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CATALYTIC PROPERTIES OF SUPERHIGH-SILICA ZEOLITES IN

# CONVERSIONS OF CERTAIN HYDROCARBONS

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One of the basic trends in the synthesis of zeolites is the development of crystalline aluminosilicates with higher and higher silica contents [1].

Superhigh-silica zeolites of the ZSM type that have been developed in other countries, as well as the TsVK and Ul'trasil that are manufactured in the USSR, are classed as narrow-pore zeolites with  $SiO_2/Al_2O_3$  ratios up to 200 or even higher; these materials, despite the small amounts of aluminum and the consequent small amounts of protons and cations, are high in acidity and hydrophobicity (they interact weakly with polar molecules) and are highly resistant to acid media [2]. Even with such obvious advantages, the catalytic properties of these zeolites have been investigated very little.

Here we are reporting on a study of the catalytic activity of type TsVK zeolites with various  $SiO_2/Al_2O_3$  ratios in reactions of isomerization of  $C_4$ - $C_6$  n-paraffins, hydrogenation and hydroisomerization of benzene, and the side reactions of hydrocracking and disproportion-ation. The studies reported previously in [3] were confined to isomerization and hydrocracking of n-decane on Pt/ZSM catalyst at atmospheric pressure.

## EXPERIMENTAL

The catalysts were prepared from these different zeolites: TsVK-1 with  $SiO_2/Al_2O_3 = 83$ , synthesized with the participation of an organic cation; TsVK-2 with  $SiO_2/Al_2O_3 = 33.3$ ; and TsVK-3 with  $SiO_2/Al_2O_3 = 47$ ; the last two of these catalysts were synthesized without an organic cation. The hydrogen forms of the zeolites were obtained by ion exchange with an NH<sub>4</sub>Cl solution with subsequent calcination at 600°C. Pd-containing catalysts were prepared from HTsVK\* by impregnation with an H<sub>2</sub>PdCl<sub>4</sub> solution and by ion exchange with a Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> solution. The hydrocarbons used in this reaction were n-butane, n-pentane, n-hexane, and benzene, grade "ch." [pure].

The experiments were performed in a single-pass flow reactor with a catalyst charge of 7.5 g. Before use in the experiments, the catalysts were pretreated as follows: The H forms of the zeolite were calcined at 520°C in a stream of air; the Pd-containing catalysts were calcined at 380°C and then reduced by  $H_2$  at this same temperature. The catalytic properties of the zeolites were investigated over a temperature range of 250-380°C at 30 atm and a hydro-carbon feedstock space velocity of 1 h<sup>-1</sup>.

The products from these runs were analyzed in an LKhM-8M chromatograph with a column containing Celite 545 with 18% triethylene glycol dibutyrate.

### DISCUSSION OF RESULTS

In order to determine the acid function of the catalysts, i.e., the ratio between their isomerizing and hydrocracking (or cracking) activities, the HTsVK and Pd/HTsVK catalysts were investigated in the reaction of n-pentane isomerization (Table 1). It will be noted that the H forms of the zeolite give high levels of n-pentane conversion, for example, 55% on the HTsVK-2 at 300°C. A common feature of the HTsVK catalysts is their high hydrocracking activity and low isomerizing activity; another feature is the occurrence of disproportionation to

\*HTsVK is the hydrogen form of the high-silica zeolite.

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TABLE 1. Conversion of n-Pentane on HTsVK Catalysts (30 atm,  $P_{H_2}/P_{C_5H_{1,2}} = 3.2$ , V = 1 h<sup>-1</sup>)

	T., °C	Conversion, %	Product yields, %		
Catalyst			<i>i</i> -C <sub>5</sub>	C <sub>1</sub> —C <sub>4</sub>	$\Sigma \mathrm{C}_{\vartheta}$
HTsVK-1, SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =83 HTsVK-2, SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =33,3 HTsVK-3, SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =47	250 250 300 250 300	37,2 42,7 55,0 13,8 40,7	10,0 9,0 9,9 4,2 8,3	21,927,041,47,328,4	$ \begin{array}{c} 6,3\\ 6,7\\ 3,7\\ 2.3\\ 4,0 \end{array} $

TABLE 2. Conversion of n-Pentane on 0.5% Pd/HtsVK Catalysts (30 atm,  $P_{H_2}/P_{C_5H_{12}} = 3.2$ , V = h<sup>-1</sup>)\*

Number in series	Catalyst	т., °С	Product Yields, %			
			<i>i</i> -C <sub>5</sub>	C <sub>1</sub> —C <sub>4</sub>	$\Sigma C_6$	
1	0.5% Pd/HTsVK-1,	330 340	56,6 56 0	2,8 6,5	1,3 1.4	
2	0.5% Pd/HTsVK-1, exchange	330 340	59,5 57,9	1,4 4,9	0,9 1,1	
3	1.3% Pd/HTsVK-1, impregnation	$330 \\ 340$	57,1 56,7	<b>1,8</b> 4,9	1,3 0,8	
4	0.5% Pd/HTsVK-2, impregnation	$330 \\ 340$	$56,3 \\ 52,7$	9,2 13,8	1,0 1,8	
5	0.5% Pd/HTsVK-2,	310	60,0	3,9	0,9	
6	exchange 0.5% Pd/HTsVK-2† impregnation	290 290 ‡	54,2 54,3	6,2 6,3	1,1 1,5	
7	0.5% Pd/HTsVK-2†	290	38,0	5,2	1,3	
8	exchange 0.5% Pd/HTsVK-3,	$\frac{310}{330}$	$^{43,4}_{33,5}$	17,0 3,0	2,7	
	impregnation	340 350	$40,3 \\ 46,7$	5,1 8,7	· 1,1 · 1,1	
9	0.5% Pd/HTsVK-3, exchange	$330 \\ 340$	$42,1 \\ 44,9$	2,8 3,7	0,5 0,5	

\*As in Russian original; no value given - Translator. †Differs in method of preparation. ‡Seventh hour of operation.

form hexanes. The n-pentane on such catalysts at 250-300°C and 30 atm is 7-40% converted to  $C_1-C_4$  hydrocarbons, 4-10% isomerized to isopentane, and 2-6% disproportionated to hexanes. The conclusion from these data is that the HTsVK materials are considerably different in catalytic properties from the cationic and H forms of faujasites and the H form of mordenite. On faujasites, for example,  $C_4-C_6$  paraffins do not undergo any conversion whatever under these conditions, whereas H mordenite at 280°C and 30 atm gives selective isomerization of n-pentane to isopentane to extent of 46% [4, 5]. These differences are apparently related to the considerably higher concentration of strong acid centers in the HTsVK in comparison with the other zeolites [3].

In Table 2 we present the results from experiments on the isomerization of n-pentane on Pd/HTsVK catalysts. The isomerization conditions were selected so that the catalysts would manifest maximum selectivity in this reaction. The best performance in this respect is shown by the Pd/HTsVK-1 catalysts obtained by ion exchange (at 330°C, the isopentane yield is 59.5%) and the Pd/HTsVK-2 obtained by ion exchange (at 310°C, the isopentane yield is 60%). Thus, the isopentane yields on these catalysts amount to 95% of the equilibrium yields; on the first of these catalysts, the selectivity is very high. Let us note, for example, that the catalyst No. 6, with a relatively high level of hydrocracking reactions (6%), did not change in activity or selectivity in 7 h of operation, thus indicating that this catalyst is stable. Finally, we should point out that there is very little disproportionation of the n-pentane to form hexanes with any of the Pd catalysts under these particular reaction conditions.

Catalyst	Hydrocar- bon	T., ℃	Product yields, %				
method			C1C3	isobutane	n-pentane	isopentane	
Exchange	n-Butane	350 380 400	 2 12,9	5,7 7,5 16,8		 13,1	
			isohexane	C <sub>i</sub> -C <sub>4</sub>	n-pentane	isopentane	
*	n-Hexane	$\begin{array}{c} 310\\ 320 \end{array}$	48,2 53,9	2,2 3,7	10,0 9,3	8,1 8,9	
			C <sub>i</sub> -C <sub>4</sub>	cyclohexane	methylcy- clopentane	∑-hexanes	
» Impregna- tion	Benzene†	200 250 280 300 310 300	- - 1,1 3,5	79,3 77,5 78,0 69,0 54,4 70,3	10,9 11,0 14,0 20,7 24,4 18,8	0,9 1,0 2,5 6,3 14,5 9,9	

TABLE 3. Conversions of Hydrocarbons on 0.5% Pd/HTsVK-1 Catalyst (30 atm,  $P_{H_2}/P_{CH} = 3.2$ , V = 1 h<sup>-1</sup>)

 $\frac{1}{P_{H_2}/P_{C_5H_6}} = 5.$ 

A comparison of the catalytic properties of HTsVK and Pd/HTsVK leads to the conclusion that there is a correlation between the hydrocracking (or cracking) activity and isomerizing activity of the catalysts included in this comparison. Actually, the HTsVK-1 and HTsVK-2 are more active than the HTsVK-3 in hydrocracking of n-pentane (Table 1). This same order of activities is observed for the Pd/HTsVK catalysts in n-pentane isomerization (see Table 2).

In connection with the overall problem of the relationship between the hydro-dehydrogenating and acid functions of metal/oxide catalysts, including metals supported on zeolites, let us note that in [3], on the Pt/HZSM-5 catalyst  $(SiO_2/Al_2O_3 = 34)$  at atmospheric pressure, no significant isomerization of n-decane could be obtained, whereas almost complete hydrocracking of this hydrocarbon was observed even at 150°C. At the same time, on a PT/ultrastable Y catalyst, the yield of isomers of n-decane at 200°C was 46%, with 37% hydrocracking. Thus, the Pt/HZSM is not a catalyst for n-decane isomerization; this was explained in [3] by the high concentration of strong acid centers and the imbalance of the above-indicated functions for such catalytic systems.

Our data show that the Pd/HTsVK catalysts, under high-pressure conditions, are selective bifunctional systems for n-pentane isomerization (see Table 2). However, the isomerization of n-butane and n-hexane on such catalysts proceeds along specific lines (Table 3). For example, on the Pd/HTsVK-1 at  $380^{\circ}$ C, we could not obtain more than 7.5% isobutane along with a high selectivity; and at 400°C, the 16.8% isobutane in the reaction products was accompanied by 12% C<sub>1</sub>-C<sub>3</sub> hydrocarbons and 30% pentane and isopentane. The n-hexane conversions gave a relatively low yield of isohexanes (in comparison with the equilibrium level) and selective hydrocarking of this hydrocarbon to pentane and isopentane (18%).

The Pd/HTsVK catalysts are active not only in paraffin conversions, but also in the exhaustive hydrogenation of benzene (see Table 3). At 200-300°C and 30 atm, the yield of cyclohexane on Pd/HTsVK-1 is 70-79%, which is comparable to the yields on the other metal-containing catalysts, including zeolitic catalysts [4]. Let us note that the TsVK catalysts that do not contain metals will also hydrogenate benzene to cyclohexane, but they are less active. At 250°C and 30 atm, on the original NaTsVK with a concentration of 1.3% Na<sub>2</sub>O in the zeolite, the cyclohexane yield was found to be 8.5%; on the decationized zeolite, it was 2%. By way of comparison, let us point out that under these same conditions on Na mordenite  $(SiO_2/Al_2O_3 = 10)$  with an 8.3% Na<sub>2</sub>O content, benzene is completely and selectively hydrogenated to cyclohexane [4]. Thus, for the TsVK zeolites without any transition elements, the same as for other crystalline aluminosilicates, the hydrogenating activity depends on the total concentration of alkali metal cations and also on the degree of decationization of the zeolite [4].

On the Pd catalysts, the hydrogenation of benzene is accompanied by hydroisomerization to form methylcyclopentane (10.9% and 20.7% at 200°C and 300°C, respectively); at 300°C,

hydrogenolysis begins, forming hexanes (6-10%). As can be seen from Table 3, the Pd-containing HTsVK materials obtained by ion exchange and by impregnation are practically the same in activity and selectivity in all of the reactions of benzene conversion at 300°C.

The results obtained in the present study lead to the conclusion that with respect to catalytic properties in hydrocarbon conversions, the superhigh-silica zeolites are substantially different from other zeolites. Modification of these superhigh-silica zeolites and adjustment of the reaction conditions can open up possibilities in the development of new catalysts for the isomerization of (for example) n-pentane to isopentane, the disproportionation and hydrocracking of hydrocarbons to n-pentane and isopentane, and the hydrogenation of benzene.

#### CONCLUSION

1. On the basis of decationized forms of superhigh-silica zeolites with a mole ratio  $SiO_2/Al_2O_3$  from 33 to 83, new and effective Pd catalysts have been synthesized for n-pentane isomerization, n-butane disproportionation, n-hexane isomerization and hydrocracking, and benzene hydrogenation.

2. A correlation has been established between the hydrocracking (or cracking) activity of the decationized forms of the zeolites and the isomerizing activity of the Pd/HTsVK catalysts in n-pentane conversions.

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# KINETIC AND MECHANISTIC STUDY OF REACTION OF C5-DEHYDRO-

CYCLIZATION OF 2,2,4-TRIMETHYLPENTANE ON PLATINIZED CARBON

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Recent studies have provided new data on the  $C_5$ -dehydrocyclization of alkanes on Pt catalysts [1-3]. However, there is still no unified opinion on the mechanism of this reaction. In [1-4], consideration was given to the possibility that the  $C_5$ -dehydrocyclization reaction proceeds through an associative activated transition complex. According to [2, 3], the reaction passes through a stage of dissociative adsorption of the original hydrocarbon, forming semihydrogenated intermediate species [2] or species of the metallocarbone and metallocarbyne types [3]. The kinetic data that have been reported on  $C_5$ -dehydrocyclization are quite limited, and these data have been obtained either under conditions of integral reactors [2, 5] or in a differential reactor at low levels of conversion [3].

With the aim of elucidating the mechanism of  $C_5$ -dehydrocyclization, we investigated the kinetics of the conversion of 2,2,4-trimethylpentane (A) to 1,1,3-trimethylcyclopentane (B) in the presence of hydrogen

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