A SURFACE SCIENCE INVESTIGATION OF THE ROLE OF POTASSIUM PROMOTERS IN NICKEL CATALYSTS FOR CO HYDROGENATION *

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The role of potassium promoters in model Ni(100) catalysts for CO hydrogenation has been studied. High-pressure kinetic measurements of the $H_2 + CO$ reaction on Ni(100) containing well-controlled submonolayer quantities of potassium adatoms have been combined with detailed surface analysis performed before and after reaction. Potassium addition decreases the steady-state rate of methane formation and increases that for higher hydrocarbons relative to clean Ni(100). These same results are reported for supported, high-surface-area Ni catalysts, indicating that metal/support interactions are not necessary in achieving the promoter effect. The activation energy for methanation (~25 kcal mole⁻¹) does not depend upon potassium coverage, suggesting that K changes neither the reaction mechanism nor the rate-limiting step. Surface carbide, a vital reaction intermediate, increases sharply in coverage upon the addition of 0.10 monolayer potassium. This is shown to result from a marked decrease in the activation energy for CO dissociation effected by potassium. The catalyst activity and selectivity are discussed in light of these results.

1. Introduction

The improvement of existing processes for the catalytic hydrogenation of CO is a vital requirement for the efficient utilization of our national energy resources through, for example, coal gasification. The catalytic methanation reaction $(3 H_2 + CO \rightarrow CH_4 + H_2O)$ over transition metals (Ni, Fe, Rh and Ru) has, thus, recently been the subject of intense interest from a fundamental, surface scientific point-of-view [1-19]. The kinetics on clean, single-crystal planes of Ni have been characterized in detail and compare favorably with results from the more practical high-surface-area, supported Ni catalysts [1,7-9]. Thus, well-defined single crystal surfaces can be, and are being, used as tractable models for studying this reaction. The reaction mechanism and the

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role of poisons in catalyst deactivation, for example, have been clarified by detailed studies using single crystals as model catalysts [1-10]. In this paper, we address the role of so-called alkali promoters in the hydrogenation of CO over Ni by comparing the kinetics on clean Ni(100) with those on a Ni(100) surface containing well-controlled sub-monolayer quantities of potassium adatoms.

Practical Ni catalysts for CO hydrogenation often include potassium promoters (as the oxide or the carbonate) [20–24], although it is doubtful whether this actually increases the methanation activity [21–23]. Potassium promoters are generally added as a precipitant [21], or to poison the support's acidity or to catalyze coke removal via hydrogen or steam reactions [20]. At atmospheric pressure, potassium increases the average molecular weight of the hydrocarbons produced over Ni catalysts presumably by increasing the chain growth process [21].

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 [25-31]. 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 N₂ [31] or CO [29,33-35], and in promoting catalytic activity in, for example, ammonia synthesis [36-38]. This role of electron donating or withdrawing additives in modifying the chemisorption properties of transition metals has been termed a ligand effect, in analogy to phenomena in organometallic chemistry. The role of electronegative adatoms (S, P) in poisoning Ni(100) methanation activity can clearly be ascribed to such an electronic ligand effect [3-5], and as such one might expect an electropositive adatom such as Na or K to have the opposite effect and to increase Ni's methanation activity. In the present study, we show this not to be the case, although certain steps in the reaction mechanism are strongly accelerated by the presence of K.

2. Experimental

The apparatus and techniques for this study have been described in detail elsewhere [1,2]. Briefly, the experiments were performed in a combined highpressure reactor/ultra-high vacuum (UHV) surface analysis chamber. Work function changes were monitored by shifts in the onset of the AES secondary electron distribution with a 15 V bias on the sample. A potassium zeolite ion source (such as described in ref. [39]) was added to the UHV chamber for dosing 200 eV K⁺ ions on the front Ni(100) surface at rates near 0.05 monolayer min⁻¹. The uniformity of the K spatial distribution over the surface was verified by AES. The sample was annealed at 600 K to remove any damage caused by the incident ions. The back face of the Ni crystal was masked with a saturation sulfur coverage (from H_2S), which has been shown to effectively quench hydrogenation kinetics [3]. The sulfur was then removed from the front face by Ar^+ ion sputtering, followed by annealing at 1400 K. In this way, product formation only occurred from the front face where K could be dosed. This type of masking using a surface pacifier such as sulfur was found to be an efficient method for reducing back-face and edge effects in surface modifier studies.

A typical experiment proceeded as follows: (1) surface cleanliness was established by AES; (2) potassium was dosed to the desired level onto the surface at 600 K; (3) the surface cleanliness and K coverage was determined by AES; (4) the sample was retracted into the reaction chamber and exposed to the reaction mixture for various times and temperatures, during which the rate of product formation was monitored with gas chromotography; (5) after evacuation, the sample was translated into the UHV chamber, briefly flashed to 600 K to remove residual CO; and (6) the AES spectrum was measured. Fig. 1 shows typical AES spectra of the clean surface, after K dosing, and after reaction.



Fig. 1. AES spectra of Ni9100) catalyst following: (a) cleaning; (b) potassium dosing at 600 K; (c) steady-state reaction on potassium-dosed Ni(100) at 120 Torr, H_2 : CO mixture (4:1) and 600 K. Spectral intensities are not normalized.

3. Results

3.1. Potassium adsorption

The work function versus exposure curve we observed was similar to that obtained previously, where a maximum work function change $\Delta \phi = -3.6$ eV and a saturation K coverage work function change of $\Delta \phi = -2.7$ eV were assigned to coverages of $\theta_{\rm K} = 0.19$ and 0.38, respectively, based upon LEED pattern assignments [30,31]. (One adatom per Ni(100) surface atom corresponds to $\theta = 1.0$). We determined K coverages using the K(250 eV): Ni(848 eV) AES ratio ($I_{\rm K}/I_{\rm Ni}$), which we assumed to be linear in $\theta_{\rm K}$ for $\theta_{\rm K} < 0.15$ and which we calibrated by comparing our observed work function changes with those reported in the references cited above [30,31]. This calibration procedure agreed to within 20% of that determined using the atomic AES sensitivities of K and Ni (obtained from bulk KCl and Ni spectra [40]) in a calculation analogous to that described in ref. [41]. (Mean free paths for the K and Ni AES electrons were taken as 10 and 17 Å, respectively [42].) By these procedures, a ratio $I_{\rm K}/I_{\rm Ni}$ of 0.23 corresponds to $\theta_{\rm K} = 0.10$ and $\Delta \phi = -3.0$ eV. (Normal incident electrons at 2 kV, 40° detection using a double-pass CMA, nonretarding.) This was the maximum coverage obtainable in UHV at 600 K (in the absence of oxygen impurity on the surface), which agrees well with the thermal stability of K reported on Ni(110) [25]. Interestingly, higher coverages of K (up to $\theta_{\rm K} = 0.18$) were stable at 600 K when dosed at lower temperatures and heated to 600 K only in the reaction mixture (typically 24 Torr CO, 96 Torr H_2). This stabilization of K must be associated with the presence of some species adsorbed under reaction conditions. It has been noted that atomically chemisorbed oxygen stabilizes K on Fe surfaces [38]. Although we observed oxygen in the AES spectrum after evacuation of the reaction mixture prior heating, it was removed easily by the 600 K flash in UHV. Its thermal instability proves that this is not atomically adsorbed oxygen (which does not desorb from Ni [43]), but rather some other species, most likely H₂O or OH. Stabilization of K at the surface by a type of "solvation" effect would not be unexpected. (That this oxygen removal is not due to CO desorption was tested by comparing the decrease in the carbon and oxygen AES signals after the 600 K flash.)

Under all the conditions reported here, no loss of K from the surface occurred during the reaction measurements.

3.2. Methanation kinetics

The effect of the adsorbed K was to decrease the steady-state rate of CO methanation under all conditions tested, as summarized in fig. 2. Extrapolating these data indicates that a coverage of about $\theta_{\rm K} = 0.22$ would be sufficient to



Fig. 2. Relative methanation reaction rate as a function of potassium coverage at various reaction conditions: (\Diamond) $P_{\rm CO} = 1.0$ Torr, $P_{\rm H_2} = 99.9$ Torr, T = 600 K; (\bigcirc) $P_{\rm CO} = 24$ Torr, $P_{\rm H_2} = 97.6$ Torr, T = 538 K; (\triangle) $P_{\rm CO} = 24$ Torr, $P_{\rm H_2} = 96$ Torr, T = 600 K; (\square) $P_{\rm CO} = 24$ Torr, $P_{\rm H_2} = 96$ Torr, T = 594 K.



Fig. 3. 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, $H_2/CO = 4/1$.

terminate the reaction completely. The presence of K did not alter the kinetics, as shown in the Arrhenius plot of fig. 3. Note that the activation energy (25 kcal mole⁻¹) remained the same at $\theta_{\rm K} = 0.10$ as for the clean surface, with a slight shifting in the curves to lower rates in the presence of K.

For the linear sections in fig. 3, the steady-state carbide coverages were essentially independent of temperature, at $\theta_C = 0.10$ for clean Ni(100) (in agreement with refs. [1,2]) and $\theta_C = 0.30$ for $\theta_K = 0.10$. (For calibration procedures for carbon coverage, see refs. [2,44].) Fig. 4 shows the K and C regions in the AES spectrum for the clean and K-dosed surfaces following reaction at $P_{\rm CO} = 24$ Torr, $P_{\rm H_2} = 96$ Torr and 600 K. Note that the carbon lineshape is unchanged by the presence of K, but that there is a marked increase in the steady-state level of carbon. As was shown on the clean surface [1,2], this lineshape is indicative of a carbidic-type of carbon overlayer (C_a), rather than a graphitic carbon.

The high-temperature departure, or rollover, in the rate from linear Arrhenius behavior shown in fig. 3 has been associated with a transition from a carbidic to a graphitic type of carbon overlayer on the clean surface [1]. These species were distinguished by their markedly different AES lineshapes [1]. The carbidic carbon is a necessary reaction intermediate which is readily hydrogenated to produce methane, while the graphitic carbon is relatively unreactive and poisons the surface [1]. This rate rollover in fig. 3 occurs at a lower temperature on the K-dosed surface. Following reaction at 750 K with $\theta_{\rm K} = 0.10$, the surface was covered with a multilayer of graphitic carbon. This indicates that the lowering in the rollover temperature is a result of a lowering in the



Fig. 4. AES spectra of the potassium and carbon regions following: (a) steady-state reaction of a clean Ni(100) catalyst; (b) steady-state reaction of K-doped catalyst with $H_2/CO = 4/1$, a total pressure of 120 Torr, and T = 600 K.

transition temperature from carbidic to graphitic carbon effected by K. This is correlated with the increase in the rate of carbon buildup in the presence of K, as discussed in section 3.4.

3.3. Higher hydrocarbon formation

As shown in fig. 5, adsorbed potassium caused a marked increase in the steady-state rate and selectivity of Ni(100) for higher hydrocarbon synthesis. Although not studied in detail, the apparent activation energy for higher hydrocarbon production was noticeably lower than that for methanation (fig. 3). The steady-state rate of conversion of CO into higher hydrocarbons (MW > 16) on the K-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 K-dosed surface; so that K may be considered a true promoter with respect to this reaction.

3.4. Carbide buildup kinetics

In a manner identical to that used for the clean Ni(100) surface [2], the rate of carbide buildup via CO disproportionation $(2 \text{ CO} \rightarrow \text{C}_a + \text{CO}_2)$ was measured for the clean and potassium-covered surfaces by observing the growth in



Fig. 5. A comparison of the product distributions (weight percent) observed for clean and K-doped catalysts at T = 500 K, $H_2/CO = 4/1$, and a total pressure of 120 Torr. Potassium coverage = 0.10 ML.



Fig. 6. The relative initial rate of reactive carbon formation from CO disproportionation as a function of potassium coverage. $P_{CO} = 24$ Torr, T = 500 K.

carbide AES signal with time in 24 Torr CO, starting from a carbon-free surface. Potassium markedly increases the rate of CO disproportionation. The increase with $\theta_{\rm K}$ of the initial (limit as $\theta_{\rm C} \rightarrow 0$) rate of carbide buildup at 500 K is shown in fig. 6. The carbide buildup kinetics at various temperatures for the clean surface [2] and for $\theta_{\rm K} = 0.10$ are compared in fig. 7. The rate of carbide buildup (i.e., the slope of fig. 7) in the presence of K at various



Fig. 7. Reactive carbon buildup via CO disproportionation at various temperatures for a clean [2] (solid curves) and K-doped (dashed curves) Ni(100) catalyst. Potassium coverage = 0.10 ML, $P_{\rm CO} = 24$ Torr.



Fig. 8. Activation energies for reactive carbon buildup as a function of reactive carbon coverage on a K-doped Ni(100) catalyst. $P_{CO} = 24$ Torr, T = 500 K, $\theta_k = 0.10$.

constant carbon coverages was analyzed in Arrhenius form for the activation energy for CO disproportionation ($E_{a,dis}$). These results are summarized in fig. 8. Note that $E_{a,dis}$ at low θ_C is much lower at $\theta_K = 0.10$ (~10 kcal mole⁻¹) than on clean Ni(100) (~23 kcal mole⁻¹ [2]). It should be noted that the limited amount of data in fig. 7 restricts this to a qualitative comparison. The rate increase may be attributed to this decrease in activation energy. At higher coverages of carbide (such as those characteristic of steady-state H₂ + CO reaction conditions in the presence of K), the activation energies for CO disproportionation become comparable on the clean and K-dosed surfaces, and approximately equal to the activation energy for the overall methanation reaction (~25 kcal mole⁻¹).

4. Discussion

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 Ni catalysts [21-23]. This agreement betwen bulk, single crystal Ni and supported Ni indicates that the major mechanism by which potassium additives alter the catalysts's activity and selectivity is not related to the support material, but that it is rather a consequence of direct K-Ni interactions. A similar conclusion has been drawn in the case of iron catalysts for ammonia synthesis [45],

where it was found that the K atoms reside upon patches of Fe and not upon iron-free areas of the support.

It was shown in fig. 3 that the activation energy for methanation was not dependent upon the presence of potassium. This suggests that the reaction mechanism and its rate-limiting step remain the same in the presence of potassium. There has been considerable discussion of the reaction mechanism on clean Ni catalysts [1,2,7,11,22,23,46-53]. Current evidence [1,2,7, 11,22,23,46-53] indicates that the mechanism must include at least the following classes of steps: (1) dissociative hydrogen adsorption; (2) molecular CO adsorption; followed by (3) CO dissociation into adsorbed carbon (surface carbide) and oxygen atoms; (4) oxygen adatom removal (rapidly, as CO_2 [54] or H_2O [55]); (5) hydrogenation of adsorbed carbon by adsorbed hydrogen; (6) chain growth via C-C bond formation; and (7) chain termination by hydrogen addition to give gaseous products.

We have shown that potassium adatoms cause a very large increase in the rate of the CO disproportionation reaction and a decrease in its activation energy for low $\theta_{\rm C}$. This may be related to the observation that traces of potassium carbonate accelerate the rate of free carbon formation in the CO disproportionation reaction on high-surface-area Ni catalysts [56]. At low $\theta_{\rm C}$ and the conditions of our measurements (24 Torr CO, 450-500 K) the surface should be covered with adsorbed CO [57] so that CO adsorption does not limit the disproportionation rate. Similarly, oxygen removal via CO₂ formation is relatively rapid [54] so that CO disproportionation must be rate-limited instead by the dissociation of adsorbed CO into adsorbed carbon and oxygen atoms (step 3 above). Our observation of a K-induced increase in the rate of CO disproportionation is then consistent with the increase in the heat of CO adsorption and the enhancement in the CO dissociation probability observed in the thermal desorption studies from alkali-covered Ni(100) [29]. These effects are also observed on other metals [33-35], and they have been explained in terms of an electronic ligand effect, whereby the electropositive K adatom denotes extra electron density to the Ni surface atoms, which in turn donate electron density to the adsorbed CO molecule [33-35]. 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 [33-35]. This model satisfactorily explains the decrease in the activation energy for carbide buildup (rate-limited by CO dissociation) brought about by potassium. This is entirely analogous to the explanation for the decrease in activation energy for dissociative N2 adsorption on K-promoted Fe [32].

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. It should be noted that

an increasing carbide level has been associated with a decreasing methanation rate on clean Ni(100) [9]. As we have shown, the most noticeable influence of K addition upon surface coverages is to markedly increase the steady-state carbide level. Potassium will also increase the coverage of molecular CO (θ_{CO}), since K increases its heat of adsorption [29]. On clean Ni(100), it was shown that increasing the carbide level increases the rate of carbide removal by hydrogenation with H₂ (in the absence of CO where the hydrogen addition step is clearly rate-limiting) [2]. The decrease in methanation activity brought about by K must therefore be related to a poisoning of either the hydrogen adsorption or hydrogen addition steps by a combination of adsorbed potassium and the consequently higher θ_{CO} . Potassium was shown to decrease the rate of hydrogen adsorption on Fe [59]; and CO is known to decelerate hydrogen adsorption on Ni(100) [59,60]. (Surface carbide is also known to decrease the hydrogen adsorption rate on Ni(100) [61].) The effects of potassium and adsorbed CO upon the rate of the hydrogen addition step $(H_a +$ $H_n C_{m,a} \rightarrow H_{n+1} C_{m,a}$) are not known.

We should point out that under no circumstances were we able to find conditions where carbide formation (CO dissociation) was rate-limiting to methane formation, even for H_2 : CO ratios as high as 10^3 . However, since this reaction proceeds much faster in the presence of K, one would expect a strong acceleration of the methanation rate due to K under those conditions where carbide formation is the rate-limiting step. This could presumably occur only at H_2 : CO pressure ratios in excess of 10^3 and total pressures in excess of 120 Torr.

The influence of adsorbed potassium upon the synthesis of higher hydrocarbons is consistent with results on supported catalysts [21] and may be analyzed by the same mechanistic model used above. For these reactions, we feel that carbon chain growth is rate-limiting. Thus, the observed effect of K 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 our 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 [10].

The effect of potassium to decrease the overall activity for methanation has been noted by several authors [21-23], but most carefully measured by Schoubye [23]. A possible contradictory result reported by Huang and Richardson [20] for Na-promoted Ni may be related to differences between Na and K, but we feel it more likely that their non-promoted results were somewhat deceptive. They observed a six-fold increase in the methanation activity for Ni catalysts upon Na loading. Note, however, that their non-promoted Ni catalyst showed an activity a factor of 7 to 16 below that reported by other authors [20]. The effect of the Na in their study was, therefore, only to restore the activity characteristic of typical non-promoted catalysts. The authors ascribe this effect to the influence of K upon the acidity of the support material (SiO₂). It is interesting to consider our results in the light of a recent study by Okamoto et al. [62], who observed an increase in Ni methanation activity when nickel-boride compounds were prepared which increased the electron density (as evidenced by XPS chemical shifts) on the Ni atoms. Since K adatoms should have the same effect upon the Ni electron density [25–31], one might have expected a similar increase in activity due to K-additive. The results of Okamoto et al. are, however, somewhat suspect in that: (1) the method for assessing the electron density on Ni completely neglected very important final-state effects in XPS; and (2) the activation energy they observed (38 kcal mole⁻¹ [1,7,9,23,53]).

A study of the effect of K promoters on iron Fischer-Tropsch catalysts has recently been completed [15]. Similar to the case of Ni, it was found that K decreases the rate of methane formation, shifts the selectivity toward higher hydrocarbons, and increases the rate of carbon deposition. The carbon coverages were, however, very high in the case of Fe, with the K thought to be "floating" upon some ten monolayers of carbon. In our case the carbon coverage at prolonged, steady-state conditions is only about 30% of a monolayer, and the K is thought to be acting directly upon the Ni substrate.

5. Summary

One-tenth monolayer of potasium decreases the rate of methane formation by a factor of two with respect to clean Ni(100), without affecting the activation energy. The rate of production of higher hydrocarbons increases in the presence of potassium. The steady-state carbide coverage, θ_C , increases from 0.1 on clean Ni(100) to 0.3 at $\theta_K = 0.1$. This is related to an increase in the CO dissociation rate and a decrease in its activation energy, effected by the potassium and understandable in terms of an electronic ligand effect. The higher carbon level is thought to explain the higher probability for reactions involving C-C bond formation. Ultra high vacuum surface analysis after the reaction at the reaction temperature indicates that the potassium adatoms do not exist as the oxide. The similarity in our present results on bulk, single-crystal Ni(100) and results on high-surface-area, supported Ni catalysts suggests that the promotion mechanism of K does not require metal-support interactions or a support material.

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