## SURFACE SCIENCE LETTERS

## THE RATE OF FORMATION OF NICKEL CARBONYL FROM CARBON MONOXIDE AND NICKEL SINGLE CRYSTALS

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We have measured the rate of Ni(CO)<sub>4</sub> formation at a total pressure of 1 atm on Ni(100), (110) and (111) single crystals cleaned by argon ion bombardment and UHV annealing. The (111) surface reacts significantly faster than the other two surfaces. The partial pressure dependence of the reaction and the effect of impurities are also discussed.

The reaction between nickel and carbon monoxide is very important, forming the basis for a commercial process for the refining of nickel. For example, INCO Ltd. operates refineries at Clydach, Wales, UK, and at Copper Cliff, Sudbury, Ontario, producing many thousands of tonnes of high purity nickel annually by processes based upon this reaction. There have been many studies of the reaction Ni + 4CO  $\rightarrow$  Ni(CO)<sub>4</sub>, but only recently has nickel been used in the form of single crystals. Some of this work was stimulated by claims that a magnetic field affects the rate of reaction [1-5], although subsequent work by several groups of workers have failed to reproduce any such effect [6-8]. Observations of faceting on the surface of low index nickel single crystals during the reaction are also relevant to interpretations of the reaction mechanism on the atomic scale [9].

In this paper we report for the first time measurements of the rate of carbonylation of three low index nickel single crystals cleaned by argon ion bombardment and UHV annealing. Unlike previously reported work, the crystals gave significantly different reaction rates in a short time.

Nickel single crystal discs, 25 mm diameter and 0.7 mm thick, of (100), (110) and (111) orientation, from Metals Research Limited were used. A crystal was mechanically polished to 0.25  $\mu$ m diamond and then electropolished before mounting in a small glass reaction vessel which formed part of an UHV system. It was cleaned on both sides by many cycles of argon ion bombardment (10<sup>-3</sup> Torr argon, 600 eV, 3  $\mu$ A cm<sup>-2</sup>, 10 min) and annealing (10<sup>-9</sup> Torr, 700°C, 20 min). The crystal was heated with an external RF coil.

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Crystals prepared in this way appeared perfectly smooth in a scanning electron microscope at magnifications of up to 30,000. It could not be demonstrated that they were atomically clean, but it is known that this cleaning technique gives atomically clean surfaces [10], while deliberately adding impurities that commonly contaminate "clean" nickel surfaces (e.g. carbon, sulphur or oxygen) gave quite different carbonylation characteristics.

A thermocouple was spot welded to the crystal support immediately adjacent to the crystal. The true crystal temperature, determined in a separate calibration experiment with additional thermocouples spot welded to the crystal, was only a few degrees higher. The true crystal temperature is the one quoted.

Carbon monoxide was purified by passing over heated copper, over a supported platinum catalyst at 200°C, over palladium and finally through a cold trap at -165°C. The carbon monoxide contained < 1 ppm oxygen, and no impurity measurable by a quadrupole mass spectrometer attached to the reaction vessel was detected. Argon was purified to < 1 ppm total impurities using a BOC rare gas purifier.

The nickel crystals were carbonylated in a flow system. The concentration of nickel carbonyl was measured by UV spectrophotometry, using a 10 cm silica cell glass-blown to the UHV system. 0.2 ppm of nickel carbonyl could be measured at a wavelength of 225 nm. Reaction rates were flow dependent at low carbon monoxide flows but were independent of the carbon monoxide flow rate at 400 ml min<sup>-1</sup>, corresponding to a gas velocity of 0.34 cm s<sup>-1</sup> across the crystal. All measurements were made using this flow rate.

After only a few minutes of reaction the crystals gave carbonylation rates that were steady with time for up to 6 h at constant temperature and pressure. Fig. 1, curve (a), shows the reaction rate on a function of time for Ni(110). This type of behaviour is different from any previously reported; the differences are probably due to different methods of crystal preparation. This is discussed later.

Table 1 shows the specific reaction rates at the temperature of the maximum carbonylation rate,  $T_{max}$ , which was  $130 \pm 2.5$ °C for all crystals. The relative magnitudes of the reaction rates for the single crystals do not bear a simple relationship to the atomic packing densities of the surfaces. By means of electron microscopy we established that no faceting occurred on any of the crystals, although the total amount of material removed was always small. The apparent activation energy for the reaction was  $8.5 \pm 0.5$  kcal mole<sup>-1</sup> for all three crystals in the temperature range 50-100°C.

Diluting the carbon monoxide with argon, at a total pressure of one atmosphere, gave the pressure dependence of the reaction rate. The reaction rate was proportional to  $P_{CO}^{\alpha}$ ;  $\alpha$  depended on temperature, and was 0.80 at 65°C, 1.9 at 130°C and 2.9 at 160°C for all three crystal surfaces.

It is well known that small amounts of impurities can affect the carbonyla-



Fig. 1. Effect of oxygen on the carbonylation of Ni(110) at 130°C. (a) <1 ppm oxygen in carbon monoxide, (b) 3 ppm in carbon monoxide.

tion reaction. When using carbon monoxide containing 3 ppm of oxygen (in fact, before the platinum catalyst was added to the carbon monoxide purification system), the results were as shown in fig. 1, curve (b). The reaction rate was clearly greater than with the oxygen-free carbon monoxide but the value of  $T_{\rm max}$  was unchanged.

Sulphur was pre-adsorbed by exposing the crystal to hydrogen sulphide at 65°C; the exposure was in excess of that required to saturate the surface [11]. The initial reaction rate increased by a factor of twenty five, but the rate decayed with time. Also  $T_{\rm max}$  decreased to 80°C and the activation energy decreased to 5.4 kcal mole<sup>-1</sup> (30-60°C). Pressure dependence measurements on the sulphided crystal gave values of  $\alpha = 1.06$  at 59°C and 2.1 at 80°C.

Table 2 shows a summary of data obtained in different laboratories on the

Crystal	Specific reaction rate (mole $cm^{-2} min^{-1}$ )	
Ni(111)	$4.4 \times 10^{-9}$	·····
Ni(100)	$1.4 \times 10^{-9}$	
Ni(110)	$1.7 \times 10^{-9}$	

Table 1 Rates of nickel carbonyl formation at 130°C

Results for the	carbonylation	of nickel single crystals						
Ref.	Crystal plane	Time for stable rate	Temp. of max. rate (°C)	Apparent activation energy (kcal mole <sup>-1</sup> )	Apparent reaction order α	Absolute r (mole cm <sup>-</sup>	ate - <sup>2</sup> min <sup>- 1</sup> )	
[3]	100	7	25	4.8 (20–75°C)			$3.0 \times 10^{-8}$ $8.7 \times 10^{-8}$	(20°C) (75°C)
[9]	100	Several days	130	5.9 (20-100°C)	I		10 <sup>-9</sup> 10 <sup>-8</sup>	(20°C) (130°C)
[7]	6.	20 min	> 100	4.9 (40-90°C)	1			
[8]	100	Continuous decay	80				ž	
[6]	001	Several days	130	9.0 (30-60°C)	1.45 at 20°C	011	5.4 × 10 <sup> 10</sup> 3.9 × 10 <sup> 10</sup> 3.0 × 10 <sup> 10</sup>	(20°C) (20°C) (20°C)
[12] <sup>a)</sup>	100	Continuous decay	120	16 (20–50°C)			$6 \times 10^{-10}$	(120°C)
This work	100 1110	20 min	130	8.5 (20-100°C)	0.8 at 65°C 1.9 at 132°C 2.9 at 165°C	001 1110	$1.4 \times 10^{-9}$ $1.7 \times 10^{-9}$ $4.4 \times 10^{-9}$	(130°C) (130°C) (130°C)

<sup>a)</sup> All work at 316 mbar pressure.

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Table 2

carbonylation of nickel single crystals. All measurements were made at atmospheric pressure apart from those of Greiner and Menzel [12] who worked at 316 mbar pressure. Kirnchik et al. [3] used a discontinuous chemical method to determine nickel carbonyl, Mehta et al. [7] used a photoionisation detector but all other workers have used UV spectrophotometry. Each group of workers has used a different method of surface preparation. It is unlikely that reduction removes all impurities from the nickel surface, and probably leaves the outer few atomic layers damaged, with reactive sites [13]. This would account for a high initial carbonylation rate decreasing to a more or less steady rate observed by most workers. Our method of argon ion bombardment and annealing is a standard method of preparing a nickel surface for LEED examination, with no damaged outer layers [10]. We observe what one might expect for the carbonylation of perfect crystal surface, a rapid increase to a constant carbonylation rate.

Comparing data in table 2, there seems to be general agreement that  $T_{max}$  is about 130°C; Greiner and Menzel's value of 120°C, obtained at a working pressure of 316 mbar would be about 10°C higher at atmospheric pressure. A lower value of  $T_{max}$  could well indicate sulphur contamination of the surface.

There is considerable scatter in the apparent activation energy determined by different groups of workers. It is impossible to assign a "correct" value, but the majority of results on all forms of nickel [9] lie within the range 5-12 kcal mole<sup>-1</sup>. One must also note the problem of diffusional resistances in any kinetic measurements. In this present study these were overcome by working at a sufficiently high gas velocity across the crystal surface. It is impossible to say whether this was true for the other studies cited.

Our measurements of the partial pressure dependence of the reaction rate do not agree with those of De Groot et al. [9]. We agree with the results of Lossmann [14] on porous nickel sheet and of Trivin [15] on nickel powder. Lossmann obtained a value of  $\alpha = 1$  at < 70°C, and calculated that  $\alpha$  increases with temperature and is equal to 4 at equilibrium. Trivin obtained a value of  $\alpha = 0.85$  for  $P_{CO} = 0.1-1$  atm at 40–90°C. Trivin proposed a reaction scheme where Ni(CO)<sub>2</sub> is the largest surface species formed, and the rate controlling process is either the Langmuir–Hinshelwood type interaction between adjacent Ni–CO species to form Ni(CO)<sub>2</sub> or a combination of this step and the desorption of Ni(CO)<sub>2</sub> from the surface. This is the only scheme consistent with his measured value of  $\alpha$ , with which we agree.

In the presence of oxygen, as shown in fig. 1, the reaction rate goes through a maximum, and then decays to a steady value. This shows that trace impurities in the gas phase can significantly affect the reaction. Presumably some of the oxygen is chemisorbed and incorporated into the nickel lattice. By analogy with sulphur, which is of course in the same group as oxygen in the Periodic Table, the presence of oxygen activates nickel atoms for carbonylation. Of the five sets of data on the absolute rate of the carbonyl formation reaction, four are very similar after allowing for the differences in the temperature and pressure of the measurements. The values obtained by Krinchik et al. are about two orders of magnitude greater, which together with their low activation energy and low value of  $T_{max}$  would suggest sulphur contamination of the crystal surface. The values given by De Groot et al. [9] do not represent true values for each crystal plane, since they could only achieve stable reaction rates after several days, when extensive faceting to (111) planes had taken place. Their most likely explanation for this was that the (111) plane reacted faster than the (100) or (110) planes, but they were unable to confirm this. We believe that we have measured a true reaction rate for each of the three crystal surfaces, verifying that the (111) surface does, in fact, react faster than the (100) or (110) surface.

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