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Tellurium-Loaded Zeolites

I. A Novel Dehydrocyclization Catalyst

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Selective dehydrocyclization catalysts are prepared by the high-temperature treatment of physical mixtures of a tellurium source and support material. An exploratory study of preparation variables—tellurium source, content and method of addition, type of support, and pretreatment conditions—has shown the most effective catalysts are produced from milled mixtures of elemental tellurium and an alkali-metal faujasite of low silica-alumina ratio, heated in a flowing hydrogen atmosphere. The catalyst is interpreted as being a highly dispersed tellurium phase coordinated to the cations of the support under the action of the reducing atmosphere.

INTRODUCTION

The activating influence of group VIA elements upon the catalytic activity of NaX-zeolite has been reported by Miale and Weisz (*1*). Of particular interest was their finding that tellurium-zeolite mixtures produce extremely selective catalysts for the dehydrocyclization of paraffins. For example, they found that the tellurium-containing catalysts at a temperature of 1000°F, produce conversions of *n*-hexane in excess of 90% with 93–94% selectivity for benzene.

In this paper, a number of exploratory experiments on this novel family of dehydrocyclization catalysts will be described. Items to be discussed include the effect on catalytic activity of tellurium source, tellurium content, and method of addition along with the influence of the support and pretreatment conditions.

EXPERIMENTAL

All the catalysts were physical mixtures of the appropriate components that had been milled, pelleted and sized to 20–30 mesh. The tellurium used was finely divided metal obtained from Matheson, Coleman and Bell and assayed 99.5% tellurium. The tellurates, tellurites, and tellurides were reagents (>99% purity) from either Alfa Inorganics, Inc. or K & K Laboratories, Inc. The primary zeolite base, NaX, was a Linde preparation (L137518, 15.1% Na, 32.8% Al_2O_3, 47.4% SiO_2) that had a silica alumina ratio of 2.45 and a Na/Al atom ratio of 0.99. The CaX (8.8% Ca, 5.7% Na, 31.5% Al_2O_3, 47.8% SiO_2) was also a Linde preparation. The NaY (9.4% Na, 21.1% Al_2O_3, 66.6% SiO_2) was synthesized in accordance with a Linde procedure (*2*) and had a silica-alumina ratio of 5.3. The alumina (F-20) base was a commercial (Alcoa) activated alumina.

A standard activity test was established for comparison purposes. The test involved the aromatization of *n*-hexane and the pertinent conditions were:

Temperature	538°C
Pressure	1 atm
Catalyst charge	1.5 cc, 20–30 mesh
Carrier gas	Helium
Helium/hydrocarbon mole ratio	4/1
Contact time	9 sec (~0.5 LHSV)
Pretreatment	1 hr at 1000°F in flowing hydrogen
Length of test	2–4 hr

The "microreactor" used in the test is similar to one already described (*3*). The helium carrier was saturated at 24°C with *n*-hexane and passed over the catalyst charge. The product stream was passed through a sample loop and vented. At established times, the product sample was charged directly to a chromatographic column by diverting the chromatographic carrier gas through the sample loop. Product analyses were based on the detected C_1–C_6 hydrocarbons and no attempt was made to complete a mass balance by coke and hydrogen analyses. The chromatographic column was silicone oil (25%, SF-96, 2.5 ft) on firebrick.

RESULTS

Catalyst Preparation by Ball-Milling or Mortar-Mixing

The tellurium containing catalysts described by Miale and Weisz had been prepared by simple mortar-mixing of the catalyst components. Since contact intimacy might be a significant variable, a series of experiments on nominal 6% Te-NaX catalysts was carried out to determine the effect of mortar-mixing and ball-milling time on catalyst activity. The effect of ball-milling time on product yields is shown graphically in Fig. 1. Results obtained by mortar-mixing the components are arbitrarily shown at ten minutes on the abscissa.

The upper curve of Fig. 1 represents the benzene yield after 30 min on stream. The middle curve represents the benzene yield after 4 hr on stream. As shown, mortar-mixing and short ball-milling time (<2 hr) have only a slight effect on the 30-min aromatization activity but a pronounced effect on catalyst aging. Optimum ball-milling time is from two to five hours after which aromatization activity begins to deteriorate.

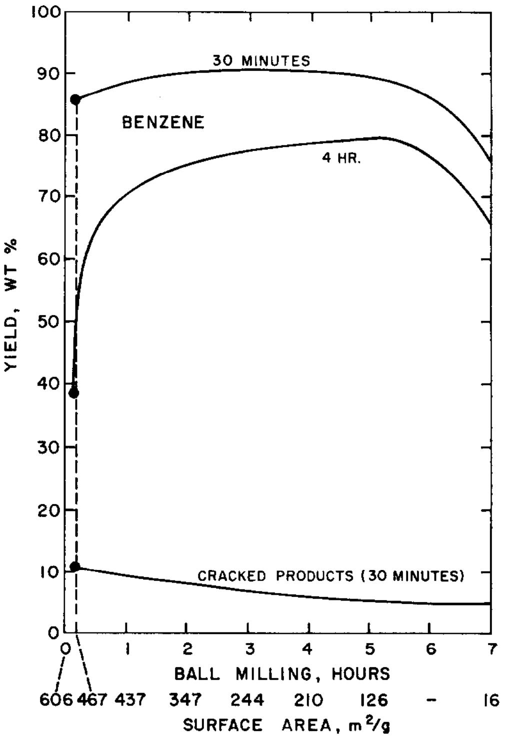

FIG. 1. Effect of ball-milling time. ● Mortra-mixed catalyst.

The surface area values (BET) of the catalysts are indexed on the abscissa of Fig. 1 by some representative values. A portion of the surface area loss might result from filling of the pores of the zeolite with tellurium, e.g., the initial drop of surface area from 606 to 467 m^2/gm. The cracked product yields are represented by the lower curve of Fig. 1—the decreasing cracking activity being a possible consequence of the decreasing surface area.

Influence of Tellurium Content

To determine the influence of tellurium content on the catalytic activity of the Te–NaX system, a series of catalysts with various tellurium contents was prepared by ball-milling tellurium with NaX for 4 hr. Results obtained from the standard activity test for these catalysts are shown in the trilinear diagram of Fig. 2 which portrays the yields of benzene, cracked products and unreacted *n*-hexane. The solid line represents data taken after ½ hr and the dotted line that taken after 4 hr. As shown, a few tenths of a percent of tellurium markedly increase the cracking activity of the NaX base. Catalysts containing 0.5–3.0% tellurium are quite active but still have relatively poor selectivity for benzene production. Optimum aromatization catalysts are obtained with tellurium contents of 3–8% beyond which the activity then begins to decline.

Tellurium Source and Method of Addition

Besides the technique of ball-milling NaX with elemental tellurium, effective aromatization catalysts have also been prepared with other tellurium sources and by using different methods of addition. Table 1 summarizes some of the results in this area.

With elemental tellurium, the best catalyst is that formed by ball-milling in a dry state. A Te–NaX catalyst prepared by mixing the components in an aqueous slurry shows good initial activity but loses this activity at a rapid rate. Vaporizing the tellurium onto the NaX-zeolite by transpiration from a bed of tellurium at high temperatures produced a catalyst of rather fair initial activity but with a decay rate far inferior to that of the ball-milled catalyst.

With sodium tellurate, the aqueous slurry method produces a better catalyst than the ball-milling technique. Both ammonium tellurate and potassium tellurite yield catalysts which are poorer than that obtained from sodium tellurate. A catalyst prepared by ball-milling tellurium dioxide with NaX-zeolite yields a catalyst which is only slightly inferior to that obtained from elemental tellurium.

In addition to the alternative tellurium sources already discussed, a series of catalysts were prepared from NaX and a

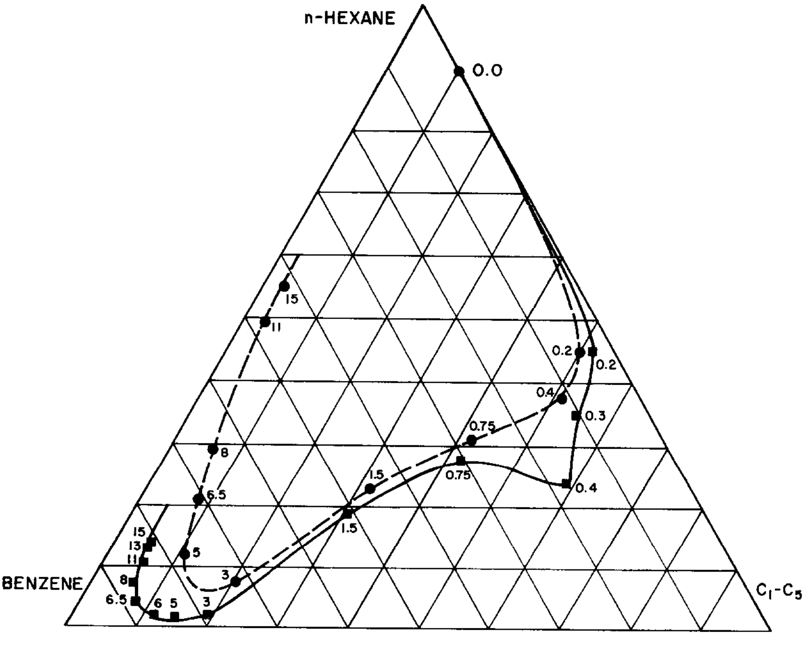

FIG. 2. Effect of tellurium content on activity of Te–NaX catalysts. Index: tellurium content, wt %.

TABLE 1

RESULTS OF STANDARD ACTIVITY TEST ON Te–NaX CATALYSTS PREPARED BY VARIOUS TECHNIQUES

% Te and Source	Method of Addition	Wt % C_1–C_5 ½ hr	Wt % Benzene		Selectivity at ½ hr
			½ hr	4 hr	
6, Te	Dry, 5 hr ball mill	4.8	89.6	79.6	94.7
6, Te	Aqueous slurry	11.5	82.3	8.0	84.2
5–10, Te	Vaporization	5.3	77.5	55.2[a]	93.7
6, Na_2TeO_4	Aqueous slurry	15.4	83.6	79.5	83.7
6, Na_2TeO_4	Dry, 2 hr ball mill	16.1	57.6	—	79.4
6, $(NH_4)_2TeO_4$	Aqueous slurry	15.3	77.9	12.1	80.1
6, K_2TeO_3	Aqueous slurry	17.7	53.8	42.5	72.7
6, TeO_2	Dry, 1 hr ball mill	11.1	84.3	67.9	88.3

[a] Run terminated after 2 hr.

number of metal tellurides. The tellurides were ball-milled with NaX-zeolite in proportions such that the tellurium/zeolite ratios would be the same as in an 11% Te–NaX catalyst—the sole exception being PbTe–NaX which was prepared to a 6% tellurium level. The activity results from the catalysts are given in Table 2. The results show that with the exception of the antimony, zinc, lead, and indium telluride, most of the metal tellurides lead to relatively active and selective aromatization catalysts. It should be noted, however, that in those cases where high aromatization activity was obtained, at least a trace of a metallic mirror was observed downstream of the reactor, indicating possible decomposition of the telluride component to elemental tellurium.

Other Zeolite Supports

Miale and Weisz (*1*) described results on CaX and NaY in addition to those on NaX. We have surveyed a number of other tellurium–faujasite systems. Table 3 lists the activity and selectivity under standard conditions for the various preparations. The X-type supports were prepared by base exchange of NaX and metals contents are given in Table 3. Tellurium catalysts derived from the alkali-metal faujasites were superior to any of the other catalysts tested—the selectivities for benzene production all being over 90%. Catalysts containing alkaline-earth cations generally exhibited lower aromatization activities, increased cracking activity, and more rapid aging rates. All the other X-based catalysts shown in Table 3 were relatively ineffectual aromatization catalysts. Although NaY provides a catalyst of moderate activity and selectivity, it is also quite inferior to Te–NaX.

TABLE 2

AROMATIZATION ACTIVITIES OF TELLURIDES SUPPORTED ON SODIUM X 2-HR, 510°C ACTIVITY TEST[a]

Telluride	Benzene Yield (wt %)	Selectivity $\left(\frac{\text{Aromatics Yield}}{\text{Conversion}} \times 100\right)$
Cr_2Te_3	80.8–77.5	93.0–93.7
$ZrTe_2$	84.8–70.6	96.6–96.8
$TaTe_2$	84.9–68.2	96.8–97.6
$TiTe_2$	79.8–65.8	96.0–96.9
WTe_2	70.3–62.8	90.0–89.0
$NbTe_2$	75.6–55.5	96.4–96.8
VTe	70.0–50.1	96.4–96.9
Bi_2Te_3	50.3–38.6	92.0–92.5
$MoTe_2$	45.1–43.9	80.0–82.0
Sb_2Te_3	15.4–14.5	92.9–93.3
ZnTe	10.2–4.5	47.9–33.3
PbTe	7.3–5.4	37–30
In_2Te_3	1.4	30

[a] Differs from standard test only in temperature.

Alumina as a Support

Miale and Weisz (*1*) have shown that alumina and silica-alumina are poor supports for elemental tellurium. We have

TABLE 3

AROMATIZATION ACTIVITIES OF OTHER TELLURIUM-FAUJASITE CATALYSTS[a]

Base (metal content, wt %)	Wt % C_1–C_5	Wt % Benzene		Selectivity
	½ hr	½ hr	4 hr	
NaX (15.1 Na)	4.8	89.6	79.6	94.7
KX (12.9 K, 6.1 Na)	5.2	72.4	67.8	93.3
RbX (22.7 Rb, 6.5 Na)	5.9	71.7	66.5	92.4
CsX (33.3 Cs, 4.4 Na)	5.8	66.2	63.0	91.9
MgX (4.4 Mg, 6.4 Na)	11.3	30.4	0.3[d]	72.8
CaX[b] (8.8 Ca, 5.7 Na)	18.9	29.2	Tr[d]	60.7
BaX (24.2 Ba, 1.3 Na)	6.9	54.3	5.9	88.8
REX[c] (28.8 RE_2O_3, 0.4 Na)	72.1	3.1	—	4.1
FeX (6.6 Fe, 5.4 Na)	13.4	3.2	0.3[d]	19.3
NaY (9.4 Na)	15.5	28.7	28.8	65.0

[a] Conditions: Catalysts contained 6% tellurium, test conditions were standard.

[b] Linde preparation.

[c] Rare earth-exchanged catalyst.

[d] Run terminated after 2 hours.

prepared a larger variety of tellurium catalysts, from F-20 Al_2O_3 and either elemental Te, TeO_2 or Na_2TeO_4. In two cases, 10% by weight of NaOH was also ball-milled into the composite catalyst. The catalytic results are given in Table 4. All the catalysts are inferior to Te–NaX. However, it is of interest that when sodium ion is present (Na_2TeO_4, Te + NaOH, TeO_2 + NaOH) far higher aromatization activity is observed than when it is absent (Te or TeO_2 alone). The sodium apparently either plays a direct role in the catalysis or else functions to prevent tellurium elution.

Effect of Pretreatment

As described in the experimental section, all the catalysts described here were pretreated in hydrogen prior to measurement of catalytic activity. However, effective catalysts had also been prepared by pretreatment in air or helium. As a result, a set of experiments was carried out to determine if any difference in catalytic behavior could be observed as a result of pretreatment in an oxidizing or reducing atmosphere.

Three aliquots of a 6% Te–NaX were pretreated at 538°C with hydrogen, air, and hydrogen followed by air. As shown in Table 5 there are no significant differences in the aromatization activity, after 10 min on stream, of the three catalysts. However, at only 5 min on a stream, the two oxidized catalysts had very low activity compared to the catalysts which had been prereduced

TABLE 4

AROMATIZATION ACTIVITIES OF ALUMINA[a]–SUPPORTED TELLURIUM CATALYSTS

Tellurium source and amount	Promoter	Wt % C_1–C_5 30 min	Wt % Benzene		Selectivity
			30 min	4 hr	
Te (6%)	—	1.7	0.3	—	23
Te (6%)	10% NaOH	2.9	10.4	12.2	84
TeO_2 (6%)	—	2.5	1.2	0.2	32
TeO_2 (6%)	10% NaOH	2.4	10.7	9.3	82
Na_2TeO_4 (12%)	—	1.5	10.7	9.5[b]	87

[a] F-20 Al_2O_3.

[b] Run terminated at 3 hr.

TABLE 5
EFFECT OF PRETREATMENT

Catalyst	Pretreatment	Wt % Benzene 5 min	10 min	30 min	60 min	90 min	120 min
Te–NaX	H_2, 538°C, 1 hr	72.5	85.3	84.7	82.1	79.9	78.3
Te–NaX	Air, 538°C, 1 hr	25.1	79.1	76.0	75.1	73.3	72.3
Te–NaX	H_2, 1 hr; air, 1 hr at 538°C	12.9	79.5	78.7	78.5	74.7	75.0

in hydrogen. The activation which occurs with the oxidized catalysts during the first 10 min on stream is presumably a result of the hydrogen produced via the aromatization reaction.

DISCUSSION

Apparently, tellurium is relatively easily dispersed into the zeolite structure. The experiments represented by Fig. 1 show that intimacy of contact has only a slight effect on *initial* catalytic activity. In addition, other observations indicate that under vacuum, tellurium begins to diffuse into the zeolite at temperatures ~100°C below its melting point of 452°C. The high mobility of tellurium may result from its hexagonal structure (*4*)—the diffusing unit probably being a polyatomic chain of atoms. It is worth noting that those metal tellurides (Table 2) which produce active catalysts with NaX zeolite all appear to have a hexagonal structure while the relatively inactive tellurides are cubic (*5*).

Comparison of results with NaX and NaY (Table 3) show again that better catalysts are obtained with faujasites of lower Si/Al ratio and consequently a greater number of cations—6% Te-faujasite corresponds to a sodium/tellurium atom-ratio of ~12 for NaX and ~7 for NaY. Also, the superior performance of the alkali-metal zeolites relative to the alkaline-earth zeolites indicates a strong dependence of catalytic activity on either the nature or the number of cations. The importance of the cations in this catalysis is further supported by the results of Table 4 in which Al_2O_3 was used as a support. The high selectivity for dehydrocyclization, the obvious influence of the cations, and the observed activating effect of hydrogen suggests the formation of a highly specific active site in which the tellurium is coordinated to the cations of the zeolite in a negative oxidation state. Further work on both the nature and catalytic properties of this class of materials will be reported later.

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