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Hydrocarbon Conversion over Crystalline Aluminosilicates Containing S, Se, and Te

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Contact with H_2S, or S followed by oxygen (air), or with SO_2 alone, raises the catalytic activity of NaX aluminosilicate for *n*-hexane cracking by a factor of five to ten. In each case, the same sulfur zeolite complex appears to be formed. The sulfur contents correspond to one sulfur atom for two of the mobile sodium atoms of the aluminosilicate lattice. Combination of NaX with Se, and with Te, leads also to active catalytic solids; however, the catalytic characteristics shift from carbon–carbon cracking to dehydrocyclization.

INTRODUCTION

Aluminosilicate structures are known that contain sulfur in a complex (*1*) of relatively unusual electronic properties. An example is the mineral, lazurite (*2*); its characteristic color is unusual when considering the usual chemical forms of its elemental constituents. Kerr and Johnson (*3*) also observed the appearance of a lazurite-like blue color on Nafaujasite (NaX-zeolite) during certain stages of its use as a catalyst in the oxidation of H_2S to elemental sulfur.

Frilette, Weisz, and Golden (*4*) showed that NaX-zeolite possesses catalytic activity for the rupture of C–C bonds in hydrocarbons. This cracking activity is comparable in magnitude to that of conventional "acidic" oxide cracking catalysts, e.g., silica-alumina; however, the product distribution differs from that of acidic catalysts, and resembles that from thermal cracking, normally assumed to proceed by a free radical mechanism.

This paper describes the properties and catalytic behavior of NaX-zeolite modified by incorporation of the group VIA elements sulfur, selenium, and tellurium.

EXPERIMENTAL

The zeolites 13X (NaX, 14.5% Na, 32.9% Al_2O_3, 47.6% SiO_2), 10X (CaX, 8.8% Ca, 5.7% Na, 31.5% Al_2O_3, 47.8% SiO_2), and 5A (CaA, 9.3% Ca, 5.8% Na, 37.4% Al_2O_3, 42.5% SiO_2) were Linde preparations. The sodium mordenite (5.5% Na, 15.7% Al_2O_3, 77.2% SiO_2) was obtained from the Norton Company. The NaY (9.4% Na, 21.1% Al_2O_3, 66.6% SiO_2) was synthesized in accordance with a Linde procedure (*5*). The S, Se, and Te were research grade materials of at least 99% purity. Other characteristics of the materials involved in this study are described in the text where deemed important.

The catalytic activity for *n*-hexane conversion was measured in a microapparatus previously described (*6*), at 1 atm pressure, 538°C, and 9-sec vapor residence time, with a reactant stream of 80% helium and 20% hydrocarbon. An integral part of the microapparatus was a sample loop, from which a trapped effluent sample could be carried into a chromatographic column—2½ ft, silicone oil (SF-96) on firebrick— and a thermal conductivity detector. The apparatus gave a convenient analysis of C_1–C_5 cracked material, unreacted *n*-hexane, and benzene.

Results and Discussion

A. *Activation by Sulfur*

Catalytic Activity. Samples of 1.5 ml of NaX powder were subjected to various treatments:

I. *H_2S + Air Oxidation:* Gaseous H_2S, at 1-atm pressure was contacted with the sample at 371°C for 5 hr. The sample was then exposed to air flowing at 20 ml/min at 1 atm, 538°C, for 30 min.

II. *Sulfur + Air Oxidation:* Flowers of sulfur were mechanically mixed with NaX powder in a weight ratio of about 3:1, i.e., in slight excess of the zeolite sorption capacity. The mixture was heated until the sulfur melts and is sorbed, producing a free flowing powder. The material was then air oxidized as in I.

III. *SO_2:* Gaseous SO_2 at 1-atm pressure was contacted with the sample for 1 hr.

IV. *SO_2 + Air Oxidation:* After treatment as in III, material is air oxidized as in I.

The catalytic results obtained on a standard silica-alumina (Si-Al) cracking catalyst, an untreated NaX, and for samples I to IV are summarized in Table 1. The distribution of cracked products, determined chromatographically, is reproduced in Fig. 1. In addition, about 2% of the hexane was converted to benzene.

TABLE 1
n-Hexane Cracking Conversion on Zeolite–Sulfur Catalysts

Sample	Treatment	Time on stream (min)	*n*-Hexane conversion (%)
Si-Al	—	5	12.5
NaX	None	5	12.9
I	H_2S + Air	10	76.2
		35	67.4
II	S + Air	10	60.3
		35	55.2
III	SO_2	10	69.4
		35	65.7
IV	SO_2 + Air	35	62.5

Compositional Tests. A mixture of 28-wt% sulfur and 72-wt% NaX powder was heated for 30 min at 204°C in a stream of helium, and these heating cycles were repeated, each one at about 30°C higher temperature; the sample weight was followed, up to a treating temperature of 563°C (Run A).

A second sulfur preloaded sample was subjected to the same weight study with air substituted for helium (Run B).

Another sample of 1.5-ml NaX was similarly studied after an initial exposure to 35 ml/min of SO_2, at 232°C, for 30 min, followed by thermal cycling in helium (Run C). A similar SO_2-preloaded sample was exposed to air treatment (Run D).

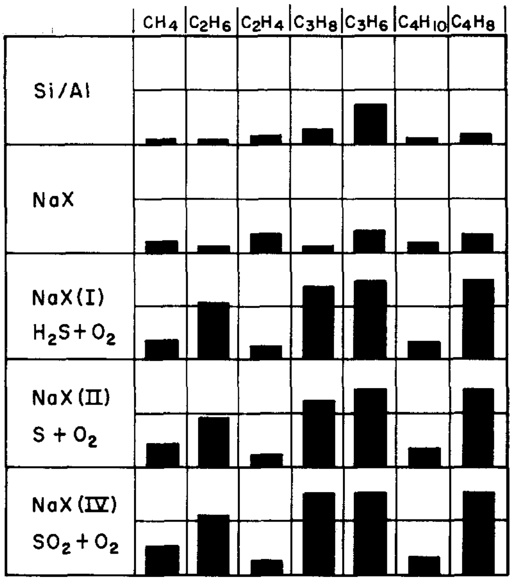

Fig. 1. Relative distribution of C_1–C_4 products from cracking of *n*-hexane.

The course of the weight loss observed for the four cases is plotted in Fig. 2. During the course of heating the SO_2-loaded sample in helium, elemental sulfur was observed depositing on the cool portion of the effluent line.

Nature of the S-Zeolite Complex. Sorbed sulfur heated in an inert atmosphere is desorbed from NaX-zeolite, in agreement with the findings of Barrer and Whiteman (7).

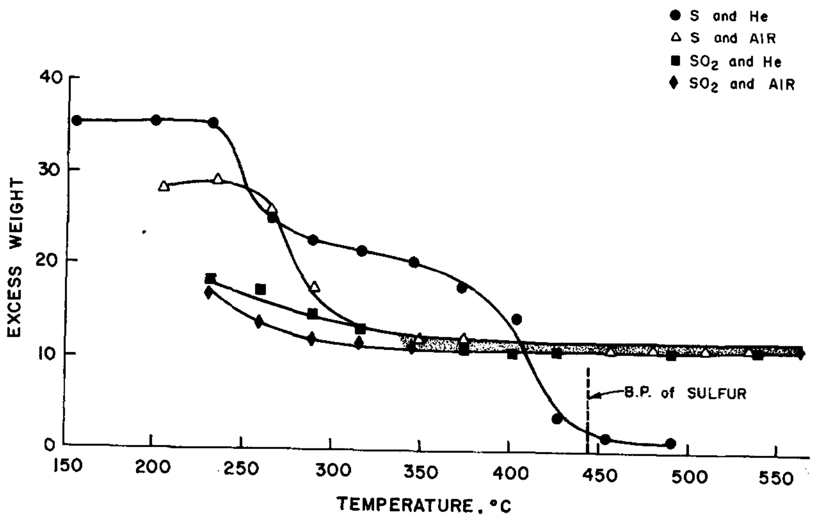

FIG. 2. Sample weight change vs temperature.

However, in an oxidizing atmosphere a constant excess weight is approached. Furthermore, sulfur dioxide (in the presence or absence of air) also reacts with NaX-zeolite resulting in the same weight excess. Sulfur analyses of the samples were obtained and are listed in Table 2, together with the observed total weight increases. The analyzed sulfur content is seen to be identical with that calculated from the total weight excess on the assumption that it is due to the stoichiometric entity SO_3.

The observations of identical weight increase and sulfur contents, and of similar catalytic activity level and product spectra are consistent with the conclusion that the same SO_3 complex is produced, either by oxidation of sorbed H_2S or S, or by the disproportion reaction $3SO_2 \rightarrow S + 2SO_3$. Indeed, elemental sulfur was observed during preparation C.

The product spectra from *n*-hexane cracking over the sulfur-zeolite complex are not characteristic of an acidic catalyst, as seen from the comparison with the products from silica-alumina. They have some of the characteristics of the NaX cracking reaction (relatively high methane and butenes concentration) and produce an unusually high ethane concentration. It is of interest that Dudzik (*8*) has reported thermal type cracking of 2,3-dimethyl butane over various ultramarines and 3A zeolite containing sulfur. He suggests that sulfur free radicals initiate the cracking reaction because of a correlation found between the amount of sulfur radicals in 3A and the catalytic activity.

TABLE 2
TOTAL WEIGHTS AND SULFUR CONTENTS

Charge	% Increase in weight	Calcd S as SO_3	Wt % S (anal)
13X + S + Air	11.2	4.48	4.40
13X + SO_2 + He	10.3	4.12	4.02
13X + SO_2 + Air	10.5	4.18	4.18

NaX-zeolite is said (*9*) to contain about 80 sodium ions per unit cell, of which 48 have been crystallographically located (*9, 10*) on six-membered rings, with the remaining 40% of the sodium ions believed to be located in the large cavities and to have some mobility. The analyzed sulfur contents of the catalysts correspond to one sulfur atom per five to six sodium ions. If we assume each sulfur to interact with two sodium ions, the fraction of sodium ions involved would be 2/(5 to 6), or 33–40%, coinciding with the number of mobile sodium ions in the large cavity. These would, in fact, be accessible to the hydrocarbon reactant.

B. *Activation by Selenium and Tellurium*

Catalytic Activity. A number of exploratory experiments were performed to investigate the possibility of an activating behavior of selenium and tellurium analogous to that observed with sulfur. Catalysts for these experiments were again made by a simple physical mixing of the components in the appropriate proportions. They were then pelleted, sized, and pretreated in flowing air or helium for 1 hr at 538°C prior to catalytic testing. Results for *n*-hexane conversion, including those with NaX and S–NaX catalysts, are summarized in Table 3.

Sulfur and selenium enhance the cracking activity of the Na-zeolite. In addition, selenium activation produces slightly more olefins in the cracked products (75%) than does sulfur activation.

A dramatic change occurs with tellurium in that the cracking and dehydrogenation activities are masked by a very selective dehydrocyclization process. The selective aromatization—90% of the converted material is benzene—is in sharp contrast with previous uses (*11*) of tellurium to catalyze oxidation processes. The sharp transition in type of catalytic activity from radical-type C—C bond cracking to dehydrogenation in the series S, Se, Te appears surprising. The structure of the tellurium site will be the subject of a separate study.

Retention of Selenium and Tellurium. Experimental results on the elution of selenium and tellurium from NaX by helium and air are given in Table 4. These results show that an oxidizing atmosphere inhibits the elution of either activator—a situation analogous with the behavior of the S–NaX system.

TABLE 4

ELUTION OF SELENIUM AND TELLURIUM

Catalyst	Elution gas	Activator concentration[a] (wt%)
Se–NaX	Helium	27.8 → 3.4
Se–NaX	Air	22.8 → 21.0
Te-NaX	Helium	33.5 → 21.5
Te–NaX	Air	No change

[a] Three cm^3 of catalyst subjected to flowing gas (35 cm^3/min) at 565°C for 2.5 hr.

Other Supports for Tellurium. Tellurium was admixed with various supports and the resultant catalysts tested under the conditions described above. The results are tabulated in Table 5.

With the zeolite supports, the aromatization activity appears to depend upon sodium ion concentration which declines with increasing silica-alumina ratio and is smaller for the divalent calcium form.

Amorphous supports—*α* alumina and silica-alumina—had negligible aromatization activity. Also they were unable to retain tellurium, as evidenced by deposition of large quantities of tellurium downstream from the heated reactor zone.

These experiments highlight some intriguing questions concerning tellurium-containing catalysts. Further studies of their selective aromatization capability and of their physical and chemical nature are reported in the following paper (*12*).

TABLE 3

ACTIVATION OF NaX BY SULFUR, SELENIUM AND TELLURIUM

		Yields (wt %)			
Activator		C_1–C_5			
Form	Wt %	Saturates	Olefins	Benzene	Olefins (% of C_1–C_5)
None	—	4.6	7.9	0	63
S	4.4	37.7	44.2	2.6	54
Se	18.7	22.7	67.0	2.8	75
Te	15	6.5	2.8	87.7	30

TABLE 5

n-HEXANE DEHYDROCYCLIZATION BY TELLURIUM-CONTAINING CATALYSTS

Base	Si/Al Ratio	Tellurium, (wt %)	C_1–C_5 Yield (wt %)	Benzene yield (wt %)
NaX	1.2	15.4	9.3	87.7
NaY	2.3	15	5.1	42.9
Na-Mordenite	4.2	8	8.1	7.3
CaX	1.3	15	6.5	44.2
α-Al_2O_3	—	15	0.6	0.2
SiO_2–Al_2O_3 (Durabead)	—	15	9.4	0.2

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