n-Hexane activation over zeolites: aromatic alkylation to 1-phenylhexane

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Terminal 1-phenylhexane was observed during alkylation of benzene with *n*-hexane over 10-membered ring zeolites at moderate temperature, whereas it was not observed when 1-hexene was the reactant.

Alkylation of aromatics and cyclic molecules is an important chemical reaction to produce fine chemicals, dyestuffs, detergents, and scents.¹ In many industrial processes alkylation reactions are still performed in the presence of the toxic and corrosive liquids, hydrofluoric and sulfuric acids. To make alkylations more effective, environmentally friendly, and cheaper, research has been devoted to replacing liquid acids by zeolites. Today, heterogeneously catalyzed alkylation of aromatics with olefins is a well-developed process.^{2,3} Because of the fast oligomerization of olefins and subsequent catalyst coking, it is necessary to work at low olefin-to-aromatic ratios. When alkylation takes place with olefins, terminal alkylation products do not form, because the primary carbenium ion intermediate is much less stable than the secondary and tertiary ion intermediates.

Replacing alkanes by olefins in aromatic alkylation leads to reduced coke formation, enables the process to proceed at a stoichiometric aromatic/alkylation agent ratio, simplifies reactor design, decreases the cost of the feed, and may enhance catalytic stability. Because alkanes are much more difficult to activate than olefins, super acids and bifunctional catalysts are required. The synthesis of alkylaromatics from alkanes and aromatics in superacidic media⁴ and over zeolites at moderate temperature has been reported.5-15 In homogeneously catalyzed reactions, C₂–C₅ alkanes were used as alkylating agents; conversions of up to 10% were reached after six hours at ambient temperature.4 Tertiary, secondary, and primary C-H and C-C bonds underwent protolysis.¹⁶ The formation of the terminal product was explained by the reaction of protonated benzene with alkane by an alkylation-cleavage mechanism.¹⁶ The heterogeneously catalyzed aromatic alkylation with alkanes has not been studied in depth. Until now, ethane^{5,6,13-15} and propane^{6-10,12} have generally been used. Over some bifunctional Pt-7,8 and Ga-modified9,10 ZSM-5 zeolites, there was considerable conversion of propane, however, the yield was usually quite low. The rationale for using a bifunctional catalyst is to dehydrogenate the alkane on the metal and to perform alkylation by means of a carbenium ion intermediate adsorbed on the acid site of a zeolite. n-Propylbenzene was observed during the alkylation of

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benzene with propane over bifunctional catalysts, and its formation was explained by the isomerization^{6,9} of cumene and by transalkylation by a bifunctional mechanism.^{17–19}

We alkylated benzene with n-hexane over ZSM-5 and observed a significant fraction of the terminal alkylated product, 1-phenylhexane. The alkylation reaction was performed at 205 °C under autogeneous pressure in a batch reactor at a benzene-to-hexane ratio of one. After 24 h, the reaction mixture was quenched in cold water and analyzed by GC/MS. Various zeolites of different pore sizes and including a (de)hydrogenation function were compared.[†] Table 1 shows the sample characterization and the results of the alkylation reaction. Over H-ZSM-5, 20% of the n-hexane reacted. The selectivity to alkylation products was 34%, about a third of which was 1-phenylhexane. The rest of the products were cracking and multialkylated products. 3-Phenylhexane was not observed; its formation was probably suppressed by the spatial restraints in the pores of ZSM-5. For alkylation over zeolites with larger pores, such as mordenite and faujasite, considerable amounts of 3-phenylhexane were observed. No phenylhexanes were detected during the reaction without a catalyst or during reaction of pure benzene or pure *n*-hexane, indicating that phenylhexanes originate from both reactants.

To understand how 1-phenylhexane formed, the reaction was carried out over the less acidic Na-ZSM-5 and metalmodified Pt/H-ZSM-5. The Si/Al ratio, the BET surface area, and the microporosity of those samples were very similar (Table 1). The conversion of n-hexane was about 30% for both samples. This increase in conversion compared to H-ZSM-5 can be explained by increased cracking and isomerization over Na-ZSM-5 and Pt/H-ZSM-5, respectively. No alkylation products were observed over Na-ZSM-5, suggesting that acid sites catalyze the alkylation. The presence of Pt induced the isomerization of *n*-hexane, suppressed multialkylation, and increased the selectivity to 2-phenylhexane. The increase in the formation of 2-phenylhexane probably originated from the bifunctional activation of n-hexane. Reacting n-hexane and benzene over metal-free zeolites of different pore size showed that 10-membered ring zeolites (MFI, TUN) showed higher selectivity to 1-phenylhexane than 12-membered rings (MOR, FAU) (Table 1). Obviously, shape selectivity plays an important role in the formation of 1-phenylhexane.

There are a few possible explanations for the formation of terminal alkylation products, notably by (a) the formation and reaction of a primary carbenium ion on the alkane, (b) the isomerization of secondary alkylaromatics, (c) ring opening of cyclohexyl benzene, (d) transalkylation, (e) a radical mechanism, and (f) the formation and reaction of a benzenium ion (Wheland intermediate).²⁰ We performed preliminary studies

Table 1 Charac	terization and a	lkylation of	benzene with	n-hexane	over the zeolite s	samples
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Sample	Si/Al	BET surface area/m ² g ⁻¹	$V_{ m micro}/ m cm^3~g^{-1}$	Conversion (%) ^a	Selectivity (%)						
					$1 \mathrm{PH}^{b}$	$2PH^c$	$3PH^d$	CHB ^e	Isomerization ^f	Cracking	Higher ^g
H-ZSM-5	24	400	0.12	20	13	21	0	1	0	12	53
Na-ZSM-5	25	400	0.12	28	0	0	0	0	0	100	0
Pt/H-ZSM-5	25	370	0.13	30	13	37	1	1	22	15	11
H-TNU-9	8	334	0.13	22	21	2	0	0	0	76	0
H-MOR	30	508	0.18	16	3	47	10	9	0	23	8
H-Y	2.6	493	0.18	21	0	19	10	10	0	24	37
^{<i>a</i>} Conversion products.	of <i>n</i> -hex	ane. ^b 1-Phenyl	hexane. ^c 2-Pheny	dhexane. ^d 3-Ph	nenylhexa	nne. ^e Cy	clohexyl	benzene.	To methylpenta	nes. ^g Multi	alkylated

to determine the possible mechanism. The formation of a carbenium ion from the alkane requires its protonation and dehydrogenation. Alkylation with olefins is known to proceed by this intermediate. Thus, if the alkylation of benzene with *n*-hexane takes place by this mechanism, then we expect 1-phenylhexane to form during alkylation with an olefin. During alkylation of benzene with 1-, 2-, or 3-hexene, we never observed the formation of 1-phenylhexane. Furthermore, monomolecular activation of n-hexane to hexenes at 205 °C was not observed; thus, the presence of benzene aids the activation of n-hexane. The hypothesis that 1-phenylhexane forms by isomerization of 2- or 3-phenylhexane was tested by exposing H-ZSM-5 to 1-phenylhexane or to a mixture of 2- and 3-phenylhexane at 205 °C. Isomerization did not occur. To test the ring opening route, cyclohexyl benzene was reacted.[‡] No 1-phenylhexane was detected in the product mixture. Transalkylation, by which n-propylbenzene forms from cumene and benzene,¹⁷⁻¹⁹ is unlikely. We reacted a mixture of 2- and 3-phenylhexane with benzene and found that 1-phenylhexane did not form. To investigate the radical nature of the reaction, reactions were performed in the presence of potassium persulfate, iodine, and hydroxyquinone as radical scavengers or propagators. The addition of potassium persulfate and iodine did not affect the reaction significantly, whereas the addition of hydroxyquinone decreased the conversion and selectivity towards 1- and 2-phenylhexane. A decrease in radicals and poisoning of the acid sites by basic hydroxyquinone may explain this. The aromatic carbenium activation of alkane requires acid sites, which we showed to be crucial for the formation of 1-phenylhexane. The reaction of benzene alone gave biphenyl, showing that benzene is activated on the zeolite. Furthermore, hydrogen-deuterium exchange on the aromatic ring over acidic zeolites is rapid at 200 °C.²¹⁻²³ This reaction occurs by means of a benzenium intermediate, which we assume is present in the reaction mixture. The alkylation of benzene with propane by a benzenium ion has been discussed elsewhere.^{1,7,8}

Alkylation of benzene with n-hexane produced a significant amount of 1-phenylhexane, which was not observed in the alkylation with 1-, 2-, or 3-hexene, suggesting that a different mechanism is operative. The formation of 1-phenylhexane was strongly dependent on the pore size. We do not exclude the possibility of an aromatic carbenium ion activation of n-hexane. Our preliminary study suggests that further investigation of the mechanism is required.

Notes and references

† H-ZSM-5 (PZ-2/50 H) and Na-ZSM-5 (PZ-2/50 Na) were obtained from Zeochem, Switzerland. Pt/H-ZSM-5 was synthesized by wet impregnation of H-ZSM-5 with $[Pt(NH_3)_4](NO_3)_2$ solution, subsequent drying in air at 300 °C and reduction in H₂ at 250 °C. Pt loading was 2.3 wt%. The average Pt particle size was 1.6 nm. H-MOR (HSZ660HOA2) was provided by Tosoh Corp., Japan. H-Y was obtained by calcination of CBV600, obtained from Chevron. H-TNU-9 was kindly provided by Suk Bong Hong from the Hanbat National University in Taejon, South Korea.

‡ Cyclohexylbenzene was detected in the reaction mixture over some catalysts (Table 1). It was shown experimentally that it can form from benzene only.

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