JOURNAL OF CATALYSIS **131**, 305–318 (1991)

# Simultaneous Polymerization and Oligomerization of Acetylene on Alumina and Fluoridated Alumina Catalysts

V. M. ALLENGER, D. D. MCLEAN,* AND M. TERNAN

*Energy Research Laboratories, CANMET, Energy, Mines and Resources, Canada KlA OGl; and*
**Department of Chemical Engineering, University of Ottawa, Ottawa, Canada KlN 9B4*

Received November 8, 1989; revised May 10, 1991

The products of the reaction of acetylene over solid acid catalysts are gases, liquids, and solids at reaction conditions. Since the products of the reaction range from low to high molecular weight polymers the process is a combination of oligomerization and polymerization. This paper reports on the product selectivities measured in a fixed-bed continuous flow reactor using a series of fluoridated alumina catalysts (0 to 4.3 wt% F) under various reaction conditions (300 to 400°C, 1 to 3 g s $ml^{-1}$, 5 to 15 mol% $C_2H_2$ in $N_2$). A comparison of the liquid product distributions in the transformation of acetylene without catalysts, over fluoridated alumina catalysts (this work) and over the ZSM-5 zeolite, revealed that the noncatalytic and catalytic product distributions did not correspond to equilibrium conversion. A mechanism is proposed for the catalytic conversion of acetylene based on our experimental observations. The mechanism involves cationic chain growth polymerization leading to both linear and cyclic products. The initiation, propagation, transfer, and termination steps are discussed. The mechanism implies two requirements for promoting the cyclization reaction. First, a sufficient number of acidic sites must be present on the catalyst surface to initiate a polymeric chain. Second, an appropriate distribution of acid sites on the catalyst surface must exist to promote the transfer reaction. A fine balance is desired between the number of sites on the catalyst surface responsible for initiation and those responsible for isomerization of the active center on the growing chain. Therefore, although alumina and fluoridated alumina are both good initiators for acetylene oligomerization reactions, the yields of aromatic products, e.g., benzene, toluene, and xylene, are lower with the fluoridated alumina catalyst since the possibility for rearrangements of the growing chain on the catalyst surface is lower.

## INTRODUCTION

The transformation of acetylene to higher molecular weight hydrocarbons must involve polymerization. Polymerization reactions of unsaturated hydrocarbons are believed to be acid-catalyzed (*1*). Alumina ($Al_2O_3$) has been used extensively as a catalyst and catalyst support for acid-catalyzed reactions such as isomerization, alkylation, and polymerization. Furthermore, fluoridation of alumina has been shown to be an effective means to alter its acidic properties and to enhance the polymerization of olefins, conjugated dienes (*2*), and acetylene (*3*).

In a previous article (*3*), we reported the high catalytic activity of a series of fluoridated alumina catalysts in the polymerization of acetylene. The products in this reaction are gases, liquids, or solids at reaction conditions. Since the products of the reaction range from low to high molecular weight polymers ($C_6$ to $C_n$), the process is a combination of oligomerization and polymerization. The term oligomerization is applied to the reactions that yield either cyclic compounds or very low molecular weight products. The term polymerization, on the other hand, is confined to describing reactions in which long, linear, or branched chains are produced.

Solid acid catalysts used to date for this reaction show severe deactivation (*4–7*). In a previous article (*4*) we reported a correspondence between the deactivation phenomenon and the ratio of aliphatic carbon to aromatic carbon in the solid reaction

0021-9517/91 $3.00

product. Three types of deposits were identified over these catalysts and it was suggested that one of these was responsible for loss in catalytic activity. The solid product appeared to be the heavy end of a continuum of products found in these reactions of acetylene over amorphous alumina catalysts. In this paper we report on the significant differences in the product selectivities brought about by changes in reaction conditions and in catalyst acidity.

A mechanism for the catalytic cyclization of acetylene to aromatic compounds, particularly benzene over solid oxides, has not yet been elucidated. The high reactivity of acetylene makes it susceptible to polymerization by anionic, cationic, or free-radical processes. Both anionic and cationic initiations have been used to produce polymers from acetylene (*8*, *9*). Based on reaction studies over amorphous fluoridated alumina, we propose a reaction mechanism in which oligomerization and polymerization occur simultaneously, the former leading to desirable products, the latter to solid product and subsequent loss in catalyst activity.

## EXPERIMENTAL

A series of fluoridated alumina catalysts was used for this study. The alumina support was impregnated with appropriate amounts of ammonium fluoride to give four catalysts containing between 0 and 4.3 wt% fluoride. The catalyst preparation procedures have been described elsewhere (*3*). Catalyst acidity (as measured by ammonia adsorption at 350°C) was found to be a complex function of the fluoride content of the catalyst. The highest acidity was exhibited by the catalyst containing 2.6 wt% F while pure alumina showed the lowest acidity.

As described earlier (*3*), reaction experiments were carried out in a tubular continuous-flow quartz reactor at atmospheric pressure and between 300 and 400°C. The concentration of acetylene in the feed gas stream varied between 5 and 15 mol%, the balance being nitrogen. The weight–time or inverse space velocity, based on weight of catalyst, was calculated at reaction conditions. Preliminary experiments showed that whether the weight of catalyst or flow rate of reactants were changed to achieve values of weight–time between 0.5 and 3 g s $ml^{-1}$, the performance results were unchanged. Product analysis was accomplished by packed column gas chromatography (light hydrocarbons) and capillary column chromatography (liquids up to 300 molecular weight). These analyses were carried out off-line by storing product gas samples in 16-port gas sampling valves. The samples were not stored for a long period of time and they were analyzed sequentially immediately after reaction. Analysis of the gas samples stored in the multiloop valves was carried out using a Carle AGC 111 Series S chromatograph equipped with a thermal conductivity detector. This chromatograph was specially configured (columns and microvalve switching) for light gas analysis, i.e., alkanes ($C_1$–$C_5$), alkenes ($C_2H_4$, $C_3C_6$), and alkynes ($C_2H_2$). Analysis of the liquid product was carried out using a Varian Vista 6000 equipped with an open-split capillary injector and flame ionization detector. Instantaneous samples of the liquid product were kept in heated sample loops and analyzed sequentially immediately after reaction. A 0.25-mm-i.d., 0.25-$\mu$m film DB-5 capillary column 30 m long was used for these analyses. A Spectra Physics 4270 integrator was used to measure peak areas and retention times on both chromatographs. A complete description of this system was given by Allenger *et al.* (*10*). Analysis of the liquid samples was also done by mass spectrometry using a Finnigan Model 700 ion trap detector. Mass spectrometric analysis assisted in fingerprinting product components.

## RESULTS

### *Product Yields*

More than 75% of the experiments were within 100 ± 35% closure of the material balance at 15 min on stream. This was

TABLE 1

Product Yields in the Tubular Reactor

| Operating conditions | Conversion (%) | Product yields[a] (%) | | |
|---|---|---|---|---|
| | | 15 min | | 60 min |
| | | Liquid | Gaseous | Solid[a] |
| | $Al_2O_3$, 2 g s ml$^{-1}$, 10% $C_2H_2$ | | | |
| 400°C | 98.1 | 90.1 | 8.8 | 28.5 |
| 300°C | 28.8 | 7.5 | 0.8 | 8.8 |
| | $Al_2O_3$, 350°C, 10% $C_2H_2$ | | | |
| 3 g s ml$^{-1}$[b] | 87.2 | 66.4 | 3.0 | 33.5 |
| 1 | 29.2 | 17.7 | 1.4 | 11.6 |
| | $Al_2O_3$, 2 g s ml$^{-1}$, 350°C | | | |
| 10% $C_2H_2$ | 72.0 | 8.4 | 2.6 | 25.9 |
| 5 | 90.3 | 13.4 | 3.7 | 17.8 |
| | 350°C, 2 g s ml$^{-1}$, 10% $C_2H_2$ | | | |
| $Al_2O_3$2.6 | 99.3 | 59.2 | 2.0 | 49.7 |
| 2.6 wt% F | 72.0 | 8.4 | 2.6 | 25.9 |

[a] Yields are expressed as a percentage (by weight) of $C_2H_2$ fed to reactor.

[b] The unit (g s ml$^{-1}$) is the inverse of the space velocity based on reactant flow at reaction conditions.

deemed to be quite respectable considering the spectrum of products obtained and the limited quantity of acetylene reacted (0.05–0.30 g). The product yield at a time-on-stream of 15 min, defined as a percentage on a weight basis, is given in Table 1. Because of the nature of the experiments the yield of the solid product was measured and is reported only at 60 min on stream.

For all experiments the yield of gaseous products ($C_1$–$C_5$) at 15 min on stream was very low (under 10 wt%). A large variation was observed in the yield of liquids (8 to 90 wt%). The yield of solid product (catalyst residue) at the end of 1 h varied between 25 and 50 wt%. An increase in the yield of liquids and gases is obtained at the expense of the solid product at high temperatures, high weight–times, and with the unmodified alumina. An increase in the initial concentration of the reactant, however, brought about a decrease in the yield of liquids and gases.

### *Distribution of Liquid Products*

The distribution of the liquid products, benzene, toluene, xylenes, and ethylbenzene (denoted as BTX) and higher hydrocarbons (denoted as $>C_9$) at 15 min on stream for all the experiments was plotted as a function of conversion and is shown in Fig. 1. The smooth curve was drawn by hand through the data. It is apparent from the overall distribution of the liquid components that significant quantities of the low molecular weight cyclic components (BTX) are obtained only at high conversions. A fairly high molecular weight product and minor amounts of BTX are observed at low conversions. The conversion level thus plays an important role in determining the liquid product spectrum.

### *Changes in Product Yield and Distribution with Time-on-Stream*

A comparison of the yields of liquid products at various times-on-stream for a single experiment is given in Table 2. Trends observed in this experiment were typical of those of others. Although the yield of liquid product decreases with longer times-on-stream, there is very little change in the selectivity to liquids with time-on-stream. Consequently, the liquid fraction is not being sacrificed at the longer times-on-stream.

The nature of the liquid product changes considerably, however, between 30 and 60

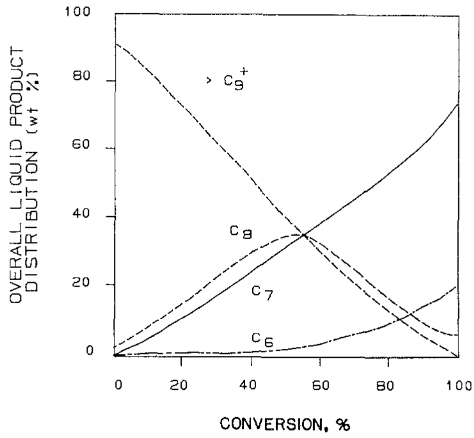


FIG. 1. Liquid product distribution as a function of acetylene conversion over alumina and fluoridated alumina catalysis in tubular flow reactor.

TABLE 2

Comparison of Liquid Yields and Selectivities with Time-on-Stream[a]

| Time-on-stream (min) | Yield | Selectivity to liquids |
|---|---|---|
| 5 | 29.2 | 42.2 |
| 15 | 22.5 | 37.8 |
| 20 | 23.6 | 41.4 |
| 25 | 23.6 | 43.4 |
| 30 | 21.6 | 42.0 |
| 35 | 19.5 | 39.6 |
| 40 | 18.3 | 38.9 |
| 45 | 17.3 | 38.9 |
| 50 | 16.6 | 38.9 |
| 55 | 16.5 | 39.5 |

[a] 375°C, 2.5 g s $ml^{-1}$, 12% $C_2H_2$, 4.3 wt% F.

min on stream. The liquid product distribution shifts increasingly to higher molecular weight components. After 60 min on stream, over 50% by weight of the liquid has a molecular weight above 160 (Table 3). A comparison of the PONA (paraffin, olefin, naphthene, aromatic) analysis of the cumulative liquid product, i.e., liquid product which is collected in a cold trap for all the experiments of 1-h and 5-h duration, respectively, is given in Table 4. The average molecular weight of the liquid product recovered after 1 h on stream is significantly lower than that of the liquid product obtained after 5 h. Furthermore, the liquids contain a higher proportion of aromatic hydrocarbons at the expense of both paraffinic and naphthenic hydrocarbons. The increase in aromaticity must correspond to the increase in the high molecular weight components which are formed in increasing proportions at long times-on-stream. Formation of condensed ring structures or polynuclear aromatics must account for the steady increase in incremental liquid product yield.

TABLE 3

Liquid Product Composition (wt%) as a Function of Time-on-Stream[a]

| Component | Molecular weight | Time-on-stream (min) | | | |
|---|---|---|---|---|---|
| | | 15 | 30 | 45 | 60 |
| Benzene | 78 | 2.18 | 2.26 | 2.69 | 1.30 |
| Toluene | 92 | 8.57 | 8.10 | 6.03 | 7.70 |
| Ethylbenzene | 106 | 33.44 | 45.48 | 19.45 | 16.59 |
| *p*-Xylene | 106 | 0.84 | — | 1.01 | 1.58 |
| *m*-Xylene | 106 | 5.16 | 0.60 | 5.02 | 6.75 |
| *o*-Xylene | 106 | 1.79 | 3.80 | — | 2.70 |
| | 120 | 1.46 | — | — | — |
| | 120 | 0.87 | — | — | — |
| Isomers[b] | 120 | 0.42 | — | — | 2.19 |
| | 120 | 26.7 | 30.35 | — | 7.15 |
| *p*-Cymene | 134 | 1.41 | — | 8.84 | — |
| n.i. | | 0.35 | — | — | |
| n.i. | 146 | — | 1.27 | — | 4.08 |
| n.i. | | 8.40 | 8.15 | — | — |
| Tetra naphthalene | 160 | — | 8.40 | 56.95 | 49.97 |
| Trimethyl naphthalene | 170 | 8.41 | — | — | — |

*Note.* n.i., Not identified.

[a] 375°C, 2.5 g s $ml^{-1}$,12% $C_2H_2$, 4.3 wt% F.

[b] Trimethylbenzene isomers.

As mentioned earlier, the total yield of gaseous products was low (<10 wt%) in all the experiments; therefore only the molar yield of the major component, ethylene, is tabulated for three experiments as a function of time-on-stream (Table 5). For the most part, a steady decrease in the yield of ethylene with time-on-stream was observed. On the other hand, the selectivity to ethylene increased slightly with time-on-stream. This increase is probably tied to the changing character of the liquid product at long times-on-stream. The presence of $H_2$, $CH_4$, and $C_2H_4$ in the gaseous products is

TABLE 4

Composition of Cumulative Liquid Product

| Time-on-stream (h) | Paraffins (wt%) | Naphthenes (wt%) | Aromatics (wt%) | Molecular weight |
|---|---|---|---|---|
| 1 | 8.7 | 49.4 { 37.6[a]<br>10.2<br>0.0<br>1.6 | 41.9 { 24.2<br>7.4<br>4.5<br>5.8 | 175 |
| 5 | 2 | 23.1 { 8.4<br>1.6<br>8.0<br>5.1 | 74.9 { 3<br>35<br>1<br>36 | 238 |

[a] Breakdown by size of rings.

TABLE 5

Yield and Selectivity of Ethylene (mol%) as a Function of Time-on-Stream

| Time (min) | Yield | | | Selectivity | | |
|---|---|---|---|---|---|---|
| | 1[a] | 9[b] | 16[c] | 1 | 9 | 16 |
| 15 | 1.77 | 5.59 | 2.49 | 3.44 | 5.70 | 2.77 |
| 30 | 1.51 | 6.43 | 1.87 | 3.34 | 6.78 | 2.69 |
| 45 | 1.24 | 5.38 | 1.46 | 5.06 | 6.34 | 2.27 |
| 60 | 1.15 | 3.80 | 1.25 | 5.75 | 8.02 | 1.99 |

[a] 385°C, 2.5 g s $ml^{-1}$, 12% $C_2H_2$, 4.3 wt% F.
[b] 400°C, 2 g s $ml^{-1}$, 10% $C_2H_2$, 2.6 wt% F.
[c] 350°C, 2 g s $ml^{-1}$, 10% $C_2H_2$, 0 wt% F.

probably a result of the dehydrogenation of naphthenes to aromatics and of the dealkylation of ring compounds.

### *Effect of Fluoridation*

The liquid product distributions over alumina and 2.6 wt% F on alumina at 15 min on stream (350°C, 2 g s $ml^{-1}$, and 10 vol% $C_2H_2$) are compared in Fig. 2. The most noticeable difference is the lack of $C_{20}^+$ compounds in the liquid product for the fluoridated alumina. The large selectivity to the solid product at 15 min on stream with fluoridated alumina (85%) compared with alumina (38%) implies that a nondesorbable carbonaceous layer forms very readily in the former case at early times-on-stream. Although high-molecular-weight species are formed over both catalysts, they do so at different rates. The narrower liquid product distribution obtained with the more acidic catalyst (2.6 wt% F) is obtained at the expense of a reduction in liquid yield (Table 1, 59.2 with alumina; 8.4 with 2.6 wt% F on alumina). This observation was made earlier in discussing the effects of the operating variables and remains consistent for the conversion of $C_2H_2$.

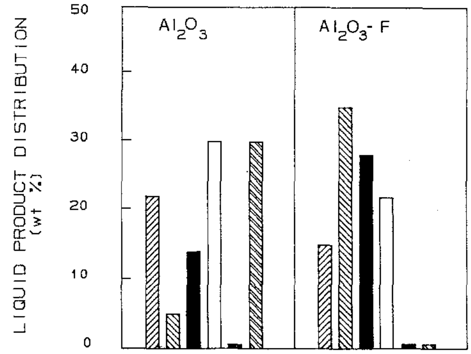


FIG. 2. Comparison of liquid product distribution with and without fluoride in the catalyst; temperature 350°C, 2 g s $ml^{-1}$, 10 mol% $C_2H_2$ in $N_2$. ▨, $C_6$; ▧, $C_7$; ■, $C_8$; □, $C_9$–$C_{18}$; □, $C_{18}$–$C_{20}$; ▧, > $C_{20}$.

The overall liquid product distribution has been shown to vary with the conversion at 15 min on stream (Fig. 1). In Fig. 3, a comparison is made of the changes in conversion and changes in the profiles of two components of the liquid product, benzene and $C_8$ isomers, with time-on-stream for catalysts with different fluoride contents. In all cases, a decrease in acetylene conversion is noticeable at 1 h on stream. An optimum in the amount of $C_8$ isomers is evident with the time-on-stream. The time at which this opti-

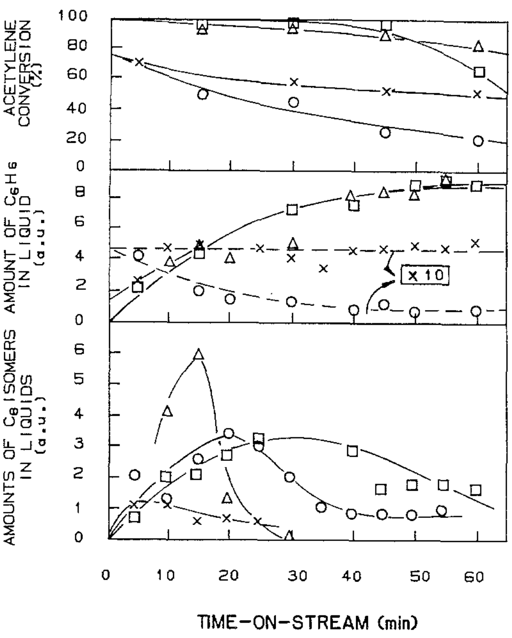


FIG. 3. Comparison of conversion, benzene $C_8$ levels as a function of time-on-stream, and catalyst fluoride content at various processing conditions. □, alumina; X, 2.6 wt% F; △, 1.5 wt% F; ○, 4.3 wt% F.

mum is reached is a function of the fluoride content, as shown below:

| Time at which maximum in $C_8$'s is reached (min) | F on alumina (wt%) | Relative acidity |
|---|---|---|
| 4 | 2.6 | 1 |
| 15 | 1.5 | 0.67 |
| 20 | 4.3 | 0.63 |
| 30 | 0 | 0.17 |

More striking, however, is the fact that this time value decreases as catalyst acidity increases. From this relationship, it can be speculated that these $C_8$ isomers may play a key role in this reaction.

Three trends are observed in the benzene content of the liquid product: an increase (0 and 1.5 wt% F), no change (2.6 wt% F) and a decrease (4.3 wt% F) with time-on-stream. No change or an increase in benzene levels would indicate that although the catalyst is deactivating, the active sites for benzene formation are not being lost or, alternatively, that the deactivation process might actually be assisting in destroying very active sites for other unfavorable reactions. In the case of high fluoride contents, benzene levels cannot be maintained, probably because of the presence of only a small number of active sites of the appropriate type.

## DISCUSSION

The observations made in this investigation and reported herein provide useful clues to the underlying mechanism for the transformations that are occurring.

### *Thermodynamic Considerations*

The thermodynamic equilibrium concentrations of the products ($C_6$ to $C_{15}$) arising from the transformation of acetylene have been calculated by Mikulec *et al.* (*11*) as a function of temperature and hydrocarbon partial pressure with and without the presence of methane. The equilibrium mixture composition based on these calculations at 350°C and 1 atm is given in Table 6. Equilibrium calculations show that paraffins are present in small amounts particularly if methane is not considered. If methane is present in the mixture, then naphthalene represents the major product. Otherwise, naphthalene, 2-methylnaphthalene, and BTX are present in considerable amounts. Mikulec *et al.* (*11*) also found that at equilibrium the overall yields of aromatics decreased with temperature whereas the yield of benzene increased. Furthermore, an increase in pressure led to an increase in the yield of aromatics at the expense of paraffins.

TABLE 6

Equilibrium Composition of Selected Hydrocarbons from Acetylene[a] (621 K and 1 atm)

| Component | Concentration (mol%) | |
|---|---|---|
| | Methane included | Methane excluded |
| Methane | 7.517 | — |
| Paraffins | 0.002 | 4.115 |
| Benzene | 1.170 | 17.52 |
| Toluene | 0.419 | 14.73 |
| Xylenes[b] | 0.0005 | 4.13 |
| $C_9$ aromatics[c] | tr | 0.51 |
| $C_{10}$ aromatics[d] | 89.18 | 36.8 |
| $C_{11}$ aromatics[e] | 2.081 | 20.15 |
| $C_{12}$ aromatics[f] | 0.0069 | 1.582 |
| $C_{13}$ aromatics[g] | 0.0018 | 0.399 |
| $C_{14}$ aromatics[h] | tr | 0.012 |
| $C_{15}$ aromatics[i] | tr | 0.061 |

[a] From Ref. (*11*).
[b] Includes ethylbenzene and styrene.
[c] Consists of ethyltoluene and trimethylbenzene.
[d] Consists of diethylbenzene, tetramethylbenzene, and naphthalene.
[e] 2-Methylnaphthalene.
[f] 1,7-Dimethylnaphthalene.
[g] 2-Ethylnaphthalene.
[h] 2-Propylnaphthalene.
[i] 2-Ethyl-6-methylnaphthalene.

The experimentally observed data on the liquid product distribution in the transformation of acetylene in the absence of catalysts (*12*), over fluoridated alumina (this work) and over the ZSM-5 zeolite (*7*), are shown in Table 7. A comparison of the data for the fluoridated alumina with those in Table 6 reveals clearly that equilibrium has not been established. The experimentally ob-

TABLE 7

Comparison of Liquid Product Distributions for the Transformation of Acetylene

| | Composition (mol%) | | | | |
|---|---|---|---|---|---|
| Catalyst: | None[a] | ZSM-5[b] | ZSM-5[b] | $Al_2O_3$-F[c] | $Al_2O_3$-F[d] |
| Time-on-stream (min): | — | 15 | 15 | 15 | 15 |
| Space velocity ($h^{-1}$): | — | 3900 | 15000 | 1175 | 885 |
| Conversion (% $C_2H_2$): | 44 | 11 | 4 | 5 | 26 |
| Benzene | 64.1 | 4.2 | 3.2 | 6.0 | 6.5 |
| Toluene | 17.5 | 6.7 | 5.3 | 2.4 | 2.1 |
| Xylenes | 4.3 | 11.8 | 8.3 | 5.8 | 20.7 |
| $C_9$–Ar | 3.5 | 1.2 | 7.3 | — | 11.2 |
| $C_{10}$–Ar | 4.4 | 39.2 | 36.4 | — | 8.2 |
| $C_{11}$–Ar | 1.9 | 36.9 | 36.4 | 9.0 | 15.1 |
| $C_{12}$–AR | 0.5 | tr | 3.1 | — | 15.6 |
| $C_{13}$–$Ar^{(+)}$ | 0.6 | tr | tr | — | 20.6 |

[a] 873 K (Ref. (*12*)).
[b] Si/Al in ZSM–5: 60, 573 K, $C_2H_2$/He = 0.133 (Ref. (*7*)).
[c] $F^-$ in $Al_2O_3$ = 4.3 wt%, 598 K, $C_2H_2/N_2$ = 0.125 (this work).
[d] $F^-$ in $Al_2O_3$ = 2.6 wt%, 573 K, $C_2H_2/N_2$ = 0.10 (this work).

served yields of $C_{10}$ and $C_{11}$ over ZSM-5 are very close to their predicted values at equilibrium. This feature was not observed over fluoridated alumina. The approach to equilibrium in the case of the zeolite is perhaps due to steric constraints imposed by the zeolite cage structure that are not present in amorphous catalysts, e.g., fluoridated alumina. Relative yields of low carbon number aromatics observed over both catalysts are significantly lower compared with the thermodynamic values (no methane).

### *Kinetic Considerations*

*Step-growth mechanism.* Flory (*13*) has given a detailed and quantitative treatment of polymerization reactions that occur by the step-growth mechanism. The Flory equation is

$$\ln (M_m) = m \ln(x) + \ln((1 - x)/x),$$

where $M_m$ is the whole fraction of a polymer with $m$ monomers, $N$ is the total number of moles, and $x$ is the extent of reaction or conversion. This equation provides a macroscopic method to predict the molecular weight distribution during polymerization. It has been applied successfully to predict molecular weight distributions of linear condensation polymers (*13*), to predict hydrocarbon distributions produced from the Fischer–Tropsch reaction (*14*), and to predict light olefin distributions in the synthesis of olefins from methanol (*15*).

The data from the polymerization of acetylene presented earlier contain valuable mechanistic information. A plot of the logarithm of the mole fraction of the product distribution found in thermal experiments carried out at 600°C in a flow reactor (*12*) is given in Fig. 4 starting with $C_5$. This plot shows a significant departure from linearity for the $C_5$ point. However, if benzene is chosen as the first product formed by the step-growth process, the Flory plot starting from benzene produces a good straight line. A high degree of correlation exists with the Flory equation observed for the products obtained from the thermal reaction of acetylene. However, this does not prove that the reaction of acetylene with benzene and higher hydrocarbons, to give the next higher molecular weight homolog, proceeds by a step-growth mechanism.

It is useful to compare the liquid product distribution obtained over ZSM-5 (*7*) and over fluoridated alumina (data from this work) with that obtained by Chang-Li (*12*) on the Flory plot (Fig. 4). A significant difference is noted between the noncatalytic

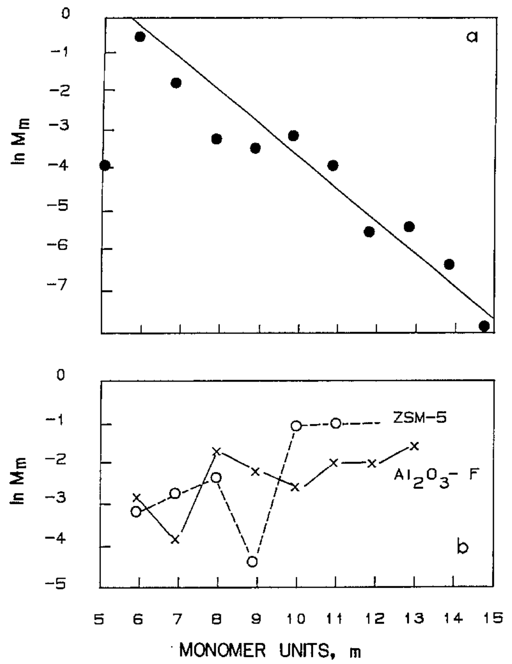


FIG. 4. Flory plot of product distribution from the transformation of acetylene: (a) thermal, (b) in the presence of ZSM-5 and 2.6 wt% F on alumina.

and catalytic product distributions. The thermal experiment was carried out at 600°C and showed a large proportion of benzene and toluene. The catalytic experiments, on the other hand, were carried out at substantially lower temperature (350°C) and showed a higher proportion of the heavier aromatics ($C_9^+$). The positive slope, ln($x$), of the product distribution obtained in the catalytic conversion of acetylene with the Flory equation implies that conversions are greater than one. Since this is not feasible, the products are derived from a mechanism different from the step-growth addition reaction. The underlying assumption of this mechanism, i.e., equal rates of formation of all the products, is not likely in the case of the catalytic reaction over solid acids.

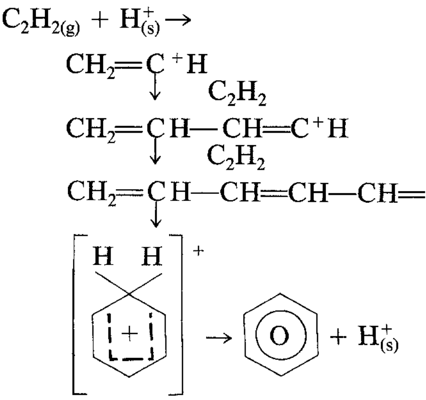
*Chain-growth mechanism.* Chain-growth polymerization differs from step-growth mechanism in that three types of reactions are believed to occur—initiation, propagation (growth), and termination. Chain-growth polymerizations are divided into ionic or radical, depending upon which type of chain carrier is involved. Back (*16*) has suggested a homogenous free-radical chain mechanism to describe the kinetics of the thermal polymerization of acetylene over a wide temperature range.

Both anionic and cationic initiation have been used to produce polymers from acetylene (*8*, *9*). The ionic chain polymerization of acetylene leads to the formation of polymers with a degree of polymerization, $m$, equal to 10, i.e., 10 repeated units in the polymeric chain (*9*). The highest molecular weight material, which was observed in the liquid product, was 275 corresponding roughly to 10 monomeric units of acetylene, which is consistent with the ionic mechanism.

One plausible mechanism for the polymerization reaction of acetylene over solid catalysts, first postulated by Tsai and Anderson (*7*) can be described by the general scheme

[acetylene → $n$-polyene → aromatic].

Polymerization of acetylene to polyene has been observed by Raman spectroscopy at the surfaces of alumina (*17*), zeolite KX (*17*), and $TiO_2$ (*19*). Although the extent of polymer formation was relatively small, its presence was beyond question. With these oxide catalysts, the polymerization mechanism is not known. Tsai and Anderson (*7*) proposed the vinyl cation route (cationic initiation) for conversion of acetylene over ZSM-5 to yield a $C_6$-polyene intermediate that cyclized to benzene:



$$C_2H_{2(g)} + H^+_{(s)} \rightarrow$$
$$CH_2{=}C^+H \xrightarrow{C_2H_2} CH_2{=}CH{-}CH{=}C^+H \xrightarrow{C_2H_2} CH_2{=}CH{-}CH{=}CH{-}CH{=}C^+H$$

It is unlikely, however, that higher carbon number aromatic compounds, e.g., toluene and xylene, are formed from a two-carbon atom precursor via cracking and isomerization reactions as suggested by Tsai and Anderson. The above mechanism falls short in attempting to explain adequately the effects of acidity, the presence of the gaseous products even at very low conversions, and the fact that significant quantities of coke do not necessarily deactivate the catalyst.

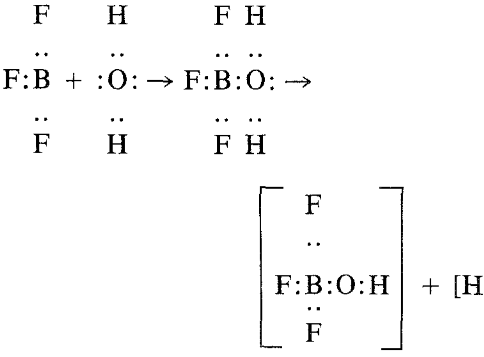
The distribution pattern shown in Fig. 6 implies that there is no reason for the polyene chain which may be formed to be limited to 6 at the outset. Analysis of the liquid product distribution obtained in the present study with alumina and fluoridated alumina (Fig. 4) corroborates this in that the polyene chain formed at the outset appears to contain more than three monomeric units. As shown in Fig. 3, under conditions of low conversion the growing chain is not starved for monomer and the polyene will grow over the length of the catalyst bed. Conversely, under conditions of high conversions, the growing chain is starved for monomer and secondary reaction of the cyclic products that are desorbed can take place over the bulk of the catalyst bed since dealkylation and condensation reactions are also acid-catalyzed.

Supporting evidence for the formation of a polyene has also emerged from work carried out in a microbalance where the conversions were low and the solid product was indeed present in the highest proportion (*19*). The low activation energies observed (12 kcal/mol) in that study are consistent with those reported for cationic chain polymerization (*20*). In addition, catalyst deactivation over these catalysts actually decreased as the temperature was increased (*4*). Many polymerization reactions are favored by lower temperatures, therefore these findings also support the premise of the polyene. The decrease in deactivation was attributed to a decrease in the surface deposit that was associated with hydrogen-rich fragments (*21*). It has been shown in a previous article (*21*) that these fragments are likely to be linear polymers and not condensed ring aromatics.

*Proposed reaction mechanism.* A modified mechanism is postulated in Fig. 5 involving cationic chain-growth polymerization leading to both linear and cyclic products. The reactions of cationic chain polymerization, specifically initiation, propagation (growth), transfer, and termination, are presented and discussed below.

*Initiation reaction.* Cationic initiation may be expected with highly unsaturated monomers such as acetylene. Moreover, strong Lewis acids behave as electron acceptors and are good initiators of cationic polymerization (*8, 20*). Little is known about heterogeneous cationic initiation of acetylene but some insight can be gained from homogeneous systems.

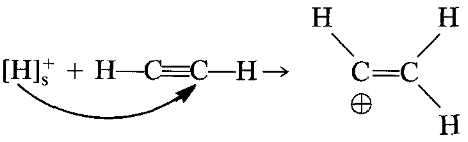
In homogeneous cationic polymerization, Lewis acids such as $AlCl_3$ and $BF_3$ are electrically neutral, but they are two electrons short of having a complete valence shell of eight electrons. These compounds require traces of co-catalyst, usually $H_2O$, to initiate polymerization, first by accepting a pair of electrons from the cocatalyst as illustrated



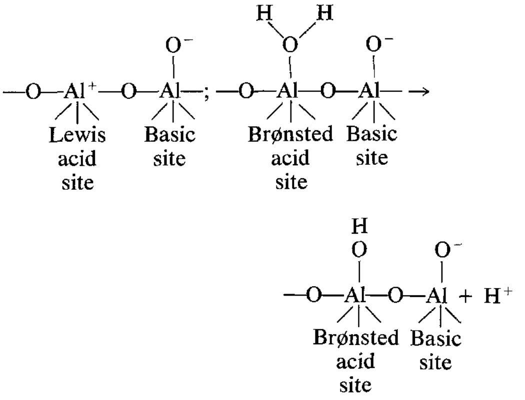
$$\mathrm{F{:}\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}} + {:}\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{O}}{:} \rightarrow F{:}\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}}{:}\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{O}}{:} \rightarrow \left[F{:}\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}}{:}O{:}H\right] + [H]^{+}}$$

The leftover proton is believed to be the actual initiating species abstracting a pair of electrons from the monomer and leaving a cationic chain end which reacts with additional monomer molecules (20).

By analogy to this homogeneous chemistry, active sites must exist on the catalyst surface to generate the polymerization initiator. Alumina and fluoridated alumina are believed to contain Lewis acid centers as well as a small number of Brønsted centers (*21*). This fact satisfies the above criterion, and favors the mechanism postulated. Tsai and Anderson (*7*) proposed that in ZSM-5 the $H^+$ from the hydroxyl groups in the zeolite (Brønsted sites) served to generate vinyl cation as the initiator:



Acidic and basic sites on the surface of alumina can be pictured according to the following scheme (*22*). The Lewis acid site is visualized as an incompletely coordinated aluminum atom formed by dehydration and the Brønsted site as a Lewis site that has adsorbed moisture, while the basic site is considered a negatively charged oxygen atom



The Brønsted acid sites could possibly be the source of $H^+$ for the initiation reaction. However, two facts make this route doubtful. First, alumina is a very reluctant Brønsted acid (*23*). Second, the gas-phase vinyl cation has a high energy and is extremely reactive, $\Delta H_f^{298} = 266$ kcal/mol (*24*). It seems more likely therefore that the initiating species is formed due to the presence of the Lewis acid sites. Octahedral coordination for Al is used as an example in illustrating the mechanism. It must be kept in mind, however, that other coordination, tricoordinate, and tetrahedral Al can also be present and affect the Lewis and Brønsted acidity.

A quantum chemical study (*25*) of the interaction of ethylene with the Lewis acid sites of zeolites has shown that the interaction of ethylene and the Al cation leading to the formation of a stable $\pi$-complex is energetically more favorable than similar interactions with zeolite hydroxyl groups. Furthermore, the $\pi$-complex may be transformed into a $\sigma$-complex which is energetically slightly more favorable than the $\pi$-complex (*25*). As a result of the formation of the ethylene–Al cation complex, donation of electron density from the $\pi$-molecular orbitals of ethylene to the unoccupied molecular orbitals of the zeolite localized on the Al cation takes place, resulting in a positive charge on the ethylene molecule. The positive charge on the ethylene molecule bonded to the Al cation has a value of about 0.2 compared with about 0.1 calculated for the ethylene molecule interacting with the Brønsted site. Both the symmetrical and unsymmetrical approaches of ethylene to the Lewis site give rise to a slight induced dipole moment in the ethylene molecule. These features have led Beran *et al.* (*25*) to speculate that the ethylene molecule interacting with the Lewis site may itself polymerize with another ethylene molecule owing to its partly cationic character. Although these types of calculations to date have not appeared with acetylene, the unsaturated nature of the two molecules would lead one to expect that a similar situation might be possible with acetylene. Additional support for this possibility comes from molecular orbital studies by Yu and Anderson (*26*) in which the binding of $C_2H_4$ and $C_2H_2$ to different $MoS_2$ sulphur sites was shown to be very similar.

Spectroscopic studies have shown that acetylene adsorbs in two modes on alumina, head on (interaction through the C–H) and flat (interaction through C–C) (*27*). The flat orientation was shown to be weakly ad-

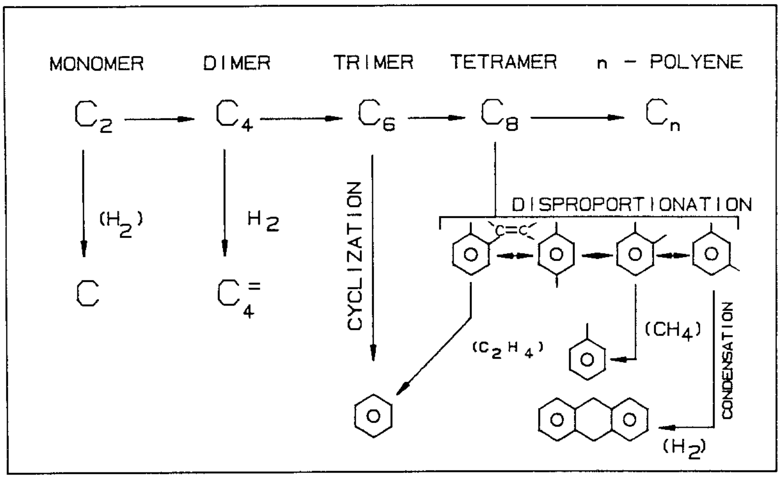
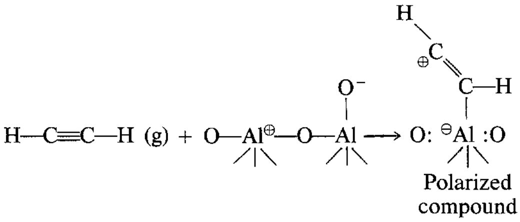


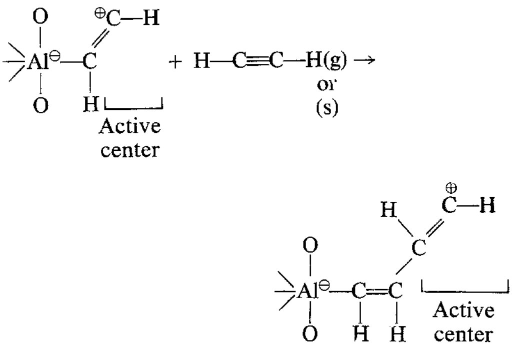
FIG. 5. Proposed mechanism for acetylene conversion over alumina and fluoridated alumina.

sorbed acetylene whereas the head-on orientation was strongly adsorbed acetylene. It is possible therefore that a polarized compound is formed upon chemisorption on the catalyst which then acts as the initiator:



The rate of initiation and thereby the concentration of the initiator should increase as the number of acid sites increases. Adsorption and polarization will be a function of acid strength. Fluoridation strengthens the Lewis acid sites and introduces some Brønsted acidity (*23*). Both features would enhance this reaction. Since the rate of polymerization is a function of the concentration of the initiator, it is expected that the rate should increase as the total acidity is increased, which has indeed been observed (*1, 20*).

*Propagation reaction.* Propagation or growth of the polymer consists of addition of monomer to the active center of the growing chain (polarized compound or vinyl cation).

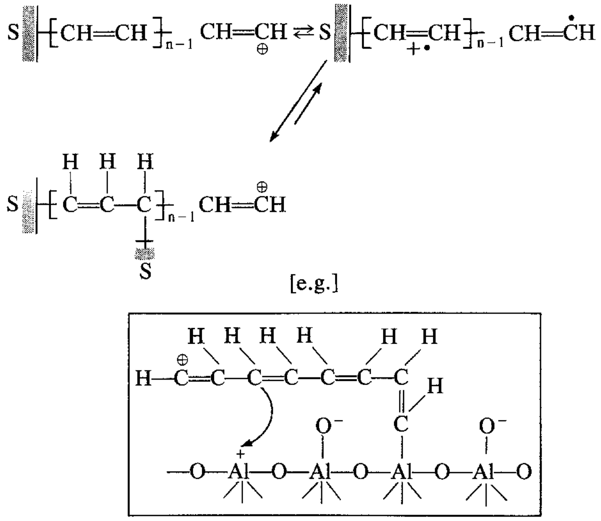


In cationic chain polymerization of acetylene, an electron is transferred from a polyene chain to an active center with formation of a radical at the end of the chain and a radical cation delocalized over the conjugation system (*8*).

$$\left[\mathrm{CH{=}CH}\right]_{n-1}\ \mathrm{CH{=}\overset{\oplus}{C}H} \rightleftharpoons \left[\mathrm{CH \overset{\bullet}{\mp} CH}\right]_{n-1}\ \mathrm{CH{=}\dot{C}H}$$

With acetylene, the isomerization of active centers (electron transfer) occurs in the first two or three units of the chain (*8*). Furthermore, formation of a ring stabilizes the ion at the end of the chain, for example, phenylacetylene. Cyclic products are obtained by intramolecular ring closure and terminate the polymerization sequence. The chief factor determining whether rings or chains will be produced is the size of the rings that will be formed. Six- and seven-membered rings are moderately stable and will usually compete with chain formation so that both products are formed. Both linear polymer and cyclic tri and tetramers have been obtained in the conversion of acetylene using homogeneous catalysts (*28*). Moreover, benzene, toluene, and ethylbenzene were obtained as cyclooligomerization products over Ziegler catalysts (*28*).

In order to have chain propagation, the catalyst must have powerful electron acceptor sites capable of forming stable donor–acceptor or radical-ion complexes with the polyene chain. For linear growth to occur, the same active site must be maintained; therefore the isomerization of the active center by electron transfer must be minimized. When the polyene chain forms a complex with the catalyst the electron density cannot be displaced in the direction away from the polyene chain (to the right).



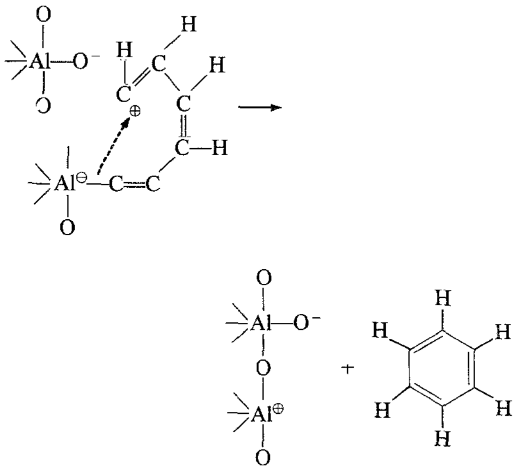
Chain propagation is therefore not prevented. In the presence of a sufficient number of electron acceptor sites (Lewis acid sites), the cationic polymerization without electron transfer will lead to a high-molecular-weight product. In fact, once a polymeric film deposits on alumina, the activity for chain growth drops drastically and an increase in the cyclic product is observed (Fig. 6). As the catalytic sites are covered with nondesorbable polymer the monomer could then react on this surface film and fewer contacts with the donor–acceptor sites occur. The chain length decreases due to an increase in the electron transfer reaction that follows from the lack of complexing. Stabilization of the chain occurs through cyclization and produces a notable increase in benzene as a function of time-on-stream.

In the mechanism proposed, the number of donor–acceptor sites plays an important role in determining the chain length. Fewer sites would imply formation of less polymer and higher possibility of cyclization brought about by the transfer reaction. In support of this, one can see that as the degree of fluoridation increases, the maximum in the tetramers produced (Fig. 4) is achieved at earlier times-on-stream in response to the fewer sites. Catalysts containing the highest number of ‘ion-pair’ sites show an increase in benzene levels with time-on-stream simultaneously with the reduction of available surface sites by polyene formation (Fig. 3).

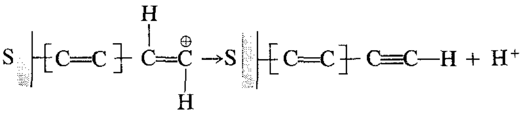
On the other hand, stronger sites would also be expected to promote the propagation and minimize the transfer reaction. When one compares the liquid product distribution over $Al_2O_3$ and fluoridated $Al_2O_3$ (2.6 wt%) in Fig. 3, it is evident that large levels of BTX are observed over the more acidic catalyst. No high-molecular-weight material appears in the vapor phase probably because macromolecules are formed very quickly and do not leave the surface. As the polyene layer continues to form, the increase in the transfer reaction, due to the higher polyene–monomer interactions as compared with the surface monomer interactions, appears to offset the loss in initiator (due to covered sites) and benzene levels are maintained ever after 1 h on stream (Fig. 4). Rucker *et al.* (*29*) have also suggested that perhaps benzene is formed on an overlayer of ethylidyne or other carbonaceous fragments onto which it is loosely bound. At higher loadings of fluoride, both the acidity and the number of sites are greatly reduced (*30*). Therefore the compensation for loss of initiator (due to the loss in acidity and the number of sites) cannot be maintained by the low polyene transfer reaction (due to the low number of sites). As a result, the yield of benzene falls steadily with time-on-stream.

An increase in the conversion of acetylene over these catalysts in the presence of infrared radiation (*31*) can probably be attributed to the ease with which the excited acetylene molecule can be converted into the polarized compound. Molecular vibrations of acetylene may be important in this reaction as has been speculated by Larsson (*32*) for catalytic HDS reactions.

*Termination reaction.* Several termination mechanisms are possible. One type of chain termination occurs when macromolecules capable of giving up an electron to the active center succeed in stabilizing the ions by cyclization



This type of termination regenerates the catalyst. Another possibility involves a disproportionation-like reaction:



$$S\text{-}[C{=}C]\text{-}\overset{H}{C}{=}\underset{H}{\overset{\oplus}{C}} \rightarrow S\text{-}[C{=}C]\text{-}C{\equiv}C\text{-}H + H^+$$

This type would generate new initiator molecules.

## CONCLUSIONS

The mechanism proposed is supported by indirect evidence from the literature and is consistent with the experimental observations of this study. Implications of this mechanism are considerable. If light cyclic products are of interest, then optimization of the chain growth to four monomeric units is desirable. Since chain propagation is prevented by the electron transfer reaction, it appears necessary to maximize the possibility for the isomerization of these active centers to take place. Catalysts that shift the ring-chain equilibrium to the left are highly desirable. To do so a catalyst should contain a minimum number of Lewis acid sites. Cationic initiation implies that high Lewis acidity is needed for the initiation of the chain. A fine balance must exist between the number of sites on the catalyst surface responsible for initiation and those responsible for the isomerization of the active center on the growing chain.

Alumina and fluoridated alumina are good initiators for acetylene oligomerization reactions. However, high yields of cyclic products may only be obtained when the possibility for rearrangements of the hydrocarbon species on the catalyst surface is high. Pure alumina satisfied this criterion to a larger extent than the fluoridated alumina catalysts. It is clear, however, from the mechanism that these solid acid catalysts cannot be used to achieve the desired result unless the two functions can be separated.

The use of external means to weaken the C–Al bond and to enhance the transfer reaction, perhaps by photoassisting the electron transfer, would be one approach to achieve this. Another approach would be to add a second component to the catalyst, which would emphasize one of these functions without sacrificing the other. In both homogeneous and heterogeneous applications to date, nickel and chromium have been used to facilitate the cyclization; however, the quantity of linear polymer formed is still unacceptably high. There is definitely a need for further work in the area of bifunctional catalysts in shifting the emphasis from polymerization to oligomerization.

## REFERENCES

1. Pines, H., "The Chemistry of Catalytic Hydrocarbon Conversions." Academic Press, San Diego, 1981.
2. Choudhary, V. R., Ind. Eng. Chem. Process Res. Dev. **16**(1), (1977).
3. Allenger, V. M., Fairbridge, C., McLean, D. D., and Ternan, M., *J. Catal.* **105**(5), 71 (1987).
4. Allenger, V. M., Clugston, D., Brown, J. R., McLean, D. D., and Ternan, M., *Appl. Catal.* **39,** 191 (1988).
5. Mardaleishvili, R. E., and Rappoport, Y. I., *React. Kinet. Catal. Lett.* **25,** 1437 (1984); *J. Catal.* **95,** 447 (1985).
6. Leglise, J., Chevreau, Th., and Cornet, D., *Catal. Zeolites,* 95 (1980).
7. Tsai, P. and Anderson, J. R., *J. Catal.* **80,** 207 (1983).
8. Reikhsfel'd, V. O., and Makovetskii, K. L., *Russ. Chem. Rev.* **34**(7), 190 (1974).
9. Matnishyan, A. A., and Kobryanskii, V. M., *Russ. Chem. Rev.* **52,** 8 (1983).
10. Allenger, V. M., McLean, D. D., and Ternan, M., *J. Chromatogr. Sci.* **24,** 3 (1986).
11. Mikulec, J., Beran, S., Wichterlova, B., and Jiro, P., *Appl. Catal.* **16,** 389 (1985).
12. Chang-Li, S., *Chemistry (Taipei)* **1,** 1 (1963).
13. Flory, P. J., "Principles of Polymer Chemistry." Cornell Univ. Press, Ithaca, NY, 1967.
14. Anderson, R. B., *J. Catal.* **55,** 114 (1978).
15. Wu, M. H., and Kaeding, W. W., *J. Catal.* **88,** 478 (1984).
16. Back, M., *Can. J. Chem.* **49,** 2199, 1971.
17. Parker, D. B. V., "Polymer Chemistry." Applied Science, New York, 1974.
18. Heaviside, J., Hendra, J., Tsai, P., and Cooney, R. P., *J. Chem. Soc. Faraday Trans. 1* **74,** 2542 (1978).
19. Rives-Arnaud, V., and Sheppard, N., *J. Chem. Soc. Faraday Trans. 1* **76,** 394 (1980).
20. Allenger, V. M., McLean, D. D., and Ternan, M., *Can. J. Chem. Eng.,* in preparation.
21. Peri, J. B., *J. Phys. Chem.* **69,** 211 (1965).
22. Tanabe, K., "Solid Acids and Bases." Academic Press, New York, 1970.
23. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyvari, A., *J. Catal.* **106,** 544 (1987).
24. Strang, P. J., "Vinyl Cations." Academic Press, New York, 1979.
25. Beran, S., Jiru, P., and Kubelokova, L., *J. Mol. Catal.* **16,** 299 (1982).
26. Anderson, A. B., and Yu, J., *J. Catal.* **119,** 135 (1989).
27. Sheppard, N., and Yates, D. J. C., *Proc. R. Soc. A* **238,** 69 (1957).
28. Ito, T., Shirakawa, H., and Ikeda, S., *J. Polym. Sci.* **12,** 11 (1974).
29. Rucker, T. G., Logan, M. A., Gentle, T. M., Muetterties, E. L., and Somorjai, G. A., *J. Phys.* **90,** 2703 (1986).
30. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somorjai, A., *J. Catal.* **96,** 115 (1985).
31. Allenger, V. M., McLean, D. D., and Ternan, M., *Fuel* **66,** 3 (1987).
32. Larsson, R., *J. Catal.* **107,** 568 (1987).