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Catalysis by Crystalline Aluminosilicates
I. Cracking of Hydrocarbon Types over Sodium and Calcium "X" Zeolites

V. J. FRILETTE, P. B. WEISZ, AND R. L. GOLDEN*
From the Socony Mobil Oil Company, Inc., Research Department, Paulsboro, New Jersey

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Crystalline sodium aluminosilicates of the three-dimensional rigid-framework type (molecular sieves) exhibit unexpected catalytic activity for cracking various hydrocarbons. The sodium "X" crystals exhibit very high activity with paraffin and olefin hydrocarbons. Paraffin cracking activity exceeds that of conventional silica-alumina cracking catalyst. The products formed are virtually free of branched chain hydrocarbons. In contrast to the conventional cracking catalyst, this salt is ineffective as a catalyst for the dealkylation of cumene.

Replacing the sodium by the calcium ion radically alters the catalytic properties of the solid. The calcium salt, even more active than the sodium form for paraffin or olefin cracking, produces considerable amounts of branched chain hydrocarbons. Furthermore, it is a highly active catalyst for the dealkylation of cumene. The relative activity toward various hydrocarbons, and the nature of the products from this salt form approach that of silica-alumina.

Available evidence indicates that the catalytic centers are located within the interstitial spaces of the dehydrated crystals. Change of the mobile cation from calcium to sodium in the same crystal changes its role from that of an acid catalyst to one which intervenes in a radical mechanism.

INTRODUCTION

Two basically different mechanisms have been proposed to explain observed product distributions in hydrocarbon cracking. One of these is the radical-chain mechanism developed by Rice and co-workers (*1*), and it applies to the so-called "thermal" cracking of paraffins and olefins in the absence of catalysts. Another mechanism, propounded by Greensfelder and co-workers (*2*), Thomas (*3*), and others, applies to cracking in the presence of acidic oxides. An essential feature of this mechanism is the postulate that the carbonium ion concepts of Whitmore apply to chemisorbed species in heterogeneous catalysis (*3*).

These two mechanisms qualitatively explain the observed behavior of amorphous oxides which influence the rate of hydrocarbon cracking. It would be desirable, however, to be able to predict catalytic behavior of the oxides from some independently measurable physical property of the solids. And, although much excellent research still is carried on towards this end, the goal seems difficult to achieve (e.g. *4*–*6*). This may be a result of the difficulty in defining unique structural parameters in such highly disordered solids.

Two crystalline forms of mixed silicon-aluminum oxides were made commercially available recently (*7*). In these crystals, all of the silicon and aluminum atoms are tetrahedrally bonded to oxygen, with the tetrahedra arranged to form three-dimensional rigid framework structures. Such crystals are sometimes called "molecular sieves." As is well known, in these struc-

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* Present address: Scientific Design Co., Inc., 33 Industrial Avenue, Litttle Ferry, N. J.

tures the tetravalency of the aluminum is maintained by electrons donated usually by alkali or alkaline earth elements, the resultant cations remaining in interstitial positions within the lattice. These interstitial cations are mobile, and in most cases readily exchangeable for other cations without alteration of the rigid three-dimensional oxide lattice. The two oxide structures have been crystallographically defined and are known as the "A" and "X" lattices, respectively (*7, 9*). Availability of these ordered oxides appeared to offer the possibility of studying acidic catalytic sites well defined in structure, amount, and homogeneity. Such sites might be introduced, e.g. by hydrogen-ion exchange.

In the ensuing studies, it was found that the salt forms of the crystals showed very high catalytic activities even when no attempts were made to deliberately introduce acidic sites. This was briefly reported in a previous note (*10*). The purpose of the present paper is to characterize the intrinsic activity, i.e., the activity inherent in the interstitial space of the sodium and calcium salts of the "X" crystals, for the cracking of paraffins, decene-1, and isopropylbenzene (cumene).

The "X" lattice, because of its large apertures, is particularly well suited to a study of intrinsic activities. In this lattice, multiple windows estimated to have a free diameter of 8–9 Å interconnect supercages with an internal free diameter of 12–13 Å, thus forming a three-dimensional array of pores (*9*). The large apertures render the interior of the crystals readily accessible to most hydrocarbon structures which contain twelve or less carbon atoms. Thus, since the present study is concerned with hydrocarbons no larger than decane, any catalytic effects of the "X" structure should be free of "molecular sieve" action on the reactants or products. In view of the irrelevancy of the molecular sieve property, it is advisable to use a designation of these solids other than "molecular sieve."

Barrer suggested that the rigid three-dimensional skeletal network characteristic of these solids may be properly regarded as "crystalline aluminosilicic acids." The commonly available salt forms of these zeolites, accordingly, become salts of the aluminosilicic acid frameworks. This nonfunctional nomenclature appears to be appropriate for the present discussion. We shall, accordingly, refer to the catalysts as salts, or aluminosilicates, of the "X" lattice (*11*).

EXPERIMENTAL

All runs were carried out in a Pyrex reactor tube charged with 50 cc of catalyst, and a hydrocarbon feed rate of 50 cc/hr, i.e., at 1 LHSV, for a period of 3 hr.

Both the CaX and the NaX aluminosilicates were clayfree products,* prepared in powder form, and pressed into $\frac{1}{8} \times \frac{1}{8}$-inch pellets without the use of a binder. The catalysts were regenerated after each run. Regenerations were carried out in air, beginning at 370–400°C and raising the temperature carefully so that it never exceeded 510°C. Regeneration was considered to be complete when the Ascarite bulb used to absorb the effluent CO_2 showed no detectable weight increase over a period of $\frac{1}{2}$ hr.

The hydrocarbons used were reagent or research grade. The cumene was percolated to remove peroxides prior to use.

The reaction products were analyzed as follows:

n-Decane. The C_1 to C_4 gases were analyzed by gas chromatography. The materials including normal pentane were removed from the liquid product by low temperature Podbielniak distillation and analyzed by gas chromatography. The *n*-decane in the total liquid product was determined by mass spectrometer. A similar procedure was used for *n*-hexane and 3-methylpentane.

Decene-1. The same procedure was used as with *n*-decane, but no attempt was made to analyze the products heavier than *n*-pentane.

Cumene. The same procedure as with *n*-decane. The fraction of the liquid boiling above *n*-pentane product was analyzed by mass spectrometer.

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* Linde Air Products Div., U.C.C. Corp.

DEPENDENCE OF CRACKING ACTIVITY ON HYDROCARBON TYPE AND SALT FORM

It was indicated in our prior publication (*10*) that both level of catalytic activity and nature of products depended on the particular salt form and hydrocarbon type. This paper presents a more detailed examination of this dependence for three types of hydrocarbons. The hydrocarbons were chosen so as to present different structural elements to the catalyst surface. Of the three hydrocarbon types, normal decane, with two methyl and eight methylene carbons is the least susceptible to primary attack by an electrophilic catalytic site. With decene-1, the dominant structural element is again methylene carbon, but the structure also contains a potentially facile point of attack in the double bond. In cumene, there is a complete absence of methylene carbons; but, as with decene-1, readily accessible electrons are present.

In Table 1 a comparison is made of the observed cracking activity levels for paraffins, among the sodium and calcium aluminosilicate and conventional high activity silica-alumina cracking catalyst (46 Activity Index; Socony Mobil Oil Co., commercial fresh catalyst; 420 m^2/g specific surface area). For the cracking of *n*-paraffins the activity increases in the order silica-alumina < NaX < CaX.

TABLE 1
ACTIVITY FOR PARAFFIN CRACKING

Hydrocarbon	Catalyst	Conversion (wt %) 470°C	Conversion (wt %) 500°C
n-decane	Silica-alumina	25.5	33.2
	NaX	31.8	49.1
	CaX	48.1	—
n-hexane	Silica-alumina	—	16.4
	NaX	—	24.5
3-methylpentane	Silica-alumina	—	33.0
	NaX	—	23.6

The dependence of cracking activity on hydrocarbon type is shown in Tables 2 and 3 for the different catalysts. At the temperatures and contact times employed, the conversions obtained are negligibly small in the absence of the catalyst. As seen in Table 2, both, *n*-decane and decene-1, are converted to cracked products with about equal facility by the sodium salt, as shown by the relatively small temperature difference required to achieve equivalent conversion.

TABLE 2
TEMPERATURE (°C) FOR 25–30% WT CONVERSION TO C_1 TO C_5 PRODUCTS (AT 1 LHSV)

Catalyst	Hydrocarbon *n*-decane	Hydrocarbon 1-decene
Silica-alumina	500	365
CaX	470	430
NaX	500	510

This stands in drastic contrast to the behavior of the conventional catalyst for which olefin cracking is well known to occur much more rapidly than paraffin cracking (*12–14*). The calcium aluminosilicate takes a position intermediate between the NaX and conventional catalyst. For cumene cracking (see Table 3), however, the conversion level over NaX is very small. Under these experimental conditions, conventional catalyst has such high activity that a true measure of conversion cannot be obtained in standard apparatus (*15*). Conversion will depend on catalyst particle size, in view of heavy diffusion effects. Again, the calcium salt shows an intermediate level of activity.

TABLE 3
CUMENE CONVERSION AT 1 LHSV

Silica-alumina[a]	>60% at 470°C
CaX	59% at 470°C
NaX	6% at 510°C

[a] See text.

NATURE AND DISTRIBUTION OF FRAGMENTS

Further information on the interaction of hydrocarbon type and salt form may be obtained by examination of the products. A detailed analysis of the lower molecular weight fragments from *n*-decane and decene-1 are summarized in Table 4. The

TABLE 4
DISTRIBUTION OF C_1–C_5 PRODUCTS FROM PARAFFIN AND OLEFIN DECOMPOSITION, MOLES PER 100 MOLES C_1–C_5

	Sodium X catalyst		Calcium X catalyst		Silica-alumina
Fragment	*n*-Decane	Decene-1	*n*-Decane	Decene-1	*n*-Decane
CH_4	15.5	19.2	9.0	5.7	5.4
C_2H_6	19.3	18.8	5.1	3.1	5.2
C_3H_8	13.7	10.6	14.9	5.4	13.8
n-C_4H_{10}	7.7	5.8	14.6	3.4	5.7
iso-C_4H_{10}	0.1	0.4	14.3	16.0	8.6
n-C_5H_{12}	5.0	3.5	3.9	2.0	3.8
iso-C_5H_{12}	0.1	0.3	14.7	17.2	8.6
C_2H_4	8.4	8.7	2.1	1.9	4.9
C_3H_6	13.4	13.3	9.5	19.0	17.0
n-C_4H_8	10.4	10.4	7.1	15.3	8.6
iso-C_4H_8	0.2	1.5	1.6	3.3	4.6
n-C_5H_{10}	5.6	5.0	1.2	3.6	9.9
iso-C_5H_{10}	0.6	2.5	2.0	4.1	3.9
	100.0	100.0	100.0	100.0	100.0
			By Carbon Number		
1-C	15.5	19.2	9.0	5.9	5.4
2-C	27.7	27.5	7.3	2.4	10.1
3-C	27.1	23.9	24.4	25.0	30.8
4-C	18.4	18.1	37.5	38.9	27.5
5-C	11.3	11.3	21.8	27.8	26.2
	100.0	100.0	100.0	100.0	100.0

products from the fragmentation of cumene are shown in Table 5.

With the sodium aluminosilicate the product and carbon number distributions obtained from *n*-decane and decene-1 are remarkably alike. The virtual absence of branched chain molecules is of particular interest. However, although skeletal isomerization is virtually absent, double bond migration took place since the butenes and pentenes were found to be mixtures of internal and terminal olefin types. More than half of the fragments contain two or three carbon atoms.

TABLE 5
PRODUCTS FORMED BY DECOMPOSITION OF CUMENE

	Mole % of converted charge	
Product	Sodium X	Calcium X
Benzene	21.5	49.1
Propylene	10.2	38.2
Hydrogen	26.4	0.0
Methane	21.2	1.3
Misc. aliphatics	7.9	6.0
Misc. aromatics	12.8	5.4
	100.0	100.0

For cracking over the Ca salt, branched fragment molecules are produced in abundance, similar to the case of silica-alumina. The carbon number distributions from *n*-decane and 1-decene are similar to each other. However, although cracking over the Na salt proceeds predominantly to C_2 and C_3 fragments, C_4 fragments predominate with the Ca salt. Again in this respect the Na salt is distinctly different in behavior from conventional cracking catalyst.

The products obtained from cumene cracking (Table 5) over the Na aluminosilicate under conditions severe enough to obtain a small but appreciable conversion

(Table 3) do not have the character of a mere dealkylation but give evidence of multiple, including dehydrogenative reactions. The products for Ca aluminosilicate are not too dissimilar to those obtained over silica-alumina, indicating rather selective dealkylation (*15, 16*).

Comparison of the cracking conversion of *n*-hexane and 3-methylpentane is of interest (Table 1), since the Na aluminosilicate shows no preference for cracking the branched chain hydrocarbon, which is the accepted experience with conventional catalyst (silica-alumina) and is usually explained on the basis of carbonium ion behavior.

INTRACRYSTALLINE CATALYSIS

Evidence that the reported catalytic reactions occur within the large interstitial spaces characteristic of zeolitic structures is not self-contained in the present study. However, data which support the concept are obtained from a comparison of cracking reactivity of various aluminosilicates including the "A" lattice, since the calcium salt of the "A" lattice excludes skeletally branched compounds from the interstices (*10*), and its sodium salt excludes both normal and branched compounds.

Table 6 shows a comparison of observed catalytic cracking activity (at 500°C) for *n*-hexane and 3-methylpentane, and accessibility of the interior crystalline space, for each of the hydrocarbon on the four aluminosilicate forms NaA, NaX, CaA, CaX. It will be noted that there exists a striking *one-to-one correspondence of penetrability and cracking activity.* It should be noted that the size of the single crystallites, and thus the exterior crystal surface area is of the same order of magnitude in each of the four cases (approx. 1 to 5 micron crystal dimensions). More detail concerning the role of intracrystalline accessibility and catalytic behavior will be covered in our accompanying paper.

Nature of Intracrystalline Catalysis

The catalytic behavior of the sodium and calcium salts differ markedly. The CaX is similar to silica-alumina in that it dealkylates cumene, cracks olefins more readily than paraffins, and produces abundant branched chain fragments. Based on analogy in behavior we may consider the calcium salt to be effective by virtue of an "acidic" mechanism. Protonic acid centers might arise in this salt by dislocation of bivalent cations to form a basic calcium salt plus the required acid, as suggested recently by Rabo *et al.* (*17*).

The catalytic behavior of the sodium salt, on the other hand, bears no resemblance to silica-alumina. Instead the products pattern resembles that from pure silica, or thermal cracking [see Greensfelder (*2*)]. Qualitative observations on the low amounts of coke formed when *n*-decane is cracked over the NaX also suggest a thermal-type mechanism. Therefore, a radical mechanism of the type invoked in thermal cracking (*2*) may be operative. Acceleration of such a mechanism by a catalyst implies, of course, that the solid intervenes in the process. This must have been the case even for the measurements with pure silica surface by Greensfelder although the catalytic enhancement was quite small. Recently, Veovodsky (*18*) has shown that the "thermal" decomposition of paraffins is at least in part a het-

TABLE 6
COMPARISON OF ACCESSIBILITY OF INTERIOR CRYSTALLINE SPACE AND CATALYTIC CRACKING ACTIVITY

Hydrocarbon		Salt form of aluminosilicate			
		NaA	NaX	CaA	CaX
n-hexane	Interior access.	no	yes	yes	yes
	Catal. cracking	no	yes	yes	yes
3-methylpentane	Interior access.	no	yes	no	yes
	Catal. cracking	no	yes	no	yes

erogeneous process, the wall taking part in the processes of chain initiation and rupture. Thus, there is an independent basis for postulating the intervention of the wall in the hitherto postulated homogeneous radical process.

The present demonstration of a major alteration of the character of the catalysis in the same crystal by change of the cation alone is unique. This finding suggests that acidic and radical mechanisms may represent special cases of a more complex but unifying mechanistic picture, involving common kinetic steps or species, with certain of the mechanistic steps predominating in each case.

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