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# $n$-Butane Isomerization Catalyzed by Supported Aluminum Chloride

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Solid superacid catalysts were prepared by the reaction of aluminum chloride vapors with each of the following supports: (i) silica, (ii) sulfated silica, (iii) sulfonated silica, and (iv) sulfonated macroporous poly(styrene-divinylbenzene). The resulting solids catalyzed the isomerization of $n$-butane at 0.1–1 atm and 23–140°C, the rate being of the order of $10^{-4}$ molecules/(Al atom · s) at 100°C for the polymer-supported catalyst. HCl in the feed to a flow reactor increased the rate of the catalytic reaction. The $n$-butane isomerization was described by Langmuir–Hinshelwood kinetics, the reaction being first order in the concentration of adsorbed reactant. The superacidic catalytic sites (of undetermined structure) were formed by the combination of aluminum chloride with Brønsted acid groups.

## INTRODUCTION

Isomerization of straight-chain paraffins has found technological application for increasing the octane numbers of light petroleum fractions, especially $C_5$–$C_6$ fractions. This cut is relatively unreactive under the typical conditions of catalytic reforming (*1*), and there is ample motivation for processing it, since its octane number is sharply decreased by the removal of lead from gasoline. The processing needs have led to the search for isomerization catalysts having high activities, since low temperatures favor the equilibrium conversion to branched isomers as well as the energy efficiency of the process.

The early paraffin-isomerization processes were carried out with strong-acid catalysts such as $AlCl_3$–HCl (*2*). The difficulties of corrosion and separation provided a motive for the application of supported $AlCl_3$, the supports being, for example, bauxite and quartz chips (*3*). The advent of bifunctional, metal-containing hydroisomerization catalysts (e.g., Pt/$Al_2O_3$), led to the elimination of $AlCl_3$, but these catalysts require high temperatures and high hydrogen partial pressures to maintain the activity. Recently a third generation of bifunctional hydroisomerization catalysts has been applied, such as Pd/H-mordenite (*2*). These are distinguished by the high acid strength of the support.

Some of the recent literature concerned with strongly acidic solids ("superacids") used to catalyze paraffin conversions is cited in Table 1. Notwithstanding this work, there has still been little quantitative characterization of paraffin isomerization and other reactions catalyzed by superacids. Our goal was to provide such characterization using solid superacids and a paraffin reactant giving a simple product distribution, namely, $n$-butane, which is converted predominantly into isobutane at temperatures < 100°C. Kinetics experiments were carried out with $n$-butane vapor as feed to a flow reactor and on-line product analysis by gas chromatography. The catalysts were highly active solid superacids, aluminum chloride supported on Brønsted acids, including sulfonated solids and silica.

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TABLE 1

Solid Superacid Catalysts Used for Hydrocarbon Conversions

| Solid acid catalyst | Reaction | Reaction conditions | Rate or turnover[a] data | References |
|---|---|---|---|---|
| Alumina-supported Lewis or Brønsted acid, e.g., $SbF_5$/alumina | Alkylation of aromatic hydrocarbons, e.g., benzene + ethylene | 0–200°C<br>20–100 atm | — | (*4*) |
| $P_2O_5$ or $AlCl_3$ supported on $\gamma$-alumina | *n*-Hexane isomerization and cracking | 100°C | | (*5, 6*) |
| $SbF_5$ supported on fluorinated $TiO_2$ or $SiO_2$–$TiO_2$ | *n*-Butane isomerization | Room temperature | >1 turnover | (*7*) |
| $XF_5$ (X = P, As, Sb, Bi, Ta, Va, Nb) reacted with inorganic oxide having surface hydroxyls, e.g., $SbF_5$/fluorinated alumina | *n*-Butane isomerization | Room temperature<br>1 atm | — | (*8*) |
| $AlCl_3$ supported on metal sulfates | Liquid-phase *n*-pentane isomerization | 23°C | ~10 turnovers | (*9*) |
| $AlCl_3$/sulfonated poly(styrene-divinylbenzene) | *n*-Butane isomerization; *n*-hexane isomerization and cracking | 100°C<br>1 atm | First-order rate constant for $n$–$C_6$ $\sim 10^{-8}$ mol/(s · g of catalyst · atm) | |
| $AlCl_3$/sulfonated poly(styrene-divinylbenzene) | *n*-Butane disproportionation | 50–100°C<br>1 atm | | (*13*) |
| Lewis acid fluorides and chlorides intercalated in graphite, e.g., $AlCl_3$/graphite | Paraffin isomerization | 0–200°C<br>1–30 atm | 200 turnovers | (*14*) |

[a] One turnover estimated to be one molecule of hydrocarbon converted per acidic site.

## EXPERIMENTAL

Catalysts were prepared by subliming aluminum chloride onto each of the following supports: (i) dry, sulfonated, cross-linked polystyrene [Amberlyst 15 (Rohm and Haas), a macroporous ion-exchange resin with a surface area of about 55 $m^2/g$]; (ii) silica gel (Davison Grade 57, which had the following properties, as specified by the supplier: pore volume, 1.1 $cm^3/g$; average pore diameter, 140 Å; surface area, 300 $m^2/g$, surface –OH group concentration, 2.5 mmol/g; impurities, 0.10% $Al_2O_3$, 0.01% $Fe_2O_3$, 0.02% $TiO_2$, 0.07% CaO, 0.06%, $Na_2O$, 0.03% ZrO); (iii) sulfonated silica; and (iv) sulfated silica.

The sulfated silica was prepared as follows. Silica gel was ground to a fine powder (about 200 mesh) and slurried with chloroform in a round-bottom flask fitted with a water-cooled condenser. Chlorosulfonic acid was added to make a 10–20% solution by volume of this regent, and the mixture was brought to boiling and allowed to reflux for 4 hr. The resulting solid was washed with chloroform and then acetone and dried overnight in a vacuum oven at 120°C. It was pale yellow.

Synthesis of the sulfonated silica was

performed according to the procedure of Cox *et al.* (*15*), who prepared β-phenylethyl-functionalized silica, and then sulfonated it. Acid-treated silica gel powder was slurried in 2% β-phenylethyltrichlorosilane (Pfaltz and Bauer) in dioxane and refluxed for 3 hr. The resulting solid was sulfonated by refluxing in 20% chlorosulfonic acid in chloroform for 3 hr.

Aluminum chloride was combined with each of the four supports mentioned above, as follows: nearly anhydrous $AlCl_3$ was placed in one chamber of a glass flow reactor, thermostated at about 120°C, where it sublimed and flowed with $N_2$ carrier gas to a second chamber, thermostated at about 140°C, where it reacted with the support, liberating HCl. The incorporation of aluminum chloride in the downstream packed bed of solid particles was nonuniform, and, consequently, catalytic activities varied from position-to-position in the bed of particles—and from one preparation to another. Details of the catalyst preparations are presented elsewhere (*13, 15, 16*).

The catalysts were handled under dry nitrogen to minimize contamination by water; samples were loaded into stainless-steel flow reactors under nitrogen and brought onstream with minimal contamination. The flow-reactor systems and details of the catalytic reaction experiments, including product analyses by on-line gas chromatography, are described separately (*13, 15, 16*). The reactant stream included *n*-butane (research grade, Phillips Petroleum, ≥99.98%), HCl (electronic grade, Linde, ≥99.99%), and He (dry grade, Linde, ≥99.995%). The helium flowed through a molecular-sieve trap to remove traces of impurity water.

Catalysts were analyzed for Al, S, and Cl (and occasionally for C and H) by Galbraith Laboratories, Knoxville, Tenn., or by Schwartzkopf Microanalytical Laboratory, New York, N.Y. The methods are reported in theses (*15, 16*).

The polymer-supported catalysts were characterized with a Nicolet 7199 Fourier transform infrared spectrophotometer. Samples were powdered with a Wig-L-Bug and prepared as mulls with water-free Nujol and placed between NaCl discs; all handling was done under nitrogen in a glove box to minimize contamination by water.

Some of the polymer-supported catalysts were examined by scanning electron microscopy and characterized by energy dispersive X-ray analysis (EDAX). The methods and results are available elsewhere (*15*).

A few experiments were done to provide a rough estimate of the swelling of the polymer by *n*-butane. Samples of the sulfonated polymer (without aluminum chloride) were equilibrated with *n*-butane vapor at 25°C in a standard volumetric adsorption apparatus (*16*). Care was taken to minimize sample contamination with water.

## RESULTS

### *Elemental Analysis of Catalysts*

The elemental analyses of the various supported aluminum-chloride catalysts are summarized in Table 2. The Al : S atomic ratios range from 0.06 to 5.4 and the Cl : Al ratios from 1.1 to 2.0. These values are consistent with those observed by Magnotta *et al.* (*10–12*), who investigated a small number of samples prepared from aluminum chloride and sulfonated poly(styrene-divinylbenzene). It is evident from the results of Table 2 that aluminum chloride reacted with each of the supports; we infer that the reactions involved the splitting off of chloride as HCl, since this was observed as a product of the syntheses.

These results indicate that the aluminum chloride combined chemically with the support and was not just physically bound. The microscopy results (obtained with the polymer-supported catalysts) confirm this conclusion, which is consistent with the inferences of Magnotta *et al.* (*10–12*). Magnotta observed that when excess aluminum chloride was used in the catalyst synthesis, it formed a crust on the surface of the poly-

TABLE 2

Elemental Analyses of the Unused Catalysts[a]

| Sample number | Support | Analysis (wt%) | | | | | Atomic ratio | |
|---|---|---|---|---|---|---|---|---|
| | | C | H | S | Al | Cl | Al/S | Cl/Al |
| 1 | Silica | | | | 4.63 | 8.63 | | 1.44 |
| 2 | Silica | | | | 5.36 | 7.64 | | 1.10 |
| 3 | Sulfated silica | | | 0.91 | 4.12 | 9.94 | 5.37 | 1.86 |
| 4 | Sulfated silica | | | 0.98 | 4.13 | 10.54 | 4.99 | 1.97 |
| 5 | Sulfonated silica[b] | 4.25 | 0.87 | 1.41 | 4.41 | 6.29 | 3.7 | 1.10 |
| 6 | Sulfonated silica[c] | 4.60 | 0.49 | 1.04 | 4.42 | 8.44 | 5.0 | 1.47 |
| 7 | Sulfonated poly(styrene-divinylbenzene)[c] | | | 9.40 | 6.73 | 12.08 | 0.84 | 1.37 |

[a] Samples 1–6 analyzed by Schwartzkopf Microanalytical Laboratory; sample 7 analyzed by Galbraith Laboratories.

[b] Sample taken from downstream end of synthesis reactor used for incorporation of aluminum chloride.

[c] Sample taken from upstream end of synthesis reactor used for incorporation of aluminum chloride.

mer (*12*)—which was not observed in this work.

### *Infrared Spectra of Polymer-Supported Catalysts*

Spectra of the sulfonated polymer and of the product of the reaction of aluminum chloride with this polymer are shown in Figs. 1 and 2. These spectra provide structural information about the sulfonic acid groups, the bands being indicative of the S—O and S=O vibrations, among others. The comparisons shown in Figs. 1 and 2 indicate changes in the sulfonic acid groups, consistent with the suggestion that these groups reacted with the aluminum chloride.

### *Catalysis of n-Butane Isomerization and the Influence of HCl*

The first catalytic reaction experiments were done with the $AlCl_3$/sulfonic acid resin catalyst and only $n$-butane and helium in the feed. The principal product was isobutane, the minor products being propane and pentanes [in equimolar amounts, as described in a separate publication (*13*)] and traces of methane and ethane, which were detected when HCl was present during the initial stages of high catalytic activity. The rate of $n$-butane conversion decreased with time onstream in the flow reactor, and the effluent stream was acidic, presumably containing HCl.

In an attempt to maintain the rate of $n$-butane conversion, HCl was added to the

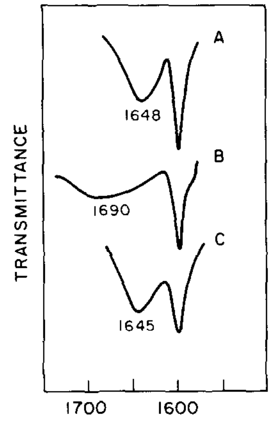

FIG. 1. Infrared spectra of sulfonated poly(styrene-divinylbenzene): evidence of the water scissor band in the range 1640–1700 $cm^{-1}$. (A) $Al^{3+}$-exchanged sulfonic acid resin membrane (gel form) (*25*); (B) macroporous sulfonic acid resin; (C) aluminum chloride/sulfonic acid resin (macroporous) after exposure to a trace of water vapor.

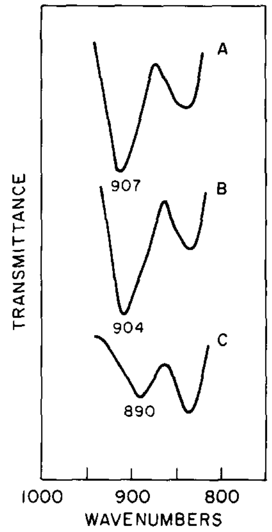

FIG. 2. Infrared spectra of sulfonated poly(styrene-divinylbenzene): evidence of the S–O single bond. (A) Sulfonic acid resin membrane (gel form) (25); (B) macroporous sulfonic acid resin; (C) aluminum chloride/sulfonic acid resin (macroporous).

feed stream, flowing steadily with the butane. The effect of HCl, shown in Fig. 3, was to increase sharply the rate of isomerization. A step change, in which the HCl was removed from the feed after flowing for a short time, led to a rapid decrease in the $n$-butane isomerization rate to a value roughly equal to that expected by extrapolation of the rate vs time curve from the period prior to the addition of HCl (*16*).

A series of experiments was done with $n$-butane feed in the absence of HCl at 23°C, a temperature so low that no HCl evolution from the polymer was observed. The decline in the rate of $n$-butane isomerization was slow enough that the reaction kinetics could be measured; the partial pressure of $n$-butane in helium was varied from 0.19 to 0.73 atm, and low (differential) conversions were measured after the catalyst had been deactivated for about 28 hr. The rates of $n$-butane isomerization calculated from these data were represented well by the following equation:[4]

$$r = \frac{k' P_{n\text{-C}_4}}{1 + K P_{n\text{-C}_4}} \tag{1}$$

where $k' = 2 \times 10^{-5}$ molecules/(Al atom · s · atm) and $K = 5.4\ \text{atm}^{-1}$.

### *Catalyst Deactivation*

The catalyst deactivation was temperature dependent, as illustrated by the data of Fig. 4. [An analysis of the deactivation process is presented separately (*16, 18*).] To achieve one of the primary objectives of this work—a determination of quantitative kinetics of the catalytic isomerization of $n$-butane—it was decided to avoid the initial period of rapid deactivation. Therefore, the most thorough experiments were done with catalysts which had been partially deactivated and were undergoing deactivation at an almost negligible rate (Fig. 4). In one of the longest experiments with an individual

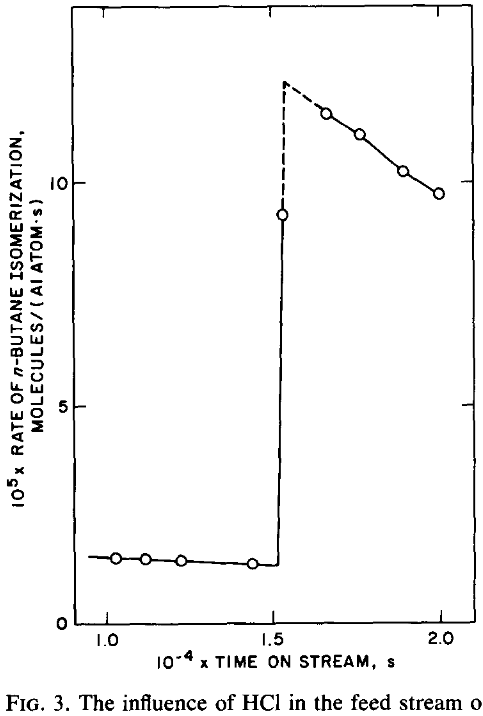

FIG. 3. The influence of HCl in the feed stream on the rate of $n$-butane isomerization catalyzed by aluminum chloride/sulfonic acid resin in a flow reactor at 100°C. The partial pressure of HCl in the feed stream was increased from zero to 0.22 atm at an onstream time of $1.5 \times 10^4$ s.

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[4] Alternatively, the data are about equally well represented by $r = 3.4 \times 10^{-6} P_{n\text{-C}_4}^{0.33}$ (*14*).

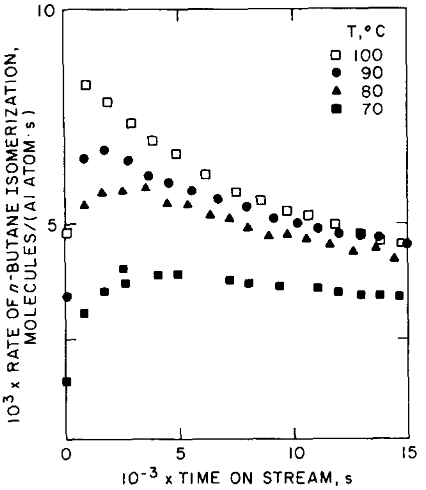

FIG. 4. Deactivation of aluminum chloride/sulfonic acid resin catalyst during *n*-butane isomerization in the presence of HCl in a flow reactor ($P_{n-C_4} = 0.33$; $P_{HCl} = 0.22$ atm).

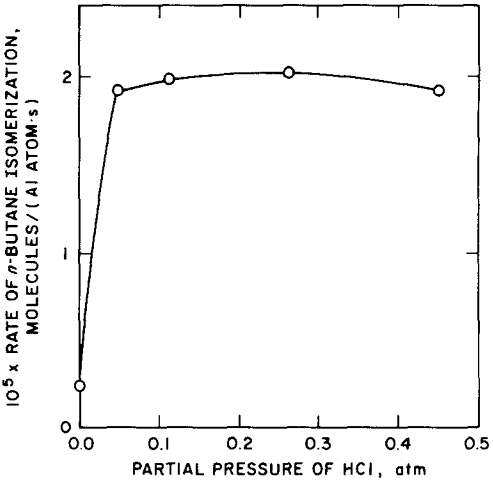

FIG. 5. Dependence of rate of *n*-butane isomerization on the partial pressure of HCl at 25°C. The partial pressure of *n*-butane was 0.44 atm. The catalyst was polymer-supported aluminum chloride.

catalyst charge, 1.9 turnovers were observed (estimated as the total number of isobutane molecules formed per Al atom in the polymeric catalyst), after which the reaction was still proceeding. We conclude from this result that the isomerization reaction was indeed catalytic.

## *Kinetics of n-Butane Isomerization*

With a sample of partially deactivated catalyst in the reactor, the partial pressures of *n*-butane and HCl were varied systematically, and low conversions of the butane were measured. In the range investigated, the conversions were proportional to inverse space velocity [as illustrated by data shown in Refs. (*13*), (*16*), and (*17*)], which

TABLE 3

Dependence of Catalytic Activity on Cl : Al Ratio

| Sample number[a] | Atomic ratio Cl/Al | Rate of *n*-butane isomerization at 100°C[b] mol/(g of catalyst · s) |
|---|---|---|
| 2 | 1.10 | $3 \times 10^{-9}$ |
| 5, 6 | 1.3[c] | $8 \times 10^{-8}$ |
| 1 | 1.44 | $2 \times 10^{-7}$ |
| 4 | 1.97 | $5 \times 10^{-7}$ |

[a] Samples specified in Table 2.

[b] Data were extrapolated to 100°C, $P_{n-C_4} = 0.42$ atm.

[c] Average for samples 5 and 6.

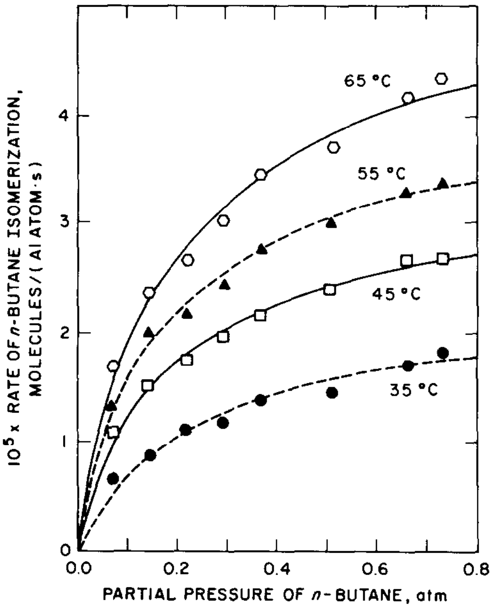

FIG. 6. Dependence of the rate of *n*-butane isomerization on the partial pressure of the reactant. The partial pressure of HCl was 0.05 atm. The polymer-supported catalyst was partially deactivated.

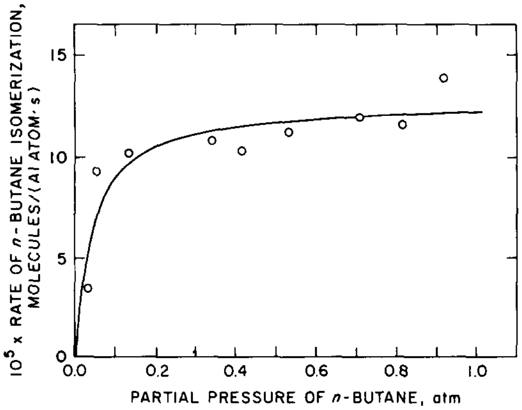

FIG. 7. Dependence of the $n$-butane isomerization rate on the partial pressure of the reactant. The catalyst was aluminum chloride supported on silica (sample 1, Table 2). Reaction conditions: $T = 25°C$; $P_{HCl} = 0.11$ atm.

demonstrates that they were differential, determining rates of the catalytic reaction directly.

Some of these rates of the $n$-butane isomerization observed with each catalyst are summarized in Table 3; the catalysts had different activities; there was apparently a pattern of increasing activity with increasing Cl : Al ratio.

The dependence of the rate of $n$-butane isomerization on the HCl partial pressure is shown in Fig. 5 for the polymer-supported catalyst. Almost all the data were obtained in the range where the rate was zero order in the HCl partial pressure. The dependence of rate on $n$-butane partial pressure under these conditions is illustrated by the data of Fig. 6, for the polymer-supported catalyst, and by the data of Fig. 7, for the silica-supported catalyst. It is evident that the order of reaction in the reactant is between 0 and 1. We therefore represent the data with an equation of the form of Eq. (1).[5] The parameter values [determined by a standard nonlinear least-squares regression analysis (*16, 17*)] for the polymer-supported catalyst are the most precise; they are collected in Table 4. Further data are given in Ref. (*17*). The temperature dependence of the rate constant for the polymer-supported catalyst is shown in Fig. 8.

TABLE 4

Kinetics of $n$-Butane Isomerization Catalyzed by Aluminum Chloride/Sulfonated Poly(styrene-divinylbenzene) (Sample 7): Parameter Values for Eq. (1)[a]

| Temperature (°C) | $10^4 \times k'$, molecules/ (Al atom · s · atm) | $K$ (atm$^{-1}$) |
|---|---|---|
| 35 | 1.02 | 4.5 |
| 45 | 1.82 | 5.4 |
| 55 | 2.39 | 5.8 |
| 65 | 2.78 | 5.2 |

[a] Data for partially deactivated catalysts.

## DISCUSSION

The results of the catalysis experiments establish the activity of supported aluminum chloride for $n$-butane isomerization under mild conditions (25°C, 1 atm). All the supports investigated, even the weakly acidic silica, allowed catalytically active species to form.

The Langmuir–Hinshelwood form of the kinetics [Eq. (1)] suggests a straightforward

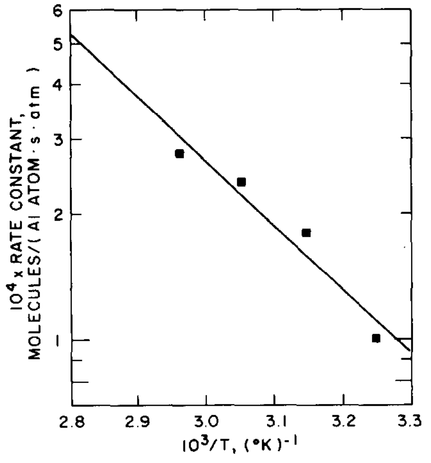

FIG. 8. Arrhenius plot: rate constant $k'$ [Eq. (1)] for $n$-butane isomerization catalyzed by aluminum chloride/sulfonic acid resin.

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[5] The data have also been fitted with about the same precision with equations of the form $r = kP^{n}_{n\text{-}C_4}$ (*16, 17*).

interpretation for the silica-supported catalyst [and for the polymer-supported catalysts, provided that the effects of transport and swelling of reactant are negligible—as is discussed elsewhere (*16*)]: the catalytic sites become saturated with HCl (when $P_{HCl} \gtrsim 0.1$ atm) and saturated with *n*-butane (when $P_{n-C_4} \gtrsim 0.2$ atm); the reaction is first-order in the concentration of *n*-butane adsorbed on the catalytic sites.

The results are consistent with the suggestion that the catalysts are strong Brønsted acids, functioning in more-or-less the same way as the superacids formed from Brønsted–Lewis acid combinations, such as $AlCl_3$–HCl, $SbF_5$–HF, and the Lewis acid–solid Brønsted acid combinations cited in Table 1. It is evident from the observation that HCl was formed in the synthesis reactions, as well as from the electron micrographs and infrared spectra, that the aluminum chloride reacted with hydrogen-containing groups on the supports, i.e., –OH groups. This pattern is borne out by the results of many workers [e.g., (*5*), (*20*)–(*22*)].

The nature of the proton-donor groups remains obscure; the complexity of the chemistry involving the Brønsted- and Lewis-acid groups is evident from the difficulty of preparation of samples having uniform aluminum chloride contents and reproducible catalytic activities; a variety of structures [suggested elsewhere (*16*)] may form, and the infrared spectra suggest that they may incorporate water (*16*). Whatever the structures of the proton-donor groups, it is clear that they were superacids. The cracking of *n*-butane to give methane and ethane suggests that carbonium ions were formed by protonation of *n*-butane; as the catalysts aged, the rates of formation of methane and ethane decreased, and the rate of formation of disproportionation products increased, and, presumably, the Cl : Al ratio in the catalyst decreased, giving less strongly acidic groups, which were perhaps no longer capable of direct protonation of the butane (*11*).

## APPENDIX: NOMENCLATURE

| | |
|---|---|
| $k$ | Reaction rate constant, variable dimensions |
| $K$ | Adsorption equilibrium constant in Langmuir–Hinshelwood rate equation, atm$^{-1}$ |
| $n-C_4$ | *n*-Butane |
| $n$ | Exponent ($0 < n < 1$) |
| $P_i$ | Partial pressure of *i*, atm |
| $r$ | Reaction rate, molecules/(Al atom · s) |

## ACKNOWLEDGMENTS

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