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LETTER TO THE EDITORS

Superactive Crystalline Aluminosilicate Hydrocarbon Catalysts

Previous publications (*1, 2, 3*) described catalytic hydrocarbon cracking activity of Na and Ca faujasites and Ca-A-zeolite comparable to or greater than that of conventional silica-alumina catalyst. Keough and Sand (*4*) reported hydrocarbon cracking activity on synthetic mordenite ("Zeolon").

Frilette and Rubin (*5*) reported H-activated natural mordenite to be a remarkably active hydrocarbon conversion catalyst, capable of cracking *n*-hexane at 200°C, demonstrating existence of activity several orders of magnitude above conventional oxide catalyst activities. They were led to compare its activity with that of HCl-promoted $AlCl_3$.

We have been able to compare the relative cracking activity rate constants of a number of very active crystalline aluminosilicate zeolite compositions revealing a span of attainable activities ranging to above 10^4 times that of conventional amorphous catalyst.

The span of activity among the catalysts of this investigation is so large that comparison tests at any chosen standard temperatures would result in either conversion percentages too low to essay analytically, or so close to complete conversion that no useful measure is attainable. We have, however, found such similarities in the *slopes* of Arrhenius plots (apparent activation energies) of activity among various compositions (see Fig. 1) that it appears justifiable to compare relative activity magnitudes by extrapolation to a standard temperature which we have chosen as 538°C.

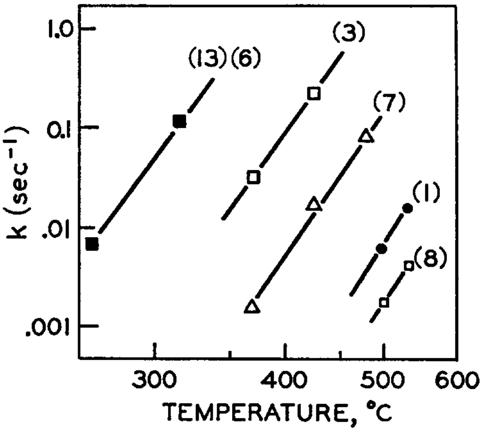

FIG. 1. Rate constants for *n*-hexane cracking measured for various crystalline aluminosilicate compositions. (Numbers refer to catalysts listed in Table 1.)

Measurements are made with *n*-hexane in a continuous flow microreactor at temperatures at which the conversions are above 5%, for accuracy of measurement, and below about 40% to avoid complications due to overcracking and transport phenomena (particle size was chosen always to be in the range of 12–28 mesh or less). Conversions were converted to per volume rate constants assuming first order behavior. Considering that these results are reported only to demonstrate magnitudes over a span of four powers of ten, the conclusions would not be altered by assumption of any other reasonable kinetic order.

For purposes of convenient comparison, we have termed the *relative* rate constant (rate of *n*-hexane conversion per unit volume of oxides composition per unit time) "alpha," and have based it on the activity of a highly active conventional amorphous silica-alumina obtained by co-gellation (*6*), containing 10% alumina, and having a surface area of 420 m^2/g, as $\alpha = 1$. This catalyst has a petroleum gas oil cracking activity in excess of that usually had by the cracking catalyst in any contemporary cracker installation. [Its activity is near "46 AI" by an industrially accepted test method (*7*).] Because of possible variability inherent in the use of cracking tests with complex petroleum gas oil charge stocks, we prefer to characterize the reference catalyst by its behavior in our standard microreactor measurement with *n*-hexane: It converts 12.5% of *n*-hexane passed as saturated vapor (25°C) in a stream of helium over the catalyst at 538°C, with a 9-sec superficial contact time (superficial catalyst volume/gaseous volume flow rate), at a time of 5 min after commencement of flow.

Table 1 summarizes zeolite structures, ionic forms, and relative "alpha" activities obtained for the samples in this investigation. The zeolite structures used include a variety of synthetic structures as well as natural samples from mineral sources as indicated. The designation $H(NH_4)$ refers to the use of NH_4 ion in the exchange solutions, where it is believed that subsequent decomposition during drying and air calcination of the sample leads to conversion to hydrogen. The zeolite ZK-5 is that synthesized by Kerr (*8*) and believed to contain alkyl ammonium ion after synthesis *per se*. Sample 7 differs from Sample 6 by having been severely steam-treated prior to catalytic test.

The exceedingly large available spectrum of magnitudes in hydrocarbon cracking activity available as a result of procedures involving introduction of hydrogen and/or multivalent elements as cations is self-evident from these data. The zeolite structures include synthetic materials as well as natural zeolites.

Attainable levels of "superactivity" of the order of magnitude of $\alpha \geqq 10{,}000$ are seen to be attainable by suitable compositions of a number of different crystallographic structures.

TABLE 1

HYDROCARBON CRACKING ACTIVITIES (α) OF VARIOUS CRYSTALLINE ALUMINOSILICATE CATALYSTS RELATIVE TO AMORPHOUS SILICA-ALUMINA

No.	Structure of zeolite	Cations in base exchanging solution	α
1	Amorphous $SiO_2 \cdot Al_2O_3$	O	1.0
2	Faujasite (syn.)	Ca	1.1
3	Faujasite (syn.)	$H(NH_4)$	6 400
4	Faujasite (syn.)	La, H	7 000
5	Faujasite (syn.)	Ce, La, H	>10 000
6	Faujasite (syn.)	Ce, La, $H(NH_4)$	>10 000
7	Faujasite (syn.)	Ce, La, $H(NH_4)$	20
8	A-Zeolite (syn.)	Ca	0.6
9	ZK-5 (syn.)	—	38
10	ZK-5 (syn.)	H	450
11	Mordenite (syn.)	Ca	1.8
12	Mordenite (syn.)	Ca, H	40–200
13	Mordenite (syn.)	H	>10 000
14	Mordenite (nat., Nova Scotia)	H	2 500
15	Mordenite (nat., Nova Scotia)	H	>10 000
16	Gmelinite (nat., Bancroft, Ont.)	$H(NH_4)$	>10 000
17	Chabazite (nat., Nova Scotia)	$H(NH_4)$	>10 000
18	Stilbite (nat., Halls Harbour, Nova Scotia)	$H(NH_4)$	120

We find that under conventional test conditions, i.e., at typically high temperature, and using accumulated effluent for determination of conversion, superactivity can remain unrevealed due to rapid deactivation during overcracking in the first moments of operation.

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