Ni(CO)₄ FORMATION ON SINGLE NI CRYSTALS: REACTION KINETICS AND OBSERVATION OF SURFACE FACETTING INDUCED BY THE REACTION

P. DE GROOT

Hochfeld-Magnetlabor Grenoble des Max-Planck-Instituts für Festkörperforschung, 166X, F-38042 Grenoble Cédex, France

M. COULON

Laboratoire d'Adsorption et de Réaction de Gaz sur Solides, ERA 368 ENSEEG, B.P. 44, F-38401 Saint Martin d'Hères, France

and

K. DRANSFELD

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, West Germany

Received 14 June 1979; accepted for publication 29 November 1979

We have studied the kinetics of the synthesis of nickel carbonyl (Ni + 4 CO \rightarrow Ni(CO)₄), using single crystalline Ni surfaces of different crystallographic orientation. A dependence of the reaction rate on the crystallographic orientation of the surface has been observed. Scanning electron micrographs showed that a very sharp (111) facetting of the surface takes place during the reaction. A reaction mechanism for the Ni(CO)₄ formation, taking into account recent experimental data of the chemisorption of CO on Ni, is discussed, which may explain the kinetic results and the observed facetting.

1. Introduction

Nickel carbonyl (Ni(CO)₄) is formed by direct interaction of Ni with CO under pressures higher than 10^{-1} mbar and at temperatures below 250° C. In spite of considerable investigation into its structure and chemistry [1-8], little is known about the mechanism and the rate controlling steps of its formation. As the reaction rate is very low (typically only one out of 200 Ni atoms is carried away per second by the Ni(CO)₄ vapour), almost all previous investigations on the Ni(CO)₄ formation have been carried out with Ni samples providing a high specific area like powders, platelets or other polycrystalline forms [1-8]. However, the surface of such polycrystalline samples is badly characterized, and the kinetic parameters found by the different authors are rather inconsistent (see table 1): the reported values of the

Table 1 Kinetic paramet	ters of the	NI(CO)4 foi	rmation by different authc	11.8		
Author	Year	Ref.	Sample form	Activation energy E_a (kcal mol ⁻¹)	Reaction order a	Reaction rate r at 20°C (mol cm ⁻² min ⁻¹)
Mittasch Goldberger Kipnis et al. Heinicke et al. Kipnis et al.	(1962) (1961) (1966) (1967) (1967) (1967)	222222	Powder Silica supported Powder Porous sheet Platelets Powder	27 (40-70°C) 7.24 (26-149°C) 6.9 (22-95°C) 24.7 (70-180°C) 13.1 (18-32°C) 7.8 (60-200°C)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
Heinicke et al. Trivin Krinchik et al. Milliams ct al. Mehta et al. Present work	(1973) (1973) (1975) (1976) (1978)	[2]] [7] [8] [13]	Platelets Powder (100) single crystal Film Polycrystal Single crystals	11.8 (40- 90°C) - 4.88 (30- 60°C) 9.0 (30- 60°C)	0.85 (0.1- 1 atm) - 1.45 (0.2- 1 atm)	$\begin{array}{c} 0.85 \times 10^{-10} \\ 7.4 \times 10^{-12} \\ 4.0 \times 10^{-8} \\ 2.8 \times 10^{-10} \\ 3.0 \times 10^{-10} \\ \end{array}$

specific reaction rate at room temperature for instance extend over several orders of magnitude.

Very recently Krinchik et al. [9-11], by reporting a spectacular influence of a magnetic field on the Ni(CO)₄ formation from a Ni single crystalline (100) surface, raised a new interest in this reaction. However, their result have not yet been reproduced elsewhere and are now questioned [12-15].

On the other hand, a detailed picture of the Ni–CO interaction at CO pressures below 10^{-3} mbar (i.e. before Ni(CO)₄ formation takes place) has now become available by the extensive studies of the chemisorption of CO on well defined single crystalline Ni surfaces [16].

We believe that the present results of the Ni(CO)₄ formation from (100), (110) and (111) Ni surfaces may lead to a better understanding of the reaction mechanism and may give a new insight into the chemisorption of CO on Ni at pressures above 10^{-1} mbar.

2. Experimental

A set-up based on a dynamic reaction chamber with on-line $Ni(CO)_4$ detection has been devised that met the following requirements:

(a) Highly sensitive detection of trace amounts of $Ni(CO)_4$ in a large CO background.

(b) High purity of the reaction gases, since the reaction is strongly affected by impurities on the Ni surface [7,17,18].

The set-up is shown schematically in fig. 1. The CO gas was obtained from gas cylinders of high purity (1). According to mass spectrometric analysis it contained less than 20 Vpm O_2 , less than 5 Vpm CO_2 and no other detectable impurities. A



Fig. 1. Schematic set-up: (1) gas cylinders, (2) destruction chamber for residual metal carbonyls, (3) copper catalyst, (4) cold trap, (5) reaction chamber, (6) Hersch detector, (7) optical spectrum analyser, (8) destruction chamber for Ni(CO)₄, (9) flow meter, (10) CO flame.



Fig. 2. Molar absorption coefficient of Ni(CO)₄ vapour.

supplementary purification of the CO gas was obtained in three steps:

(a) First it was heated up to 300° C (2) in order to eliminate residual metal carbonyls that may be formed by the reaction of the CO gas under high pressure with the stainless steel walls of the gas cylinders and other Ni containing surfaces.

(b) In the next step residual O_2 was removed on a bed of a highly active copper catalyst (BASF R3-99) maintained at 200°C (3).

(c) Finally the remaining traces of H_2O and CO_2 were frozen out in a liquid Ar cold trap (4).

The resulting O_2 concentration, measured with a Hersch [19] detector (6) (sensitivity 0.1 Vpm O_2) was lower than 1 Vpm and the remaining H_2O and CO_2 traces were estimated to be less than 0.1 Vpm and 1 Vpm respectively.

The measurement of the Ni(CO)₄ concentration in the outlet flow (7) was based on the strong UV optical absorption of Ni(CO)₄ vapour as shown in fig. 2. The outlet flow passed through the quartz cell of an UV spectrophotometer. The detection was carried out at 210 nm, which was sufficiently separated from the CO adsorption line (206 nm) to avoid interference. The absorption coefficient was obtained by integrating the absorption versus time plots during the Ni(CO)₄ formation and comparing this with the mass difference of the Ni samples before and after the experiment. With an optical path length of 10 cm, a detection limit of 0.05 Vpm of Ni(CO)₄ was obtained. Because of its extreme toxicity, the Ni(CO)₄ was decomposed immediately after detection by heating the gas to 350°C (8) and the remaining CO gas was burnt (10). Flow rates were varied between 0.4 and 12 cm³ s⁻¹ and were measured by means of a soap bubble flow meter (9). In this way specific reaction rates as low as 10^{-11} mol cm⁻² min⁻¹ could be measured.

Partial pressures of CO lower than 1 atm were obtained by diluting the CO with

highly purified Ar under a total pressure of 1 atm. In this case the cold trap was maintained at -100° C in order to prevent condensation. The CO concentration was determined spectroscopically by measuring the sharp absorption peak of CO at 206 nm (fig. 2).

The quartz reaction chamber (5) contained three identical single crystals in the form of thin disks of about 1 mm thick and about 20 mm in diameter, providing a total working surface of about 30 cm². Less than 7% of the working surface was composed of the lateral surfaces of the disks which have random crystallographic orientation.

All crystals were spark cut from the same ingot along the three principal crystallographic planes, with a misalignment smaller than 1° , as revealed by the X-ray diffraction pattern. The ingot was obtained from a Ni ex-carbonyl powder (Mond Company) of high purity and contained, according to emission spectrographic analysis, only small traces of Mg and Fe.

The disks were mechanically polished on both sides with a solution containing 2.4 g/l Na, 0.07 g/l K and 330 g/l SiO₂, down to a grain size of 0.05 μ m. Afterwards they were chemically etched in a solution of 30% HNO₃, 10% H₂SO₄, 10% H₃PO₄ and 50% CH₃COOH at 60°C for 30 s. Before the exposure to CO the samples were reduced under pure hydrogen atmosphere (99.999% H₂) at 600°C for 30 min. Each surface was photographed with an electron scanning microscope before and after reaction.

The reaction chamber could be heated up to 700° C and the reaction rate was directly recorded as a function of the temperature, measured with a thermocouple in direct contact with the samples, at sweep rates lower than 1° C/min.

3. Observed reaction kinetics

3.1. Time dependence

The initial value of the reaction rate and its time dependence were found to be strongly dependent on the preliminary treatment of the Ni surface. This is not surprising since the reaction is very sensitive to the surface roughness and surface impurities, which are both strongly influenced by the cleaning procedure.

Most authors [7,8,13,20] report a strong decay of the reaction rate towards a steady state value. However, the reported time constant of this decay varies between several minutes [13] and several days [20].

The observed time dependence of the reaction rate in the present experiments is illustrated in fig. 3 for differently prepared (111) surfaces. On the samples that have been polished mechanically, etched chemically and reduced at $600^{\circ}C$ (curves 1 and 2) the reaction rate remains very low during the first hours and then increases strongly to reach a maximum after about 24 h. Since this stagnation of the reaction during the first hours was not observed with samples that were not chemically



Fig. 3. Time dependence of the reaction rate on a (111) surface at different temperatures and for different preliminary treatments. $P_{CO} = 1$ atm.

etched (curve 3), it may be a consequence of remnants of the etchant on the surface, which may inhibit $Ni(CO)_4$ formation. The early maximum of the rate may be due to highly reactive clusters or atoms in a low coordination state, generated by the reduction of the NiO layer [7]. This assumption is supported by the fact that a preliminary oxidation of the surface at 200°C, followed by reduction at 600°C increases this effect (curve 4), whereas in the case of an already used sample, reexposed to CO after moderate reduction, no maximum is observed (curve 5).

The reaction rates during the first days are essentially irreproducible and depend strongly on the surface preparation. After about five days, however, we found that in all cases the reaction rate reaches a well reproducible steady state value, which is characteristic for the crystallographic orientation of the surface and independent of the surface preparation. All kinetic measurements described below were therefore carried out after stabilization of the reaction rate.

3.2. Temperature and crystallographic orientation dependence

The temperature dependence of the stationary reaction rate between 30 and 60° C is illustrated in fig. 4 for three different crystallographic orientations. The experiments were repeated several times for each of the three orientations, using each time freshly polished samples. From this figure the following important conclusions can be drawn.

- Between 30 and 60°C the reaction rate obeys the Arrhenius law. The apparent activation energy $E_a = 9.0 \pm 0.5$ kcal mol⁻¹ (~0.39 eV) is the same for the three crystallographic orientations.

- Repeated experiments on different samples of the same crystallographic orienta-



Fig. 4. Arrhenius plot of reaction rate for different crystallographic directions; for each direction the results of repeated experiments are shown.



Fig. 5. Temperature dependence of the Ni(CO)₄ pressure at the reactor outlet for different flow rates (in cm³ s⁻¹): (a) 0.37, (b) 2.8, (c) 12.0. Broken line: Ni(CO)₄ pressure at chemical equilibrium; $P_{CO} = 1$ atm.



Fig. 6. Observed dependence of the reaction rate on the CO flow rate at different temperatures.

tion give nearly the same value of the specific reaction rate (defined as the reaction rate relative to the macroscopic surface area of the disks.

- A significant difference between the reaction rates on surfaces of different crystallographic orientation is observed: The specific reaction rates on a (100) and (110) surface are respectively about 1.8 and 1.3 times higher than on a (111) surface.

As the temperature increases the reaction passes through a maximum at 125° C and then decreases rapidly. This is illustrated in fig. 5. Generally, the decrease of the reaction rate is attributed to the reverse reaction that becomes predominant at higher temperatures: The broken line in fig. 5 represents the partial pressure of Ni(CO)₄ at chemical equilibrium, computed from the data in (7). According to this, the temperature at which the maximum occurs should depend on the partial pressure of Ni(CO)₄. However no such dependence could be found. Moreover, it can be seen from fig. 6 that at temperatures up to about 130° C (i.e. in the vicinity of the maximum), the reaction rate is almost independent of the CO flow rate, thus indicating that in the present experimental conditions the system is still far from chemical equilibrium. These observations suggest that the decrease of the reaction at higher temperatures may not be due solely to the approach of equilibrium but also to the nature of the reaction mechanism itself.

At temperatures higher than 160° C, the kinetic data ceased to be reproducible and showed again a time dependence. It is known that at these temperatures dissociation of the CO molecule may take place [22,23], thus leading to a surface contamination with carbon and oxygen. These temperatures were therefore avoided.



Fig. 7. Dependence of the reaction rate on the partial pressure of CO. Solid points: observed values. Solid line: according to $\alpha = 1.45$.

3.3. CO pressure dependence

The observed dependence of the reaction rate on the partial pressure of CO $(P_{\rm CO})$ is shown in fig. 7 for a (111) surface (solid points). For the (100) and (110) surface a similar dependence was found. In all cases the reaction rate is proportional to $P_{\rm CO}^{\alpha}$, with an apparent reaction order $\alpha = 1.45$, independent of the crystallographic orientation of the surface.

3.4. Summary of the main kinetic results

The steady state value of the specific reaction rate is independent of the surface cleaning procedure. The activation energy $E_a = 9.0 \pm 0.5$ kcal mol⁻¹ and the apparent reaction order $\alpha = 1.45 \pm 0.1$ are independent of the crystallographic orientation of the surface. However, at fixed temperature and CO partial pressure, a characteristic dependence of the reaction rate on the crystallographic orientation of the surface has been observed: the highest rate is observed on (100) surfaces and the lowest on the (111) surfaces. A comparison of our observations with previous rather divergent results is given in table 1.

4. Observations of the surface facetting by SEM

Fig. 8 shows an electron scan micrograph of a (110) surface after mechanical and chemical polish *before* reaction. (Similar pictures were obtained for the (111) and (100) surfaces.) Scratches caused by the mechanical polish are apparent. Fig. 9



Fig. 8. (110) surface before reaction.



Fig. 9. (110) surface after reaction.



Fig. 10. (100) surface after reaction.

shows the same surface *after* a reaction with CO for two weeks during which an Ni layer, about 5 μ m thick, has been removed. Instead of the initially smooth (110) surface the micrograph displays a very sharp faceting. The etched surface is composed of two series of parallel planes of alternate orientation. By tilting the sample until vanishing of either series we have been able to determine that each of them form an angle equal to $35^{\circ} \pm 3^{\circ}$ with respect to the (110) plane. The intersections of these planes, more or less regularly spaced. are found to be parallel to a (110) direction of the crystal.

A (100) surface presents, after reaction, also a very well defined faceting under the form of square based pyramidal pits and peaks (fig. 10). The edges of the square bases are also found to be parallel to the (110) directions of the crystals.

In striking contrast to these observations, (111) surfaces, even after removal of several microns of Ni, never displayed any faceting at all. Instead, the surface remained as smooth and featureless as before the reaction. In order to demonstrate this unique behaviour of the (111) surface more clearly, a slight scratch creating a polycrystalline surface, was internationally carved on a (111) surface before reaction. Micrographs 11a and 11b show the sharp contrast between the uniform etching of the undisturbed (111) plane and the formation of facets in the polycrystalline area of the scratch.



Fig. 11. (a) (111) surface after reaction. (b) (111) surface, magnification of the border of the scratch.

These observations show unambiguously that the etching of Ni by the Ni(CO)₄ formation leads to a (111) faceting. The faceted (110) surface displays two (111) planes, which are theoretically inclined by 35.5° with respect to the (110) surface, in excellent agreeement with our observations quoted above. The pyramidal structure of the etched (100) surface corresponds evidently to the (111) faced hemioctahedron.

Faceting of a Ni surface by Ni(CO)₄ formation has so far only been reported by Heinicke et al. [20], who used a polycrystalline sample and ascribed their observations to the tribomechanical treatment that was given to the surface. Edmonds et al. [24] discussed the possibility of facetting of single crystalline Ni by Ni(CO)₄ formation but none was observed. This, in retrospect, seems understandable since unfortunately a (111) surface was chosen in their experiments.

It may be argued that the faceting, instead of being related to the reaction mechanism, should rather be due to a thermal reconstruction of the Ni surface induced by the adsorbed layer. This seems, however, improbable: the surface energy of a (111) face, for example, has been calculated to be 0.73 times lower than the surface energy of a (100) face [25]. Hence the increase of the surface energy, corresponding to the enlargement of the surface area (a factor 1.73 in the case of a (100) surface), exceeds the decrease due to the change of the crystallographic orientation, leading to a net increase of the total surface energy.

The (111) faceting during $Ni(CO)_4$ formation should therefore be closely related to the nature of the reaction mechanism itself.

5. Discussion of the results

Although most authors agree that the Ni(CO)₄ formation involves one or more intermediate complexed, very little is known about the reaction mechanism. According to Goldberger [2] the reaction rate is controlled by a combination of gas adsorption and surface reaction. Trivin [7] concludes that Ni(CO)₄ is most probably formed after desorption of the intermediate Ni(CO)₂ complex and the decrease of the reaction rate at high temperatures is ascribed to the approach of chemical equilibrium. According to Kipnis et al. [26] the Ni(CO)₄ formation involves three intermediate complexes: Ni(CO), Ni(CO)₂ and Ni(CO)₃, where the formation of the first one is the rate controlling step. These mechanisms are rather incomplete and differ considerably from each other. Moreover, none of these mechanisms seems to lead in a simple way to the observed facetting.

The present SEM observations have shown that the Ni(CO)₄ formation induces a surface rugosity under the form of linear furrows on the (110) surface and of pyramidal pits or peaks on the (100) surface. In order to find the true specific reaction rates of these surfaces, one has to relate them not to the macroscopic geometrical surface A but to the larger total area A' of all microscopic (111) facets existing on these surfaces. If γ is the angle between the (111) facets and the macroscopic

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plane of the crystal the ratio A'/A is given by $(\cos \gamma)^{-1}$. The theoretical values of this factor for the (100) and (110) surfaces are respectively 1.73 and 1.22. As the observed reaction rates on these surfaces are found to be respectively factors of 1.8 and 1.3 higher than on the macroscopic (111) surface, it can be concluded that the *true* specific reaction rates, corresponding to the total microscopic surface areas are *independent* of the macroscopic orientation of the surface.

This important result has the following implication: The reaction rate is only proportional to the total area of the (111) facets and thus independent of the density of the macroscopic edges and peaks on the etched (110) and (100) surfaces. Since these exposed edges and peaks are stationary during the reaction although they contain many Ni atoms in a low coordination state, as compared to a smooth (111) surface, we are led to the rather unexpected conclusion that the Ni atoms in such low coordination states are less reactive than the Ni atoms on the most densely packed (111) faces. Perhaps the edges and peaks are stabilized by inhibitors, which remain in the same position as successive layers of Ni are etched off and inpede the reaction at these exposed positions. Such inhibitors may be surface carbon atoms from dissociated CO. Indeed, partial dissociation of CO on Ni at high pressures has been observed at room temperatures [27] and occurs below 150°C exclusively at surface steps [28,29]. On the other hand we cannot exclude the possibility that the edges and peaks are intrinsically less reactive than the (111) planes (without the action of inhibitors). In any case, if the reaction at these exposed positions would proceed faster than for Ni atoms within a (111) surface, the formation of the sharp edges and peaks would be difficult to understand.

At present it is not known what processes are responsible for the formation of the observed (111) facets, nor is it entirely clear whether the reaction on (111) surfaces is slower or faster than it would be on other microscopic surfaces, since we have no reliable reaction data for real (100) or (110) surfaces, i.e. before the formation of the (111) facets. We can, however, show that for example in the case of an uncontaminated (110) surface the reaction rate on the (110) face (r_{110}) cannot be higher than on the (111) face (r_{111}) : Let A and B be two surface sites at which initially no reaction takes places (for instance because of local defects) (fig. 12a). Initially the surface may evolve towards a structure as pictured in fig. 12b. However, after some duration A and B will perhaps be undermined and removed and the atoms at the apex will now be able to react (fig. 12c). If now $r_{110} > r_{111}$, the initially small (110) facet at the top will extend its surface area at the expense of the more slowly reacting (111) facets (fig. 12d). Therefore, (110) facets should always be visible, which is in conflict with our observations. Thus, in order to explain the observed faceting on uncontaminated surfaces, we would have to assume that the $Ni(CO)_4$ formation on the (111) faces is intrinsically faster than on all other faces. This conclusion is quite surprising, as one would rather expect the reaction rate to be lowest on the (111) faces because of their higher density and the consequently stronger binding of the Ni surface atoms.

The alternative explanation, which takes into account the above consideration,



Fig. 12. The evolution of an uncontaminated (110) surface during Ni(CO)₄ formation under the assumption that $r_{110} > r_{111}$.

is that the $Ni(CO)_4$ formation on the (111) faces is actually the slowest, but that the more reactive patches are blocked by surface carbon atoms from locally dissociated CO.

At present we cannot choose definitely between these different and conflicting interpretations. However, whatever the true mechanism for this faceting, the above results suggest that in the steady state the reaction proceeds according to a Langmuir-Hinshelwood mechanism (reaction between adspecies) rather than by an Eley-Rideal mechanism (reaction between adspecies) rather than by an Eley-Rideal mechanism (reaction between adspecies and gaseous molecules). Indeed the latter can probably be ruled out, since it would favour the reaction on Ni atoms in a low coordination state (because of their greater accessibility to impinging CO molecules) and hence lead to a reaction rate which would not be compatible with the observed surface rugosity. In contrast, the Langmuir-Hinshelwood mechanism predicts a reaction rate only proportional to the surface area, in agreement with our observations.

Let us now consider the Langmuir-Hinshelwood process in more detail. Chemisorption studies on Ni have shown that CO mainly adsorbs under two forms: linearly and bridge-bonded molecules [30-33] Ni(CO) and Ni₂(CO). The commonly assumed intermediate Ni(CO)₂ complex may then be formed by a reaction between three neighbouring linearly bonded CO molecules such as

 $3 \operatorname{Ni}(\operatorname{CO}) \rightarrow \operatorname{Ni}(\operatorname{CO})_2 + \operatorname{Ni}_2(\operatorname{CO})$.

This reaction requires a triplet of neighbouring linearly adsorbed species, the occurrence of which is proportional to θ_1^3 , where θ_1 is the fraction of Ni surface atoms covered by linearly bonded CO. At low coverages CO only adsorbs at twofold or even threefold sites, whereas linearly bounded CO only occurs at coverages $\theta > 0.5$ [30,33]. Even at saturation ($\theta \sim 0.57$), which is certainly achieved in our experimental conditions, only a small portion of the CO molecules is in the "on top" position ($\theta_1 \sim 0.14$), but at higher CO pressures θ_1 will increase. In our experimental pressure range of Ni(CO)₄ formation ($P_{\rm CO} > 10^{-2}$ mbar) probably an adsorption equilibrium

Ni₂CO + CO \rightleftharpoons 2 Ni(CO) with $K = 2\theta_1^2 / P_{CO}(1 - \theta_1)$

can be assumed. Therefore we find $\theta_1 = (P_{CO}K/2)^{1/2}$ for low θ_1 and for the reaction rate $r \sim \theta_1^3 \sim P_{CO}^{3/2}$. The reaction order $\alpha = 3/2$ for this Langmuir-Hinshelwood process is in good agreement with the observed value of 1.45 (see fig. 7).

This reaction mechanism may also explain the decrease of the reaction rate above 125° C: Recent investigations have actually shown that θ_1 is rather temperature independent between 20 and 100°C, whereas it strongly decreases at temperatures above 120° C [34,35].

Although at present we cannot exclude other processes, the Langmuir– Hinshelwood reaction mechanism described here seems to account for the experimental data of the Ni(CO)₄ formation on single crystalline Ni surfaces. In order to get more information about this reaction, IR investigations on single crystalline surfaces in the 10^{-2} –10 mbar range, as well as high resolution surface analysis after reaction, seem highly desirable.

Acknowledgements

We gratefully acknowledge the efficient assistance of R. Molins and J. Garden in the SEM observations. We wish to thank G. Greiner and D. Menzel for the helpful and stimulating discussions and for the communication of their results, prior to publication.

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