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The Cracking of Cumene on HZSM-5

The cracking of cumene has served as a model reaction in the extensive studies of the nature of the active sites on HY, LaY, and amorphous Si/Al (*1–6*). It is therefore interesting to examine the effect of catalyst pore size by repeating the previous work done with HY and LaY but this time using HZSM-5 as the catalyst.

In previous studies the methodology of establishing initial reaction networks was documented and applied to many reactions (*7–11*). The method of identifying primary and secondary products has therefore been well tested and its application here to identify the mechanism of cumene cracking on HZSM-5 is consistent with previous work.

EXPERIMENTAL

The experimental apparatus and procedures have been described in previous publications (*7, 14*).

The HZSM-5 was prepared by the method described by patent (*12*) and repeatedly exchanged using 1 *M* ammonium nitrate solution at 80°C followed by calcination at 520°C for 2 h after the final exchange. Particles of 100–140 mesh were sieved out and used in the reactor in a mixture with crushed glass of 60–80 mesh.

The HZSM-5 was found to have a Si/Al ratio of 37 and a sodium content of <0.2 wt%. X-Ray diffraction patterns identical to those reported for ZSM-5 (*13*) were obtained with our preparation.

Cumene supplied by Aldrich Co. was purified through silica–alumina column to remove traces of hydroperoxide. All runs were done at ambient pressure and at 430°C over a range of times on stream and catalyst/oil ratios.

RESULTS

We were able to detect minute quantities of α-methyl styrene and methane in our blank run with our newly improved chromotographic methods. We have therefore performed blank runs and subtracted yields from those runs from the yields of catalytic runs. These residual catalytic yields show that propylene, *n*-propyl benzene, and "coke" are the only primary products of cracking of cumene on HZSM-5. "Coke" is defined here as the material which remains on the catalyst surface after a post reaction stripping purge with nitrogen for 30 min at the reaction temperature. Product initial selectivities and characterizations are reported in Table 1.

Secondary products are shown in Table 2. Most of the secondary products are olefins although trace amounts of aromatics were detected. No olefins whose molecular weight is higher than C_6 were found in the products.

DISCUSSION

We see from the results that the cracking of cumene on HZSM-5 is much more selective than it is on LaY. The primary products on HZSM-5 are only those which can form by monomolecular reaction, i.e., benzene and propylene by cracking and *n*-propyl benzene by internal rearrangement. All primary products due to bimolecular process are prevented from forming on HZSM-5 by the steric constraints of the small pores.

In the case of cumene cracking on LaY a "corrected" initial benzene selectivity had to be calculated by accounting for the excess benzene produced by disproportiona-

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TABLE 1

Selectivities of Primary Products

Catalyst:	HZSM-5		LaY	
	Product type[a]	Selectivity	Product type[a]	Selectivity
Reaction Products				
Benzene	1S	0.96	1S	0.870[b]
Propylene[c]	1U	0.96	1U	0.870
n-Propyl benzene	(1+2)S	0.028	(1+2)S	0.0031
"Coke" (adsorbed C_3H_6)[d]	(1+2)S	0.010		—
Cymene		—	1S	0.0033
m-Diisopropyl benezene		—	1U	0.0335
p-Diisopropyl benezene			1U	0.0199
i-Butene		—	(1+2)S	0.0040
n-Butene		—	(1+2)S	0.0048
Total (aromatic)		0.998		1.0041

[a] 1, Primary product; 2, secondary product; S, stable product; U, unstable product.

[b] Corrected benzene selectivity.

[c] Redundant value. Equal to benzene selectivity.

[d] Molar selectivity.

TABLE 2

Secondary Products

	Product	HZSM-5	LaY
Major quantities	Methane	Yes	Yes
	Ethylene	Yes	Yes
	Ethane	No	Yes
	Propane	Yes	Yes
	n-Butane	No	Yes
	i-Butane	No	Yes
	i-Butene	Yes	Yes (primary)
	cis-2-Butene	Yes	N/A
	trans-2-Butene	Yes	N/A
	Residue (coke)	Yes (primary and secondary)	Yes
Trace quantities	1-Pentene	Yes	No
	2-Methyl 1-butene	Yes	Yes
	2-Methyl 2-pentene	Yes	Yes
	2,3-Dimethyl 1-butene	Yes	No
	4-Methyl 2-pentene	Yes	Yes
	2-Methyl 1-pentene	Yes	No
	3-Methyl 2-pentene (*cis* and *trans*)	Yes	Yes
	2-Hexene	Yes	No
	Toluene	Yes	Yes (major secondary)
	Ethyl benzene	Yes	Yes (primary)
	Styrene	Yes	No

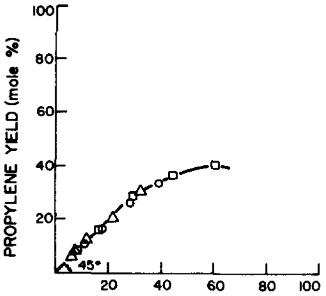

FIG. 1. Propylene vs Benzene yields in cumene cracking on HZSM-5.

tion reactions (*7*). This procedure is not necessary here and a plot of propylene yield vs benzene yield shown in Fig. 1 shows that up to ~30% conversion the two are equal. After this, a shortage of propylene is observed due to secondary reactions. Such reactions yield the C_1 to C_6 products shown in Table 2. It was found that the secondary products of propylene dimerization-cracking reactions and the tertiary products produced by oligomerization of secondary products are more plentiful on HZSM-5 than on LaY. We attribute this observation to the fact that the small pores of HZSM-5 encourage the dimerization of propylene molecules which are small enough to achieve the necessary transition state inside the HZSM-5 pores.

Most of the secondary products we observed are olefins although it has been reported that olefins readily form aromatics by dehydrocyclization and hydrogen transfer on HZSM-5 (*16*). This may be due to the Si/Al ratio of HZSM-5 used in our reaction (Si/Al = 37) which is higher than that of catalysts reported (*16*) to facilitate such reactions.

The selectivity for cracking on HZSM-5 is overall somewhat higher than on LaY mainly because no bimolecular process take place on this catalyst. However, there is a remarkable tenfold increase in selectivity for rearrangement to *n*-propyl benzene which deserves note. In previous publications we have postulated that this process occurs on Lewis sites (*7*). This explanation can also serve here and the fact that the selectivity is so much higher for *n*-propyl benzene is therefore either due to a higher proportion of Lewis sites in HZSM-5 than in the Y catalyst or due to some steric advantage in the rearrangement of isopropyl benzene to *n*-propyl benzene within the narrow confines of the ZSM-5 pore. At this time we are unable to say which of the two is the probable cause.

A major and significant difference in HZSM-5 and LaY behavior is the fact that the "coke" on HZSM-5 is a primary product whereas on LaY (*7*) and HY (*15*) the residue which was designated as coke was secondary. Figure 2 shows the HC/ratio of the coke as a function of conversion. Due to the nature of the analysis and the very small yield the data are scattered. Nevertheless we observe a decrease in the H/C ratio with increasing conversion and obtain the extrapolated value of ~1.9 at zero conversion. This falls between the ratio in cumene (1.4) and that in propylene (2.0) and closer to that of pure olefins.

In cumene cracking on LaY and HY (*14, 15*) coke was found to be formed from side chain carbons. It appears that here the same is true except that dehydrogenation is less effective and there may well be some trapping of benzene rings behind residue "plugs" in the small pore structure.

On the assumption that there is no dehydrogenation and all the residue formed consists of oligomerized propylene (H/C = 2) and some trapped benzene (H/C = 1.0), molar selectivity of propylene and benzene

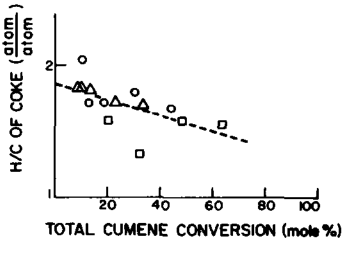

FIG. 2. H/C ratio in residue formed in cumene cracking on HZSM-5.

in the residue can be calculated as 0.010 and 0.00057, respectively. This shows that there are only about 5 molecules of benzene per 100 molecules of propylene in the residue, confirming the previously identified provenance of coke (*14*) in this reaction, namely propylene.

The high H/C ratio of the residue also suggests that hydrogen transfer is less likely on this catalyst than on Y catalyst, perhaps because of a lower site density.

CONCLUSION

Our study of cumene cracking on HZSM-5, combined with previous studies of the same reaction on HY and LaY, confirms that the pore structure of HZSM-5 has a profound influence on the course of the various reactions cumene is known to undergo on acid catalysts.

Only monomolecular reactions of cumene occur on HZSM-5. Diisopropyl benezenes are not formed at all and neither is cymene. We conclude that the cumene molecule is too large to form the bimolecular transition state necessary for disproportionation on HZSM-5.

At the same time propylene dimerizes and cracks in the pores of HZSM-5. This linear molecule can clearly achieve the transition state necessary for dimerization and thereafter follows a cracking mechanism similar to that which has previously been reported for other olefins on this catalyst.

In the course of propylene oligomerization some species become attached in a way which precludes diffusion out of the pores. These exist in a dynamic steady state involving cracking and polymerization with an occasional dehydrogenation event contributing to the coking reaction. The result is that the coke formed in HZSM-5 is initially made up of almost pure propylene oligomer and becomes dehydrogenated as time on stream is increased.

It should be noted that the "coke" oligomer is unlikely to be a long chain since there is no detected trace of olefins higher than C_6. It seems that the "coke" here is simply strongly adsorbed propylene or at best its dimer.

At this point all the observed differences between the behavior of HZSM-5 and HY or LaY can be ascribed to pore structure, confirming the shape selective nature of HZSM-5 without invoking any new phenomena or changing our view that the nature of the active sites on this catalyst is the same as that of the active sites in HY, LaY, and amorphous Si/Al.

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