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Chemisorption of Sulfur on Metal Oxide Catalysts

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The chemisorption of sulfur on nickel oxide, nickel sulfide, and vanadium pentoxide, each of which was supported on high-area alumina, was investigated over the temperature range 600–750°C.

Adsorption of sulfur on nickel oxide was shown to be irreversible, since sulfur could only be desorbed in the form of SO_2. The kinetic and thermodynamic features of the adsorption suggest that sulfur is simultaneously chemisorbed and incorporated in the oxide lattice, gaseous SO_2 being formed via intermediate chemisorbed SO_2.

In contrast, the adsorption of sulfur on both nickel sulfide and vanadium pentoxide is reversible. The difference between the isosteric heats of adsorption on these two adsorbents infers that covalent-type surface bonds are formed in the case of adsorption on nickel sulfide and ionic-type bonding in the case of vanadium pentoxide. Estimation of the entropy losses on adsorption indicates that adsorbed sulfur is more mobile on nickel sulfide than it is on vanadium pentoxide.

The synthesis of carbon disulfide from hydrocarbons and sulfur is a process which has attracted considerable attention, especially in view of the increasing exploitation of the world's resources of natural gas. Previous investigators concerned with the overall kinetics of the catalyzed reaction between methane and sulfur (*1–6*) have not considered the possible influence which the major products of reaction may have on the rate of conversion to carbon disulfide. A more recent and detailed study in these laboratories (*7*) has revealed that when carbon disulfide is formed from methane and sulfur in the presence of a vanadium pentoxide catalyst the rate of formation of product is retarded by the addition of carbon disulfide and hydrogen sulfide to the reactant gases. The main features of the kinetic results may be explained in terms of either of two mechanisms. One of these assumes that the rate of CS_2 formation is controlled by surface chemical reaction and that other rate processes, embracing mass transfer, adsorption, and desorption of reactants and products are fast in comparison with the surface reaction. On the other hand, an alternative model is one in which the rate-controlling step is assumed to be the rate of desorption of CS_2. Both of these hypotheses lead to equations, in qualitative agreement with the experimental results, which describe the rate of formation of CS_2 as first order with respect to methane, less than first order with respect to sulfur, and retarded by the products H_2S and CS_2. An unequivocal decision concerning these alternative mechanisms could not be taken without studying the adsorption and desorption of the reactant and product gases on the catalyst. This paper deals with the adsorption of sulfur on catalysts active in CS_2 synthesis; a later paper will be concerned with the adsorption of H_2S and CS_2.

EXPERIMENTAL

Apparatus

A volumetric technique was adopted for studying both adsorption and desorption. Thus, a measured volume of the heated vapor was expanded into the silica reaction vessel containing the sample of

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adsorbent and the corresponding equilibrium pressure recorded by means of a calibrated Pirani gauge.

The whole of the apparatus, excepting the McLeod gauge and sulfur reservoir, had to be maintained at a temperature, ~250°C, sufficient to prevent condensation or adsorption of sulfur on the glass walls of the connecting tubing. Electrical heating tape was used for this purpose. Since it would be impracticable to utilize ordinary greased vacuum stopcocks under these conditions, electromagnetically operated high-temperature taps, similar to those designed by Sykes and White (*8*), were employed. Details of the construction of these is given elsewhere (*9, 10*). The rate at which gas leaked across a tap was determined by admitting various initial pressures of dry air to the upstream side of the tap and observing the rate of increase in pressure at the downstream side of the tap, using two additional McLeod gauges specially for this purpose. The rate of increase in pressure was a linear function of the time a tap was in the closed position and the ratio of the leak rate to the initial pressure was constant, $\sim 8 \times 10^{-4} \mathrm{min}^{-1}$. In general, the maximum time for which an adsorption experiment was followed was about 60 min. Since the amount of gas leaking across the tap in this time represents only about 5% of the original charge, the error introduced by use of such a tap does not exceed the error in pressure measurement.

Pressures were measured by means of the Pirani gauge which had previously been calibrated for sulfur vapor using as a standard the vapor pressure of sulfur at a fixed temperature. The vapor pressure data of Neumann (*11*) were used to calculate the proportions of S_6 and S_8 present in the sulfur vapor. Since, during calibration, various parts of the apparatus were usually at different temperatures, in addition to the usual correction for thermomolecular flow (*12*) allowance was also made for the variation in the molecular complexity of sulfur vapor with temperature. The method of applying such a correction has been formulated by Sykes and White (*8*). In the case of SO_2 a McLeod gauge was used as a standard for calibrating the Pirani gauge. Corrections for thermomolecular flow were also applied in this case.

The amount of sulfur remaining in the vapor phase after adsorption was determined chemically by oxidizing with excess oxygen at the prevailing temperature of 250°C, condensing out the SO_2 formed, and finally measuring the residual oxygen with the Pirani gauge. Less than 2% of the SO_2 is converted to SO_3 under these conditions (*9*). Mixtures of sulfur and SO_2 were analyzed by condensing out sulfur at 0°C and measuring the residual pressure of SO_2. These analytical procedures were reproducible and were checked with known mixtures of components.

The silica reaction vessel was heated by a nichrome-wound electrical furnace, the temperature of which was controlled to ±0.5°C by means of a platinum resistance thermometer in conjunction with an AEI-type PT3R temperature controller. Temperature was measured with a calibrated chromel-alumel thermocouple inserted in the thermal well of the reaction vessel.

Materials

Sulfur. Analytical grade sulfur was recrystallized from analytical grade CS_2. The first crystals were rejected and the subsequent crop dried *in vacuo* for one week. Gases. Spectroscopically pure oxygen from B.O.C. Ltd. (UK) was used without further purification. SO_2 from BDH Ltd (UK) was distilled *in vacuo* prior to storage and subsequent use.

Adsorbents. Messers. Peter Spence Ltd. (UK) supplied the 10% (w/w) NiO supported on ⅛-inch pellets of porous alumina and also the 10% (w/w) V_2O_5 supported on the same material. Nickel oxide was also used in a sulfided form by passing H_2S or sulfur vapor in argon carrier gas over the solid at 400°C for 8 hr before use. V_2O_5 can only be sulfided under extreme reducing conditions above 700°C (*13*) and it was therefore considered that this catalyst does not essentially alter its bulk composition when exposed to sulfur vapor.

Prior to any adsorption experiment 5.0 g of the adsorbent was outgassed at 750°C *in vacuo* for 36 hr and then cooled to the temperature chosen for the experiment. The monolayer capacity of each adsorbent was determined by the BET technique using N_2 as adsorbate at $-195°C$.

RESULTS AND DISCUSSION

A comparison was made of the adsorption and desorption characteristics of sulfur on the adsorbents nickel oxide, sulfided nickel oxide, and vanadium pentoxide, each of which was supported on high-area alumina. The effect of the support was not separately investigated. The results for each system bear similarities, but there are also important differences.

Nickel Oxide

When sulfur was admitted to the NiO adsorbent between 400° and 600°C, the first dose was adsorbed rapidly and completely in less than 1 min. Subsequent doses were adsorbed somewhat less rapidly and gave a residual gas pressure which did not change further. Figure 1 shows the way in which the gas pressure (expressed arbitrarily as the Pirani gauge reading) decreased with time. After each dose had reached a steady equilibrium pressure, the residual gas was analyzed and shown to be entirely SO_2. Sulfur could only be desorbed from the surface as gaseous SO_2. To ascertain the amount of SO_2 formed and sulfur remaining after any desired interval of time (from the time at which sulfur was admitted), gas samples were taken from the reaction vessel by isolating the dosing section and subsequently analyzing for sulfur and SO_2. Thus the course of the reaction could be followed as a function of time. Figure 2 shows how the reaction proceeded after 1.8×10^{-6} moles sulfur

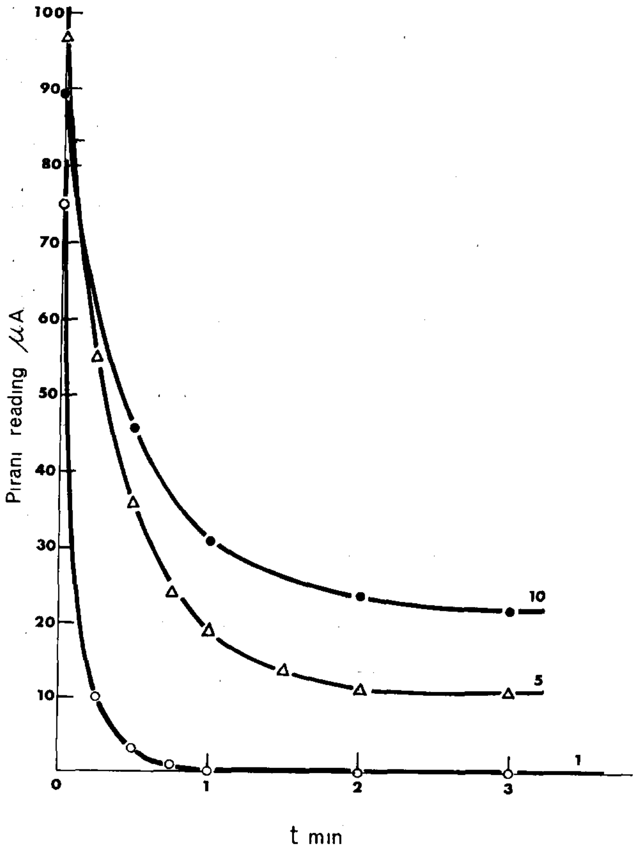

FIG. 1. Uptake of S_2 on supported NiO at 500°C. Figures on curves indicate dose number.

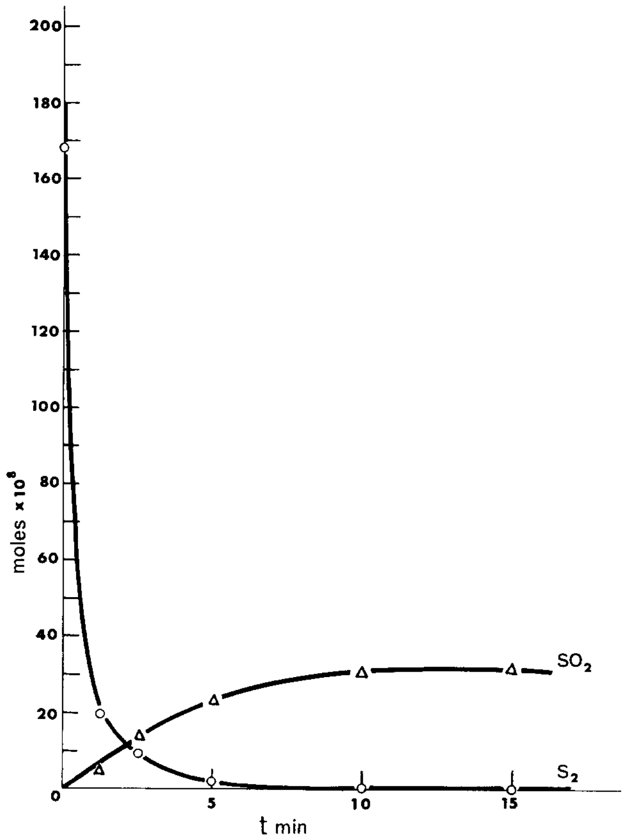

FIG. 2. Disappearance of S_2 and formation of SO_2 over supported NiO at 600°C.

(expressed arbitrarily as S_2) had been admitted to an outgassed sample of 5.0 g of NiO at a temperature of 600°C. Only small amounts of SO_2 appeared in the gas phase in the first 2 min after admitting a dose of sulfur to the catalyst, yet all of the sulfur had been consumed before 5 min had elapsed. Furthermore, the amount of SO_2 produced was always considerably smaller than the original dose of sulfur admitted to the adsorbent.

The delay in the appearance of gaseous SO_2 may be accounted for by its retention at the surface in the adsorbed state. It should therefore be possible to desorb SO_2 from the adsorbent after evacuation of the surface. Figure 3 shows that when the catalyst was evacuated for 1 min, SO_2 was desorbed from the surface at approximately the same rate as it was produced when sulfur was admitted to the fresh baked-out NiO surface. Figure 2, illustrating the formation of SO_2 and disappearance of S_2, shows that only 0.40×10^{-6} moles of SO_2 appeared in the gas phase after 15 min of contact with the NiO. In this time all of the gaseous S_2 had been consumed and the rate of formation of SO_2 had become immeasurably small. This means that 55% of the S_2 charge had not been oxidized to SO_2 and must therefore be considered to be present at the surface or within the subsurface layers of the oxide lattice. Published data (*14, 15*) indicate that reduction of the bulk oxide by sulfur is thermodynamically feasible, the process

$$2NiO + 1.5S_2(g) = 2NiS + SO_2(g) \qquad (1)$$

occurring with a standard free energy change of —84 kcal. Any reasonable interpretation of the changes observed should

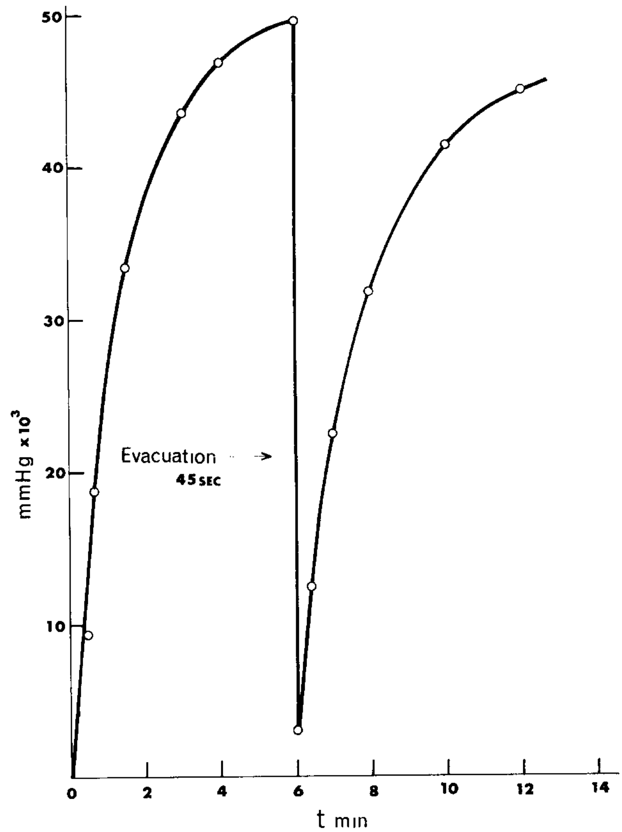

FIG. 3. Desorption of SO_2 from supported NiO at 600°C.

therefore include the possibility of sulfur incorporation within the oxide lattice.

The kinetics of sulfur adsorption was examined by drawing tangents to curves of pressure versus time obtained from adsorption experiments at 500°, 600°, and 700°C. Figure 4 shows a typical plot of the rate of disappearance of sulfur (expressed as moles S_2 $min^{-1}g^{-1}$) as a function of the number of moles of diatomic sulfur in the gas phase. Clearly, the order of reaction is greater than unity in the initial stages of reaction when the dose of sulfur is first admitted to the adsorbent. However, by the time the gas pressure has decreased by about 30% the rate of adsorption follows first order kinetics and is directly proportional to the pressure of diatomic sulfur. Such behavior has been noted before by Madley and Strickland-Constable (*16*), who studied the oxidation of charcoal by N_2O, and also by White (*9*), who reacted sulfur with charcoal. In both cases initial rates were greater than first order with respect to reactant, but after a relatively short time the reaction rate could be represented by first order kinetics. Madley and Strickland-Constable (*16*) explained their observed fall in first order rate constant with decrease in initial pressure by assuming that a labile surface oxide blocked some of the available adsorption sites. Their interpretation also implies that the initial reaction rate is numerically greater than that predicted from the first order kinetic rate equation obeyed during most of the reaction. A similar explanation is also possible in this case. In terms of the hypothesis of Madley and Strickland-Constable (*16*) the fraction of free surface available for adsorption changes rapidly in the initial stages of

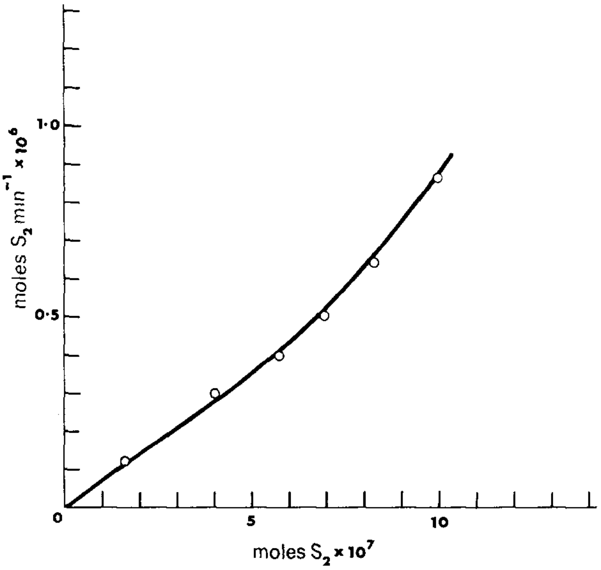

FIG. 4. Rate of adsorption of S_2 on supported NiO at 500°C as a function of amount of S_2 in gas phase.

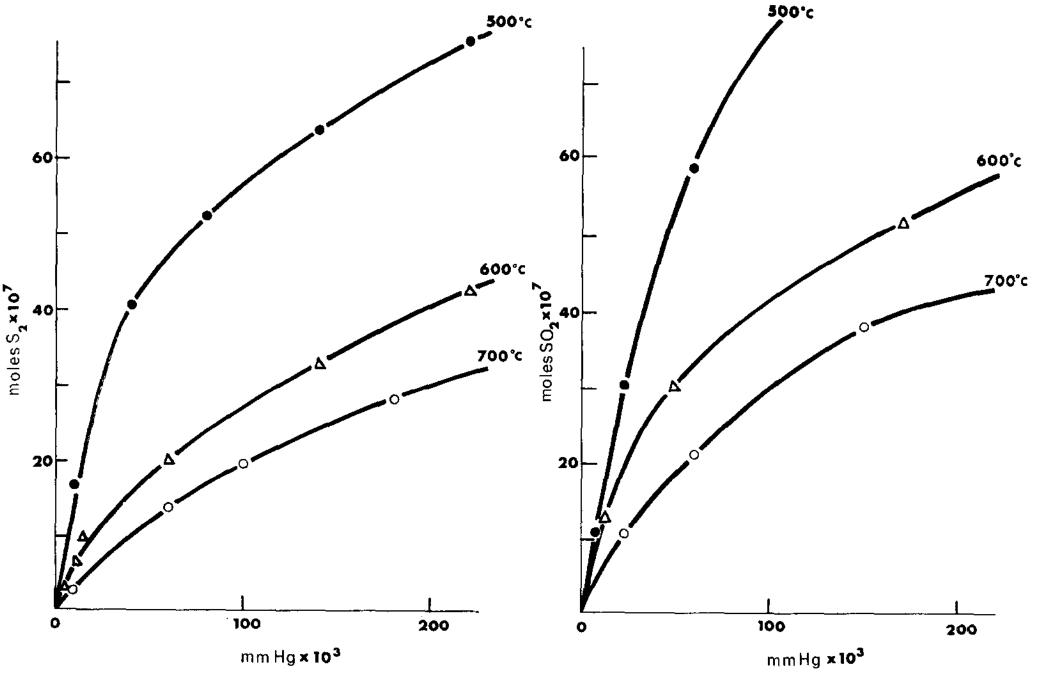

FIG. 5. *Left:* Isotherms for adsorption of S_2 on supported NiO. *Right:* Isotherms for adsorption of SO_2 on supported NiO.

reaction but later becomes sensibly constant. The values of the first order rate constants for the uptake of sulfur by NiO (derived from the linear portion of the rate curve) at 500°, 600°, and 700°C are 0.71, 1.08, and 1.15 min^{-1}, respectively. These values give an average activation energy of 3.6 kcal mole^{-1}. If the labile surface oxygen which oxidizes the sulfur to SO_2 originates from beneath the subsurface layers of the oxide lattice, then it is likely that the rate of oxidation will be limited by the diffusion of oxygen ions to the surface when the surface has been depleted in oxygen. It is difficult to assess which would be the rate-determining process in such an event but, in this work, the total charge of sulfur ($\sim 2 \times 10^{-6}$ moles) admitted to the fresh outgassed NiO surface was less than 0.001% of the BET monolayer capacity and it is likely that surface oxygen was in excess. The observed rates, therefore, probably represent the adsorption process.

By allowing each dose of sulfur to establish equilibrium with the oxide, it was possible to construct isotherms representing the total amount of sulfur adsorbed (expressed as g-atoms of S) as a function of the equilibrium pressure of SO_2 in the gas phase. The isotherms are portrayed in Fig. 5. (left). In addition, isotherms for the adsorption of SO_2 on the oxide were obtained and are shown in Fig. 5 (right). Since the isotherms representing the adsorption of SO_2 on NiO could be retraced on desorption, then it must be concluded that the SO_2-NiO system is reversible. The reversible adsorption of SO_2 on Cu_2O, a *p*-type semiconductor similar to NiO, has been explained (*17*) in terms of the formation of SO_3^{2-} surface ions and a similar interpretation is probably correct for the reversible adsorption of SO_2 on NiO. Comparison of the isotherms in Fig. 5 indicates that the amount of sulfur adsorbed for a given equilibrium pressure of SO_2 is higher when equilibrium is approached from gaseous S_2 than it is when approached from gaseous SO_2. This is consistent with the view that an additional amount of sulfur is adsorbed by virtue of incorporation of sulfur atoms within the oxide lattice.

From the above results it appears that although supported nickel oxide is a good adsorbent for sulfur, and hence may possibly be utilized as a catalyst for the methane–sulfur reaction, it would not produce CS_2 as a product until the metal oxide had first been converted to the sulfide by conditioning with sulfur. SO_2 produced during this conditioning would be quite likely to have a deleterious effect on the ultimate formation of CS_2. Some qualitative experiments in which a mixture of methane and sulfur was passed over a supported nickel oxide catalyst at 600°C showed that no CS_2 was formed until all traces of SO_2 in the product gases had disappeared.

Nickel Sulfide and Vanadium Pentoxide

The adsorption of sulfur on both supported nickel sulfide and vanadium pentoxide in the temperature range 600° to 750°C differs from the adsorption on baked-out nickel oxide. Initially the rate of uptake was comparatively fast and there was no residual pressure in the gas phase until several doses had been admitted. Further charges of sulfur were adsorbed more slowly. At the end of a series of admissions of sulfur vapor there was no SO_2 present in the gas phase either with nickel sulfide or with vanadium pentoxide. The reaction vessel was then evacuated for a period of about 45 sec (sufficient to remove all gaseous sulfur) and the desorption followed for about 10 min. Figure 6 shows the course of events following the evacuation of nickel sulfide and it is evident that sulfur may be removed from the surface in small amounts without too much difficulty.

On both adsorbents the kinetics of adsorption were strictly first order throughout the whole range of pressure studied. This marks a contrast with the adsorption of sulfur on NiO, the kinetics of which (Fig. 4) were greater than first order in the initial stages of adsorption. When inserted in an Arrhenius equation, the first order rate constant (Table 1) gives an average value of 2.6 kcal mole^{-1} for nickel

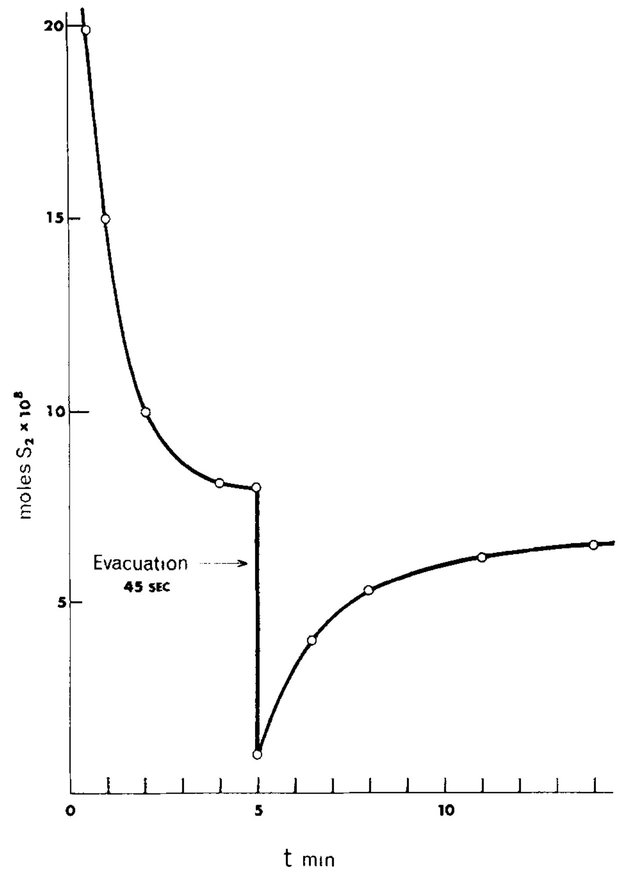

Fig. 6. Desorption of S_2 from supported NiS at 600°C.

sulfide and 15 kcal $mole^{-1}$ for nickel sulfide and 15 kcal $mole^{-1}$ for vanadium pentoxide.

TABLE 1

Kinetics of Adsorption of S_2 on Nickel Sulfide and Vanadium Pentoxide

T (°C)	Nickel sulfide k(min^{-1})	Vanadium pentoxide k(min^{-1})
600°	0.92	0.51
650°	1.11	0.82
700°	1.18	1.23

Adsorption isotherms for both adsorbents were obtained by noting the pressure p in the gas phase corresponding to definite amounts q of sulfur adsorbed. Sulfur could be desorbed easily from both adsorbents and the isotherms retracted on admitting further doses of sulfur. This indicates reversible adsorption and it is unlikely therefore that sulfur is incorporated in either the sulfide or oxide lattices. Figures 7 and 8 show, respectively, the isotherms obtained for nickel sulfide and vanadium pentoxide.

The maximum capacity q_m of the surface toward sulfur adsorption was found empirically by plotting, for each catalyst, p/q versus p. This is equivalent to assuming obedience to a nondissociative Langmuir adsorption isotherm. Good straight and almost parallel lines were obtained (*10*) for nickel sulfide at 600°, 650°, and 700°C and for V_2O_5 at 700° and 750°C. Values for q_m obtained in this way are 4.9×10^{-6} moles g^{-1} for nickel sulfide and 3.8×10^{-6} moles g^{-1} for vanadium pentoxide.

If we define θ, the fraction of active surface covered, as the ratio of the actual

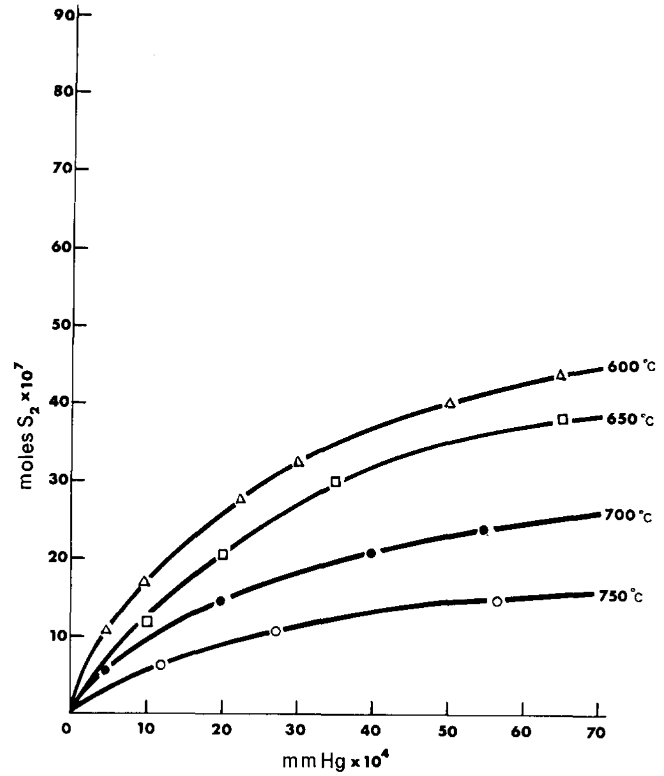

FIG. 7. Isotherms for adsorption of S_2 on supported NiS.

quantity of sulfur adsorbed to the maximum quantity adsorbed, then application of the Clausius-Clapeyron equation to the experimental isotherms gives values for isosteric heats of adsorption q_{ist} as a function of coverage. Table 2 shows that the isosteric heats of adsorption of sulfur on both adsorbents are essentially independent of coverage but are larger in the case of vanadium pentoxide than for nickel sulfide. It is not possible to explain this fact in terms of the catalyst crystal geometry. If sulfur dissociation occurs as the first step in a dissociative adsorption mechanism, then the net result of the process is the breakage of a sulfur–sulfur double bond and the formation of two new metal–sulfur bonds. However, if sulfur requires two sites for adsorption and forms a bridged structure with the metal atoms of the adsorbent, then the net result is the formation of two metal–sulfur bonds and the cleavage of only a π-bond between the sulfur atoms. Thus adsorption requiring the rupture of only the π-bond may lead to a higher heat of adsorption than adsorption involving complete dissociation. Considering NiS (which forms a hexagonal three-dimensional crystal habit) the distance between neighboring nickel atoms in the principle {0001}, {1100}, {0110}, and {1010} planes is 2.5 Å (*18*). Too great a strain would be imposed on the S–S distance (2.1 Å) to envisage adsorption in any form other than at single sites, either as discrete S atoms or S_2 molecules. However, militating against the possibility of

TABLE 2

ISOSTERIC HEATS OF ADSORPTION

NiS catalyst		V_2O_5 catalyst	
θ	q_{ist} (kcal mole^{-1})	θ	q_{ist} (kcal/mole)
0.15	13.0	0.02	35.0
0.30	8.9	0.18	34.0
0.45	9.9	0.27	33.5
0.52	9.8	0.32	34.9

an S_2 molecule being adsorbed on V_2O_5 in the form of a bridge-type structure is the large distance between vanadium atoms (>3.0 Å). A more plausible explanation of difference between the heats of adsorption is that the bond formed with sulfur at the surface of NiS is possibly covalent or may even involve weak dispersive forces (though the latter possibility is remote since the adsorption temperature is about 200°C above the normal boiling point of sulfur), whereas at the surface of V_2O_5 the bond may be more ionic. The type of chemical bond formed during chemisorption will certainly depend on the nature of the interatomic forces in the bulk adsorbent itself. In both NiS and Ni_3S_2 the bonding tends to be covalent in character and so an atom of nickel situated at the surface of the solid is quite likely to form a covalent bond with chemisorbed sulfur. V_2O_5 on the other hand, has distinct *n*-type semiconductor properties, its crystal lattice being deficient in anions. Ionic bonding of sulfur to vanadium cations is thus possible and in terms of the electronic theory of chemisorption the quantity of adsorbate taken up at the surface should be small since one would envisage a depletive type of chemisorption in these circumstances. The maximum amount of sulfur adsorbed at the supported V_2O_5 catalyst ($\sim 10^{-6}$ moles) is about 0.05% of the total BET capacity. In terms of the vanadium ions utilized as adsorption sites this amounts to only 1% of the total number of cations exposed at the surface. The fact that NiS adsorbs no more sulfur than V_2O_5 need not necessarily conflict with the postulate that adsorption on nickel sulfide involves covalent bonding. Since a heat of adsorption of only 10 kcal/mole and an activation energy for adsorption of about 2-3 kcal/mole is involved, then the activation energy for desorption will be no greater than 12–13 kcal/mole. Desorption will therefore not be difficult and at temperatures of 600–700°C the amount of gas adsorbed would be likely to be small for adsorption involving weak bonding.

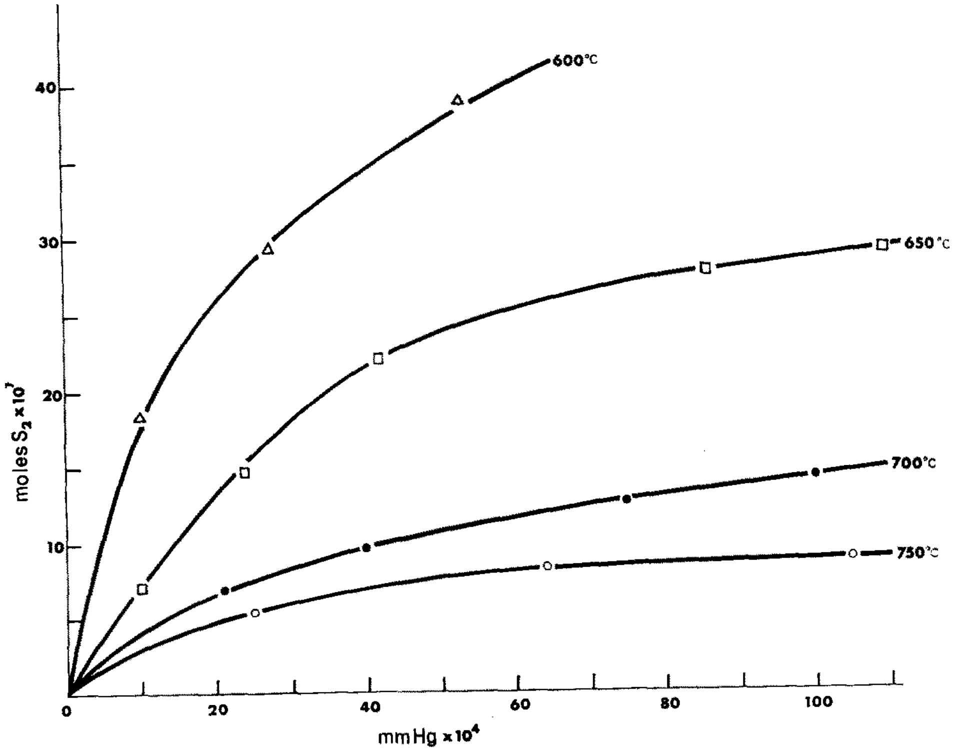

FIG. 8. Isotherms for adsorption of S_2 on supported V_2O_5.

The loss in entropy on adsorption may be estimated from the isosteric heat of adsorption q_{ist} and the equilibrium gas pressure at half-coverage (*19*). Values of q_{ist} are given in Table 2 while p (expressed in atmospheres) may be obtained from the isotherms portrayed in Figs. 7 and 8. At 600°C the experimental entropy loss turns out to be 31.2 e.u. when sulfur is adsorbed on NiS and 55.5 e.u. for adsorption on V_2O_5. The value of 55.5 e.u. for the loss in entropy on adsorption of sulfur at V_2O_5 is consistent with values calculated on the basis of the loss of three translational and one rotational degrees of freedom. The entropy per mole of the gas at $\theta = \frac{1}{2}$ may be calculated from the Sackur-Tetrode equation (*19*), while the configurational entropy for $\theta = \frac{1}{2}$ can also be computed from the accepted expression relating the configurational entropy to the degree of coverage. Allowing 7 e.u. for the loss of one degree of freedom of rotation in the S_2 molecule, then, at 600°C and for $\theta = \frac{1}{2}$, the calculated entropy loss is 59.6 e.u., which concurs closely with the experimental value for adsorption on V_2O_5. One might therefore tentatively suggest that when sulfur is adsorbed reversibly on nickel sulfide the adatoms have a greater degree of mobility than when adsorbed reversibly on vanadium pentoxide.

Comparing nickel sulfide and vanadium pentoxide as catalysts for the reaction between methane and sulfur it may be concluded that the reversible adsorption of sulfur on both catalysts augurs well for the requisite that sulfur should be transferred from reactant to product with the minimum amount of energy. The mobility of absorbed sulfur may be expected to enhance the ability of NiS to transfer sulfur between reactant and product. On the other hand the more localized adsorption of sulfur on V_2O_5 need not necessarily be a disadvantage in forming CS_2 for it still offers a route with a lower activation energy than the homogeneous gas-phase reaction (*7*).

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