A 'Superacid' Polymer Catalyst: a Complex of Aluminium Trichloride with Crosslinked Polystyrenesulphonic Acid for the Cracking and Isomerization of n-Hexane at 358 K

By VINCENT L. MAGNOTTA, BRUCE C. GATES,* and GEORGE C. A. SCHUIT
(*Department of Chemical Engineering, University of Delaware, Newark, Delaware* 19711)

Summary A catalyst has been synthesized from $AlCl_3$ and beads of macroporous, sulphonated poly(styrene-divinylbenzene); it has the catalytic character of a 'superacid,' as shown by conversion data for cracking and isomerization of n-hexane in a flow reactor at 358 K and 1 atm.

THE strongest acid solutions known are combinations of Brønsted and Lewis acids such as $HF + SbF_5$. These 'superacids' are highly active catalysts for hydrocarbon reactions proceeding through carbonium ion (carbocation) intermediates,[1] but they have the processing disadvantages of being corrosive and difficult to separate from reaction products. We have tried to design a solid polymer catalyst having 'superacid' properties analogous to those of the solutions but lacking the processing disadvantages. The catalyst was synthesized from anhydrous $AlCl_3$ and a solid polymeric Brønsted acid, macroporous beads of sulphonated poly(styrene-divinylbenzene) (Amberlyst 15, Rohm and Haas). The beads were contacted in a fixed bed at 388 K with a stream of N_2 containing sublimed $AlCl_3$. $AlCl_3$ formed a complex with the sulphonated polymer, liberating HCl. The resulting polymer had a Cl:Al atomic ratio of *ca.* 2:1 and an Al:S atomic ratio of *ca.* 1:2, as determined by analysis of digested samples. The Al and Cl were dispersed uniformly throughout each polymer bead on a macroscale (*ca.* 1 μm) determined by electron microprobe *X*-ray analysis.

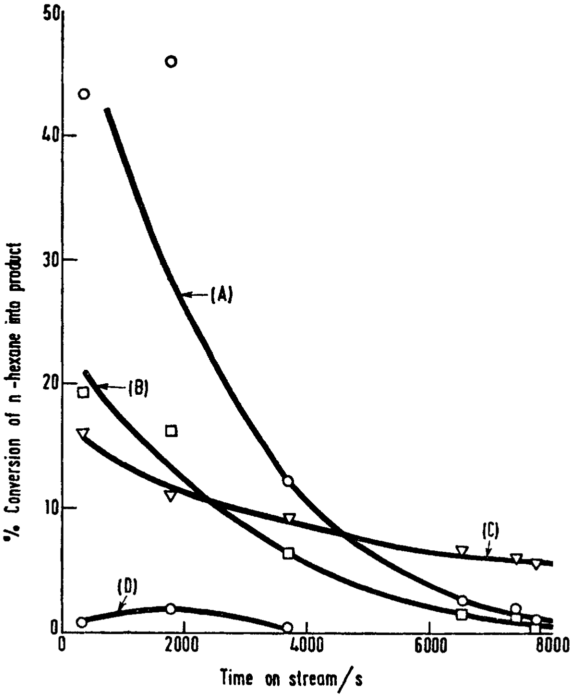

Figure. Cracking and isomerization of n-hexane as a function of time on stream in a steady-state flow reactor. Conditions: catalyst weight, 24·9 g; hydrocarbon feed rate, $1{\cdot}09 \times 10^{-5}$ mol/s; partial pressure of n-hexane in helium, 0·72 atm; reactor temperature, 358 K; reactor pressure, 1 atm; the feed n-hexane contained 0·1 mole % hex-1-ene. (A), isobutane; (B), isopentane; (C), branched C_6 isomers; (D), n-pentane.

The catalytic character of the polymer beads was investigated in an experiment with a flow reactor. The feed was n-hexane containing 0·1 mole % of hex-1-ene; it flowed at steady state with negligible axial dispersion in the packed-bed reactor operated at 1 atm and 358 ± 0·5 K. The products flowed directly into the sampling valve of a gas chromatograph and were analysed periodically during the experiment; products were identified by their mass spectra.

The Figure shows the conversion of n-hexane into each of the observed products as a function of time on stream. The overall initial conversion was *ca.* 80%; besides the products shown, traces of n-butane were also identified initially. The catalyst lost activity during the experiment, and the initially high selectivity towards isoparaffinic cracking products having 4—5 carbon atoms decreased with time, so that finally the isomerization products predominated.

The results show that the polymer catalyst was highly active compared with commercial cracking catalysts such as zeolites and silica–alumina, which require temperatures $>$ *ca.* 600 K for comparable conversions.[2] The activity of the polymer is roughly comparable to that of $AlCl_3$ promoted with HCl and H_2O[3] and is also similar to that of silica–alumina-supported $AlCl_3$, which, however, also requires promotion by H_2O and HCl.[4] The absence of low-molecular-weight products ($C \leqslant 3$) is characteristic of promoted aluminium halide catalysts.[3]

The highly active polymer catalyst defines a new class of solids, 'organometallic superacids.' These could find applications, for example, as insoluble catalysts for Friedel-Crafts reactions, and perhaps even for industrially important reactions such as paraffin isomerization and alkylation.[5]

(*Received*, 16*th February* 1976; *Com.* 163.)

---

[1] G. A. Olah, ed., 'Friedel-Crafts and Related Reactions,' Interscience, New York, 1963.

[2] H. Heinemann, *Acta Cientif. Venezolana*, 1974, **24**, Supplement 2, 5.

[3] F. E. Condon, 'Catalysis,' Vol. VI, ed. P. H. Emmett, Reinhold, New York, 1958, Ch.2.

[4] J. M. Oelderik and J. C. Platteeuw, Proceedings of the Third International Congress on Catalysis, eds. W. H. M. Sachtler, G. C. A. Schuit, and P. Zwietering, Vol. 1, North Holland, Amsterdam, 1965, 736.

[5] T. S. Huang and S. Yurchak, U.S.P. 3,855,343 (1974).