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# Tellurium NaX Zeolites

## II. Nature of Active Sites

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An unusual dehydrocyclization catalyst can be prepared from an intimate mixture of NaX zeolite and tellurium metal. Careful X-ray diffraction studies by researchers at Mobil Research and Development Company indicated that the active site was a $Te^{2-}$ species nestled in the supercage of the zeolite and coordinated to sodium ions in the zeolite. Our ESCA spectra, however, point toward elemental $Te^0$ as the active sites, and sodium NMR data confirm that the Te is coordinated to sodium ions in the host oxide. These sites are capable of accommodating up to 2H/Te in an activated adsorption process. A dehydrogenation mechanism consistent with the observed kinetics involves the simultaneous removal of two hydrogen atoms by these $Te^0$ sites in a rate limiting step.

## INTRODUCTION

Maile and Weisz (*1*) first reported the discovery of an unusual dehydrocyclization (DHC) catalyst which was prepared from an intimate mixture of elemental tellurium and sodium–X zeolite. Activation was achieved by treatment in hydrogen at a temperature of about 500°C. A subsequent study by Lang *et al.* (*2*) described optimal preparation techniques for the system, and they suggested that tellurium was coordinated to the sodium cations in the zeolite support.

Mikovsky *et al.* (*3*) and Olson *et al.* (*4*) later published interrelated papers containing information about the structure of the active sites. From a careful X-ray crystallographic study, they concluded that there are two types of Te sites. The first site is a $Te^{2-}$ species coordinated to $Na^+$ ions within the sodalite cage, and the second site is $Te^{2-}$ coordinated to Site II and Site III sodium atoms in the supercage of the zeolite. The second type of site was considered to be the one responsible for aromatization activity since it is the only site accessible to reactant molecules. The main argument supporting the assignment of a negative valence $Te^{2-}$ species as the active site was the X-ray crystallographic work. The interatomic distance between the Te species and the $Na^+$ ions is approximately the same as the sum of the Pauling radii for $Te^{2-}$ and $Na^+$. However, the low occupancy of tellurium in the zeolite (about 4.5% by weight) made the detection of this site difficult, and the assignment of a negative oxidation state for Te is not absolutely conclusive.

If a $Te^{2-}$ species does exist, then hydrogen, which is necessary for activation of the catalyst, must be responsible for its reduction from the original elemental state. The question that remains is what happens to the $H^+$ ions produced in the reduction step, and do they have any catalytic effect? In addressing these issues, Mikovsky *et al.* (*3*) and Olson *et al.* (*4*) studied Te retention and selectivities of Te/NaX and Te/KX, hydrogen sorption, and diffuse-reflectance spectroscopy of the Te/NaX catalyst. Some of their results are summarized as follows.

(1) Catalysts with very low Te contents

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(0.2–0.4% Te on NaX) show much more cracking activity than the support alone, but these materials have little DHC activity. Addition of small amounts of Te to KX causes a marked increase in DHC but no increase in cracking activity (*2*).

(2) All the tellurium can be eluted from the catalyst at high temperature in an inert atmosphere. However, an atmosphere of hydrogen gas will cause the catalyst to stabilize at a loading of about 3.5% by weight on the NaX support at 538°C. No more Te is eluted so long as the $H_2$ atmosphere is present.

(3) Diffuse-reflectance spectra showed a band at 3650 $cm^{-1}$ which was assigned to $H^+$ ions on the zeolite.

(4) Approximately one hydrogen molecule is sorbed per Te atom.

From the results, it was concluded that $H^+$ ions were indeed on the surface and were responsible for the cracking activity of the low concentration samples. The authors attributed the high cracking activity of these catalysts to an initial deposition of the Te in the sodalite cage which would not be accessible to the reactants. The mobile $H^+$ ions, produced in the reduction of the Te, would then be available for cracking Further Te loading would populate the supercage sites and cause a shift in selectivity to DHC. The explanation for the high aromatization activity of Te/KX even at low Te levels was that Te is not able to get into the sodalite cages of the KX zeolite due to the large size of the $K^+$ ions. Thus, essentially all the Te sites would be in the supercage locations and active for aromatization.

We (*5, 6*) have recently reported information about the pathways, mechanisms, and rate limiting steps involved in the DHC reactions. The purpose of this paper is to describe some experiments designed to provide additional information about the nature of the active sites. Evidence we have accumulated in some cases supports and in other cases contradicts the conclusions of the Mobil investigators.

## EXPERIMENTAL METHODS AND RESULTS

### *Catalysts*

The sodium based catalyst used in this study was kindly donated by R. J. Mikovsky of the Mobil Research and Development Laboratories. As mentioned in the previous paper (*6*), it contained 11% elemental Te by weight and 89% NaX (13X) zeolite. The two constituents were dry ball milled for 4 hr before being activated in flowing hydrogen at 500°C.

A LiX zeolite was prepared in a manner similar to the procedure described for the preparation of the KX zeolite (*3*), except that both LiCl and $LiNO_3$ were used as the exchange agents. This 11% Te on LiX zeolite catalyst was inactive for the aromatization of cyclohexane even though we were easily able to prepare active Te/NaX zeolites by this method (*7*). After treatment with hydrogen, the Te/LiX catalyst did not show the characteristic brownish color reported by the Mobil researchers (*4*) and observed in our laboratory for the Te/NaX catalyst.

### *Hydrogen Isobar*

A conventional Pyrex volumetric adsorption apparatus was used to measure a hydrogen adsorption isobar. A 1-g sample of Te/NaX was evacuated overnight at 200°C to remove moisture. Evacuation at higher temperatures caused loss of Te as evidenced by the formation of a metallic mirror in the cool section of the sample tube above the heater. After evacuation, the sample tube was isolated and cooled to 100°C. One atmosphere of hydrogen was admitted to the system and allowed to equilibrate with the catalyst. The volume of the system was adjusted periodically during a 15-min adsorption period to keep the pressure constant at 1 atm. The amount of hydrogen adsorbed was determined, and the sample was heated to 200°C for another adsorption measurement. This process was repeated at 100°C temperature increments to 500°C. Corrections were made for the expansion of the gas phase due to increasing temperature; a blank run with the support alone showed no hydrogen adsorption. Figure 1 shows the results of the experiment.

During the course of this experiment, a small amount of Te was seen plated out in the cool section above the heater. If we assume that the catalyst contained 3.5% Te by weight after $H_2$ treatment (this is the "stable" Te after high temperature reduction (*3*, *4*)), the maximum adsorption in the isobar corresponds closely to two H atoms per Te atom. If none of the Te had been lost during the $H_2$ treatment, the maximum would correspond to about 0.6 H/Te. The amount adsorbed declines after the maximum is reached, which is typical of an activated chemisorption process.

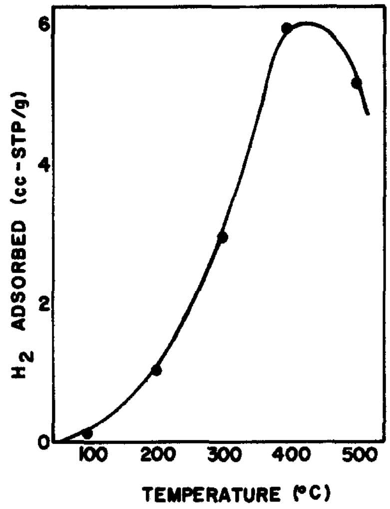


FIG. 1. Hydrogen isobar at 1 atm pressure, 1 g Te/NaX zeolite.

### *ESCA*

To determine the valence state of Te in the catalyst, ESCA spectra were taken at the Shell Development Westhollow Research Center. The catalyst samples were prepared in a U-tube Pyrex reactor connected to a four-way stopcock via O-ring ball and socket joints. The sample could be pretreated in the reactor and then isolated by closing the stopcock. One sample of NaX support alone and one sample of the Te/NaX were prepared by treating each in flowing hydrogen for 12 hr at 500°C. The samples were cooled under flowing hydrogen and isolated. They were opened in a nitrogen glovebox and transferred directly into the ESCA spectrometer without being exposed to air. The spectrometer was a Varian IEE instrument equipped with a high intensity aluminum X-ray anode operated at 10 kV and 100 mA. The analyzer pressure was between $2 \times 10^{-6}$ and $5 \times$

TABLE 1

ESCA Data

| Species | NaX Alone | | Te/NaX | |
|---|---|---|---|---|
| | Binding[a] energy (eV) | Relative no. of atoms | Binding[a] energy (eV) | Relative no. of atoms |
| Te(3*d*) | — | — | 573.6 | 0.42 ($Te^0$) |
| Te(3*d*) | — | — | 576.6 | 0.35 ($Te^{+4}$)[b] |
| Na(1*s*) | 1072.55 | 29.4 | 1072.40 | 17.5 |
| Al(2*s*) | 119.15 | 17.3 | 119.20 | 13.6 |
| Si(2*p*) | 102.3 | 23.4 | 102.3 | 18.9 |
| O(1*s*) | 531.4 | 94.0 | 531.5 | 87 |
| Na(*α*) | 574.0 | | 574.2 | |
| O(*α*) | 552.8 | | 552.8 | |

[a] Binding energies corrected to C(1*s*) = 284.6 eV.

[b] $Te^{4+}$ dropped to zero after 30 min of irradiation.

$10^{-6}$ Torr. Table 1 shows the results for NaX alone and for Te/NaX.

No $Te^{2-}$ was observed and, surprisingly, $Te^{4+}$ was observed along with $Te^0$. The $Te^{4+}$ peak disappeared after about 30 min of irradiation in the spectrometer; this was possibly due to reduction caused by the photoelectrons. No corresponding growth in the $Te^0$ peak was observed. There was also a slight shift in the $Na^+$ lines when comparing the NaX with the Te/NaX. Since the shift was only slightly larger than the expected experimental error, the shift may not be significant.

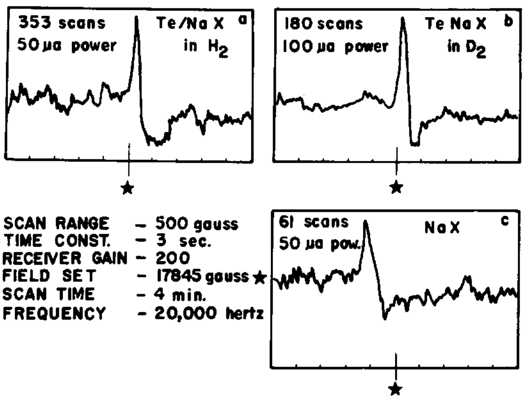


FIG. 2. Derivative NMR spectra for sodium at ambient conditions.

*Sodium NMR*

Samples for sodium NMR spectroscopy were prepared in a similar fashion to those described above except that after the samples were cooled, the hydrogen was evacuated to 10 Torr (1 Torr = 133.3 N $m^2$) and the sample tube sealed. Three samples were analyzed at the Exxon Corporate Research Labs in Linden, N.J. The first was tellurium on NaX zeolite activated in hydrogen ($Te/NaX/H_2$), the second was the same material activated in deuterium ($Te/NaX/D_2$), and the last was the NaX zeolite support alone. A Varian model WL-112 wide-line NMR instrument with a 12″ Varian magnet was used for these measurements. A General Radio frequency synthesizer operated from 3 to 35 MHz, and the magnetic field was oscillated sinusoidally at 35 Hz. The samples were transferred from the sealed tubes into other tubes in a helium drybox. The results are shown in Fig. 2.

The spectrum of the NaX support is quite different from the other two spectra. The main line is much broader and shifted very significantly to the left with respect to the other spectra. This indicates that the Te indeed has an effect on the sodium in the NaX sieves. Note that the spectrum of the $Te/NaX/D_2$ is very similar to the $Te/NaX/H_2$ spectrum. The major difference is that the $Te/NaX/H_2$ spectrum has several small satellite peaks on both sides of the main peak; these peaks are absent from the spectrum of the material activated in $D_2$. The satellite peaks could be due to the spin–spin splitting of the sodium lines by the hydrogen nuclei, which would indicate that hydrogen may be an integral part of the Te–Na coordination complex which provides the active sites.

## DISCUSSION

From these results, we propose that the active site is an elemental $Te^0$ atom coordinated to sodium ions in the zeolite. This site is capable of adsorbing two hydrogen atoms per Te atom. Our results do not point to any particular position for the Te to occupy, nor do they give an indication of the nature of the Te–Na stoichiometry.

The ESCA results are mostly responsible for leading us to speculate about the $Te^0$ species. The $Te^{4+}$ observed was probably due to a surface contamination by oxygen even though care was taken to avoid catalyst exposure to $O_2$. We must admit the possibility that $Te^{2-}$ was oxidized to $Te^0$ and $Te^{4+}$ by contamination, but we feel that a color change of the catalyst would have been noticed if a serious contamination had occurred. No change from the usual brown color was noted after the ESCA spectra were taken, while activated catalysts generally turn white after several hours of exposure to the atmosphere.

The sodium NMR spectra show clearly

that Te addition to the zeolite significantly alters the chemical environment of the sodium ions. Although the complete interpretation of the NMR spectra would require considerable systematic work (*8*), information about the actual position of the $Na^+$ ions that are coordinated with the Te atoms may be contained in such an analysis. Mikovski *et al.* (*3*) and Olson *et al.* (*4*) present strong evidence that Site II and Site III sodium ions are responsible for the coordination of the Te.

An elemental Te site which chemisorbs two hydrogen atoms also explains the hydrogen isobar in that chemisorption processes are frequently activated and reversible. Our stoichiometric value of two hydrogen atoms per tellurium atom agrees well with the results of Olson *et al.* (*4*).

Chemisorption of hydrogen on the Te/Na coordination complex can also explain the possibility that spin–spin splitting is observed in the $Te/NaX/H_2$ sample. For spin–spin splitting to occur, the hydrogen would have to be relatively near the sodium ions. If $H^+$ ions were formed and associated with the zeolite, as the Mobil workers propose, these ions would not necessarily be coupled to the sodium ions. In such a case the $Te/NaX/H_2$ NMR spectrum should be identical to the $Te/NaX/D_2$ spectrum; it was not.

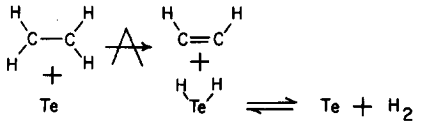
One might also ask why hydrogen is required to maintain the stability of the Te site after the initial activation (reduction) step. The $Te^{2-}$ species proposed earlier (*3*, *4*) could undergo Te elution by helium only if $Te^{2-}$ were able to lose two electrons to establish electrical neutrality. In light of the $Te^{2-}$ site proposed, these observations could be explained by assuming that the activation process simply reverses itself, viz.,

$$H_2 + Te^0 \underset{\text{inert}}{\overset{H_2}{\rightleftharpoons}} 2H^+ + Te^{-2}.$$

Our proposed site would be capable of simply desorbing hydrogen, and the Te could then be eluted in the elemental state in a helium atmosphere. Chemisorbed hydrogen might cause a partial negative charge on the Te atoms, and this induced charge could help attract the Te to the positive $Na^+$. Thus, the Te would remain in place so long as the hydrogen atmosphere was in place.

One interesting point resulted from the work with the inactive Te LiX zeolite catalyst: apparently the Li is missing some property common to both Na and K which is required for the production of active dehydrogenation sites. Size of the ions is one obvious possibility. It is also possible that the Te–alkali metal coordination may involve *p* electrons of the alkali metal. Li, in contrast with Na and K, contains no *p* electrons and cannot participate in a coordination of this type.

Another piece of evidence supporting this $Te–Na–H_2$ complex is its prediction of a rather simple dehydrogenation mechanism. The mechanism can be written as follows.



This mechanism is also consistent with the lack of intermolecular hydrogen atom scrambling (*6*) and the conclusion that the catalyst serves mainly as a dehydrogenation promoter (*5*) with cyclization of *n*-paraffins occurring homogeneously through hexatriene intermediates. The rate limiting step is cleavage of the C–H bonds (*6*). The active Te sites are actually coordinated with $Na^+$.

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