JOURNAL OF CATALYSIS 29, 316–318 (1973)

# Tellurium-Loaded Zeolites

## IV. Effect of Hydrogen Partial Pressure on Dehydrocyclization Activity

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Received December 11, 1972

The effect of hydrogen partial pressure on the *n*-hexane dehydrocyclization activity of Te/NaX catalyst has been determined and compared with that observed for $Cr_2O_3/Al_2O_3$. The relative benzene formation rates measured for both catalyst types show an essentially identical dependence on hydrogen pressure. Kinetic analysis of the results is consistent with a stepwise reaction mechanism.

Tellurium in combination with alkali metal-X zeolites yields selective dehydrocyclization catalysts (*1–4*). The catalytic results described in previous reports had been obtained at atmospheric reaction pressure. In this paper we wish to summarize our findings on the influence of hydrogen partial pressure (HPP) on the reactivity of this novel catalyst system.

The experiments described here were carried out in a pressure-balanced glass flow reactor. The *n*-hexane used was Phillips pure grade. Reaction conditions were: temperature, 950°F; hexane partial pressure, 0.2 atm; and HPP as noted. The catalysts used were 20–30 mesh. The 6% Te/NaX catalyst was prepared by ball-milling as previously described (*3*). The chromia–alumina catalyst was a cogelled preparation containing 33% $Cr_2O_3$ (*5*).

A series of experiments in which the HPP was varied from 1 to 10 atm was carried out on the Te/NaX catalyst. Results on overall conversion and rate of benzene production are summarized in Table 1. As shown, increasing HPP significantly depresses dehydrocyclization activity; the rate of benzene formation dropping approximately two orders of magnitude over the range of HPP examined. In Fig. 1, the ln of the benzene formation rate is plotted versus the ln of the HPP. The results indicate that the dehydrocyclization activity is not a function of a single integral power

TABLE 1
EFFECT OF HYDROGEN PARTIAL PRESSURE ON CONVERSION OF *n*-HEXANE WITH Te/NaX CATALYST

| Hydrogen pressure (atm) | % Conversion | Product distribution (wt %) | | | Av rate of benzene production (moles/hr g) ($\times 10^3$) |
|---|---|---|---|---|---|
| | | Benzene | Other $C_6$ products[a] | $C_5^-$ products | |
| 1 | 50.85 | 33.44 | 7.70 | 9.71 | 9.02 |
| 2 | 38.91 | 20.04 | 10.56 | 8.31 | 5.41 |
| 3 | 26.04 | 8.47 | 10.51 | 7.06 | 2.28 |
| 5 | 16.79 | 2.58 | 8.55 | 5.66 | 0.696 |
| 7.5 | 13.54 | 1.20 | 7.25 | 5.09 | 0.324 |
| 10 | 9.35 | 0.43 | 5.52 | 3.40 | 0.116 |

[a] Primarily isohexanes.

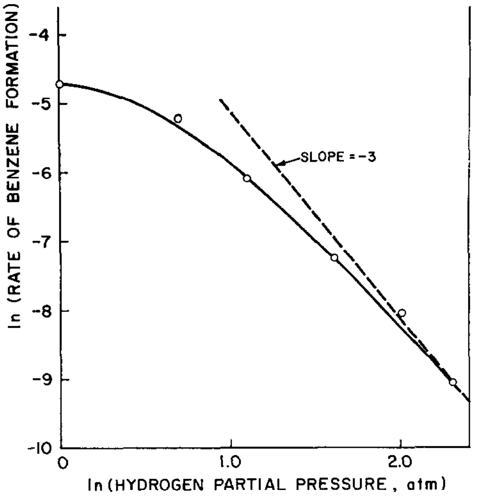

FIG. 1. Log-log plot of dehydrocyclization rate for Te/NaX catalyst as a function of hydrogen partial pressure.

of the HPP although a third order dependency is approached as the HPP is increased.

It is well known that the paraffin dehydrocyclization activity of chromia-alumina catalysts is also strongly decreased by increasing HPP (*6*). In order to compare the effect of HPP on the dehydrocyclization activity of Te/NaX and $Cr_2O_3/Al_2O_3$, a series of experiments similar to that described above was also carried out on the latter catalyst. Arbitrarily setting benzene formation rates for both catalysts equal to 100 at a HPP of 1 atm yields the comparison given by Table 2 and by the data points of Fig. 2. This comparison shows that for *n*-hexane, the relation between dehydrocyclization activity and HPP is essentially the same for both catalyst systems implying a common reaction mechanism.

TABLE 2

EFFECT OF HYDROGEN PARTIAL PRESSURE ON RELATIVE DEHYDROCYCLIZATION ACTIVITIES OF $Cr_2O_3/Al_2O_3$ AND Te/NaX CATALYSTS

| Hydrogen partial pressure (atm) | Relative benzene formation rates | |
|---|---|---|
| | Te/NaX | $Cr_2O_3/Al_2O_3$ |
| 1 | 100 | 100 |
| 2 | 59.9 | 50.5 |
| 3 | 25.3 | 24.6 |
| 5 | 7.70 | 8.53 |
| 7.5 | 3.57 | 2.20 |
| 100 | 1.29 | 1.67 |

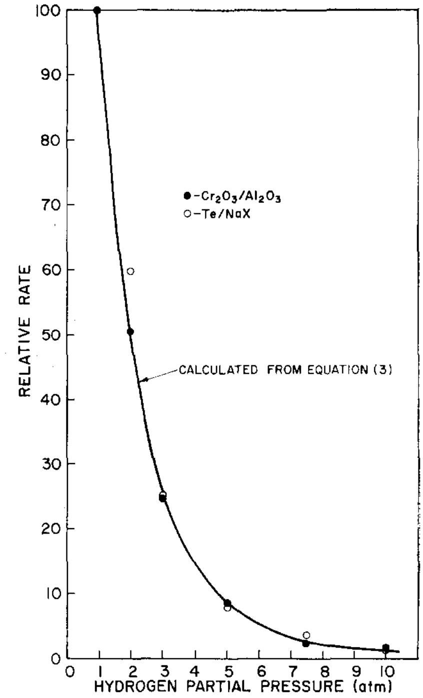

FIG. 2. Relative dehydrocyclization activities for Te/NaX and $Cr_2O_3/Al_2O_3$ catalysts as a function of hydrogen partial pressure.

In a recent paper (*7*), Kazansky and co-workers presented evidence that the dehydrocyclization of *n*-hexane on chromia catalysts proceeds by the stepwise mechanism shown below:

$$\text{hexane} \xrightleftharpoons[k_{12}]{k_{21}} \text{hexene} + H_2,$$

$$\text{hexene} \xrightleftharpoons[k_{23}]{k_{32}} \text{hexadiene} + H_2,$$

$$\text{hexadiene} \xrightleftharpoons[k_{34}]{k_{43}} \text{hexatriene} + H_2,$$

$$\text{hexatriene} \xrightleftharpoons[k_{45}]{k_{54}} \text{cyclohexadiene},$$

$$\text{cyclohexadiene} \xrightleftharpoons[k_{56}]{k_{65}} \text{benzene} + H_2.$$

Assuming that all hydrocarbon intermediates between hexane and benzene are at steady state, the above reaction scheme yields the following rate equation for benzene formation:

$$\frac{d[\text{benzene}]}{dt} = \frac{1}{\Delta}\left[\theta_{61}[\text{hexane}] - \theta_{16}[\text{benzene}][\text{HPP}]^4\right], \qquad (1)$$

where

$$\theta_{61} = k_{21}k_{32}k_{43}k_{54}k_{65},\ \theta_{16} = k_{12}k_{23}k_{34}k_{45}k_{56}$$

and

$$\Delta = (k_{32}k_{43}k_{54}k_{65}) + (k_{43}k_{54}k_{65}k_{12})[\text{HPP}] + (k_{54}k_{65}k_{12}k_{23})[\text{HPP}]^2 + (k_{12}k_{23}k_{34}k_{45} + k_{12}k_{23}k_{34}k_{65})[\text{HPP}]^3.$$

At 950°F, thermodynamics requires that $(\theta_{61}/\theta_{16}) = 1.4 \times 10^5$. As a result, the minimum (benzene/hexane) equilibrium ratio of interest in this study (i.e., at a HPP of 10 atm) is 14. Thus, the reverse reaction can be neglected and Eq. (1) becomes

$$\text{rate} = \frac{\theta_{61}[\text{hexane}]}{\Delta}. \qquad (2)$$

Due to the constant initial hexane partial pressure (0.2 atm), even accounting for variable conversion levels, shows that the average hexane concentration in these experiments only varied from about 0.15 to 0.19 atm. Thus, assuming the hexane concentration to be constant, the following equation

$$\text{relative rate} = [C_1 + C_2[\text{HPP}] + C_3[\text{HPP}]^2 + C_4[\text{HPP}]^3]^{-1}, \qquad (3)$$

describing the dependence of dehydrocyclization activity on HPP can be written.

Application of a regression procedure to Eq. (3) and the data in Table 2 yields the following values of the constants $(\times 10^4)$: $C_1 = 59.9$, $C_2 = 23.8$, $C_3 = 9.84$, $C_4 = 6.45$. Using these values in Eq. (3) generates the solid curve shown in Fig. 2. Although the actual values of the constants are probably of little meaning due to the large number of parameters, the comparison given in Fig. 2 shows that the observed relation between dehydrocyclization activity and hydrogen partial pressure for both Te/NaX and chromia–alumina is consistent with the mechanism proposed by Kazansky *et al.* (*7*).

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