

Effect of Hydrogen on the Selectivity of Pt-Containing Pentasil Catalysts in *n*-Hexane Transformations

O. V. BRAGIN,* T. V. VASINA,* E. G. HELKOVSKAYA-SERGEeva,*
M. A. DOBROVOLSZKY,† AND Z. PAÁL†

*"Zelinsky" Institute of Organic Chemistry of the USSR Academy of Sciences, Leninsky Prospect 47, Moscow, USSR; and †Institute of Isotopes of the Hungarian Academy of Sciences, P.O. Box 77, Budapest, H-1525 Hungary

Received January 14, 1987; revised August 4, 1987

Transformations of *n*-hexane were studied over ZSM-5-type Na-, H-, and Pt/H-pentasil ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 35$; Pt: 0.5%) in flow and pulse systems and in the presence of hydrogen or nitrogen. The Na-form was almost inactive; the H-form showed the expected acidic properties, with hardly any hydrogen effect. Aromatization and isomerization were enhanced over the Pt/H zeolite; the former is bifunctional, the latter are metal-catalyzed reactions. Hydrogen influenced the yields of both reactions in a way similar to that of other Pt-containing catalysts. © 1988 Academic Press, Inc.

INTRODUCTION

Pentasil-type zeolites of high silica content are well-known highly active and selective catalysts for several processes (1-3). Among the factors influencing their catalytic properties we have to mention the composition of the gas phase in which the reaction is carried out. This factor has often been neglected. Recently it was found that the presence and/or amount of hydrogen has a very marked influence on hydrocarbon transformations over catalysts containing Group VIII B metals (such as Pt black, Pd black, Pt/C, Pt/Al₂O₃, Pt-Re/Al₂O₃, etc.) (4-7). Hydrogen may be a reagent in some cases; however, its influence is considerable even when it does not appear in the stoichiometric equation.

Up to now, the effect of the gaseous medium on hydrocarbon reactions in the presence of pentasil-type catalysts has not been studied in proportion to its true significance (8, 9). The present work reports the transformation of *n*-hexane over several mono- and bifunctional ZSM-5-type catalysts: Na-, H-, and Pt/H-pentasil (Russian abbreviation: ZVM). There have been a few studies of the catalytic properties of Group VIII B-element-containing zeolites in al-

kane reactions. For example, Pt/Na, Pt/Ca, and Pt/La-Y zeolites have been used for reacting neohexane and neopentane (10). Hydrogenolysis and, up to 35% selectivity, isomerization were observed. Pt/Ba KL zeolite was an efficient catalyst for aromatization of naphtha cut and *n*-octane (11). Alkali zeolites are active in skeletal isomerization of olefins; *n*-hexene gave isohexene on Na-ZSM (12); methylcyclohexene gave alkylcyclopentenes and also toluene on PtNaY (13). Na- and La-Y isomerized neopentane at temperatures 100 K higher than did Pt zeolites (10). These works, however, do not stress the effect of gaseous medium. In this study we compare hydrogenolysis/hydrocracking, isomerization, aromatization, and buildup reactions in H₂ and N₂, and we report a remarkable effect of H₂ on the catalytic action of Pt/H-pentasil.

EXPERIMENTAL

Catalysts. Three high-silica zeolites were used: Na-, H-, and 0.5% Pt/H-pentasil. These zeolites were produced by crystallization of alumina gels and silica gels under hydrothermal conditions without addition of any organic compounds. The synthesis produced the sodium form of a ZSM-5-type

high-silica zeolite (Na-form: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$; $\text{Na}_2\text{O} = 3.3\%$, static pore water immersion volume: 0.10; heptane pore volume: $0.19 \text{ cm}^3 \text{ g}^{-1}$) (14). The H-form was obtained by twofold ion exchange with a NH_4Cl solution at 80°C and a subsequent decomposition of NH_4 -pentasil at 550°C . Pt/H-zeolite was prepared by exchange of NH_4^+ ions of the NH_4 zeolite by Pt^{2+} ions, by means of an aqueous solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$. Actual Pt content, 0.48%.

Experimental methods. Two types of apparatus were used. The amount of catalyst in a flow reactor (15) was 1.7–1.8 g (2.5 cm^3). The catalyst was pretreated before each series of experiments in air flow for 5 h (520°C for Pt-pentasil, 550°C for H- and Na-pentasil). The runs lasted for 1.5 h. Runs were carried out between 250 and 450°C . The space velocity of *n*-hexane feed was 0.9 h^{-1} , diluent gas (H_2 or N_2) was added in amounts between 300 and $1500 \text{ cm}^3 \text{ h}^{-1}$.

The chromatographic analysis of gaseous and liquid products was performed separately (15). The pulse apparatus has been described earlier (16); here 250 or 500 mg catalyst was used and 0.5 or $1.0 \mu\text{l}$ of *n*-hexane was introduced into the 60-ml min^{-1} flow of H_2 or N_2 carrier gas. Again, the reaction temperature varied between 250 and 450°C . A packed squalane column was used for analysis with a temperature program (17) to identify higher aromatics also.

RESULTS

The three types of zeolites show rather different catalytic properties (Tables 1 and 2). The sodium form is practically inactive in our reactions, as was reported for NaY for methylcyclohexene dehydrogenation (13). Under similar conditions, *n*-hexane reacts with conversions up to 100% on the H-form. The transformation of *n*-hexane over the H-form starts at 250°C (hydro-

TABLE I
Transformation of *n*-Hexane over Pentasil-Type Catalysts in the Pulse System^a

Catalyst	Carrier gas	T (°C)	Effluent composition ^b (%)							
			<C ₆	2MP	3MP	<i>n</i> H	MCP	Bz	Tol	C ₈ ar ^c
Na-pentasil	N ₂	Up to 450	1–2	—	—	98–99	—	—	—	—
H-pentasil	N ₂	250	18.4	—	0.2	81.4	—	—	—	—
		300	53.5	1.3	0.2	44.1	0.7	tr.	tr.	0.2
		350	90.2	0.5 ^d	0.1	7.4	0.3	0.1	tr.	1.1
		450	92.1	0.4	0.2	3.5	0.2	1.1	tr.	2.9
0.5% Pt/H-pentasil	H ₂	350	94.8	0.4	0.2	4.2	0.2	tr.	—	0.2
		450	89.4	0.5 ^d	0.1	3.5	0.3	1.4	—	4.4
	N ₂	250	19.2	0.7	—	79.7	0.4	—	—	—
		300	61.5	0.5	0.1	37.5	0.3	0.1	—	—
		350	77.4	0.5	0.1	14.3	0.2	1.0	6.1	0.4
		400	89.0	0.3	0.1	3.2	0.1	2.7	0.8	3.8
		450	71.3	tr.	—	—	—	9.7	14.6	4.4
		H ₂	250	22.0	33.6	8.5	35.8	—	—	—
300	40.2		21.4 ^d	7.1	25.9	0.3	—	—	—	
350	88.1		6.8 ^d	2.8	1.6	0.5	0.1	—	tr.	
400	99.4		0.1	0.1	tr.	—	0.4	—	tr.	
		450	99.4	—	—	—	tr.	0.5	0.1	tr.

^a $1 \mu\text{l}$ *n*-hexane pulses into 60 ml min^{-1} carrier gas.

^b 2MP, 3MP = 2- and 3-methylpentane; *n*H = *n*-hexane; MCP = methylcyclopentane; Bz = benzene; Tol = toluene.

^c Negligible ethylbenzene, mainly xylenes.

^d 2,2-Dimethylbutane detected in amounts to make 100%.

TABLE 2
Transformations of Hexane over Pentasil Catalysts^a

Catalyst	Gas added	T (°C)	Effluent composition (%)									
			<C ₆	2,2-DMB + 2MP	3MP	nH	Bz	C ₇ nonaromatic	Toluene	Xylenes	C ₉ -C ₁₁ aromatic	
Na-pentasil	N ₂ or H ₂	up to 450	2-3	—	—	97-98	—	—	—	—	—	—
H-pentasil	N ₂	250	23.8	2.5	0.3	55.4	—	18.0	—	—	—	—
		350	78.7	0.3	0.2	0.9	2.2	0.2	7.4	6.5	3.6	—
		450	79.0	tr.	0.1	0.2	4.3	—	7.6	4.8	4.8	—
	H ₂	250	18.3	2.3	0.6	75.7	—	3.1	—	—	—	—
		350	72.3	0.3	0.2	1.2	2.0	0.2	8.6	8.3	6.9	—
		450	70.8	tr.	0.1	0.1	6.6	—	10.9	5.9	5.3	—
Pt/H-pentasil	N ₂	250	17.9	2.6	0.6	77.5	—	1.4	—	—	—	—
		350	69.8	0.5	0.3	1.4	1.6	0.1	11.0	13.2	2.1	—
		450 ^b	67.1	tr.	—	0.4	6.4	—	13.7	7.7	4.7	—
	H ₂	250	55.2	7.8	2.7	31.4	—	2.9	—	—	—	—
		350	73.5	0.1	0.1	—	2.8	—	9.6	8.9	5.4	—
		450	73.3	0.1	—	—	5.9	—	10.1	5.6	4.9	—

^a Flow reactor, LHSV = 0.9 h⁻¹; feed rate of diluent gas: 300 ml h⁻¹.

^b According to separate DTG-DTA measurements, the amount of nondesorbing condensation products formed from *n*-hexane under the most severe conditions (450°, N₂) is less than 1% of the catalyst mass (calculated to carbon). This corresponds to <1% of the *n*-hexane feed.

cracking, skeletal isomerization: Tables 1 and 2). Above 300°C, aromatization occurs also. We have to emphasize that the conversion of *n*-hexane in hydrogen and nitrogen exhibits similar values in the temperature range 350–450°C and that the product composition is analogous also (Table 2). Thus, the gaseous medium does not noticeably influence the activity and selectivity of H-pentasil in *n*-hexane transformations. The high cracking selectivity in both carrier gases is noticeable, especially in the pulse system.

The introduction of platinum into H-pentasil changes the picture dramatically. More aromatics (especially in the flow reactor) and more isomers (especially in the pulse reactor) are formed. Some aromatization occurs on H-pentasil, too, but the observation of large amounts of isomers instead of cracking over Pt-containing pentasil (Table 1) is, as far as we know, a completely new result. The absolute isomer yield is low in the flow reactor (Table 2), yet it is still three times higher than that observed with H-pentasil. At higher temperatures cracking and/or aromatization prevails on both catalysts. It is interesting to note that the conversion of *n*-hexane feed

may approximate 100% by 350°C; raising the temperature to 450°C could nevertheless increase aromatic yields still further. Most aromatics are buildup products with more than six C atoms (Table 2).

Hydrogen effects are more marked here. Isomerization on Pt/H-pentasil is promoted in the presence of hydrogen, whereas aromatization is much more significant in nitrogen. In particular, the overall conversion at 250°C is three times higher in H₂ than in N₂ (Table 1); also, the relative amount of aromatics in the pulse system is not too high, but the relative gains in N₂ are significant.

The suppression of aromatization by hydrogen was reported earlier with other Pt-containing catalysts (4, 5), but this observation is new as far as Pt-containing zeolites are concerned. Further study of this effect involved runs where the rate of hydrogen flow was changed with constant feed rate of *n*-hexane (Table 3). This effect may be due, on the one hand, to decreasing contact times at higher diluent gas rates. This effect, in fact, can be observed, as shown by the experiments with Ar in Table 5. However, the decrease by a factor of 2 is much less than the drop by nearly an order of

TABLE 3

Effect of Diluent Gas Rate on the Transformations of *n*-Hexane over Pt/H-Pentasil

Carrier gas and rate, liters h ⁻¹	T (°C)	<C ₆	2,2-DMB + 2MP	3MP	<i>n</i> H	C ₇ nonaromatic	Bz	Tol	C ₈ aromatic	C ₉ aromatic
H ₂ , 0.3	250	55.1	7.8	2.7	31.4	2.9	—	—	—	—
	350	73.5	0.1	0.1	0.1	—	2.8	9.6	8.4	5.4
	450	73.4	0.1	—	—	—	5.9	10.0	5.6	4.9
H ₂ , 0.5	250	27.6	3.0	1.0	67.2	1.2	—	—	—	—
	350	84.0	0.4	0.4	3.8	0.3	0.7	5.1	4.8	0.5
	450	89.1	—	—	0.2	—	2.2	4.9	2.8	0.8
H ₂ , 0.8	250	56.2	7.6	3.3	31.7	0.9	—	—	—	—
	350	97.9	0.1	0.1	0.1	—	0.2	0.9	0.6	0.1
	450	94.6	—	—	0.1	—	0.9	2.8	1.4	0.2
H ₂ , 1.5	250	56.9	4.1	1.7	36.3	1.0	—	—	—	—
	350	92.8	0.6	0.5	4.0	0.2	0.2	0.7	0.8	0.1
	450	~97	—	—	—	—	~3			—
Ar, 0.3	450	77.6	—	—	1.9	—	2.3	7.9	5.8	3.8
Ar, 1.5	450	91.2	—	—	0.3	—	1.3	2.8	2.8	1.6

magnitude in hydrogen. Therefore, one has to assume an effect of hydrogen on the catalytic process, too.

A closer look at the fragment composition (Tables 4 and 5) reveals the predominance of C₃ fragments on both catalysts. (Different product classes come from slightly different analyses with pulse and flow systems.) C₄ and C₅ fragments are significant at the lowest temperatures only; however, their complementary fragments C₁ and C₂ do not appear in the gas phase in the flow system. They are more significant

in the pulse system. No dramatic differences can be seen between H-pentasil and Pt/H-pentasil. In the flow system, we can also see some hydrogen effects: more hydrogen favors the formation of higher amounts of C₄ and C₅ fragments. Perhaps the above phenomena are related to contact time. In the pulse reactor, the hydrocarbon injection is periodic. Thus, as the carrier gas flushes the last traces of hydrocarbons from the catalyst, they may suffer a deeper fragmentation than in the flow reactor, where a steady state should be established between gas phase, the outer catalyst surface, and the inner pores. With more hydrogen present (Table 5, lowest part), the partial pressure of hydrocarbons in the gas phase must be lower, hence the desorption of C₄-C₅ fragments should be facilitated.

TABLE 4

Fragmentation Selectivity on Pt/H-Pentasil in the Pulse System^a

Carrier gas	T (°C)	Fragment selectivity (%)					
		C ₁ -C ₂	C ₃	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₅	<i>n</i> -C ₅
N ₂	300	2.5	44.5	21.5	20.5	5	6
	350	11.5	46	17	18.5	4	3
	400	30	55	6	6	2	1
H ₂	300	59	58	8	14	4	7
	350	12	72	3	8	3	2
	400	25	55	5	12	2	1
	450	35	60	2.5	2.5	tr.	—

^a Conditions, see Table 1.

DISCUSSION

The high activity of the H-form indicates that the main reactions of *n*-hexane (hydrocracking, isomerization, aromatization) take place on Brønsted acid centers by acidic catalysis. In fact, it was shown previously (18) that the IR spectrum of Na-pentasil contains valence vibrations only in the range of absorption bands of nonacidic OH

TABLE 5
Typical Fragment Compositions Obtained in the Flow System^a

Catalyst	Gas	Gas flow rate, liters h ⁻¹	T (°C)	Fragment selectivity (%)						
				CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈ ^b	C ₄	C ₅	
H-pentasil	N ₂	300	250	tr.	2	tr.	28	33	38	
			350	tr.	2	1.5	80	14	2.5	
			450	6.5	1.5	15	71.5	5	0.5	
	H ₂	300	250	tr.	tr.	0.5	16.5	35.5	47.5	
			350	tr.	tr.	1	71	26.5	1.5	
			450	5	1	12.5	73.5	7.5	0.5	
Pt/H-pentasil	N ₂	300	250	—	—	1	28	46	25	
			350	1	—	12	54	27	6	
			450	1	1	11	75	11	1	
	H ₂	300	250	tr.	—	1	23	34	42	
			1500	250	—	0.5	1	38.5	44	16
			300	350	tr.	—	10	71.5	17.5	1
		800	350	—	0.5	8	64.5	27	1	
				1500	350	—	—	5	58	35
		300	450	4	tr.	36	55	5	tr.	

^a Conditions, see Table 2.

^b C₃H₆, max. 0.6%.

groups of silica. On the other hand, the IR spectrum of H-pentasil contains an intense absorption band with its maximum around 3610 cm⁻¹, corresponding to bridged OH groups giving rise to Brønsted acid centers (19). It is most likely that these centers serve as active sites for primary splitting of alkanes to give unsaturated fragments of low molecular weight (20).

On the basis of the predominance of C₃ hydrocarbons among the fragments one could suspect that a selectivity for shape occurs in fragmentation (21). One may recall the earlier observation (22) that cracking of C₁₀–C₂₃ alkanes on small-pore (4.3 Å) erionite gave product maxima at C₃–C₄ as opposed to large-pore zeolite X. However, the cracking of 3-methylpentane over amorphous aluminosilicate and shape-selective zeolites gave a product composition very close to this, namely, a predominance of C₃ (23). Since almost no shape selectivity was previously observed between *n*-hexane and 3-methylpentane on the zeolite types used in our experiments (24), shape selectivity

may not be the true explanation for the cracking pattern observed.

Considering that Pt/H-pentasil essentially remains acidic after incorporating Pt and also that—unless a very low heating rate is applied—Pt forms crystallites on the outer surface of the zeolite (25), our catalyst should be regarded as bifunctional, with both acidic and metallic functions. Electron microscopy of these catalysts revealed, in fact, two types of Pt crystallites: the catalyst contains metal particles 3 to 15 nm in diameter on the external surface together with finely dispersed Pt crystallites of about 1 nm diameter located in the channel mouths. The fraction of the latter type seems to be higher when the sample was pretreated in air (26). Aromatization on Pt was suggested to take place by the alkane–olefin–diene–triene–cyclodiene–aromatics route (27, 28). The zeolite-catalyzed route involves the combination of low-molecular-weight unsaturated fragments being the products of primary breakdown of *n*-hexane molecules in the channels of high-silica

zeolites (20). In both cases hydrogen may suppress the formation of unsaturated intermediates. Lower aromatic yields are in agreement with the assumed higher hydrogenation rates of unsaturated surface species in the pulse reactor where the surface hydrogen concentration of hydrogen is higher than in the flow system. Also, combination reactions are favored by the longer contact times in the flow system. These reactions continue also when *n*-hexane is practically consumed: overall conversion may approach 100% at 350°C; still, aromatic yields do not drop considerably at 400–450°C (Tables 2, 3); they may even increase at the expense of fragments (Table 1, N₂). All these indicate that the combination route of aromatization—suggested also for Pt/Al₂O₃ (29)—is more likely. A uniform scheme for aromatization of ethylene and C₆ hydrocarbons was proposed earlier (24). This scheme regards C₁–C₅ fragments as important intermediates for both types of feed. The ratio benzene:toluene:xylenes was between 1:(2–4.5):(1.3–5), i.e., considerable toluene excesses were observed. The same can be seen from the data in Tables 2 and 3. This is possible only if C₁ fragments have an important role in forming odd-numbered buildup products. That may be the reason why fewer C₁ (and also C₂) fragments were observed. At the same times coking of the catalyst even under the most severe conditions is not important (<1%, Table 2). Analogously, 1-hexene gave no C₁ fragments over Na-pentasil at 92% conversion level, although the proportion of C₄–C₅ fragments was around 13% (12).

Maximum yields were reported for various hydrocarbon reactions as a function of hydrogen pressure (4–6, 30, 31); that is, in various *P*(H₂) ranges hydrogen either promotes or hinders the reactions. In low *P*(H₂) ranges the formation of deeply dehydrogenated surface species blocking active sites is gradually suppressed by increasing the hydrogen pressure—hydrogen acceleration is observed. After a maximum rate,

hydrogen and hydrocarbon species compete with each other. The plot of yield of aromatics (Fig. 1) may correspond to this latter, descending branch of the maximum curves. Such a hydrogen effect is reported for the first time with Pt-zeolite catalyst.

An interesting and important observation is that at lower temperatures, metal-containing zeolites promote isomerization; under the same conditions the acid-catalyzed isomerization over H-pentasil is negligible. Increasing temperatures would lead to enhanced cracking in the latter case, where isomerization is still considerable on Pt/H-pentasil (Table 1). Hydrogen is necessary for this. Acid-catalyzed reaction produces 2MP and 3MP close to the thermodynamic ratio (~1.5) (32). The predominance of 2MP points to some metal-catalyzed pathways. Of the two possibilities (33, 34), the C₅-cyclic mechanism (33) would give 2MP/3MP ratios close to 2, whereas with a predominant bond shift, the ratio 2MP to 3MP can be very high (29). Also, with a significant C₅-cyclic isomerization, more methylcyclopentane ought to appear. Thus, we attribute the enhanced isomer yields to a metal-catalyzed bond shift reaction. Its occurrence points to the presence of Pt particles larger than 2 nm, since bond shift stops with particles smaller than 2 nm (35). This again points to the activity of Pt crystallites on the outer surface of the zeolite grains (24).

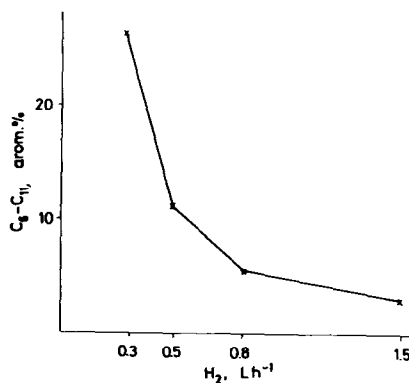


Fig. 1. Yield of aromatic products as a function of hydrogen flow rate. T = 450°C.

Above 350°C, the yield of isomer hexanes drops drastically (down to <0.5%) because of enhanced hydrogenolysis on Pt sites as well as cracking on acidic sites. The appearance of *i*-C₄ and *i*-C₅ fragments even when hardly any skeletal isomerization occurs points to their formation by other mechanisms, perhaps by acidic isomerization of fragments (29).

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