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Poisoning of Ni/SiO_2 Catalysts with H_2S: Chemisorption of H_2, CO, C_6H_6, and C_2H_2 Studied by Magnetic Methods

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The poisoning of Ni/SiO_2 catalysts by H_2S adsorption and the subsequent chemisorption of CO, H_2, C_2H_2, and C_6H_6, which are involved in reactions on Ni where the presence of sulfur is known to change activity and selectivity, were studied by magnetic methods. When H_2S is introduced by small successive increments at 20°C, the surface nickel layer is first covered with H_2S (four or five Ni atoms involved in the bond, suggesting dissociation), and then deeper layers of the metal are attacked. The poisoning probably occurs with a two-dimensional phase growth from nuclei. H_2 and CO subsequent chemisorptions are specific to the free nickel surface, and have the same characteristics as on pure Ni. This result establishes the validity of the method of H_2 adsorption to estimate the unperturbed nickel surface area. In contrast, unsaturated hydrocarbons (C_2H_2, C_6H_6) are adsorbed on both free and poisoned nickel. Hydrogen from adsorbed H_2S probably interacts with the hydrocarbon molecule to give a hydrogenated adspecies. This behavior is different from that observed when the Ni surface is precovered with H from molecular hydrogen; in that case, the hydrocarbon molecules subsequently adsorbed do not interact with H. Moreover, H_2S seems to inhibit the cracking of hydrocarbons on nickel.

INTRODUCTION

The presence of sulfur, combined or not, is known to have a great influence on the activity and selectivity of Ni catalysts. For example, an enhancement of the selectivity for heavier hydrocarbons in the CO + H_2 reaction and a decrease of the overall activity were observed when small quantities of H_2S were introduced into the catalytic system (*1–3*). Increases of the selectivities for partial hydrogenation of acetylene to ethylene, of polyolefins or cyclic polyenes to corresponding monoolefins, and of nitrobenzene to aniline were also reported (*4–8*).

Interaction between H_2S and nickel has been studied by various techniques, including magnetism (*9, 10*), volumetric methods and gas analysis, and H_2–D_2 exchange (*11–13*). The chemisorption was not detected by infrared spectroscopy (*14*). These studies point to the fact that H_2S is dissociatively adsorbed with a more or less pronounced incorporation of sulfur and H_2 evolution. However, the behavior of H_2S with Ni is complicated, and a number of points remain obscure. Moreover, there are very few reports on chemisorption of gases on partially poisoned nickel powders (*15*).

In this paper we report results on the poisoning of Ni catalysts by H_2S and some observations concerning the subsequent chemisorption of CO, H_2, C_2H_2, and C_6H_6 which are involved in the above-mentioned reactions, with the help of magnetic

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methods which have been shown capable of shedding some light on the nature of the gas–nickel bond (*16*).

EXPERIMENTAL METHODS

Catalyst preparation. Ni/SiO_2 catalysts were obtained by adding aerosil silica (200 m^2/g) into a solution of nickel nitrate hexamine (*17*). The solution was filtered. The adsorbed complex was decomposed by evaporating ammonia, and $Ni(OH)_2$ was precipitated on the support. The solid was washed and dried. The powder was agglomerated under 2 tons/cm^2, and a pellet ca. 0.15 g in weight, 0.5 cm in diameter, and 1.0 cm in length was thus obtained. The reduction was performed for 4 hr in a H_2 stream (2 liters/hr) at 650°C. After reduction, the sample was outgassed at 450°C for 2 hr at 10^{-6} Torr. Adsorptions were performed in a volumetric apparatus equipped with a Texas Instruments pressure gauge. The nickel content was 12 wt%, and the degree of reduction calculated from saturation magnetization (*18*) was higher than 95%. The average nickel particle diameter calculated by low- and high-field magnetic methods (*13*) was found to be 5.3 nm. This value agrees with that calculated from H_2 chemisorption at room temperature at 100 Torr (ca. 33 ml [NTP]/g of Ni) assuming a nearly complete coverage in these conditions and (111) and (100) planes on the Ni surface.

Magnetic methods. After chemical treatments (outgassing, adsorption), the sample holder containing catalyst was introduced into an electromagnet providing moderate fields up to 21 kOe, and Ni magnetization (M) was measured at 300, 77, and 4.2 K using the "axial" Weiss extraction method (*19*).

Variations of saturation magnetization (M_s) due to gas adsorption were calculated by plotting ΔM (variation of magnetization) against $1/H$ and extrapolating to $1/H = 0$ (H, field strength). For measurements performed at 300 and 77 K, ΔM_s was multiplied by k, a coefficient nearly equal to 1 (1.055 and 1.01 at 300 and 77 K, respectively) to account for the variations of M_s with temperature. Magnetic "bond numbers," n, were calculated, in some cases, assuming that nickel atoms in interaction with adsorbed molecules cease to participate in the collective ferromagnetism of Ni (*16*). Values of n can be calculated by dividing α, the change in saturation magnetization per adsorbed molecule, by the magnetic moment of Ni atoms expressed in the same units as α (e.g., in Bohr magnetons, B.M.); in that case, $n = \alpha$ [B.M./molecule]/0.6).

In previous papers (*10–22*), it was shown that the decrease of saturation magnetization per adsorbed molecule was nearly independent of the temperature of measurement (300, 77, and 4.2 K) for this type of catalyst (prepared in almost identical conditions and having the same particle size). This is the reason why most of the magnetic measurements reported here were performed at room temperature.

EXPERIMENTAL RESULTS

Adsorption of H_2S

Small amounts of H_2S were successively adsorbed at room temperature on the Ni/SiO_2 catalyst. Addition of H_2S was stopped when the pressure of the gas phase (which was shown to consist of H_2) was ca. 3 Torr. In those conditions the adsorbed volume is $V_0 = 47$ ml (NTP)/g of Ni, and the ratio S_{ads}/H_{ads} is nearly equal to 1.9. The effect of H_2S adsorption on magnetization is shown in Fig. 1, where it can be compared to that due to H_2 adsorption. It can be seen that the ΔM_s vs V_{H_2S} curve can be best described by two linear parts: The first of which yields an α value of 2.5 B.M. per adsorbed molecule while the second part yields an

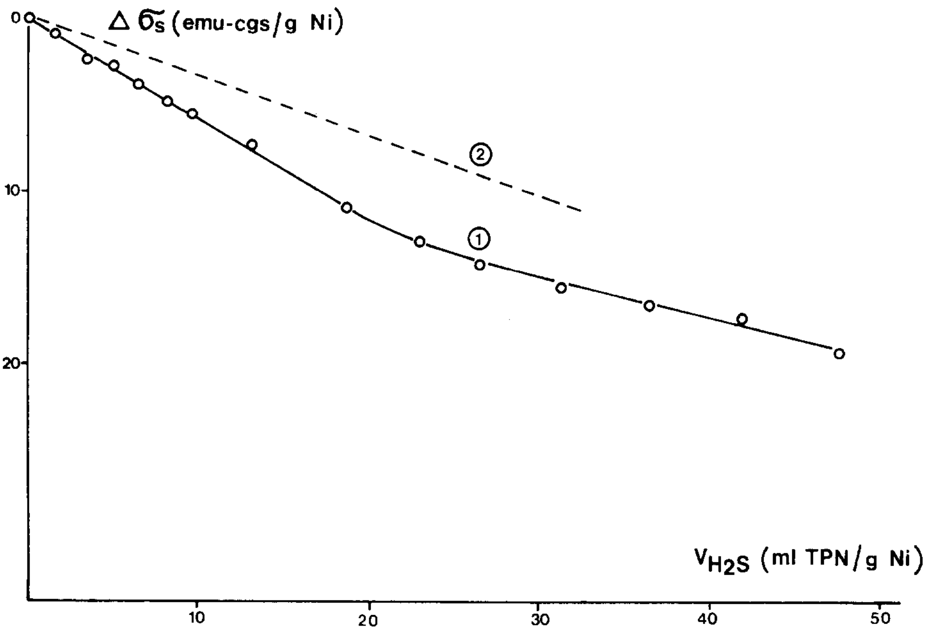


FIG. 1. Saturation magnetization change as a function of adsorbed volume at room temperature for H_2S, curve 1, and for H_2, curve 2 [see ref. (*17*) and Dalmon, J. A., Martin, G. A., and Imelik, B., *Colloq. Int. Cent. Nat. Rech. Sci.* **201**, 593 (1971)].

α value of 1.0. B.M. per molecule, suggesting a change of the nature of adsorbed species.

When the introduced amounts are very large, they lead to higher values for α (typical values are 3–3.3 B.M./molecule) which could be attributed to local heating due to the heat of adsorption.

The loss of magnetization caused by H_2S adsorption in the first part of the isotherm shown in Fig. 1 is nearly equal to that produced by H_2 adsorption at complete coverage. Assuming that H_2 is capable of destroying the ferromagnetism of each surface nickel atom (*16*), then it is reasonable to suppose that the first part of the H_2S isotherm corresponds to the almost complete coverage of the first nickel layer. The same type of reasoning may suggest that the second part of the H_2S isotherm involves more than the surface layer of nickel atoms, in agreement with conclusions of Den Besten and Selwood (*9, 16*). It means that after saturation of the surface nickel layer ($\alpha = 2.5$ B.M./molecule), H_2S is able to attack the nickel particle in depth ($\alpha = 1$ B.M./molecule).

Samples covered with H_2S at room temperature were heated stepwise up to 450°C; after each thermal treatment, catalysts were cooled down to room temperature, and magnetic measurements were performed. The variations of α thus observed against the holding temperature t are shown in Fig. 2, where it can be seen that α does not vary to a great extent as t increases.

Another set of experiments was performed in the following way: Samples having adsorbed H_2S were submitted to pumping (10^{-6} Torr) for 20 min at successively increasing temperatures, then cooled down to room temperature for magnetic measurements. The only gas detected was H_2. The volume evolved was calculated from the pressure increase in the rough vacuum tank of the pumping

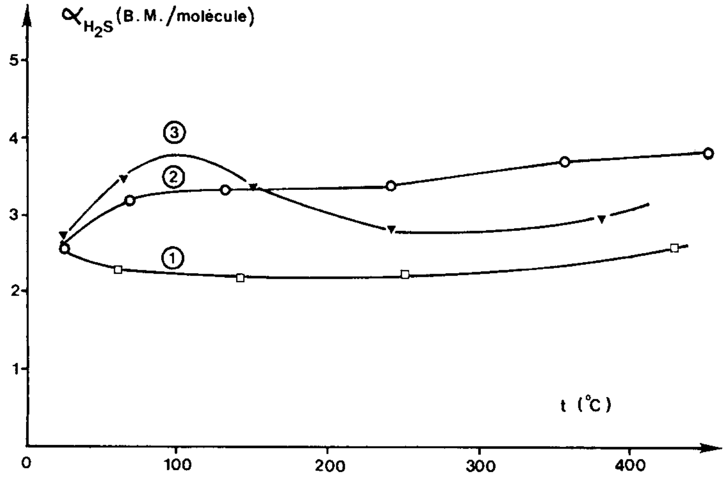


FIG. 2. α as a function of the holding temperature for H_2S. Curves 1, 2, and 3 correspond, respectively, to V_{H_2S} = 4.5, 9, and 18 ml [NTP]/g of Ni.

system (*23*). The volumes thus measured are shown as a function of the treatment temperatures in Fig. 3. It can be seen that the ease of H_2 evolution decreases as the poisoning increases: At 300°C, the extent of H_2 evolution is nearly equal to unity on unpoisoned catalysts; it is equal to 0.85 and 0.6 for two samples having adsorbed, respectively, 6.6 and 17 ml [NTP]/g of Ni of H_2S. This observation is in good accordance with the results obtained by Den Besten and Selwood (*9*) by thermodesorption and Saleh *et al.* (*12*) by H_2–D_2 exchange. It suggests that the system Ni–adsorbed H_2S can give up its hydrogen relatively easily (however, less easily than H_2 adsorbed on pure nickel). This hydrogen may react with adsorbed

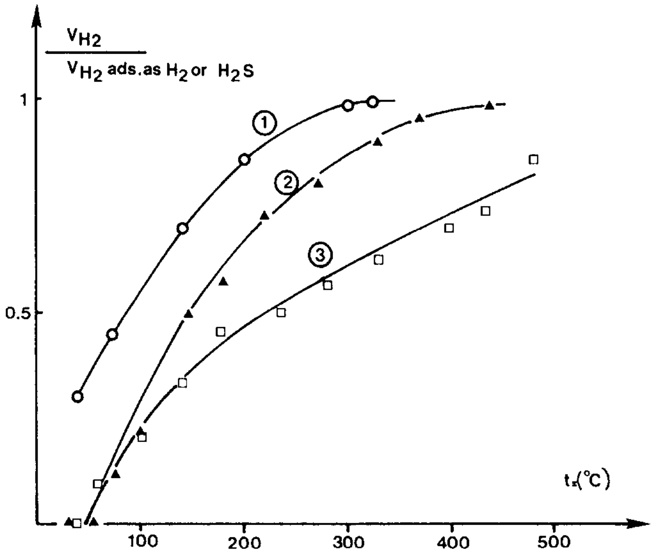


FIG. 3. Amount of desorbed $H_2(V_{H_2})$ from Ni/SiO_2 with various H_2S coverages as a function of the temperature, *t*. Curve 1, Ni covered with H_2; curve 2, Ni covered with 6.5 ml [NTP]/g of Ni; curve 3, Ni covered with 17 ml [NTP]/g of Ni.

molecules in a different way than H_2 over pure Ni.

When H_2 is evolved upon heating under vacuum, does sulfur remain in the same chemical state? In Fig. 4 we have plotted α_S against the treatment temperature. For temperatures at which H_2 evolution was nearly complete α_S was calculated directly from magnetic measurements. At lower temperatures, it was assumed that the contribution due to the remaining H_2 was equal to that observed for H_2 on pure nickel (α_{H_2} = 1.4 B.M./molecule). From the curves of Fig. 4, it can be observed that α_S does not remain constant, indicating some chemical transformation of sulfur. For low degree of poisoning, large values for α_S are observed: A maximum of 4 is attained at 120°C, and at higher temperatures α_S tends to 3 (in that case H_2 is completely evolved). For samples containing more H_2S, α_S is smaller.

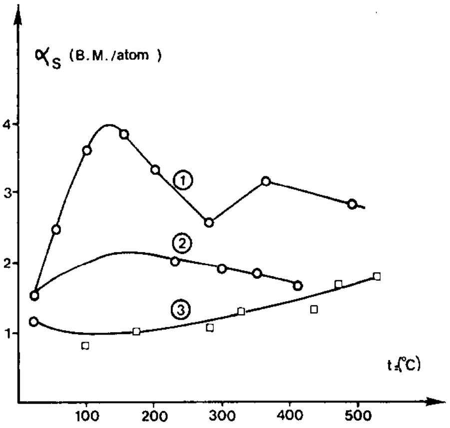


FIG. 4. α for sulfur as a function of the temperature of treatment (sample submitted to heat treatment with H_2 pumping) for various degrees of coverage in H_2S. Curve 1, V_{H_2S} = 4.5 ml, [NTP]/g of Ni; curve 2, V_{H_2S} = 8 ml [NTP]/g of Ni; curve 3, V_{H_2S} = 17 ml [NTP]/g of Ni.

It is of interest to compare the results of Fig. 4 with those of Fig. 2. It can be seen that chemical transformations of the system Ni–S are much more pronounced when H_2 is evolved by pumping, indicating that the presence of hydrogen stabilizes the surface sulfur.

Figure 5 shows the magnetic isotherm of readsorption of H_2 on a sample treated with H_2S (V_{H_2S} = 6.4 ml [NTP]/g of Ni)

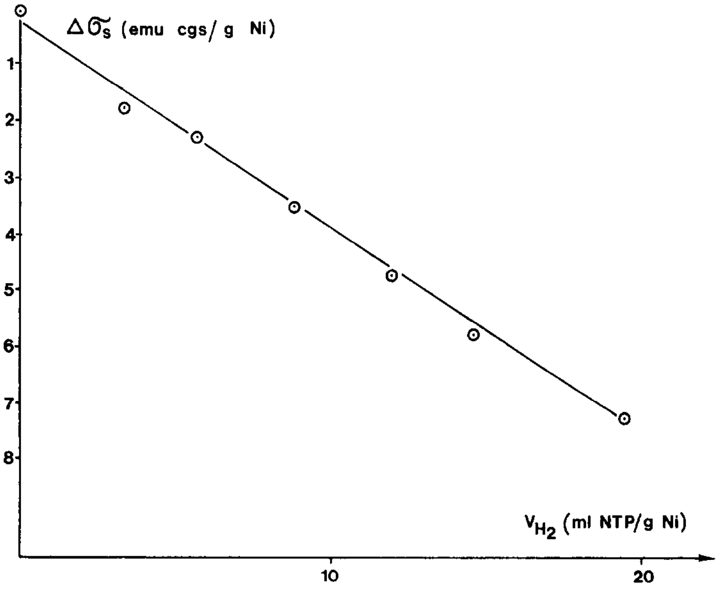


FIG. 5. Saturation magnetization change of a Ni catalyst treated with H_2S at 20°C and outgassed at 450°C as a function of the amount of adsorbed H_2 at room temperature.

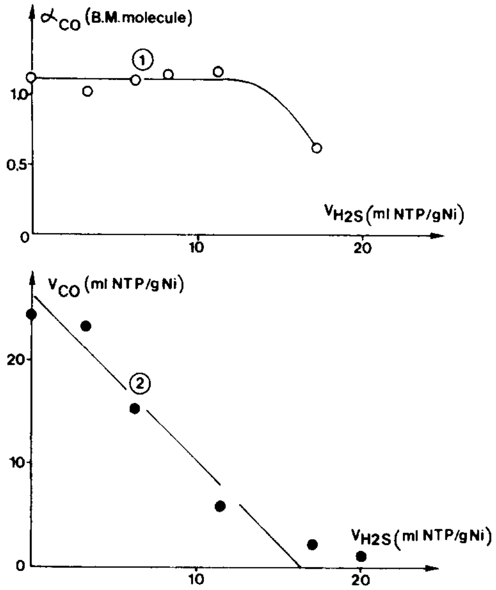


FIG. 7. Volume of adsorbed CO at room temperature and 1 Torr and α_{CO} vs the volume of preadsorbed H_2S.

and completely desorbed at 450°C. The value of α_{H_2} derived from it (1.45 B.M./molecule) is very near to that observed for H_2 on pure nickel. This means that H_2 readsorbed is quite free from perturbation of S already in the sample. The volume of readsorbed hydrogen was found to be 19 ml [NTP]/g of Ni at 1 Torr which was significantly smaller than the corresponding value for a pure Ni surface (28 ml [NTP]/g of Ni at 1 Torr), showing that a part of the surface perturbed by remaining S cannot be used for H_2 chemisorption, the other part showing the same behavior as unperturbed Ni.

Adsorption of H_2 on Poisoned Catalysts

From Fig. 6 one can see that the amount of H_2 adsorbed at room temperature at ca. 5 Torr decreases linearly with the amount of preadsorbed H_2S. The curve thus obtained intercepts the x-axis at

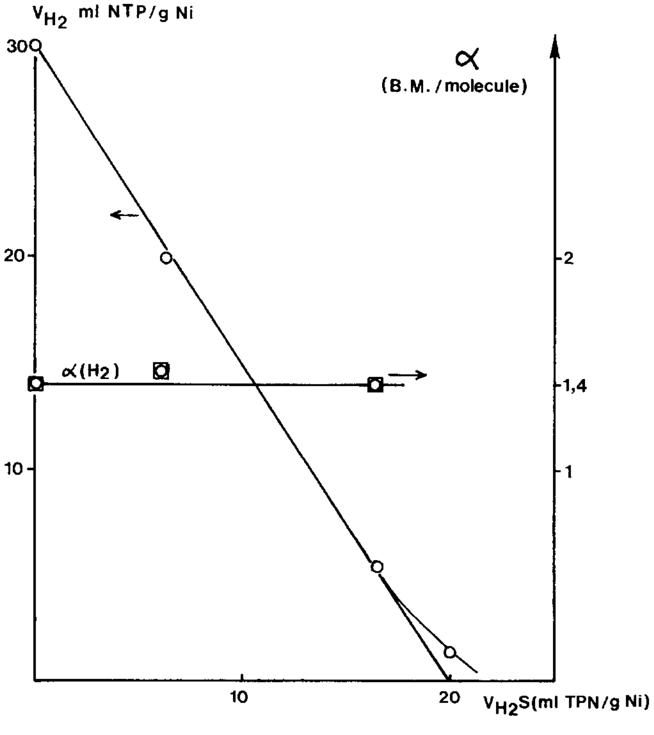


FIG. 6. Volume of adsorbed H_2 at room temperature and ca. 5 Torr and α_{H_2} vs the volume of preadsorbed H_2S.

V_{H_2S} = 20 ml [NTP]/g of Ni. This value is nearly equal to that which was supposed to correspond to the completion of the surface nickel in the previous section. H_2 is not chemisorbed on the part of the surface which is covered with H_2S; chemisorption occurs only on the nickel surface which remains free. The independence of α_{H_2} with the volume of preadsorbed H_2S suggests that the free nickel surface is not strongly perturbed by the part of Ni on which H_2S is adsorbed.

Adsorption of CO

Results concerning the CO adsorption are shown in Fig. 7 (they were partly reported and discussed in a preliminary note (*24*)]; in many respects they are similar to those observed for H_2. The amount of adsorbed CO at 1 Torr at room temperature decreases linearly as the volume of preadsorbed H_2S increases. It vanishes at ca. 16.5 ml [NTP]/g of Ni of H_2S, a value nearly equal to that observed for H_2. CO, like H_2, is only ad-

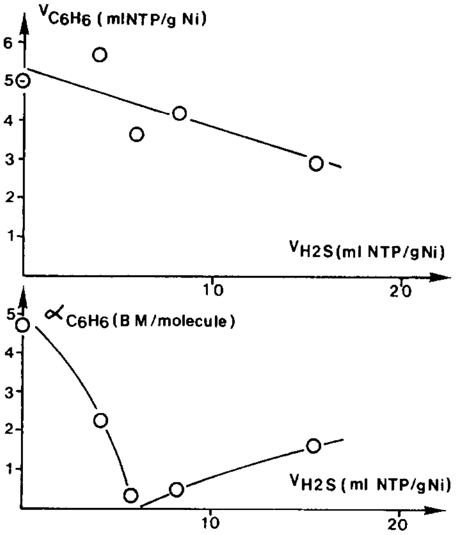


FIG. 8. Volume of irreversibly adsorbed benzene and $\alpha_{C_6H_6}$ at room temperature as a function of the volume of preadsorbed H_2S.

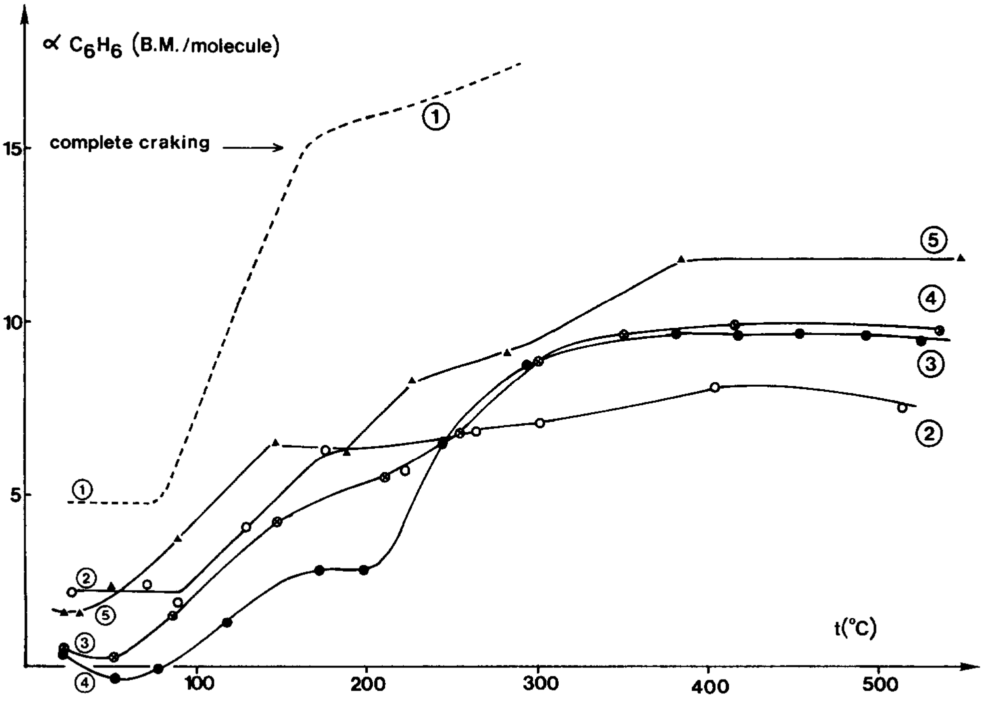


FIG. 9. α for irreversibly adsorbed benzene at room temperature as a function of the holding temperature. Curves 1, 2, 3, 4, and 5 refer to catalyst precovered with 0, 4.1, 5.9, 8.2, and 15.5 ml [NTP]/g of Ni of H_2S, respectively.

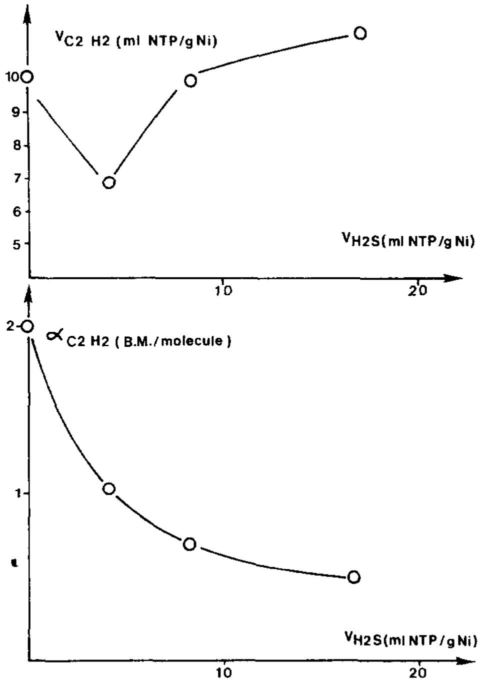


FIG. 10. Volume of adsorbed acetylene and $\alpha_{C_2H_2}$ as a function of the volume of preadsorbed H_2S.

sorbed on the nickel surface which is free. α_{CO} and the corresponding bond number n_{CO}, directly proportional to α_{CO}, remain constant up to $V_{H_2S} = 14$ ml [NTP]/g of Ni. As n_{CO} has been shown to be directly correlated to x, the ratio of linear to bridged species concentrations (*18–21*), it can be concluded that x, which has been shown to be very sensitive to the Ni environment (*18–21*), remains unchanged as the amount of preadsorbed H_2S increases up to 14 ml.

Adsorption of C_6H_6

After poisoning by H_2S, C_6H_6 was admitted at room temperature at ca. 1 Torr. After equilibrium, reversibly adsorbed benzene was removed in a liquid nitrogen trap (*25*). As shown in Fig. 8, the behavior of C_6H_6 is quite different from that of CO and H_2 in the sense that it can be adsorbed on the catalyst when the surface is nearly completely covered with H_2S. For smaller coverages of H_2S, C_6H_6 is probably adsorbed both on free and poisoned surface.

The variation of $\alpha_{C_6H_6}$ with the volume of preadsorbed H_2S reveals a rather complex situation: As V_{H_2S} increases, $\alpha_{C_6H_6}$ decreases down to 0 at $V_{H_2S} = 6$ ml [NTP]/g of Ni, then increases up to ca. $\alpha = 2$ B.M./molecule.

After adsorption, the catalyst was heated stepwise up to 500°C; after this thermal treatment the system was cooled to room temperature and a magnetic measurement was performed (Fig. 9). At low poisoning ($V_{H_2S} = 4.1$ ml [NTP]/g of Ni), the thermal variations of $\alpha_{C_6H_6}$ follow narrowly those corresponding to adsorption on pure nickel. For higher degree of coverage in H_2S, $\alpha_{C_6H_6}$ drops to negative values, then increases again as the temperature increases. Finally, when the volume of preadsorbed H_2S is large enough, $\alpha_{C_6H_6}$ again has a positive value. In all cases, it can

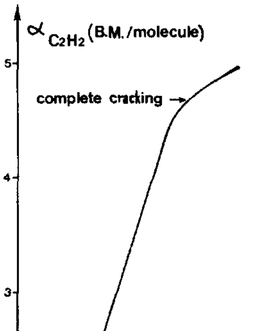


FIG. 11. α for C_2H_2 as a function of t, the holding temperature. Curves 1, 2, 3, and 4 refer to catalyst precovered with 0, 4.1, 8.2, and 17 ml [NTP]/g of Ni, respectively.

be seen that $\alpha_{C_6H_6}$ relative to adsorption on a precovered with H_2S catalyst is smaller than $\alpha_{C_6H_6}$ on pure nickel. Particularly the $\alpha_{C_6H_6}$ value of 15 B.M./molecule which has been shown to correspond to the complete cracking of the molecule on pure nickel (*21*) is never attained, which suggests an inhibiting effect of H_2S on the cracking properties of Ni.

Adsorption of Acetylene

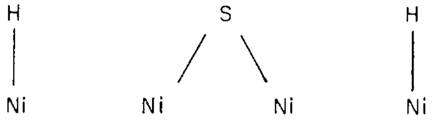
The change in saturation magnetization upon adsorption of C_2H_2 at room temperature for various coverages of H_2S is not linear, indicating some changes in the nature of the chemisorptive bond with the degree of coverage. The variations of $\alpha_{C_2H_2}$ (average value at complete C_2H_2 coverage) and of the C_2H_2 uptake (at room temperature and 1 Torr) with the volume of preadsorbed H_2S are shown in Fig. 10. Like benzene, acetylene is adsorbed when the nickel surface is completely covered with H_2S, indicating a combination with the system Ni, H_2S. The corresponding α value is ca. 0.5 B.M./molecule.

After C_2H_2 adsorption, the catalysts were heated as in the previous section. Results are reported in Fig. 11, where it can be seen that α is nearly temperature-independent and in any case much smaller than the α values corresponding to adsorption on pure nickel (*21*). α values corresponding to complete cracking (α = 4.8 B.M./molecule) are never attained once the nickel surface is precovered with H_2S. These observations are very similar to those previously reported for C_6H_6.

DISCUSSION

Nature of Chemical States of H_2S

For H_2S, two states were observed: The first one which corresponds to the initial part of the curve in Fig. 1 has an α value of 2.5 B.M./molecule and a bond number of 4.1. These values are in reasonable agreement with those previously reported for a thermostable state (*21*) observed at temperatures slightly lower on a nearly similar catalyst (α = 2.95 B.M./molecule, n = 4.8). They are also in good agreement with those measured by Den Besten and Selwood (*9*) on a Ni/kieselguhr catalyst by low-field techniques (n = 4). These authors suggest that H_2S could be adsorbed dissociatively according to the following model:



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This model is in agreement with the fact that H_2 was detected in the free space over the sample and that the only gas evolved upon thermal treatment was molecular H_2. However, our results show that when H_2 is evolved upon heating, S does not remain in the same chemical state as when hydrogen remains on the surface, indicating some synergetic effect between H, S, and Ni, which tends to stabilize the surface molecule. This is the reason why we suggest writing this species as (Ni, H_2S), without speculating how S, H, and Ni are bonded together.

The second chemical state for H_2S is observed at high degree of coverage. The corresponding α value is much smaller (α = 1 B.M./molecule). This result is also in good agreement with that reported in (*9*). As noted earlier, it results from an attack by H_2S on the second layer with a possible chemical rearrangement of the first one.

Chemical State of S in (on) Ni

Another point of interest is the chemical state of S which remains in the catalyst after H_2 evolution. α_S values as high as 3 or 4 B.M./atom are observed for small S contents; when the S amount in the catalyst increases, α_S decreases.

Two bulk sulfides are well-known, namely, NiS and Ni_3S_2; their formation would yield α values too small (0.6 and 0.9 B.M./atom, respectively, assuming that 1 and 1.5 Ni atoms per S atom cease to participate in the collective ferromagnetism and that the magnetic moment in ferromagnetic Ni is 0.6 B.M.) to account for the observed values, and hence they can be ruled out.

The high magnetic effect of S is best interpreted by assuming that the outer electrons of S atoms are given up to the d band of the host metal. A similar explanation was already proposed (*26*) to account for high α values observed in the case of the C–Ni system. α can be as high as the number of outer electrons, and in the case of the S atom it can reach 6. The decrease of α_S observed when the sulfur amount increases could be due to the formation of S clusters which are expected to give smaller magnetic effects owing to the fact that some electrons are used for the S–S bond.

The position of the sulfur atoms (at the surface or in the bulk) deserves some discussion. Sulfur solubility into bulk nickel is known to be small (0.005%), so this is a first indication that S is located on the surface instead. However, the solubility could vary with the degree of dispersion of the host metal. A more convincing argument for S being present on the surface is that the volume of adsorbed hydrogen is smaller on nickel containing sulfur (Fig. 5).

This study helps us to understand the state of sulfur in a procedure described by Takeuchi *et al.* (*5, 6*) and commonly used to obtain Ni–S catalysts. H_2S is introduced at 300°C, and the evolved H_2 is evacuated at the same temperature. This procedure is very similar to one which is used here, where the surface sample is saturated at room temperature (V_{H_2S} = 20 ml [NTP]/g of Ni) and then heated under vacuum. If the temperature of treatment is 300°C, it can be seen from Fig. 3 that H_2 is not completely evolved (more than 40% remains in the system). It may be concluded that the catalysts obtained by this procedure are probably complex: S is present on the surface as a mixture of (Ni, H_2S) and of sulfur more or less clustered, combined with Ni.

Mechanism of Poisoning

When H_2S is introduced in successive small quantities at room temperature, it has been shown that the surface nickel layer is first covered with H_2S to give the adspecies (Ni, H_2S) and that the remaining free surface shows the same behavior toward CO and H_2 adsorption as a pure Ni surface. This suggests that a part of the surface is completely poisoned with H_2S, the other part being apparently quite free from any perturbation. Then, all catalytic reactions rate taking place on nickel are expected to decrease in a parallel way as the poisoning by H_2S increases. As far as we know, there are no experimental data on Ni catalysts, but Maurel *et al.* (*27*) have reported that H_2S acts as a "nonselective" poison for Pt catalysts.

The origin of this phenomenon may be found by taking into account the results of Richardson (*10*) who showed that poisoning of Ni catalysts by H_2S, H_2 mixtures occurs at the front of the bed and moves through the reactor with increasing time (or H_2S amounts); in our experiments, H_2S would be adsorbed on the external part of the bed, the inside remaining free from adsorption. A part of the nickel particles would be completely sulfided, the other being unperturbed.

Another possibility would be that the (Ni, H_2S) complex forms a two-dimensional phase growing from nuclei. Each nickel particle would contain a small number of nuclei. In that case the free nickel surface would be in the neighborhood of the perturbed metal and could be more easily influenced by it. However, this influence would not be sufficient to change α_{H_2} and α_{CO} at room temperature. We will see below that results obtained for C_6H_6 adsorption are in best accordance with the last hypothesis.

Adsorption of Gases on Poisoned Catalysts

We can distinguish gases which are adsorbed only on free nickel and gases which are adsorbed on both free and poisoned nickel. H_2 and CO may be classified in the first category. From a practical viewpoint, this result establishes the validity of the method of H_2 and CO adsorption to estimate the free nickel surface area of partially poisoned catalysts. It was previously suggested that it be measured from O_2 chemisorption (*11*). However, as O_2 is known to adsorb on a variable number of nickel layers (*28*), we recommend using H_2 and CO, and preferably H_2 owing to the possibility of nickel carbonyl formation in the case of CO.

In contrast with CO and H_2, benzene and acetylene are both adsorbed on free and poisoned nickel. When the nickel surface is completely precovered with H_2S, the adsorption of these two gases causes the saturation magnetization to decrease ($\alpha_{C_6H_6} = 2$ B.M./molecule; $\alpha_{C_2H_2} = 0.5$ B.M./molecule). As the first Ni layer is supposed to be completely demagnetized by H_2S chemisorption, we are led to believe that deeper nickel layers, initially unperturbed, become concerned by this adsorption. The hydrocarbon adsorption may repulse the H_2S molecule as a whole toward deeper layers. This mechanism is quite plausible since it has been shown that when the nickel surface is saturated with H_2S, other H_2S molecules may react with deeper nickel layers (Fig. 1). Another possibility is that a part of the H_2S molecule, namely hydrogen, may be consumed by the hydrocarbon to give a less unsaturated adspecies, the remaining sulfur atom being no longer stabilized by hydrogen migrating into deeper layers. Without further experiments, it seems hazardous to decide between these two hypotheses.

How is it possible to account for variations of α for hydrocarbons against the volume of preadsorbed H_2S? To a first approximation, it could be considered (i) that the volume of adsorbed hydrocarbons on free or perturbed nickel is proportional to the respective surface areas, (ii) that one should attribute to α, on free nickel and on poisoned nickel, the values which are observed on a pure and completely H_2S-covered nickel surface (linear approximation). This would lead to a linear variation of α with H_2S coverage. This is in sharp contradiction to the experimental data (Fig. 8 and 10). It means that, in fact, the phenomena are much more complicated.

We can tentatively suggest the following mechanism in the case of benzene where small and even negative values for α are observed. Benzene adsorbed on free nickel would be capable of extracting hydrogen from adsorbed H_2S, thus liberating nickel atoms which would return to ferromagnetism and thus would contribute to the decrease of α to negative values. A very similar reasoning was used by one of us in the case of the poisoning of Raney nickel (in fact, Ni–Al alloys) by thiourea. Al and thiourea alone each decrease the saturation magnetization of Ni: However, when they are present together, the initial saturation magnetization of Ni is partially restored because Al and thiourea are reacting together and cease to influence nickel (*29*).

To illustrate this hypothesis in the case of C_6H_6 adsorption we can propose the following reaction:

$$C_6H_{6\ \mathrm{gas}} + 2H_2S_{\mathrm{ads}} \rightarrow C_6H_{10\ \mathrm{ads}} + 2S_{\mathrm{on\ Ni}}.$$

Thus

$$\alpha_{C_6H_6} = \alpha_{C_6H_{10}} + 2\alpha_S - 2\alpha_{H_2S}$$

and we can suppose that C_6H_{10} is bonded to two Ni atoms by two α bonds; then $\alpha_{C_6H_{10}} = 1.2$ B.M./molecule. Taking for α_{H_2S} the observed value (2.5 B.M./molecule) and for α_S a value between 1 and 4 (Fig. 4), one obtains:

$$-1.8 \leqslant \alpha_{C_6H_6} \leqslant 4.2$$

which shows clearly that α may have negative values.

This type of mechanism is only possible if hydrogen coming from adsorbed H_2S is not too far from the hydrocarbon molecule, or in other words, that free nickel atoms are in the neighborhood of poisoned nickel. This would be in better accordance with the second hypothesis which we have proposed on the poisoning mechanism, namely, formation of a two-dimensional phase growing from a nucleus. Naturally, this does not preclude that the external part of the sample could simultaneously be more sulfided.

It seems to us rather hazardous at this time to attempt a quantitative interpretation of the well-defined minimum observed in the $\alpha_{C_6H_6} = V_{H_2S}$ curve at $V_{H_2S} = 6$ ml [NTP]. More work is needed, for example, from infrared spectroscopy, to make this interesting point clearer.

It should be noted that acetylene and benzene do not react with preadsorbed hydrogen on a nickel surface free from H_2S to give hydrogenated adspecies (*16*, *20*); this behavior is in sharp contrast with that described here, where hydrogen coming from the complex (Ni, H_2S) seems capable of hydrogenating the hydrocarbons. The specific properties of this type of hydrogen could explain the selectivity for hydrogenation reactions which is generally observed on Ni–S catalysts.

The last point which deserves some comment is the inhibiting effect of H_2S on the cracking properties of Ni catalysts (Figs. 9 and 11). The origin of this behavior does not seem clear. However, it can be considered that it is in good agreement with the results reported by Dalla Betta *et al.* (*3*) who observed an increase of the selectivity toward heavier hydrocarbons in the CO + H_2 reaction on nickel when partially poisoned with H_2S (an increase of cracking properties would probably lead to the opposite effect).

To summarize, our main results are:

(i) When H_2S is introduced in small successive quantities at room temperature, the surface nickel layer is first covered with H_2S (four or five Ni atoms involved in the bonding), and then deeper layers are attacked;

(ii) Poisoning occurs probably with a two-dimensional phase growth from nuclei;

(iii) H_2 (and CO) chemisorption are specific to the free nickel surface;

(iv) Unsaturated hydrocarbons are adsorbed on both free and poisoned nickel: There is a possibility of interaction between the hydrogen from H_2S to give a hydrogenated adspecies, in sharp contrast with preadsorbed hydrogen from molecular H_2; and

(v) H_2S seems to inhibit the cracking of hydrocarbons on nickel.

This work will be pursued with the aim of clarifying these postulates and of elucidating the exact mechanism of the increase of selectivity for various reactions on this type of catalyst.

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