

Sulfur Poisoning of Carbon Monoxide Adsorption on Ni(111)

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Received September 13, 1977; revised January 2, 1978

CO adsorption on Ni(111) precovered with varying amounts of sulfur has been investigated using LEED, AES, flash desorption, and work function measurements. Sulfur strongly reduces CO adsorption and blocks it completely for $\theta_s > 0.3$. Besides a single CO adsorption state observed for the clean surface flash desorption spectra reveal a second state at lower energy for $\theta_s > 0.1$. With increasing sulfur coverage the following sequence of LEED structures is observed: $p(2 \times 2)$, $(3^{\frac{1}{2}} \times 3^{\frac{1}{2}}) R 30^\circ$, $c(20 \times 2)$. The latter complex pattern, already described in previous publications and attributed to a reconstructed surface, could also be obtained by additional CO adsorption onto the $p(2 \times 2)$ sulfur structure. In connection with further experimental findings it is proposed that the complex pattern results from a coincidence structure of a chemisorbed sulfur overlayer.

INTRODUCTION

Sulfur poisons technically important catalytic reactions involving CO adsorption on Ni catalysts (methane formation, Fischer-Tropsch synthesis). In basic research, sulfur acts as the main contaminant on nickel surfaces. It segregates to the surface at elevated temperatures and may markedly influence adsorption/desorption studies if no special care is taken to deplete the bulk crystal from S impurities. In view of these implications, coadsorption studies of CO and S deserve considerable attention. There is one further incentive which makes this system attractive. Perdreau and Oudar (1) reported strong structural changes of sulfur overlayers on Ni(111) after thermal treatments. According to these studies, sulfur forms two-dimensional Ni-S compounds at elevated temperatures, as derived by LEED observations. One might expect differences in the CO adsorption properties depending on whether sulfur

forms a chemisorbed overlayer on Ni(111) or a reconstructed Ni-S compound layer of effectively the same surface coverage.

Carbon monoxide adsorption on clean Ni(111) surfaces has been the subject of numerous investigations (2-8). Several studies dealt also with the coadsorption of CO with various gases, e.g., hydrogen (9, 10), oxygen (11, 12), and nitric oxide (13) on Ni(111). The results indicate that small amounts of such coadsorbates considerably influence the adsorption/desorption behavior of CO. Sulfur poisoning of CO adsorption on Pt has been studied by Bonzel and Ku (14). The same effect on silica-supported Ni was recently investigated by Rochester and Terrell (15) using infrared spectroscopy.

The present investigation shows that sulfur poisons CO adsorption very effectively and inhibits the CO uptake completely for $\theta_s > 0.3$. No differences in CO adsorption properties have been found

because of heat treatment of sulfur predeposits. In connection with further experimental findings, it seems questionable whether sulfur actually forms two-dimensional Ni-S compounds on Ni(111). According to the LEED results of the present study, the interpretation of Perdereau and Oudar (1) can only be maintained by invoking reversible phase changes between S adsorption layers and reconstructed Ni-S compound layers.

EXPERIMENTAL

The experiments were performed in a UHV system capable of a base pressure of 1×10^{-8} Pa equipped with a four-grid LEED/Auger optic and provisions for thermal flash desorption measurements and able to record continuously work function changes by the retarding field method. The details of the apparatus as well as the procedures of preparing a clean, well-defined Ni(111) surface have been reported in previous publications (8, 16). Carbon monoxide exposures were carried out at room temperature and a partial pressure of 1.3×10^{-5} Pa. Flash desorption spectra were recorded by a quadrupole mass analyzer (QMA) tuned to the 28 mass peak. The heating rate was 10 K s^{-1} over the effective temperature range. Sulfur coverages between $0 < \theta < 0.40$ monolayers can be achieved either by S segregation from bulk impurities or by dissociative adsorption of H_2S . Because the bulk impurity concentration of sulfur had been effectively depleted by thermal treatment in an oxygen partial pressure during the cleaning procedure (8), the S coverages were produced by H_2S adsorption.

The calibration of the CO Auger signal in terms of monolayer fractions θ_{CO} was the same as that reported in Ref. (8) and the respective calibration for the S Auger signal was taken from Perdereau's data (17), which agreed well with the sequence of the LEED patterns observed in the present work.

RESULTS

(a) CO Flash Desorption Spectra from a Ni(111). Surface as a Function of Sulfur Precoverages

The following results were obtained for sulfur coverages produced by H_2S adsorption followed by heating the sample up to 1100 K prior to CO exposure. The clean and S precovered Ni(111) surfaces were given a CO exposure of 4 L ($= 5.3 \times 10^{-3}$ Pa·s). This exposure is sufficient to reach the stationary CO coverage at 1.3×10^{-5} Pa and at room temperature. After stopping the CO gas inlet and reaching nearly base pressure flash desorption traces were recorded as reproduced in Fig. 1. If prior to the flash no electron beam interactions with the Ni surface by LEED or AES measurements were allowed, the total amount of adsorbed CO desorbed during the flash. No dissociation products of C and O could be detected within the sensitivity of the Auger measurements ($\theta_{\text{C}} < 0.01$ for C and $\theta_{\text{O}} < 0.02$ for O) after completion of the flash. Dissociative CO adsorption has been observed (18) on stepped Ni(111) surfaces.

For the clean Ni(111) surface, a single

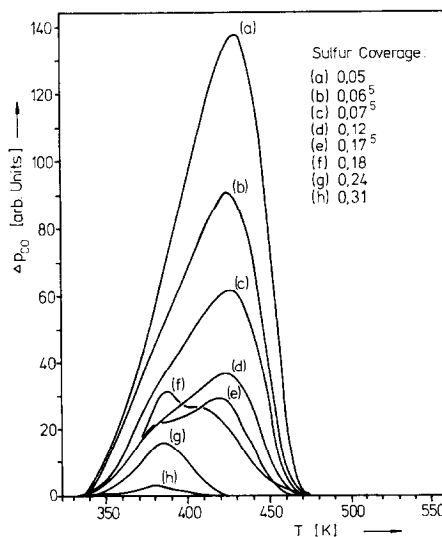


FIG. 1. CO flash desorption spectra from Ni(111) with varying sulfur precoverage.

CO desorption peak centered around 430 K is observed. This desorption temperature agrees very well with published data (4) for similar CO coverages on Ni(111) and the same heating rates. Also, in the region of low S precoverage ($0 < \theta_s < 0.1$) a single desorption peak is observed. The desorption peak temperature, however, shifts slightly to lower temperatures with increasing S coverage. Above a sulfur coverage of $\theta_s = 0.1$ a second desorption peak develops around $T = 385$ K and this is the only one observed for $\theta_s > 0.25$.

The area under the flash desorption traces is proportional to the total amount of adsorbed CO. Figure 2 shows the integrated spectra as a function of sulfur precoverage. For $\theta_s < 0.03$ the CO coverage is independent of the S precoverage. In the region $0.03 < \theta < 0.1$, the CO uptake decreases strongly with increasing sulfur coverage and follows a nearly linear dependence on θ_s . Above $\theta_s = 0.1$ the adsorbed amount of CO decreases with a much smaller rate up to $\theta_s \simeq 0.18$. At this sulfur coverage the observed two CO desorption peaks attain about equal maximum height. For even higher S coverages up to $\theta_s = 0.22$, the amount of adsorbed CO decreases more strongly again. In this sulfur coverage range the higher temperature desorption peak disappears completely. Finally, the CO uptake approaches the experimental detection limit around $\theta_s = 0.33$.

(b) *CO Flash Desorption and Work Function Measurements Starting from a $p(2 \times 2)$ Sulfur Overlayer on Ni(111)*

Perdereau and Oudar (1) reported that dissociative H_2S adsorption on Ni(111) at room temperature leads to the sequential appearance of $p(2 \times 2)$ and $(3^{\frac{1}{2}} \times 3^{\frac{1}{2}})$ R 30° LEED patterns characteristic of chemisorbed S overlayer structures. Upon high temperature annealing, these structures are reported to transform irreversibly into complex structures, which Perdereau

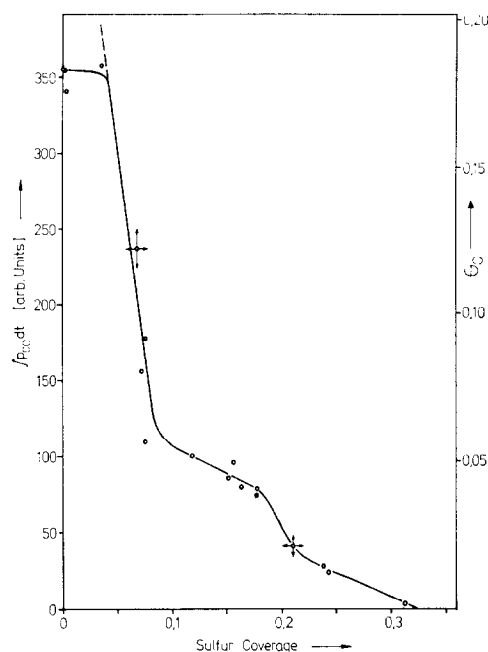


FIG. 2. Area under CO flash desorption curves as function of sulfur precoverage.

and Oudar referred to as surface two-dimensional I (SBAI) and II (SBAILI), respectively. They interpreted these structures in terms of two-dimensional Ni-S compounds, i.e., reconstructed surfaces with Ni and S in the top surface layer. One may expect that the irreversible phase changes cause changes (i) in work function and (ii) in the CO adsorption properties.

For this reason the following experiment was performed. The sample was exposed at room temperature to H_2S which led after an exposure of 0.5 L ($= 0.67 \times 10^{-3}$ Pa·s) to a sulfur coverage of $\theta = \frac{1}{4}$ as measured by AES using the calibration of Perdereau (17). This coverage results in a sharp $p(2 \times 2)$ LEED pattern as reported in Ref. (1) and as described in more detail in the following LEED section and caused the work function to increase by 0.4 eV. Subsequently, CO was introduced at 1.3×10^{-5} Pa, leading to a further work function increase of 0.5 eV. (Note that in this experiment the sulfur-covered Ni surface

was not heated to 1100 K, as in the experiments described in the preceding section.) A stationary CO coverage was reached after about 2.5 L. A flash desorption run (heating rate 10 K s^{-1}) revealed a single desorption peak centered around 385 K. The maximum temperature did not exceed 523 K, which is below the temperature of 670 K at which Perdereau and Oudar (1) observed the transition from the (2×2) into the SBAIL structure. The work function decreased during the flash by 0.5 eV and reached the same value as obtained prior to CO adsorption. The CO adsorption-desorption process did not change the S (152 eV) Auger peak height. Auger measurements did not reveal any C or O residues after flash.

Integration of the flash desorption trace yielded within experimental error the same value as that obtained in the adsorption-desorption experiment described in the preceding section for a sulfur-covered Ni(111) surface with $\theta_s = 0.25$ which had been heated to 1100 K prior to CO adsorption. This temperature is well above the transition temperature of 670 K stated in Ref. (1).

Heating the S-covered Ni(111) surface with $\theta_s = 0.25$ to temperatures well above the transition temperature does not cause the work function to change appreciably. The slight decrease with increasing temperature is well accounted for by the negative temperature coefficient of the work function of the Ni(111) surface of $-1.7 \times 10^{-4} \text{ eV K}^{-1}$ (9).

Because of the identical CO adsorption-desorption behavior obtained for the Ni(111) surface covered by a chemisorbed S overlayer of $p(2 \times 2)$ structure and for the annealed S-covered Ni surface with the same S coverage and because of no marked work function changes upon temperature treatment, we decided to reinvestigate the formation of sulfur structures on Ni(111) during H_2S adsorption and upon heat treatments by LEED.

LEED Results

With increasing H_2S exposure at room temperature, the following sequence of LEED patterns was observed: $p(2 \times 2)$, $(3^{\frac{1}{2}} \times 3^{\frac{1}{2}}) \text{ R } 30^\circ$, and a more complex pattern as reproduced in Fig. 3. The $p(2 \times 2)$ structure which appeared after an exposure of about 0.3 L disappeared upon heating the sample to 370 K. Above this temperature no ordered structure developed but rather an increased background prevailed. Cooling the sample below 370 K caused the $p(2 \times 2)$ pattern to reappear. Even heating the sample to 1300 K had no effect on the reappearance of the $p(2 \times 2)$ structure below 370 K. This is in contrast to the observation of Perdereau and Oudar (1), who obtained instead the complex structure which they designated surface two-dimensional II (SBAIL).

With increasing H_2S exposure, superstructure spots characteristic of a $(3^{\frac{1}{2}} \times 3^{\frac{1}{2}}) \text{ R } 30^\circ$ structure appeared in coexistence with the $p(2 \times 2)$ spots. The $(3^{\frac{1}{2}} \times 3^{\frac{1}{2}}) \text{ R } 30^\circ$ superstructure spots were not stable even at room temperature. Without further H_2S adsorption a slow transition to the complex structure identical to the SBAIL structure occurred. Upon further H_2S adsorption this structure is fully developed at a sulfur coverage of $\theta_s = 0.4$, as determined by AES. Starting from the well-developed (SBAIL) structure and reducing the sulfur coverage either by ion sputtering or by reaction with oxygen to about $\frac{1}{4}$ monolayer caused the $p(2 \times 2)$ S superstructure to reappear provided the surface was allowed to cool below 370 K.

Exposure of the well-ordered $p(2 \times 2)$ S structure to CO also resulted in the disappearance of the $p(2 \times 2)$ spots after 2 L and again the complex pattern identical to SBAIL emerged. Heating the sample to 450 K caused the chemisorbed CO to desorb. Further heating to 670 K and subsequent cooling below 370 K resulted in the reappearance of the sharp $p(2 \times 2)$ sulfur

pattern. This procedure was repeated many times and complete reversibility of the LEED pattern sequence was observed. The complex sulfur structures SBAl and SBAlII both observed by Perdereau and Oudar (1) after heat treatment could not be reproduced in this study.

DISCUSSION

(a) Flash Desorption

The functional dependence of the integrated flash desorption spectra (Fig. 2),

i.e., the stationary CO coverage related to the sulfur precoverage, can be qualitatively discussed in conjunction with the observed LEED patterns. In a similar way, Bonzel and Ku (14) interpreted their experimental results on the flash desorption spectra for CO on Pt(110) precovered with various amounts of sulfur.

The sulfur $p(2 \times 2)$ LEED structure appeared at room temperature only above $\theta_s > 0.2$ and became fully developed at $\theta_s = 0.25$. This observation shows that the

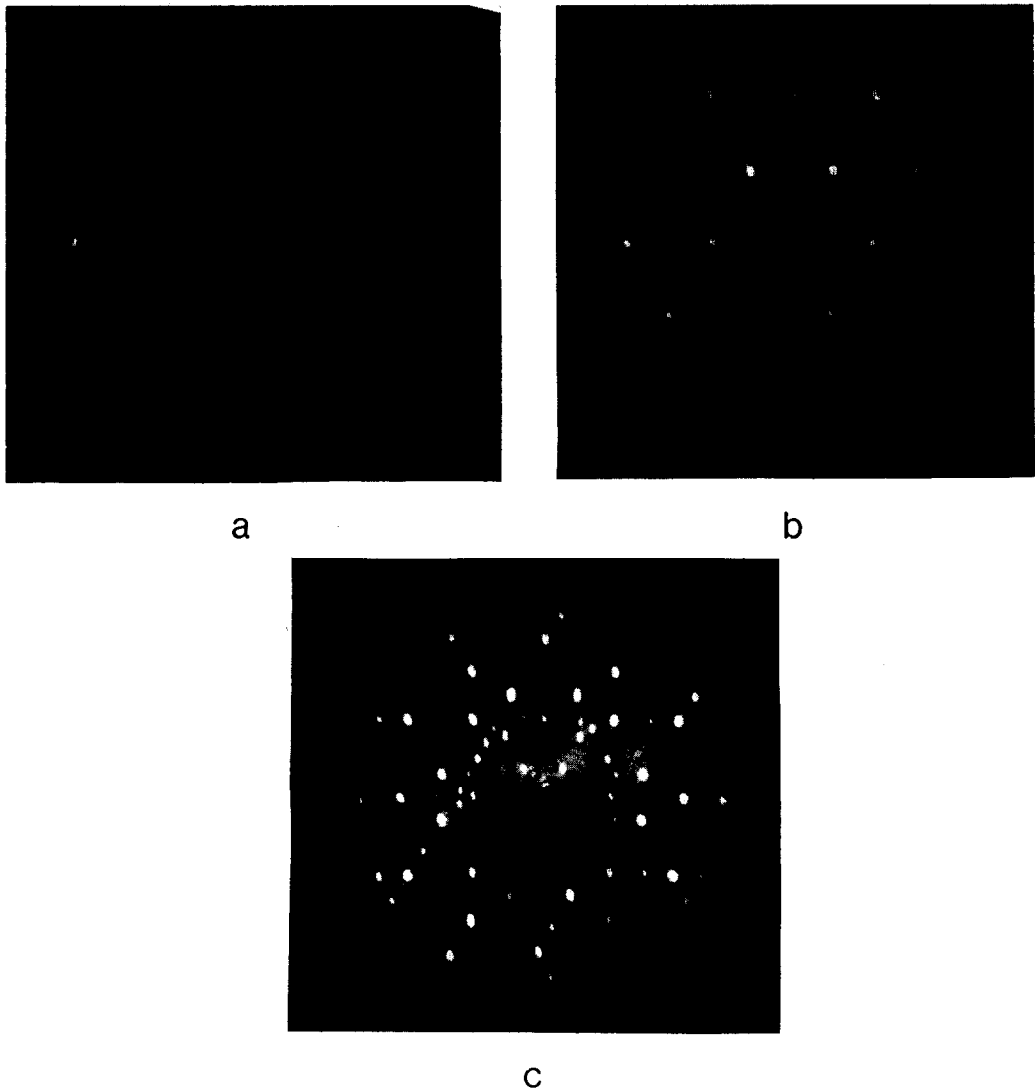


Fig. 3. LEED pattern from (a) clean Ni(111), 80 V, (b) $p(2 \times 2)$ sulfur overlayer, 85 V, and (c) $c(20 \times 2)$ sulfur overlayer, 71 V.

sulfur atoms do not form well-ordered $p(2 \times 2)$ domains below $\theta_s = 0.25$ but rather are distributed more or less randomly in the low coverage regime. The steep decrease of the CO coverage (Fig. 2) for $0.05 < \theta_s < 0.1$ can therefore be correlated with the absence of potential CO adsorption sites which are blocked by randomly distributed sulfur atoms. By approximating the steep decrease by a straight line, one can estimate that about nine equivalent sites are blocked for CO adsorption by one sulfur atom. This number seems reasonable by considering that already the site occupied by the sulfur atom and the six equivalent nearest neighbors make up a total of seven sites which are not available for CO adsorption. Extrapolation of the straight line to zero sulfur coverage yields a maximum CO coverage around 0.3 monolayer, which agrees with our previous finding (8). The higher coverage values were not reached in the present experiment because the lower CO partial pressure being used was not sufficient to establish the maximum CO coverage possible at room temperature.

The break of the CO coverage plot around $\theta_s = 0.1$ may become plausible by considering that with increasing sulfur coverage the effective areas blocked by single S atoms overlap causing a slower decrease of the CO uptake. In view of the LEED results discussed below for $\theta_s = 0.25$, it may be quite possible that CO adsorption causes the randomly distributed sulfur atoms to form islands with higher θ_s values. In this case, the number of sites "blocked" by each S atom would decrease.

The peak temperature of the flash desorption spectra changes only slightly toward lower temperatures for $0 < \theta_s < 0.1$. This behavior indicates that the CO adsorption state in this sulfur coverage range is barely influenced by neighboring S atoms and supports the above-mentioned view that the sulfur precoverage blocks potential adsorption sites.

With increasing sulfur coverage beyond $\theta_s = 0.12$, a second lower temperature desorption peak develops which is the only one remaining for $\theta_s \geq 0.25$. This adsorption state may well arise from repulsive interactions exerted by sulfur atoms in neighboring positions to the CO adsorption site. At first glance one could expect this to happen for a sulfur coverage of $\theta_s \sim 0.25$ corresponding to the $p(2 \times 2)$ sulfur LEED structure. If, however, a CO molecule could be accommodated within the (2×2) sulfur unit mesh, one would expect a much higher CO uptake to occur. In fact, the LEED pattern observed upon additional CO coverage on the sulfur $p(2 \times 2)$ structure reveals that the (2×2) unit mesh disappears and the complex sulfur structure (SBII) appears, which is the same as the structure observed at even higher sulfur coverages. One is led to the conclusion that additional CO adsorption on the S $p(2 \times 2)$ structure causes the sulfur atoms to move closer together and to form higher coverage domains. This view is supported by the observation that the sulfur $p(2 \times 2)$ structure returns after CO flashing and allowing the sample to cool below 370 K. It should, however, be mentioned that the complex structure exhibits a certain stability, as shown by the observation that the sample had to be heated beyond the flash temperature of 385 K to about 700 K to produce the $p(2 \times 2)$ structure again.

The two CO adsorption states are simultaneously present within the sulfur coverage range $0.12 < \theta_s < 0.2$. The disappearance of the flash desorption peak around 430 K is accompanied by an additional steeper decrease in CO coverage around $\theta_s = 0.18$. The adsorption of CO stops completely within detection limits for $\theta_s = 0.33$.

The reversible change of the $p(2 \times 2)$ into the complex SBII structure by CO adsorption raises again the question whether the complex structure described by Perd-

ereau and Oudar (1) actually corresponds to reconstructed Ni-S compound layers. McCarroll *et al.* (20) took a different view in rationalizing very similar LEED patterns obtained by H₂S adsorption on Ni(111) at a variety of surface temperatures. These authors find close agreement with the observed patterns by invoking sulfur adsorption on a slightly distorted (100) layer of nickel supported on the (111) face. This interpretation also requires reconstruction, viz., the formation of a Ni layer of (100) symmetry.

According to the present findings, the complex structure forms at room temperature if the local coverage exceeds $\theta_s = 0.25$ because of additional CO adsorption or approaches $\theta_s = 0.4$ by sufficient H₂S adsorption. In addition, reduction of sulfur coverage causes the $p(2 \times 2)$ structure to reappear, corresponding to a coverage $\theta_s = 0.25$. We are therefore tempted to conclude that the complex pattern corresponds to a higher S coverage without taking recourse to a surface reconstruction process. The fact that Perdereau and Oudar (1) observed an irreversible transition from the $p(2 \times 2)$ structure to the complex SBII structure may be explained as follows. Perdereau and Oudar calibrated and measured the S coverage by a radioactive tracer method. The sulfur signal was therefore only proportional to the radioactive sulfur species adsorbed from the gas phase. It may well be that upon heating the sample the overall sulfur coverage increased by segregation of S bulk impurities to the surface without changing the radioactive sulfur concentration.

Figure 4 shows a structural arrangement of sulfur atoms on top of the Ni(111) plane which is compatible with the observed LEED pattern of Fig. 3c and the sulfur coverage as measured by AES. The depicted S arrangement forms a coincidence mesh described by a $c(20 \times 2)$ structure in Wood's nomenclature or by the matrix notation $\begin{pmatrix} 10 & 1 \\ 0 & 2 \end{pmatrix}$. Three equivalent domains

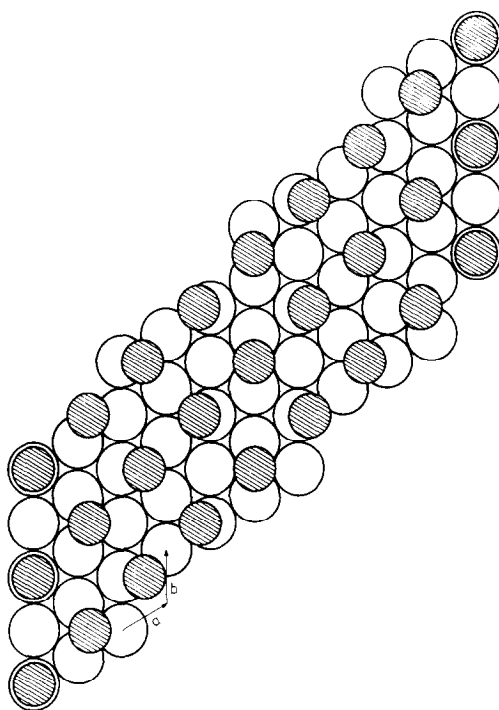


FIG. 4. Model for sulfur $\begin{pmatrix} 10 & 1 \\ 0 & 2 \end{pmatrix}$ structure. In Wood's nomenclature this structure is denoted by $c(20 \times 2)$.

rotated by 60° against each other are possible and give rise to the hexagonal symmetry of the observed LEED superstructure. At present, no physical or chemical arguments can be given which favor such a sulfur adsorption structure. Coincidence structures of adsorption layers, however, have been observed with other systems for which physical insight into the special structural arrangement has not been reached. As an example one can quote the recent study of Bauer and Engel (21) on oxygen adsorption on W(110) for $\theta_o > 0.5$. A number of experimental facts lead the authors to the conclusion that the coincidence structure observed by LEED is not caused by surface reconstruction but rather results from an oxygen adsorption layer in which the oxygen atoms are placed on several low symmetry adsorbent sites.

CONCLUSION

Sulfur very effectively poisons CO adsorption on Ni(111). In the low S coverage regime ($\theta_s < 0.1$), each sulfur atom blocks about nine potential CO adsorption sites. The CO adsorption energy deduced from flash desorption spectra is only slightly changed by the presence of coadsorbed S atoms. For higher sulfur precoverages, a second desorption peak at lower temperature develops which is attributed to the influence of sulfur atoms in close proximity to adsorbed CO molecules. Above a sulfur coverage of $\theta_s = 0.33$, CO adsorption stops completely, at least for stationary CO partial pressures below 1.3×10^{-5} Pa.

Contrary to previous publications (1, 20) it is proposed that sulfur does not cause reconstruction of the Ni(111) face.

ACKNOWLEDGMENTS

We wish to thank Mrs. C. Damerow for technical assistance and Dr. H. P. Bonzel and Prof. H. Ibach for valuable discussions.

REFERENCES

1. Perdereau, M., and Oudar, J., *Surface Sci.* **20**, 80 (1970).
2. Germer, L. H., Scheibner, E. J., and Hartmann, C. D., *Phil. Mag.* **5**, 222 (1960).
3. Edmonds, T., and Pitkethly, R. C., *Surface Sci.* **15**, 137 (1967).
4. Christmann, K., Schober, O., and Ertl, G., *J. Chem. Phys.* **60**, 4719 (1974).
5. Eastman, D. E., and Demuth, J. E., *Japan. J. Appl. Phys. Suppl.* **2**, 827 (1974).
6. Demuth, J. E., and Rhodin, T. N., *Surface Sci.* **45**, 249 (1974).
7. Apai, G., Wehner, P. S., Williams, R. S., Stör, J., and Shirley, D. A., *Phys. Rev. Lett.* **37**, 1497 (1976).
8. Erley, W., Besocke, K., and Wagner, H., *J. Chem. Phys.* **66**, 5269 (1977).
9. Lapujoulade, J., *J. Chem. Phys.* **68**, 73 (1971).
10. Conrad, H., Ertl, G., Küppers, J., and Latta, E. E., in "Proceedings of the Sixth International Congress on Catalysis (London 1976)," p. 427. Chemical Society, London, 1977.
11. Edmonds, T., and Pitkethly, R. C., *Surface Sci.* **17**, 450 (1969).
12. Conrad, H., Ertl, G., Küppers, J., and Latta, E. E., *Surface Sci.* **57**, 475 (1976).
13. Latta, E. E., Ph.D. Thesis, Hannover, 1975.
14. Bonzel, H. P., and Ku, R., *J. Chem. Phys.* **58**, 4617 (1973).
15. Rochester, C. H., and Terrill, R. J., *Faraday Trans. II* **73**, 609 (1977).
16. Erley, W., and Wagner, H., *Surface Sci.* **66**, 371 (1977).
17. Perdereau, M., *Surface Sci.* **24**, 239 (1971).
18. Erley, W., and Wagner, H., *Surface Sci.*, in press.
19. Christmann, K., Ertl, G., and Schober O., *Z. Naturforsch.* **29a**, 1516 (1974).
20. McCarroll, J. J., Edmonds, T., and Pitkethly, R. C., *Nature (London)* **223**, 1260 (1969).
21. Bauer, E., and Engel, T., *Surface Sci.* **71**, 695 (1978).