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Reactions of Carbon Dioxide on Pyrophoric Nickel-on-Silica Surfaces

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Reactions of carbon dioxide on pyrophoric nickel-on-silica catalysts have been studied in a flow system at atmospheric pressure from 450° to 1000°C. Initially, carbon dioxide reacted rapidly with preadsorbed hydrogen to give carbon monoxide and water vapor. In the absence of hydrogen, carbon dioxide was decomposed to carbon monoxide and oxygen. The oxygen was then incorporated by the solid to give nickel oxides of compositions which varied with reaction temperature. The decomposition rate showed zero order kinetics with respect to carbon dioxide and fractional dependence on oxygen partial pressure.

Kinetic results were supplemented by X-ray, thermogravimetric, infrared, magnetic, and chemical analysis.

INTRODUCTION

Reduction or activation by hydrogen is employed generally in the final stages of preparation of finely divided nickel catalysts for hydrogenation reactions. This treatment results in a catalyst surface covered with chemisorbed hydrogen (*1*), and the system is often pyrophoric in air.

For metallic nickel supported on silica, prepared by coprecipitation of a basic nickel carbonate and silica (*2*), the reduction stage is followed by cooling in carbon dioxide or nitrogen (*3*). This treatment enables the catalyst to be handled easily and, in particular, prevents spontaneous ignition on contact with air. While the activity of such catalysts depends on the reduction temperature (*2*) and nickel content (*4*), the influence on the surface of treatment with carbon dioxide or nitrogen has been ignored so far.

Consequently, an attempt has been made to see if surface chemical changes are implemented on activated nickel-on-silica catalysts, during such treatments, by making a kinetic study of the reactions of carbon dioxide from 450° to 1000°C at atmospheric pressure. These results are supplemented by thermoanalytical, X-ray, magnetic susceptibility, and infrared data.

EXPERIMENTAL

Materials. Nickel-on-silica catalysts were prepared as described previo sly (*2*, *5*), and reduced in a mullite tubular furnace with catalytically purified hydrogen under the optimum conditions of 30 min at 450°. The material was used as a fine powder. Iodine pentoxide was prepared by the standard method of recrystallization of G. P. R. iodic acid from 60% v/v nitric acid with final drying at 120°.

For the kinetic experiments cylinder carbon dioxide (Distillers Company Ltd.) of initial oxygen content 0.1% v/v, was purified through alkaline pyrogallol. Since with continuous usage, the oxygen content of these cylinders decreases to negligible proportions, the pyrogallol purification train was removed in later experiments to avoid anomalously high carbon monoxide analysis arising from possible pyrogallol decomposition. All other materials, unless stated below, were of "AnalaR" specification.

Apparatus and procedure. Thermogravimetric determinations were made with a Stanton thermobalance with 0.3 g samples in silica crucibles, and magnetic susceptibilities measured on a Gouy balance.

Kinetic measurements were made with a

standard design flow system in which carbon dioxide was passed into a 10 liter reservoir followed by a splash-trap, flow meter and drying column. The flow was adjusted by separate coarse and fine control needle valves. The reaction was studied in a recrystallized alumina tube placed in a noninductive furnace. The catalyst was contained in the middle zone of the reactor by a fine mesh copper basket. This was shaped as a thin cylinder and fitted snugly against the tube walls. Temperatures were measured by thermocouples placed between the reactor and the furnace wall just below the basket.

Effluent gases were passed through concentrated sodium hydroxide and then to the analysis train. This consisted of a 200 mm long by 14 mm internal diameter horizontal Pyrex tube packed closely with iodine pentoxide. The tube was jacketed with propionic acid which when refluxed into a condenser enabled the pentoxide to be maintained at around 120°. The iodine liberated by carbon monoxide from the dissociation was taken up in dimpled absorption units containing 20% w/w sodium hydroxide. The liberated iodine was then analyzed by the method of Urbánek (*6*).

During the course of every kinetic run samples of gas from the I_2O_5 reactor were tested for traces of carbon monoxide by aspiration through a calibrated silica gel/palladous chloride detector. This was capable of detecting 1 in 10^6 parts of CO, and ensured that the iodine pentoxide was reacting satisfactorily. (The test was essential, particularly at high CO_2 decompositions, as the I_2O_5 became partially inhibited with usage and freshly prepared crystals were substituted.)

Alternative gas streams similar to that described for CO_2, were provided up to the catalyst reactor to carry hydrogen, oxygen, and nitrogen.

RESULTS

Thermogravimetric Analysis

Preliminary studies were made of the behavior of reduced catalyst samples when heated in air. These had been cooled quickly from 450° to room temperature in either hydrogen or carbon dioxide, before final exposure to carbon dioxide for 5 hr at room temperature. The effect of "aging" catalysts in CO_2—storing under the gas in closed containers at room temperature—was also examined. The rate of heating was 4°C/min.

Apart from catalysts "aged" 18 months, the trend in all cases was to an intial slight loss of weight up to 150° followed by a rapid increase (Fig. 1). For the catalysts quenched in hydrogen and examined immediately following carbon dioxide exposure, the increase of weight with temperature was apparently parabolic. This was confirmed by separate isothermal experiments in which samples were heated, in air, successively at 354°, 460°, and 610° until a constant increase of weight was recorded. For the power relationship $W^2 = 2kt$, where W is the gain in weight/m^2 of surface in time t (min) a plot of t/W against W should give a straight line from which k can be deduced from the slope. The equation was used first by Wagner and Grunewald (*7*) to describe the parabolic nature of the oxidation of copper under various oxygen pressures. It was used here as a confirmatory test for the growth of a thick oxide layer on the nickel component of the catalyst (Fig. 2). The nitrogen adsorption value of the catalyst surface area (180 m^2/g) was used in determining W. Deviations from linearity at the higher temperatures show that all the available nickel has been oxidized.

Catalyst samples quenched to room temperature in CO_2, after reduction, were covered noticeably with a pale-green surface skin. In separate experiments, these layers were carefully skimmed off and examined. Their behavior on heating was similar to that of the 18 months "aged" catalyst (Fig. 1) and they were resistant to oxidation. A maximum weight loss of 8.1 mg/g was recorded, followed by an increase of 20.4 mg/g with no further increase from 180° to 600°.

Infrared spectra were determined on 1 mg samples of mean particle range 60–120 mμ, using the KCl disc and Nujol mull techniques. All samples gave absorption bands at 3450 cm^{-1} and from 1650 cm^{-1} to 1680 cm^{-1}. These were attributed to physically adsorbed

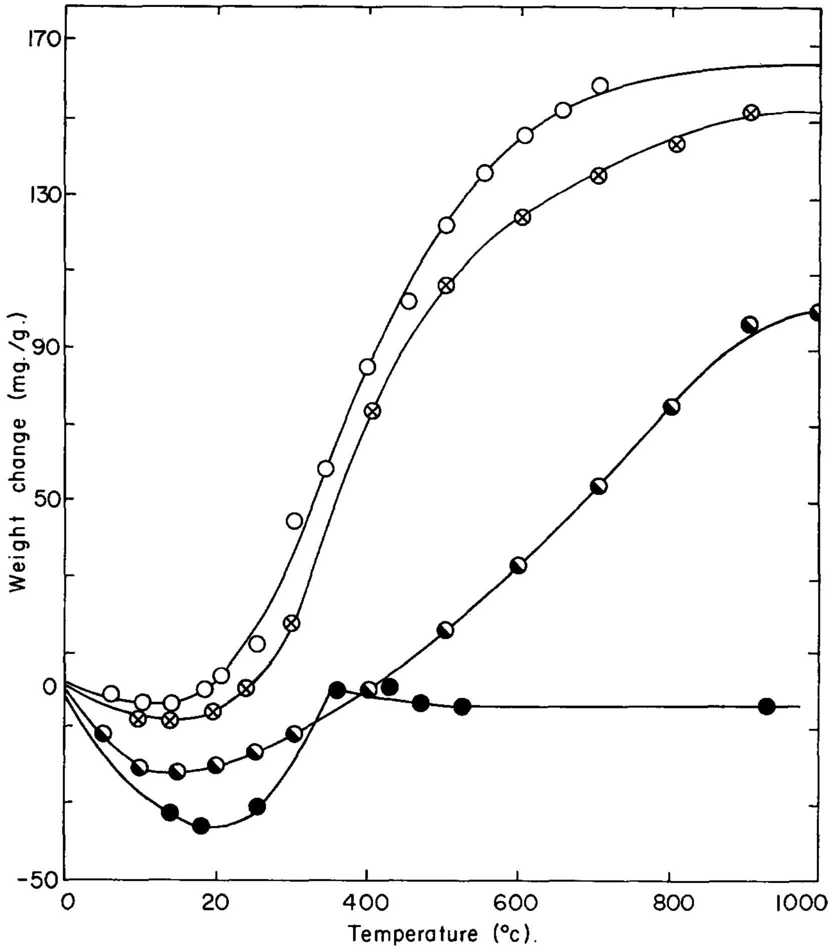


FIG. 1. Effect of temperature on catalysts weight changes. (1) ○, "Fresh" catalyst, quenched to room temperature in hydrogen. (2) ⊗, As (1), "aged" 30 days. (3) ◐, "Fresh" catalyst, quenched in carbon dioxide. (4) ●, As (1), "aged" 18 months.

water (*8*), while the intense bands at 1020 to 1050 cm^{-1} were assigned to Si–O bond vibrations (*9*). In addition, a weak band was found at 2400 cm^{-1} with samples of green surface skins. This could still be detected after allowing the sample to stand in air for a further 7 days. A similar absorption band was found by Eischens and Pliskin (*10*) in the spectrum of carbon dioxide physically adsorbed at 30° on "Ca-bo-sil," a finely divided nonporous silica.

These preliminary data indicated that carbon dioxide was dissociatively adsorbed at the catalyst surface. This could occur by interaction, (a) with the catalyst surface, thus initiating oxide layer growth, (b) with preadsorbed hydrogen, or (c) by both (a) and (b) competitively or sequentially. To obtain this information, it was decided to proceed with a detailed kinetic study.

Kinetic Experiments

Runs were carried out at a fixed CO_2 flow rate of 55 ml/min at 20°, 450°, 600°, 800°, and 1000° using an empty reactor. In all cases, 0.054 mg of CO were collected per minute. This showed that no CO_2 was decomposed thermally, as expected, but that there was a small amount of CO impurity present in the gas stream.

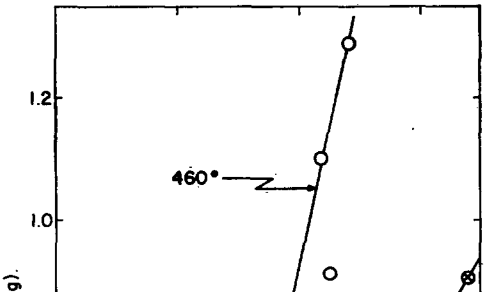


FIG. 2. Wagner plot illustrating growth of oxide layer.

(i) *Variation of Space Velocity*

CO_2 was passed over 1 g of catalyst at 450° using space velocities of 6200, 4550, 230, and 100 ml/ml catalyst/hr and the amount of CO produced measured over 10 min intervals. These results are plotted in Figs. 3 and 4. In all cases there was a rapid increase in the initial rate of formation of CO (r) to a maximum value. The rate then declined with similar rapidity to a steady level at the highest space velocity (Fig. 3), while at the other settings a secondary peak showed up after the decline in about 50–60 min. In all cases a steady rate was achieved after 80–90 min exposure. This value of r lies at 0.080 mg CO/min and was independent of space velocity while r_{max} values are dependent on space velocity.

Experiments were made to establish whether rate maxima were due to reaction of CO_2 with H_2 (ads) from the reduction stage, i.e.

$$CO_2 + H_2\,(ads) \rightleftharpoons H_2O + CO \qquad (1)$$

Initially, catalyst samples were activated with hydrogen at 450°C for 1–2 hr to ensure the complete removal of traces of physisorbed water from silica pores. CO_2 was then passed for 30 min and the water produced collected by anhydrous copper sulfate. This was compared with the gas absorption by the copper sulfate in blank runs. The average amount of water collected was 0.0054 g, which corresponds to 0.0084 g of CO from reaction (1). This quantity of CO was about 20% less than that of the directly analyzed amount and may indicate that a separate CO_2 decomposition process occurs simultaneously, i.e.,

$$CO_2(g) \rightarrow CO + \tfrac{1}{2}O_2 \qquad (2)$$

Secondly, after hydrogen reduction for 30 min at 450°, the catalyst was flushed with high-purity nitrogen (99.998%; $O_2 < 10$ v.p.m.; $Ar = 5$ v.p.m.; $CO_2 < 5$ v.p.m.; $H_2 < 1$ v.p.m.) for the same time. CO_2 was then passed at 230 ml/ml/hr and CO analysis obtained. The initial CO rate maxima fell to a very low value, almost vanishing, while the secondary peak occurred later than in the normal runs, but at approximately the same value of r. No ammonia was detected in the effluent during these experiments.

Thirdly, after activation at 450°, 5.1 mm Hg partial pressure water vapor was added to the CO_2 streams and passed over the catalyst. A constant, steady r value was obtained with no evidence of rate maxima (Fig. 4).

These experiments showed that chemical reaction between CO_2 and preadsorbed hydrogen took place, that the rate maxima were due to reaction (1), and that this reaction is sensitive to space velocity. The equilibrium position of (1) is upset readily, while the ease of displacement of preadsorbed hydrogen by nitrogen indicates that it is held loosely.

Frequent attempts were made to achieve a mass balance for the reaction by additional

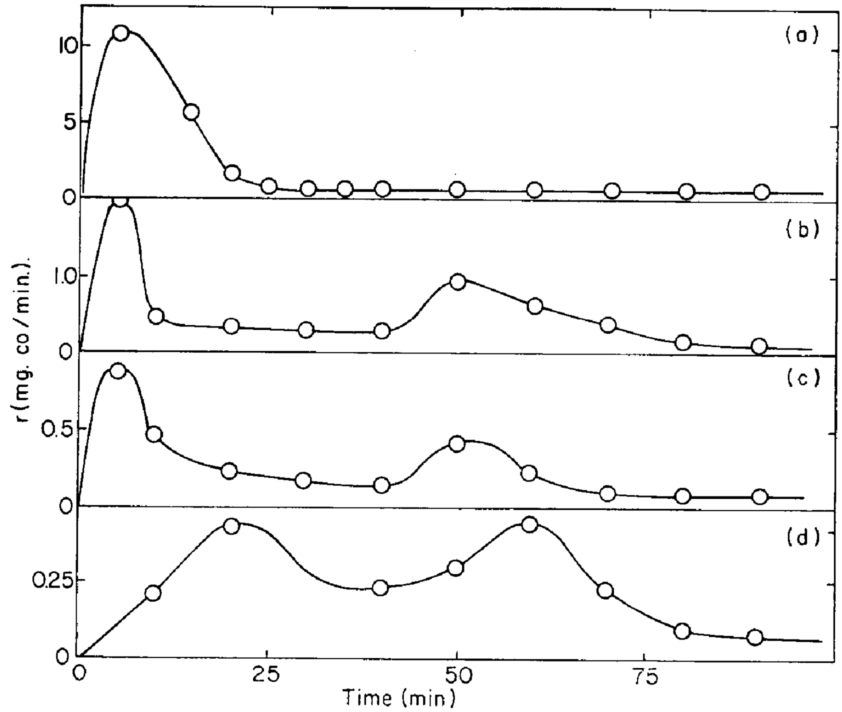


FIG. 3. Variation of r with space velocity at 450°. Space velocities—(a) 6200, (b) 4550, (c) 230, and (d) 100 ml CO_2/ml catalyst/hr.

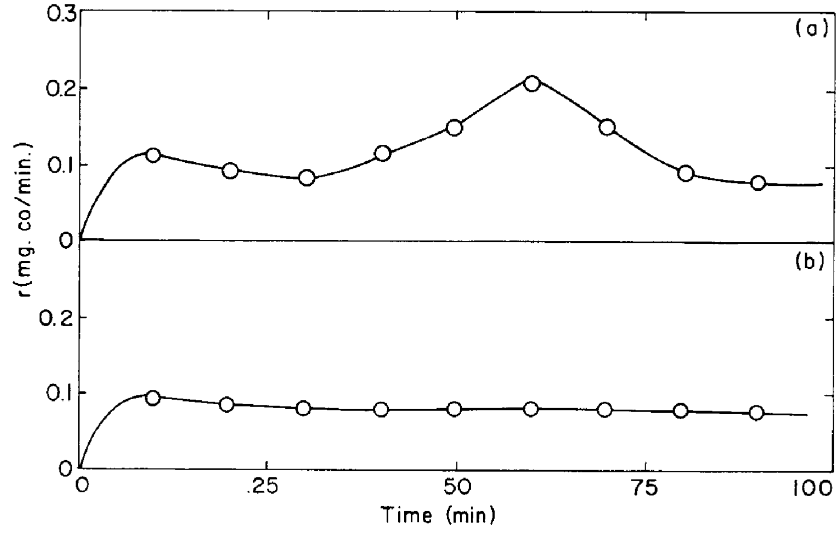


FIG. 4. Carbon dioxide dissociation patterns at 450° and space velocity 230 ml CO_2/ml catalyst/hr. (a) Catalyst flushed with nitrogen before introduction of CO_2. (b) Catalyst activated with hydrogen then exposed to CO_2 stream containing 5.1 mm Hg (pH_2O). [Compare Fig. 3(c).]

quantitative estimation of CO_2. Determinations were made from 30 to 120 min at 450°. However, the effluent CO_2 was 6 to 6.5% by weight less than that required to balance. It will be shown later that strong evidence of the presence of chemisorbed CO_2 on the catalyst surface was obtained from infrared work, which may account for the discrepancy.

(*ii*) *Variation of r with Carbon Dioxide and Oxygen Partial Pressures*

The dependence of r on CO_2 and O_2 partial pressures was studied at 450° and 950°. For CO_2, the partial pressure was varied by addition of quantities of high purity nitrogen while maintaining a constant flow rate. The results are given in Table 1.

TABLE 1

DEPENDENCE OF STEADY REACTION RATE LEVEL ON CARBON DIOXIDE PARTIAL PRESSURE[a]

Temperature (°C)	Partial pressure of CO_2 (mm Hg)	Partial pressure of N_2 (mm Hg)	r (mg CO/min)
450	759.6	—	0.089
450	552.7	206.9	0.095
450	345.5	414.1	0.096
450	207.3	552.3	0.096
950	759.6	—	1.509
950	552.7	206.9	1.503
950	345.5	414.1	1.503
950	207.3	552.3	1.506

[a] Space velocity—230 ml gas/ml catalyst/hr.

These results show that the reaction rate is independent of the CO_2 partial pressure from 200 to 760 mm at both temperatures.

In a similar fashion the influence of oxygen pressure was examined from 138–550 mm Hg while keeping the CO_2 pressure constant. At both temperatures the increase in rate (Δr) moves in step with increasing oxygen concentration (Table 2).

TABLE 2

EFFECT OF OXYGEN PRESSURE ON STEADY LEVEL OF REACTION RATE[a]

Temperature (°C)	Partial pressure of CO_2 (mm Hg)	Partial pressure of O_2 (mm Hg)	Δr (mg CO/min)
450	207.3	552.7	0.042
450	207.2	414.5	0.021
450	207.3	276.4	0.015
450	207.3	138.2	0.001
950	207.3	552.7	0.055
950	207.3	414.5	0.032
950	207.3	276.4	0.021
950	207.3	138.2	0.015

[a] Space velocity—230 ml gas/ml catalyst/hr.

$\log_{10} r$ when plotted against $\log_{10} (pO_2)$ gives a good straight line for 450° results but with some scatter for the higher temperature. These data indicate that $r \propto (pO_2)^{0.40-0.48}$.

(*iii*) *Effect of Temperature*

At 1000°C and CO_2 space velocity of 230 ml/ml/hr, studies were made with separate catalyst masses of 1 g and 3 g. The maximum value of r on the "water vapor" peak was 38.0 mg/min with 1 g mass, dropping to 17.0 mg/min with 3 g, although the latter peak was considerably broadened. An apparent level rate of 6.7 mg/min was found after 100 min and this was independent of catalyst mass. However, after 5–10 hr exposure to CO_2 or after air admission for 30 min and re-exposure to CO_2, the rate level at this temperature deteriorated to 0.1 mg/min, that is about twice the blank value.

Similar runs were made at 600°, 800°, and 950°.

For a zero order reaction in which a gas is decomposed by passage over a solid catalyst:

$$k = C_i D/t \qquad (3)$$

where k, the rate constant, includes certain nonseparable surface factors such as variations in activity of different particles, D is the absolute fraction of gas decomposed during a single traverse, and t is the contact time. C_i, the initial concentration, is taken in moles/min and t is then assumed proportional to the reciprocal of the space velocity (S_v). The working expression for the rate constant becomes:

$$k = C_i D\ (fS_v) \qquad (4)$$

where f is introduced to allow for space velocity variations with temperature and is arbitrarily taken as directly proportional to T_2/T_1, where T_2 is the reaction temperature and T_1 the flow-meter temperature (both in °K).

A plot of $\log_{10} k_{100}$ (conditions at 100 min exposure) against $1/T$°K shows a distinct break at around 800° (Fig. 5). Below 800°, k changes slowly with temperature, $E_a =$

5.5 kcal mole^{-1}, while above 800° the rate increases rapidly and E_a = 45.0 kcal mole^{-1}.

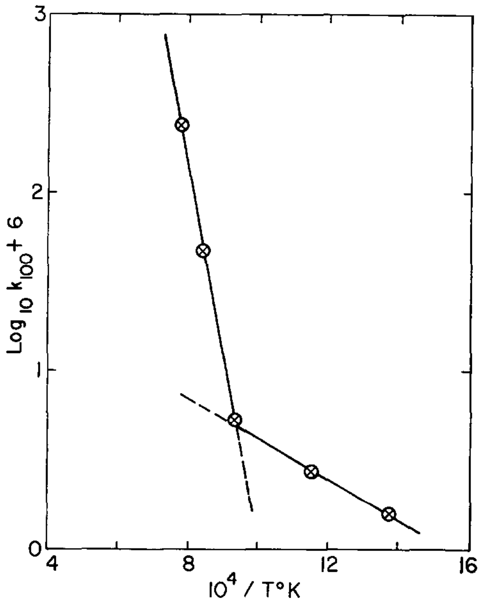


Fig. 5. Activation energy plot. Rate constants measured after 100 min exposure to CO_2.

(*iv*) *Catalyst Specifications*

Catalysts were specified by chemical analysis for nickel and by magnetic susceptibility measurements at 1400 and 6100 oersteds (room temperature). The results in Table 3 refer to analysis of nickel/silica mixtures after 2 hr exposure to CO_2 in each case.

TABLE 3
Chemical and Magnetic Analysis of Nickel/Silica Catalysts

Temperature of exposure to CO_2 (°C)	Color	Nickel content (% w/w)	Magnetic susceptibility (c.g.s. units)
450	Brown	52.14	Ferromagnetic
800	Slate-gray	58.85	Ferromagnetic
1000	Apple-green	58.80	9.5×10^{-6}

Debye-Scherrer powder photographs using copper K_α radiation gave a strong pattern with the 450° sample. This was wholly attributable to nickel oxide (A.S.T.M. 4-0835). No nickel, nickel carbonate, or silica lines were detected. Infrared spectra showed a peak of medium intensity at 1610 cm^{-1}, which could be attributed to chemisorbed CO_2 (*10*). Several samples of catalysts from the 1000° studies were examined after stagewise leaching with dilute nitric acid. All gave nickel oxide and crystalline silica patterns with nickel silicates and nickel carbide absent. No infrared absorption bands were detected.

(*v*) *Separate Effects of Nickel Oxide and Silica*

Nickel oxide was prepared by thermal decomposition of the nitrate at 1000° until a steady weight level was achieved, silica by thermal dehydration of high-purity silica gel at 850° for 16 hr followed by 16 hr at 1000°.

These samples were tested separately at 450°. Both showed some initial activity (Table 4) which dropped to the blank value in 20 min (SiO_2) and 30 min (NiO).

TABLE 4
Activities of Nickel Oxide and Silica at 450°[a]

Time of exposure to CO_2 (min)	r (mg CO/min) Nickel oxide	Silica
10	0.158	0.096
20	0.069	0.054
30	0.054	0.054
40	0.054	—

[a] CO_2 space velocity—230 ml/ml/hr.

Discussion

The thermogravimetric results are interpreted as showing an initial loss of adsorbed water from catalyst pores up to 150–200°. (Even freshly reduced samples will readsorb traces of moisture in cooling to room temperature and transferring to the thermal balance.) This is followed by the growth of a nickel oxide layer in the absence of a protective surface skin. This skin forms increasingly with catalyst "aging" and its formation can be accelerated by exposure to CO_2 at 450°. The composition of the skin was not examined. However, studies of hydrogen chemisorption and of the convertibility of nickel to nickel carbonyl (*1*) with similar catalysts suggest that a proportion of the nickel is not accessible to adsorption. Some of the nickel crystalloids may be covered by a protective silica layer or caged within a silica matrix. Such explanations may hold for studies with coprecipitated catalysts reduced at 300–650°. However from the nickel content of the present series the expected gain in weight on heating in air at 1000°C, assuming the eventual formation of stoichiometric nickel oxide, is 157 mg/g. This is very similar to the experimental result of 160 mg/g for freshly reduced catalysts (Fig. 1), and suggests that all the nickel content is available for oxidation to nickel oxide at these temperatures. Silica, if present as a coherent covering on the small nickel particles, might be expected to act similarily to borate coatings on nickel, which protect the metal from high temperature oxidation (*11*).

It seems conclusively proved that CO_2 dissociates to give nickel oxide and carbon monoxide, so it may be that the protective surface skin is of a nickel oxide which, on aging or on exposure to CO_2 at 450°, effectively bars the balanced migration of further nickel atoms to the surface and oxide growth stops. Also, it is worth noting that nickel carbonate decomposes below 100° and even if the weight loss for surface films was due entirely to CO_2 desorption, it would approximate to a CO_2 surface coverage of only about 16% of a monolayer.

Turning now to the kinetic experiments, it seems fairly certain that the adsorption of hydrogen on nickel above room temperature involves transfer or partial transfer of electrons from hydrogen to nickel *d* orbitals (*12*). The ease with which this hydrogen may be displaced from the catalyst surface by nitrogen and the initial rapid reaction with carbon dioxide indicates that the gas is, in fact, chemisorbed weakly. For the reaction:

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad (5)$$

ΔG at 723°K [calculated from the data of Prigogine and Defay (*13*) and including Kirchoff corrections] is -2.8 kcal. In the absence of any surface mechanistic barrier the reaction should proceed readily, as was found. The variation in initial and maximum rates in the space velocity region 100–6200 ml/ml/hr indicates that the rate of transport of CO_2 to the catalyst surface is slow compared to the depletion rate of chemisorbed hydrogen.

For the decomposition of CO_2 into gaseous products (Eq. 2), $\Delta G_{723} = 53.7$ kcal. On energy considerations reaction (2) would be expected to proceed only in the absence of (5). At the same time, although (2) is noncompetitive with (5) it may proceed concurrently on active surface sites which have become denuded of hydrogen earlier. The analytical figures confirm this. Once reaction (2) initiates, then oxidation of nickel becomes possible—the heat of formation of nickel oxide being 57.5 kcal at this temperature.

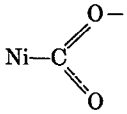
While the steady catalytic rate is independent of flow parameters, r_{max} of the secondary CO peak, which occurred after 50–60 min of exposure at all space velocities, varied from 0.4–1 mg/min. The peak areas are nearly constant so the actual quantity of CO produced was invariable. Again, this rate was depressed considerably by added water vapor, which upsets the equilibrium position of reaction (5). The time lag in the appearance of the secondary peak may be controlled simply by the time taken for hydrogen, from interstitial positions and deep pores within the catalyst, to diffuse to the surface and react with CO_2.

It has been implied earlier that at the steady level of "catalytic" rate at all temperatures between 450° and 1000°, CO_2 dissociates to CO + O. Previously, from the results of isotherm determinations at 200° and 300°, Kwan (*14*) suggested from statistical conclusions that CO_2 adsorbed on reduced nickel gave three dissociated species—C, O, and O. If so, then we might anticipate some traces of carbon deposition or perhaps nickel carbide formation at the higher temperatures. No traces of either were detected in X-ray photographs of bulk catalyst samples nor in those of solid fractions isolated at various stages of dissolution in weak acids. It may be, however that carbon once deposited on the nickel surface could react quantitatively with fresh CO_2 thus:

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g) \qquad (6)$$

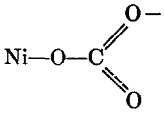
This reaction is favored thermodynamically with increase of temperature (*15*) ($\Delta G_{823} =$ 4 kcal; $\Delta G_{923} = 0$), and has been shown to be catalyzed by iron (*16*), for example. However, there was no direct experimental evidence for the occurrence of reaction (*6*).

The adsorption of CO_2 on nickel probably involves one adsorption center and the intermediate structure



has been proposed by Eischens and Pliskin (*10*). This complex could decompose by electron acceptance to give carbon monoxide and adsorbed O^{2-} or, initially, adsorbed O^- ions. At the temperatures studied O^{2-} ions adsorbed on nickel would be expected to initiate oxide growth. Since fresh quantities of CO_2 are continually dissociated, the limit to oxidation is reached when all the nickel is used up.

During oxide growth on the catalyst the surface complex formed may be of the bicarbonate (*11*) type



Dissociation would be by electron acceptance from an adjacent Ni^{2+} surface ion giving O^- (ads), CO(g), and Ni^{3+}. Although O_2^- (ads) has been named as the most probable intermediate ion in the adsorption of oxygen on NiO at room temperature (*17*), with CO_2 the formation of O^- (ads) would require less rearrangement and bond fission. The O^- adsorbed ions would then incorporate into the growing nickel oxide lattice by an oxide-growth mechanism—electron acceptance and occupation of vacant anion sites. And so long as the solid surface exhibits deviations from chemical stoichiometry then so long will dissociation proceed. Such considerations lead to a realization of the importance of oxygen in determining the reaction rate but do not appear to fit, on a quantitative numerical description, the exact dependence of reaction rate on oxygen pressure as found by experiment, i.e. $r \propto (pO_2)^{0.4}$.

The break in the value of the activation energy, from 5.5 kcal/mole below 800° to 45.0 kcal/mole above this temperature, is striking. Initially, it was felt that the overall rate might be controlled simply by the slow step in the oxidation of nickel. If this were so then the high temperature activation energy should be much nearer the value of 35.5 kcal/mole given by Kubaschewski and Von Goldbeck (*18*) for the oxidation of nickel by oxygen at similar temperatures. For the moment, it is believed that the E_a break is connected with a switch in the rate-controlling step which is enforced by some change in the solid. This change may be connected with a rearrangement or disturbance of lattice positions of the catalyst components so that, for example, surface Ni^{2+} ions become more abundant or available perhaps through an alteration in solid environment.

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