

NOTES

Unusual Inhibitory Effects on Shape-Selective Reactions over Erionite

The cage structure of erionite (and zeolite T) has been known to exert an unusual effect on the rate of diffusion and reaction of *n*-paraffins of varying chain lengths (1, 2). Hence it was not unexpected that the relative rate of hydrocracking of C₁₀ to C₁₆ *n*-paraffins in a mixture with non-normal hydrocarbons varies with the chain length. Figure 1 compares experimental results obtained with nickel/H-erionite and a non-shape-selective catalyst, Ni/REFX. The reaction was carried out, at 2000 psig and a 27/1 mole ratio of hydrogen/hydrocarbon, with a hydrocarbon mixture containing 25% *n*-paraffins (C₁₀-C₁₆). With erionite a decrease in cracking rate with increasing chain length is noted; with zeolite X, more non-normal hydrocarbons are converted than *n*-paraffins, and the conversion increased with increasing chain length.

Hydrogen pressure, however, has an unexpected effect on conversion of normal and non-normal hydrocarbons over erionite. High partial pressure of hydrogen appears to be necessary for the selective conversion of *n*-paraffins. The experimental results on the effect of hydrogen pressure on conversion are shown in Fig. 2. A sharp decrease in the rate of conversion of *n*-paraffins is noted as the hydrogen pressure is lowered from 1000 to 500 psig, while the rate of conversion of non-normals is hardly affected by pressure.

Replacing hydrogen with a mixture of hydrogen and nitrogen at the same total

pressure also has a disastrous effect on shape selectivity. Pressure should not have any effect on intracrystalline diffusion of hydrocarbon molecules in a zeolite. The fact that the nature of the gas has such a strong effect on catalyst activity suggests that the experimental results cannot be explained on the basis of simple diffusional effects.

The addition of 1 wt% sulfur as thiophene in the feed also has a significant effect on conversion. Under the reaction conditions used, more than 95% was converted to H₂S and butane. Since thiophene is too large a molecule to enter the pores

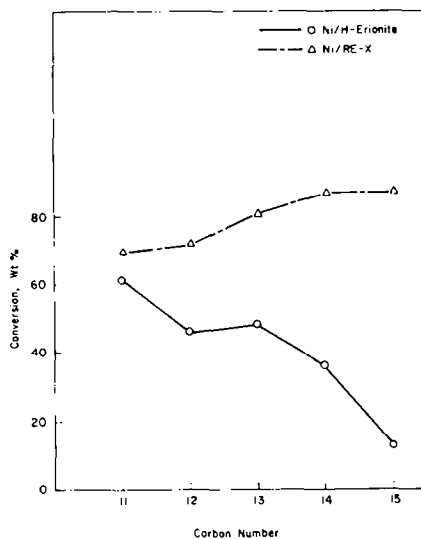


FIG. 1. Relative rate of conversion at 2000 psig and a hydrogen/hydrocarbon ratio of 27/1.

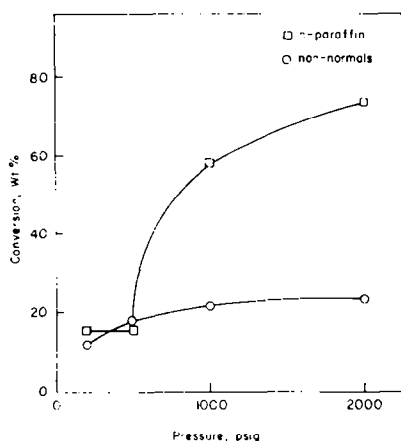


Fig. 2. Effect of pressure on conversion. Reaction conditions: Ni/H-erionite catalyst; 27/1 hydrogen/hydrocarbon mole ratio; 700°F; 14 LHSV.

of erionite, the thiophene reaction must have taken place external to the erionite crystals. From the data shown in Table 1, in the presence of thiophene, the conversion of *n*-paraffins is inhibited, while the conversion of non-normals is promoted, particularly at 137 atm. The activation of NaX by SO₃ complex was reported by Miale and Weisz (3). Dudzik and Preston (4) reported activation of K-A by sulfur-containing free radicals in cracking 2,3-dimethylbutane, a molecule too large to

TABLE I
Effect of Sulfur^a

	Total pressure (atm)			
	137	137	69	69
Sulfur in feed (wt%)	0	1	0	1
Conversion (wt%)				
<i>n</i> -Paraffins	73.8	28.1	58.2	6.5
Non-normals	22.7	34.4	21.8	21.2

^a Reaction conditions: Ni/H-erionite catalyst; hydrogen/hydrocarbon mole ratio of 27/1; 400°C; 14 LHSV.

enter the pores of K-A. Since the erionite catalyst contains 2.7% potassium, the observed activation effect may be attributed to external surface activation effects. However, the inhibition of intracrystalline activity by sulfur is unexpected.

We propose that the inhibition effect of sulfur and hydrogen pressure on the intracrystalline catalytic activity is related to the build-up of equilibrium concentrations of bulky and strongly sorbed reaction intermediates within the pores of the zeolite. These molecules could not only reduce the concentration of available sites but also impede the passage of the reacting molecules by blocking the intracrystalline channels. The inhibition of the rate of hexane conversion by the presence of *n*-pentane reported earlier (5) is another example. However, positive identification of the "inhibitors" or alternative interpretation of the experimental results awaits further investigation.

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