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CATALYSIS =

Modification of the Alumina-Supported Platinum Catalyst of Reforming

R. I. Kuz'mina, V. T. Liventsev, V. P. Sevost'yanov, and N. V. Dogadina

Chernyshevsky Saratov State University, Saratov, Russia Saratov Oil Refinery, Open Joint-Stock Company, Saratov, Russia

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Abstract—The catalytic activity of alumina-supported platinum catalysts modified with rare earth metal (samarium, europium, gadolinium, ytterbium, yttrium) complexes in C_6 hydrocarbon reforming was studied.

Production of aromatic hydrocarbons, in particular, benzene, which is a raw material for chemical industry, is an important direction of the catalytic reforming, since the production of polyamide, polyester, and other fibers and, in addition, some types of plastics and specialty rubbers is based on conversion of benzene and its nearest homologs.

Alumina-supported platinum catalysts, which were for many years the main catalysts of hydrocarbon aromatization, now give place to the catalytic systems with a low platinum content, containing other metals (iridium, rhenium, germanium, tin) as modifiers [1].

Modifying additives introduced into the platinum catalyst can affect the properties of both active metal itself and a support. With regard to bifunctionality of the alumina-supported platinum catalyst, whose platinum catalyzes hydrogenation and dehydrogenation, while alumina catalyzes paraffin isomerization and hydrocracking, we took rare-earth metals (REMs) differing in the dehydrogenation and dehydrocyclization power as modifying additives [2]. It was interesting to find how the initial REM compound affects the catalyst activity.

EXPERIMENTAL

The catalyst properties were studied with a flowtype laboratory device within $440-540^{\circ}$ C in a hydrogen atmosphere. *n*-Hexane was used as a feed in reforming.

To study the influence of REMs on the aluminasupported platinum catalyst and to develop a highperformance catalyst with a low platinum content, a series of catalysts containing 0.25 wt % platinum and 0.1-0.4 wt % samarium, europium, gadolinium, ytterbium, or yttrium were considered. The activity of the catalysts was evaluated by the content of benzene (aromatization) and C_1 - C_5 hydrocarbons (hydrocracking) in the catalyzate. We found that the catalytic activity of the modified catalysts decreases in the order Gd > Y > Eu > Sm > Yb (Table 1).

The catalysts that were more active in aromatization also showed the elevated selectivity. Taking this into account, we studied the properties of the gadolinium-containing catalyst in the *n*-hexane conversion in more detail and found that, in the presence of the catalyst with gadolinium additives (0.1-0.4 wt %), the yield of benzene is higher than in the case of the REM-free alumina-supported platinum catalyst (Figs. 1, 2). Although the Gd-modified alumina-supported platinum catalyst is characterized by the elevated activity in hydrocracking, the ratio of the benzene concentration to the total concentration of C_1-C_5 hydrocarbons $[C_6H_6]/\Sigma(C_1-C_5)$ on the gadoliniummodified alumina-supported platinum catalyst is also higher than on the unmodified alumina-supported platinum catalyst, which indicates higher selectivity of the former in the aromatization.

Table 1. Influence of REMs on catalytic properties of thealumina-supportedplatinumcatalystat500°C

REM	Composition of reaction product, wt %						
	$\Sigma C_1 - C_5$	iso-C ₆ H ₁₄	MCP*	C ₆ H ₆	$C_6H_6/\Sigma C_1-C_5$		
Sm Eu Yb Gd	10.1 12.2 9.8 22.0	20.1 20.3 17.7 28.7	17.5 19.9 21.6 8.1	5.5 10.6 3.6 30.4	0.5 0.9 0.4 1.4		
Y	20.0	28.1	10.1	15.2	0.7		

* Methylcyclopentane.



Fig. 1. Influence of the Gd content on the distribution of the products of *n*-hexane conversion on the modified alumina-supported platinum catalyst with the platinum content of 0.25 wt %. Temperature (°C): (1) 460, (2) 500, (3) 520, and (4) 540.

It should be noted that an increase in the Gd content to 0.25 wt % increases the aromatization activity of the catalyst. However, at a further increase in the Gd content, the benzene yield decreases (Fig. 1). The effect of the temperature on *n*-hexane conversion on the modified catalysts is shown in Fig. 3. As seen, the Gd content weakly affects the temperature dependence of the product yield. The benzene and Σ (C₁–C₅) content increases with temperature; at 520–540°C, the degree of aromatization substantially exceeds the degree of hydrocracking. The temperature dependence of the content of isohexane (*i*-C₆) and C₅ dehydrocylization (C₅-DHC) products has a maximum at 460– 520°C. The catalyst selectivity with respect to aromatization increases with temperature (Fig. 3).

To study the effect of Gd additives on the activity of the alumina-supported platinum catalyst, gadolinium was introduced into the catalyst with a gadolinium metanilate solution. A series of catalysts with the platinum content from 0.1 to 0.4 wt % and Pt : Gd ratio from 1:4 to 4:1 was prepared. As a whole,



Fig. 2. Temperature dependence of the content of the products of *n*-hexane conversion, *A*, on the Pt/Al₂O₃ catalyst. Platinum content 0.25 wt %; the same for Figs. 3 and 5. (1) Σ (C₁-C₅), (2) benzene, (3) isohexanes, (4) products of C₅-DHC, and [C₆H₆]/ Σ (C₁-C₅); the same for Fig. 3.



Fig. 3. Temperature dependence of the contents of the products of *n*-hexane conversion, A, on the alumina-supported platinum catalysts modified with gadolinium. Gadolinium content (wt %): (a) 0.1, (b) 0.15, (c) 0.25, and (d) 0.4.

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Cotolyct wit %	T, °C	Product composition, wt %					
Catalyst, wt %		$\Sigma C_1 - C_5$	iso-C ₆ H ₁₄	МСР	benzene	$C_{6}H_{6}/\Sigma C_{1}-C_{5}$	
0.1Pt + 0.1Gd	520	9.1	27.8	11.5	9.5	1.0	
0.4Pt + 0.4Gd	520	27.9	25.9	8.8	23.7	0.7	
0.25Pt + 0.25Gd	500	20.2	5.0	2.7	61.0	3.0	
	520	23.5	_	_	72.5	3.0	
	540	21.4	_	_	72.6	3.0	
0.25Pt + 0.1Gd	520	32.4	4.3	0.6	62.5	1.9	
0.25Pt + 0.5Gd	520	16.3	23.2	10.8	13.7	0.8	
0.25Pt + 0.05Gd	520	7.3	15.8	10.5	17.1	2.3	
0.4Pt + 0.1Gd	520	45.9	13.8	2.6	33.3	0.7	
0.1Pt + 0.4Gd	520	20.7	8.4	8.4	23.2	1.0	

Table 2. Conversion of n-hexane on the Gd-modified alumina-supported platinum catalysts

the Gd added increases the activity and selectivity of the catalyst in the *n*-hexane aromatization.

The effect of the Pt : Gd ratio (wt %) on the catalyst activity in various directions of *n*-hexane conversion (0.1 Pt : 0.4 Gd, 1 : 4; 0.25 Pt : 0.5 Gd, 1 : 2; 0.25 Pt : 0.25 Gd, 1 : 1; 0.4 Pt : 0.1 Gd, 4 : 1) is shown in Fig. 4. The benzene yield grows with in-



Fig. 4. Influence of the Pt : Gd ratio on the composition of the products of *n*-hexane conversion, *A*, at (a) 540 and (b) 500°C. Contact time 0.24 s. (1) Σ (C₁-C₅, (2) benzene, (3) isohexanes, and (4) products of C₅-DHC.

creasing Pt : Gd ratio to 1 : 1 at a slight increase in the yield of C_1-C_5 products (Fig. 4, curves 1, 2). The catalyst containing 0.25 wt % Pt and 0.25 wt % Gd showed the highest activity. The yield of the target product on this catalyst at 540°C and contact time of 0.6 s reaches 72.6 wt %. The selectivity in aromatization at 500–540°C is 3. At Pt : Gd > 1, the yield of hydrocracking products exceeds the yield of benzene. The decrease in the selectivity of the aromatization at increasing Pt : Gd ratio and a maximum in the benzene yield at 540°C show that the Pt : Gd ratio of 1 : 1 is optimal for the catalyst modification in the *n*-hexane conversion.

At the same Pt : Gd ratio, the content of the active components affects the catalyst activity. At the Pt : Gd ratio of 1 : 1, the aromatizing activity increases with increasing platinum and gadolinium content up to 0.25 wt %. Further increase in the Pt and Gd content is accompanied by a decrease in the catalyst activity. Thus, the catalyst sample containing 0.25 wt % Pt and 0.25 wt % Gd is the most active (Table 2).

The experimental data were treated with the Bassett–Habgood equation for first-order heterogeneous catalytic reactions [3]:

$$kK = \frac{F_0}{273Rm} \ln [1/(1 - x)],$$

where k is the rate constant (s⁻¹); K, adsorption equilibrium constant; F_0 , carrier gas flow rate recalculated to the normal conditions (ml s⁻¹); x, degree of conversion; and m, catalyst amount (g).

From the $\log(1/m)\ln[1/(1 - x)]-1/T$ dependence, we calculated E_{app} of *n*-hexane aromatization. The *n*-hexane aromatization on the industrial alumima-sup-

ported platinum catalyst proceeds mainly through the C_5 -DHC with the subsequent methylcyclopentane dehydroisomerization. The apparent activation energy of the *n*-hexane aromatization amounts to 134 kJ mol⁻¹. On the base-modified industrial alumina-supported platinum catalyst, when methylcyclopentane dehydroisomerization is suppressed because of blocking of acid centers, the *n*-hexane aromatization proceeds through the C_6 -DHC. In this case, the apparent activation energy of the *n*-hexane aromatization is equal to 164 kJ mol⁻¹ [4].

 $E_{\rm app}$ on a Gd-modified alumina-supported platinum catalyst is 163 kJ mol⁻¹, i.e., coincides with $E_{\rm app}$ of the *n*-hexane aromatization on base-modified aluminasupported platinum catalyst (Fig. 5). Hence, modifying Al₂O₃ with the Gd compounds blocks active centers responsible for isomerization in the stage of methylcyclopentane isomerizatrion, which causes aromatization through the C₆-DHC [5, 6].

Thus, modifying the alumina-supported platinum catalyst with REM (samarium, europium, gadolinium, ytterbium, yttrium) increases its aromatization activity in the *n*-hexane conversion. Among the REMs studied, gadolinium is the most active.

Modifying alumina-supported platinum catalyst with REM suppresses the acid function of the support, which is accompanied by a decrease in the contribution of the C₅-DHC reaction in favor of benzene formation by successive dehydrogenation. In the REM series, the dimensions of atom and ion decrease with increasing atomic number, which decreases the basicity of REM oxides. Although the chemical properties of all the lanthanides(III) are similar, they regularly change from La to Lu. Yttrium has an ionic radius intermediate between those of Dy and Ho, which causes its similarity with lanthanides. The basicity of gadolinium oxide is higher than that of ytterbium oxide, which is manifested in their different influence on the support acidity.

To confirm this suggestion, we studied the IR spectra of the catalyst modified with Gd and Yb, which occupy the first and the last place, respectively, in the order of the activity of the modified alumina-supported platinum catalysts in the *n*-hexane aromatization. After the interaction with pyridine, the bands at 1630, 1580, 1490, and 1440 cm⁻¹ appear in the IR spectrum of Al_2O_3 (Fig. 6). In accordance with the published data [7, 8], the bands at 1630 and 1490 cm⁻¹ belong to vibrations of pyridine molecule coordinated to Lewis acid centers of the alumina surface, while the bands at 1580 and 1440 cm⁻¹ correspond to physically adsorbed pyridine molecules.



Fig. 5. The $\log(1/m)\ln[1/(1 - x)]-1/T$ dependence for *n*-hexane aromatization on (1-4) Gd-modified alumina-supported platinum and (5) alumina-supported platinum catalysts. Gadolinium content (wt %): (1) 0.1, (2) 0.15, (3) 0.25, and (4) 0.4.



Fig. 6. IR spectra of (1, 2) Al₂O₃, (3, 4) Yb/Al₂O₃, and (5, 6) Gd/Al₂O₃. (*T*) Transmittance and (v) wave number. (1, 3, 5) Initial samples and (2, 4, 5) after pyridine adsorption.

Under the action of ytterbium as a modifying additive, the relative power of the active surface centers substantially changes. Although the bands at 1630 (Lewis acid centers) and 1440 cm⁻¹ (physically adsorbed pyridine) are present in the IR spectrum of the catalytic system with sorbed pyridine, their intensities are substantially lower than after pyridine adsorption on the initial aluminum oxide, suggesting a substantial decrease in the surface acidity due to modification with ytterbium. It follows from the

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IR spectrum that aluminum oxide modified with gadolinium contains almost no acid centers. Indeed, after slight evacuation, the bands of free and physically adsorbed pyridine completely disappear, bands characteristic for pyridinium ion are not observed, and the band at 1630 cm⁻¹ assigned to pyridine molecules coordinated to Lewis acid centers is very weak. Thus, these data show different influence of REMs on the support acid function, which is manifested in the different catalytic activity of the modified alumina-supported platinum catalysts.

The apparent activation energy of the *n*-hexane conversion on the Gd-modified alumina-supported platinum catalyst, coinciding with E_{app} on the base-modified alumina-supported platinum catalyst, which is characterized by consecutive mechanism of the *n*-paraffin aromatization, confirms the REM influence on the acid properties of the support.

CONCLUSIONS

(1) An order of the activity and selectivity of modifying REMs in the *n*-hexane aromatization was determined: in the series Gd > Y > Eu > Sm > Yb; the catalyst modified with gadolinium is the most active.

(2) The optimal composition of the Gd-modified alumina-supported platinum catalytic system was found for the *n*-hexane aromatization.

(3) On the basis of the study of physicochemical and catalytic properties, the mechanism of the influence of the modifying additives on the activity and selectivity of the catalysts studied was suggested. Modification of the alumina-supported catalyst with rare-earth metals suppresses the acid centers of the support responsible for isomerization of hydrocarbons and, as a result, aromatization of *n*-paraffins proceeds through their successive dehydrogenation.

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