Promotion and Inhibition of Ni(CO)₄ Formation on Ni(100): A Kinetic Investigation Coupled with ESCA Measurements

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The rate of formation of Ni(CO)₄ on a Ni(100) surface was investigated by continuous spectroscopic detection of the reaction product at and above room temperature, as a function of reaction time and surface composition (coverage with C, S, and O). To determine the latter, ESCA spectra of the surface were taken in the same apparatus. An initially clean surface starts with a high rate which drops off very fast to below the detection limit (of about 10^{11} molecules $cm^{-2} s^{-1}$); this is accompanied by carbon deposition, probably through CO disproportionation. After a few hours, the rate is roughly stationary and exhibits a maximum at about 390 K and an apparent activation energy of about 67 kJ/mol between room temperature and 320 K. Sulfur precoverage has a strong promoting effect; the rate at room temperature increases exponentially with S coverage for $\theta_S > 0.3$. By S-saturation the rate maximum shifts down to 335 K, and the apparent activation energy around 300 K decreases to 8 kJ/mol. Contrary to common belief, oxygen also increases the rate for the "clean" surface, probably because of removal of C contamination; it decreases the rate for an S-precovered surface because of partial removal of S. Practical surfaces obtained at high vacuum and less stringent purity conditions lead to very complicated behavior of the rate with prehistory which can only be understood qualitatively. The results are discussed in terms of factors controlling the reaction mechanism.

1. INTRODUCTION

This work was prompted by an attempt to reproduce the reports of Krinchik *et al.* (*1*) of an oscillatory dependence of Ni(CO)₄ formation rate on an external field, which we could not repeat (*2*) as had been the case for other groups (*3, 4*). During this work, which has focused on stringently defined conditions of cleanliness of surface and gas, it became obvious that surface conditions very strongly influence the rate of formation of Ni(CO)₄ (subsequently termed "the rate"). Some of these, for instance the promoting influence of sulfur, have been well known for a long time (*5*), but they have never been quantified from the standpoint of surface compositions.

Because of its technical importance, this reaction has been investigated by many authors since Mittasch's days (*1–16*), but prior to 1973 all work has been carried out with powders (*5–8*), porous sheets (*9*),

platelets (*10–12*), or films (*13, 14*). Single crystals have been used only recently (*1–4, 15, 16*), but even then not under UHV conditions. From the earliest investigations (*5*) a change of the rate with reaction time, a promoting influence of sulfur, and an inhibiting effect of oxygen have been observed. The reported rates and activation energies vary widely (see the compilation in Ref. (*16*)); in most cases a decay of the rate with reaction time is observed. The first work using high vacuum techniques was done by Brown in 1965 (*13*) and continued by Milliams *et al.* (*14*). Using evaporated films, Milliams *et al.* found an increase of activation energy from 32 to 68 kJ/mol with reaction time, a different behavior of the rate during heating or cooling, and a maximum rate at a temperature T_m; nickel carbide formation was assumed as the main cause. They also found a strong promoting effect of treatment with H₂S above a minimum dosage of $6 \times 10^{14} cm^{-2}$ which leads to

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a shift of T_m from about 360 K to as low as 310 K; this effect was attributed to suppression of CO dissociation by adsorbed S. Promotion by Hg adsorption was also found. De Groot et al. (16) found a strong faceting effect at long times. Mehta et al. (15) reported a Hedvall II effect (17) for Ni/Cu alloys, i.e., a change of activation energy at the Curie point. References (14) and (16) constitute the most careful work to date and contain a number of conclusions which are relevant to the present work despite the lack of direct surface analysis. They will be discussed below.

In order to obtain better access to the influence of surface conditions, we coupled the rate determination apparatus to an ESCA spectrometer such that the surface composition of the Ni crystal used could be analyzed before and after carrying out the reaction or other treatments, by transferring the crystal under UHV. Ultrahigh vacuum techniques and stringent conditions of cleanliness were used throughout. Also, we focused on the initial behavior of the rate, i.e., after removal of between <1 and a few 100 Ni layers. Therefore our conditions do not correspond to the steady-state faceting observed by de Groot et al. (16). A number of interesting but somewhat complicated results have thus been obtained which shed additional light on the mechanism of this comparatively simple heterogeneous reaction.

2. EXPERIMENTAL

The experimental set-up is sketched in Fig. 1. It was constructed to conform to the following requirements:

(1) Extreme cleanliness of the whole system including supply gas to avoid undefined contamination of the reacting surface and to make controlled changes of the surface possible.

(2) A method to check the surface composition *in situ* while maintaining cleanliness.

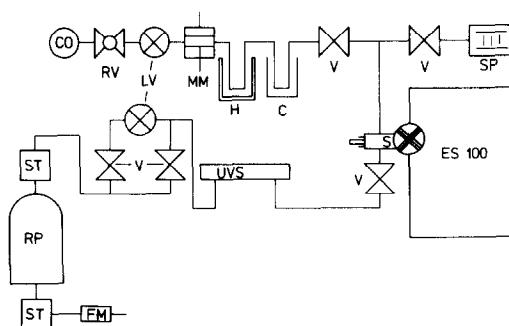(3) A continuous method of monitoring the rate at high sensitivity and with high

FIG. 1. Sketch of the experimental set-up. CO, gas supply; RV, reduction valve; LV, leak valves; MM, membrane manometer; H, hot zone; C, LN cooled zone; V, metal valves; SP, sorption pump; S, transfer system; UVS, uv spectrometer; ST, sorption traps; RP, rotary pump; FM, flow meter; ES100, ESCA spectrometer with pumps.

relative accuracy (the latter was of particular importance in the work checking for magnetic field influences (2).

Standard UHV techniques were used throughout. The base pressure in the reaction cell was in the upper 10^{-10} mbar range. The CO used (99.99%, Linde) was further purified in a Cu tube with an active surface area of 160 cm² which was heated to 400°C to remove oxygen, hydrogen, and Ni or Fe carbonyls. Residual gases (CO_2, H_2O, hydrocarbons) were frozen out in a liquid nitrogen-cooled trap. To avoid CO condensation in the latter the CO pressure was limited to 316 mbar. These procedures had the result that no extrinsic contamination of the Ni surface was detectable with ESCA even after reaction times of some hours (i.e., no peaks other than those of Ni, C, and O were observable). To make such measurements possible (condition 2), the reaction cell was coupled to an ESCA spectrometer (AEI ES 100, with Mg anode) via a UHV transfer system constructed of welded bellows and a UHV valve. This proved of utmost importance as illustrated by results obtained using a standard AEI transfer system with Teflon bushings (see below). Although the pressure in the latter transfer system with pumps connected was, at some 10^{-9} mbar, less than an order of magnitude higher than

in the UHV transfer system, the contamination in transfer strongly influenced the rate, as will be described briefly at the end of this paper. This must have been due to the composition of the residual gas.

The sample was a Ni(100) disc of 12 mm diameter and about 1 mm thickness cut by spark erosion from a single crystal rod (MRC Corp.) after orientation to 0.5° by X-ray diffraction, and polished mechanically. It was cleaned by repeated heating to 1200 K alternately in NO and H_2 which has been found to remove C, S, and O impurities effectively (18); the cleanliness was checked by XPS.

The third condition was met by the construction of a differential uv absorption spectrometer working at 220 nm and employing a hydrogen lamp with band filters, and thermostated photocells and amplifiers. Using an absorption path length of 50 cm, a carbonyl partial pressure of about 10^{-5} mbar in 316 mbar CO, i.e., less than 1 in 10^8, could be detected. With a gas flow of 1 cm^3 s^{-1} the minimum detectable rate was 1.6×10^{11} molecules/cm^2 s^{-1}, i.e., about 10^{-4} Ni monolayers per second.

3. RESULTS

3.1. The "Clean" Surfaces

3.1.1. Time dependence, roughness, and carbidization. When a freshly prepared clean crystal was used for the reaction, the rate at room temperature was initially very high ($>100 \times 10^{11}$ cm^{-2} s^{-1}) but dropped off fast (Fig. 2, line 1). ESCA spectra taken after a few minutes or 2 hr showed two C 1s and one O 1s peaks (Fig. 3), of which the C_I (285.7 eV) and the O (531.7 eV) peaks disappeared upon heating to ~480 K indicating that they are due to adsorbed CO. Indeed the binding energies (BE) are as expected for this assignment, and the relative intensities are equivalent to a 1:1 atomic ratio if corrected for the different cross-sections and spectrometer sensitivities (this was calibrated by taking spectra

from a thick condensed $Ni(CO)_4$ layer). The C_{II} peak at 283.6 eV is removed by heating to 900 K. It is certainly due to deposited carbon which diffuses into the bulk at these temperatures (see below); judging from the binding energy, it is likely to be bonded to Ni ("carbidic" carbon (19)) and not segregated. (Atomic C in dissociated β-CO on W (110) has a BE of 283.0 eV (20). On the other hand, graphitic carbon as measured, e.g., for an Aquadag film, has a BE of 284.6 eV; see also below, Fig. 6.) As no O 1s peak attributable to dissociated CO (which should be observable at about 530 eV (20)) was ever seen, and as no oxygen stayed behind after desorption of the CO layer, the carbon must be formed via disproportionation of CO at the high pressures used, with subsequent desorption of CO_2, and not by CO dissociation. As shown by ample evidence in the literature, dissociation does not occur below the desorption temperatures on smooth Ni surfaces (21), but does occur on stepped (22) and disordered (21) surfaces even at room temperature, and on low index faces above 460 K and at high CO pressures (23, 24). CO disproportionation has been reported from early on (25), but could also be explained by dissociation followed by removal of adsorbed O with further CO to form CO_2 (24).

If another cleaning cycle was performed after curve 1 of Fig. 2, the initial rate was much smaller, but fell off as rapidly (curve 2); a third repetition led to a rate at (or below) the detection limit from the start which was roughly constant with reaction time. As the carbide layer was formed every time in the first minutes, the high initial rate and its rapid drop-off cannot be (solely) caused by its initial absence and subsequent formation. Rather it is probable that the high initial rate is due to surface faults and disorder which are present after crystal preparation and are removed by reaction (during the first minutes of curve 1 above five layers are removed).

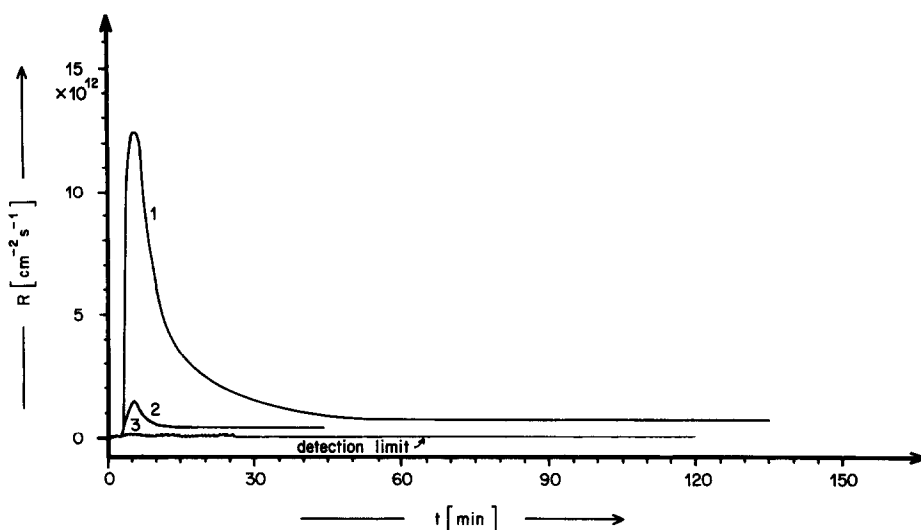The results suggest that surface disorder strongly enhances the rate, and that an ini-

FIG. 2. Time dependence of the room temperature rate of a freshly cleaned surface (1, 2, 3, three successive runs).

tially clean surface always contains carbidic carbon under reaction conditions.

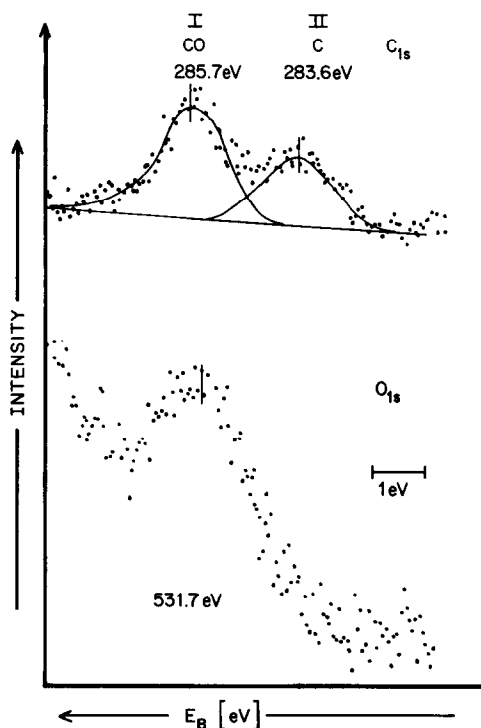*3.1.2. Temperature dependence.* Measurements of the temperature dependence

were reasonable only for the roughly stationary state corresponding to the end of curve 3 or further reaction. For such a surface (rate at room temperature below detection limit) the temperature dependence is shown in Fig. 4. Apart from a decrease of the height of the maximum, the dependence is essentially the same on heating or cooling if the heating or cooling is done slowly enough (≤ 0.05 K s^{-1}). In the example of Fig. 4 T_m is found at 391 K; it varied slightly (by some K) with initial conditions.

Obviously a dependence of the type of Fig. 4 does not lend itself easily to deduction of a physically meaningful activation energy. If we nevertheless plot the data in a
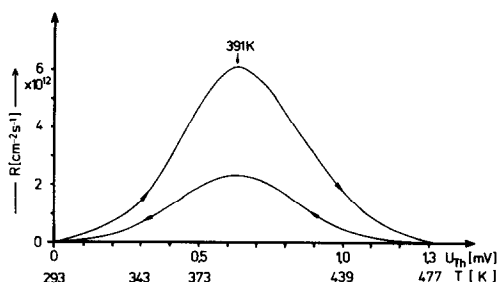

FIG. 3. The C 1s and O 1s region of the ESCA spectrum after a few minutes or hours of reaction.

FIG. 4. The variation of the rate on a "clean" annealed surface with heating and cooling (at 0.05 K s^{-1}). The temperature scale is slightly nonlinear as it is derived from a thermocouple reading.

log R vs $1/T$ diagram for the sake of comparison with other work, we find that the data up to about 320 K can be considered as roughly conforming to a straight line equivalent to a formal activation energy of about 67 kJ mol^{-1}. At higher temperatures the slope decreases, and between 320 and 370 K gives an average value of 42 kJ mol^{-1}.

That the difference between heating and cooling in Fig. 4 is due to a persisting slow decrease of the rate with reaction time can be seen in Fig. 5 where we plot the time dependence of the rate at T_m after stepwise heating to T_m from room temperature. Obviously the surface condition corresponding to the maximum rate needs some time to be established (the maximum is reached after about 10 min while the temperature is constant after about 10 s). Subsequently, the rate decays by about $\frac{1}{3}$ in 3 hr. After this time, about 30 layers have been removed, and ESCA spectra show a broadened C 1s peak which cannot easily be resolved any more into the CO and carbidic peaks. This suggests that additional carbon contamination builds up and is the reason for the slow decay of R. Nevertheless, the type of reactivity appears to be the same, as shown by the constancy of T_m (Fig. 4).

A dramatic change in reactivity as well as surface composition can be brought about if the sample is heated to higher temperatures under CO (Fig. 6). Although the rate remains undetectable above 480 K, the rate maximum shifts strongly to lower temperatures upon cool-down (in the example shown, where the maximum temperature of heating was 720 K, T_m is 329 K; different initial maximum temperatures led to different T_m values). Subsequent ESCA spectra (Fig. 6, inset) show a strongly diminished O 1s peak and a very strong C 1s peak at 284.6 eV, i.e., intermediate to C_I and C_{II} of Fig. 3, and corresponding to graphitic C (see above). This suggests that the heating in CO leads to carbon build-up which consists of species with C–C bonds. This species suppresses part of the normal CO layer and changes the reactivity (lower R_m at lower T_m).

If a carbon deposit produced in this way is heated $in\ vacuo$, the carbon concentration decreases as shown in Fig. 7 and disappears around 900 K; it does not come back
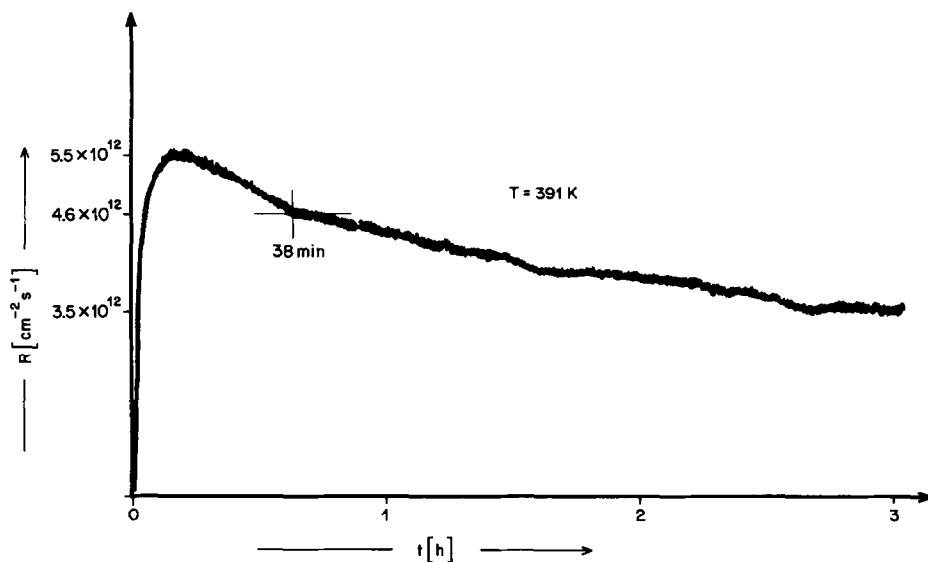

FIG. 5. Time dependence of the rate after stepwise heating to 391 K for a crystal corresponding to the start of Fig. 4.
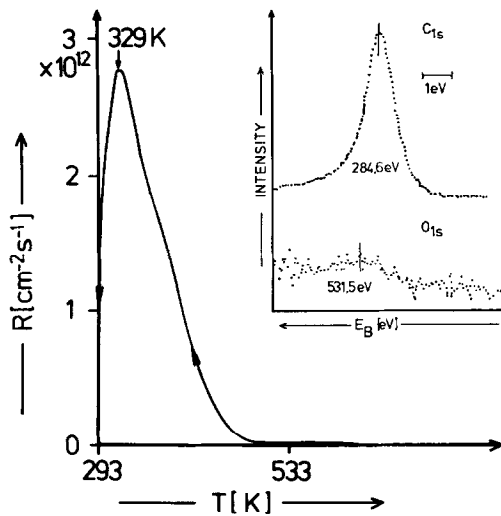
upon cooling. This must be due to carbon diffusion into the bulk (*19*). The rate after cool-down is *normal* as for the annealed "clean" surface (i.e., as in line 3 of Fig. 2, and Figs. 4 and 5).

3.2. The Influence of Extrinsic Surface Contamination on the Rate

It has been shown in Section 3.1 that even an initially clean Ni surface does not stay clean under reaction conditions as carbon deposits of various types, depending on conditions, are formed. In the following we describe the influence of intentional precoverage by S and O, as these species have been reported to be of importance (see Introduction). In Section 3.3 we consider the behavior of realistic surfaces which are obtained by only slightly less stringent attention to cleanliness.

3.2.1. The influence of sulfur coverages. As mentioned, sulfur has been known as a promoter of the Ni(CO)₄ formation since the earliest days (*5, 14*). Therefore, a quantitative investigation of its influence appeared to be of particular interest.

A precoverage of S was produced by exposure to a certain dose of H₂S at room temperature and heating the layer to 670 K, and the resulting S coverage was determined by ESCA. A calibration curve was established using the S 2p peak area (peak location and shape stayed constant with coverage; therefore we do not believe that surface reactions toward sulfide formation (*26*) played any role). The saturation coverage reached at >100 Ex [1 Ex = 10¹⁸ m⁻² (*27*)], corresponding to 100 × 10¹⁴ cm⁻², and staying constant up to 5000 Ex probably corresponds to the ordered c (2 × 2) overlayer described by various authors (*28*) and believed to be due to S : Ni = 1 : 2. We will give θ_S relative to the saturation coverage (θ_S ≡ 1 corresponding to half a monolayer relative to Ni). Figure 8 shows the rates obtained at S-covered surfaces as functions of reaction time. Obviously the rate is strongly increased by S coverages above θ_S = 0.3. The decay with time is less pronounced than for "clean" unreacted surfaces which is consistent with the fact that the crystal had been used for reaction prior to S coverage so that roughness and faults should have been removed. No changes in the magnitude of the S peak before and after the reaction were detectable, so that removal of S during the reaction is an unlikely cause of the rate decay. ESCA after reaction also showed that for θ_S > 0.3 *no* C 1s or O 1s peaks were detectable showing that neither irreversible chemisorption of CO nor CO disproportionation
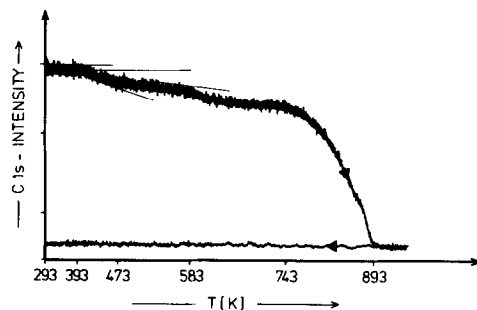

FIG. 7. Behavior of the C 1s peak produced by the procedure of Fig. 6, upon heating.
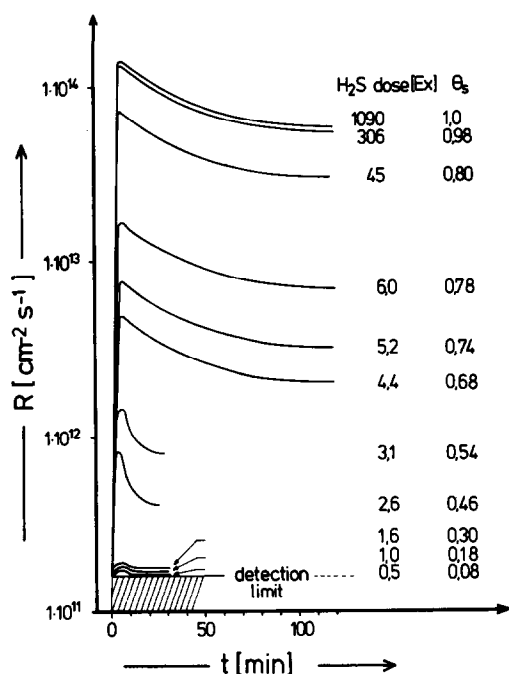
FIG. 8. Dependence of the rate on reaction time for various sulfur coverages to saturation ($\theta_S = 1$ corresponding to half a monolayer of S), at room temperature.

An Arrhenius plot for 293 to 323 K leads to a very low formal activation energy of 8 kJ/mol both for the up and down curves. The maximum rate at $\sim$330 K (about 10^{14} cm^{-2} s^{-1}) is about equal to the initial rate of the S-saturated surface at room temperature.

3.2.2. The influence of oxygen. Oxygen on Ni (100) can lead to adsorption as well as oxidation depending on exposure and temperature (*30*). In order that the results are not influenced by these different possible surface compositions or by changes during reaction and heating, the crystal was always heated to 900 K for some seconds after exposure to an oxygen dose. This led to O 1s peaks identical in location (BE: 530.3 eV) and shape. To produce thicker oxide layers the crystal was heated in oxygen. To
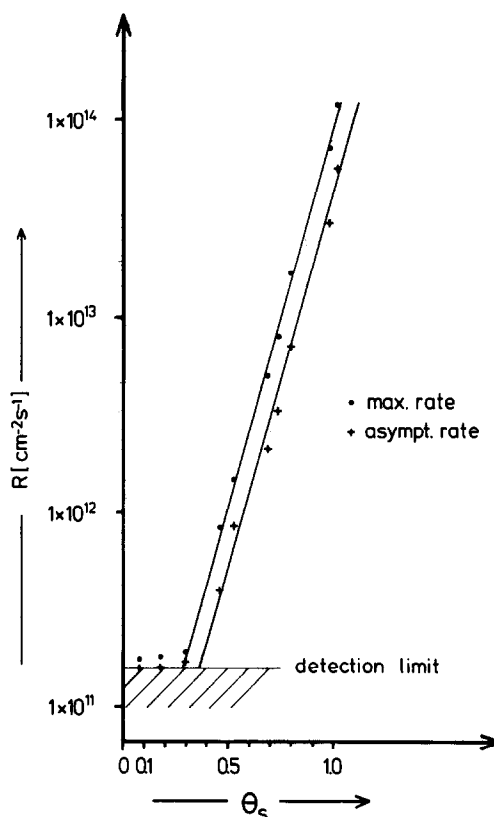
takes place on such a surface. Below $\theta_S = 0.3$ (S : Ni = 0.15), both C_I and C_{II} decreased with increasing θ_S (due to the small signals a quantitative statement is not possible here). If the (roughly constant) rates after 2 hr are plotted against the S coverage, an *exponential* dependence becomes obvious above $\theta = 0.3$; a similar dependence holds for the initial rates (Fig. 9). This is an unexpected relation for a catalytic effect; it will be discussed in Section 4.

The temperature dependence of the rate on an S-saturated surface (after 2 hr reaction) is shown in Fig. 10. T_m is strongly decreased, in qualitative agreement (*29*) with Milliams *et al.* (*14*). A hysteresis upon heating and cooling is found, part of which may be due to a parallel decrease of the rate with time. Again the S peak was *not* diminished by the reaction sequence during which roughly 200 Ni layers were removed. This shows that the S contaminants always manage to stay "on top."

FIG. 9. Initial and asymptotic room temperature rates of Fig. 8 vs sulfur coverage ($\theta_S = 1$ corresponds to half coverage relative to surface Ni atoms). An *exponential* dependence is obvious.
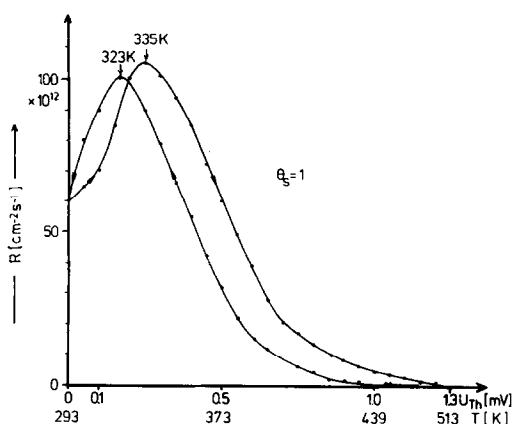
FIG. 10. Temperature dependence of the rate on a sulfur-saturated surface upon heating and cooling.

indicate the amount of oxygen present, θ_O is given relative to the O 1s intensity obtained by saturation with oxygen at 6 × 10^{-7} mbar at room temperature ($\theta_O \equiv 1$). Figure 11 shows the time dependence of the rates on such oxide surfaces. As seen, all surfaces are characterized by a *high* initial rate (compared to "clean" surfaces) which decreases rapidly. Up to an intermediate amount of oxygen ($\theta_O \approx 4$) the rates increase but then fall again and stay constant above $\theta_O \simeq 7$. For thin oxide layers ($\theta_O \leq 1.4$) the oxygen is completely removed in a reaction time for 80 min, and the surface coverage after reaction (CO, C) resembles that of an initial clean sample, but with lower intensities. Thicker oxide layers show a decrease of oxygen content which is smaller even on an absolute scale; no C_{II} peak (carbide) is found, and the amount of chemisorbed CO (C_I peak) is smaller and becomes undetectable above $\theta_O = 4.2$. This suggests that the initial increase of rate with θ_O is due to the suppression of CO disproportionation (and possibly to induced roughness), while the decrease above $\theta_O = 4$ is due to the suppression of adsorbed CO. The decay of rate with time may be due to removal of Ni from the oxide layer.

The temperature dependence of the rate over a thick oxide layer ($\theta_O = 10$), measured after the rate had decayed below the

detection limit, is shown in Fig. 12. In heating up, a rate maximum is reached at 397 K, while on cool-down, a fourfold higher maximum is reached at 377 K. Both rate maxima exceed those obtained for a "clean" reacted surface, i.e., oxide layers do *not* act as inhibitors. An "activation energy" cannot reasonably be extracted (changing slopes between 25 and 80 kJ/mol are obtained from an Arrhenius plot). This behavior suggests that processes occurring during heating or cooling are important to determine the rate. This is further illustrated by the effects of temperature jumps (Fig. 13): if T is increased stepwise from room temperature to 400 K (the "upward" T_m) for a sample whose activity had been allowed to decay below detectability at room temperature, the rate climbs slowly to its maximum, while if a step is made from 500 to 383 K (the "downward" T_m), the R shows the fast reaction-induced decay, and the height of the step depends on the time elapsed at the high T. Both effects can best be rationalized by diffusion and reaction: at high temperatures oxygen diffuses into the
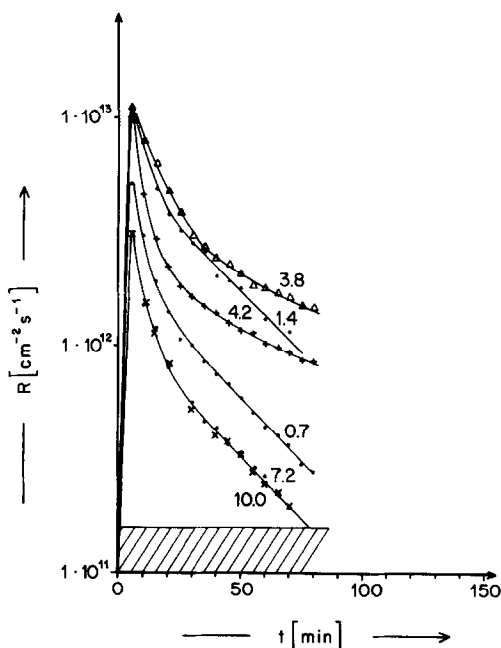

FIG. 11. Rate dependence on reaction time for various "oxygen" coverages at room temperature.
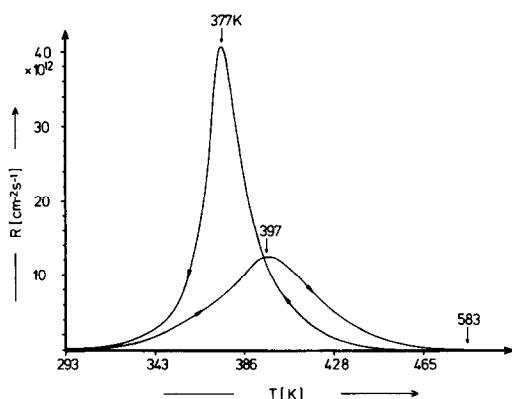
FIG. 12. Temperature dependence of the long-time rate over a thick oxide layer ($\theta_O = 10$) upon heating and cooling (0.05 K s^{-1}).

crystal leaving accessible Ni behind; reaction of an Ni-rich oxide leads to Ni-depletion and therefore rate decay. The coupling of both processes leads to the sharp maximum during cool-down and to the changing temperature dependences.

3.2.3. The influence of oxygen on a sulfur layer. Oxygen is consistently reported to be an inhibitor of carbonyl formation in the literature (*5, 9, 10*). As shown in Section 3.2.2, however, oxygen—at least in the form of thin oxide layers—promotes the reaction compared to the "clean" surface. One possible explanation for this apparent contradiction is that oxygen in fact does
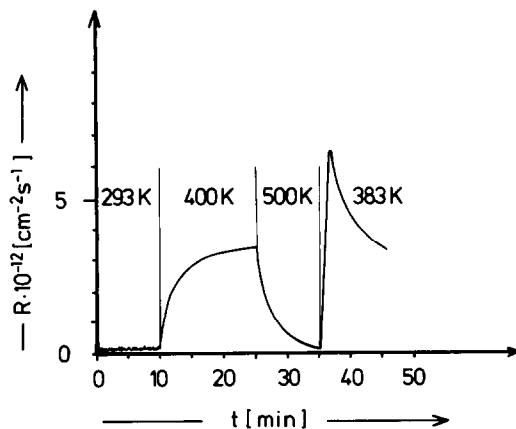
not inhibit the reaction itself but reduces the promoting effect of S: under most conditions of less than stringent cleanliness, S contamination on Ni can be expected, and would not be reduced by the reaction (see above).

Therefore we examined the effect of oxygen on a sulfur-saturated surface. Figure 14 shows the behavior of the S-content of such a surface which was postexposed to 10^{-3} mbar oxygen at 353 K for 4 hr (this would correspond to the integrated effect of 1 ppm oxygen around the rate maximum). The S-content decays to about half in an hour and more slowly thereafter. After 4 hr the nominal oxygen content was $\theta_O \simeq 6$ (!). Even if the simultaneous presence of CO were to slow the S removal by O, it is likely that S is indeed removed by oxygen under reaction conditions also. This can explain the reported inhibiting effect.

3.3. "Technical" Conditions

In the early stages of this work some preliminary tests were made using the original air-lock system of the AEI spectrometer which uses sliding Viton seals. While this degrades the residual vacuum in the sample chamber by a factor below 10, considerable contamination on the crystal is produced during transfer into the spectrometer, probably caused by friction-induced desorption and opening of virtual leaks in the gaskets. This contamination apparently consisted mainly of partly cracked hydrocarbons. It

FIG. 13. Response of the rate over a surface corresponding to Fig. 12, to stepwise temperature increases and decreases above and below T_m.
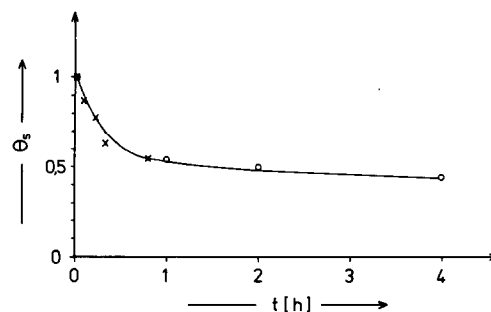

FIG. 14. Decrease of the S_{2p} intensity with exposure of an initially sulfur-saturated surface to 10^{-3} mbar oxygen at 353 K.

was characterized by a very broad C 1s peak centered at about 285.6 eV (diffusion pump oil produced a peak with the same BE) which was about seven times more intense than the total signal (C_I + C_{II}) produced by CO adsorption or reaction under clean conditions; the O 1s signal was only $\frac{3}{4}$ of that of a CO layer.

Although such a layer is rather badly defined, we show some results for it because surfaces maintained under poorer vacuum conditions would probably be similar.

Even though the carbon intensity corresponds to several monolayers, the rate on such a surface was initially (i.e., without annealing) also around 5×10^{13} cm^{-2} s^{-1}, and decreased to below the detection limit in a few hours. Subsequent T variation between room temperature and 470 K led to distinct hysteresis with, e.g., $T_m \simeq 385$ K (up) and 363 K (down). However, depending on the maximum temperature attained, it was also possible to produce regions of roughly constant rate with temperature (Fig. 15a), of changing hysteresis (Fig. 15b) and of shifting pronounced maxima (Fig. 15c). Even though the heating rate was low (0.04 K s^{-1}) these curves also contain time effects as was deduced from temperature jump experiments where isothermal changes with time constants of the order of 20 min were seen.

If such a surface is saturated with S, the initial rate is brought back to about 2×10^{13} cm^{-2} s^{-1}, but the temperature dependence is stronger than for the C-free surface. Reproducible measurements are difficult because again the memory of the layer for its prehistory is strong (see Fig. 16 for an example).

Obviously any number of rate parameters could be derived from such surfaces. Qualitatively this is probably due to diffusion processes of Ni in the carbonaceous layers. Fast diffusion of Ni through carbonaceous layers has indeed been reported (31). Any attempt to go further in the interpretation does not appear sensible. However, we consider it worthwhile to mention these

results briefly for two reasons: (i) The conditions leading to these surfaces are not very "dirty" at all and could well have existed in other investigations. (ii) The fact that comparable rates are found on almost clean and almost totally contaminated surfaces stresses how few surface sites take place in the reaction.

4. DISCUSSION

The main results of Section 3 can be summarized as follows:

(1) Under reaction conditions, initially clean Ni(100) surfaces are immediately covered with "carbidic" carbon (to a coverage corresponding to about 15–30% of a Ni monolayer). The reactivity under such conditions depends strongly on surface roughness; if the latter is low, the reactivity at room temperature is below 10^{11} cm^{-2} s^{-1}. The activation energy around room temperature is 67 kJ mol^{-1}, with a pre-exponential of $R_0 = 7 \times 10^{22}$ cm^{-2} s^{-1} (at 316 mbar CO), and a rate maximum occurs at 390 K.

(2) Precoverage with sulfur to more than 30% of saturation suppresses the formation of irreversibly chemisorbed CO as well as of carbidic C, and strongly increases the rate. The latter effect becomes stronger the higher the S coverage: quantitatively, an exponential dependence of R on θ_S is found. For $\theta_S = 1$ (half a monolayer relative to Ni), the rate of a smooth surface at room temperature is increased by a factor of more than 600 compared to the sulfur-free surface; E_a around room temperature is decreased to 8 kJ mol^{-1} ($R_0 = 1 \times 10^{15}$ cm^{-2} s^{-1}), and the rate maximum occurs at 335 K.

(3) Thin oxide layers also increase the rate at room temperature as compared to untreated surfaces, and decrease the activation energy and T_m; the formation of surface carbon is suppressed.

Qualitatively, most of these results agree with earlier reports about work with powders, films, and polycrystalline material, and in particular with the work of Milliams et al. (14), showing that the principal ef-

fects must be independent of the form of Ni used, so that our conclusions can also be carried over to other surfaces. Our work, however, is the first in which definite knowledge is available about qualitative and quantitative surface coverages, thus making the conclusions safer and independent of inferences from unrelated data.

In the following these findings will be dis-

cussed in context with the possible influences of impurities on the reaction, and an attempt will be made to draw some conclusions about the general mechanism. In doing so, we shall use the working hypothesis that the energy necessary to remove a Ni atom from the bulk (428 kJ/mol (*32*)) is gradually fed into the reaction by the sequential bonding of the four CO molecules
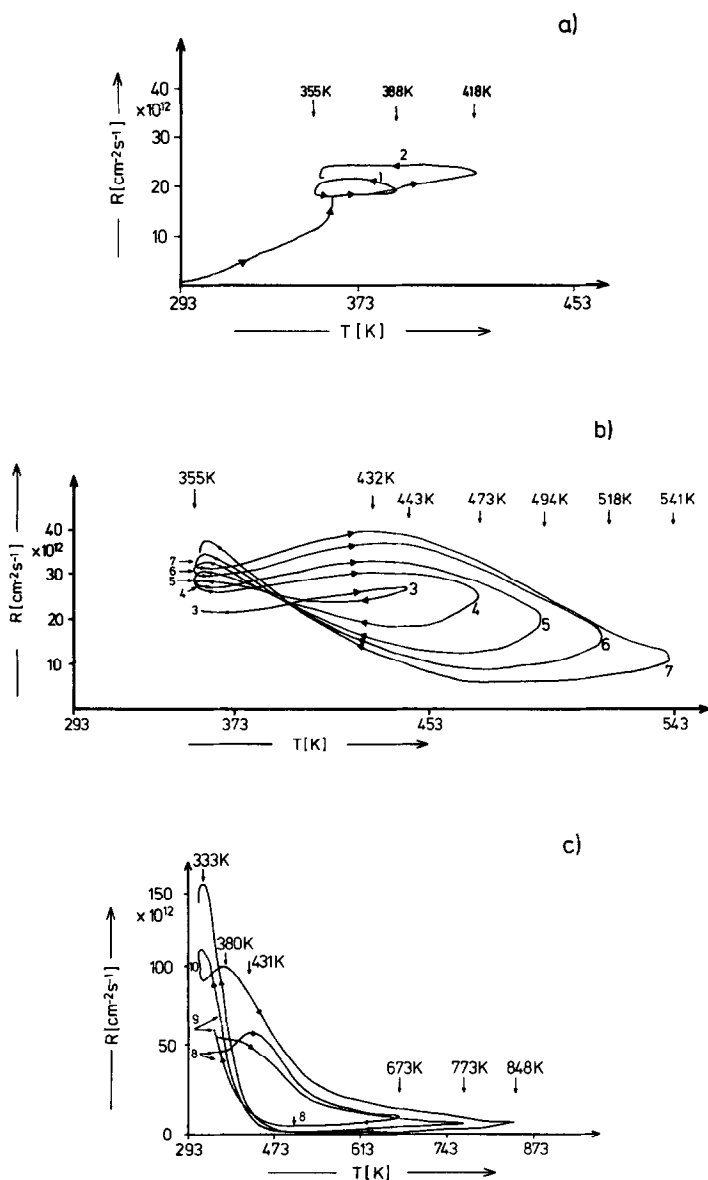

FIG. 15. (a–c) Examples of various kinds of temperature dependences on a hydrocarbon-contaminated Ni surface (see text). The reaction cycles 1 through 10 have been run subsequently.
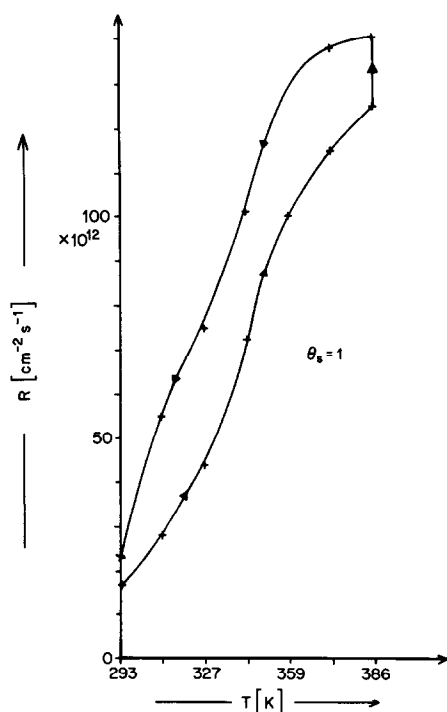
FIG. 16. Temperature dependence of the rate over a hydrocarbon-contaminated surface saturated with sulfur.

(575 kJ/mol total (32)), leaving open at what stage the slow step of the reaction occurs. This suggests that the two important energetic parameters are the Ni–surface bond strength and the CO adsorption bond of the molecules actually taking part in the reaction.

All results make it quite obvious that the Ni(CO)₄ formation is a very slow reaction. If referred to the total number of Ni atoms present, the turnover number would become of the order of 10^{-3}, but the strong dependence on surface roughness and/or disorder, as well as the fact that it can still go on at surfaces covered by thick carbonaceous deposits, suggest that only a very small part of surface atoms actually participate in the reaction. On the "smooth" surface reached after extensive cleaning or reaction the likely candidates are the Ni atoms in half-crystal (i.e., kink) sites, as this leads to a repeatable step. Another possibility would be that screw dislocations are

involved. This should lead to pitting after long reaction times; de Groot et al. (16), however, observed the formation of (111) facets (33). On rougher surfaces, adsorbed Ni atoms or atoms in disturbed areas probably possess higher reactivities, if not blocked by contaminants. This, of course, stresses the importance of breaking the Ni–Ni bonds in the slow step of the reaction. The inhibiting influence of carbidic carbon can be twofold: if there is a tendency of C to diffuse into half-crystal sites or to disturbed areas (or to form there to start with: it is quite likely that the observed CO disproportionation takes place at the same exposed sites responsible for the rate), then these could be blocked for the necessary CO adsorption. Furthermore, the incorporation of C between Ni atoms (formation of local carbidic structure) is expected to strengthen the Ni–surface bond which will also make the reaction less likely. The effect of oxygen can then simply be the suppression of this C influence. In addition, Ni oxide has been shown to be partially reduced by CO under reaction conditions, leaving accessible Ni atoms at the surface.

The effect of S is the most interesting. S is well known to be a strong poison for catalytic reactions on Ni and other transition metal surfaces involving CO and H₂ (see, e.g., Goodman and Kiskinova (34) and work cited therein); usually a small S coverage (less than 0.2 of a monolayer) suffices to saturate this effect. This seems to be connected with the suppression of strongly (irreversibly) chemisorbed CO (where one S affects more than 10 Ni) which has been found here as well, and a considerable weakening of the hydrogen chemisorption bond. Here a very different qualitative and quantitative relationship $R(\theta_S)$ is observed: S leads to an increase of the rate; while the effect appears to be small or negligible at low θ_S, it increases exponentially with θ_S above a threshold. The fact that S does suppress both the strongly chemisorbed CO and the formation of carbidic C (with this

effect becoming complete for $\theta_S \approx 0.3$, i.e., $S : N \approx 0.15$), while the main effect on the rate comes in only at much higher θ_S, shows that the latter is not directly connected with the former (contrary to the assumption of Milliams et al. (14)). Two effects of S appear possible, namely, a decrease of the Ni bonding energy at the relevant sites, and a change of the CO bonding character. It is known (35) that S adsorbs in fourfold coordination up to a c (2 × 2) structure. This makes it likely that the half-crystal sites are not affected by S adsorption, except at high coverages. Furthermore, Goodman and Kiskinova have shown that, while the strongly chemisorbed β_2-species are suppressed by 20% S, weakly adsorbed CO species (desorption temperature around 130 K) come in above S/Ni ≈ 0.3. The CO binding energy appears to decrease gradually with S coverage. Such weakly adsorbed CO is likely to be of importance in carbonyl formation; under high pressures its coverage should be considerable even at 300 K and more.

We suggest, therefore, that the observed S influence is a combination of weakening of the Ni-to-surface and of the CO-to-surface bond. Formally, a behavior of the kind observed here, viz. exponential dependence of the rate on S coverage, $R_S \sim R_0 \exp(a \cdot \theta_S)$, can be explained if the activation energy of reaction behaves roughly like $E_S = E_0 - b \cdot \theta_S$. This effect could work on either or both of the Ni and CO binding energies; the weakening of the bond would have to be roughly proportional to the surface density of S atoms. Unfortunately our results do not allow more detailed conclusions here. However, Block and co-workers (36) have seen evidence in field desorption for the slow step of the reaction to be the displacement of Ni atoms from kink sites to adatom sites. If this is correct, then the linear decrease of activation energy may be connected to the difference of overall binding energy of an $Ni(CO)_2$-entity at a kink site and an $Ni(CO)_3$-entity at an adatom site, where the latter would appear

more likely to be influenced by S adsorption. The reason for the threshold for the S effect may then be that up to $\theta \approx 0.3$ the overall rate is still determined by reaction at irregularities (whose density may have reached a steady state) while above the threshold the S-covered surface parts compete successfully and take over for the overall rate. To be sure, the real effect will be much more complicated as shown by the strong influence of S not only on E_a but also on the preexponential (unfortunately only measured for $\theta_S = 1$) which counteract each other. This must mean that the number of favorable low-energy paths is much smaller than that at higher energy.

This brings us to a discussion of the rate maximum at T_m. It has been suggested (8–12) that this is due to the decomposition of $Ni(CO)_4$ at higher temperatures. This may indeed be so for the high T_m values (around 400 K) as the decomposition pressure of $Ni(CO)_4$ becomes quite low there (37), although this interpretation is questionable even in that case (16). The very low T_m values observed, e.g., for the S-covered surfaces, are definitely in contradiction with this explanation since a catalyst cannot change the equilibrium dissociation pressure. It is more likely, therefore, that the rate decay above the maximum is due to the decrease of coverage of weakly bonded CO with temperature. The decrease of T_m by both S and oxide becomes understandable then, as both decrease the CO bond strength. Attention is called to the fact that the found curve shapes in the decay region cannot be explained by a constant CO–surface bond, but that a rather strong coverage dependence must be assumed.

To sum up, by combining rate measurements with surface analysis in the same apparatus, we have been able to show directly the influence of surface composition on the rate of $Ni(CO)_4$ formation. In particular the very strong promoting effect of sulfur has been quantified. Oxygen has been shown to be a promoter rather than an inhibitor; the main inhibitor is carbon. The occurrence of

a rate maximum at a certain temperature cannot be explained by the reverse reaction (Ni(CO)$_4$-dissociation) setting in, but must be an intrinsic property of the mechanism. It is believed that the main influences governing the rate are the surface bond strengths of Ni and of CO; for both, weakening of the bond makes the reaction easier.

ACKNOWLEDGMENTS

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