

Model Catalytic Studies over Metal Single Crystals[†]

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Received July 11, 1983 (Revised Manuscript Received December 16, 1983)

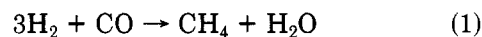
Heterogeneous catalysis is of major importance to most chemical and fuel technologies. Little is known, however, about surface reactions at the molecular level because the tools for such investigations have only become recently available. During the past 2 decades, modern surface science¹ has provided an array of techniques to characterize the surface region and, consequently, the ability to study molecular adsorption and reaction on a molecular level. The ordering of surface atoms in ideal cases can be ascertained with precision by using low-energy electron diffraction (LEED), and their oxidation states can be probed by using X-ray photoelectron spectroscopy (XPS). The surface composition can be determined in most cases with a sensitivity better than 1% with Auger spectroscopy (AES) and XPS. Other techniques such as ultraviolet photoelectron spectroscopy (UPS), high-resolution electron energy loss spectroscopy (HREELS), secondary ion mass spectrometry (SIMS), ion scattering spectroscopy (ISS), and molecular scattering permit study of adsorption and reaction on atomically clean surfaces. The data obtained by these sensitive techniques provide an important link to the understanding of reaction mechanisms and the relationship between the reactivity of a surface, its structure, and its composition.

Most surface techniques require an ultrahigh vacuum environment and generally are best utilized in studying low-surface materials such as single crystals with areas of $\sim 1 \text{ cm}^2$. Correlating information between such an idealized system and high-area, supported catalysts at atmospheric conditions understandably can be criticized. Indeed, if metal single crystals are to be used as catalyst models, it is essential to demonstrate the relationship of their kinetic parameters to high-area, supported catalysts at realistic reaction conditions. The measurement of these parameters for single crystals and their relationship to working catalysts are essential features of our research program.

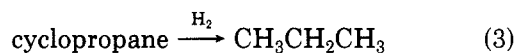
These studies use the specialized apparatus² shown in Figure 1. The custom-built catalytic reactor, contiguous to the surface analysis system, employs a retraction bellows that supports the metal crystal. The samples can be translated in situ from the reactor to the surface analysis chamber. Typically, the single crystals are spotwelded to short, high-purity leads and resistively heated. High-purity gases are used to mea-

sure kinetics at up to $\sim 2 \text{ atm}$; gas chromatography provides a convenient and sensitive technique for product analysis. Auger spectroscopy is used to document surface composition prior to and subsequent to reaction rate measurements.

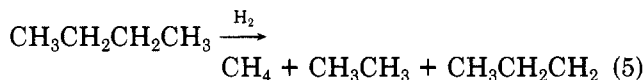
This apparatus has been used to study the reactions in eq 1-6, over single crystals of nickel, ruthenium, and rhodium. These reactions exemplify two major types methanation



hydrogenation



hydrogenolysis



of catalytic progresses,³ namely, those that are sensitive to catalyst particle morphological changes and those that are not. Reactions 1-3 are structure insensitive, whereas reactions 4-6 are sensitive ones.

Structure-Insensitive Reactions over Clean Single-Crystal Surfaces

Methanation⁴ (reaction 1) has a critical role in the production of synthetic natural gas from hydrogen-deficient materials. In addition, this reaction is an obvious starting point in studies of fuel and chemical synthesis, in general, from a carbon source. Historically this reaction was considered to be structure insensitive⁴ in that, generally, changes in catalyst morphology produce, at most, small changes in the catalytic activity. Catalytic activity is usually expressed in terms of specific activity, i.e., the catalytic rate normalized to the number of exposed metal sites. Specific activity is expressed as a turnover frequency or molecules of product pro-

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[†]This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract No. DE-AC04-76DP00789.

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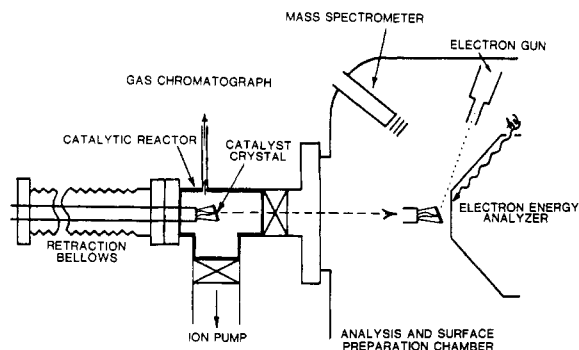


Figure 1. An ultrahigh vacuum apparatus for studying single-crystal catalysis before and after operation at atmospheric pressure in a catalytic reactor.

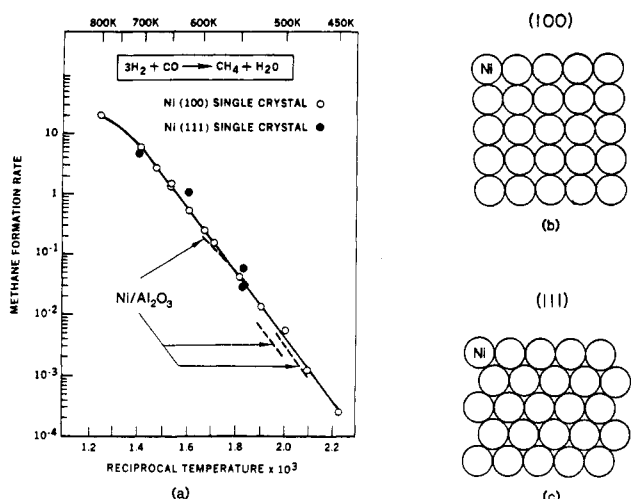


Figure 2. (a) A comparison of the rate of methane synthesis over single-crystal nickel catalysts and supported Ni/Al₂O₃ catalysts at 120-torr total reactant pressure. (b) Atomic conformation of a Ni(100) surface. (c) Atomic conformation of a Ni(111) surface.

duced per metal atom site per second.

For methanation on nickel it has been possible to correlate kinetic parameters with those found for supported, high-area catalysts.⁵ The data in the Arrhenius plot of Figure 2 represent *steady-state*, specific reaction rates. The measurements were conducted over a period of months, using several crystals with a reproducibility of the specific rates within 5%. The data in Figure 2a are for a Ni(100) surface (Figure 2b) and for another low-index crystal plane, Ni(111)⁶ (Figure 2c). The similarity between the close-packed (111) and the more open (100) crystal plane of Ni is evident in both the value of the specific rates and activation energy (103 kJ mol). In the temperature range of 450–700 K, methane production rates vary by almost 5 orders of magnitude. It should be pointed out that such measurements are difficult, if not impossible, with high-area catalysts due to heat and mass transfer limitations.

These single-crystal results are compared in Figure 2 with three sets of data taken from ref 7 for nickel

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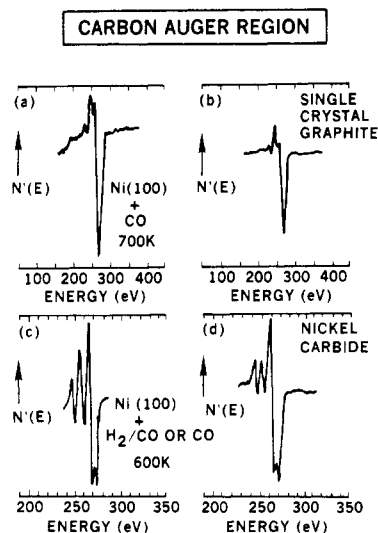


Figure 3. A comparison of AES carbon signals on a Ni(100) crystal with those from single-crystal graphite and nickel carbide. (a) Following 1000 s of heating at 700 K in 24 torr of CO. (b) Single-crystal graphite. (c) Following 1000 s of heating at 600 K in 24 torr of CO. (d) Nickel carbide.

supported on alumina, a high-surface-area catalyst. This comparison shows extraordinary similarities in kinetic data taken under nearly identical conditions. Thus, for the H₂/CO reaction over nickel, there is *no significant variation* in the specific reaction rates nor the activation energy as the catalyst changes from small metal particles to bulk single crystals. These data provide convincing evidence that the methanation reaction rate is insensitive to the surface structure of the nickel catalyst.

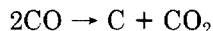
For reactions insensitive to structural effects, the surface characteristics of the single-crystal catalyst should simulate the active metal of a supported catalyst in the same reactant environment. This proves to be most fortunate since the advantages of single crystals are retained along with the relevance of the measurements. Moreover the use of single crystals allows the assessment of the crystallographic dependence of structure-sensitive reactions.

For the methanation reaction, surface characterization subsequent to reaction has provided data addressing the reaction mechanism. Auger spectroscopic analysis of an active nickel catalyst following reaction at atmospheric pressure⁵ has been accomplished by transferring the crystal to the surface analysis chamber. Auger analysis after such a procedure shows a carbonaceous species present on the surface at a concentration equivalent to approximately 10% of a monolayer (a monolayer, ML, in this context is defined as one atom per one substrate metal atom). The Auger spectrum shown in Figure 3c indicates this carbon to be a "carbide" form with a line shape distinctive from that of graphitic carbon^{5,8} shown in Figure 3b. This carbide-type carbon can be readily removed by heating the crystal to 600 K in H₂, with the product formed being methane. A carbon species with these same characteristics can be produced by heating the Ni crystal in CO in the absence of hydrogen. Figure 3 shows the AES carbon signal⁵ measured after heating

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a Ni(100) crystal in several torrs of CO at 600 K (Figure 3c) and at 700 K (Figure 3a). These carbon peaks are compared with those observed with single-crystal graphite (Figure 3b) and with bulk nickel carbide (Figure 3d). On the basis of this comparison, the active carbon form has been designated "carbide" and the inactive "graphitic". The deposition of an active carbon and the absence of oxygen on the nickel surface following heating in pure CO is consistent with a well-known disproportionation reaction, the Boudouard reaction



which has been studied on supported Ni catalysts^{9,10} and on Ni films.¹¹ Studies, such as those described here, showed that methane could be catalytically synthesized over Ni by an active (carbide) carbon formation via the Boudouard reaction and its subsequent hydrogenation to methane. However, to demonstrate that this surface carbon route is the major reaction pathway, kinetic measurements of both carbon formation from CO and its removal by H₂ were carried out.¹²

In the first set of measurements¹² a Ni(100) sample was cleaned by using standard procedures.⁵ The rate of carbon buildup on the surface was measured at various temperatures as follows: (1) surface cleanliness was established by AES, (2) the sample was then retracted into the reaction chamber and exposed to several torrs of CO for various times at a given temperature, (3) after evacuation the sample was transferred to the analysis chamber, and (4) the AES spectra of C and Ni were measured. Two features of this study are noteworthy: (a) Two kinds of carbon forms are evident—a carbide type that occurs at temperatures <650 K and a graphite type at temperature >650 K. The carbide form saturates at 0.5 monolayer. (b) The carbon formation data from CO disproportionating indicates a rate equivalent to that observed for methane formation in a H₂/CO mixture. Therefore, the surface carbon route to product is sufficiently rapid to account for methane product with the assumption that kinetic limitations are not imposed by the hydrogenation of this surface carbon.

A second set of experiments¹² further supported the surface carbon route to methane. In these experiments a Ni(100) surface was precarbided by exposure to CO and then treated with hydrogen in the reaction chamber for various times. Steps 3 and 4 above were then followed to measure the carbide level. This study showed that the rate of carbon removal in hydrogen compared favorably to the carbide formation rate in CO and to the overall methanation rate in H₂/CO mixtures. Thus in a H₂/CO atmosphere the reaction rate is determined by a delicate balance of the carbon formation and removal steps, and neither of these is rate determining in the usual sense.

According to this mechanism, if the surface coverage of atomic hydrogen is close to saturation, it is predicted that (a) further increases in hydrogen pressure would have almost no effect on the methane rate and (b) a low surface carbon level will result. This is the condition believed to exist under the reaction conditions of Figure

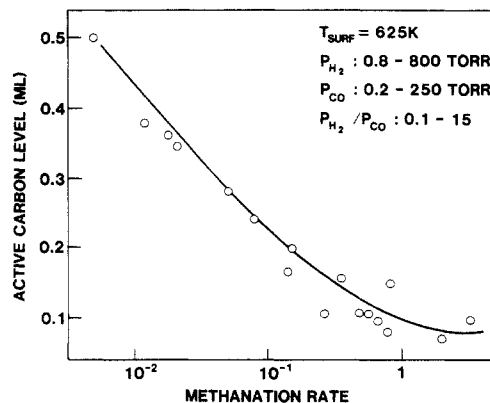


Figure 4. Methane production rate at 625 K over a Ni(100) catalyst as a function of surface carbon coverage at various reaction conditions.

2a. However, if reaction conditions are altered such that the surface hydrogen concentration decreases (e.g., low H₂ pressure and/or high temperature), then the mechanism demands a correlation of decreasing methane yield with increasing surface carbide. This correlation between the rate of production of methane and the steady-state surface carbide concentration holds very well as evidenced by the data in Figure 4.⁶ Here all reaction rate data measured over a Ni(100) catalyst at 625 K lie on a smooth curve when plotted against the measured steady-state carbide level, regardless of H₂/CO ratio or total pressure.

Thus, the proposed reaction mechanism involving the dissociation of CO and the subsequent hydrogenation of the resulting carbon species (C_{ads}) accounts quite satisfactorily for the effect of pressure on the methanation rate, for the variation in the measured surface carbon level as reaction parameters are changed, and for the formation at a characteristic temperature and pressure conditions of a catalyst-deactivating graphitic carbon. Recent studies¹³ using isotopically labeled CO have shown that the CO dissociation step is essentially unidirectional in that the rate of C_{ads} and O_{ads} recombination is insignificantly slow compared to the C_{ads} hydrogenation rate.

Methanation over Ni, over Ru,^{6,14} and over Fe¹⁵ shows remarkable similarities in many critical parameters, suggesting that the three metals behave essentially the same catalytically. This conclusion finds support in recent studies with nickel, ruthenium, and cobalt high-surface-area, supported catalysts^{9,10,16,17} and with studies using Ni, Co, and Ru films in UHV.¹⁸

The close correspondence between the catalytic studies using single metal crystals and results for high-area, supported catalysts attests to the structure insensitivity of the methanation reaction. Other reactions are believed to be structure insensitive and should be amenable to relevant modeling with metal single-crystal catalysts. Two such reactions have been studied recently: ethylene hydrogenation¹⁹ (reaction 2) and

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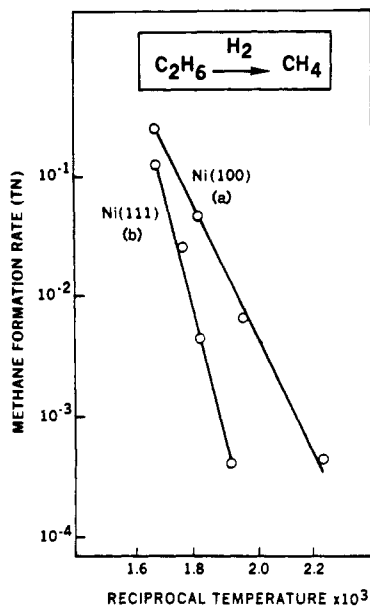


Figure 5. (a) Methane production from ethane over a Ni(100) catalyst at a total reactant pressure of 100 torr, $H_2/C_2H_6 = 100$. (b) Methane production from ethane over a Ni(111) catalyst at a total reactant pressure of 100 torr, $H_2/C_2H_6 = 100$.

cyclopropane hydrogenation²⁸ (reaction 3). The details of these studies will not be discussed in this account; however, these data, as those for methanation, show similar correlations between the model systems and the supported, high-area catalysts.

Structure-Sensitive Reactions over Clean Single-Crystal Surfaces

The activity of metal catalysts toward alkane hydrogenolysis (reactions 4–6) generally depends markedly on the metal particle size and upon the nature of the metal.^{20,21} These reactions therefore have been described as structure sensitive. Although there is a consensus in the literature regarding the relationship of particle size to activity, no such consensus exists in detailing the origins of the effect. Recent work by Martin²² suggests that different activities of different crystal planes toward a given reaction could be responsible for the observed rate attenuation with increasing particle size. For example, if (111) orientations become dominant as the metal particles become larger and if these crystal planes exhibited a lower activity toward hydrogenolysis, then the activity of the catalyst would fall with particle growth. Martin further speculated that the lower activity of the (111) facet relative to other facets could be intrinsic or could arise from preferential poisoning of the (111) crystal plane by reactants or products. These studies emphasized the need for kinetic measurements over single metal catalysts. Such studies have been carried out for the hydrogenolysis of ethane,²³ *n*-butane,²⁴ and cyclopropane.²⁸ These results confirm that the (111) surface is indeed significantly less active toward hydrogenolysis than the

(100) surface. This reduced activity has been shown to be intrinsic and not due to selective poisoning of the (111) surface by carbon.

Figure 5a shows the specific reaction rate for methane formation from ethane over a Ni(100) catalyst. At a given temperature the rate of methane production over an initially clean crystal was constant with no apparent induction period. The carbon level during reaction remained constant at a submonolayer coverage. The methane frequency turnover during a fixed time (typically 1000 s) was determined with use of the Ni(100) atom density of 1.62×10^{15} atoms/cm².

Figure 5b shows the kinetic data for ethane hydrogenolysis over a Ni(111) catalyst. As observed for the (100) catalyst, the carbon level during reaction remained constant at submonolayer coverages. The specific rate was determined with use of the Ni(111) atom density of 1.88×10^{15} atoms/cm². It is evident that the activity of the (111) surface toward ethane hydrogenolysis is considerably less than that observed for the (100) surface as suggested by Martin.²² The kinetic results for the Ni(111) catalyst agree favorably with the data of Martin²² for Ni/SiO₂ catalysts reduced at high temperature with a resulting larger particle size. Such severely fired catalysts are expected to contain metal crystallites exposing predominantly (111) faces.²⁵

The origin of the lower activity associated with the (111) surface compared with the (100) is not presently understood. We can speculate that electronic differences, which most certainly exist, are responsible. An additional contribution could be the spatial distribution of the high-coordination bonding sites,²³ those on the (111) surface being more favorable for stabilization of C₂ fragments. The result of this stabilization is that the (111) surface is less effective in cleaving carbon-carbon, an obvious crucial step in hydrogenolysis.

Although the chemistry of these observations is not well-understood, it is clear that these kinds of studies are necessary in detailing the origins of this most intriguing aspect of catalysis by metals.

Reactions over Chemically Modified Surfaces

Electronegative Modifiers. One particularly promising extension of the previously discussed work is surface modification by additives and their influence on reaction kinetics. Current ultrahigh vacuum surface techniques permit experiments to be carried out with a level of atomic characterization precluded using classical catalytic methods. Examples are recent studies into the nature of poisoning by sulfur of the catalytic activity of nickel toward methanation of CO²⁶ and CO₂,²⁷ hydrogenolysis,^{28,29} and hydrogenation.¹⁹

Previous work^{30,31} using LEED, UPS, and other surface techniques has shown that sulfur is chemisorbed on the Ni(100) surface in an ordered sequence. The sulfur forms a p(2 × 2) structure (Figure 6a) at 0.25 monolayer and a c(2 × 2) structure (Figure 6b) at 0.5 monolayer, which corresponds to a saturation coverage.

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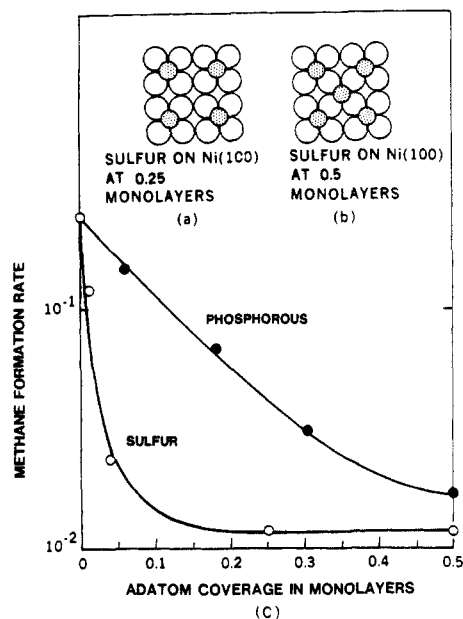


Figure 6. Methanation rate as a function of sulfur and phosphorus coverage on a Ni(100) catalyst. Pressure = 120 torr, $H_2/CO = 4/1$, reaction temperature = 600 K.

This well-behaved system provides an excellent model for studying poisoning of nickel by sulfur. The ordered LEED patterns allow sulfur coverage determination by AES by providing calibration points. Kinetic studies²⁶ have been carried out for several reactions as a function of sulfur coverage over Ni(100) and Ni(111) surfaces. The sulfur levels were established by exposure of the sample to H_2S at 300 K followed by heating to 600 K. The surface coverage of sulfur was determined by measuring the S_{152}/Ni_{848} AES peak height ratio.

For the methanation reaction the sulfided surface²⁶ shows behavior remarkably similar to results for the clean surface at considerably reduced hydrogen partial pressure. For clean Ni(100),⁵ a departure from Arrhenius linearity is observed at ~ 700 K. Associated with the negative deviation of this plot is a rise in the surface carbon level that continues until the carbon level reaches 0.5 ML, the saturation level. This deviation, or rollover, of the Arrhenius plot has been interpreted⁵ as reflecting the departure of the surface concentration of atomic hydrogen from a saturation or critical coverage. For a sulfur surface coverage of 4%, the reaction rate at identical conditions departs similarly from linearity at ~ 600 K,²⁶ some 100 degrees lower reaction temperature. Here, too, an increase in surface carbon level is associated with this deviation from linearity. This behavior indicates that the sulfur is very effective in reducing the steady-state surface atomic hydrogen coverage that results in an attenuation of the rate of surface carbon hydrogenation. The effectiveness of sulfur in poisoning both H_2 dissociation as well as the total atomic hydrogen coverage has been measured directly by using thermal programmed desorption (TPD). These studies²⁶ reveal that both H_2 sticking coefficients, as well as the capacity of the Ni(100) surface for atomic hydrogen, fall dramatically upon the addition of small amounts of sulfur.

The kinetics and the TPD studies show that the poisoning effect of sulfur is very nonlinear. Figure 6c shows this nonlinear relationship between the sulfur coverage and the methanation rate at 600 K. A rapid

drop is seen for the catalytic activity at low sulfur coverages. The poisoning effect quickly maximizes and no further reduction in reaction rate is found at sulfur levels exceeding 0.2 monolayer. An identical reduction of methanation activity for supported Ni/ Al_2O_3 has been observed by Rostrup-Nielsen and Pedersen for sulfur poisoning.³² These authors as well observed a nonlinear effect of sulfur on the reaction rate. Likewise, other workers³³ have shown a similar reduction in steady-state methanation activity in the presence of sulfur on supported nickel. Apparently sulfur bonded in the $p(2 \times 2)$ configuration sufficiently deactivates the nickel surface for methanation that further addition of sulfur produces no reaction rate attenuation. The unoccupied fourfold nickel sites remaining at a sulfur coverage of 0.25 monolayer are effectively poisoned for carbon formation and carbon hydrogenation catalysis. The initial change in the reaction rate poisoning in Figure 6c suggests that 10 or more equivalent nickel sites are deactivated by one sulfur atom. There are two possible causes for this effect: (a) a long-range electronic effect (ligand effect) or (b) an ensemble effect, the requirement that a certain number or conformation of surface atoms are necessary for a reaction to occur. Experimentally these two possibilities can be distinguished. If long-range electronic effects are most important, then the reaction rate is expected to be a function of the relative electronegativity of the poison. If indeed a 10-nickel atom ensemble is required for methanation, then changing the electronic character of the poison should produce little change in the reaction rate attenuation. Substituting phosphorus for sulfur in a similar set of experiments^{34,35} results in a marked change in the magnitude of poisoning at low coverages as indicated in Figure 6c. Phosphorus, because of its less electronegative character, poisons only the four nearest-neighbor metal atom sites. These results support the conclusion that long-range electronic effects are playing a major role in the deactivation process.

Similar nonlinear poisoning of nickel by sulfur has now been seen for other catalytic reactions, including cyclopropane hydrogenolysis,²⁸ ethylene hydrogenation,¹⁹ and CO_2 methanation.²⁷ The data also suggest that the dominant sulfur poisoning mechanism is electronic and extends over distances larger than the sulfur atomic radius.

Chemisorption studies^{26,35,36} of H_2 and CO on a C, N, S, P, and Cl precovered Ni(100) surface support the conclusion drawn above. For H_2 and CO chemisorption, a correspondence exists between the relative electronegativity of the preadsorbed atom and the inhibition of sticking coefficients and the capacity of the surface for adsorption. At this point little theoretical work has been undertaken to address directly the predicted magnitude of the near-surface electronic perturbations by impurity atoms. Work by Grimley and others³⁷ has suggested that atom-atom interactions through several lattice spacings should occur, although these studies did

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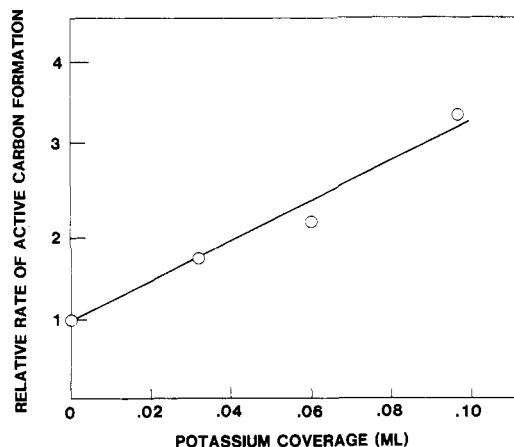


Figure 7. The relative initial rate of reactive carbon formation from CO disproportionation as a function of potassium coverage. $P_{\text{CO}} = 24$ torr, $T = 500$ K.

not specifically address the effects of sulfur. Calculations expressly addressing the surface electronic perturbation by sulfur have recently been reported.³⁸

Electropositive Modifiers. The addition of electron-donor compounds such as potassium is known to increase the activity, the resistance to poisoning, as well as the selectivity of metallic catalysts toward various reactions.³⁹ In the hydrogenation of CO over iron catalysts, it is essential that a certain amount of potassium compound be present on the catalyst.³⁹ This promoter increases the CO conversion and shifts the selectivity toward the more useful long-chain hydrocarbons and toward olefins. Although the result of adding such promoters is recognized, the mechanism of their action is not well-understood.

Alkali adatoms on a transition metal surface are known to exist in a partially ionic state, donating a large fraction of their valence electron to the metal, resulting in a work function decrease.⁴⁰ This additional electron density on the transition-metal surface atoms has been shown to be a major factor in explaining the role of alkali adatoms in altering the chemisorptive bonding of adsorbed molecules such as N_2 ⁴¹ or CO ⁴² and in promoting catalytic activity in ammonia synthesis.⁴³ As has been shown in this account, the role of electronegative adatoms (S, P) in poisoning Ni(100) methanation activity can be ascribed, to a large extent, to an electronic effect. Thus, one might expect an electropositive adatom such as potassium to have the opposite effect and to increase nickel's methanation activity. A recent study⁴⁰ has shown that this is not the case although certain steps in the reaction mechanism are strongly accelerated by the presence of potassium.

In a manner identical with that used for the clean Ni(100) surface,¹² the rate of carbide or reactive carbon formation via CO disproportionation ($2\text{CO} \rightarrow \text{C}_{\text{ads}} + \text{CO}_2$) was measured for the clean and potassium-covered surfaces by observing the growth in carbide AES with time in CO, starting from a carbon-free surface. Po-

tassium markedly increases the rate of CO dissociation. The increase of the initial rate of carbide buildup at 500 K with potassium coverage is shown in Figure 7. Of particular significance is the reduction of the activation energy of reactive carbon formation from ~ 23 kcal mol^{-1} for the clean Ni(100) surface to ~ 10 kcal mol^{-1} for a 10% surface coverage of potassium.

Kinetic measurements of methanation over a Ni(100) catalyst containing well-controlled submonolayer quantities of potassium adatoms show a decrease in the steady-state rate under a variety of reaction conditions. The presence of potassium did not alter the apparent activation energy associated with the kinetics. The potassium did, however, change the steady-state carbide coverage, which increased from 10% of a monolayer for clean Ni(100) to 30% of a monolayer for a potassium coverage of 10% of a monolayer. No apparent change was observed in the carbon AES line shape in the presence of potassium.

Adsorbed potassium caused a marked increase in the steady-state rate and selectivity of Ni(100) for higher hydrocarbon synthesis. The steady-state rate of conversion of CO into higher hydrocarbons on the potassium-dosed surface approached that of CO conversion into methane at low temperatures (< 500 K) but was only a small percentage of methane production at 600 K. At all temperatures studied, the overall rate of higher hydrocarbon production was faster on the potassium-dosed surface, so that potassium may be considered a true promoter with respect to this reaction, Fischer-Tropsch synthesis.

The effects of potassium upon the kinetics of CO hydrogenation on this model single-crystal Ni(100) catalyst are to (1) decrease the rate of methane formation and (2) increase the rate of higher hydrocarbon production. These same effects have been reported for high-surface-area, supported nickel catalysts. This agreement between bulk, single-crystal nickel and supported nickel indicates that the major mechanism by which potassium additives alter catalytic activity and selectivity is not related to the support material but that it is rather a consequence of direct K-Ni interactions.

Potassium adatoms, then, cause a very large increase in the rate of the CO disproportionation reaction and a decrease in its activation energy for low carbon coverages. These effects can be explained in terms of an electronic ligand effect, whereby the electropositive potassium adatom donates extra electron density to the nickel surface atoms, which in turn donate electron density to the adsorbed CO molecule. This increases the extent of π -backbonding in the metal-CO complex, resulting in an increased metal-CO bond strength and a decrease in C-O bond strength. This model satisfactorily explains the decrease in the activation energy for carbide buildup brought about by potassium.

In spite of this increase in the rate of CO dissociation or carbide buildup, the overall rate of methanation decreases and the activation energy is unchanged in the presence of potassium. This indicates that another step in the methanation sequence, either hydrogen adsorption or hydrogenation but not CO dissociation, is rate limiting for methane production under these conditions.

The influence of adsorbed potassium upon the synthesis of higher hydrocarbons is consistent with results on supported catalysts. For these reactions, it is likely

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that carbon chain growth is rate limiting. Thus, the observed effect of potassium to increase the steady-state carbide coverage can be related to the increase in supply of reactants for chain growth. That is, the more carbon present on the surface, the greater the chances for reaction events leading to C-C bond formation. This satisfactorily explains the observation that the activity for higher hydrocarbon production increases upon dosing with potassium. This is also consistent with the observation on clean Ni(100) that conditions leading to higher equilibrium carbide coverages shifts the product distribution toward higher hydrocarbons.

Conclusions and Outlook

This account has dealt with a portion of studies now being carried out integrating surface science techniques with kinetics at realistic reaction pressures.^{1,15} These studies are offering a new perspective to the fundamental understanding of heterogeneous catalysis. These new techniques cannot, by any means, displace

the traditional methods employed but serve rather to complement them. Their power lies mainly with the ability to tie the model surface studies to parallel studies on high-area, supported catalysts. Thus far these comparisons, as we have seen, are most comforting. The future success of the surface science approach to catalysis will be determined by the ability of the workers in the area to fully appreciate the wealth of catalytic information that has accumulated over the years in the literature, to understand the current research and problems of catalysis, and to attack those problems most suitable for study using modeling techniques. This, coupled with a close interplay between the surface science community and the traditional catalytic community, promises that the future for fundamental research in the catalytic area will be both fruitful and exciting.

We acknowledge with pleasure the partial support of this work by the Department of Energy through the Division of Basic Energy Sciences.