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Investigation of palladium catalysts in n-hexane isomerization reaction

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Abstract

Pd/SO₄²⁻/ZrO₂/Al₂O₃ catalysts are prepared and investigated in reaction of isomerization of N-hexane in the work. For comparison Pt/SO₄²⁻/ZrO₂/Al₂O₃ catalysts are investigated. It is established that in the field of low temperatures (140 °C) the catalyst on the basis of palladium shows high rates comparable to the Pt-containing catalyst. At more high temperatures yielding of isomers for Pd/SO₄²⁻/ZrO₂/Al₂O₃ catalyst are lower, than for Pt/SO₄²⁻/ZrO₂/Al₂O₃. However, isomerization depth (the maintenance of a 2, 2-dimethylbutan in mix of C₆ isomers) for the palladic catalyst in all studied range of temperatures exceeds for 6-10% a similar indicator for the platinum catalyst. For clarification of the role of condition of palladium the catalysts Pd/Al₂O₃, Pd/SiO₂ were prepared and investigated. It was established that the best indicators are reached on the aluminum oxide systems in which palladium is in the oxidized state.

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1. Introduction

Today an actual task is the search of effective catalysts of the process of isomerization for production of the component of gasolines of ecological classes 4 and 5. Much attention is paid to catalysts on the basis of sulfate dioxide of zirconium which combine high activity, poisons resistance and work in thermodynamic favorable interval of temperatures 140-180 °C. Traditionally, platinum is used as an active component in catalysts of isomerization of alkanes, however palladic catalysts also possess high isomerizing ability [1, 2]. At the moment palladic the

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sulphate zirconia of catalysts is paid much less attention to research in literature than to studying platinum systems on the basis of $\text{SO}_4^{2-}/\text{ZrO}_2$.

The research of activity of palladic catalysts on the basis of sulfate dioxide of zirconium in reaction of isomerization of N-geksana was the purpose of this work. The researches were conducted on $\text{Pd}/\text{SO}_4^{2-}/\text{ZrO}_2/\text{Al}_2\text{O}_3$ catalysts (Pd/SZA is designated) and $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2/\text{Al}_2\text{O}_3$ (Pt/SZA is designated). Oxide aluminum was added to $\text{SO}_4^{2-}/\text{ZrO}_2$ to facilitate molding and to increase durability of granules of the catalyst, and also to stabilize isomerizing active tetragonal modification of crystal lattice of ZrO_2 [3, 4]. Activity of palladic catalysts was compared to activity of catalysts on the basis of Pt. Besides we used the approach based on the research of difficult catalytic system by comparison with simpler and well characterized catalysts for studying of the role of the condition of palladium in Pd/SZA. We used the palladium applied on oxides of silicon and aluminum as catalysts.

2. Experimental

2.1. Preparation of catalysts

SZA ($\text{SO}_4^{2-}/\text{ZrO}_2/\text{Al}_2\text{O}_3$). Dioxide of zirconium was prepared with sedimentation of hydrate of dioxide of zirconium ammonia from water solution of salt $\text{Zr}(\text{SO}_4)_2$. The received deposit was washed out, dried at 120 °C and then processed with 12% solution of sulfuric acid. Aluminum hydroxide in the amount of 10% was added to the dried material. Further the received weight was formed in extrudate with the diameter of 1.5 mm. In the beginning extrudate was dried at the room temperature for 3 hours, then for 2 hours at 120 °C, further it was calcinated in the muffle furnace at 650 °C. Textural characteristics of SZA: $S_{\text{ud}}=114$ of sq.m/g , $\Sigma V_{\text{por.}}=0,34 \text{ m}^3/\text{g}$.

Pd/SZA, Pt/SZA. Sulfate zirconium dioxide prepared as it is described above, was vacuumized for removal of air from the pores, then it was impregnated with the acidified water PdCl_2 and H_2PtCl_6 solution, respectively. Then the samples were dried at 120 °C and calcinated in the running of the drained air at 450 °C.

$\text{Pd}/\text{Al}_2\text{O}_3$, Pd/SiO_2 . $\text{Pd}/\text{Al}_2\text{O}_3$, Pd/SiO_2 . For preparation of $\text{Pd}/\text{Al}_2\text{O}_3$ powder of hydroxide of Pural SB-1 aluminum (SASOL) was used. At the peptization stage water solution of oxalic acid was injected into the powder (7% Mas.). The received weight was also formed in extrudate (mm d=1.5), Extrudate was dried for 3 hours at the room temperature and at 120 °C – for 2 hours. Calcinating of the supplier was carried out in the running of the drained air at 520 °C. Textural characteristics of Al_2O_3 – $S_{\text{BET}}=250 \text{ m}^2/\text{g}$, $\Sigma V_{\text{por.}} = 0,46 \text{ m}^3/\text{g}$; SiO_2 – $S_{\text{BET}} = 340 \text{ m}^2/\text{g}$, $\Sigma V_{\text{nop}} = 1,0 \text{ cm}^3/\text{g}$.

The received suppliers before applying palladium was vacuumized for removal of air from pores, and then there was impregnation with palladium containing solution. As initial compound of palladium for catalysts $\text{Pd}/\text{Al}_2\text{O}_3$, Pd/SiO_2 the acidified water PdCl_2 solution was used, and $\text{Pd}(\text{CH}_3\text{COO})_2$ solution was applied in acetone to $\text{PdAc}/\text{Al}_2\text{O}_3$. After impregnation the catalysts were dried at 120°C and calcinated in the running of the drained air at 450°C. The Pd/SiO_2 catalyst was only dried.

The nomenclature, the prepared catalysts, and also their processings are given in Table 1.

Table 1. Catalyst compositions and pretreatments.

Catalyst	Metal predecessor	C_{Pd} , % mas.	$T_{\text{прок}}$, °C	$T_{\text{восст}}$, °C
Pd/SZA	PdCl_2	0.6	450	250
Pt/SZA	PdCl_2	0.4	450	250
Pd/SiO_2	PdCl_2	0.3	-	250
$\text{Pd}/\text{Al}_2\text{O}_3$	PdCl_2	0.4	450	500
$\text{Pd}_{\text{Ac}}/\text{Al}_2\text{O}_3$	$\text{Pd}(\text{CH}_3\text{COO})_2$	0.6	450	500

2.2. Techniques of experiments

Research of porous structure was conducted on isotherms of adsorption of N_2 at 77 K on the Sorptomatic device. At calculation of a specific surface it was accepted that value of the molecular airfield of nitrogen in the filled monolayer makes $0,162\text{nm}^2$. The total volume of pores determined by the size of adsorption of nitrogen at 77 K and $P/P_s = 0.996$. The molar volume of liquid nitrogen was accepted as $34.68\text{ cm}^3/\text{mol}$.

The adsorptive researches for the assessment of dispersion, amounts of the adsorbed oxygen and hydrogen conditions of superficial atoms of platinum were carried out by means of a technique of oxygen-hydrogen (O_2-H_2) titration and adsorption of oxygen [5].

The isomerization of N-geksana was investigated on flowing installation with the isothermal tubular reactor with the stationary layer of the catalyst in the range of temperatures of 140-500 °C with the pressure of 1.5 MPa, the volume speed of giving of liquid raw materials of 2 h^{-1} and molar ratio $H_2/n-C_6 = 3/1$. Raw materials is the N-geksan of the "hch" brand drained on the molecular sieve of NaX. Products of reaction were analyzed on-line by means of the "Colour-800" chromatograph with the flaming=ionized detector on the capillary column "Petrocol DH 50.2".

3. Results and discussion

3.1. Hexane isomerization over Pd/SZA and Pt/SZA

In Fig. 1a the exit of isomers of geksan on Pd/SZA and Pt/SZA catalysts is presented. It is visible that at the temperature of 140°C , exits of isomers of N-geksana for platinum and palladic catalysts are close and reach 84-87%. The exit of isomers on both catalysts decreases at reaction temperature increase. Decrease in the exit of isomers from temperature for the palladic catalyst is more considerable.

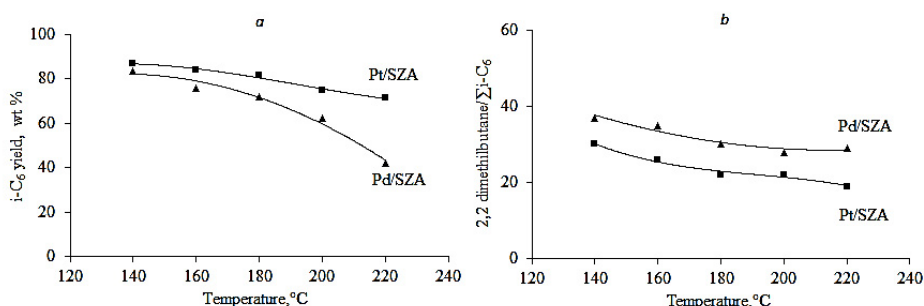


Fig. 1. An exit of isomers of a geksan (a) and depth of an isomerization (b) on Pd/SZA and Pt/SZA catalysts depending on the temperature. Conditions of catalytic tests: $P=15\text{ atm}$, $H_2/n-C_6=3\text{ mol/mol}$, $OSPS=2\text{ h}^{-1}$.

However on the depth of isomerization (Fig. 1b) characterizing the maintenance of a 2,2-dimethylbutane in mixes of C₆ isomers, activity for the Pd/SZA catalyst on all studied range of temperatures, exceeds the activity of Pt/SZA approximately on 6-10%. Isomerization depth is an important indicator which reflects the share of a high-octane component 2,2-dimethylbutane (IOCh=93) in isomerizate and in many respects defines its octane characteristics.

3.2. Research of the condition of palladium in isomerization catalysts

There are different opinions on the condition of palladium in the sulfate zirconia systems in literature. According to authors [6] palladium poorly interacts with the supplier on the surface of zirconium dioxide which isn't modified by sulfate, and, like the platinum applied on SiO_2 , palladium is on the surface in nulvalent state. Modifying of the surface ZrO_2 promotes strengthening of interaction of metal supplier, on the surface Pd^+ particles, and also Pd^0 , by $Pd^{\delta+}$ are mainly observed. There is also other point of view – in [2] it is reported about mainly metal condition of Pd in catalysts on the basis of sulfate dioxide of zirconium.

3.2.1. O_2 - H_2 - titration and O_2 -chemisorbtion

Sizes of absorption of oxygen from data (O_2 -Nads) - titration and O_2 - chemisorption which were received for Pd/SiO₂, Pd/Al₂O₃, and also for the Pd/SZA catalyst are shown in Table 2.

Table 2. Adsorption characteristics of Pd in the catalysts.

Catalyst	Oxygen consumption, O atoms/Pd _t atoms		OT/OC	Dispersion, Pd _s /Pd _t ,%	Amount of adsorbed hydrogen, H atom/Pd _s atom	
	OT	OC				
I	Pd/SiO ₂	0.55	0.3	1.83	0.37	1.35
	Pd _{Ac} /Al ₂ O ₃	0.40	0.27	1.48	0.27	0.96
II	Pd/Al ₂ O ₃	0.51	0.17	3.0	0.34	2.0
	Pd/SZA	1.65	0.21	7.9	>1	2.6

OT – the amount of oxygen spent for O_2 - H_2 - titration; OC – absorption of oxygen at a chemisorption; Pd_t – total number of atoms of palladium; Pd_s – number of superficial atoms of palladium

The ratio of OT/OC characterizes metal oxidation level in the applied catalysts [5]. The value of this indicator equal to 1,83-1,48 for Pd/SiO₂ and Pd_{Ac}/Al₂O₃ catalysts (we will allocate them in group I), is characteristic for the zero oxidation level of metal. The calculated size of specific absorption of hydrogen by superficial atoms of palladium $N/P_{ds}=0,96-1,35$ also indicates the possibility of reference of palladium to the metal in these catalysts. For catalysts of group II (Pd/Al₂O₃, Pd/SZA) the ratio OT/OC = 3,0-7,9 that is characteristic for atoms of palladium in the oxidized state, and oxidation level in Pd/SZA is significantly higher, than in Pd/Al₂O₃. The size of specific absorption of N/P_{ds} hydrogen = 2-2,6 also testifies in favor of the oxidized condition of palladium. It was shown similarly for platinum sulfate zirconia catalysts [7] that Pt in these systems are in the oxidized state in atoms that it was later confirmed with the IK method (CO_{ads}) [8].

3.2.2. An isomerization of *N*-geksana on Pd/SiO₂, Pd/Al₂O₃

The exit of isomers of a geksan on palladic catalysts depending on temperature is presented in Fig. As we see, catalysts Pd/SiO₂, Pd_{Ac}/Al₂O₃ in which palladium is in the metal state show the activity in the field of high temperatures of 440-500 °C. The maximum exit of isomers for Pd_{Ac}/Al₂O₃ and Pd/SiO₂ mass made 45 and 25%. at 480 and 450 °C respectively.

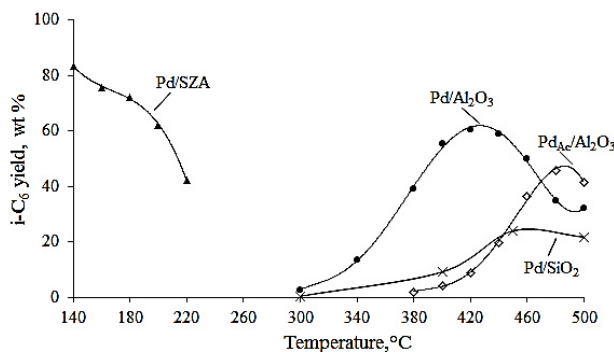


Fig. 2. An exit of isomers of geksan on catalysts Pd/SiO₂, PdAc/Al₂O₃, Pd/Al₂O₃, Pd/SZA. Reaction conditions: P = 1.5 MPa, OSPS = 2 h-1, H₂/H-C₆ = 3/1.

The oxidized palladium in the Pd/Al₂O₃ catalyst displaces reaction course area approximately on 80°C. The maximum exit of isomers for this catalyst made 60% mass at 420 °C. Oxidation level, characteristic for palladium in the Pd/SZA catalyst promotes the course of reaction of isomerization of N-geksana in low-temperature area.

4. Conclusion

Palladic sulfate zirconia catalysts effectively catalyze isomerization of N-geksana in the field of low temperatures (140-220 °C). The activity of these systems expressed by isomerization depth exceeds for 6-10% activity of platinum sulfate zirconia catalysts. Thus, palladium containing catalysts on the basis of sulfate zirconia dioxide zirconium are perspective catalysts of isomerization. Considering significantly smaller cost of Pd, these catalysts can be considered as an alternative to catalysts on the basis of Pt.

Catalysts with metal palladium are active in reaction of isomerization of N-geksana in high-temperature area. The oxidized condition of metal in palladic catalysts promotes the course of reaction in the field of low temperatures.

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