

Catalytic Activity of a Cobalt Powder in NH₃ Synthesis in Relation with the Allotropic Transformation of the Metal

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A kinetic analysis of ammonia synthesis over powdered Co showed that the rate law is of the type

$$r = kP_{N_2}(1 + KP_{H_2}^{1/2})^{-2}(1 + K'P_{NH_3})^{-2}$$

The reaction was rate limited by N₂ chemisorption and inhibited, albeit moderately, by H₂ and NH₃. Within the temperature domain where the reaction could be studied, Co underwent the hcp \rightleftharpoons fcc phase transformation. Little variation of the active area was entailed but a significant change was observed for the rate constant of N₂ chemisorption, the equilibrium constant of H₂ chemisorption and also the equilibrium constant of chemisorbed nitrogen. Every step (or group of steps) of the reaction was therefore involved, leading to a variation of the overall rate of reaction. Another striking effect of the phase transformation was the display of reversible hysteresis cycles as a function of the temperature. © 1985 Academic Press, Inc.

INTRODUCTION

We have previously reported experiments carried out on an industrial-type Fe catalyst (1) and on powders of Ru (2) and Os (3) with the aim of comparing catalytic behavior in NH₃ synthesis throughout an extended range of temperature and composition of the reactant mixture. New ways of examining the action of the catalyst resulted from these and related studies (4, 5). We considered it advisable to extend our experimental analysis to the next column of the Periodic Table. Cobalt, in spite of its lesser activity compared to Fe and Ru, appeared nevertheless much more active than Rh and Ir. Little information concerning pure Co is available as it has most frequently been used in addition to other metals (6-8), in a supported form (9), or added with promoters (6, 7, 9). Moreover, activity tests rather than detailed mechanistic studies were the main purpose of most of the previous works. Their main result was that Co is not a good catalyst for NH₃

synthesis. The present article supports that conclusion. Nevertheless, accurate kinetic determinations enabled a remarkable catalytic behavior to be revealed, namely the sensitivity not only of the rate of reaction but also of the main kinetic factors to the allotropic modification displayed by Co in a temperature range which includes that used for NH₃ synthesis.

EXPERIMENTAL

Kinetic measurements. The experiments were performed at atmospheric pressure in a flow-type apparatus which has already been described (2, 3).

The steady rates of production of NH₃, R_s , were determined by measuring the time required to neutralize a known and appropriate sample of acid solution.

Transient productions of NH₃ occurred by hydrogenating nitrogen preadsorbed on the metal surface. The amounts of NH₃ thus produced were derived from the corresponding amounts of acid which were re-

acted and determined by measurements of conductivity.

Catalyst. We used 10 g of a very pure Co powder (Johnson Matthey, Specpure sponge, 20 ppm total impurity). The powder was first reduced under a stream of stoichiometric mixture ($N_2 + 3H_2$) while the temperature was increased up to 500°C within a few hours.

For X-ray diffraction experiment, the catalyst was reduced in the X-ray cell under a stream of H_2 . The measurements were made with a diffractometer (C. G. R. θ 60) using $CoK\alpha$ radiation and a scan speed of $0.5^\circ/\text{min}$ in flowing H_2 from 20 to 600°C.

The total surface area of the fresh powder after reduction was determined by adsorption of Kr at 77 K and was found to be $0.4 \text{ m}^2 \text{ g}^{-1}$, that is to say, three or four times as high as that which could be deduced from N_2 chemisorption experiments which will be reported later. The stoichiometry of N_2 chemisorption on Co surfaces is not known. If reference is made to bulk compounds, stoichiometries such as Co_3N or Co_4N might be expected and could explain a difference between physisorption and chemisorption results.

RESULTS

The Co powder appeared to be a poor catalyst under the ($N_2 + 3H_2$) mixture as 10 g were required to obtain rates comparable with those corresponding to 1 g of Os powder, and moreover the Os activity was roughly two orders of magnitude lower than that of Fe and Ru (3). Consequently we tried to activate the powder by submitting it to successive oxidizing and reducing treatments but only with moderate success.

Cobalt Activation

The powder was first oxidized by a stream of air at 600°C. The temperature increased to 750°C within minutes, then decreased slowly to its initial value ($\frac{1}{2}$ hr). It is well known that a strong oxidation takes place in such conditions (10, 19). At the end of the thermal effect, the powder was

flushed with the stoichiometric mixture ($1000 \text{ cm}^3/\text{min}$) after a brief N_2 injection had cleared the reactor of O_2 . By periodically decreasing the temperature to 400°C it was possible to probe the catalytic activity and to monitor its variation under these reference conditions. At the end of the reduction process the rate had increased by a factor of 2.5, evidently due to some surface roughening as the active area was increased to the same extent. No improvement resulted from new similar treatments. Furthermore, the rate increase was not permanent and tended to disappear slowly. Nevertheless, the catalyst decay was slow enough to remain negligible within the time required to investigate the influence of all the required kinetic factors upon the rate of reaction (a few days).

Arrhenius Plots

Figure 1 shows the logarithmic variation of the steady reaction rate versus $1/T$ corresponding to a constant flow rate of the stoichiometric reactant mixture. Curiously, two plots were obtained as the temperature was increased from 300°C (line 1) or decreased from 550°C (line 2).

The transition between these two approximately parallel straight lines took place between 460 and 500°C by increase of temperature and between about 380 and 340°C by decrease of temperature. When the catalyst was heated from 300°C or less to any constant temperature lying between 380 and 460°C, its activity remained constant and roughly twice as high as that it would have displayed if the same temperature had been reached by cooling from 500°C or more.

If the temperature exceeded 500°C even only for a while and did not thereafter decrease lower than 380°C, the rate varied as depicted by line 2 whether the catalyst was heated or cooled. In particular the rate remained constant for tens of hours at 380°C; however, if the temperature was decreased only a few degrees lower the transition toward line 1 occurred immediately. Had the

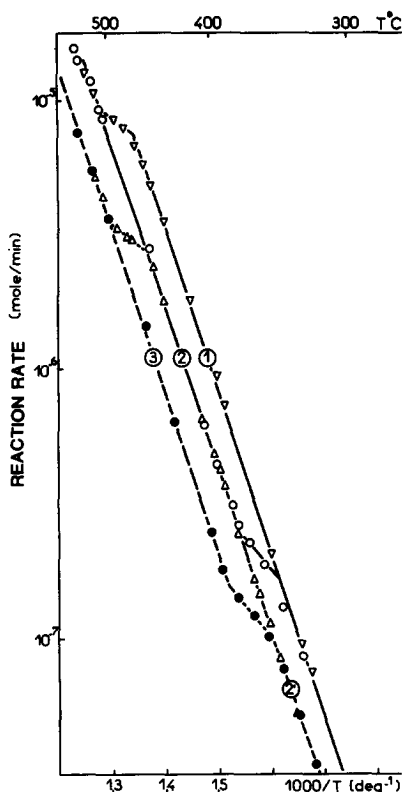


FIG. 1. Arrhenius plots corresponding to 1000 cm³/min of the mixture N₂ + 3H₂. Fresh catalyst: measurements at temperature increasing from 300°C (∇) or decreasing from 550°C (○). Aged catalyst: measurements at temperatures increasing from 300°C (Δ) or decreasing from 550°C (●).

temperature been fixed at any particular value between 380 and 360°C a steady state would have been reached, corresponding to a point of the curve joining the straight lines 1 and 2. If the catalyst was reheated from this particular state a new straight line parallel to lines 1 and 2 would have been obtained. Such intermediate Arrhenius plots have not been reported in order to avoid overloading Fig. 1.

In the same way, if the temperature was decreased below 340°C the rate variations were represented by line 1 whether the catalyst was heated or cooled provided its temperature never exceeded 460°C. However, if the temperature passed but a few degrees beyond 460°C the transition toward line 2 started at once.

Figure 2 displays similar hysteresis cycles corresponding to 20% H₂ and either 80% N₂ (cycle 1–2) or 27% N₂ (cycle 2'–3). They were obtained as the temperature increased from 300°C (curve 1: 80% N₂; curve 2': 27% N₂) or decreased from 550°C (curve 2: 80% N₂; curve 3: 27% N₂). In their upper parts curves 1 and 2' reach the equilibrium regions which were rendered more accessible because of a lowering of the equilibrium NH₃ pressure due to the decrease of P_{H_2} . The transition from one curve to the other one was therefore hindered in the upper part of every cycle but appeared little affected in the lower part when the composition of the reactant mixture changed. Nevertheless, one can easily see that a broadening of the cycle was entailed by the decrease of P_{H_2} as the rate ratio changes from 2 in Fig. 1 to 2.5 in Fig. 2. Both Arrhenius lines appear parallel, from which it results that the difference between the corresponding activation energies, if any, cannot be higher than 1 kcal/mol. Figure 1 also displays the cycle 2'–3 which was obtained with the stoichiometric mixture after long

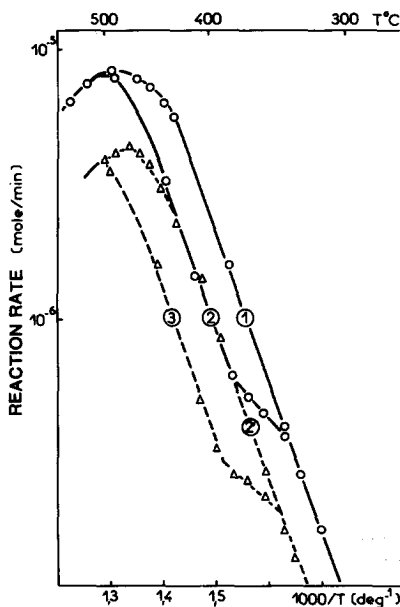


FIG. 2. Arrhenius plots corresponding to 1000 cm³/min of mixtures containing 20% H₂ and either 80% N₂ (○) or 27% N₂ and the complement of He (Δ).

use of the catalyst. Some deactivation had occurred as in its most active form the powder then exhibited a rate which was closely the same as that corresponding to the less active form of its fresh state. That loss of activity entailed no appreciable modification of the transition temperature and the cycle breadth remained constant.

Active Area

The active area of the cobalt powder could be derived from the titration by H_2 of the nitrogen chemisorbed on its surface. To this end the catalyst was first fed with pure N_2 for a given time and then with H_2 . Any disturbing effect able to proceed from the mixing up of both gases was avoided by an intermediate flush of purified helium. A common flow rate was used for each gas ($750 \text{ cm}^3/\text{min}$) and we could estimate that the catalyst bed was cleared almost instantaneously (0.5 s). The amount of nitrogen chemisorbed was deduced from the corresponding amount of NH_3 produced by hydrogenation.

We observed that the total amount of nitrogen chemisorbed on the surface ceased to depend on the exposure time as soon as the latter exceeded a few minutes at 450°C and about 10 min at 400°C . That amount was the same when the temperature was lying between 400 and 450°C . We could then reasonably estimate that it corresponded to a complete N_{ads} monolayer from which the molar amount of active sites was found equal to 2.0×10^{-6} or 1.8×10^{-6} per gram of powder freshly activated (Fig. 1, cycle 1–2) according to its previous thermal treatment (heating from 300°C or cooling from 550°C). In its final state corresponding to the cycle 2'–3 of Fig. 1 we could measure 1.0×10^{-6} (curve 2') and 0.9×10^{-6} (curve 3) mol of sites per gram. The activity decrease turned out to be therefore proportional to the active area decrease.

The same procedure applied in an intermediate state of the catalyst deactivation (Fig. 2) led to 1.5×10^{-6} and 1.35×10^{-6} mol of sites.

A systematic increase of active area of 10% was therefore observed after a stay of the powder at a low temperature ($<300^\circ\text{C}$). The reverse was true after a stay at a high temperature ($>550^\circ\text{C}$).

Other Kinetic Features of the Reaction

Experiments were carried out to determine the kinetic orders of the reaction with respect to each chemical partner. As NH_3 is frequently reported to exert an inhibition effect such an influence was looked for first.

A convenient way of revealing the possible influence of NH_3 on the reaction rate was to vary the flow rate of the reactant mixture at constant H_2 and N_2 pressures. As explained elsewhere (3), the rate R_0 corresponding to $P_{NH_3} = 0$ can be calculated from the equation

$$R_0 = R_s \left(1 + mP_s + \frac{m^2 P_s^2}{3} \right), \quad (1)$$

where P_s is the pressure of NH_3 at the end of the catalyst bed whereas m is a parameter which depends on P_{H_2} but not on P_{N_2} . Consequently, the values of R_s and P_s corresponding to two particular flow rates of the reactant mixture permit R_0 and m to be found and therefore the variation of R_s as a function of P_s to be derived.

Figure 3 shows the variations of R_s as a function of P_s corresponding to two different reactant mixtures containing 25% N_2 and either 75% H_2 (curves 1 and 2) or 17% H_2 (curves 3 and 4). Moreover, curves 1 and 3 were obtained at 401°C after preheating of the catalyst at 300°C whereas curves 2 and 4 were obtained at 414°C after preheating of the catalyst at 550°C . One can thus easily see that an approximate 15°C temperature increase was needed for the activity loss caused by the stay of Co at an elevated temperature ($>550^\circ\text{C}$) was almost compensated for. Each of the four curves can easily be represented by Eq. (1).

Although the effect of P_{NH_3} upon the reaction rate could not be neglected the dif-

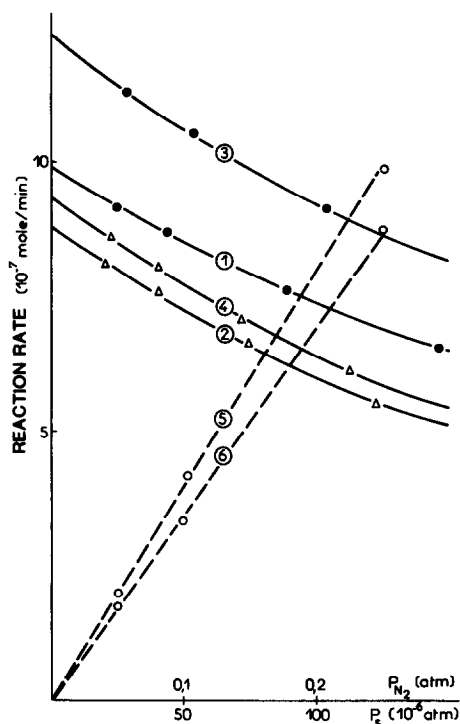


FIG. 3. Rates of NH₃ production as a function of P_{NH_3} at the reactor exit. As measured at 401°C for mixtures containing 25% N₂ and either 75% H₂ (1) or 17% H₂ and the complement of He (3) after preheating at 300°C. As measured at 414°C for mixtures containing 25% N₂ and either 75% H₂ (2) or 17% H₂ and the complement of He (4) after preheating at 550°C. Rates of reaction at $P_{\text{NH}_3} = 0$ as a function of P_{N_2} . As measured at 401°C after preheating at 300°C (5). As measured at 414°C after preheating at 550°C (6).

ferences between the R_0 values (curve intercepts) and the highest R_s values which could experimentally be obtained remained small. They could hardly be perceived on the logarithmic representation so that linear Arrhenius plots were obtained throughout the main part of the temperature range investigated.

The strength of the NH₃ inhibition depended very little on P_{H_2} as the ratio between two R_s values corresponding to a same NH₃ pressure varies very little along curves 1 and 3 or 2 and 4. This statement held whether the catalyst was in a state of high or low activity.

A clear though moderate H₂ inhibition is

also evident in Fig. 3. Moreover, this effect was less small when the catalyst had been cooled at 300°C prior to measurements (curves 1 and 3) rather than heated at 550°C (curves 2 and 4). The H₂ adsorption was bound to increase when the catalyst was cooled, as already reported (11).

The reaction order with respect to N₂ could be obtained by substituting helium for a part of N₂ into the reactant mixture while P_{H_2} was kept constant (0.75 atm) and the flow rate as well (1000 cm³/min). A decrease of P_s resulted as well as a parallel decrease of mP_s since m does not depend on P_{N_2} . The NH₃ inhibition became still smaller than with the stoichiometric mixture so that the difference between R_s and R_0 lessened. Figure 3 shows how R_0 depended upon P_{N_2} at 401°C after cooling at 300°C (line 5) and at 414°C after heating at 550°C (line 6). The reaction was therefore of the first order in N₂ on Co whatever thermal pretreatment was applied.

Hydrogenation of Preadsorbed Nitrogen

The reactivity of preadsorbed nitrogen toward H₂ could also be easily measured. To this end the powder surface was first fed with a flow of pure N₂ until saturation. The subsequent substitution of H₂ to N₂ led to a transient production of NH₃ which could be measured without any difficulty.

Figure 4 shows such variations of the total amount of NH₃ which were produced as a function of the hydrogenation time. Completion of the nitrogen monolayer as well as subsequent hydrogenation were carried out at 400°C. The powder had first been heated at 550°C (curves 1, 2, 3, and 4) or cooled at 300°C (curves 5 and 6). In every case the total amount of NH₃ produced within a given time was proportional to the time of the hydrogenation and to the flow rate of H₂. The pressure of NH₃ was therefore constant at the reactor exit, thus illustrating that there was equilibrium between chemisorbed nitrogen and gaseous H₂ and NH₃. The constancy of P_{NH_3} was obeyed until nitrogen chemisorbed on the end layer of

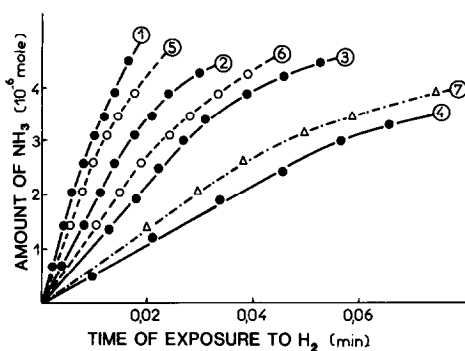


FIG. 4. Amount of NH_3 resulting from hydrogenation of the surface saturated first with N_2 , as a function of the time elapsed under H_2 . The measurements were made at 400°C , after heating at 550°C , under H_2 flow rates of 900 (1), 480 (2), 270 (3), and 135 (4) cm^3/min or after heating at 300°C and under H_2 flow rates of 490 (5) and 240 (6) cm^3/min . Curve 7: Hydrogenation at 100°C under H_2 flow rates of 960 or 480 cm^3/min of the surface saturated with N_2 at 400°C .

the catalyst bed started being reacted. The situation was similar to that observed on Os (3) and Ru (2) powders. Comparison between curves 2 and 5 on the one hand and curves 3 and 6 on the other shows clearly that the initial equilibrium NH_3 pressure was higher when the catalyst had first been cooled at 300°C than when it had been heated at 550°C instead.

In another series of experiments the catalyst was cooled at 200 and 100°C after completion of the chemisorbed nitrogen monolayer at 400°C . Exposures to H_2 began once the lower temperature was attained. At 200°C the same hydrogenation equilibrium continued to operate. However, the rate of NH_3 production did not depend any more on the H_2 flow rate at 100°C thus showing that the hydrogenation proceeded irreversibly at that temperature.

Allotropic Transformation of Cobalt

Within the temperature range where a dual kinetic behavior was displayed, Co is able to undergo an allotropic transformation from the hcp structure (ϵ) into the fcc one (α). The exact transition temperature may vary according to the direction of the

modification. Large hysteresis effects result and their extents have been a matter of discrepancy as they depend on metal pretreatments which may be chemical (13, 14), thermal, or mechanical (15, 16) in nature. Data concerning the transition in powders are scarce (15) as most of the techniques used to reveal the modification require test bars (12, 17). Consequently an examination of our sample by X-ray diffraction was in order in an attempt to detect the phase transformation under conditions closely related to those used during catalytic reaction.

The powder was maintained under a permanent flow of pure H_2 and could be heated from room temperature to 600°C during irradiation.

Figure 5 shows the beginning of the photometric record of the Debye-Scherrer diagram given by the powder at room tempera-

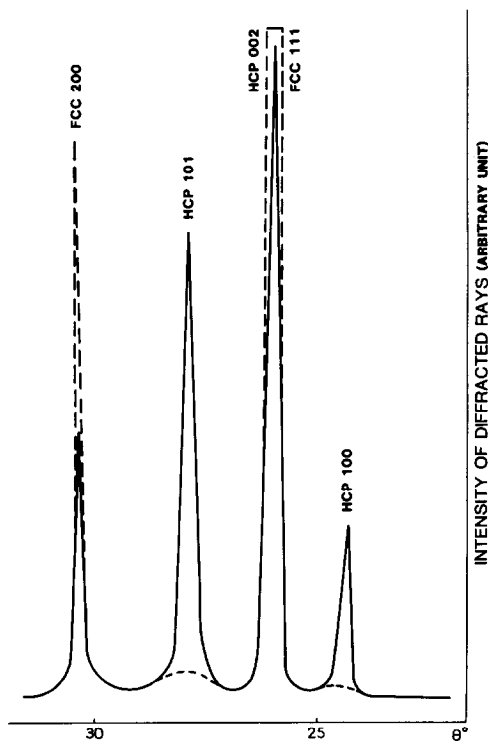


FIG. 5. X-Ray diffraction lines characteristic of each Co structure at room temperature (full lines) or at 600°C (dotted lines).

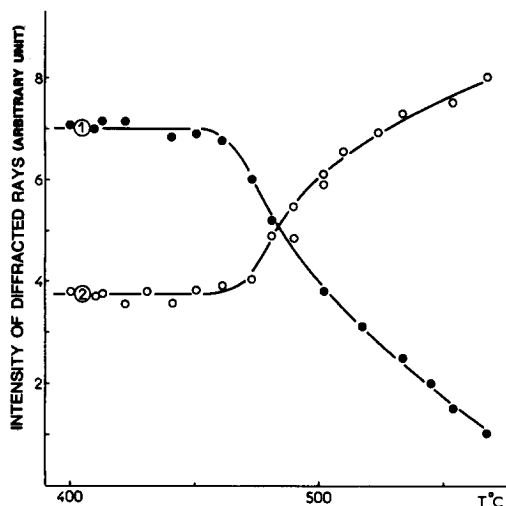


FIG. 6. Intensity variation of the diffracted rays characterizing each Co structure as a function of the temperature when the latter increases from 20 to 600°C. Curve 1: (101) ray. Curve 2: (200) ray.

ture or at 600°C. Diffracted rays, (101) and (200), were selected to characterize hexagonal and cubic phases since they have a maximum intensity among the rays which are different for the respective structures. In Figs. 6 and 7 are shown the variations of the (101) peak height (curves 1) and those of the (200) peak height (curves 2) as a function of temperature when the latter increased from 20 to 600°C (Fig. 6) or decreased from 600 to 20°C (Fig. 7). Of course, curves 1 of Figs. 6 and 7 met at 20°C as they did at 600°C and the same was true for curves 2.

At 600°C the hexagonal Co disappeared almost completely (Fig. 5) and it was necessary to drop the temperature below 380°C (Fig. 7) to make it reappear (curve 1) to the detriment of the cubic phase (curve 2). The hexagonal form grew then as the temperature decreased and continued to do so until room temperature was reached. There then remained a great amount of cubic Co (Fig. 5) which could not grow again if the sample was not reheated to more than 460°C (Fig. 6). When that was done cubic Co spread out again (curve 2) at the expense of hexag-

onal Co (curve 1) and did not stop doing so before about 600°C.

After a temperature change, the diffracted rays became constant in intensity in less time than that needed for the diagram to be obtained (about 10 min). The peak heights remained constant inasmuch as the temperature was maintained constant and that was even observed in the regions of phase transformation. For example, no change could be observed for about 10 h after the sample was heated from room temperature to 460°C; however, heating the powder to a temperature a few degrees higher made the transformation start at once. In the same way cubic Co remained stable at 380°C but a small cooling was enough to make some hexagonal Co appear. The amount of transformed metal remained then constant in the absence of a new temperature change and immediately varied after a new temperature change.

We also tried to examine the sample under ($N_2 + 3H_2$) instead of pure H_2 as it was possible that the allotropic transformation might be sensitive to the chemical composition of the gaseous environment (13). No variation of the transformation temperature

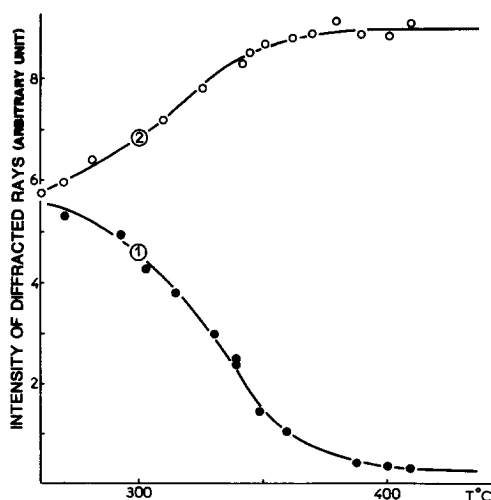


FIG. 7. Intensity variation of the diffracted rays characterizing each Co structure as a function of the temperature when the latter decreases from 600 to 20°C. Curve 1: (101) ray. Curve 2: (200) ray.

resulted from the replacement of a part of the H_2 by N_2 . Nevertheless, the peak heights were seriously decreased. The corresponding curves are not presented as they would give no additional information.

DISCUSSION

Reaction Mechanism

As for Fe, Ru, and Os the reaction is of first order with respect to N_2 and this kinetic property shows that the reaction is rate limited by N_2 chemisorption. This is the only kinetic limitation which is consistent with the fact that preadsorbed nitrogen was shown to be hydrogenated under equilibrium conditions at $T > 200^\circ C$. Hydrogenation of chemisorbed nitrogen was even evidenced easily at $100^\circ C$ whereas the steady production of NH_3 required $300^\circ C$ to be visible.

Under such conditions the rate law can be written as formerly (3):

$$r = \frac{kLP_{N_2}}{[1 + (KP_{H_2})^{1/2}]^2(1 + mP_{NH_3})^2} = \frac{R_0}{(1 + mP_{NH_3})^2}$$

with m being defined by

$$m = \left[\sum_{x=0}^{x=3} \frac{1}{K_{NH_x} P_{H_2}^x} \right] [1 + (KP_{H_2})^{1/2}]^{-1}$$

In these equations the symbols have the following definitions:

- k , rate constant of N_2 chemisorption
- L , total amount of active sites upon the sample
- K , equilibrium constant for H_2 chemisorption
- R_0 , reaction rate corresponding to $P_{NH_3} = 0$
- K_{NH_x} , equilibrium constant for the hydrogenation of the surface species NH_x .

This rate law assumes that N_2 chemisorption occurs irreversibly, which was true under the reacting conditions corresponding to Fig. 3.

Equation (1) previously referred to is obtained by integration of the present rate law taking the plug-flow character of the reactor into account.

The influence of P_{H_2} upon the reaction rate is not as clear on Co as on Fe (zero order) or on Ru and Os (-1 order). Moreover, it depends on the thermal pretreatment to which the metal was subjected. The overall H_2 effect consists of a moderate inhibition of the reaction which clearly appears in Fig. 3. However, comparison of Figs. 1 and 2 shows that a broadening of the hysteresis cycle resulted from the decrease of P_{H_2} . Such a broadening must directly or indirectly originate in the decrease of P_{H_2} . The only indirect way through which the decrease of P_{H_2} could be imagined to act upon the catalyst activity seems to rest on the corresponding increase of the NH_3 inhibition. Now Fig. 3 shows that the rate inhibition by NH_3 varied but very little when two different values were ascribed to P_{H_2} for one and the same state of Co. No cycle broadening could have resulted from that. The simplest remaining explanation is therefore to assume that the H_2 inhibition is not the same on either states of the metal. More precisely, H_2 must exert a greater inhibition upon the metal heated from $300^\circ C$ which was the most active since the reverse would have caused a cycle shrinking.

The influence of P_{H_2} upon m appears very limited in every case. For taking that behavior into account one can reasonably assume that NH_3 is the most abundant nitrogenated species upon the surface as in this case

$$m = \frac{1}{K_{NH_3}[1 + (KP_{H_2})^{1/2}]}$$

and thus displays the least dependence upon P_{H_2} .

Modification of the Catalytic Properties of Cobalt in Relation with its Allotropic Transformation

Cooling the catalyst at about $300^\circ C$ made the reaction rate increase by a factor of 2 or

2.5 according to the H₂ pressure whereas the growth of the sample area did not exceed 10%. The reverse changes occurred when the powder was heated beyond 550°C. Even though they were limited in extent those modifications implied that the rate per active center varied.

The existence of hysteresis cycles added to the steady character of any reacting state between 380 and 460°C constitute a behavior which appears rather unexpected. Moreover, the break of metastability within the transition regions occurred in a progressive way as the evolution could be stopped as soon as the temperature was kept constant. Numerous Arrhenius plots and therefore numerous narrower hysteresis cycles could have been represented in Fig. 1.

There seems to be little possibility for explaining such an odd behavior by the effect of any impurity which might have been carried by the reactant mixture or which might have segregated from the bulk to the surface. In either of these cases one would need to ask why the activity should have remained constant for hours at 380°C and why it should suddenly have changed its law of variation against the temperature when the catalyst was just cooled slightly. Why did just the opposite effects happen at 460°C during heating?

The catalyst behavior becomes quite clear if account is taken of the allotropic transformation which Co is known to undergo in those temperature regions and which was directly proved to occur. The change of hcp Co (ϵ -Co) which is stable at low temperatures to fcc Co (α -Co) stable at higher temperatures belongs to the group of martensitic transformations which are commonly referred to as diffusionless phase transformations since they make atomic movements occur in a collective manner. In the present case both phases only differ in the stacking of the planes of maximum density. Adequate slip of such planes is sufficient to change the binary stacking of hcp Co into the ternary stacking of fcc Co. It is easily conceived that for such collective movements to occur into the parent phase

the resistance opposed by obstacles (such as dislocation arrays or grain boundaries) has to be overcome. Consequently a sufficient amount of driving force has to be accumulated into the solid and a delayed start of the transformation results. That was the reason for which the martensite (hcp Co in our case) began to appear at 380°C by cooling the sample whereas it began to disappear at 460°C only when the sample was heated. The true transition temperature can be estimated to be 420°C (12) which was the average value of the two temperatures of starting transitions in the opposite directions.

Another striking kinetic feature of martensitic transformations can be understood from the preceding remarks. Since the resistance to the phase transition may be viewed as essentially mechanical in nature the transformation proceeds to some extent as soon as the corresponding required energy is available. Hence the total change which can be obtained at every temperature within the metastable region is *immediately* obtained so that nothing else happens if the temperature does not continue to vary in order that the driving force can go on increasing in the domains not yet transformed. Therefore we can understand why an incompletely transformed powder could give rise to steady catalytic states since the metal required an ever-increasing driving force (and thus an ever-varying temperature) to continue being transformed.

There is another aspect of the Co phase transition which has recently been reported (18). When undergoing the $\epsilon \rightarrow \alpha$ transformation spherical grains of Co are turned into ellipsoids with about 10% larger surface area which compares very well with the increase of active area mentioned above.

Similarities between the crystallographic and the catalytic behavior are so strong that it would be difficult not to explain the kinetic effects observed as resulting from the phase transition. Kinetic consequences of the same transformation have already been reported in the case of Co oxidation (19)

TABLE 1
Catalytic Activities of Metallic Powders^a

Metal	10^{-8} (mol min ⁻¹ g ⁻¹)	10^{15} molecules (s ⁻¹ m ⁻²)	Turnover frequency (10^{-4} s ⁻¹)	References
Co hcp	10	3	8	This work
Co fcc	5	1.5	4	This work
Co + 3% Al ₂ O ₃	40	0.5		6
Fe + 3% Al ₂ O ₃	7×10^2	18.9		6
Ru	10^3		600	2
Os	20		5	3

^a 673 K, stoichiometric mixture.

and in that of the catalytic methanation of CO₂ upon the same metal (20). Nevertheless, two questions can be raised and will now be examined in turn.

The first question is whether there is any influence of the composition of the gaseous environment upon the effects under study. H₂ has been claimed as responsible for the existence of hysteresis effects (13). Although it may be expected on a thermodynamical basis that any dissolved impurity may affect the transition temperature inasmuch as the solubility would be different in both solid phases, the reason for related memory effects is not clear. Moreover, the very small H₂ solubility into Co does not display any peculiarity in its variation (30–80 ppm) from 300 to 600°C (21). No evidence in favor of such an effect was brought out by our experiments.

The second question relates to the obvious differences which exist between the hysteresis cycles obtained either by rate measurements or by X-ray diffraction. Although there was good agreement between both kinds of experiment as to the temperatures at which the transformation started in one or another direction, there was a large discrepancy as to the end temperatures. In particular a large amount of cubic phase remained at room temperature and it is known that cubic Co does not ever disappear completely even at low temperatures. Hexagonal Co disappeared by increase of temperature but not below 600°C. On a catalytic ground the whole transformation

seemed to take place between 380 and 340°C by cooling and between 460 and 500°C by heating of the sample.

Such a difference may well be linked with the fact that X rays reveal what takes place in the solid as a whole whereas catalysis is only concerned with the powder surface. Now the obstacles opposed to gliding planes can reasonably be assumed to be stronger inside the bulk of the solid rather than when the planes project themselves out of the crystal. Moreover the particles of which the powder is composed contribute to the total area and hence to the overall activity, the more so as they decrease in size. Hysteresis effects are known to be less pronounced in that case (12) and that also may cause the difference observed.

Comparison of Cobalt and Other Metals

Taking 400°C and the stoichiometric mixture as common references, the Co sample used in this work can be compared to another sample of the same metal (6) as well as to other metals. For the sake of comparison the turnover frequency measured in this work by reference to the surface area deduced from N₂ chemisorption (8×10^{-4} or 4×10^{-4} s⁻¹ according to the structure) has been converted into the units used in Ref. (6) and taking the BET area into account. The data are collected in Table 1.

Co used in Ref. (6) was coprecipitated with 3% Al₂O₃ used as a structural stabilizer. The activity measured can be expected to refer to the cubic phase as metal-

lic Co resulted from reduction of the oxide at 580°C. Although it appears a little less active than the powder used in this work the agreement can be considered as reasonable concerning the rates and quite good for the activation energies (115 kJ mol⁻¹).

Structure Sensitivity of the Reaction

That the crystallographic transformation which Co undergoes may result in rate effects clearly means that NH₃ synthesis is a structure-sensitive reaction on Co. More can be said, however, about the structure sensitivity of the different steps of which the overall reaction is composed. We have explained early in the Results section why the cycle broadening evidenced in Fig. 2 with respect to Fig. 1 and which resulted from a decrease of the H₂ pressure meant that the H₂ inhibition was greater on the powder previously cooled at 300°C rather than when it had been heated at 500°C. We can now rephrase this fact by stating that hexagonal Co is more inhibited by H₂ than cubic Co and hence that the equilibrium constant of H₂ chemisorption is increased when the cubic variety turns into the hexagonal one. However, the latter transformation does not prevent hexagonal Co displaying a higher turnover frequency in the absence of any NH₃ inhibition (that is to say when $P_{\text{NH}_3} = 0$). We can therefore deduce that the ratio between the rates of N₂ chemisorption upon hexagonal and cubic Co is higher than that of the overall reaction rates. Finally, Fig. 4 shows that the equilibrium constant of the hydrogenation of chemisorbed nitrogen is also modified by the transformation. It can therefore be asserted that the rate of N₂ chemisorption as well as the equilibrium constants of the H₂ chemisorption and of the hydrogenation of N_{ads} are sensitive to the crystallographic state of Co. As the equilibrium of the H₂ chemisorption is able to take place independently of the NH₃ synthesis, other reactions bringing this step into play can be expected to give rise to a sensitivity of the catalytic activity to the allotropic modification of cobalt.

Although the rate is but little affected by the allotropic transition, the structure sensitivity of the reaction to the crystal structure must be high as the latter only consists in a change of the distance between every atom and its next-nearest neighbor. In addition to that, attention must be paid to the fact that not all of the surface planes are concerned with the crystal transformation.

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