

## Kinetics of Hydrogenation on Supported and Bulk Nickel-Tungsten Sulfide Catalysts

R. J. H. VOORHOEVE\* AND J. C. M. STUIVER

*Koninklijke/Shell-Laboratorium, Amsterdam, Netherlands*

Received February 25, 1971

The kinetics were studied of the hydrogenations of cyclohexene and benzene and the hydrogenolysis of carbon disulfide on mixed sulfide catalysts. Comparison of bulk and alumina-supported Ni-W-S shows that the same types of active sites are present in the two catalysts. Anion-vacancies appear to be the active centers. The alumina carrier has no effect on the intrinsic properties of the sites; only their numbers increase by dispersion of the sulfide. Centers active in the conversion of cyclohexene, benzene, or carbon disulfide appear to be different. Simultaneous hydrogenation of cyclohexene and carbon disulfide shows that the hydrogenation sites are blocked by hydrogen sulfide, but particularly by carbon disulfide.

### NOMENCLATURE

Indices  $n = 1, 2, 3, 4$  indicate the compounds benzene, cyclohexene, carbon disulfide, and hydrogen sulfide, respectively.

$A$	pre-exponential factor in rate equation
$E$	apparent activation energy
$f$	volume fraction in liquid feed
$F$	liquid feed rate
$k$	hydrogenation rate constant, dependent on sulfur content of the feed
$k'$	same, independent of sulfur content of the feed
$K$	adsorption equilibrium constant
$p$	partial pressure at the entrance of the catalyst bed
$W$	weight of catalyst in the reactor
$x$	fractional conversion
$\alpha$	activity ratio
$\theta$	fractional coverage of the active sites
$\tau_0$	"threshold" value of reciprocal space velocity

### 1. INTRODUCTION

Mixed sulfide catalysts, such as cobalt-molybdenum sulfide and nickel-tungsten

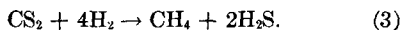
sulfide have attracted interest as hydrocracking, hydrodesulfurization, and hydrogenation catalysts (1). This study aimed at finding the clue to their favorable catalytic properties in hydrogenation and hydrogenolysis reactions.

Commercially used catalysts, mostly prepared by impregnation of a carrier or by coprecipitation, are characterized by a poorly developed crystal structure. Their physical and structural properties are difficultly accessible to measurements. In the present investigation, therefore, "bulk" model compounds of a much better developed structure were prepared from the elements at high temperature. These were used to study the relation between the catalytic properties and the structural and physical characteristics of the ternary sulfides under consideration. A close similarity between the catalytic behavior of bulk and supported sulfides was found and this is the subject of the present paper. Hydrogenations of benzene, and particularly cyclohexene [Eqs. (1) and (2)] were used as test reactions.



\* Present Address: Bell Telephone Laboratories, Murray Hill, New Jersey 07974.

Carbon disulfide, added to the feed to maintain a steady-state sulfur content of the catalyst, is hydrogenolyzed rapidly to hydrogen sulfide, Eq. (3):



This reaction is very much faster than (1) but of comparable velocity as (2). This latter fact makes it possible to study reactions (2) and (3) simultaneously.

## 2. EXPERIMENTAL PROCEDURES

### Catalysts

The commercial catalyst used (BASF No. 8376) contains 22.6% w tungsten and 3.8% w nickel as sulfides supported on alumina. The atomic ratio Ni:W is 0.53. A specific surface area of the sulfided catalyst of 143 m<sup>2</sup>/g was determined by the Brunauer *et al.* (2) nitrogen adsorption method. The catalyst pellets were crushed before use, to particles smaller than 50  $\mu$ .

The bulk model catalyst is prepared by heating tungsten disulfide and nickel (molar ratio 2:1) in an evacuated quartz tube for 20 hr at 800°C, cooling, homogenizing the contents of the tube, firing for another 80 hr at 800°C, and cooling slowly to room temperature. Immediately before use the catalyst is ground in a ball mill to particles smaller than 50  $\mu$ . Samples of 0.80, 0.86 and 0.95 m<sup>2</sup>/g specific surface area were used in the hydrogenations of cyclohexene/carbon disulfide, carbon disulfide/pentane, and benzene/carbon disulfide, respectively. These surface areas were determined with the Shell-Perkin Elmer Sorptometer. During the initial stages of the hydrogenation/hydrodesulfurization process the fresh catalyst (NiW<sub>2</sub>S<sub>4</sub>) takes up additional sulfur to reach a steady-state sulfur content depending on the sulfur content of the feed.

### Materials

In the preparation of NiW<sub>2</sub>S<sub>4</sub> catalysts specpure nickel (ex Johnson-Matthey), specpure tungsten and tungsten disulfide (ex Sylvania) were used. In the hydrogenation tests pure benzene (ex Noury-Baker, <0.003% w sulfur, evaporation residue 0.001% w, <0.017% w water), redistilled

gas-chromatographically pure cyclohexene and pure carbon disulfide (ex Union Chimique Belge, <0.02% w water) were used. Hydrogen was freed from oxygen by passing it through a BTS activated copper catalyst at 400°C; it was predried with Linde 4A sieves.

### Hydrogenation Procedure

The kinetic parameters were determined with a microflow technique, at a fixed pressure of 48 atm and a hydrogen/hydrocarbon molar ratio of 35. Samples of 0.1 to 5 g of catalyst, possibly diluted with quartz powder, were packed in the reactor. Further variables were: temperature 200–400°C; space velocities 0.14–36 ml of liquid feed/g of catalyst/hr; benzene and cyclohexene conversions 1–95%, carbon disulfide conversion always 100%.

Conversions in the empty reactor were negligible up to 400°C.

### Analysis

The reactor effluent was analyzed by gas-liquid chromatography over a column of dihexyl dinitrodiphenic ester. Automatic sampling and injection was used.

## 3. ANALYSIS OF THE KINETIC BEHAVIOR OF THE HYDROGENATION PROCESS

To characterize the catalytic properties of the nickel-tungsten sulfide catalysts the rate constants for the hydrogenation reactions have to be extracted from the variation of hydrocarbon conversion with space velocity.

For benzene a simple first order rate law (see Nomenclature above) was found (Eq. 4):

$$f_1 F dx_1 = k_1 p_1 (1 - x_1) dW. \quad (4)$$

From the integrated form of (4) it is possible to determine  $k_1$  in a plot of  $\ln(1 - x_1)$  versus the reciprocal space velocity  $W/F$  (Eq. 5).

$$-\ln(1 - x_1) = \frac{k_1 p_1}{f_1} \cdot \frac{W}{F} \quad (x_1 = 0 \text{ at } W = 0). \quad (5)$$

The hydrogenation of cyclohexene/carbon disulfide mixtures is more complicated in that the lines  $\ln(1 - x_2)$  versus  $W/F$  are

straight only at lower space velocities, or higher  $W/F$  values (see Fig. 1). This indicates that the reaction is first order in cyclohexene, but is inhibited in the first part of the catalyst bed. Figure 1 shows the inhibition to be more severe as more carbon disulfide is admixed with the feed. Hence it is supposed that preferential adsorption of  $CS_2$  blocks the hydrogenation sites. Conversion of  $CS_2$  into less strongly adsorbing  $H_2S$  in the first part of the catalyst bed results in higher cyclohexene hydrogenation rates at higher  $W/F$  values. The difference in adsorption strength of  $CS_2$  and  $H_2S$  has been found earlier on platinum black and on nickel sulfide (3-5).

The cyclohexene/carbon disulfide conversion kinetics is analyzed on the basis of these observations. Assuming rather insignificant coverage of active sites with cyclohexene, the first order rate law for cyclohexene conversion is:

$$\frac{dx_2}{dW/F_2} = k'_2(1 - x_2)(1 - \theta_3 - \theta_4)p_2. \quad (6)$$

As hydrogenolysis of carbon disulfide in pentane over the model  $NiW_2S_4$  catalyst shows zero order kinetics (Table 1), it is assumed that its conversion is controlled by reaction of hydrogen with chemisorbed carbon disulfide:

$$\frac{dx_3}{dW/F_3} = k'_3\theta_3. \quad (7)$$

The differential equations (6) and (7) must be solved simultaneously for the boundary conditions  $x_2 = x_3 = 0$  for  $W/F_2 = W/F_3 = 0$ . Adsorption equilibria for carbon disulfide and  $H_2S$  are given by

$$\frac{\theta_3}{1 - \theta_3 - \theta_4} = K_3p_3(1 - x_3), \quad (8)$$

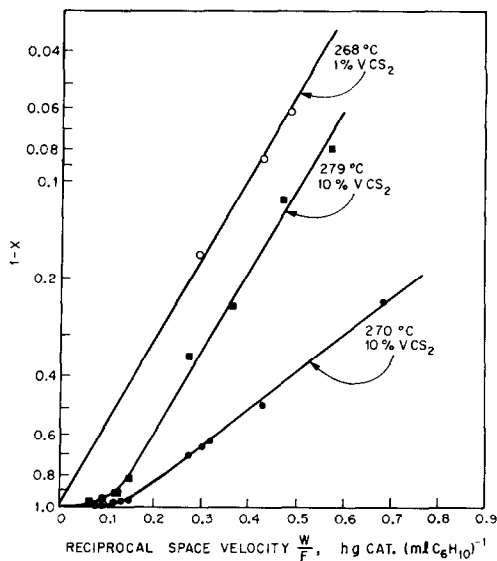


FIG. 1. Hydrogenation of cyclohexene-carbon disulfide mixtures on  $Al_2O_3$ -supported nickel-tungsten sulfide.

$$\frac{\theta_4}{1 - \theta_3 - \theta_4} = 2K_4p_3x_3. \quad (9)$$

To obtain a relation between  $W/F_2$  and  $x_2$  we solve  $\theta_3$  and  $\theta_4$  from Eqs. (8) and (9) and substitute these in Eqs. (6) and (7). Integrating and combining the resulting equations yields

$$\begin{aligned} \frac{W}{F} = & \frac{-f_2(1 + 2K_4p_3)}{k'_2p_2} \ln(1 - x_2) \\ & + \frac{f_3(K_3 - 2K_4)}{k'_3K_3} \{1 - (1 - x_2)^{k'_3K_3f_2/k'_2p_2f_3}\}. \end{aligned} \quad (10)$$

Equation (10) is depicted in Fig. 2, showing its initial and final slope, its asymptote, and the intercept  $\tau_0$  of the asymptote with the  $W/F$  axis. As the conversion rate for carbon disulfide is much higher than the rate of

TABLE 1  
HYDROGENOLYSIS OF CARBON DISULFIDE ON BULK Ni-W-S

Reactants	Temp (°C)	Rate constant [ml CS <sub>2</sub> (m <sup>2</sup> cat.) <sup>-1</sup> hr <sup>-1</sup> ]	Reaction order in CS <sub>2</sub>	$E_3$ , (kcal/mole)
CS <sub>2</sub> (10% v) in pentane, H <sub>2</sub> (190 mol/mol CS <sub>2</sub> ) <sup>a</sup>	250	0.053	~0	29
	273	0.17		
CS <sub>2</sub> (1 and 4% v) in cyclohexene <sup>b</sup>	275	0.03	~0	32

<sup>a</sup> Specific surface area of catalyst 0.86 m<sup>2</sup>/g.

<sup>b</sup> For details see text.

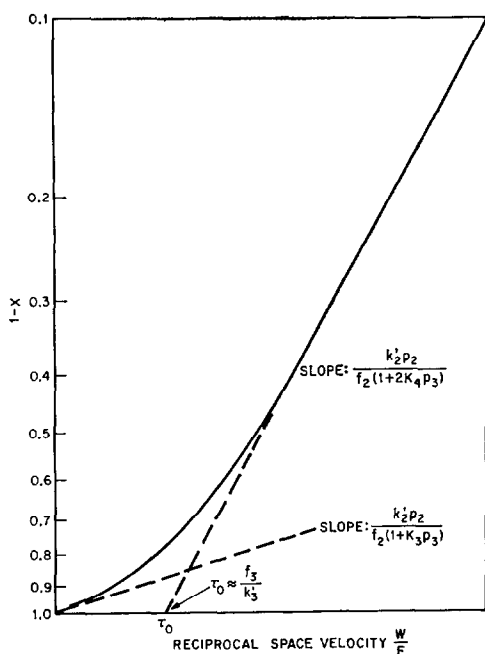


FIG. 2. Kinetics of cyclohexene-carbon disulfide conversion, Eq. (10).

cyclohexene conversion, the exponent of  $(1 - x_2)$  in the term between braces in Eq. (10) is rather large. This means that with increasing  $x_2$  the term will rapidly approach unity, causing Eq. (10) to near its asymptote rapidly also. From the ratio of initial and final slopes of Eq. (10) in Fig. 2, it can be inferred that  $K_3$  is rather bigger than  $2K_4$ . Therefore, the expression for the asymptote can be simplified to

$$\begin{aligned} \frac{W}{F} &= \frac{-f_2(1 + 2K_4 p_3)}{k'_2 p_2} \ln(1 - x_2) + \frac{f_3}{k'_3} \\ &\equiv \frac{-f_2}{k_2 p_2} \ln(1 - x_2) + \frac{f_3}{k'_3} \quad (11) \end{aligned}$$

This asymptote describes the hydrogenation of cyclohexene after all  $\text{CS}_2$  has been converted into  $\text{H}_2\text{S}$ . Applying Eq. (11) to the experimental results yields  $k_2$ , which is dependent on  $p_3$  or the sulfur content of the feed, and also yields  $k'_3$ .

The validity of this analysis of the curves in Fig. 1 is shown by the proportionality found experimentally between the intercept  $\tau_0$  and the sulfur content of the feed,  $f_3$  (see below). Moreover, the rate constants and activation energy for the carbon disulfide

hydrogenolysis extracted from Eq. (11) agree satisfactorily with independently determined values (Table 1).

#### 4. RESULTS FOR BULK AND ALUMINA-SUPPORTED Ni-W-S

##### *Alumina-Supported Catalyst*

The hydrogenation of cyclohexene/carbon disulfide mixtures on the BASF 8376 catalyst is an example of the kinetic behavior described in the previous section, including the effects of the sulfur content of the feed on the slope of the  $\ln(1 - x_2)$  versus  $W/F_2$  curves and on the magnitude of the intercept  $\tau_0$  (see Fig. 1). Measurements with 1% v and 10% v  $\text{CS}_2$  in the feed were performed in the range of 214 to 329°C and yielded rate constants  $k_2$  spanning two orders of magnitude. These are shown in curves I and II of the Arrhenius plot in Fig. 4. Comparing these curves shows the marked effect of the sulfur content of the feed. The Arrhenius curves are nonlinear, indicating an activation energy that depends on temperature (Table 2).

The rate constant for hydrogenolysis of carbon disulfide,  $k'_3$ , is calculated from the intercepts  $\tau_0$  and presented in Fig. 5, curve I, in an Arrhenius plot. The value of  $k'_3$  is seen to be independent of the sulfur content of the feed. The activation energy is constant at  $E_3 = 32$  kcal/mole, the pre-exponential factor is  $A_3 = 4.4 \times 10^{12}$  ml  $\text{CS}_2$  per g catalyst and per hour.

The hydrogenation of benzene on this catalyst proved to be slower than the cyclohexene hydrogenation by a factor of about 300 at 280°C. The rate constant  $k_1$ , for 1% v  $\text{CS}_2$  in the feed, is given as curve III in Fig. 4.

##### *Bulk Model Catalyst*

The kinetic behavior of the cyclohexene/carbon disulfide hydrogenation process on this catalyst also fits the kinetic analysis in the previous section. Some experiments are shown in Fig. 3. Values for  $k_2$  and  $k'_3$  were again determined from the slope and intercept of curves like those in Fig. 3.

Results for  $k_2$  for 1 and 4% v  $\text{CS}_2$  in the feed are given in Fig. 4, curves IV and V, respectively. Here, as in the case of the alumina-supported catalyst, the activation energy appears to depend on the tempera-

TABLE 2  
ACTIVATION ENERGIES FOR HYDROGENATIONS OF BENZENE, CYCLOHEXENE, AND  
CARBON DISULFIDE

Test	Bulk Ni-W-S catalyst		Ni-W-S/Al <sub>2</sub> O <sub>3</sub> catalyst	
	Temp (°C)	Activation energy (kcal/mole)	Temp (°C)	Activation energy (kcal/mole)
C <sub>6</sub> H <sub>6</sub>			300-400	17
CS <sub>2</sub>	280-350	32	210-330	32
C <sub>6</sub> H <sub>10</sub>	280	28	230	46
	300	22	260	36
	320	19	280	28
	360	15	300	22
	400	15	320	19

ture. At constant temperature, the rate constants are shown to depend on the CS<sub>2</sub> content of the feed.

For carbon disulfide, the hydrogenation rate constants  $k'_3$  calculated from  $\tau_0$  are plotted in Fig. 5, curve II. Points for 1 and 4% v CS<sub>2</sub> are shown to fit the same line, establishing again the linear relation between  $\tau_0$  and  $f_3$  required by Eq. (11). The activation energy is  $E_3 = 32$  kcal/mole, the same value

as found for the BASF 8376 catalyst. The pre-exponential factor is  $A_3 = 13 \times 10^{11}$  ml CS<sub>2</sub> per m<sup>2</sup> catalyst surface area and per hour. Benzene with 1% v CS<sub>2</sub> was hydrogenated over this catalyst at 400°C, yielding a rate constant of  $k_1 = 0.16$  ml (m<sup>2</sup> cat.)<sup>-1</sup> hr<sup>-1</sup> atm<sup>-1</sup>.

## 5. DISCUSSION

### Nature of the Active Sites

The rate constants  $k_1$  and  $k_2$  for benzene and cyclohexene, respectively, are valid when

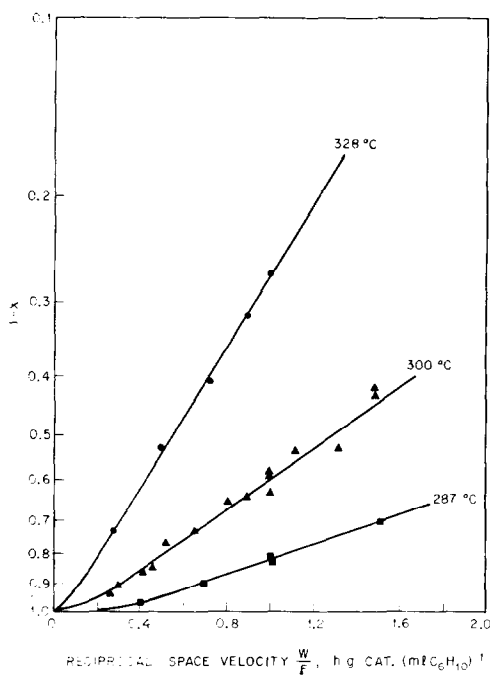


FIG. 3. Hydrogenation of cyclohexene (1% v CS<sub>2</sub>) on bulk Ni-W-S.

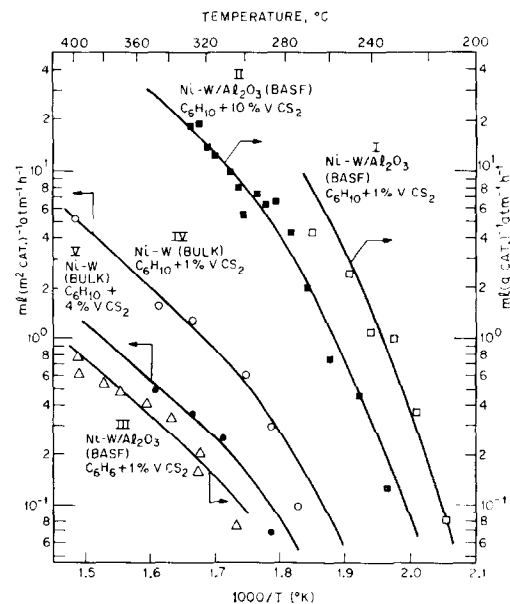


FIG. 4. First order rate constants for benzene and cyclohexene hydrogenation.

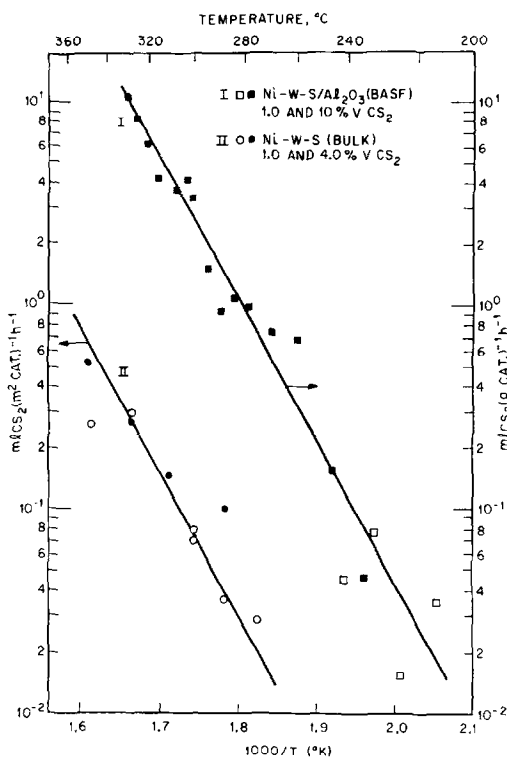


FIG. 5. Zero order rate constants for carbon disulfide hydrogenolysis.

the  $\text{CS}_2$  in the feed has been converted to hydrogen sulfide. Hence, the influence of the sulfur content of the feed on the rate constants reflects the effect of the hydrogen sulfide partial pressure. Comparison in Fig. 4 of curves for higher and lower sulfur contents of the feed, shows clearly that an increase in hydrogen sulfide partial pressure decreases the rate. The apparent activation energy does not change, however, only the pre-exponential factor. This appears from the fact that curves for different sulfur contents can be made to coincide by simple vertical displacement of one relative to the other. This has been done to construct Fig. 6. Thus it is the number of active sites and not their intrinsic activity that is affected by  $\text{H}_2\text{S}$ . The active sites are evidently sulfur deficient metal centers in the surface of the catalyst. These anion vacancies are in equilibrium with the hydrogen sulfide and hydrogen pressures via the equation

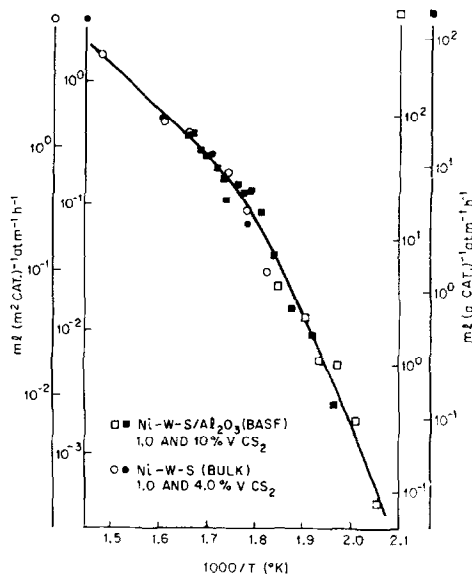
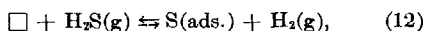


FIG. 6. Cyclohexene hydrogenation rate constants, supported and bulk Ni-W-S, with 1.0, 4.0, and 10% v  $\text{CS}_2$  in the feed.

with  $\square$  denoting a vacancy. The centers active in the hydrogenations of benzene and cyclohexene, however, cannot be identical, as their numbers are affected differently by the dispersion of the sulfide catalyst on a carrier (see below).

#### Effects of the Alumina Carrier

The Arrhenius curves in Fig. 4 for the hydrogenation of cyclohexene on the bulk and the alumina-supported catalysts can all be made to coincide by appropriate vertical displacements (see Fig. 6). Evidently, the hydrogenation process on the two catalysts is characterized by the same, temperature-dependent, activation energy. The difference in rate is brought about by the difference in the number of active sites. The similarity of the sites on the two catalysts is further substantiated by the analogous kinetics and sulfur-dependence of the reaction on bulk and supported Ni-W-S. The effect of the carrier is exclusively to stabilize a much greater dispersion of the sulfide. The same observation holds for the carbon disulfide hydrogenolysis: the Arrhenius lines for this reaction on the two catalysts are parallel, with an activation energy in both cases of 32 kcal/mole (Fig. 5). Our data for

benzene are not sufficient for a similar conclusion; but, in view of the results for the other two reactions, no specific effect of the carrier on the activity of the benzene sites is expected either. In hydrocracking, on the other hand, the acid function of the support is expected to be important.

The effect of the dispersion on alumina on the number of active sites for each test reaction is determined by comparing the number of sites in 1 g of sulfide supported on alumina with the number of sites in 1 m<sup>2</sup> of unsupported sulfide surface area. For this purpose we define:

$$\alpha_n = \frac{\text{rate [ml(g cat)}^{-1} \text{ hr}^{-1}] \text{ on supported catalyst}}{\text{rate [ml(m}^2 \text{ cat)}^{-1} \text{ hr}^{-1}] \text{ on bulk catalyst}}$$

with  $n = 1, 2, 3$  for benzene, cyclohexene, or carbon disulfide, respectively. For the supported catalyst the rate is expressed per gram of nickel-tungsten sulfide (and not per gram of alumina-containing catalyst as in the figures). The  $\alpha$ -values, which are independent of the temperature, are given below.

Reaction	Activity ratio	Specific surface area of bulk catalyst (m <sup>2</sup> g <sup>-1</sup> )
C <sub>6</sub> H <sub>6</sub>	$\alpha_1 = 15$	0.95
C <sub>6</sub> H <sub>10</sub>	$\alpha_2 = 180$	0.80
CS <sub>2</sub>	$\alpha_3 = 100$	0.80

Although the difference between the activity ratios for carbon disulfide and cyclohexene may not be too significant, it is quite evident that the dispersion of sulfide on a carrier influences the number of hydrogenation sites much less for benzene than it does for cyclohexene. One further point deserves attention. There is no doubt that dispersion of the catalyst on alumina in the form of particles which are mainly amorphous to X-rays increases the specific surface area of the sulfide by much more than a factor 15. The low  $\alpha_1$  value (see above) is an indication that we deal with crystal features (faces, edges, corners, etc.) of widely different activity. The relative contribution of active

sites for benzene hydrogenation to the total surface area may be larger in bulk than in alumina-supported nickel-tungsten sulfide.

#### Diffusion Limitations

The apparent activation energy for the cyclohexene hydrogenation  $E_2$  is dependent on temperature (Fig. 6). Nevertheless, it is considered unlikely that the reaction is limited by diffusion. First, at any given temperature,  $E_2$  is independent of the changes in reaction rate caused by variations in the CS<sub>2</sub> content, and also independent of the specific surface area of the catalyst. Secondly, the activation energy for the even faster CS<sub>2</sub> hydrogenolysis in these same catalysts does not depend on temperature (Fig. 5). Moreover, calculations following Yoshida *et al.* (6) show that no significant temperature or concentration gradients are to be expected.

## 6. CONCLUSIONS

In previous sections the activities of nickel-tungsten sulfide, in the form of a bulk high-temperature preparation and as an alumina-supported industrial catalyst were compared in the hydrogenations of cyclohexene and benzene mixed with carbon disulfide. This study allows the following conclusions regarding the nature of the active sites in Ni-W-S and the effect of the alumina carrier.

The active centers for hydrogenation of cyclohexene and benzene are sulfur-deficient metal sites, or anion vacancies, the activity of which does not depend on the coverage of the surface with sulfur. Their number decreases with increasing sulfur content of the feed, as they are reversibly blocked by hydrogen sulfide, but particularly by carbon disulfide. Centers active in the hydrogenations of benzene and cyclohexene are different. Active sites present in bulk and in alumina-supported nickel-tungsten sulfide are the same; the alumina carrier does not affect their intrinsic activity, but increases their number. This is particularly effective for cyclohexene hydrogenation. This study shows that bulk nickel-tungsten sulfide may be used in further studies of the mechanism

of the catalytic activity and may be regarded as representative for supported sulfide. The unraveling of the hydrogenation kinetics for cyclohexene-carbon disulfide mixtures shows the conversion of cyclohexene to be first order in cyclohexene, whereas the hydrogenolysis of carbon disulfide is zero order in CS<sub>2</sub>.

#### ACKNOWLEDGMENTS

The authors thank Dr. P. Cossee and Dr. W. M. H. Sachtler of Koninklijke/Shell-Laboratorium, Amsterdam for suggestion of this subject and for discussions, and Mr. J. Gaaf of that laboratory for preparation of the bulk Ni-W-S catalyst.

#### REFERENCES

1. (a) BERKMAN, S., MORRELL, J. C., AND EGLOFF, G., "Catalysis," pp. 277-279, 848-887, 924-930. Reinhold, New York, 1940. (b) MCKINLEY, J. B., in "Catalysis," Vol. 5, p. 405. (P. H. Emmett, Ed.). Reinhold, New York, 1957.
2. BRUNAUER, S., EMMETT, P. H., AND TELLER, E., *J. Amer. Chem. Soc.* **60**, 309 (1938).
3. MAXTED, E. B., AND EVANS, H. C., *J. Chem. Soc., London* **1937**, 603.
4. CRAWLEY, B., AND GRIFFITH, R. H., *J. Chem. Soc. London* **1938**, 720.
5. TARAMA, K., TERANISHI, S., HATTORI, K., AND NISHIDA, S., *J. Fuel Soc. Jap.* **42**, 156 (1963).
6. YOSHIDA, F., RAMASWAMI, D., AND HOUGEN, O. A., *AIChEJ.* **8**, 5 (1962).