

Kinetics of the Reaction of Hydrogen Sulfide with Unsupported and Supported Nickel Oxide*

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The kinetics of the reaction of gaseous hydrogen sulfide with unsupported, silica-supported, and silica-alumina-supported nickel oxide have been measured. Each system exhibits a different kinetic form for this reaction. As with the reduction of silica-alumina-supported nickel oxide, Elovich kinetics also describe the sulfiding of this catalyst. However, the kinetic equations which describe the sulfiding of the other two systems are unlike the equations that describe their reduction. Some possible mechanisms are proposed for the reaction of hydrogen sulfide with these nickel systems.

INTRODUCTION

Recently there has been reported a considerable amount of experimental work that has characterized the kinetics of hydrogen reduction of supported nickel catalysts (1-3). These studies have shown that the reducibility of nickel catalysts depends very much on the nature of the support and the manner of catalyst preparation. Although it is commonly known that the presence of hydrogen sulfide gas can greatly affect the catalyst's activity for hydrogenation of olefins and cracking of hydrocarbons (4), no comparable effort has been directed toward elucidating some aspects of the reaction of this commonly encountered gas with supported nickel catalysts.

In this paper we describe a technique for measuring the kinetics of a gas-solid reaction. This technique is used to measure the kinetics of the reaction of gaseous hydrogen sulfide with unsupported NiO powder, silica-supported nickel oxide, and silica-alumina-supported nickel oxide catalysts. We find that the rate equation describing this reaction is different for each of these nickel systems. Comparison of these results with the

published hydrogen reducibility measurements (1, 2) shows that with two of these nickel systems, hydrogen sulfide also reacts differently than does hydrogen. As with the reduction of silica-alumina-supported nickel, the reaction of hydrogen sulfide with this catalyst is also described by Elovich kinetics [for a general review see ref. (5)]. Some mechanisms are suggested for the reaction of hydrogen sulfide with nickel in these three systems.

EXPERIMENTAL

Apparatus. The reactant gas mixture of 5 mole % H₂S in He was passed across the reference side of a thermal conductivity cell, through the catalyst bed, then across the other side of the thermal conductivity cell. The thermal conductivity cell was a diffusion-type cell with tungsten filaments. The signal from the thermal conductivity cell was recorded on a 1-mV recorder. The signal response was linear with H₂S concentration up to at least 5 mole % H₂S in He. The tubular Vycor and Pyrex reactors (23-mm o.d.) had a total volume of about 100 cc, most of which was filled with Pyrex beads during a run. Packed Dry Ice-acetone traps were on the effluent side of the reactor in order to trap water.

Procedure. One gram of catalyst (60-100 mesh powder) was diluted with 10 g of quartz chips (50-200 mesh) and loaded into the

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reactor along with enough Pyrex beads to fill the dead space. The total sweepout volume of the lines and the reactor was about 50 cc. The catalysts were heated to 500°C in nitrogen for 30 min, then cooled to the temperature of the run. The gas stream was switched from pure nitrogen to 5 mole % H₂S in He, and the amount of H₂S taken out of the He was recorded as a function of time on the 1-mV recorder. The integral of this curve is proportional to the total amount of H₂S reacted with the catalyst.

Catalysts. Baker C.P. grade nickelous oxide powder (6.4 wt %) was mixed with Davison 950 grade silica gel (93.6 wt %) for measurements of the rate of nickel oxide powder sulfiding. The NiO powder had a surface area of 0.9 m²/g. Ni/SiO₂ was prepared by impregnation of Davison 950 grade silica gel with nickelous acetate. The Ni/SiO₂-Al₂O₃ was prepared by impregnation of American Cyanamid's MS-A-3 silica-alumina cracking catalyst with nickelous acetate. The metal loadings on these catalysts were 5 wt %. They were calcined before use by heating them slowly to 500° or 750°C in flowing air. They were held at the calcining temperature (500° or 750°C) for 3 hr.

Gases. The H₂S/He gas mixture was obtained premixed in 1500 psig cylinders from the Matheson Company. They stated composition was 5 mole % H₂S. However, Ascarite trapping, and also mass spectral analysis, indicated the mixture to be 4.2 mole % H₂S in He.

RESULTS AND DISCUSSION

NiO Powder

The reaction of hydrogen sulfide with NiO powder has been studied by following the weight change of the solid with time using a quartz helix balance (6). These measurements were carried out in pure hydrogen sulfide at a pressure of 12 mm Hg. By contrast, we have measured the rate of this reaction by following the uptake of hydrogen sulfide gas as a function of time using the technique outlined in the experimental section. In our system the partial pressure of H₂S is 32 mm Hg and there is an inert gas (He) present at a pressure of about 728 mm Hg.

The uptake of H₂S by this NiO powder sample as a function of time and temperature is illustrated in Fig. 1. The results have been

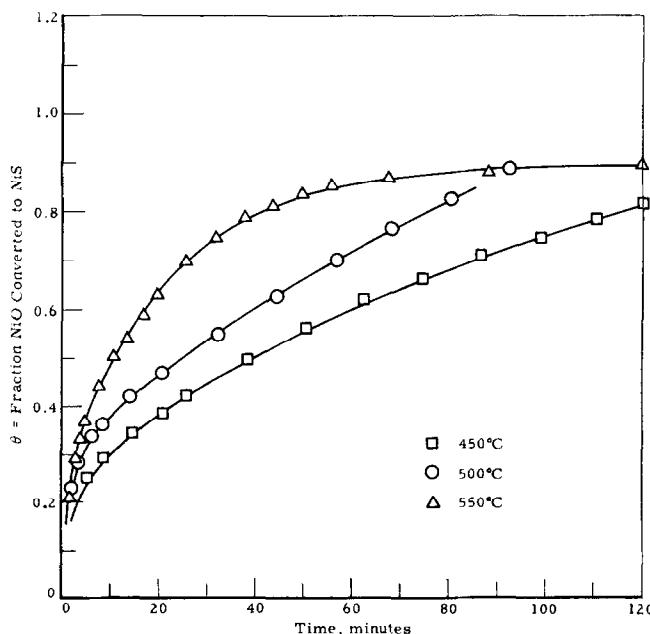


FIG. 1. Reaction of H₂S with NiO powder.

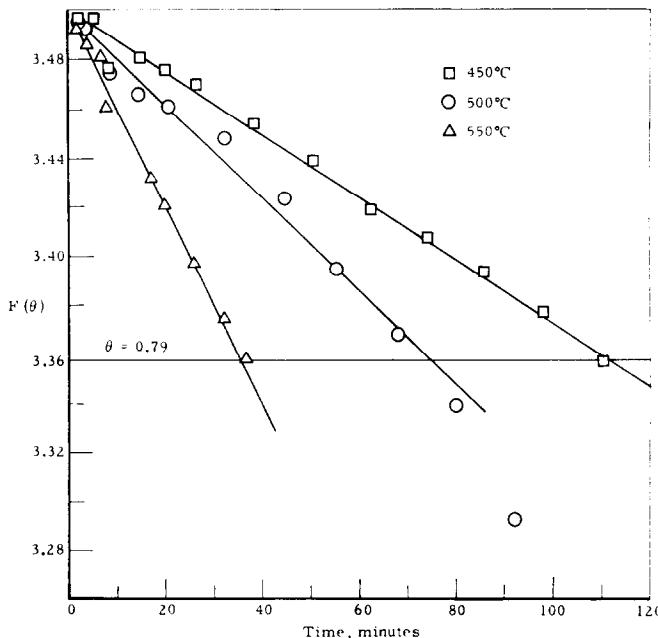


FIG. 2. Reaction of H_2S with NiO powder; $F(\theta) = (1-\theta)^{2/3} + \frac{1+0.4\theta)^{2/3}}{0.4}$

normalized to NiS, i.e., θ is the fraction of the original NiO that has reacted to form NiS. The rate of H_2S uptake on NiO powder was too slow at temperatures below 450°C for accurate rate measurements with this technique. We found, however, that at 300°C, $\theta = 0.08$ after 1 hr. Since NiO powders are essentially completely reduced by hydrogen under these conditions (7), reduction of NiO by hydrogen is much faster than the reaction of H_2S with NiO. The reduction of NiO by hydrogen is sigmoid with time, indicating the mechanism involves first nucleation followed by growth of the nuclei (1, 8). No induction period is evident in Fig. 1 for the reaction of H_2S with NiO.

The rate of reaction of H_2S with NiO has been proposed to be limited by the rate of ion migration across the newly formed NiS layer. The reaction occurs at the gas-solid boundary, forming water and sulfide ions, but the rate is controlled by the rate of oxide and sulfide ion migration through the NiS layer (6). The parabolic rate law is customarily applied to these types of diffusion-controlled reactions (9). A correct derivation of the rate equation describing such a diffu-

sion-controlled reaction with spherical particles was first made by Valensi (10). Recently Carter has derived this equation and discussed its application (11). For sulfiding spherical particles of NiO the fractional amount of NiO converted to NiS, θ , is related to time, t , by (6)

$$F(\theta) = (1 - \theta)^{2/3} + \frac{[1 + (A - 1)\theta]^{2/3}}{A - 1} = \frac{A}{A - 1} - \frac{Kt}{r_0^2} \quad (1)$$

where A is the ratio of the molar volumes of NiS to NiO (1.4); K , a constant proportional to the rate constant for ion diffusion across the NiS layer; and r_0 , the initial radius of the NiO particle.

Carter has shown that this equation is applicable to systems of spheres of uniform radii, but if data for powders consisting of particles with a distribution of sizes and shapes are plotted according to Eq. (1), they will deviate from a straight line for larger values of θ . Further, since the reaction is too fast in the beginning due to the large surface area of the irregularly shaped par-

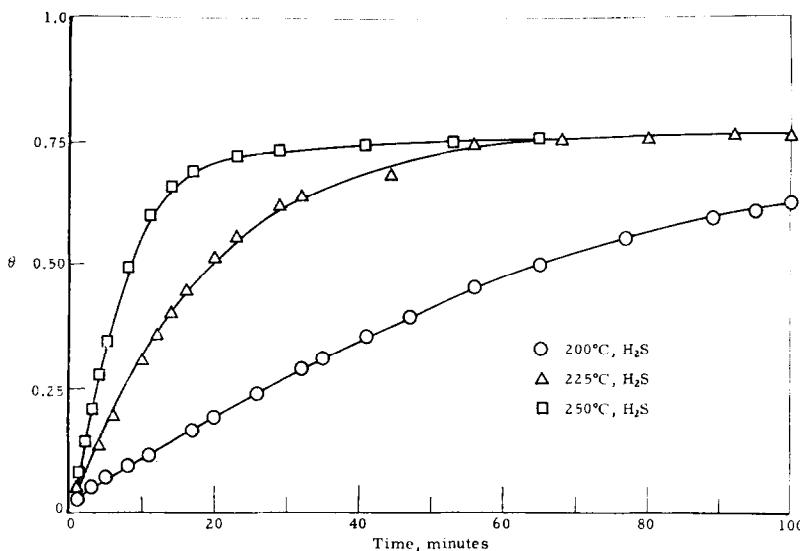


FIG. 3. H₂S reaction with Ni/SiO₂; 500°C calcination.

ticles, and it is too slow during the last part of the reaction since the remaining particle size will be large, the rate constant, K , obtained from the linear portion of the plot for a multiradii system will not be directly proportional to the true rate constant for ion diffusion. Its temperature dependence, however, will give the correct activation energy (provided the sample has identical size distribution and shapes in all experiments) (11).

Equation (1) was found by Colson *et al.* (6) to describe adequately the reaction of H₂S with NiO powders as measured by their technique. They obtained an activation energy of 19.6 kcal mole⁻¹. Equation (1) also gives a good fit to the data obtained by the technique used here up to $\theta \approx 0.8$ (Fig. 2). The activation energy obtained from the slopes of the lines in Fig. 2 is about 15 \pm 4 kcal mole⁻¹; the sparsity of the data prohibits an accurate activation energy determination.

The present technique then reproduces the correct kinetic behavior for the reaction of H₂S with NiO powders. The reaction seems to be adequately described by a diffusion-controlled mechanism with an activation energy of \sim 19 kcal mole⁻¹. Sulfiding NiO with H₂S is much slower than reduction of NiO by hydrogen, and the rate-controlling steps of these two reactions are different.

Impregnated Ni/SiO₂ Catalysts

The data for reaction of H₂S with 5 wt % nickel impregnated on Davison 950 grade silica gel calcined at 500°C are illustrated in Fig. 3. Although the data in Fig. 3 have again been normalized to a final stoichiometry of NiS, it appears from Fig. 3 that the final stoichiometry is about NiS_{0.76}. This catalyst was also reacted with H₂S at 375°C (data not shown). There was an initial rapid uptake of H₂S to $\theta = 0.7$ followed by further slow H₂S uptake going beyond $\theta = 0.83$. The Ni/SiO₂ catalyst calcined at 750°C also gave the same type of θ vs. t curves as shown in Fig. 3, except that the rate was about a factor of 10 slower than the catalyst calcined at 500°C, and the maximum was $\theta = 0.67$ instead of $\theta = 0.76$. Since a maximum stoichiometry of Ni₃S₂ is not indicated by either the bulk NiO data or the higher temperature (375°C) sulfiding of Ni/SiO₂, a probable explanation is that the surface NiO, or perhaps Ni silicate, is rapidly sulfided at these temperatures, but any bulk NiO present reacts very slowly. Bulk sulfiding of NiO is relatively slow at temperatures below 400°C.

The sulfiding of Ni/SiO₂ does not follow Elovich kinetics as does its reduction by hydrogen (1). No simple order in unreacted nickel ions over the entire range of θ is indicated by the data in Fig. 3.

If the fractional uptake of H₂S is renormalized to the experimentally determined maximum amount for these Ni/SiO₂ systems, we can then call θ' the fraction of the total accessible NiO converted to NiS. For reasons already stated this could be considered to be the surface NiO (or nickel silicate). One may also think of θ' as the fraction of all of the nickel ions that have been sulfided to a final stoichiometry of NiS_{0.76} for the 500° calcined catalyst and NiS_{0.67} for the 750° calcined catalyst. Figures 4 and 5 illustrate that for values of $\theta' > 0.2$, the reaction of H₂S with these catalysts is first order in unreacted accessible nickel ions. The rate is given by

$$d\theta'/dt = k_1(1 - \theta') \quad (2)$$

However, the data illustrated in these figures show that a simple first order kinetic equa-

tion does not adequately describe the reaction over the entire range of θ' . Evidently a more complex mechanism is involved.

A plausible mechanism that gives first order kinetics after an initial period is one involving nucleation and growth of the nuclei over the small NiO crystals. If growth of the nuclei is sufficiently fast and nucleation occurs by an exponential rate law, first order kinetics will be experimentally observed for the uptake of H₂S after an initial reaction period (12).

The surface might be thought of as being made up of small uniform crystals of NiO (or nickel silicate) and their conversion to NiS occurs by nucleation according to the rate law

$$dN/dt = k_1(N_0 - N) = k_1 N_0 \exp(-k_1 t) \quad (3)$$

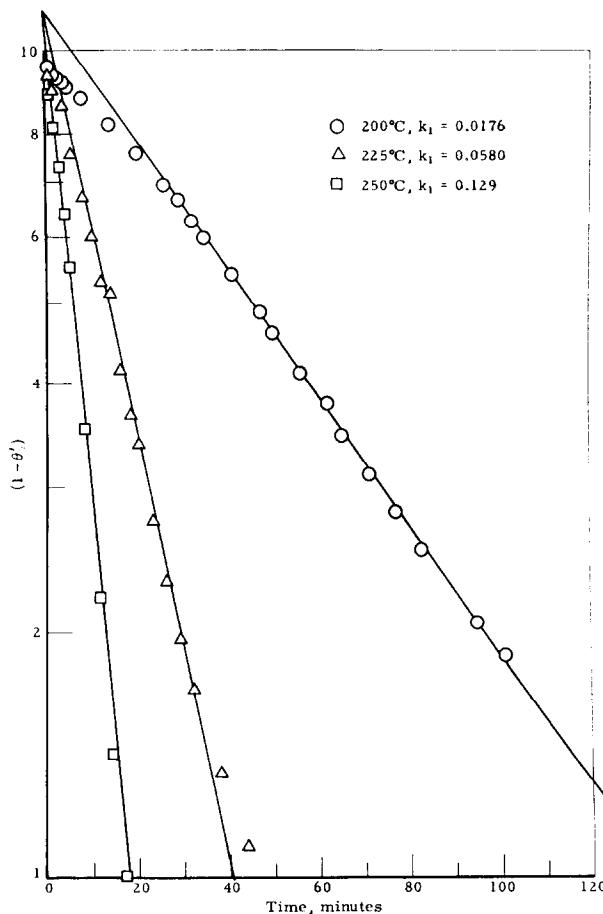
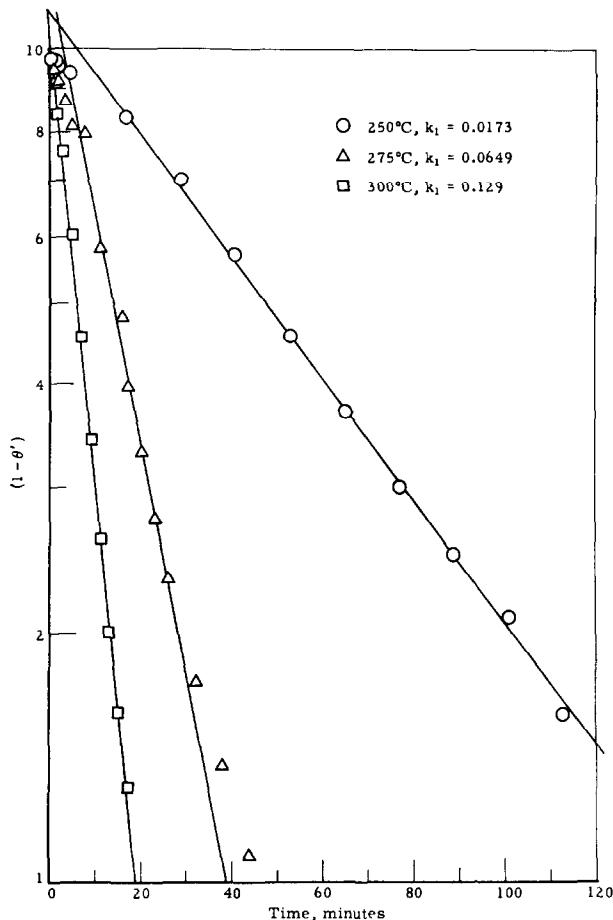


FIG. 4. H₂S reaction with Ni/SiO₂; 500°C calcination.

FIG. 5. H_2S reaction with Ni/SiO_2 ; 750°C calcination.

followed by linear growth of the nuclei over the surface of the crystals. N_0 is the number of potential nuclei forming sites at $t = 0$ and N is the number of sites that have reacted to form nuclei.

The radius of a nucleus at time, t , that was formed at $t = y$ is

$$r(t, y) = k_2(t - y) \quad (4)$$

Its area will be

$$A(t, y) = \pi k_2^2(t - y)^2 \quad (5)$$

The total area sulfided after time t is then given by

$$\begin{aligned} A(t) &= \int_0^t A(t, y) [dN/dt]_{t=y} dy \\ &= N_0 \pi k_1 k_2^2 \int_0^t (t - y)^2 \exp(-k_1 y) dy \end{aligned} \quad (6)$$

However, at $t_1 = r_0/k_2$, where r_0 is the NiO particle diameter, those crystals that were nucleated at $t = 0$ will be completely sulfided, and they should not be included in Eq. (6). The integral should be divided into two parts; one part for those crystals nucleated between t_1 and t_2 , and one part for those crystals nucleated between 0 and t_1 where

$$t_1 = t_2 - r_0/k_2 \quad (7)$$

The total area sulfided at t_2 is then

$$\begin{aligned} A(t_2) &= N_0 k_2^2 k_1 \pi \int_{t_1}^{t_2} (t_2 - y)^2 \exp(-k_1 y) dy \\ &\quad + N_0 r_0^2 k_1 \pi \int_0^{t_1} \exp(-k_1 y) dy \end{aligned} \quad (8)$$

Defining θ' as being equal to $A(t)/A_0$ where A_0 is the total accessible sulfiding surface area, integration of (8) gives for $t > r_0/k_2$

$$\theta' = 1 - B \exp(-k_1 t) \quad (9)$$

B is a constant dependent on the values of k_1 , r_0 , and k_2 . Therefore for $t > r_0/k_2$ plots of $\ln(1 - \theta')$ vs. t will, by Eq. (8), be linear, i.e., the reaction will follow first order kinetics. The rate constant, k_1 , obtained from these plots is the first order rate constant for formation of nuclei.

For $t < r_0/k_2$, the kinetics will not be described by Eq. (9). This model would predict a deviation from first order kinetics at times short enough such that a negligible number of the crystals are completely sulfided. The data illustrated in Figs. 4 and 5 for the sulfiding of Ni/SiO₂ deviate from first order behavior for $\theta' < 0.2$.

We can summarize by saying that the sulfiding of silica-supported nickel is first order in unreacted nickel for values of $\theta' > 0.2$. One mechanism consistent with the experimental results involves nucleation according to an exponential rate law followed by rapid two-dimensional growth of the nuclei over the surface of the crystals. The activation energy of the first order rate constant is 20 kcal mole⁻¹ for the catalyst calcined at 500°C and 24 kcal mole⁻¹ for the 750°C calcined catalyst. The uncertainty in these E_a values is about $\pm 20\%$ due to the sparsity

of the data. In terms of the nucleation model the increased activation energy may result from high-temperature calcination annealing the crystals, causing nucleation to be more difficult.

Hydrogen reduction of impregnated Ni/SiO₂ catalysts is described by Elovich kinetics, and silica-supported nickel is reduced more slowly than is NiO powder (1). Sulfiding of an impregnated Ni/SiO₂ catalyst does not follow Elovich kinetics and silica-supported nickel is sulfided much faster than is NiO powder. Moreover, we find that H₂S reacts with Ni/SiO₂ calcined at 500°C to give $\theta = 0.7$ in 4 min when the reaction temperature is 375°C. This is much faster than the reaction of hydrogen with this catalyst (1). Sulfiding of NiO powder and impregnated Ni/SiO₂ catalyst seem to have no relation kinetically to the reduction of these systems by hydrogen.

Impregnated Ni/SiO₂-Al₂O₃ Catalysts

The uptake of H₂S by an impregnated 5% Ni on MSA-3 catalyst is illustrated in Fig. 6. The reaction of H₂S with this catalyst follows Elovich kinetics (5) as does its reduction by hydrogen (1, 2). A reasonable interpretation of the Elovich equation,

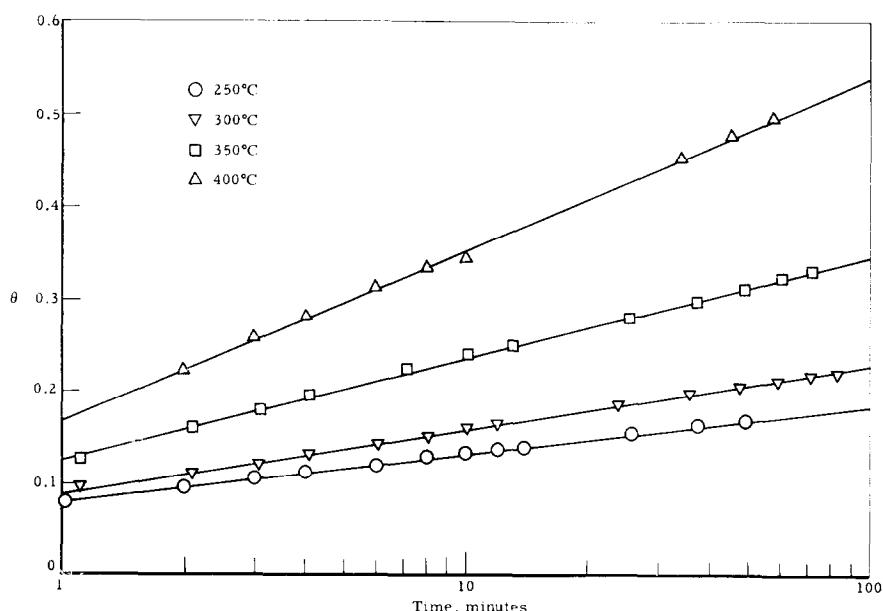


FIG. 6. H₂S reaction with Ni/MSA-3; 500°C calcination.

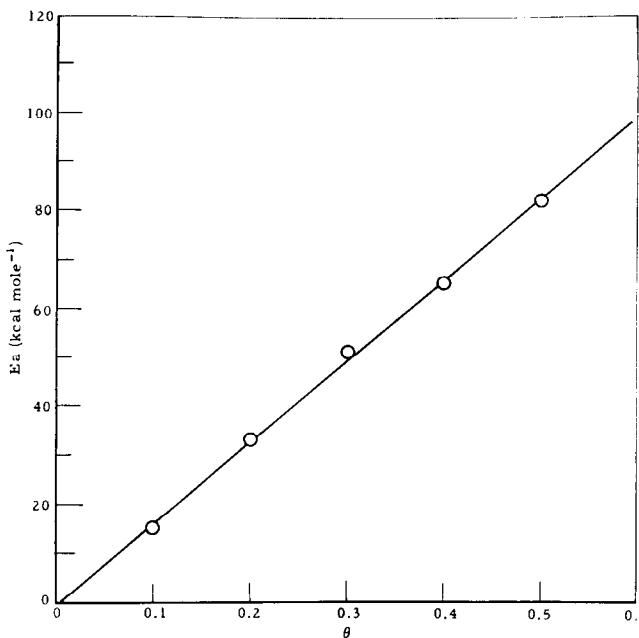


FIG. 7. Apparent activation energy for Ni/MSA-3 as a function of θ ; 500°C calcination.

$$d\theta/dt = a \exp(-b\theta) \quad (11)$$

where a is a constant independent of θ , is that it applies to rate processes on heterogeneous surfaces, and b is related to the spread in activation energy over the surface (1, 5). It has been shown that a sum of simultaneously occurring independent first order or second order reactions will approximate Elovich kinetics (13). If the reaction is H₂S with the nickel is zero order in unreacted nickel, but the activation energy is a linear function of the extent of reaction, Elovich kinetics are exactly obeyed, and b is equal to the spread in activation energy. Further discussion about the significance of Elovich kinetics can be found in the literature (1, 5).

The apparent activation energy, E_a , as a function of the extent of reaction, θ , can be extracted from the experimental data by using the relation

$$d\theta/dt = a \exp(-b\theta) = A(\theta) \exp[-E(\theta)/RT] = \text{rate} \quad (12)$$

$$\ln(\text{rate}) = \ln a - b\theta = \ln A(\theta) - E(\theta)/RT$$

The parameters a and b were obtained from the data in Fig. 6. Plots of $\ln(\text{rate})$ vs. $1/T$ for constant values of θ (plots are not shown) were linear, except for $\theta = 0$. The variation

in a is only a factor of 2 over the temperature range, 250–400°C, and therefore, $d \ln a / d(1/T) \approx 0$.

The apparent activation energy, E_a , as a function of θ is illustrated in Fig. 7. Over the range of the measurements, $0 \leq \theta \leq 0.5$, the apparent activation energy can be expressed by

$$E_a = 163\theta \text{ kcal mole}^{-1} \quad (13)$$

The values of E_a for $\theta < 0.1$ are lower than any values observed for NiO powder or Ni/SiO₂, and E_a values for $\theta > 0.15$ are higher than activation energies observed for those systems. These results certainly imply a heterogeneity in the reactant nickel ions on MSA-3 support, and few of these nickel ions are like the nickel ions in NiO powders or on a silica support.

The intercepts for $1/T \rightarrow 0$ of the linear plots of $\ln \text{rate}$ vs. $1/T$ (not shown) are, by Eq. (12), equal to $\ln A(\theta)$. We find that the intercepts have a functional dependence on θ of the form (see Fig. 8)

$$\ln A(\theta) = -2 + 115\theta \quad (14)$$

when the rate is expressed in units of fraction nickel reacted per minute to form NiS. Of course $\ln A(\theta)$ must be linearly dependent

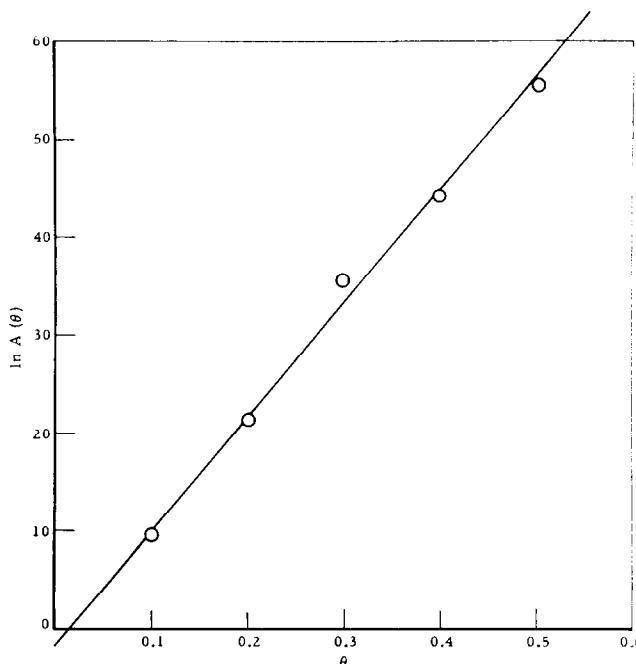


FIG. 8. Frequency factor as a function of θ for H₂S reaction with Ni/MSA-3; 500°C calcination.

or independent of θ if the overall kinetic expression is of the Elovich form. The rate of reaction of H₂S with this catalyst can then be expressed as

$$\ln(d\theta/dt) = -2 + 115\theta - (163/RT)\theta$$

Therefore,

$$-b = 115 - (163/RT)$$

$$\ln a = -2$$

and

$$d\theta/dt = \exp(-2) \exp[115 - (163/RT)]\theta \quad (15)$$

This equation has the form of

$$d\theta/dt = A_0 \exp[-\Delta F^\ddagger(\theta)/RT] \quad (16)$$

where $\Delta F^\ddagger(\theta)$ is the free energy of activation. It appears that at $\theta = 0$, the reaction has an activation energy and free energy of activation of nearly zero. The free energy of activation increases linearly with the extent of reaction; the linear increase in entropy somewhat compensates for the increase in activation energy.

These results are very different from either

NiO or Ni/SiO₂ and imply that the nickel ions on MSA-3 are quite unlike the Ni ions in these simpler systems. It seems unlikely that there is actually a zero activation energy at $\theta = 0$ for the reaction with Ni, since such low values have not been seen in other systems. Since the pure MSA-3 support does not chemisorb a significant amount of H₂S, this low apparent activation energy may be associated with initial, rapid chemisorption of H₂S on Ni ion sites.

Reduction with hydrogen (1, 2) and sulfiding with hydrogen sulfide of silica-alumina-supported nickel both are kinetically described by the Elovich equation. These results seem to be consistent with a picture (1) that the nickel oxide forms compounds with the silica-alumina support in several ways and that this mixture of oxides display a heterogeneity in reactivity toward hydrogen and hydrogen sulfide.

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