PROPERTIES OF PENTASIL-CONTAINING CATALYSTS

IN HYDROCARBON CONVERSIONS.

7.* BENZENE ALKYLATION BY LOWER ALKANES IN THE PRESENCE OF MODIFIED ZEOLITES

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A novel catalytic synthesis of alkylaromatic hydrocarbons (AArH) containing C_7 - C_8 has been achieved using C_2 - C_4 alkanes as alkylating reagents on high silica zeolites of the pentasil type. It has been established that the yield of AArH during the reaction between benzene and alkanes varies in the order $C_2H_6 < C_3H_8 \leq C_4C_{10}$ (450-600°C). Modification of the zeolite by additions of Pt, Zn, and Ga results in a lowering of the reaction temperature (by ~100°C) and alters the selectivity of the alkylation process. On passing from flow to static conditions and raising the pressure to 2-4 MPa the AArH yield doubles and reaches 70-75% in the case of C_3-C_4 hydrocarbons.

The development of economically profitable methods of processing the lighter hydrocarbons is one of the real problems in current petrochemistry. A possible solution would be to combine these alkanes with other compounds, in particular aromatic hydrocarbons. However, published accounts of alkylation reactions are concerned as a rule with the reaction of benzene with olefins, oxygen-containing compounds, etc. [2-4]. The aim of this present study was to investigate the basic principles governing reactions between low molecular mass alkanes (ethane, propane, and isobutane) and benzene on pentasil-containing catalysts and to establish the effect of the nature of the modifying additive (Pt, Zn, Ga) on the catalytic properties of zeolites in this process.

EXPERIMENTAL

The experiments were conducted in a flow type apparatus [5] at atmospheric pressure and under pressure in a rotary autoclave [6]. The catalysts used were pentasil HZSM $(SiO_2/Al_2O_3 = 42; Na_2O < 0.1\%)$ and modified forms of the zeolite: 0.5% Pt; 2.0% Zn and 2.0% Ga/HZSM. The initial reagents ethane, propane, isobutane, and benzene had a purity >99% (GLC). The preparation and preliminary activation of the catalysts have been described elsewhere [6, 7]. The sample mass in the flow system was 3.4-3.6 g (5 cm³). The feed rate of benzene was 2.2 ml/h (liquid) and of the alkanes 300-800 ml/h (gas). The conditions for experiments conducted under pressure have been described in [6]. The reaction products were analyzed by GLC.

RESULTS AND DISCUSSION

It has been shown [6, 8] that AArH can be synthesized catalytically from C_2-C_3 alkanes and benzene. It can be seen from our data (Table 1) that in the presence of HZSM the AArH yield is directly related to the stability of the alkane molecule and increases in the order $C_2H_6 < C_3H_8 \leq$ C_4H_{10} . Thus, from ethane and benzene the maximum yield of AArH is ~9%. By using propane (or isobutane) the yield can be increased ~4 times; under comparable conditions it is 32-36% (550-600°C). Propane (isobutane) and benzene react under milder conditions (450-500°C) the AArH yield being higher for isobutane than for propane and benzene. Under more stringent conditions (550-600°C) the AArH yield for these two alkanes is comparable (see Table 1).

*For previous communication, see [1]. +Deceased.

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	т, с	X, %		Yield,* mass %										
Reagent		C ₈ H ₅	al- kane	tolu- ene	xy1- ene	с ₉₊	Σaarh	СН₄	c2 [‡]	c ₃ ‡	с ₄ ‡			
C ₂ H _e	450	No conversion												
-2 0	500	7	6	1.	-	1	2	1	<u> </u>		-			
	5 50	25	20	1	3	3		1						
	600	18	24	6	1	2	9	1		2	-			
C ₃ H ₈	450	7	17	9	3	3	15	3	3	-	1			
	500	27	60	10	7	6	23	4	4)	1			
	550	- 38	70	20	6	10	- 36	6	6	-	Traces			
	600	30	90	18	3	11	32	7	6		Traces			
i-C4H10	450	5	68	12	9	8	29	1	1	15	-			
	500	26	80	16	8	10	34	4	5	20	-			
	550	36	94	18	6	11	35	10	8	8	- 1			
	600	45	97	15	2	10	27	8	13	3	- 1			

TABLE 1. Benzene Alkylation by Alkanes on HZSM (mole ratio of reagents 1:1)

*Condensation product (CP) content 8-10%. +Mainly naphthalene and its homologs. +In addition to initial alkane.

It can be seen from Table 1 that the reaction temperature has a considerable effect on the activity and selectivity of alkylation. In the case of ethane and benzene there is a continuous increase in AArH yield as the temperature is increased to 600°C while for C_3 - C_4 alkanes and benzene the variation in AArH yield with temperature passes through a maximum at 550°C. During this the values for conversion (X) of the two reagents differ; so, for example, in the case of ethane X increases steadily with increasing temperature, while for benzene X passes through a maximum. The features noted above can be explained both by an increase in the direct aromatization of the alkane to form benzene [9, 10] and by the formation of a certain amount of benzene by dealkylation of AArH at 600°C.

The results also show (see Table 1) that considerable amounts of toluene are formed during the reaction between the alkanes and benzene (especially at 600°C). This probably results not just from the immediate reaction between alkane and benzene molecules but also from decomposition of polyalkylbenzenes that have formed.

From a comparison of the results in the table with those obtained earlier on alkane aromatization on pentasil-containing catalysts [10] we can assume that there are two concurrent routes for the formation of alkyl benzenes from alkanes and benzene: alkylation of a benzene molecule by the alkane and direct aromatization of the alkane to alkylbenzenes. The contribution of each route in the formation of AArH is quite difficult to estimate in the absence of special kinetic investigations, but nevertheless it can be seen that at 500-550°C ArH are not formed on HZSM from pure ethane while in the presence of benzene the AArH yield at this temperature reaches 7%. An analogous picture emerges for propane but at lower temperatures. This supports the idea that at relatively low temperatures (450-500°C) benzene, introduced into the reaction zone, is an unexpected acceptor of active unsaturated fragments of the original alkanes formed on the catalyst.

In order to optimize the reaction conditions the effect of the reagent flow rate and pressure on the yield and selectivity of AArH formation was studied. It was established (Fig. 1) that under the experimental conditions the maximum AArH yield for all three reacting systems was in the region $v = 250 h^{-1}$. An increase in the reagent flow rate resulted in a lowering of X and a corresponding decrease in the AArH yield, the decrease in X for benzene being greater than for the alkane. Cracking of the initial and final reagents intensified as the contact time lengthened also resulting in a decrease in the AArH yield.

A very favorable effect was produced by increasing the pressure of the reaction zone to 3 MPa (Table 2). It can be seen that at 450°C the AArH yield from propane and benzene increases 4.5 times to reach 70-72%, and in the case of ethane and benzene from 0 to 17 and 30% on H and Pt pentasil, respectively [8]. Raising the pressure in the reaction zone to 5 MPa lowers the AArH yield from 70 to 30%. It should be noted that the high AArH yield (up to 72%) is achieved at lower temperatures while there is only a slight reaction (C_3H_8) at atmospheric pressure, or none at all (C_2H_6) (Table 1).



Fig. 1. Variation in AArH yield with reagent flow rate for reaction between alkanes and benzene on HZSM at the optimum temperature for each system: 1) ethane + benzene (600°C); 2) propane + benzene (550°C); 3) isobutane + benzene (550°C).

Fig. 2. Variation in AArH yield with reaction temperature for reaction between ethane and benzene at a mole ratio 1:1 on the catalysts: 1) HZSM; 2) Pt/HZSM; 3) Ga/HZSM.

The effect of modifying additives (Pt, Zn, and Ga) on the reaction between the alkanes and benzene was studied using a flow type apparatus at atmospheric pressure (Table 3, Fig. 2). The results have been given for the optimum temperature (with respect to AArH yield) for each alkane so that the fullest evaluation can be made of the modifying action of the additives on the selectivity of the process.

It can be seen that the nature of the modifier affects the catalytic properties of the zeolite in this reaction in different ways. This is particularly obvious for ethane and benzene where the AArH yield is increased by ~2.5 times while the reaction becomes more selective toward higher molecular mass AArH mainly in the form of condensation products (naphthalene and its homologs). At the same time there is a significant decrease in the reaction temperature on these modified pentasils (see Fig. 2). In the case of benzene alkylation by C_3-C_4 alkanes the effect of the modifying additives is less marked: The AArH yield hardly changes and in other cases even decreases somewhat, which is most probably associated with the acceleration of side reactions, primarily methane formation as a result of cracking of the initial alkanes.

Overall it should be noted that the reaction between alkanes and benzene is quite complicated and its selectivity mainly depends on the molecular mass of the alkane, the properties of the molecular sites on the zeolite, and lastly on the nature of the modifier.

Introduction of a modifier has a significant effect on the variation in selectivity of formation of the different components. For example, in the reaction between propane and benzene (550°C) the catalysts can be placed in the following sequence according to the distribution of the main products (yield, mass %):

Toluene	H > Ga > Pt > Zn
Xylene	$\mathrm{H}>\mathrm{Pt}>\mathrm{Ga}>\mathrm{Zn}$
∑ ArH C ₉ +	$Zn \geqslant Ga > H > Pt$
CH_4	Ga > Zn > Pt > H

It can be seen that these modifiers, besides catalyzing the main process, catalyze cracking, disproportionation, condensation, and other reactions, the degree to which these occur depending mainly on the nature of the cation. The H-form of the zeolite exhibits the highest selectivity toward formation of C_7 - C_8 AArH and the least toward methane. On Zn- and Ga-containing pentasils the selectivity favors formation of methane and high molecular mass ArH mainly in the form of condensation products. Pt/HZSM occupies an intermediate position.

It should be noted that in the reaction between C_3-C_4 alkanes and benzene on Pt/HZSM the processes of cracking and gas formation are accelerated significantly leading to a de-

	-	Yield, mass %	Selectivity			
Catalyst	P. MPa	AArH	C7—C8- AArH *			
Ethane + benzene	0, 1 3	() 47 30	22			
Propane + benzene	3 + 0,1 3	0 15 70 30	0 80 77 61			
Isobutane + benzene	3 + 0,1	7 29 55	7 72 69			
Benzene	3	6	42			

TABLE 2. Benzene Alkylation by C_2-C_4 Alkanes on H and Pt Pentasils at Increased Pressure (T = 450°C, alkane:benzene = 1:1)

*Content of C₇-C₈ AArH in liquid products. +Pt/HZSM.

#Alkane conversion in absence of benzene.

TABLE 3. Effect of Modifier on Catalytic Properties of HZSM in Reaction of C_2-C_4 Alkanes with Benzene (1:1 mole)

	_		1/0		Yield, mass %									
Catalyst		C _e H _e	alkane			CH4	t	toluene		lenes		C ₉₊		∑ AArH
$C_2H_6 + C_8H_8 (600^{\circ}C)$														
HZSM Pt/HZSM Ga/HZSM		15 30 25		24 30 24		1 4 7		6 14 11	ĺ	1 1 1		2 9 10		9 24 22
$C_{3}H_{8} + C_{6}H_{6}$ (550°C)														
HZSM Pt/_HZSM Ga/HZSM Zn/HZSM		36 41 30 37		70 84 98 90		6 8 10 12		20 14 18 12		6 4 3 3		10 7 13 15		36 25 34 30
$i-C_4H_{10}+C_6H_6$ (500°C)														
HZSM Pt/.HZSM- Ga/HZSM		30 15 19		80 82 98		4 5 6		16 13 22		8 5 8		10 7 13		34 25 43

crease in the yield of liquid products and an increase in conversion of the alkanes. A different picture emerges for the reaction between the more stable ethane and benzene. On Pt/ HZSM ethane conversion and the AArH yield are comparable, ~30 and 24%, respectively. This indicates that ethane reacts mainly with the benzene.

We should also note that AArH formation from benzene and the C_2-C_4 alkanes is most successful on HZSM; modification of the zeolite does not always play a positive role in increasing the AArH yield. We can assume that the acidic zeolite centers are directly involved in this process. It is evident that initially activation of the alkane and benzene molecules occurs on bridging OH groups of the pentasil [11, 12] with the formation of activated particles (unsaturated low-molecular-mass fragments, cation radicals, CH_3 ', etc.), which then react among themselves.

These investigations have established that in reactions between alkanes and benzene the AArH formed include considerable amounts of toluene and xylenes and in the gaseous products alkanes with n - 1 carbon atoms, where n is the number of carbon atoms in the initial hydrocarbon (see Table 1). This would indicate that benzene reacts with the single carbon fragment CH_3 '.

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