

SURFACE SCIENCE LETTERS

CHEMISORPTION AND REACTIVITY STUDIES OF H₂ AND CO
ON SULFIDED Ni(100)

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Sulfur segregation to the surface poses a perplexing problem in basic research on low surface area nickel materials. In addition sulfur effectively poisons catalytic reactions involving CO adsorption on nickel as well as other transition metal catalysts in technically important processes such as methanation and Fischer–Tropsch synthesis. It is not surprising then that considerable attention has been given the sulfur/nickel system [1–7]. For the Ni(100)/sulfur system investigators [6,7] using LEED, photoemission, as well as other techniques, agree that sulfur is chemisorbed with fourfold site coordination. The sulfur forms a $p(2 \times 2)$ structure at one-quarter monolayer coverage and a $c(2 \times 2)$ structure at one-half monolayer. The one-half monolayer corresponds to a saturation coverage.

Carbon monoxide and hydrogen adsorption on clean Ni(100) have been investigated previously [8–10]. Adsorption of H₂ and CO lead to the formation of an interacted complex but no product other than H₂ and CO was observed to desorb upon heating [10]. In the presence of a monolayer of CO, hydrogen is desorbed at a lower temperature; however, the surface coverage of hydrogen is the same as for the clean surface [10]. For Ni(111), sulfur at low coverages effectively poisons CO adsorption [2]. CO adsorption is completely inhibited for $\theta_s > 0.3$. For hydrogen on Ni(111) the sticking coefficient approaches zero as the sulfur coverage is increased to saturation [11].

The present investigation combines thermal programmed desorption (TPD) measurements with reaction rate measurements at elevated pressures. These results for a sulfided Ni(100) surface show a striking correspondence between the kinetic data at a given sulfur coverage and the observed H₂/CO chemisorption behavior. The experimental apparatus and procedures have been described previously [12,13]. Fig. 1 shows an Arrhenius plot for kinetic data obtained for the methanation reaction over a Ni(100) catalyst with varying amounts of preadsorbed sulfur. These sul-

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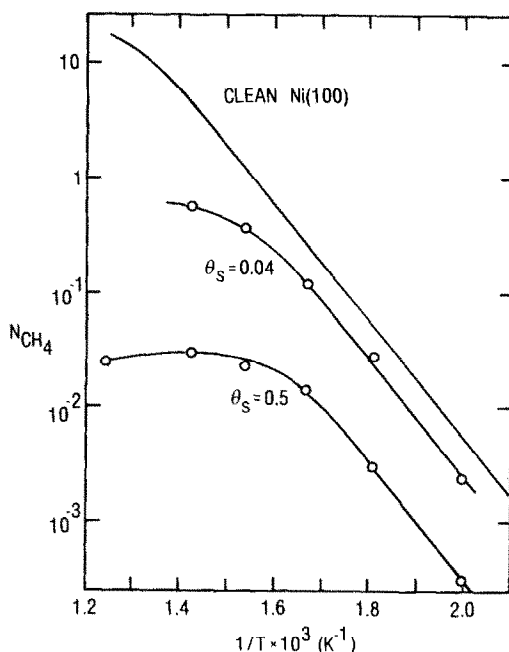


Fig. 1. An Arrhenius plot of the rate of methanation over a sulfided Ni(100) catalyst at 120 Torr and at a H₂/CO ratio equal to four. θ_s 's are expressed as fractional monolayers (1 cm² Ni(100) equals 10¹⁵ atoms). N_{CH_4} is the number of methane molecules produced per nickel atom site per second (turnover number).

fur levels were established by exposure of the sample to H₂S at 300 K followed by a sample heating to 600 K. The surface coverage of sulfur was determined by monitoring the S₁₅₂/Ni₈₄₈ Auger peak height ratio and referencing this to that ratio found for a saturated sulfur coverage. As mentioned above, this saturation level corresponds to one-half monolayer. Previous work [13] has demonstrated that for clean Ni(100) the reaction proceeds with a low level of a carbide-like carbon (~10% monolayer) on the catalyst. At 120 Torr this level is constant throughout the temperature region of linear Arrhenius behavior (450–700 K). However, at 700 K, as the rate diverges from linearity, the surface carbon level rises to one-half monolayer, a value found to be the saturation carbon level [14]. At lower hydrogen pressures similar behavior is observed at lower temperatures. These curvatures in the Arrhenius plots have been explained as arising from an onset of a departure of the hydrogen coverage from a saturation value. This reduction of hydrogen coverage leads to an increase in the active carbon level under reaction conditions.

For identical reaction conditions the sulfided surfaces show behavior remarkably similar to results for the clean surface at considerably reduced hydrogen partial pressure. For $\theta_s = 0.04$ the reaction rate at 120 Torr departs from linearity at

600 K. For the clean surface a nearly identical plot was found at 10 Torr. For θ_s equal to 0.04, the surface carbon level begins to rise to the saturation level as the reaction rate begins to fall. The response of the reaction rate to higher levels of sulfur ($\theta = 0.5$) is very similar. Here, however, as the rate departs from linearity, no surface carbon is found following reaction. This may result from one of two causes: (1) the high sulfur coverage has led to the carbon formation step becoming rate-determining or (2) the sulfur and carbon compete for sites such that sulfur precludes any carbon buildup on the surface. In the latter case the minority sites leading to product formation could be saturated with undetected carbon. The chemisorption data suggest that the first interpretation is correct. It should be noted that at temperatures <600 K, the reaction rate plots for the sulfided surface parallel that for the clean surface. This suggests that although the reaction rate is slowed no fundamental change has occurred in the reaction mechanism.

It is clear from the results shown in fig. 1 that the poisoning effect of sulfur on nickel for the methanation reaction is very nonlinear. Fig. 2 shows more completely this nonlinear relationship between the sulfur coverage and the methanation rate at 600 K. A precipitous drop is seen for the catalytic activity at lower sulfur coverages. The poisoning effect quickly maximizes and no further reduction in reaction rate is found at sulfur levels exceeding 0.2 monolayers. Apparently sulfur bonded in the $p(2 \times 2)$ configuration sufficiently deactivates the nickel surface for methanation that further addition of sulfur produces no perceptible attenuation of the reaction rate. This suggests that the unoccupied four-fold nickel sites remaining at a sulfur coverage of one-fourth monolayer are quite effectively poisoned both for carbon formation as well as carbon hydrogenation. Chemisorption studies of hydrogen and carbon monoxide support this conclusion.

Fig. 3 presents results for CO thermal desorption from Ni(100) with varying amounts of surface sulfur. The top curve shows the TPD from the clean surface. Three states designated α , β_1 , and β_2 are evident above 250 K. The saturation coverage is dominated by the β_2 state which desorbs near 460 K. With increasing sulfur coverage the occupancy of the β_2 state is rapidly attenuated. It is important to note, however, that no apparent change occurs in the β_2 state desorption energy as the occupancy of the state falls. At $\theta_s = 0.3$ virtually no desorption from the β_2 state is observed. Neither the α or β states are appreciably affected as the sulfur coverage rises. In the 100–200 K region new states are observed to populate at $\theta > 0.3$.

Estimates of the occupation of the various states with sulfur coverage have been made. These are shown in fig. 3. The integrated total CO coverage falls smoothly with increasing sulfur coverage until $\theta_s = 0.3$. CO desorption from higher θ_s shows no further attenuation of CO adsorption. Of particular interest is the desorption area for the β_2 state. Just as in the case of the methanation rate, its population falls abruptly with θ_s such that at $\theta_s = 0.3$, population of the β_2 state is essentially zero. At this point, as seen in fig. 2, the methanation rate reaches its minimum. The population of the α and β_1 states, with the exception of a small increase near $\theta_s =$

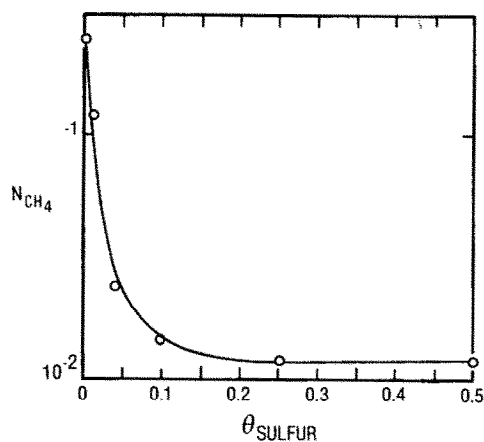


Fig. 2. Methanation rate as a function of sulfur coverage on a Ni(100) catalyst. Pressure = 120 Torr, $H_2/CO = 4/1$, reaction temperature = 600 K.

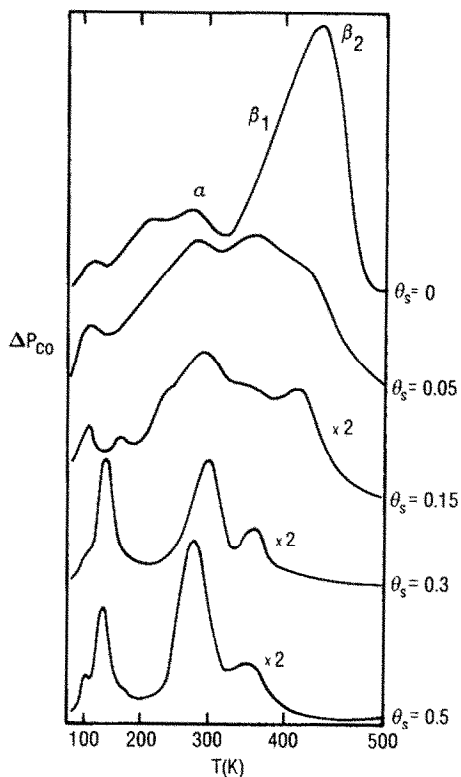


Fig. 3. Thermal programmed desorption spectra of CO (mass 28) as a function of sulfur coverage on Ni(100).

0.1, remain unaffected with change in the sulfur level.

Chemisorption of hydrogen on Ni(100) has also been carried out. The integrated results of the TPD data are shown in fig. 4. As with the β_2 state of CO, uptake of total hydrogen falls rapidly with θ_s . The zero intercept occurs approximately at the sulfur saturation coverage.

It is evident from the above chemisorption data that long range electronic effects are important at low sulfur coverages in inhibiting chemisorption of both hydrogen and the β_2 state of CO. Initial slopes of the population curves in fig. 4 for hydrogen and CO β_2 suggest that about ten equivalent nickel sites are blocked for adsorption by one sulfur atom. The combined effect of this reduction in coverage of CO and hydrogen is manifested in the methanation kinetics as a sharp attenuation of the rate at $\theta_s < 0.2$. Initially the rate appears to be affected primarily by a reduction of

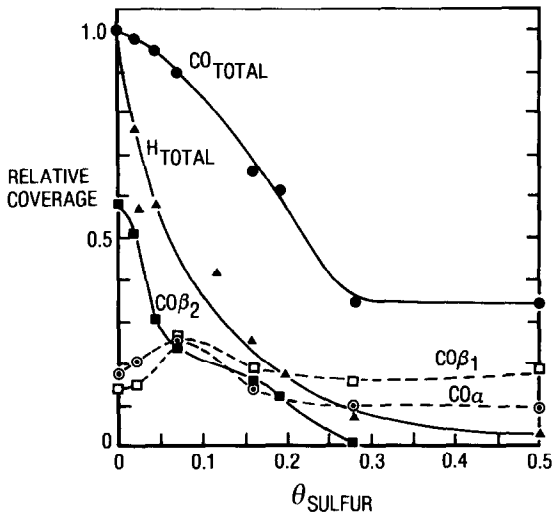


Fig. 4. Area under thermal programmed desorption spectra for H₂ and the α , β_1 , β_2 , as well as total CO curves as a function of sulfur precoverage.

the hydrogenation rate. This is evidenced by an increase at $\theta_s < 0.1$ of the steady-state carbon level present under reaction conditions. At sulfur levels less than 0.1, the reaction still remains essentially independent of the CO partial pressure in the the nonlinear portion of the Arrhenius line and first order in hydrogen partial pressure. As in the case of the clean surface, the steady-state carbon level in the non-linear Arrhenius region rises to the saturation level. This is consistent with the hydrogenation step being rate-limiting. As the sulfur level rises to $\theta_s \geq 0.25$ the reaction rate in the non-linear region becomes first order in CO partial pressure as well as hydrogen partial pressure. From the chemisorption data we anticipate this after observing that the binding energy of CO at $\theta_s > 0.25$ is reduced to approximately that for hydrogen.

Therefore for high θ_s , the reaction is inhibited both in the carbon formation step as well as in the carbon hydrogenation step. Poisoning is maximized at $\theta_s = 0.25$. The reaction rate at $\theta_s = 0.25$ corresponds to that characteristic of a surface at saturation sulfur coverage. An identical reduction of methanation activity for supported Ni/Al₂O₃ has been observed by Rostrup-Nielsen and Pedersen for sulfur poisoning [15]. These authors also observed a strong nonlinear effect of sulfur on the reaction rate and, as here, a constant activation energy with sulfur coverage. They concluded that the nonlinear sulfur poisoning effect correlates with the reaction requirement of an ensemble of nickel atoms of perhaps four. Likewise work by Dalla-Betta, Peken, and Shelef [16] on supported nickel on alumina showed a factor of 50 reduction in steady-state methanation activity in the presence of sul-

fur. The excellent agreement between the results for both Ni(100) and supported nickel after sulfur deactivation illustrates, as has been shown for clean Ni(100) [13], how single crystals can be successfully employed as a convenient model for technical catalysts.

To summarize, sulfur at $\theta_s < 0.2$ very effectively poisons the Ni(100) surface both for catalytic methanation, CO_{β2} adsorption, as well as hydrogen chemisorption. This poisoning effect is nonlinear – one sulfur atom deactivates approximately ten nickel atom sites. The results of chemisorption studies suggest that the attenuation of H₂ and CO_{β2} chemisorption is responsible for the reduction of catalytic activity. These data are consistent with electronic effects playing a major role at low sulfur coverages in reducing the reaction rate. Work is in progress with other surface additives of varying electronegativity to define in more detail the nature of catalytic deactivation.

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