MODIFICATION OF CHEMISORPTION PROPERTIES BY ELECTRONEGATIVE ADATOMS: \( \text{H}_2 \) AND \( \text{CO} \) ON CHLORIDED, SULFIDED, AND PHOSPHIDED \( \text{Ni}(100) \)

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The effect of preadsorbed electronegative atoms Cl, S and P on the adsorption-desorption behavior of \( \text{CO} \) and \( \text{H}_2 \) on \( \text{Ni}(100) \) has been studied using thermal desorption, LEED and AES. It is found that the presence of the electronegative atoms causes a reduction of the adsorption rate, the adsorption bond strength and the capacity of the \( \text{Ni}(100) \) surface for \( \text{CO} \) and \( \text{H}_2 \) adsorption. The poisoning effect becomes stronger with increasing electronegativity of the preadsorbed atoms. In the case of \( \text{CO} \) adsorption the most tightly bound \( \beta_2 \)-state is suppressed most significantly. The variation of the initial sticking coefficient of \( \text{CO} \) as a function of the adlayer precoverage shows that at low Cl and S coverages the effective number of the influenced Ni surface atoms is more than four. The observed reduction of \( \text{CO} \) and \( \text{H}_2 \) adsorption and the difference in the poisoning effect of Cl, S and P is generally interpreted in terms of the changes in the surface electron density in the presence of electronegative atoms.

1. Introduction

The effect of foreign atoms on the adsorption kinetic of gases on metal surfaces is of considerable interest in view of explaining the role of poisons and promoters in heterogeneous catalysis. The purpose of this paper is to show the influence of preadsorbed electronegative elements on adsorption-desorption behavior of \( \text{CO} \) and \( \text{H}_2 \) on \( \text{Ni}(100) \). We have chosen for this study Cl, S and P which have different electronegativities but similar atomic and covalent radii. Kinetic data for the methanation reaction on \( \text{Ni}(100) \) with preadsorbed sulfur and phosphorus have been collected and will be reported elsewhere. A striking correlation is found between the observed methanation rate attenuation and the changes which occur in the adsorption behavior of \( \text{CO} \) and \( \text{H}_2 \) in the presence of these adatoms.

\( \text{CO} \) and \( \text{H}_2 \) adsorption on a clean \( \text{Ni}(100) \) has been extensively studied [1–8].

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Recently several papers have appeared reporting the effect of sulfur on CO and H₂ adsorption on metal surfaces [9–13]. The results in ref. [9] indicate that sulfur poisons CO adsorption on Ni(111) — each sulfur atom blocking ∼9 adsorption sites at low S coverages.

The present paper shows that the poisoning effect on CO and H₂ adsorption increases in the sequence P, S, Cl. In the case of CO adsorption the most pronounced effect is on the more tightly bound β₂ state.

2. Experimental

All experiments were performed in UHV chamber equipped with a double-pass cylindrical mirror analyzer, LEED optics and quadrupole mass-spectrometer. The detailed description of the apparatus as well as the procedure of obtaining a clean Ni(100) surface and cooling the crystal is given in ref. [5].

The adsorption experiments were performed at crystal temperature of 80K. Sulfur and phosphorus coverage were built up by adsorption of H₂S and H₃P, and Cl coverages were achieved by exposure of the crystal to Cl₂. The coverages of S, Cl and P were determined using AES peak-to-peak ratios which are calibrated to monolayer (ML) coverage. Temperature programmed desorption (TPD) spectra were recorded at a heating rate of ∼15°C/s with the sample in line-of-sight of the QMS.

3. Results

3.1. Structure and composition of Cl, S and P overlayers on Ni(100)

Since no reports on Cl₂ and H₃P adsorption on Ni(100) surface were available, their chemisorption behavior has been studied using LEED, AES and TPD measurements. The chlorine coverage was determined measuring the AES Cl(181)/Ni(848) peak height ratio. Because of the significant electron stimulated desorption of Cl caused by the electron beam, the chlorine level was established after each exposure with the crystal at a new position. Ni(100) exposure to Cl₂ at a partial pressure of ∼1 × 10⁻⁸ Torr causes a sequence of p(2 × 2) and c(2 × 2) LEED patterns with increasing Cl coverage. The saturation coverage was achieved at ∼4 L exposures and a Cl/Ni Auger signal ratio of ∼5. The observed ordered c(2 × 2) structure at high Cl coverages implies a saturation coverage value of 0.5 ML. (Coverages are normalized to 1 ML for an overlayer that has one atom per one substrate atom.) No changes in the chlorine coverage as well as in the LEED picture were detected after heating the sample up to 600 K. We should like to note that as reported in ref. [14] no desorption of atomic or molecular chlorine was detected by QMS upon heating to 1300 K, but the Cl AES signal decreases and completely disappears at temperatures higher...
than 1300 K. Since some chlorine diffuses into the substrate bulk, several heating-cooling cycles were required to achieve a clean surface after chlorine desorption. Using the coverage calibration as assumed from the LEED pattern, the initial sticking coefficient from the adsorption kinetic plot is estimated to be equal to 0.8.

Phosphorus coverages were built up by dissociative adsorption of H₃P. As in the case of chlorine the Auger peak ratio P(120)/Ni(848) was used for determination of phosphorus surface concentration. The intensity of the P Auger signal increases gradually with H₃P exposure with an almost constant rate up to a P/Ni Auger ratio ~1.2 followed by a very slow continuous increase with further H₃P exposure. The LEED diffraction patterns representing clean Ni(100) change very little with initial H₃P exposure and only a general decrease of intensity was observed. At intermediate H₃P coverages (P/Ni ratio ~0.8) weak new features between the substrate spots emerge whereas at exposures higher than 8 L (P/Ni ratio ~1.2) the LEED pattern completely disappears. Heating the sample to temperatures above 1000 K causes attenuation of the P Auger signal and the reappearance of the Ni(100) pattern. This implies penetration of the phosphorus into the bulk of the sample since no desorption of species in the mass range (30–35) was observed.

The absence of an ordered LEED pattern with a P adlayer can be explained by formation of an amorphous structure. The lack of an ordered LEED pattern makes difficult the coverage calibration of the Auger P(120)/Ni(848) peak height ratio. The following TPD measurements were performed to obtain more information regarding the absolute level of adsorbed P. The sample, cooled to 100 K, was exposed to H₃P flux using a molecular beam doser and the evolution of H₂ monitored during adsorption. No H₂ evolution was observed by QMS during the period of adsorption. After adsorption the Auger P(121)/Ni(848) peak-to-peak ratio was recorded and the sample was heated in line-of-sight of the mass spectrometer while monitoring the H₂, PH₃, PH₂, and PH signals. The observed PH₃, PH₂ and PH signals were negligibly small in comparison with the H₂ evolution. From the area under the H₂ TPD curve recorded after PH₃ adsorption, we determine \( \theta_p = 0.5 \) to correspond to an AES P/Ni ratio = 1.2. This value corresponds to the break point in the P(120)/Ni(848) versus exposure plots and to the value P/Ni at which the LEED pattern disappears.

The structural arrangement of sulfur atoms on Ni(100) has been extensively studied. No discrepancy with the results reported in refs. [15–17] was observed in the present study. H₂S adsorption on Ni(100) results in formation of p(2×2) at quarter-monolayer and c(2×2) at a half monolayer. (The latter corresponds to saturation coverage.) No changes in the LEED pattern and AES signal were observed upon heating the sample to 1200 K, in agreement with results of Wagner and Erley [9] for the S/Ni(111) system. These authors showed evidence that no reconstructed Ni–S layers are formed as a result of heating. The calibration of sulfur coverage was made assuming that the saturation Auger signal ratio \( S(152)/N(848) = 2.4 \) corresponds to half monolayer.
3.2. Adsorption/desorption behavior of CO on Cl, S and P precovered Ni(100) surfaces

As was mentioned in section 1, CO adsorption on Ni(100) has been extensively studied [1–5]. It is known that at low coverages CO adsorbs top-site whereas at higher coverages terminal and bridge-bonded forms coexist at about a 1:1 ratio.

In the present study the sample was exposed to CO at pressures ranging from $10^{-9}$ to $10^{-7}$ Torr. An exposure of 5 L was sufficient to reach a stationary CO coverage. The thermal desorption spectra of CO following adsorption at 100 K at high coverages consists of four TPD peaks. As shown in figs. 1, 2, and 3, (top curves) these peaks are labeled as $\alpha_2$, $\alpha_1$, $\beta_2$, and $\beta_1$ states. According to LEED and ratio tracer data [2,4], the saturated CO coverage corresponds to 0.62 ML ($1.1 \times 10^{14}$ atoms/cm$^2$) and is the value used in the evaluation of the initial sticking coefficient. At low CO exposures up to 1 L only the $\beta_2$ state is detected and, as is seen in figs. 1–3, remains the dominating state at high coverages [1]. The lower temperature peaks appear with further CO exposure. From the initial slope of the adsorption kinetic plot ($\theta_{CO}$ versus exposure) we estimate the initial sticking coefficient for CO to be equal to 0.68. Using the simple Readhead equation and assuming $\nu = 10^{13}$:

$$E_d/RT_p = \ln[(\nu_1 T_p)/(dT/d\nu)] - 3.64,$$

the desorption energies corresponding to each desorption peak can be estimated. The values of $E_{\beta_2}$, $E_{\beta_1}$, $E_{\alpha_2}$, and $E_{\alpha_1}$ were found to be 28.5, 22.0, 18.1, and

![Figure 1](image.png)

Fig. 1. Effect of varying chlorine precoverage on CO thermal desorption from Ni(100). CO exposure of 6 L.
The influence of different Cl, S and P coverages on the adsorption/desorption behavior of CO was studied as follows. The precovered Ni(100) surface was given an increasing CO exposure until the stationary CO coverage was achieved. As in the case for clean surface adsorption, exposures of ∼5 L are necessary for saturation coverage. From the area under the TPD traces the amount of the adsorbed coverage was determined assuming θ = 0.62 for the saturation clean surface value. The observed effect of the pre-adsorbed layers of Cl, S and P on CO TPD curves is shown.

13.0 kcal/mole, respectively. A similar value for $E_p$ has been reported previously [5].

Fig. 2. Effect of varying sulfur precoverage on CO thermal desorption from Ni(100). CO exposure of 6 L.
in figs. 1, 2 and 3. The CO curves represent the total CO desorption for different preadsorbed adlayer coverages after a CO exposure sufficient to reach the stationary CO coverage. As can be seen the CO uptake decreases markedly in the presence of the preadsorbed adlayer. The effect of P, however, is much less pronounced than for Cl or S. Fig. 4b shows the observed dependence of the total CO uptake on the precoverage of Cl, S and P, respectively. In the case of Cl no CO desorption was detected at coverages $\theta > 0.4$ whereas even for saturated S and P precoverages, some low temperature desorption peaks were detected. Since the changes observed in the lower temperature range of the TPD spectra are very complicated, we should like to note only that for low and medium P, S and Cl precoverages there is a slight increase of the CO population in the lower temperature state. In the case of P (see fig. 3) even at high P precoverages a considerable amount of a weakly bound CO is adsorbed on the surface. Compared with the CO saturation coverage on the clean surface, the total of this weakly bound CO is equivalent to 0.40 ML. Its desorption energy, however is appreciably lower (15 kcal/mol). As can be seen in fig. 4 the presence of foreign atoms affects most strongly the tight bonded $\beta_2$ CO state. Its population decreases sharply with the first doses of preadsorbed atoms. The $\beta_2$ state disappears completely at the following preadsorbed adatom coverages: $\theta_{Cl} = 0.15$, $\theta_S = 0.25$, and $\theta_P = 0.6$. No significant shift of the $\beta_2$ peak to lower temperatures is detected. Fig. 4a presents the dependence of the $\beta_2$ coverage on adlayer precoverage. The amount of CO adsorbed in the $\beta_2$ state was determined by resolving the TPD curve assuming first order desorption kinetics for the $\beta_2$ state.
Comparing the effect of Cl and S precoverages one can see that in the low pre-
coverage region ($\theta < 0.1$) the $\beta_2$ CO population decreases with approximately the 
same rate. However, for $\theta > 0.1$, the effect of sulfur is less pronounced. From a 
series of TPD curves representing the CO uptake with exposure, the adsorption 
kinetic plots were obtained for every Cl, S and P precoverage under investigation. 
From the initial slope of these plots the initial sticking coefficient can be estimated. 
As is shown in fig. 5 this value strongly depends on the foreign atom precoverage. 
Dotted lines in fig. 5 show the $\beta_2$ state sticking coefficient dependence. Since the 
$\beta_2$ state is the only state detected at low CO exposures for precoverages $\theta < 0.1$ ML, 
the initial part of the $\theta_0$ plot is the same for the $\beta_2$ state as for the total $\theta_{CO}$ plot. 
The data in fig. 5 demonstrate again that the poisoning effect of P is much less pro-
nounced.

### 3.3. Adsorption–desorption behavior of H$_2$ on Cl, s, and P precovered surfaces

Adsorption–desorption behavior of H$_2$ was studied at pressures ranging from $5 \times 10^{-9}$ to $1 \times 10^{-7}$ Torr at an adsorption temperature of 100 K. Thermal desorption 
spectra of H$_2$ from Ni(100) are more simple than those of CO. At low and medium 
hydrogen exposures only a single desorptive peak is observed. This peak shifts to 
lower temperatures with increasing coverage implying a second order desorption
process. At exposures higher than 5 L a second lower temperature state arises, however, its population is much less than those of the main desorption state. Exposures of \(~10\) L are sufficient for establishing the saturation H\(_2\) coverages both for clean and precovered Ni(100). Since H\(_2\) adsorption on a clean Ni(100) has been extensively studied \([6-8]\) we should like to summarize that our results are in good agreement with those reported in refs. \([6,7]\). An adsorption energy of 22.0 kcal/mole was evaluated for the main H\(_2\) adsorption state. Since the saturation coverage value, \(\theta_H(\text{max})\), assumed in the different studies varies considerably and no data for the absolute adsorbed H\(_2\) amount at 100 K are available, an attempt was made to evaluate this value from the desorption curve corresponding to saturation coverage. Because the TPD experiments were performed in line-of-sight of the QMS, edge

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**Fig. 5.** Variation of the initial sticking coefficient of CO, \(S_0\), as a function of additive precoverage. Short dashed lines represent the variation of the \(\beta_2\) CO state initial sticking coefficient. Long dashed line represents the theoretical dependence according to the relationship \(S = S_0 (1 - 4\theta)\).

**Fig. 6.** Effect of varying chlorine precoverage on H\(_2\) thermal desorption from Ni(100). H\(_2\) exposure of 10 L.
effects can be neglected. A value of \( \sim 0.7 \) for \( \theta_{H\text{max}} \) at an adsorption temperature of 100 K was found. Using this value we estimate the initial sticking coefficient \( (S_0) \) for clean Ni(100) to be 0.6. This sticking coefficient value is higher than the values reported in refs. [6–8]; however, these studies deal with adsorption at room temperature. It should be noted that according to Christmann et al. [6] \( H_2 \) adsorption on Ni(100) is disordered at room temperature.

Adlayers of Cl, S and P cause a reduction of hydrogen uptake and a shift of the TPD peak maxima to a lower temperature. As shown in figs. 6, 7, and 8, at higher foreign atom precoverages a lower temperature state becomes more pronounced.
The extent of the effect increases in the sequence P, S, Cl. As shown in fig. 9 the reduction of H₂ coverage is most rapid in the presence of Cl atoms such that at θ₁ Cl higher than 0.2 a negligibly small amount of desorbing hydrogen is detected. For S precoverages a small amount of H₂ occupying a weakly bonding state was detected even at saturation coverages. As in the case of CO a less pronounced effect was observed for P. For H₂ adsorption kinetic curves the initial sticking coefficient was determined and its dependence on Cl, S and P adlayer concentration is presented in fig. 10.

4. Discussion

The present data show that the electronegative atoms on Ni(100) results in an attenuation of the adsorption rate, the adsorption bond strength and the capacity of the Ni surface for CO and H₂ adsorption. Because of the considerable interest in nickel as a catalyst for methanation and the well known sulfur poisoning effect, considerable data on sulfur overlayer structures on Ni(100) are available. Recent results of Fisher [16] give a complete interpretation of the structure and bonding of sulfur on Ni(100). He concludes that S occupies a four-fold hollow site independently of adatom density. The sulfur structure and bond coordination, however, changes with coverage from four-fold bond coordination corresponding to p(2 × 2) one-fourth monolayer to two-fold bond coordination at c(2 × 2) one-half monolayer coverage. The Ni–S bonding involves 3d surface Ni orbitals which, as it is well known, participate in the formation of the Ni–CO chemisorption bond.

The same sequence of LEED patterns, p(2 × 2) and c(2 × 2), was observed in the present work for Cl adsorption on Ni. In the case of P, however, no ordered structure was found and the disappearance of the LEED pattern at high P coverages
implies formation of islands or an amorphous Ni-P surface phase. As is known [19], Ni and P react easily according to a complex Ni-P phase diagram with phosphorus compositions ranging from 0 to 70%.

Prior to the interpretation of the poisoning effect of the Cl, S and P it is useful to review the character of the bonding of CO and H on the surface. According to Blyholder [20] CO chemisorption bond is formed through the carbon atom when occupied 5\sigma CO orbitals donate electrons to the metal d-electron states and, in turn, d-electrons from the metal are back donated to the antibonding 2\pi^* CO orbitals. This donor-acceptor bond is bonding with respect to the C-M bond and antibonding with respect to the C-O bond.

Identification of specific adsorption sites for hydrogen atoms is difficult because of atom size. As reported in ref. [21] both terminal and bridge bonding is possible on single crystal surfaces and the transition from the former to the latter states occur in the presence of other adsorbates. Comparing the work function changes and the chemisorption bond strength upon H\textsubscript{2} and CO adsorption [6], it is clear that the charge transfer from Ni to H required for the H-Ni chemisorption bond is smaller than for CO. On the other hand, however, two neighboring surface sites are necessary for H\textsubscript{2} dissociative adsorption.

The effect of the preadsorbed electronegative atoms on CO and H\textsubscript{2} adsorption observed in the present work generally increases with increasing the electronegativity of the preadsorbed atoms which is 2.1, 2.5 and 3.0 for P, S and Cl, respectively. Recently Benziger and Madix [13] have shown by LCAO calculations that the reduction of CO binding energy on Fe(100) in the presence of S, C and O is due not only to reduced Fe(3d)-C0(2\pi^*) interactions but also to direct interactions between CO and the foreign atoms, the latter depending on the size of the preadsorbed atoms.

Since the Cl, S and P atomic and covalent radii are similar (0.99, 1.02 and 1.04 Å, respectively) we conclude that the electronegativity factor plays a major role in explaining the difference in their poisoning effect. In comparing the suppression of \(\beta_2\) (CO) states with increasing the preadsorbed overlayer, it is seen that overlayer coverages at which \(\beta_2\) state population drops to zero is 0.17, 0.21, 0.5, respectively, for Cl, S and P. In the case of Cl and S the ratio 0.17/0.21 correlates with the relative poisoning effect predicted from their electronegativities (2.1 versus 2.5). The effect of P, however, is much less than those predicted by this electronegativity factor compared with those for S and Cl. This fact implies that in addition to the electronic factor and atomic size, the surface structure of the overlayer has to be taken into account. As summarized above, in contrast to Cl and S ordered overlayers, no ordered structure was observed for the P overlayer. It is assumed that both the Ni-P surface phase and free Ni surface coexist such that fewer surface atoms are influenced by adsorbed P atoms.

On the base of the observed LEED pattern for S and Cl we assume that the influence of the preadsorbed atom is spread over the four nearest neighbor Ni atoms. We have estimated the dependence of the initial sticking coefficient on the
overlayer precoverage using the relationship $S = S_0 \left(1 - 4\theta\right)$ for CO and $S = S_0 \left(1 - 4\theta\right)^2$ for H$_2$ adsorption. The calculated curves are presented by the dashed lines in fig. 5 and 10. As can be seen from fig. 5, the effect of low Cl and S precoverages is stronger than the predicted by a simple site blocking model. The initial sticking coefficient of the $\beta_2$ state drops to zero at lower Cl and S precoverages than would be predicted by such a model. This fact shows that at low Cl and S precoverages the adatom influence involves a long-range electronic interaction. This is consistent with the interpretation that the surface modification is mainly due to the variation in the density of the surface 3d Ni electronic states. Because of the reduced 3d electron density in the vicinity of the preadsorbed atoms and the possible adlayer-CO interaction, the $\beta_2$ CO adsorption is not observed at medium and high overlayer coverages.

The reduction in the rate of change of the CO uptake and $S_0$ at medium and high coverages can be ascribed to the modifications of the bonding and the structure of the overlayers. With increasing overlayer coverage the effective number of the influenced Ni atoms by one foreign atom decreases. It is noteworthy that the effect of P, although lacking adlayer order, is not in contradiction with general electronic factor considerations.

Comparing the predicted and experimental values of $S_0$ for H$_2$ (fig. 10) as a function of adatom coverage it is seen that the model for four Ni atoms deviates slightly from the experimentally obtained curves for Cl and S. This is consistent with the less electron charge transfer required for H$_2$ adsorption. As in the case of CO, however, the reduction of the electron surface density in the presence of electronegative atoms and the possible adatom-adatom interactions cause a decrease in the hydrogen binding energy. The results presented here correlate very well with the studies on the effect of S and P overlayers on the methanation reaction kinetics [22]. It is found that the effect of S is stronger and, with increasing precoverage, the reaction becomes dependent on CO and H$_2$ partial pressures. The results are quite understandable in view of the observed suppression of H$_2$ and $\beta_2$ CO population in the presence of S and P. In the case of Cl overlayers, however, no change in the methanation rate was observed. Subsequent AES showed no Cl remaining on the surface shortly after initiation of the reaction. At reaction conditions of 120 Torr, 4/1 H$_2$/CO and 600 K, H$_2$ reacts with Cl(ads) forming HCl. This reaction prohibits the study of Cl effect on the methanation kinetics.

5. Conclusions

In this study we compare the effect of three electronegative elements, Cl, S and P, on CO and H$_2$ adsorption on Ni(100). It is shown that less than one-tenth monolayer precoverage causes a strong reduction of the most tightly bound $\beta_2$ CO state. The observed suppression of CO and hydrogen adsorption is explained in terms of changes in the surface electron density in the presence of the electronegative atom
precoverage. We show generally the important role of the electronic factor in explaining the observed effects. The increasing of the influence on CO and H₂ adsorption in the sequence P, S, Cl correlates with the increasing electronegativity of the preadsorbed atoms.

The observed influence of S and P adlayers on CO and H₂ adsorption relate to the variations in the kinetics of the methanation reaction on Ni(100) observed in the presence of S and P [22]. A strong correlation between poisoning effect on the methanation reaction and the reduction of the H and β₂ CO state adsorption is observed. This work demonstrates the utility of surface studies applied to fundamental catalytic problems such as poisoning.

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