## ALKYLATION OF BENZENE BY PROPANE OVER ZEOLITE-CONTAINING PENTASIL—ALUMINA COMPOSITIONS AND DEALUMINATED PENTASILS

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The alkylation of benzene by propane over pentasil-aluminum compositions  $(HTsVM-\gamma-Al_2O_3)$  has been studied for a wide range of compositions and also over dealuminated and dehydroxylated samples. It has been established that  $Al_2O_3$  plays little if any part in this reaction. As the proportion of HTsVM in the composition is increased the yield of alkyaromatic hydrocarbon increases, reaching a maximum (36%) for pure HTsVM. Dealumination and dehydroxylation of the HTsVM led to a significant reduction in the yield of alkylation products. It was concluded the Brønsted acid centers of the zeolite are responsible for bringing about the alkylation of benzene by the lower alkanes.

Keywords: alkylation of benzene, zeolites, alumina, alkylaromatic hydrocarbons, Brønsted acid centers.

It has been established previously [1-4] that lower  $(C_2-C_4)$  alkanes react with benzene over pentasil-containing catalysts to form alkylaromatic hydrocarbons (AAH).

It is known that in the preparation of catalysts,  $Al_2O_3$  is often used as a binder and this consists essentially of Lewis acid centers [5]. The present work was devoted to a study of relationships in the reaction of propane with benzene over catalytic systems based on pentasil with different concentrations of Brønsted and Lewis acid centers: compositions of pentasil and alumina (HTsVM $-\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and dealuminated or dehydroxylated pentasils.

## EXPERIMENTAL

Materials used in this study were HTsVM,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and samples with varying proportions of HTsVM and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (70, 50, and 30% by weight HTsVM) which were prepared by the method of [5] by suspending and peptizing Al(OH)<sub>3</sub> and NH<sub>4</sub>TsVM in water. Dealuminated samples were prepared by treating HTsVM with steam for 1 h at 600, 700, and 850°C, respectively [6]; dehydroxylation was carried out at 750°C (2 h) and 800°C (3 h). Experiments were carried out in a flow-type apparatus [7] at atmospheric pressure. The reactants were benzene and propane of >99% purity by GLC. Weighed samples of catalyst of 3.4 to 3.6 g (5 ml) were used, and the benzene feed was at the rate of 2.2 ml/h (liquid) and propane at 600 ml/h (gas) giving a 1:1 molar ratio of reactants. In the experiments with propane alone the latter was diluted 1:1 with He and passed at a rate of 1200 ml/h which corresponds to the contact time in experiments with a propane – benzene mixture. Each experiment was run for 3 h; the yield is given overall for this period calculated on the overall reactants. The reaction products were analyzed by GLC [7]. The quantity of coke formed [condensation products (CP) not desorbed under the experimental conditions] was

<sup>\*</sup>Deceased.

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TABLE 1. Reaction of Benzene and Propane over HTsVM-Al<sub>2</sub>O<sub>3</sub> Compositions (550°C, molar ratio 1:1)

HTsVM, by wt.	%	Yield, $%$ , on $\Sigma$ reactants passed								
		benzene	toluene	xy1enes	с <mark>†</mark>	Сн.	$\Sigma C_2$ hydcbns	C <sub>3</sub> H <sub>6</sub>	C,H	
100 70 50 30 0		35 42 48 46 56	20 18 14 10 0.4	6 4 3 4 0.2	10 5 4 3 0.7	13 13 9 8 0,4	6 7 6 3 0.5	1 1 1 	7 7 12 23 39	

\*CP content, 1.6-3.0%.

†Including naphthalene and its homologs.

TABLE 2. Propane Conversion over  $HTsVM - Al_2O_3$  Compositions (550°C, molar ratio  $C_3H_8/He$  1:1)

HTsVM in composi- tion, % by wt.	Yield, %*									
	benzene	toluene	xylenes	С <sup>†</sup> 9+	CH4	ΣC <sub>2</sub> hydcbns	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>		
100 70 50 30 10	2 4 3 2 -	13 8 4 4 -	8 5 3 3 -	2 2 3 2	25 22 17 6 4	20 21 17 7 4	3 - - 2	20 33 48 70 84		

\*CP content.  $\sim 3\%$ .

†Including naphthalene and its homologs.

determined by TGA-DTA on a MOM Q-1000 derivatograph. Observed effects were recorded in the course of linear heating up to 1000°C at a rate of 10 K/min under static conditions in air [8].

## **RESULTS AND DISCUSSION**

The principal results are set out in Tables 1 and 2 and Fig. 1. It can be seen that in the reaction of benzene and propane under the conditions examined  $Al_2O_3$  displayed no activity. On introducing 30% HTsVM into the  $Al_2O_3$ , 17% AAH was formed from propane and benzene and as the HTsVM content, and consequently also the quantity of Brønsted centers in the composition, was increased, the yield of AAH increased reaching its highest value on HTsVM alone. The results of the catalytic experiments are in agreement with the earlier IR spectroscopic results for the concentration of Brønsted and Lewis centers in the HTsVM $-\gamma$ - $Al_2O_3$  system [5]. The highest activity (yield of AAH 35%) in the alkylation of benzene by propane was shown by the H form of TsVM which contains many strong Brønsted centers (bridging OH groups absorbing at 3610 cm<sup>-1</sup>) and only a small number of Lewis centers. On the other hand,  $Al_2O_3$  containing predominantly Lewis centers is virtually inactive in the alkylation process (Table 1). The results definitively show that the Brønsted centers of the zeolite are critical in the alkylation of benzene by lower alkanes.

Figure 2 shows the results obtained on dealuminated or partially dehydroxylated samples of HTsVM. It can be seen as the molar ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> increases and hence the concentrations of Brønsted centers falls, the yield of AAH is markedly reduced (samples 1-4). Thus, comparing an extensively dealuminated sample with the initial HTsVM the yield of AAH is reduced by a factor of  $\sim 3.5$  (sample 4). Partial dehydroxylation of HTsVM also results in a significant fall in the yield of AAH (samples 5 and 6).



Fig. 1. Alkylation of benzene by propane (a) and conversion of pure propane (b) over pentasil-alumina compositions: 1) propane conversion; 2) yield of AAH; 3) yield of methane.



Fig. 2. Variation in yield of AAH in the reaction of  $C_3H_8$  with benzene (550°C) as a function of the extent of dealumination and dehydroxylation of HTsVM: 1) initial HTsVM; 2-4) dealuminated samples (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 42, 120, 200, and ~500, respectively); 5, 6) dehydroxylated HTsVM samples, respectively at 750°C (2 h) and 800°C (3 h).

Thus, the Lewis centers formed as a result of dealumination and dehydroxylation [9] do not make a significant contribution to the process under study. It follows from the results obtained that when using catalyst samples with different ratios of Brønsted and Lewis centers prepared by the three methods noted above, reduction in the concentration of Brønsted centers and increase in the concentration of Lewis centers leads to a fall in the yield of AAH.

To study the contribution of propane and benzene to the formation of AAH a series of experiments was carried out under the same conditions over  $HT_sVM - \gamma - Al_2O_3$  compositions with propane diluted with helium (Table 2). We note that benzene, in the absence of propane, remains unchanged under the conditions of the experiments whereas propane forms various products, including AAH.

A comparison of the results obtained in the reaction of propane with benzene and in the conversion of propane alone (Fig. 1) points to a significant difference in the selectivity of formation of the reaction products. Thus, for the reaction of

propane and benzene there is a sharp fall in the yield of methane (by a factor of  $\sim 2$ ) and simultaneously an increase in the yield of AAH (by a factor of 1.5-2) compared with the conversion of propane alone.

It follows from these results that when propane and benzene are used together as reactants, the latter is a typical acceptor of unsaturated fragments formed from the alkane [4]. The definitive role of the zeolite matrix is apparent here. Thus, in [10-14] it was shown by means of a combination of physical and physicochemical methods, that when benzene is adsorbed on pentasils there is a strong interaction of the  $\pi$ -electrons of the benzene ring with the OH groups of the zeolite.

ESR, IR, and UV spectroscopy were used [12] to study the oxidation-reduction processes taking place on the adsorption of benzene with the formation of cation-radicals [13] on the Lewis acid centers of the pentasil lattice. Such centers can be  $Fe^{3+}$  ion impurities or radical centers of one-electron transfer type  $\equiv$ Si-O' able to ionize aromatic compounds with the formation of the corresponding radicals. The possibility of the interaction of cation-radicals with alkane molecules activated on Brønsted centers (unsaturated low-molecular-weight fragments, CH<sub>3</sub><sup>+</sup> particles, etc.) was not excluded [4, 15]. However, the results obtained in the present work show that there is no significant contribution by the Lewis centers to the alkylation process.

Examination of the CP formed in relatively small quantities (1.5-3%) in the alkylation of benzene by propane showed that coke formation was more evident on compositions than on individual HTsVM or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Two exothermic effects were detected here, both associated with weight loss, at  $T_{\text{max}} \sim 530$  and  $\sim 470$  °C, which provided evidence of different types of CP on HTsVM and on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [8]. We note that the least amount of CP (1.6%) is formed when the yield of AAH is at a maximum under the given conditions on HTsVM and when the alkylation process is proceeding at a lower efficiency (on HTsVM $-\gamma$ -Al<sub>2</sub>O<sub>3</sub>), or almost not at all (on Al<sub>2</sub>O<sub>3</sub>), CP formation is markedly greater. This shows that the Lewis centers are apparently facilitating the formation of polyconjugated structures ("coke").

On the whole, the results obtained provide evidence that Brønsted acid centers (bridging OH groups absorbing at  $3610 \text{ cm}^{-1}$ ) play a decisive role in the alkylation of benzene by alkanes. It seems that the Lewis centers take part in the formation of polyconjugated structures. The results obtained in the reaction of propane with benzene and in the conversion of propane alone point to the participation of the benzene in the formation of AAH.

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