Chapter III: Catalytic Activation of CO Over Single Crystals

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ABSTRACT

The catalytic activation of CO single crystal surfaces is reviewed. Examples are provided which demonstrate the relevance of single crystal studies for modeling the behavior of high surface area supported catalysts. The coupling of an apparatus for the measurement of reaction kinetics at elevated pressures with an ultrahigh vacuum system for surface analysis allows detailed study of structure sensitivity, the effects of promoters and inhibitors on catalytic activity, and, in certain cases, identification of reaction intermediates by post-reaction surface analysis. Studies of CO methanation over single crystal surfaces provide convincing evidence that this reaction is structure insensitive, and that it occurs in the presence of an active carbidic overlayer on the catalytic surface. For the water-gas shift reaction (a structure-sensitive reaction), model single crystal studies allow correlations to be drawn between surface structure and catalytic activity. The effects of both electronegative (S and P) and electropositive (alkali metals) impurities on the catalytic activity of metal single crystals for CO methanation and the water-gas shift reaction are discussed.
III.1 INTRODUCTION

One of the important challenges in basic and applied science is to understand how the atomic structure and composition of the surface of a catalyst determine catalytic activity and selectivity. Over the past 20 years many electron spectroscopies have been developed that permit the study, on the molecular level, of surfaces and adsorbates in ultrahigh vacuum (UHV) conditions [1,2]. This has furthered our understanding of the chemistry of metal surfaces [1-3]. Unfortunately, the conditions under which the analytical techniques of surface science can be applied are highly idealized.

The very low pressures required for surface science studies are typically many orders of magnitude below the pressures used in practical catalytic processes. In order to overcome this problem, several laboratories have developed experimental systems which combine a high pressure reactor system with an UHV analysis chamber [4-9]. The high pressure reactor allows the kinetics of catalytic reactions to be measured on a given surface, while analysis of the structure and composition of the surface both before and after reaction can be accomplished in the UHV analysis chamber. In many high-pressure/UHV studies a clean and well-defined, single-crystal plane is used to model a site or set of sites expected to exist on practical high-surface-area catalysts. This approach allows direct comparison of reaction rates measured on single crystal surfaces with those measured on more realistic supported metal catalysts, and also allows detailed study of structure sensitivity, the effects of promoters and inhibitors on catalytic activity, and, in certain cases, identification of reaction intermediates by post-reaction surface analysis.
In this chapter, we review existing literature that deals with the catalytic activation of CO on single-crystal surfaces. The following reactions are considered:

- methanation

\[ 3H_2 + CO \rightarrow CH_4 + H_2O \]  

(1)

- water-gas shift

\[ H_2O + CO \rightarrow H_2 + CO_2 \]  

(2)

- methanol synthesis

\[ CO + 2H_2 \rightarrow CH_3OH \]  

(3)

Examples are provided which demonstrate the relevance of single crystal studies for modeling the behavior of high surface area supported catalysts.

### III.2 METHANATION OF CO ON SINGLE CRYSTAL SURFACES

The reaction of low concentrations of CO in a mixture with H₂ to form CH₄ was developed as a gas-purification process in the 1950s [10]. At the present time, the methanation reaction has a critical role in the production of synthetic natural gas from hydrogen-deficient carbonaceous materials [10-12]. In addition, the reaction is an obvious starting point in studies of fuel and chemical synthesis from carbon sources [10-12]. In the last ten years the methanation reaction over single crystal surfaces has been the subject of many investigations. Here we review the results of these investigations. We begin with a discussion of the studies on monometallic (section III. 2.1.1) and bimetallic (section III. 2.1.2) single crystal surfaces. Next the results of studies dealing with the effects of electronegative (section III. 2.2.1) and electropositive (section III. 2.2.2)
impurities on the kinetics of the methanation reaction are presented. Finally, we show studies concerned with metal-support interactions and the methanation reaction (section III. 2.3).

III.2.1 CO Methanation on clean metal single crystals.

III.2.1.1 Monometallic surfaces

A. Ni(100) and Ni(111)

The data in the Arrhenius plot of fig. 1a represent steady-state specific methanation rates (CH$_4$ molecules/site-s) on both the Ni(111) and Ni(100) surfaces [13]. At a given temperature the rate of production of CH$_4$ over an initially clean catalyst crystal was constant, with no apparent induction period [13]. The atomic configurations of the Ni(100) and Ni(111) surfaces are shown in figs. 1b and 1c, respectively. The similarity between the data for the close-packed (111) and for the more open (100) crystal plane of Ni is evident in both the specific rates and activation energy (103kJ/mol).

The single crystal results are compared in fig. 1a with three sets of data taken from ref. [14] for alumina supported nickel catalysts. This comparison shows extraordinary similarities in kinetic data taken under nearly identical conditions. Thus, for the H$_2$ + CO reaction over nickel, there is no significant variation in the specific reaction rates or the activation energy as the catalysts change from small metal particles to bulk single crystals. These data provide convincing evidence that the methanation reaction rate is indeed structure insensitive on nickel catalysts.

Post-reaction analysis of the surface of the Ni crystal catalysts with Auger electron spectroscopy (AES) showed a low level of a carbon species and
the absence of oxygen [6,13]. The Auger lineshape for the carbonaceous residue was similar to that of nickel carbide, indicating that the carbon was in a "carbidic" form [6]. Experiments were carried out studying the interaction of CO (24 Torr, 0-1000s exposures) with Ni(100) at different temperatures (450-800K) [15]. AES data showed the deposition of carbon on the surface and the absence of oxygen. Two kinds of carbon were formed on the surface: a carbidic type which occurs at temperatures <650K and a graphite type at temperatures >650K. The carbide type saturates at 0.5 monolayers, and can be readily removed from the Ni(100) surface by heating the crystal to 600K in 1 atm of H₂ with methane formed as the product. In contrast, the graphite type is a poison. The deposition of an active carbon residue 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,

\[ 2\text{CO} \rightarrow \text{C}_2 + \text{CO}_2 \quad (4) \]

which has been studied on supported Ni catalysts [16,17] and on Ni films [18]. On Ni(100), the carbon formation data from CO disproportionation 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 production with the assumption that kinetic limitations are not imposed by the hydrogenation of this surface carbon.

A set of experiments was performed [15] in which a Ni(100) surface was precarbided by exposure to CO and then treated with hydrogen in the reaction chamber for various times. This study showed that the rate of carbon removal in hydrogen compared favorably to the carbide formation rate from CO and to the overall methanation rate in H₂/CO mixtures. Thus in a H₂ + CO atmosphere
the methanation 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 [6,13-15]. More recent studies [19] using isotopically labeled CO have shown that the CO dissociation step is essentially unidirectional in that the rate of Cₐ and Oₐ recombination is insignificantly slow compared to the Cₐ hydrogenation rate.

Figure 2a shows the changes in the methanation reaction rate as the total pressure is increased from 1-120 Torr at a fixed H₂:CO ratio [13]. At low temperatures the rates fall on the same straight line at all pressures. As the temperatures is increased, a deviation from linearity is seen - the higher the pressure the higher the deviation temperature. Accompanying this non-linear rate behavior is an increase in the active carbon level on the surface of the catalyst crystal [13]. It has been proposed [13] that this departure from the linearity of the rate in fig. 2a and the accompanying increase in the surface carbon level is due to a decrease in the surface coverage of hydrogen and thus a decrease in the rate of hydrogenation of surface carbon. According to the mechanism proposed above for CO methanation, if reaction conditions are altered such that the surface hydrogen concentration decreases (e.g. low H₂ pressure and high temperature) then a correlation between decreasing methane yield and increasing surface carbide should be observed. This correlation holds very well as evidenced by the data in fig. 3. Thus, the proposed reaction mechanism involving the dissociation of CO and the subsequent hydrogenation of the resulting carbon species (Cₐ) 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 characteristic temperature and pressure conditions of a catalyst-deactivating graphitic carbon.

**B. Ru(110) and Ru(001)**

Figure 2b displays steady state specific rates for CO methanation on two faces of ruthenium: the zig-zag, open (110), and the close-packed (001) [13]. While the comparison is limited, it is clear that the \( \text{H}_2 + \text{CO} \) reaction is quite similar in regard to the specific reaction rate and the activation energy for these two crystal planes of ruthenium. Thus, it appears that CO methanation is structure insensitive on ruthenium surfaces [13].

Post-reaction surface analysis of the Ru crystal catalysts with AES showed the presence of carbidic carbon [13]. The hydrogenation of this carbonaceous residue can be followed readily [13,20]. Furthermore, the specific rates of carbide formation on ruthenium surfaces from CO decomposition are equal to the rates of methane formation in CO + \( \text{H}_2 \) mixtures [13,20]. This experimental evidence suggests that the reaction mechanism for CO methanation on ruthenium surfaces is similar to that mentioned above for methanation over nickel surfaces. In fig. 2 the variation of the reaction rate with pressure is very similar for the Ni(100) and Ru(110) crystals. In both cases, the non-linear rate behavior is accompanied by an increase in the active carbon level on the surface of the catalyst crystal. It has been proposed [13] that the departure from linearity of the rate in fig. 2 is due to a decrease in the surface coverage of hydrogen, which causes a decrease in the rate of hydrogenation of surface carbon. In fact, since the binding energy of hydrogen on Ru is lower than on Ni [13,21], the deviation from
linearity should be expected at lower temperature for ruthenium. This is particularly evident in the 1 Torr data of figs. 2a and 2b.

C. W(110)

The methanation activities for W(110) [22] and Ni(100) [12] are compared in fig. 4 over a range of temperatures (fig. 4a) and H\textsubscript{2} partial pressures (fig. 4b). The data clearly indicate that W(110) is an active methanation catalyst, with an activity that in some cases can surpass the activity of Ni(100). Plotting the data in an Arrhenius fashion (fig. 4a) yields an apparent activation energy of 56 kJmol\(^{-1}\) for W(110), as compared to 103 kJmol\(^{-1}\) for Ni(100). The activation energy over W(110) is in reasonable agreement with the value of 63 kJmol\(^{-1}\) observed on catalysts prepared by decomposition of W(CO)\textsubscript{6} on alumina [23].

Auger electron spectra of the W(110) surface after steady-state reaction conditions indicated that the active methanation surface was highly carbidic [22], in contrast to the case of nickel, where the active methanation surface is the metal itself with only a low surface coverage (0.05-0.1 monolayers) of carbidic carbon species present [6,13]. The idea that the active W surface is carbidic is consistent with the significant hydrogenation activity reported for W carbide catalysts [22].

D. Rh(111)

CO hydrogenation over clean Rh(111) was studied at a temperature of 573K and partial pressures of 4.5 atm of H\textsubscript{2} and 1.5 atm of CO [24]. Under these reaction conditions the Rh catalyst produced primarily methane (90 wt\%) at an
initial rate of 0.15 molecules/site-s. Small amounts of C₂ and C₃ hydrocarbons were also formed, but no oxygenated hydrocarbons were detected. The rates of formation of all the products were found to be the same on the Rh(111) single crystal and on a polycrystalline Rh foil suggesting that CO hydrogenation is structure insensitive on these surface [24]. The results of AES showed the presence of ~1 monolayer of carbon on the surface of the Rh catalysts after 3 hours of reaction [24]. The close proximity of the Rh 256 and 302 AES peaks to the C 272 AES peak prevented an analysis of the lineshape of the carbon peak in order to determine the chemical nature of the carbonaceous residue.

**E. Fe(111)**

The hydrogenation of CO on the (111) face of iron was examined at partial pressures of 4.5 atm of H₂ and 1.5 atm of CO and at a temperature of 573K [25]. The major product of the reaction was methane (~70 wt%), which was formed at an initial rate of 1.35 molecules/site-s. The formation of C₂ (~20 wt%), C₃ and C₄ products was also observed.

**F. Mo(100)**

Figure 5 shows the effects of temperature and pressure on the rate of CO methanation over Mo(100). On this surface, the hydrogenation of CO produced primarily methane (~90 mol%), ethene and propene [26]. An activation energy of ~100 kJ/mole was found for the methanation reaction on Mo(100). The observed rate law for methanation (see fig 5b) is given by:

\[ r_{\text{CH}_4} = kP_{\text{CO}}^{+0.32} P_{\text{H}_2}^{+1.0} \]  \hspace{1cm} (5)
The positive power of rate dependence on the pressure of CO is unusual since the methanation rate has a negative-order dependence on CO partial pressure over Ni, Ru, Fe and Co catalysts [5,26,27].

Auger electron spectra taken after the hydrogenation reaction indicate that the "active" surface is covered by a submonolayer of a carbidic carbon species. The reaction is poisoned as the carbidic species is converted to graphitic carbon. The rate of poisoning is determined by the ratio of CO to H$_2$ in the reaction mixture and by the reaction temperature (lower CO:H$_2$ ratios and lower temperatures prolong the lifetime of the active catalyst).

The following set of elementary steps was proposed for the methanation reaction on Mo(100) [26]:

1. $\text{CO}_\text{g} \rightarrow \text{CO}_\text{a}$ (6)
2. $\text{H}_2,\text{g} \rightarrow \text{H}_2,\text{a}$ (7)
3. $\text{CO}_\text{a} + \text{H}_2,\text{a} \rightarrow \text{CHOH}_\text{a}$ (8)
4. $\text{CHOH}_\text{a} + \frac{1}{2} \text{H}_2,\text{a} \rightarrow \text{CH}_\text{a} + \text{H}_2\text{O}$ (9)
5. $\text{CH}_\text{a} + \frac{3}{2} \text{H}_2,\text{a} \rightarrow \text{CH}_4,\text{g}$ (10)

In terms of this model the rate-determining step is reaction (9) and all the steps preceding it are in quasiequilibrium. A mathematical analysis of this kinetic model [26] leads to a rate expression of the form:

$$r_{\text{CH}_4} = k_{\text{CO}}^{0.5} P_{\text{H}_2}^{1.0},$$

which is in reasonable agreement with the experimental results of fig. 5b. Reactions (6) to (10) probably take place on top of a carbidic overlayer [26].

This overlayer will deactivate by forming graphite on the surface, which will block the reaction sites.
No differences in either rates or product distributions were observed between CO hydrogenation on Mo(100) and over polycrystalline Mo foils [26]. Thus, the reaction does not appear to be structure sensitive on molybdenum surfaces.

G. Summary

Table I shows the apparent activation energies observed for CO methanation on different single crystal surfaces. In general, the energies are close to the value of 110 kJ/mol. The only exception is W(110), with an apparent activation energy of 56 kJ/mol. The studies reviewed in this section provide convincing evidence that the methanation reaction is structure insensitive on surfaces of Ni, Ru, Rh, Fe and Mo. On these metals the methanation of CO occurs in the presence of an active carbidic overlayer. The transformation of this overlayer into graphite leads to a decrease in the catalytic activity of the metal surfaces.

III.2.1.2 Bimetallic surfaces

Catalytic properties of metal surfaces can be altered greatly by the addition of a second transition metal [28]. In many cases, mixed-metal systems are superior over their single-metal counterparts in terms of catalytic activity and/or selectivity [28]. Many fundamental studies have focussed on trying to understand the roles of "ensemble" and "ligand" effects in bimetallic catalysts [28,29]. Ensemble effects are defined in terms of the number of surface atoms needed for a catalytic process to occur. Ligand effects refer to those modifications in catalytic activity or selectivity that
are the product of electronic interactions between the components of a bimetallic system. In gathering information to address these issues, it has been advantageous to simplify the problem by utilizing models of bimetallic catalysts such as the deposition of metals onto single-crystal substrates. Work on ultrathin metal films supported on well-defined metal surfaces (Cu on Ru(0001) [30-33]; Cu, Ni, Pd and Pt on W(110) and W(100) [34-38]; Fe, Ni and Cu on Mo(110) [39,40]; and Fe and Cu on Re (0001) [40,41]) has shown that a metal atom in a matrix of a dissimilar metal can be significantly perturbed, and that this perturbation can dramatically alter the chemical and electronic properties of both constituents of the mixed-metal system.

The studies reviewed here are part of a continuing effort to identify those electronic and structural properties of bimetallic systems which can be related to their superior catalytic abilities.

**A. Ni/W(110) and Ni/W(100)**

The Ni/W(100) and Ni/W(110) systems are particularly interesting because they involve the addition of an active metal for CO methanation (Ni) to relatively inactive tungsten surfaces.

At ~100K, Ni is adsorbed layer by layer on W(110) and W(100) [36]. The results of low-energy electron diffraction (LEED) indicate that at coverages up to 1 ML the Ni films grow pseudomorphically with respect to the W(110) and W(100) substrates [36]. This growth pattern leads to Ni monolayer densities on W(110) and W(100) which are 21% and 38% less than the corresponding monolayer densities for Ni(111) and Ni(100), respectively.

Specific rates of CH₄ production, expressed as turnover frequencies (CH₄
molecules/Ni atom-s), over Ni covered W(110) and W(100) surfaces are shown in fig. 6 [38]. Under the experimental conditions of this figure, the reaction rates on the clean W surfaces were ~10^2 times lower than on the Ni covered surfaces. Figure 6a shows that for a total pressure of 120 Torr, Arrhenius behavior is observed over the entire temperature range studied (450-700K) as the CH₄ production rates vary by almost 3 orders of magnitude. The similarity between Ni/W(110) and Ni/W(100) at all the coverages studied is evident in both the turnover frequencies and activation energy, 77 ± 4 kJ/mole. The activation energy for the Ni covered W surfaces is lower than the value of 103 kJ/mole reported for Ni(100) and Ni(111) [13]. However, the specific rates for CO methanation on Ni/W(110) and Ni/W(100) correlate well with those observed on supported Ni catalysts, Ni single crystals and Ni films [38]. These results are further manifestations of the structure insensitive behavior of the CO methanation reaction and suggest that the mechanistic steps which control the rate of CO hydrogenation are the same in all these surfaces.

Lowering the total pressure has a significant effect on the rate of methane production (Figure 6b) for Ni supported on W(110) [38]. A similar effect was observed for Ni(100) (see figure 2a), and was attributed to a decrease in the concentration of atomic hydrogen on the surface as the pressure was lowered and the temperature was increased (see section 2.1.1) [13]. The departure from Arrhenius behavior occurs at lower temperature for Ni/W(110). This correlates [38] with the fact that the activation energy for H₂ desorption from Ni/W(110) (~71 kJ/mol [36]) is lower than that from Ni(100) (96 kJ/mol [42]).
B. Cu/Ru(001) and Ag/Rh(111)

A bimetallic system that has been extensively studied in supported catalyst research is copper on ruthenium [28,32,33]. The immiscibility of copper in ruthenium circumvents the complication of determining the three dimensional composition. The adsorption and growth of copper films on the Ru(0001) surface have been examined [30,31,43,44] by work function measurements, LEED, AES and TPD. The experimental evidence indicates that for submonolayer depositions at 100K the Cu grows in a highly dispersed mode, forming 2-D islands pseudomorphic to the Ru(001) substrate upon annealing to 300K. The pseudomorphic growth implies that the copper-copper bond distances are strained approximately 6% beyond the equilibrium bond distances found for bulk copper.

Copper surfaces are inactive catalysts for CO methanation. A study of the rate of CO methanation over Cu/Ru(001) [33] indicates that copper merely serves as an inactive diluent, blocking the active sites of the ruthenium surface in a one-to-one basis. Similar results have been found in analogous studies [45] introducing silver onto a Rh(111) methanation catalyst.

C. Co/W(110) and Co/W(100)

Cobalt forms pseudomorphic monolayers on W(110) and W(100) which are thermally stable to 1300K [46]. The cobalt overlayers are geometrically strained with respect to bulk cobalt surfaces. The pseudomorphic monolayer of Co/W(110) has an atomic density 21% less than Co(0001), while the pseudomorphic monolayer of Co/W(100) has an atomic density 45% less than Co(0001) [46]. However, the CO hydrogenation activity of these Co/W surfaces
is very similar [46]. A fact that suggests that CO hydrogenation is structure insensitive on cobalt surfaces [46].

AES spectra show the after-reaction Co/W surfaces to have high coverages of both carbon and oxygen, with carbon lineshapes characteristic of carbidic carbon [46]. The catalytic activity is apparently not correlated with surface carbon level [46].

III.2.2 CO Methanation in chemically modified surfaces.

The addition of impurities to a metal catalyst can produce dramatic changes in the activity, selectivity and resistance to poisoning of the catalyst. For example, the selectivity of some transition metals can be altered greatly by the addition of light metals such as potassium, and the activity can be reduced substantially by the addition of electronegative species such as sulfur. Although these effects are well-recognized in the catalytic industry, the mechanisms responsible for chemical changes induced by surface additives are poorly understood. An important question concerns the underlying relative importance of ensemble (steric or local) versus electronic (nonlocal or extended) effects. A general answer to this question will improve our ability to design efficient catalysts.

Catalyst deactivation and promotion are extremely difficult questions to address experimentally [47]. For example, the interpretation of related data on high-surface area supported catalysts is severely limited by the uncertainty concerning the structural characterization of the active surface. Specific surface areas cannot always be determined with adequate precision. In addition, a knowledge of the crystallographic orientation, the
concentration and the distribution of impurity atoms, as well as their electronic states is generally poor. The use of metal single crystals in catalytic reaction studies essentially eliminates the difficulties mentioned above and allows, to a large extent, the utilization of a homogeneous surface amenable to study using modern surface analytical techniques. In this section we review studies dealing with the effects of electronegative and electropositive surface impurities on the rates of CO methanation over single crystal catalysts. Although the studies to date are few, the results appear quite promising in addressing fundamental aspects of catalytic poisoning and promotion.

III.2.2.1 Electronegative impurities

Impurities whose electronegativities are greater than those for transition metals generally poison a variety of catalytic reactions, particularly those involving H₂ and CO. Of these poisons sulfur is the best known and is technologically the most important [10,47].

A. Atomic chlorine, sulfur and phosphorus on Ni(100)

The effects of preadsorbed Cl, S and P atoms on the adsorption-desorption of H₂ and CO on Ni(100) have been extensively studied [48-52] using Auger electron spectroscopy, low-energy electron diffraction and temperature programmed desorption. Figure 7 shows the variation of the saturation coverage of H₂ and CO on Ni(100) with the coverage of Cl, S and P. Both CO and H₂ adsorption decrease markedly in the presence of surface impurities. The effects of P, however, are much less pronounced than for Cl and S. The
similarity in the atomic radii of Cl, S and P (0.99, 1.04 and 1.10Å, respectively [53]) suggests a relationship between electronegativity and the poisoning of chemisorptive properties by these surfaces impurities [48-50]. Impurities that are strongly electronegative with respect to nickel, Cl and S, modify the chemisorptive behavior far more strongly than would result from a simple site blocking model. The initial effects of these impurities as shown in Fig. 7 indicate that a single impurity atom can successfully poison more than just its nearest-neighbor nickel atoms. This type of poisoning supports an interaction that is primarily electronic in nature.

The experimental results [48-50] indicate that the presence of electronegative Cl, S and P atoms causes a reduction of the adsorption rate, the adsorption bond strength and the capacity of the Ni(100) surface for CO and H₂ adsorption. In general, these poisoning effects become stronger with increasing electronegativity of the adsorbed impurity.

Kinetic studies [48-50] have been carried out for CO methanation over Ni(100) surfaces covered with chlorine, sulfur and phosphorus impurities. Figure 8 shows the rate of CO methanation as a function of sulfur and phosphorus coverage over a Ni(100) catalyst at 120 Torr and a H₂/CO pressure ratio equal to 4. In the case of Cl overlayers no change in the methanation rate was observed. At the reaction conditions of fig. 8, H₂ reacts with the adsorbed Cl forming HCl. This reaction "cleans" the Ni(100) surface and prohibits the study of the effects of Cl on the methanation kinetics. The results presented in fig. 8 correlate very well with the studies on the effects of S and P overlayers upon the adsorption of H₂ and CO on Ni(100) ([48-50] and fig. 7.)
Figure 8 shows a non-linear relation between the sulfur coverage and the methanation rate. A steep drop in catalytic activity is observed at low sulfur coverages, and the poisoning effect maximizes quickly. A similar reduction of methanation activity by sulfur poisoning has been observed for alumina supported nickel catalysts [54]. The initial attenuation of catalytic activity by sulfur suggests that ten or more equivalent nickel sites are deactivated by one sulfur atom. There are two possible explanations for this result: (1) an electronic effect that extends to the next-nearest-neighbor sites or (2) an ensemble effect, the requirement being that a certain number of surface atoms is necessary for a reaction to occur. If extended electronic effects are significant, then the reaction rate is expected to be a function of the relative electronegativity of the poison. In contrast, if an ensemble of ten nickel atoms is required for the critical step of methanation, then altering the electronegative character of the poison should produce little change in the poisoning of the reaction. Substituting phosphorus for sulfur (both atoms are approximately the same size [53]) results in a marked change in the magnitude of poisoning at low coverages as shown in fig. 8. Phosphorus, because of its less electronegative character, effectively poisons only the four nearest-neighbor metal atom sites. These results support the conclusion that extended electronic effects do play a major role in catalytic deactivation by sulfur.

B. Atomic Sulfur on Ru(001), Rh(111) and W(110)

Figure 9 presents the effects of sulfur coverage on the rate of CO
methanation on Ru(001) and Rh(111) catalysts [45,55]. As for the case of Ni(100), a precipitous drop in the catalytic activity is observed for low sulfur coverages. The initial changes in the rates suggest that more than ten Rh or Ru atom sites are deactivated by one sulfur atom.

Kinetic data for sulfur-covered W(110) surfaces indicate that the activation energy of the methanation reaction does not change with sulfur coverage [56]. In this respect tungsten is similar to nickel [48]. Sulfur decreases the rate of CO methanation on W(110) [56]. In fig. 10 the relative change in rate is plotted as a function of sulfur coverage. For comparison, the data for the Ni(100) surface [48] are included. While sulfur clearly exhibits long-range effects on nickel, the operation of long-range effects over tungsten occurs only at the lowest coverages. At very low sulfur coverages (~0.03 ML), the decrease in activity is quite steep and extrapolates to between 10 and 12 atoms sites deactivated per sulfur atom adsorbed [56]. Apparently the adsorption of sulfur occurs initially in a random, disordered fashion, so that there is little overlap of the inhibiting effect of sulfur atoms on open sites. As the sulfur coverage increases, clustering into islands occurs [56]. Thus, the inhibiting effect of additional sulfur atoms is diminished due to overlap with the effect of previously adsorbed sulfur atoms.

III.2.2.2 Electropositive impurities

We have discussed above the role of electronegative impurities in poisoning Ni(100), Ru(001), Rh(111) and W(110) toward methanation activity. These results have been ascribed, to a large extent, to an electronic effect.
In the context of this interpretation it is expected that an electropositive impurity might have the opposite effect, i.e. to increase the methanation activity of a metal surface. A study of CO hydrogenation over potassium covered Ni(100) [50,57] has shown that this is not the case, although certain steps in the reaction mechanism are strongly accelerated by the presence of the electropositive impurity.

A. Potassium on Ni(100)

Figure 11 shows kinetic measurements of CO methanation over a Ni(100) catalyst containing well-controlled submonolayer quantities of potassium adatoms [57]. These data indicate a decrease in the steady-state rate of methanation with potassium coverage. A coverage of about 0.22 ML of potassium would be sufficient to terminate the reaction completely. The presence of K did not alter the apparent activation energy associated with the kinetics, as shown in the Arrhenius plot of fig. 11b. However, the potassium did change the steady-state coverage of active carbon on the catalyst. This carbon level changed from 10% of a monolayer on the clean catalyst to 30% of a monolayer for a catalyst covered with 0.1 ML of potassium [57].

As shown in fig. 12, adsorbed potassium caused a marked increase in the steady-state rate and selectivity of Ni(100) for higher hydrocarbon (MW>16) synthesis [57]. At all the temperatures studied, the overall rate of higher hydrocarbon production was faster on the potassium-dosed surfaces, 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 over Ni(100) (i.e. a decrease in the rate of methane formation
and an increase in the rate of higher hydrocarbon production) are similar to those reported for high-surface-area supported Ni catalysts [58-59]. This agreement between bulk, single crystal Ni and supported Ni indicates that the major mechanism by which potassium additives alter the activity and selectivity of industrial catalysts is not related to the support material, but that it is rather a consequence of direct K-Ni interactions.

Adsorbed potassium causes a marked increase in the rate of CO dissociation on a Ni(100) catalyst [57]. The increase of the initial formation rate of "active" carbon or carbidic carbon via CO disproportionation is illustrated in Fig. 13. The relative rates of CO dissociation were determined for the clean and potassium covered surfaces by observing the growth in the carbon Auger signal with time in a CO reaction mixture, starting from a carbon-free surface. The rates observed in fig. 13 are the observed rates of carbon formation extrapolated to zero carbon coverage. The presence of K adatoms leads to a reduction of the activation energy of reactive carbon formation from 96 kJ/mol on clean Ni(100) to 42 kJ/mol on a 10% potassium covered surface [57].

In spite of increasing the rate of CO dissociation or carbide buildup, potassium decreases the overall rate of methanation. This reduction in methanation activity must be related to a poisoning of either the hydrogen adsorption or the hydrogen addition steps [57]. The enhancement of steady-state carbide coverage caused by potassium favors C-C bond formation and the synthesis of heavy hydrocarbons (MW>16).

**III.2.2.3 Related theory**
CO is generally thought to be adsorbed on transition-metal surfaces by the Blyholder mechanism [60,61], which involves \( \sigma \)-donation of electron density from CO into the unoccupied metal orbitals and \( \pi \)-back-donation of electron density from occupied metal orbitals into the lowest unoccupied molecular orbitals (\( 2\pi' \)) of the CO molecule. The mechanism is similar to that observed for CO bonding in transition metal compounds [62]. Theoretical results with the constrained space orbital variation (CSOV) method show that, in this type of synergistic bond with \( \sigma \)-donation/\( \pi \)-back-donation, \( \pi \)-back-donation is energetically more important in determining the character of the bond than is \( \sigma \)-donation, at least for the case of Cu surfaces [63-65]. Recently, inverse photoemission results have supported the predominant importance of \( 2\pi' \) back-donation in CO chemisorption on Pd and Ru [66]. The thought that the antibonding \( 2\pi \) orbitals of CO are populated upon adsorption is consistent with the results of HREELS [67,68], which show that the C-O stretching frequency and the C-O force constant of CO adsorbed on metals are lower than those of free CO.

The standard picture used to describe the effects of electron-transferring species upon CO chemisorption is an extension of the basic Blyholder model. Electropositive impurities donate charge to the metal. This excess charge is partially accommodated in increased \( \pi \)-back-donation to the \( 2\pi' \) orbitals of CO. This increases the metal-CO bond strength, while decreasing the C-O bond strength. Opposite effects are expected for coadsorption with electronegative impurities. In a few coadsorption cases, this general picture has been to some extent substantiated by calculations with different quantum-chemical methods [69-75, 107].
Theoretical work has been undertaken to address directly the predicted magnitude of the near surface electronic perturbations by impurity atoms. Early work was concentrated on the indirect interactions between adsorbates which occur via the surface conduction electrons [76-78]. These calculations suggested that atom-interactions through several lattice spacings can occur. Recent theoretical studies have expressly addressed the surface electronic perturbations by sulfur [79] as well as by Cl, P and Li [80]. The sulfur-induced total charge density vanishes beyond the immediately adjacent substrate atom site. However, the Fermi-level density of states, which is not screened, and which governs the ability of the surface to respond to the presence of other species, is substantially reduced by the sulfur even at nonadjacent sites. The results for several impurities indicate a correlation between the electronegativity of the impurity and its relative perturbation of the Fermi-level density of states [79,80], a result which could be very relevant to the poisoning of CO methanation by S and P as discussed above. Finally, an alternate model, which produces the same final results, involves an electrostatic, through-space (as opposed to through-metal) interaction between the charge distribution of the coadsorbed species [81,82].

Both sets of theories, that is, "through-metal" or "through-space," are consistent with adsorbate perturbations sufficiently large to effect chemically significant changes at next-nearest-neighbor metal sites. This perturbation length is sufficient to adequately explain the observed poisoning of catalytic activity by surface impurities discussed above.

III.2.3 Metal-support interactions and CO methanation.
The early concept of a support or a carrier was that of an inert substance that provided a means of spreading out an expensive catalyst over a large surface area. However, the support may actually modify the activity of the catalyst, depending upon the reaction and reaction conditions [10,83,106]. The oxidic support materials (e.g. $\text{La}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$, $\text{ZnO}$, $\text{MgO}$, $\text{TiO}_2$, $\text{ZrO}_2$...) can favorably or adversely influence the performance of a metal in a particular catalytic process [83,106]. Titania ($\text{TiO}_2$) is a typical example of an "interacting" support [83,106].

Surface science methods have been applied to study the CO hydrogenation activity of nickel overlayers on the $\text{TiO}_2(100)$ surface [84]. Results of ultraviolet photoelectron spectroscopy indicate that there is an electron transfer from $\text{TiO}_2(100)$ to Ni when Ni is deposited onto a reduced $\text{TiO}_2(100)$ surface [84]. When the Ni/$\text{TiO}_2(100)$ surface was used as a methanation catalyst, the $\text{CH}_4$ yield varied as a function of the Ni coverage, as shown in fig. 14a. At a temperature of 190°C, an average Ni thickness of ~5Å gave optimum activity. An Arrhenius plot of the specific rate of methane formation over the 5Å Ni-covered $\text{TiO}_2(100)$ surface is included in fig. 14b. The methane yields from the Ni/$\text{TiO}_2(100)$ catalyst are 3.3-3.7 times that from a pure Ni(111) catalyst. The apparent activation energy for methane production over the Ni/$\text{TiO}_2(100)$ surface ($105.5 \pm 2.5 \text{ kJ/mol}$) is very close to that seen over Ni(111) ($111.8 \pm 3.8 \text{ kJ/mol}$) [84].

A study of the methanation activity of a Ni(111) surface containing controlled amounts of TiO$_x$ (x=1.0-1.5), showed that the nickel catalyst is optimally promoted at a titanium coverage of ~0.1 monolayer, displaying an activity and product distribution similar to those seen over 8Å Ni-covered
TiO$_2$(100) catalysts [85]. The fact that TiO$_x$/Ni(111) and Ni/TiO$_2$(100) are so similar in their catalytic behavior, suggests [85] that in high-surface area Ni/TiO$_2$ catalysts, TiO$_x$ species diffuse from the support material to the nickel. Dispersal of the oxide on the metal and the formation of nickel-titanium bonds modify the catalytic properties of the surface.

III.3 WATER-GAS SHIFT REACTION ON SINGLE CRYSTAL SURFACES

The water-gas shift reaction (CO + H$_2$O $\rightarrow$ H$_2$ + CO$_2$) is widely used industrially in various hydrogen production or enrichment processes [10,86]. Many materials are able to catalyze this reaction [10,86]. Originally, the most commonly employed industrial catalysts were based on iron oxides and operated at high temperatures (570-820K) [10,86]. A substantial improvement came about by the development of Cu/ZnO-based catalysts, which operate at relatively low temperatures (470-530K) and allow higher thermodynamic conversions [10,86]. In these catalysts, copper is the active species, and the principal role of the zinc oxide is to act as a support for the copper [10,87-91]. It is not clear why ZnO is a superior support [86-91]. In this section we review the results of studies in which the kinetics and mechanism of the water-gas shift reaction have been investigated using the modern techniques of surface science and copper single crystals.

III.3.1 Kinetics on Cu(110) and Cu(111) catalysts.

Figure 15 illustrates the effect of temperatures on the rate of the water-gas shift reaction over Cu(110) [88] and Cu(111) [87] surfaces. For the same geometric area, Cu(110) is 2.5-7.0 times more active than Cu(111) between
550 and 650K [88]. On a "per copper surface atom" basis, this difference is 1.63 larger due to the higher surface atom density of Cu(111). The slopes in fig. 15 give apparent activation energies of 10 and 17 kcal/mol for the water-gas shift reaction on Cu(110) and Cu(111). These results indicate that the reaction is structure sensitive on copper surfaces. A fact that is consistent with data for high-surface area supported catalysts, which show an increase in the catalytic activity as the Cu particle size decreases [91]. High area supported and unsupported catalysts show apparent activation energies in the range of 13 to 16 kcal/mol [87], well within the range between Cu(110) and Cu(111) (10-17 kcal/mol).

A study of the influence of CO and H₂O partial pressures on the reaction rate over Cu(110) [88] and Cu(111) [87], revealed that on both surfaces the rate is nearly independent of P$_{CO}$ (order _ 0) and strongly positive order in H₂O (0.5-1.0). Analysis of the surface of the catalysts with AES and XPS after reaction conditions showed essentially oxygen-free copper surfaces [87,88]. To further prove that Cu surfaces are fully reduced under water-gas shift conditions at low conversion, experiments were carried out using a heavily preoxidized Cu(111) crystal [87]. After a few minutes reaction time, the surface displayed a fully metallic Cu(2p) XPS spectrum, and gave no oxygen signal in AES or XPS [87]. This suggests that metallic Cu is the active ingredient for high-surface area Cu/ZnO or Cu-based catalysts [87].

The following mechanism has been proposed [88] for the water-gas shift reaction on Cu(110) and Cu(111):

\[
\begin{align*}
H_2O_g & \rightarrow H_2O_a \quad (12) \\
H_2O_a & \rightarrow OH_a + H_a \quad (13)
\end{align*}
\]
\[ \text{OH}_a \rightarrow \text{O}_a + \text{H}_a \quad (14) \]
\[ 2\text{H}_a \rightarrow \text{H}_2 \text{,g} \quad (15) \]
\[ \text{CO}_g \rightarrow \text{CO}_a \quad (16) \]
\[ \text{CO}_a + \text{O}_a \rightarrow \text{CO}_2 \text{,g} \quad (17) \]

In this mechanism the rate-determining step involves O-H bond cleavage in H\text{O}_a (reaction (13)). The enhanced catalytic activity of Cu(110) compared to Cu(111) has been attributed \[88\] to a lower barrier for O-H bond cleavage on the Cu(110) surface. Reaction (14) may not necessarily be an elementary step, but a consequence of the process \[88\]:
\[ \text{H}_2\text{O}_g \rightarrow \text{H}_2\text{O}_a \quad (18) \]
\[ \text{H}_2\text{O}_a \rightarrow \text{OH}_a + \text{H}_a \quad (19) \]
\[ 2\text{OH}_a \rightarrow \text{O}_a + \text{H}_2\text{O}_a \quad (20) \]
\[ \text{H}_2\text{O}_a \rightarrow \text{H}_2\text{O}_g \quad (21) \]

\[ \text{net } \text{OH}_a \rightarrow \text{O}_a + \text{H}_a \quad (14) \]

Reaction (20) provides an easy pathway for converting \text{OH}_a to \text{O}_a, which proceeds rapidly even at 290K on Cu(110) \[92,93\].

Figure 16 shows a potential energy diagram for the water-gas shift reaction on Cu(110). The diagram was constructed \[88\] using kinetic and thermochemical data for reactions (12) to (17). The activation energy for the rate determining step (H\text{O}_a \rightarrow \text{OH}_a + \text{H}_a) is \(~20\, \text{kcal/mol}\). A value of 27 kcal/mol has been estimated for this step on Cu(111) \[87\]. This difference is probably due to the fact that the (110) plane is much more open, offering Cu surface atoms which are much more coordinatively unsaturated and hence more active for breaking O-H bonds.
III.3.2 Sulfur poisoning of Cu(111) catalysts.

The poisoning of Cu/ZnO catalysts by sulfur is one of the most serious problems in the water-gas shift process [86,94]. Figure 17 shows the effect of pre-adsorbed sulfur atoms upon the rate of the water-gas shift reaction over Cu(111) [94]. Sulfur addition causes a linear decrease in the rate of the reaction, with the rate going to zero at saturation sulfur coverage ($\theta_S = 0.39$). The decay in the rate with $\theta_S$ can be easily understood in terms of a simple site-blocking model, where sulfur adatoms sterically prevent the dissociation of water [94]. The rate decay of Fig. 17 is well fit by the expression: $(1-2.6\theta_S)$. According to a statistical analysis [94], this linear function indicates that each sulfur atom blocks about 2.6 Cu atoms, and that the ensemble required for $\text{H}_2\text{O}$ dissociation is rather small (1 or 2 Cu atoms).

This is not unexpected, given the small size of the $\text{H}_2\text{O}$ molecule and its dissociation products ($\text{OH}_a + \text{H}_a$).

III.3.3 Cesium promotion of Cu(111) and Cu(110) catalysts.

Cesium has been shown to promote the water-gas shift reaction over Cu/ZnO catalysts [95,96]. Kinetic data for the reaction on Cs promoted Cu(110) surfaces [88] are displayed in fig. 18. The optimum Cs coverage to promote the reaction is $\theta_{\text{Cs}} = 0.25$ ML. At this coverage, the reaction rate is five times faster than the clean surface rate at any reaction temperature [88]. The coverage dependence and optimal coverage for cesium promotion shown in Fig. 18 for Cu(110) are similar to those observed over Cu(111) [97].

An apparent activation energy of 11 kcal/mol was determined for the water-gas shift reaction on an optimally-promoted Cs/Cu(110) surface ($\theta_{\text{Cs}} = \ldots$)
found for the clean surface. A tendency toward a slightly higher apparent activation energy was also observed in experiments with Cu(111), where the optimally-promoted Cs covered surface had an activation energy of 20 kcal/mol versus 17 kcal/mol for the clean Cu(111) surface [97].

A study of the pressure dependence of the water-gas shift reaction over optimally-promoted Cs/Cu(110), shows that on this surface the reaction orders in $P_{CO}$ and $P_{H2O}$ are very different from those on clean Cu(110) [88]. This fact rules out the possibility that the same elementary step is rate determining with Cs present or absent.

In order to understand the role of Cs promoters in the water-gas shift reaction, detailed studies were carried out investigating the effects of Cs upon the surface chemistry of H$_2$O, CO and CO$_2$ on Cu(110) [93,98,99]. Post-reaction surface analysis of the Cs-promoted Cu(110) catalysts show that the dominant form of Cs is a surface cesium-carbonate complex (Cs•CO$_3$) [100]. This same species can be produced by dosing CO$_2$ to Cs/Cu(110) under ultra-high vacuum (UHV) conditions [98]. It decomposes in UHV at 450-600K (for $\theta_{Cs} < 0.25$) via: $\text{Cs•CO}_3,a \rightarrow \text{Cs•O}_a + \text{CO}_2,g$ [98]. The equilibrium:

$$\text{CO}_2,g + \text{Cs•O}_a \rightleftharpoons \text{Cs•CO}_3,a$$ (22)

occurs rapidly under water-gas shift reaction conditions [99,100]. The Cs•O$_a$ species is readily reducible with CO gas via: $\text{CO}_g + \text{Cs•O}_a \rightarrow \text{CO}_2,g + \text{Cs}_a$ [88,100]. Thus, a mechanism involving the species Cs•O$_a$ (produced by the reaction of H$_2$O and Cs [93,99,100]) rather than simply O$_a$ may be operative on the Cs promoted catalysts. The species Cs•O$_a$ should be thought as a cesium-stabilized oxygen adatom, with a dominant bond to Cu and some degree of
bonding to a neighboring Cs adatom [93,99].

III.4 METHANOL SYNTHESIS

Methanol is synthesized from carbon monoxide and hydrogen by the reaction: \( \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \). The selective synthesis of methanol is a process of major industrial importance because of the use of methanol as a chemical intermediate, its potential use as a starting material for fuel production, and many other applications [10,101,102]. The most commonly employed industrial catalysts are based on Cu supported on ZnO, or a mixture of ZnO and other oxides such as \( \text{Cr}_2\text{O}_3 \) [10,101,102]. It has been demonstrated that under certain conditions Pd is also an active methanol synthesis catalyst, and that the nature of the support has great influence on both the rate and selectivity [103]. Here we review studies that deal with methanol synthesis on Pd(110), Cu(111), ZnO/Cu(111) and Cu/ZnO(0001) single crystals.

III.4.1 Kinetics on Pd(110).

Figure 19a illustrates the effect of temperature on the rate of methanol production over a Pd(110) catalyst. The rate shows approximately Arrhenius behavior with an apparent activation energy of 18.4 ± 1.9 kcal/mol and a pre-exponential factor of 8 x 10^4 s^-1 over the temperature range of 493 to 553K [104]. The activation energy is in good agreement with values reported for Pd on "noninterating" supports such as SiO\(_2\) and basic supports such as ZnO and La\(_2\)O\(_3\) [104,108,109]. In addition, the pre-exponential factor determined for Pd(110) agrees well with reported values for Pd/SiO\(_2\) [104,109]. The activation energy for Pd(110) is, however, significantly different from values
obtained on acidic Al₂O₃ and TiO₂ supports [104,108].

Figure 19b shows the variation of the reaction rate with pressure at 553K. Methanol production was roughly first order (1.2 ± 0.2) in total pressure. The specific rates seen on Pd(110), extrapolated to pressures typical of most methanol synthesis works, are in good agreement with rates observed for Pd dispersed on SiO₂ [104,108,109]. Thus, Pd metal is an active methanol synthesis catalyst, and no specific support interaction is required. Highly interacting supports exhibit rates and/or selectivities substantially different from those of Pd(110) [104]. The rates on Pd(110) are higher than those seen over Pd supported on zeolite and acidic supports (e.g., PdNaY and Al₂O₃) [104,108,110], but much lower than those observed on highly active La₂O₃-supported Pd [104,108,109].

After reaction on Pd(110), submonolayer quantities of a carbonaceous residue (generally between 0.05 to 0.25 carbon monolayers) were detected by Auger electron spectroscopy on the surface of the catalyst [104]. Significant adsorption of hydrogen into the bulk, determined by post-reaction temperature programmed desorption, was not observed [104].

### III.4.2 Studies on Cu(111), ZnOₓ/Cu(111) and Cu/ZnO(0001) surfaces.

The synthesis of methanol from CO and H₂ was attempted on Cu(111) and over model catalysts consisting of well-defined Cu overlayers on ZnO(0001) [105]. For temperatures between 500 and 600K, H₂ + CO total pressures up to 1500 Torr, and reaction times of 40 minutes, no production of methanol was observed. The same result was obtained when ZnOₓ films on Cu(111) were used as catalysts.
On the basis of these data, an upper limit of \( <2 \times 10^{-3} \) CH\(_3\)OH molecules/site-s was obtained for the catalytic activity of Cu(111), ZnO\(_x\)/Cu(111) and Cu/ZnO(0001) surfaces [105]. This limit is consistent with the rates expected for high-surface area Cu/ZnO catalysts (extrapolate from a somewhat higher pressure regime) [105].

III.5 CONCLUSIONS

The use of a high pressure reactor combined with an ultra-high vacuum surface analytical chamber to study catalytic reactions can provide detailed information about the relation between surface structure and catalytic activity. Using these techniques, the concepts of structure sensitivity and structure insensitivity can be investigated. For CO methanation (a structure insensitive reaction), excellent agreement is obtained between studies on single crystal surfaces and studies on high surface area supported catalysts, demonstrating the relevance of kinetics measured on well-ordered single crystal surfaces for modeling the behavior of practical catalysts.

Model studies on single crystal surfaces are also helpful in developing a better understanding of the effects of surface additives (poisons and promoters) on catalyst performance. The influence of additives on the surface chemistry of adsorbed reactants, products and intermediates can be studied using UHV techniques, and this information can be related to the effects of the additives upon the activity and selectivity of a catalyst. Of particular interest is the possibility that these types of studies will help to clarify the relative importance of electronic and geometric effects in determining additive effects. The types of studies reviewed here, in conjunction with
studies on high-surface are supported catalysts, hold great promise for contributing to an overall understanding of CO activation.

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REFERENCES


FIGURE CAPTIONS

Figure 1. (a) A comparison of the rate of methane formation (CH₄ molecules/site-s) over single crystal nickel catalysts and supported Ni/Al₂O₃. Reaction conditions: 120 Torr, H₂/CO ratio = 4 (from ref. [13]). (b) Atomic configuration of a Ni(100) surface. (c) Atomic configuration of a Ni(111) surface.

Figure 2. (a) Arrhenius plot of CH₄ synthesis on a Ni(100) catalyst at total reactant pressures of 1, 10 and 120 Torr. The ratio H₂ / CO is 4 (from ref. [13]). (b) Arrhenius plot of CH₄ synthesis on a Ru(110) catalyst at total reactant pressures of 1, 10 and 120 Torr. The ratio H₂ / CO is 4. Data at two temperatures for a Ru(001) catalyst at 120 Torr are plotted with the symbol X (from ref. [13]).

Figure 3. Methane production rate (molecules/Ni surface atom-s) at 625K over a Ni(100) catalyst versus surface carbon coverage (under steady-state conditions). The H₂ / CO ratio and the total pressure (Torr) for each point are indicated in the insert (from ref. [13]).

Figure 4. (a) The methanation activity for W(110) compared to that for Ni(100), plotted in an Arrhenius fashion (from ref. [22]). (b) The H₂ dependence of the methanation activity for W(110) compared to that of Ni(100) (from ref. [22]).

Figure 5. (a) Arrhenius plot for CO methanation on Mo(100) (from ref. [26]). (b) Rate of formation of methane over Mo(100) versus the partial pressure of each reactant. Constant H₂ pressure of 3 atm for determination of CO dependence, and constant CO pressure of 3 atm for determination of H₂ pressure dependence. In all the cases the total pressure was 6 atm, with nitrogen or argon used as a buffer gas (from ref. [26]).

Figure 6. (a) Arrhenius plot for CH₄ synthesis over several different Ni coverages on W(110) and W(100) at a total reactant pressure of 120 Torr (H₂/CO = 4) (from ref. [38]). (b) Arrhenius plot for CH₄ synthesis over several different Ni coverages on W(110) at total reactant pressures of 1, 10 and 120 Torr (H₂/CO = 4) (from ref. [38]).

Figure 7. Variation of the saturation coverage of CO (part (a)) and H₂ (part (b)) on Ni(100) with the precoverage of Cl, S and P (from ref. [50]).

Figure 8. Plot of the rate of methanation (CH₄ molecules/site-s) over a sulfide and phosphided Ni(100) catalyst at 120 Torr and a pressure ratio of H₂ to CO of 4 (from ref. [50]).

Figure 9. Methanation rate as a function of sulfur coverage on: (a) Ru(001) (from ref. [55]), and (b) Rh(111) (from ref. [45]) catalysts. Pressure = 120 Torr, H₂/CO = 4, reaction temperature = 600K.

Figure 10. Relative change in methanation rate over W(110) as a function of sulfur coverage (from ref. [56]). For comparison the data for Ni(100) is also
shown (from ref. [50]).

Figure 11. (a) Relative methanation rate as a function of potassium coverage at various reaction conditions: (◊) $P_{\text{CO}} = 1.0$ Torr, $P_{\text{H}_2} = 99.9$ Torr, $T = 600$K; (O) $P_{\text{CO}} = 24$ Torr, $P_{\text{H}_2} = 97.6$, $T = 538$K; (▃) $P_{\text{CO}} = 24$ Torr, $P_{\text{H}_2} = 96$ Torr, $T = 600$K; (□) $P_{\text{CO}} = 24$ Torr, $P_{\text{H}_2} = 96$ Torr, $T = 594$K (from ref. [57]). (b) A comparison of the rate of methane synthesis over a clean single crystal Ni(100) catalyst with the rate over a potassium doped catalyst. Total reactant pressure is 120 Torr, $H_2/CO = 4$ (from ref. [57]).

Figure 12. A comparison of the product distributions (weight percent) observed for clean and K-doped catalysts at $T = 500$K, $H_2/CO = 4$, and a total pressure of 120 Torr. Potassium coverage = 0.10 ML (from ref. [57]).

Figure 13. 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. (From ref. [57]).

Figure 14. (a) The methane yield from Ni/TiO$_2$(100) as a function of the average Ni thickness. $P_{\text{H}_2} = 60$ Torr, $P_{\text{CO}} = 20$ Torr, $T = 190^\circ$C (from ref. [84]). (b) Arrhenius plots of the methane turnover number (CH$_4$ molecules/site-s) for Ni(111) and 5Å Ni/TiO$_2$(100), $P_{\text{H}_2} = 60$ Torr, $P_{\text{CO}} = 20$ Torr (from ref. [84]).

Figure 15. Variation of the water-gas shift reaction rates on Cu(110) and Cu(111) with temperature, in Arrhenius form. $P_{\text{H}_2O} = 10$ Torr and $P_{\text{CO}} = 26$ Torr. (From ref. [88] and [87]).

Figure 16. Potential energy diagram of the water-gas shift reaction on Cu(110) (from ref. [88]).

Figure 17. Rate of water-gas shift reaction over Cu(111) as a function of sulfur coverage (from ref. [94]).

Figure 18. The water-gas shift reaction rate as function of Cs coverage ($\theta_{\text{Cs}}$) on Cs/Cu(110) at 493, 523 and 573K. $P_{\text{H}_2O} = 10$ Torr and $P_{\text{CO}} = 26$ Torr (from ref. [88]).

Figure 19. (a) Turnover frequency (CH$_3$OH molecules produced/Pd surface atom-s) versus inverse temperature at a total pressure of 244 kPa and a 3.9:1 H$_2$/CO mixture (from ref. [104]). (b) Turnover frequency plotted as a function of total pressure at 553K, for a 3.9:1 H$_2$/CO mixture (from ref. [104]).
### TABLE I

**Metal Single Crystal Catalysts:**
Specific Activities and Activation Energies in CO Methanation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (K)</th>
<th>P$_{H_2}$ (Torr)</th>
<th>P$_{CO}$ (Torr)</th>
<th>TOF$^a$ (site$^{-1}$s$^{-1}$)</th>
<th>E$_a$ (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Ni(100)</td>
<td>450-700</td>
<td>96</td>
<td>24</td>
<td>0.0002 - 8</td>
<td>103</td>
<td>[13]</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>550-700</td>
<td>96</td>
<td>24</td>
<td>0.04 - 5</td>
<td>103</td>
<td>[13]</td>
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<tr>
<td></td>
<td>440-540</td>
<td>60</td>
<td>20</td>
<td>0.0002 - 0.05</td>
<td>111</td>
<td>[84]</td>
</tr>
<tr>
<td>Ru(110)</td>
<td>500-700</td>
<td>96</td>
<td>24</td>
<td>0.002 - 10</td>
<td>123</td>
<td>[13]</td>
</tr>
<tr>
<td>Ru(001)</td>
<td>550-650</td>
<td>96</td>
<td>24</td>
<td>0.01 - 0.8</td>
<td>~120</td>
<td>[13]</td>
</tr>
<tr>
<td>W(110)</td>
<td>480-750</td>
<td>100</td>
<td>0.1</td>
<td>0.002 - 0.5</td>
<td>56</td>
<td>[22]</td>
</tr>
<tr>
<td>Mo(100)</td>
<td>510-640</td>
<td>1100</td>
<td>220</td>
<td>0.001 - 0.2</td>
<td>100</td>
<td>[26]</td>
</tr>
</tbody>
</table>

$^a$TOF = turnover frequency = CH$_4$ molecules/site-s
The figures in the review were taken from the following articles:

Fig. 1: Fig. 1 in: R.D. Kelley and D.W. Goodman, Surf. Sci. 123 (1982) L743.

Fig. 2: Fig. 2 in: R.D. Kelley and D.W. Goodman, Surf. Sci. 123 (1982) L743.

Fig. 3: Fig. 3 in: R.D. Kelley and D.W. Goodman, Surf. Sci. 123 (1982) L743.

Fig. 4: Figs. 1 and 2 in: T.J. Udovic et al., Surf. Sci. 150 (1985) L71.

Fig. 5: Figs. 3 and 5 in: M. Logan et al., J. Catal. 94 (1985) 60.

Fig. 6: Figs. 1 and 3 in: C.M. Greenlief et al., J. Phys. Chem. 91 (1987) 6669.

Fig. 7: Figs. 3 and 5 in: D.W. Goodman, Appl. Surf. Sci. 19 (1984) 1.

Fig. 8: Fig. 7 in: D.W. Goodman, Appl. Surf. Sci. 19 (1984) 1.


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Fig. 11: Figs. 2 and 3 in: C.T. Campbell and D.W. Goodman, Surf. Sci. 123 (1982) 413.

Fig. 12: Fig. 5 in: C.T. Campbell and D.W. Goodman, Surf. Sci. 123 (1982) 413.

Fig. 13: Fig. 6 in: C.T. Campbell and D.W. Goodman, Surf. Sci. 123 (1982) 413.

Fig. 14: Figs. 7 and 8 in: C.C. Kao et al., J. Catal. 73 (1982) 136.

Fig. 15: Fig. 2 in: J. Nakamura et al., submitted for publication.

Fig. 16: Fig. 7 in: J. Nakamura et al., submitted for publication.

Fig. 17: Figs. 4 and 5 in: C.T. Campbell and B.E. Koel, Surf. Sci. 183 (1987) 100.

Fig. 18: Fig. 4 in: J. Nakamura et al., submitted for publication.

In each figure caption, we mention the original article from which the figure was taken. It may be necessary to obtain an authorization from the journals before using the figures in the book.
Fig. 1
Fig. 2
Methanation Rate Versus Surface Carbon Level

\[ T = 625\text{K} \]

<table>
<thead>
<tr>
<th>Pt. No.</th>
<th>( \frac{H_2}{CO} ) Ratio</th>
<th>Press. (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>4.0</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>4.0</td>
<td>500</td>
</tr>
<tr>
<td>8</td>
<td>4.0</td>
<td>1000</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
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</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>200</td>
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<tr>
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</tr>
<tr>
<td>13</td>
<td>0.1</td>
<td>110</td>
</tr>
<tr>
<td>14</td>
<td>0.4</td>
<td>34</td>
</tr>
<tr>
<td>15</td>
<td>2.7</td>
<td>89</td>
</tr>
</tbody>
</table>

Fig. 3
Fig. 4
Fig. 5
Fig. 6

(a) CO + H₂ → CH₄

(b) CO + H₂ → CH₄

METHANE TURNOVER FREQUENCY (s⁻¹)

1000/T (K⁻¹)

NI/W (110)

0.3 ML Ni

0.4 ML Ni

0.6 ML Ni

1.0 ML Ni

P = 120 Torr

P = 10 Torr

P = 1 Torr
Fig. 7
Fig. 8

SULFUR ON Ni(100) AT 0.25 MONOLAYERS

SULFUR ON Ni(100) AT 0.5 MONOLAYERS

PHOSPHOROUS

SULFUR
Fig. 9

- **Graph a**: Relative rate of sulfur coverage (monolayer) for ruthenium.
- **Graph b**: Relative rate of sulfur coverage (monolayer) for rhodium.
Inhibition of Methanation over W (110) by Adsorbed Sulfur

- 750 K: Reaction Temperatures
- 700 K: $P_{H_2} = 100$ Torr
- 600 K: $P_{CO} = 1$ Torr

x Similar Data for Ni (100)

600 K: $P_{H_2} = 96$ Torr
$P_{CO} = 24$ Torr

Fig. 10
Fig. 11
PRODUCT DISTRIBUTION OVER A Ni(100) CATALYST

- Methane: 93%
- Ethylene: 53%
- Ethane: 4.9%
- C₃⁺: 22%

CLEAN
θₓ = 0.1

Fig. 12
Fig. 14
TEMPERATURE / K

LOG_{10} [ RATE / (10^{15} \text{ molecules cm}^{-2} \text{ s}^{-1}) ]

Cu (110)
Ea = 10 kcal/mole

Cu (111)
Ea = 17 kcal/mole

H_2O + CO \rightarrow H_2 + CO_2
10 Torr H_2O
26 Torr CO

○ H_2
△ CO_2

1000 K / TEMP.

Fig. 15
Fig. 17
H₂O + CO → H₂ + CO₂

Cs/Cu(110)

P_{H₂O} = 10 \text{ torr} \quad P_{CO} = 26 \text{ torr}

Cs/Cu AES Ratio

Rate / (10^{15} \text{ molecules cm}^{-2} \text{ s}^{-1})

Cesium Coverage (θ_{Cs})

Fig. 18
Fig. 19