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Dehydrocyclodimerization

I. Dehydrocyclodimerization of Butanes over Supported Platinum Catalysts

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Dehydrocyclodimerization is a new process converting C_3–C_4–C_5 paraffins to aromatics. The reaction is carried out at temperatures over 430°C by dual-functioning catalysts having dehydrogenation and acid-type activities. Platinum on acidic alumina is a suitable catalyst. The aromatics formed from butanes are principally xylene and toluene with smaller quantities of benzene and C_9 and C_{10} aromatics. With strong acidic catalysts, product distribution obtained from iso- and *n*-butanes is the same. Ethylbenzene and styrene are the predominant C_8 aromatics formed from *n*-butane over weakly acidic catalysts.

Dehydrocyclodimerization is a new catalytic process which converts light (C_3–C_4–C_5) paraffins to aromatics. The reaction is quite different from the well-known dehydrocyclization reaction in which C_6 and higher paraffins are converted to aromatics containing the same number (or less) carbon atoms than those in the feed. In dehydrocyclodimerization the product aromatics always contain more carbon atoms than the reactant paraffins. Here we describe the main features of the dehydrocyclodimerization reaction of butanes.

Dehydrocyclodimerization is carried out above 430°C over acidic dehydrogenation catalysts. The reaction is favored by high temperatures. Equilibrium constants for the reaction;

$$2 \text{ isobutane} = p\text{-xylene} + 5H_2,$$

are 16.23 at 427°C and 1.225×10^4 at 527°C [calculated from Rossini and coworker's data (*1*)]. Because the equilibrium concentration of aromatics is inversely proportional to the fifth power of the hydrogen concentration, the reaction is carried out without hydrogen dilution. However, without hydrogen present, the rate of coking is high. Coking deactivates the catalyst, requiring frequent regenerations. Operation is cyclic; dehydrocyclodimerization, regeneration, purging, and reduction cycles follow each other.

EXPERIMENTAL METHODS

Apparatus

The apparatus consisted of the feed system, the reactor, and the product traps. Reaction-effluent samples were withdrawn with a Beckman sampling valve for gas chromatographic analyses. The reactor was a 46-cm long, 6.35-mm o.d. stainless steel tube with Swagelok fittings on each end. In most experiments, the reactor held 1.3 or 2.6 ml of catalyst. Alundum was used to fill the space below and above the catalyst. A separate reactor was made for each catalyst sample.

Analytical Apparatus

Gas samples were withdrawn several times during each experiment for gas chromatographic analyses. Each time two analyses were carried out with the use of separate columns in different instruments. A 6.1-m long column with 33% dimethylsulfolane on GC 22 support was used at room temperature for the detailed analyses of C_1–C_5 hydrocarbons. Aromatics were analyzed on a 6.1-m long column with 15% polar silicone on Gas Chrome P support. This column was operated with a programmed temperature rise of 42°C/min between 24 and 140°C. The C_1–C_5 hydrocarbons on this column were combined into five poorly separated peaks. A 10.7-m foot long column with 15% Carbowax 20M on 42/60 mesh GC 22 Sil-O-Cel firebrick support was also used for some of the analyses. This column was temperature programmed between 65 and 190°C with a temperature rise of 42°C/min. The Carbowax column resolved most of the C_1–C_5 hydrocarbons but retained the aromatics boiling above the trimethylbenzenes. Relative retention times of the different hydrocarbons over the dimethylsulfolane and Carbowax columns have been given by Csicsery and Pines (*2*).

Reaction product analyses were based on data obtained over the polar silicone or Carbowax columns, unless otherwise specified. Distribution of the C_1–C_5 hydrocarbons and isobutylene/*n*-butene ratios were calculated from the data obtained over the dimethylsulfolane column. Because isobutylene and 1-butene peaks were poorly separated, the amount of 1-butene had to be determined from the amount of the other *n*-butene isomers, assuming complete equilibration between the double-bond isomers. The equilibrium values used in the calculation at 560°C were: 32% 1-butene, 29% *cis*-2-butene, and 39% *trans*-2-butene. In some cases, propylene and isobutane were poorly resolved. Concentrations of these two hydrocarbons are combined in such experiments.

Occasionally some compounds had to be identified and determined from analyses of the liquid products. Liquid reaction products were collected in a Dry Ice–acetone-cooled condenser and then analyzed by a combination of vapor-phase chromatography and mass spectroscopy. Certain samples were hydrogenated after passing from the detector of the gas chromatograph to the mass spectrometer. Molecular structures were obtained from the mass spectra of the hydrogenated hydrocarbons. Spectra of the unsaturated compounds revealed molecular weights. The number of double bonds was calculated from the mass gain after hydrogenation. Double-bond positions were not determined. A 15-m long, 6.35-mm o.d. copper gas chromatographic column containing 20% Carbowax 1000 on 42/60 mesh GC 22 firebrick was used with H_2 carrier gas (60 ml/min flow rate). The hydrogenation was done at 254°C over 0.7% platinum-on-silica catalyst. A Consolidated Electrodynamics Corporation Model No. 21-103 mass spectrometer was used. Higher (C_{12}–C_{20}) aromatics were determined by low voltage mass spectroscopy.

"Coke" values were obtained either from the carbon content of used catalysts or from the CO_2 content of the regeneration offgases. Carbon dioxide was analyzed by absorption on known weights of Ascarite.

Hydrogen yields were calculated from coke and hydrocarbon product analyses. Mass spectroscopic analyses of the reaction offgases indicated a fair agreement between calculated and observed hydrogen values.

Procedure

The catalysts were ground to 20/60 mesh size. Catalyst pretreatment consisted of 1-hr heating in hydrogen at 370°C and another hour at the temperature of the experiment. The hydrogen flow was stopped when the hydrocarbon feed was started. Experiments varied from 1 min to several hours long. Depending on the length of the experiment, several reaction-effluent samples were taken for gas chromatographic analyses. In 90-min experiments, the samples were taken at 10- and 75-min onstream times. Reaction exit gas rates were measured at the same time. After the hydrocarbon feed was turned off, the reactor was purged for 30 min with hydrogen. If the catalyst was not regenerated, the reactor was removed and the catalyst was submitted for carbon analysis. Metal oxide catalysts were regenerated repeatedly. The regeneration was done with a 1:1 air:nitrogen mixture. The exit gases were checked by gas chromatography for CO_2 content. The regeneration was discontinued when the exit gas did not contain any more CO_2. The regeneration was followed with a 3-min purge with hydrogen at the temperature of the next experiment. Between the hydrogen and air cycles, the reactor was purged for 2 to 5 min with an inert gas (helium).

Ultimate recycle yields ("Yields") were calculated assuming that all C_3–C_4–C_5 hydrocarbons are recycled:

$$\text{Yield (wt \%)} = \frac{\text{aromatics (wt \%)}}{\text{aromatics} + CH_4 + C_2 + H_2 + \text{coke (wt \%)}}.$$

Materials

n-Butane (Phillips, instrument grade) 98.1% pure, contained 1.3% isobutane, 0.05% propane, and 0.05% ethane.*

Isobutane (Phillips, instrument grade) 99.36% pure, contained 0.1% *n*-butane and 0.54% propane.*

Catalysts

Pure aluminas were prepared from either hydrolyzed aluminum isopropoxide (HAI) or potassium aluminate (KA), as described by Pines and Haag (*3*). The eta-alumina used was manufactured by the Davison Chemical Division of W. R. Grace and Company. Chloride-containing platinum–alumina catalysts were prepared by impregnating the different aluminas with solutions of H_2PtCl_6. Chloride-free catalysts were obtained using either $[Pt(NH_3)_4](NO_3)_2$ or $[Pt(NH_3)_2(NO_2)_2]$ complexes. The impregnated catalysts were dried overnight at 150°C in a helium stream, then reduced in dry H_2 1 hr each at 370 and 560°C. Pt–silica–alumina was similarly prepared on a 72:28 silica–alumina support. Platinum surface areas were determined according to the method of Hughes *et al.* (*4*).

RESULTS AND DISCUSSION

The main products of the reaction of isobutane over an 0.8% Pt–alumina at 560°C as a function of space velocity are shown in Fig. 1. Conversion to aromatics is substantial. Other reaction products are butenes, butadiene, C_5 and higher aliphatics and naphthenes, methane, C_2 and C_3 hydrocarbons, hydrogen, and coke.

Figure 1 shows the rapid dehydrogenation to butenes which reach a maximum concentration at about 1.5-sec contact time. The concentration of aromatics increases more gradually. The concentration of butene plus aromatics reaches a maximum value

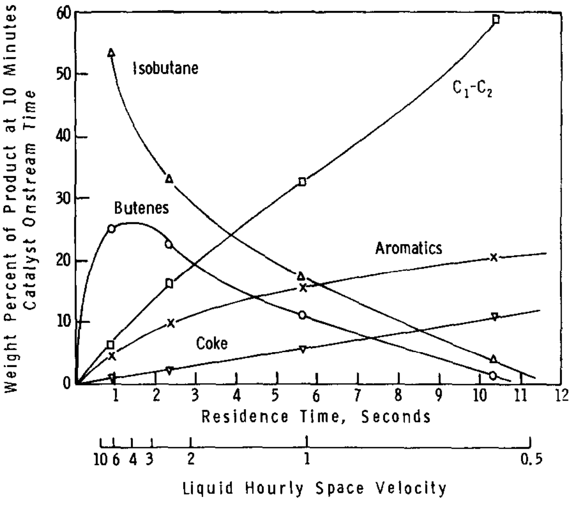

FIG. 1. Effect of space velocity on product composition in the dehydrocyclodimerization of isobutane at 560°C over 0.8% platinum-on-alumina catalyst.

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* Mass spectrographic analysis.

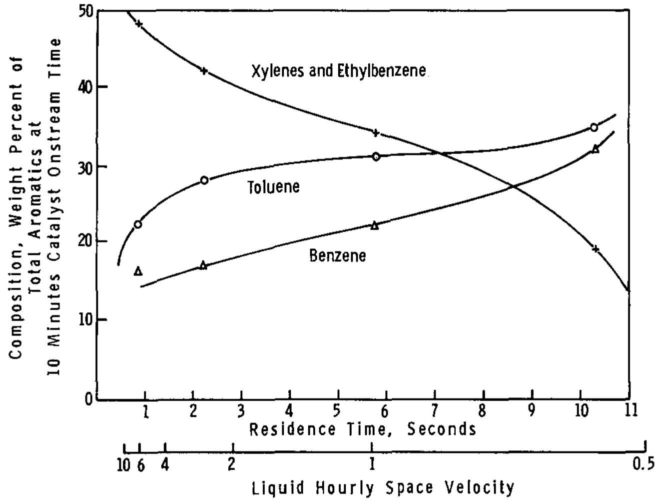

FIG. 2. Effect of space velocity on the composition of aromatics produced in the dehydrocyclodimerization of isobutane at 560°C over 0.8% platinum-on-alumina catalyst.

(about 32%) at about 2.3-sec residence time. The shapes of the butene curve and of the aromatic curve are characteristic of consecutive reactions in which the aromatics are formed from butene intermediates. Coking and cracking increases nearly linearly with residence time. At 11-sec residence time, excessive cracking converts all feed and the previously produced other aliphatics to methane. Skeletal isomerization of the butenes is fast. At 0.9-sec residence time, the isobutylene/*n*-butenes ratio is 0.84. At longer contact times, this ratio approaches the equilibrium value (0.73).

The change in composition of the aromatics fraction is shown in Fig. 2, which indicates that xylenes and ethylbenzene are the major aromatics produced at short residence times. At longer residence times,

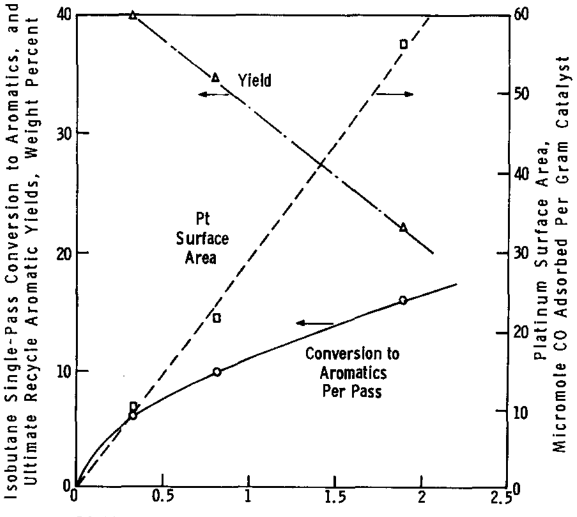

FIG. 3. Effect of platinum concentration of Pt-alumina catalysts at 560°C, 1 atm total pressure, and with an LHSV of 2.5 at 10 min onstream time.

TABLE 1

DEHYDROCYCLODIMERIZATION OF ISOBUTANE OVER PLATINUM ALUMINA CATALYSTS AT 560°C AND 1 ATM WITH AN LHSV OF 1

Catalyst support	Davison eta-alumina			Alumina from HAI	Alumina from K-aluminate[d]
Platinum concentration (wt %)	0.5[a]	0.5[b]	0.5[c]	0.8[c]	0.98[c]
Platinum surface area (μmole CO/g)	17.8	13.8	18.3	Not measured	17.6
Chloride concentration	0.5	0	0	0	0
Product composition (wt %)[e]					
Unreacted isobutane	17.9	43.4	56.4	18.5	72.4
n-Butane	8.4	3.8	1.4	3.9	
Butenes	14.2	16.1	12.3	19.0	19.2
Butadiene	0.4	0.3	0.3	0.4	
Pentenes, pentadienes, and higher olefins	0.3	0.3	0.3	0.3	
Methane	11.0	7.9	6.0	19.5	4.4
Ethane, ethylene	6.4	3.1	2.1	7.3	0.1
Propane, propylene	12.4	7.6	5.2	9.5	1.1
Hydrogen	2.3	1.6	1.5	1.0	0.55
Total aromatics	22.4	12.0	10.0	15.5	0.95
Composition of C_5 + fraction (wt %)[f]					
Methylbutenes	1.35	5.9	6.7	6.0	3
n-Pentenes	0.68	2.8	3.6	1.9	
Isoprene	0.22	1.4	1.2	1.3	1
n-Pentadienes	0.31	1.4	1.1	1.1	
Cyclopentane	0.07	0.2	0.1	0.2	
Cyclopentene	0.20	0.5	0.7	0.5	
Cyclopentadiene	0.30	1.4	0.9	1.9	3
Hexenes	0.11	0.7	0.6	0.3	
Hexadienes	0.20	0.5	0.7	0.3	
Methylcyclopentenes	0.20	0.5	0.5	0.3	
Methylcyclopentadienes	0.25	1.2	0.5	0.6	1
Heptenes, C_7 naphthenes	0.08	0.7	1.0	0.3	
Octenes, C_8 naphthenes	0.33	0.2			
Benzene	11.50	17.7	15.5	24.6	47
Toluene	28.63	23.6	20.0	17.7	3
Ethylbenzene	2.72	2.1	1.2	1.6	
o-Xylene	9.75	5.7	3.2	3.9	
m-Xylene	23.64	20.5	11.8	15.0	
p-Xylene	6.93	5.5	3.4	4.3	
Styrene	0.80	0.5	0.3	0.3	
Propylbenzenes	0.43	0.2	0.7	0.2	
Methylethylbenzenes	1.39	1.0	0.7	0.3	
Trimethylbenzenes	3.05	2.1	1.0	0.8	
Methylstyrenes	0.35	0.2	0.1		
Indan	0.13	0.2	0.3	0.2	
Indene	0.68	0.4	0.7	0.3	

TABLE 1 *Continued*

Catalyst support	Davison eta-alumina			Alumina from HAI	Alumina from K-aluminate[d]
Platinum concentration (wt %)	0.5[a]	0.5[b]	0.5[c]	0.8[c]	0.98[c]
Platinum surface area (μmole CO/g)	17.8	13.8	18.3	Not measured	17.6
Chloride concentration	0.5	0	0	0	0
Tetramethylbenzenes	0.41	0.7	0.2		
Other C_{10} alkylbenzenes	0.33	0.5	0.6	0.2	3
Methylindans	0.22	0.5	0.7	0.3	
Naphthalene	2.66	0.7	4.1	3.2	35
Methylnaphthalenes	2.08	0.5	4.1	3.2	1
C_{12}–C_{24} Polycyclic aromatics	Not analyzed		13.6	9.2	3
Coke[g]	4.3	3.9	4.5	5.1	1.3
Yield of aromatics (wt %)[e]	49	42	41	32	13
Isobutylene/*n*-Butenes[e]	0.85	1.64	1.43	2.3	38
Methylbutenes/*n*-pentenes[f]	2	2	2	3	∞
Isoprene/*n*-pentadienes[f]	0.7	1	1.1	1.1	∞

[a] Made from H_2PtCl_6.

[b] Made from $[Pt(NH_3)_2(NO_2)_2]$.

[c] Made from $[Pt(NH_3)_4](NO_3)_2$.

[d] Contains 3.78% potassium.

[e] From reaction-effluent sample analyses at 10-min sampling times.

[f] From liquid product analyses.

[g] Coke was calculated from the carbon content of the used catalyst.

[h] "Yields" were calculated assuming that all C_3–C_4–C_5 hydrocarbons are recycled.

most of the alkylbenzenes are dealkylated. Small quantities of C_9–C_{10} alkyl aromatics and traces of polycyclics are also formed.

Dehydrocyclodimerization of *n*-butane under comparable conditions gives a similar product distribution to that shown in Table 1 for isobutane.

Effect of Platinum Content

The effects of platinum concentration on isobutane conversions and yields are shown in Fig. 3. Platinum surface areas are roughly proportional to platinum concentrations. Conversions to aromatics increase, but ultimate recycle yields decrease with increasing platinum concentration because cracking is high at high Pt levels. Although optimum platinum concentration may depend on the nature of the support, the space velocity, and other process variables, under our conditions it appears to be around or below 0.8%.

Effect of Catalyst Acidity

Catalyst acidity has a strong effect on dehydrocyclodimerization conversion. Since the isobutylene $\rightleftharpoons$ *n*-butenes reaction is acid catalyzed, we used the ratios of isobutylene to *n*-butenes produced from isobutane to rank catalysts. The more acidic a catalyst, the closer equilibrium between isobutylene and the *n*-butenes is approached. Now, the lowest ratio observed with isobutane feed at 560°C is around 0.75; whereas, with *n*-butane the highest ratio is 0.71. The equilibrium ratio probably falls midway between these two values, at about 0.73. [The value calculated from Rossini's data is 0.786 (*1*).]

The relative acidities of the different catalysts (a) depend on the acidity of the support, (b) increase with chloride content, and (c) may be influenced by interactions between the support and the metal or metal oxide. To study these effects, three catalysts containing 0.5% Pt on eta-alumina were made. Different Pt complexes were used in the preparation of each sample (Table 1). Conversions and yields to aromatics are about twice as high over the catalyst containing chloride than over the others. The isobutylene/*n*-butene ratio is 0.85 over the chloride-containing catalysts versus 1.4–2 over the other two samples, showing that the chloride-containing catalyst is significantly more acidic.

The acidity of aluminas may depend on the method of preparation. Alumina made from hydrolyzed aluminum isopropoxide (HAI) has relatively strong acidity, as shown by Pines and Haag (*3*). Alumina prepared from potassium aluminate (KA) usually has very weak acidity (*3*). Catalysts prepared by impregnating $[Pt(NH_3)_4](NO_3)_2$ on these two aluminas are compared in Table 1. Dehydrocyclodimerization conversion is about 16 times higher over the catalyst made from HAI alumina than over the one prepared from KA alumina. Isobutylene/*n*-butenes ratios are 2.3 versus 38, respectively.

Over the catalyst made from KA alumina (containing 3.78% K), benzene is the predominant aromatic hydrocarbon formed (77% of all aromatics at 10-min onstream time). This is rather surprising. The crude correlation between the relative amounts of benzene and propane plus propylene observed over other catalysts suggests benzene as the initial product of the dehydrocyclodimerization of propane. Due to the low C_3 level in this experiment (1%), this route is unlikely here. Over this catalyst, benzene (and toluene) are probably formed from demethylation of xylenes catalyzed by potassium ions.

When potassium is removed from KA alumina by repeated washings, the catalyst exhibits reasonably strong acidity. As the potassium is reduced from 3.78 to 0.003%, the conversion to aromatics increases from 0.9 to 19 wt %.

Mixtures of Dehydrogenation and Acid Catalysts

The importance of catalyst acidity was outlined above. Here we show that dehydrogenation and acid sites need not be present on the same catalyst particle. As Table 2 shows, aromatic production is higher over 1:3 mixtures of Pt–alumina and acidic alumina or silica–alumina than over Pt–alumina alone. These "physical mixtures" are prepared by mixing 20/60 mesh size particles with each other. Note that the sum of the amounts of butenes, butadienes, and aromatics is approximately the same over the three catalysts. The added acid component helps convert bu-

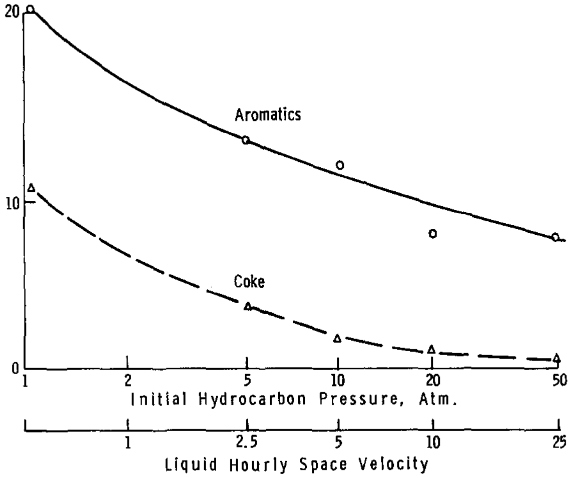

FIG. 4. Effect of hydrocarbon pressure on the dehydrocyclodimerization of isobutane over Pt(0.8%)–alumina at 560°C with a constant residence time of 11 sec.

TABLE 2

DEHYDROCYCLODIMERIZATION OF ISOBUTANE OVER CATALYST MIXTURES AT 560°C WITH A FEED RATE OF 2.6 ml LIQUID FEED/HR

Wt of dehydrogenation-component (0.8% Pt-Al_2O_3) (g)	0.42	0.42	0.42
Acid component	None	Alumina	Silica–alumina
Wt of acid component (g)	—	1.26	1.26
Aromatics produced at 10-min onstream time	10.8	19.8	20.3
Butenes and butadiene at 10 min	22.1	14.5	9.0

tenes to aromatics, but the rate of butane dehydrogenation is not increased.

Effects of Hydrogen and Hydrocarbon Pressure

Yields and conversions to aromatics are significantly reduced in the presence of hydrogen diluent because of increased hydrogenolysis. For example, over Pt–alumina at 10-min onstream time, 85% of the butane is converted to methane; and a large fraction of the aromatics is demethylated (Table 3).

Pressure effects were studied between 1 and 50 atm and without a diluent gas. At a constant residence time, the fraction of isobutane converted to aromatics decreases with increasing hydrocarbon pressure (Fig. 4). Other changes observed with increasing pressure are:

TABLE 3

DEHYDROCYCLODIMERIZATION OF *n*-BUTANE DILUTED WITH H_2 OVER Pt(0.8%)–ALUMINA AT 560°C AND AT AN LHSV OF 0.4 (H_2/*n*-BUTANE MOLE RATIO = 1.27)

Reaction effluent sampling time (min)	10	20	67
Product composition (wt %)			
n-Butane			3.1
Isobutane and propylene		1.3	7.1
Butenes and butadiene		0.03	5.3
Pentenes and pentanes			0.2
Benzene	6.9	5.0	3.1
Toluene	0.2	3.5	3.4
Xylenes and ethylbenzene		1.2	3.0
Methane	85.3	54.4	32.8
Ethane, ethylene		25.2	23.7
Propane		1.8	10.7
Coke	←	7.6	→
Ultimate recycle yield (wt %)	7	10	13

The rate of aromatization (as milligrams of isobutene converted per minute per gram of catalyst) increases (Fig. 5).

Cracking rates (milligrams of cracked per gram of catalyst per minute) increase

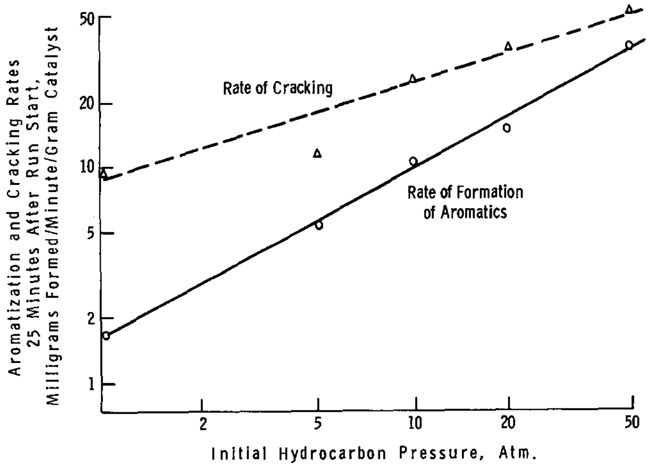

FIG. 5. Effect of hydrocarbon partial pressure on the rates of formation of aromatics and cracking from isobutane at a constant residence time of 11 sec at 560°C over Pt (0.8%)–alumina.

also. However, cracking is less affected than aromatization.

The $C_3/(C_1 + C_2)$ ratio changes from 0.2 to 1.4 between 1 and 50 atm, indicating a change in the mechanism of cracking.

Butane/butenes, butenes/butadiene, and pentane/pentenes ratios increase.

CONCLUSIONS

Butanes are converted to aromatics over Pt–alumina catalysts. The principal aromatics are xylenes and toluene. Benzene and C_9 and C_{10} aromatics are also formed. With strong acid catalysts iso- and *n*-butanes give a similar product distribution. Over a weakly acidic catalyst *n*-butane forms predominantly ethylbenzene and styrene, and *p*-xylene forms isobutane.

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