2. The framework iron in the ferrisilicate determines the catalytic properties of its hydrogen and modified forms in transformations of n-hexane; out-of-lattice iron has no significant effect on the properties of these ferrisilicates.

3. The selectivity of transformations of n-hexane on Pt(Pd)-elemental silicates is a function of the gas medium: skeletal isomerization predominates in  $H_2$ , and aromatization and cracking predominate in the absence of a carrier gas or in Ar.

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STUDY OF THE CATALYTIC ACTIVITY OF METAL COMPLEXES FIXED ON SOLID SUPPORTS. 7. SYNTHESIS OF Pd—Sn COMPLEXES ATTACHED TO MACROPOROUS ANION EXCHANGERS AND STUDY OF THEIR ACTIVITY IN THE HYDROGENATION OF 1-HEXENE

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UDC 541.49:541.128:542.941.7:
547:313.6

Recently heterogenization has been used for production of new metal complex catalysts. Polymeric materials [1], including ion exchange resins [2], have served as supports. Macroporous anion exchangers which have a highly developed surface are especially interesting. Heterogenization of palladium chloride on anion exchangers produced active and selective hydrogenation catalysts for unsaturated compounds [3]. Homogeneous complexes of platinum group metals with halostannyl ligands are active and selective in transformations of many hydrocarbons. Ru and Os complexes selectively catalyze hydrogenation; Rh and Ir complexes, isomerization of olefins [4].

This work develops a synthetic method for palladium complexes with trichlorostannyl ligands which are fixed on macroporous anion exchangers and studies their catalytic properties in the conversion of 1-hexene.

## EXPERIMENTAL

Anion exchangers which were synthesized based on macroporous copolymers of styrene and divinylbenzene containing various functional groups (Table 1) were used as supports. The

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TABLE 1. Characteristics of Anion Exchangers

Anion exchanger	Quantity of linker, %	Functional group	$s, m^2/g$	Pore volume, cm <sup>3</sup> /g
AV -17-2 P	2	$-CH_2 - \overset{+}{N}(CH_3)_3$	15	0,25
ANV221	8	$-CH_2 - \dot{N}(CH_3)_3$	30	0,35
AN -221	12	$-CH_2-NH-CH_2-CH_2-NH_2-CH_2-NH-CH_2-CH_2-NH_2$	50	0,60

TABLE 2. Conversion of 1-Hexene by Pd-Sn Compounds Fixed on Macroporous Anion Exchangers ( $PH_2 = 5$  MPa, 323 K, 4 h, ethanol solvent, 0.17 g catalyst ( $2 \cdot 10^{-5}$  g at Pd/g),  $10^{-3}$  mole 1-hexene, 2 M HC1)

	Anion	Fixed compound	Content in catalysate, mass%		
Catalyst	exchanger		1-hexene	2-hexene	Hexane
(I) <b>*</b>	AN-17-2P	(A)	37,9	49,1	13,0
(II) (II) *		(B)	36,6 91,1	32,5 6,4	1,9 2,5
(III) (IV) (IV) *	<b>ANV</b> -221	(A) (B)	44,3 62,6 71,9	42,6 35,4 17,1	13.1 2,0 11,0
(V) (V) *	<b>AN-22</b> 1	(A) <u></u>	$65.5 \\ 42.6$	23,5 39,7	11,0 17.7
(VI) (VI) *		(B)	57,4 62,1	33,1 24,9	9,5 13,0
(VII) *	·	(A.)	25,0 19,9	70,3 72,8	3,7 7,3

\*Experiments without HC1.

cluster  $[Pd_4(SnCl_2)_2(SnCl_3)_8]^{5-}$  (A) was prepared according to [5]. To 10 ml of a 0.01 M solution of PdCl\_2 (10<sup>-4</sup> mole Pd) in 3 M HCl with argon flow were added 0.12 g (5·10<sup>-4</sup> mole) SnCl\_2·2H\_2O. The mixture was stored for 3 h. To this solution was added 2 g anion exchanger in the Cl-form. This mixture was stored for 48 h under argon. The solution was poured off, the anion exchanger was washed with 1 M HCl and alcohol and dried in air (Table 2, catalysts (I), (III), and (V)). The complex  $[Pd(SnCl_3)_4]^{2-}$  (B), fixed on the anion exchangers in the Cl-form (catalysts (II), (IV), and (VI)), was prepared according to [6]. Complex (B) fixed on anion exchanger AN-221 in the OH-form was prepared as follows. To 2 g anion exchanger were added 6 ml of a 0.01 M solution of PdCl\_2 acidified to pH 2 with HCl. Upon completion of sorption the solution was poured off, the anion exchanger was washed with water, and the aqueous solution of SnCl\_2·2H\_2O (0.1 g) was added. The anion exchanger containing the complex was washed with water and alcohol and dried in air.

The structure of the fixed compounds was studied using both Mössbauer (<sup>119</sup>Sn) spectroscopy on a NGRS-4 instrument with an AI-4096 analytical pulse analyzer at liquid nitrogen temperature and long wave IR spectroscopy using a double beam Hitachi FIS-3 spectrometer. The content of palladium in the solutions was determined by atomic absorption on the AAS-1 instrument.

The catalytic properties of the compounds were studied in the conversion of 1-hexene in alcohol solution. The experiments were done in a rotating autoclave at  $P_{H_2} = 5$  MPa at 323 K, also in a catalytic "flask" at  $P_{H_2} = 0.1$  MPa at 273-323 K. The activity of the catalysts was evaluated in hydrogenation (A<sub>h</sub>) and isomerization (A<sub>is</sub>) of 1-hexene. Reagent 1-hexene and 96% ethanol were used.

The catalysate composition was determined by GLC using a 6 m  $\times$  3 cm column and a stationary phase of  $\beta$ , $\beta$ '-oxydipropionitrile (17%) on chromosorb P at 298 K.

## DISCUSSION

Attachment of Pd-Sn complexes to an anion exchanger can be accomplished by various methods depending on the nature and state of the functional group (C1- or OH-form). Ionic reaction [7] is characteristic for supported complex compounds on the salt forms of all types of anion

exchangers. Fixation of Pd-Sn compounds on the highly basic anion exchanger AV-17-2P occurs only by ion exchange. The complex anion occupies the position of the counter ions of the ionic groups of the support.

 $\begin{array}{c} = -CH_2 - \ddot{N}(CH_3)_3 Cl^- \\ + [Pd(SnCl_3)_4]^{2-} \rightarrow \end{array} \xrightarrow{=} \begin{array}{c} = -CH_2 - \ddot{N}(CH_3)_3 \\ = -CH_2 - \ddot{N}(CH_3)_3 Cl^- \end{array} \xrightarrow{=} \begin{array}{c} = -CH_2 - \ddot{N}(CH_3)_3 \\ = -CH_2 - \ddot{N}(CH_3)_3 \end{array}$ 

Fixation of Pd-Sn compounds on the moderately basic anion exchanger ANV-221 can occur both by ion exchange and partially by coordination of the metal ion to the nitrogen atom of the amino group.

Binding of Pd-Sn compounds to the weakly basic AN-221 in the OH-form is done mainly through coordination of the palladium to nitrogen atoms of the amino group.



Two types of Pd-Sn compounds, clusters (A) and complexes (B), were attached to macroporous anion exchangers in the Cl-form. IR spectra of the first type of compounds (catalysts (I), (III), and (V)) showed two broad absorption bands due to v(Sn-Cl) near 290 and 315 cm<sup>-1</sup>, which indicate the presence of two types of chlorostannyl ligands which are specific to cluster compounds [5]. Mössbauer (<sup>119</sup>Sn) spectra appeared as a superposition of two doublets with isomer shifts  $\delta$  of 1.87 and 2.10 mm/sec and a quadrupole splitting  $\Delta$  of 1.53 and 2.01 mm/sec, respectively. The Mössbauer spectral parameters of (A) correspond to [5].

The values of the isomer shifts in the Mössbauer spectra ( $^{119}$ Sn), observed at 1.70-2.20 mm/sec and v(Sn-Cl) between 330-310 cm<sup>-1</sup> indicate coordination of Sn(II) to Pd in the supported (B) complexes. These spectral characteristics are identical to those found earlier for the isolated complex [4].

Thus, the structures of the fixed Pd-Sn compounds are close to the structures of their homogeneous analogs according to the data obtained.

Study of the hydrogenation properties of (I) toward 1-hexene showed that reaction in acidified ethanol (T = 323 K,  $P_{H_2}$  = 0.1 MPa) for the first 3 h occurs predominantly by shifting of the double bond with formation of up to 45% 2-hexene. Later, A<sub>h</sub> increases and A<sub>is</sub> decreases (Fig. 1). The degree of conversion in experiments at elevated pressure ( $P_{H_2}$  = 5 MPa) with (I) after 4 h reaches 62% and A<sub>is</sub> exceeds A<sub>h</sub> by  $\sim$ 4 times.

Carrying out the reaction in neutral media gives a different picture. In this case, the hydrogenation reaction dominates at  $PH_2 = 5$  MPa and use of a larger ( $\sim 2.5$  times) quantity of catalyst increases the degree of reduction of 1 hexene to 96%.

Catalyst (II) becomes active only at high  $H_2$  pressure. It accelerates primarily the double bond isomerization reaction (Table 2). The degree of double bond isomerization in 1-hexene is 97% after 4 h.

Apparently, the specificity of catalyst action is related to the state of palladium in the Pd-Sn compounds. In agreement with [5], the oxidation state of palladium in the (A) cluster is near +1 (electron binding energy  $E_{bi} Pd3d_{5/2} = 336.2 \text{ eV}$ ) and in the (B) complex is +2 (Ebi = 337.3 eV). It can be assumed that this difference in the metal oxidation state is preserved in the supported compounds.

Thus, the Pd-Sn compounds which are supported on the Cl-form of anion exchangers of various types (ionic bonding character) have relatively low catalytic activity and produce hydrogenation and isomerization of the olefin only at elevated  $H_2$  pressure. In contrast to this, a highly active catalyst is produced upon supporting the complex on weakly basic AN-221 in the deprotonated state (OH-form). The time for half conversion of 1-hexene was 10 min upon carrying out the reaction under mild conditions (292 K, 0.1 MPa). The catalysate at this moment contained 35% 2-hexene and ~15% n-hexane (Fig. 1). Thus, the activity of this



Fig. 1. Conversion of 1-hexene at 20°C and  $PH_2 = 0.1$  MPa on catalyst (I) (a), and complex (B) fixed on AN-221 in the OH-form (b). 1) 1-hexene; 2) trans-2-hexene; 3) cis-2-hexene; and 4) n-hexane.

catalyst is more than an order of magnitude higher than for the complex which is supported on this same anion exchanger in the Cl-form. This is probably explained by a different reaction of the complex with the functional groups of the resin. Weakly basic anion exchangers (including AN-221) are known to exhibit their complex-forming properties more fully when they are in the coordinatively active OH-form [7].

We note that the supported Pd-Sn compounds are stably held on the surface of the exchangers. Palladium is not observed in the catalysate after the reaction. The homogeneous complex (B) is decomposed in  $H_2$ . In contrast to the palladium chloride complexes which are fixed on the anion exchangers [3, 4], all studies of the Pd-Sn catalysts do not require preliminary activation by sodium borohydride. Apparently, the presence of trichlorostannyl ligands aids the formation of hydride forms which are active in the conversion of olefins [8].

It follows from these results that heterogenization of Pd-Sn compounds, in contrast to the homogeneous analogs, produces high catalytic activity and elevated stability in reducing media.

#### CONCLUSIONS

1. New catalysts, Pd-Sn compounds, were synthesized and fixed to macroporous anion exchangers. They are active in hydrogenation and isomerization reactions of 1-hexene.

2. The catalytic properties of the Pd-Sn systems depends on the structure of the fixed compound (cluster, complex), the nature and state of the exchanger functional groups (Cl- or OH-form), and the reaction conditions (pH,  $PH_2$ ).

3. The cluster  $[Pd_4(SnCl_2)_2(SnCl_3)_8]^{5-}$  on the highly basic anion exchanger AV-17-2P (Cl-form) catalyzes mainly the hydrogenation reaction, while the complex  $[Pd(SnCl_3)_4]^{2-}$  catalyzes the isomerization reaction.

4. The complex  $[Pd(SnCl_3)_4]^{2-}$ , fixed to the weakly basic anion exchanger AN-221 (OH-form), is active in the isomerization and hydrogenation of 1-hexene under mild conditions.

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