Zr/Al ₂ O ₃	Pt-Re/Al ₂ O ₃	Pt-Re-Zr/Al ₂ O ₃
A_{av} (490°C), (g toluene) (g Cat) $^{-1}$ h $^{-1}$	2.2	2.4	2.3	2.9
S	0.52	0.59	0.35	0.50
E_a , kJ/mol	127	97	180	148
k_d (520°C)	0.78	0.89	0.90	0.95
$k_{ef} = ASk_d$	0.89	1.26	0.73	1.38

Note: Reaction conditions: $P = 1.0$ MPa; $H_2/C_7 = 5$ (mol); $T = 460, 480, 500$, and 520°C. Catalyst composition, wt %: Pt, 0.25; Re, 0.3; Zr, 0.3; Cl, 1.2.

activation energy decreased from 180 to 148 kJ/mol. These considerable changes suggest the possible transformation of the transition complex on the catalyst surface as a result of a change in the state of platinum.

Figure 2 shows data on the composition of gaseous reaction products in heptane conversion. As the reaction temperature was increased, the yield of C_1 – C_4 gases increased and their composition changed. The average ratio $(C_1 + C_2)/(C_3 + C_4)$ (so-called cracking number) changed from 0.1 on Pt–Re/ Al_2O_3 to 0.3 and 0.7 on Pt–Re–Zr/ Al_2O_3 with zirconium contents of 0.2 and 0.4 wt %, respectively. This is indicative of the effect of zirconium on the selectivity of hydrocarbon conversion on active platinum sites. It is well known [12] that cracking and complexation reactions occur through the steps of formation of strongly bound transition complexes at the active sites of the catalyst. A decrease in the yield of C_1 – C_4 hydrocarbon gases and an increase in their molecular weight, as well as an increase in the stability of catalysts modified with zirconium to coke deactivation (k_d , Table 1), suggest that zirconium affects the state of platinum to hinder the formation of strongly bound states. The modification results in an increase in the contribution of isomerization and dehydrocyclization processes, which occur through less strongly bound states, to the conversion of heptane [22].

In the course of the study, we found an important role of the nature of the starting zirconium compounds used for support modification. Table 2 summarizes the results. It was found that modification effects increased in the order hydroxide–acetate–nitrate–sulfate. The similarity of reaction rate parameters on the samples modified with the use of the first three compounds may be a consequence of the identical hydrolysis products of zirconium compounds upon the interaction with aluminum hydroxide, whose aqueous suspension is characterized by pH 9 [23].

It is believed that, in the case of modification with easy-to-hydrolyzed compounds (nitrates and acetates) by their interaction with the aluminum hydrox-

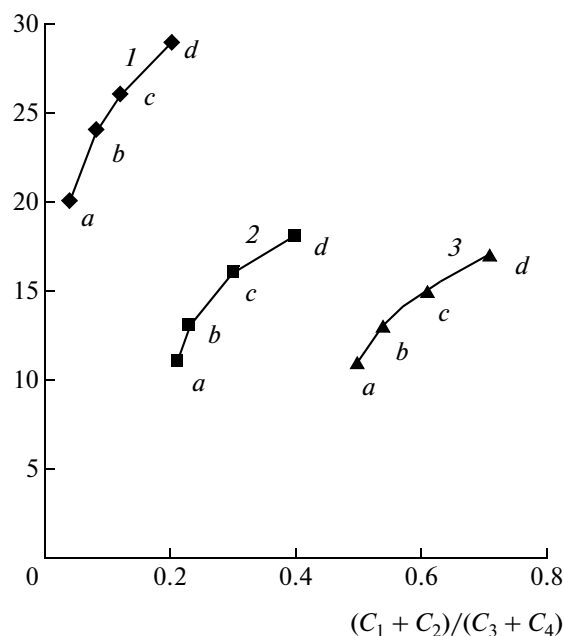
Yield of C_1 – C_4 , wt %

Fig. 2. Effect of the modification of the Pt–Re/ Al_2O_3 catalyst with zirconium on the composition of hydrocarbon gases formed upon the reforming of *n*-heptane at (a) 460, (b) 480, (c) 500, and (d) 520°C on the following samples: (1) Pt–Re/ Al_2O_3 , (2) (Pt–Re + 0.2% Zr)/ Al_2O_3 , and (3) (Pt–Re + 0.4% Zr)/ Al_2O_3 .

ide $AlOOH$, zirconium hydroxides are formed. These hydroxides form oxide phases under conditions of the subsequent calcination at a temperature higher than 500°C. Zirconium sulfates are more difficult to decompose; therefore, hydroxo sulfates can be immobilized on the surface of Al_2O_3 . The effects of supported platinum modification observed in these cases can be due to an increase in the metal–support interaction as a result of a change in the chemical composition of the support.

Table 2. Effect of the nature of the starting zirconium compound on the catalytic properties of the Pt–Re–Zr/ Al_2O_3 system

Characteristic	Chemical composition of the starting zirconium compound				
	Zr(OH) ₄	ZrO(Ac) ₂	ZrO(NO ₃) ₂	ZrOSO ₄	Zr(SO ₄) ₂
A_{av} (490°C), (g toluene) (g Cat) ^{−1} h ^{−1}	1.7	1.54	2.25	2.9	1.9
S	0.45	0.44	0.43	0.50	0.40
E_a , kJ/mol	195	177	180	148	210
k_d (at 520°C)	0.91	0.9	0.92	0.95	0.96
$k_{ef} = ASk_d$	0.69	0.60	0.83	1.38	0.72

Note: Reaction conditions: $P = 1.0$ MPa; $H_2/C_7 = 5$ (mol); $T = 460, 480, 500$, and 520°C.

Table 3. Effects of the modification of Pt/Al₂O₃ catalysts (from adsorption measurements)

Sample*	Degree of dispersion, %	Pt ^σ fraction, %
Pt/Al ₂ O ₃	70	30
Pt/Al ₂ O ₃	93	60
Pt–Zr/Al ₂ O ₃	90	80
Pt–Re/Al ₂ O ₃	70	90
Pt–Re–Zr/Al ₂ O ₃	100	90

* The Al₂O₃ support was prepared from mixed-precipitation aluminum hydroxide in the first sample or from continuous-precipitation aluminum hydroxide in the other samples.

The occurrence of modification effects was supported in a study of the dispersity and state of catalysts using oxygen chemisorption and oxygen–hydrogen titration. Table 3 summarizes the results of adsorption studies. They suggest that the procedure used for sample preparation in this work resulted in a higher dispersity of platinum (70–100%) than that in traditional Pt/γ-Al₂O₃ catalysts with the predominant fraction of the ionic species Pt^σ. From this point of view, the test catalysts can be considered as model systems based on ionic platinum species.

Figure 3 shows the temperature dependence of the adsorption of hydrogen on catalysts with different compositions. The amount of adsorbed hydrogen considerably increased with temperature; this fact suggests the activated character of adsorption. The isobars of hydrogen adsorption on platinum modified with zirconium are more gently sloping; this suggests a higher regularity of platinum sites.

The greatest adsorption of hydrogen was observed on platinum–rhenium catalysts; at the same time, these catalysts exhibited high activity in cracking reactions. Thus, a correlation between the presence of strongly bound hydrogen and the ability of the catalyst to form strong bonds with adsorbed hydrocarbons can be assumed, which led to an increase in the fraction of cracking in the total substrate conversion. On the contrary, a decrease in the activated adsorption of hydrogen on the catalysts promoted with zirconium, as well as the higher regularity of their active sites, facilitated an increase in the contribution of aromatization and isomerization processes, in which less strongly bound states participated.

To study the acid properties of the samples, we performed the IR-spectroscopic studies of the γ-Al₂O₃ support, the support modified with 0.25 wt % zirconium, and the (0.24%Pt + 0.25%Zr)/Al₂O₃ catalyst. Figure 4 shows the resulting IR spectra in the region of OH-group vibrations, and Table 4 specifies the assignment of particular absorption bands to support fragments [20]. The first three bands (3793, 3775, and 3760 cm^{−1}) correspond to terminal OH groups, which are bound to aluminum cations in different coordinations. The absorption band intensity at 3775 cm^{−1} (Al_sOH) qualitatively characterizes the defect structure of alumina [20]. The alumina sample modified with zirconium contained the greatest amount of these groups. After supporting platinum, the intensities of absorption bands due to all of the terminal OH groups, especially, bands at 3775 and 3793 cm^{−1}, considerably decreased. It is believed that platinum is immobilized at defect sites of the alumina surface modified with zirconium.

Figure 5 shows the IR spectra of CO adsorbed at a pressure of 10 Torr, when CO occupied all of the oxygen sites. A band in the region of 2155–2165 cm^{−1} (B₁) belongs to CO adsorbed at the weakly acidic OH

Table 4. Positions, nature, and intensities of absorption bands due to OH groups in the IR spectra

Absorption band position, cm ^{−1}	Assignment*	Relative intensities of absorption bands due to OH groups, arb. units/g		
		γ-Al ₂ O ₃	0.25% Zr/Al ₂ O ₃	(0.24% Pt + 0.25% Zr)/Al ₂ O ₃
3793	Al _t OH	3	4	0
3775	Al _p OH	8	19	0
3760	Al _o OH	9	12	5
3732	Al _o OH Al _o	14	21	15
3709	Al _o OH Al _p	8	17	13
3687	Al _o OH Al _t	9	20	16
3667	Al _p OH Al _t	10	22	17

* The subscripts at Al atoms correspond to the following coordination numbers with respect to oxygen: t, tetrahedron; p, pentahedron; o, octahedron.

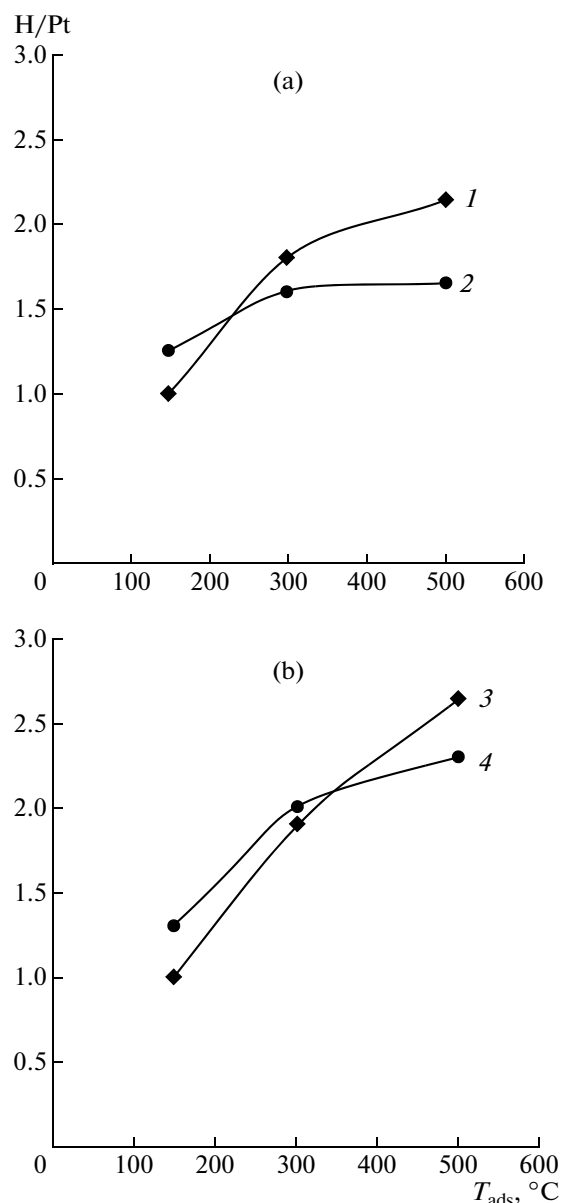


Fig. 3. Adsorption of hydrogen on the following samples: (1) Pt/Al₂O₃, (2) Pt-Zr/Al₂O₃, (3) Pt-Re/Al₂O₃, and (4) Pt-Re-Zr/Al₂O₃.

groups of alumina [19, 20]. The spectra exhibited absorption bands due to the Lewis sites of two types. The LASs of the first type belong to weak sites, which were most likely formed by aluminum cations on the low-index faces of alumina crystals. They are characterized by a band at 2175–2180 cm⁻¹ (L_1). The LASs of the second type (L_2) are characterized by a band at 2190–2195 cm⁻¹; they correspond to pentacoordinated aluminum atoms, which likely occur on defect faces. From Fig. 5, it follows that the concentration of L_2 sites considerably increased upon the modification of Al₂O₃ with zirconium.

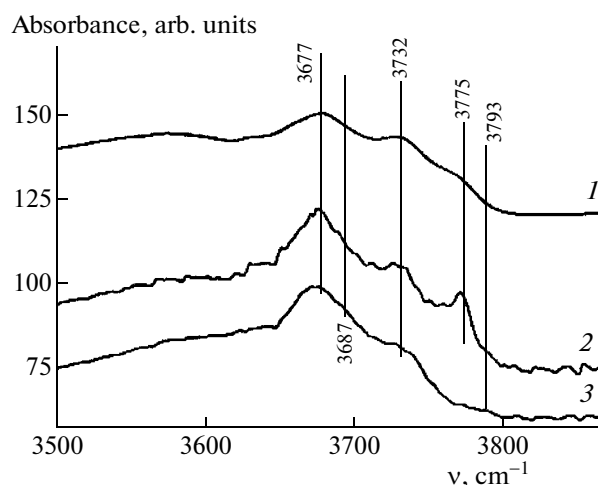


Fig. 4. IR spectra of samples measured at 77 K in the region of absorption bands due to OH groups: (1) γ -Al₂O₃, (2) 0.25% Zr/Al₂O₃, and (3) (0.24% Pt + 0.25% Zr)/Al₂O₃.

In the course of CO adsorption at a pressure of 0.1 Torr, the IR spectra exhibited very weak absorption bands in the region of 2228–2440 cm⁻¹. According to published data [19], this suggests the occurrence of the most acidic sites. Table 5 specifies the concentrations of these sites. The strongest LASs (absorption band at 2240 cm⁻¹) occurred in zirconium-containing samples; however, their concentration was low, and it did not exceed 1 $\mu\text{mol/g}$. For comparison, the concentration of platinum in the catalyst was 12.2 $\mu\text{mol/g}$.

The shape of IR spectra did not allow us to distinguish between the adsorption of CO at coordinatively unsaturated aluminum and zirconium ions. However, it is well known [19] that the LASs of zirconium are weaker than those of aluminum. Therefore, a considerable increase in the concentration of sites that correspond to an absorption band at 2176 cm⁻¹ (Fig. 5) can be caused by the introduction of zirconium into alumina.

Published data suggest that the stabilization of charged platinum species in alumina–platinum catalysts reduced with hydrogen is a consequence of the metal–support interaction [5, 6, 15, 16, 22]. The state of platinum reached in this case depends on the strength of this interaction, which, in turn, depends on the preparation procedure and the nature of the support. The results of this work indicate that the surface concentrations of terminal hydroxyl groups (especially, an absorption band at 3775 cm⁻¹; Al_sOH) and LASs (absorption bands at 2190–2195 cm⁻¹), which were attributed [19, 20] to coordinatively unsaturated aluminum cations, probably, localized on defect faces, considerably increased after the introduction of 0.2–0.4 wt % zirconium into the composition of alumina. We can hypothesize that the introduction of zirconium salts into AlOOH from an acetic acid solution (1–2%

Table 5. Positions of the absorption bands of CO and the concentrations of the strongest LASs in various samples

Positions of absorption bands due to CO corresponding to strong LASs, cm^{-1}	Concentration of strong LASs, $\mu\text{mol/g}$		
	$\gamma\text{-Al}_2\text{O}_3$	0.25% Zr/ Al_2O_3	(0.24% Pt + 0.25% Zr)/ Al_2O_3
2240	—	0.31	0.16
2236	0.2	—	—
2233–2230	1.4	5.15	4.0
2228–2223	2.5	—	—

on a stoichiometric basis) at the stage of plastification was accompanied by the formation of mixed basic salts of aluminum and zirconium on the surface of primary pseudoboehmite crystals. On the subsequent oxidative calcination, the oxidation of organic ions (the residual carbon content was lower than 0.1%) and the pseudoboehmite \rightarrow γ -alumina phase transition occurred simultaneously. As a result of these processes, defects were formed on the surface of the resulting alumina crystals. On the supporting of platinum, it was primarily immobilized at these defects. This is evident from IR-spectroscopic data on the surface hydroxyl coverage and the adsorption of CO. The effect of zirconium manifested itself in an increase in the dispersity and the fraction of charged platinum species (Table 3). A gently sloping shape of hydrogen adsorption isobars suggests an increase in the regularity of active sites, which facilitated the equalization of the strength of the resulting bonds with hydrogen and the decrease of the fraction of especially strongly bound hydrogen. It is likely that the higher regularity of platinum sites is a consequence of an increase in the regularity of the acidity of the alumina surface modified with zirconium.

This most clearly manifests itself in a decrease in the contribution of reactions that occur through strongly bound transition states (cracking and coke formation) and in an increase in the activity, selectivity, and rate constant of heptane dehydrocyclization. It is evident that the observed effects demonstrate that the metal–support interaction exerts an important effect on the state and catalytic properties of platinum.

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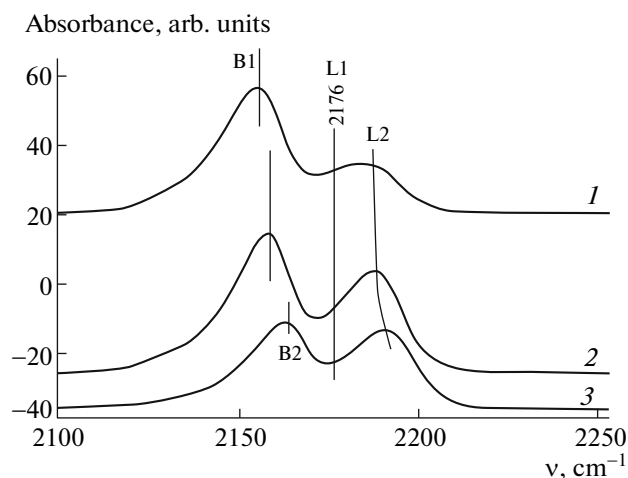


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