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Ammonia Decomposition in the Presence of Water Vapor

I. Nickel, Ruthenium and Palladium Catalysts

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The activity of different catalysts used for the catalytic decomposition of ammonia in the presence of water vapor was studied so as to obtain selective catalysts for the reduction of NO by H_2 into N_2. Ni, Ru, and Pd base formulas and Ni–Ru and Ni–Pd associations from different preparation methods were investigated. The catalytic species appears to be reduced metal despite the presence of water vapor. Ruthenium proves to be the most active metal, while palladium is inactive. If the initial catalyst is in an oxidized form, reduction by the reaction medium becomes necessary. With NiO this reduction is slow and requires a temperature of about 600°C, but it appears to be extremely fast with oxidized Ru. With reduced Ru, an activation appears necessary around 530°C. This activation has been interpreted as expressing a reconstruction of the metal surface. The addition of the noble metals Ru and Pd to nickel oxide enhances the reducibility of this oxide but does not appear to introduce any synergetic effect for the preparation method used.

INTRODUCTION

The catalytic reduction of nitrogen oxide by hydrogen in the purification of exhaust gases leads to the simultaneous production of nitrogen and ammonia (*1,3*). Investigating numerous catalysts, certain authors have found a clear correlation between the desired selectivity in the production of nitrogen, and the activity in the decomposition of ammonia (*4*)–(*6*). Thus in the context of our general researches concerning catalytic purification of exhaust gases, we have found it useful to study the activity of different catalysts for ammonia decomposition. Abundant literature exists on this reaction, and has led to the following classifications based on the activity:

$$\mathrm{Ru} \gg \mathrm{Fe} \sim \mathrm{Ni} \sim \mathrm{Co} \sim \mathrm{Rh} > \mathrm{Re} > \mathrm{Pt}\ [\text{Refs. } (9, 10)],$$

and

$$\mathrm{Ru} > \mathrm{Ni} \gg \mathrm{Pt, Pd, Cu}\ [\text{Ref. } (6)],$$

in accordance with the known selectivity of Ru and Ni. On the other hand, catalyst preparation conditions, and therefore the initial form of the catalyst (e.g., oxidized or reduced) has been shown to be important, especially in the case of Ru catalysts (7). Finally, interest in some metal combinations has been recognized (*8*).

Our investigation has consequently been directed to study the influence of the initial form of the catalyst and to examine the type of transformation arising during the transient period, as well as to determine the final stationary activity. We have chosen Ru and Ni catalysts, as being the most efficient ones, then their combination, and lastly the combination of Ni with Pd, this last metal being known as inactive but able to enhance the reducibility of NiO. We have chosen to operate in the presence of water vapor to simulate the exhaust gases atmosphere. In Part II (*17*), a kinetic in-

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vestigation was undertaken to obtain a fundamental characterization of the catalytic performances.

EXPERIMENTAL METHODS

1. Equipment

Catalyst spheres with a diameter of 2.5 to 4 mm were placed in a vertical quartz reaction tube, with a volume of 16 cm^3, between two silicon carbide plugs. A preheater-mixer filled with silicon carbide preceded the reactor. Blank experimentation showed that the filling was catalytically inert. The reactants were fed to the preheater, the ammonia being in the form of an aqueous solution. The gaseous mixture leaving the reactor passed through a system of bubblers in which the undecomposed ammonia could be continuously titrated by acidimetry.

2. Procedure

For a fixed temperature and flow rate, NH_3 conversion was constantly monitored by measuring the time required to neutralize a specific volume of acid. As soon as this time had become stable, the actual measurement was made by integrating the amount of acid consumed in 30 min. Standard test conditions were as follows:

$$P_{NH_3} = 1.8 \times 10^2 \, N \, m^{-2};$$

$$P_{H_2O} = 3.7 \times 10^3 \, N \, m^{-2},$$

$$P_{N_2} = 9.6 \times 10^4 \, N \, m^{-2};$$

$$\mathrm{GHSV} = 20{,}000 \, hr^{-1}.$$

For each catalyst the conversion was measured versus temperature. The error in the conversion measurement was in general less than 2% in absolute value; the temperature accuracy was about ±1°C. The reproducibility of performances for several preparations of the same catalyst were verified, as illustrated in Fig. 1.

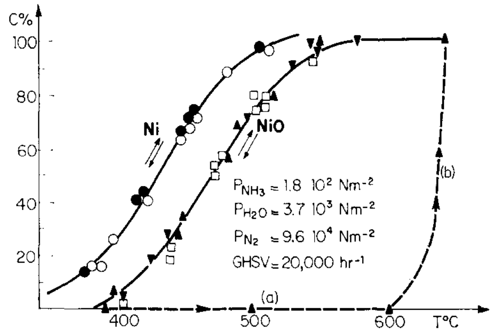

FIG. 1. Transient activity (a) and (b) for NiO catalyst; and steady state activity (⇄) for NiO and Ni catalysts. (▼) Decreasing temperature and (▲) increasing temperature for the first sample of NiO catalyst; (□) decreasing or increasing temperature for the second sample of NiO catalyst; (●) decreasing or increasing temperature for the first sample of Ni catalyst; (○) decreasing or increasing temperature for the second sample of Ni catalyst.

3. Catalyst Analysis

The specific surface areas of the catalysts were measured with a Perkin-Elmer Shell 212 sorptometer. The specific surface areas of metals were measured by dynamic hydrogen chemisorption (*12*). The degree of nickel oxidation was measured either by X-ray diffraction, or by weight loss during reduction in thermogravimetric measurements (TGA). The former technique could be used with a small amount of catalyst, but it required a careful prior calibration to be made from physical mixtures of NiO and metallic Ni deposited on alumina; it had an accuracy of about 5%. TGA measurements were performed on a large fraction of the catalytic bed. The sample was reduced by H_2 for 3 hr at 700°C. With such conditions it was checked that the reduction was almost complete for the supported catalysts used. With ruthenium catalysts the active phase contents (0.05%) were too small to be characterized.

4. Gas–Solid Reactions

The reduction of various oxidized catalytic species was analyzed by a Mettler

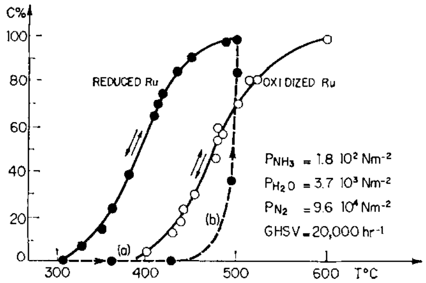

FIG. 2. Transient activity (a) and (b) for reduced Ru; and steady state activity (⇄) for oxidized Ru (○) and reduced Ru (●) catalysts.

thermobalance. With a sample mass of 100 mg, accuracy was ±0.01 mg.

5. *Catalyst Preparation*

Ru, Ni and Pd based catalysts were prepared by impregnation on alumina carriers. An alumina with a small surface area (8 m^2/g) was chosen so as to reduce interaction with the carrier.

In the case of *ruthenium*, the very high activity of this element led us to deposit very small amounts, approximately 0.05% weight. Impregnation was done with a hydrochloric solution of $RuCl_3$, and brought about an exchange phenomenon between the solute and the support, which resulted in an approximately 95% reduction in the concentration of the solution. After drying for 2 hr at 150°C, two fractions were separated. One of them was calcined in air at 500°C for 3 hr. The other was directly reduced by pure hydrogen at 350°C for 3 hr (hydrogen GHSV = 1000 hr^{-1}). In this way, two types of products were obtained, containing either ruthenium in an oxidized form or ruthenium in a reduced form. These products are the initial form of the catalysts and will be called, respectively, *oxidized Ru and reduced Ru catalysts.*

In the case of *nickel,* the weaker activity led us to deposit amounts of about 10% weight. Impregnation was performed by a nitrate solution and did not cause any appreciable interaction during wetting. Impregnation was performed without excess of solution. The drying stage at 150°C for 2 hr was very important because it determines the number, size and distribution of salt crystallites, which are precursors of the active species. The subsequent calcination stage in air at 600°C for 2 hr transforms the nickel nitrate into nickel oxide. Two fractions were then also separated. One of them was placed directly in the reactor while the other was reduced by H_2 at 500°C for 3 hr with a GHSV = 1000 hr^{-1}. These products are the initial form of the catalysts and will be called, respectively, *NiO* and *Ni* catalysts.

Palladium was deposited in a comparable amount to ruthenium from a solution of its nitrate, which does not cause any appreciable exchange during wetting. Drying and calcination were performed as for the oxidized Ru catalyst. The product obtained will be called *oxidized Pd catalyst.*

Bimetallic catalysts containing Ni and Ru, or Ni and Pd were prepared in the same way as oxidized Ru catalysts and oxidized Pd catalysts, but with *NiO catalyst* used as the carrier. They will be called *NiO-oxidized Ru* and *NiO-oxidized Pd catalysts.*

RESULTS AND DISCUSSION

For each catalyst we shall successively present for given experimental conditions:

1. The existence of a transient period of activation.
2. The existence of stationary activity, which enables single curves to be plotted which give the value of this activity versus temperature.
3. The stationary state of the catalyst, when stationary activity is attained.

Some simple and partial interpretations can be directly made after each successive experimental result. A more general interpretation is proposed below.

The ammonia decomposition reaction is practically complete from the thermodynamic point of view, for the partial pressure and temperature range used.

I. NICKEL-BASED CATALYSTS

A. NiO Oxide Catalyst (14% wt Ni)

Figure 1 shows that up to about 600°C, conversion is zero (period a, with a temperature rise of 1°C/min). At around 600°C, conversion increases quickly to attain 100% around 650°C (period b). If the temperature is then decreased the activity can be plotted by a single curve that can be considered to be reversible. In Fig. 1, a differentiation is made between points obtained for an increase or decrease in temperature.

This reveals the need for activation by the reaction medium at high temperature and the existence of a stationary activity curve. After a series of tests (final temperature = 500°C), the catalyst was cooled under nitrogen, then removed from the oven for analysis. The color change (turning from light gray to black along the bed) suggested a reduction to metallic nickel. TGA performed on the entire bed effectively revealed that the overall fraction of reduced nickel was 0.41. Furthermore, an X-ray diffraction analysis showed that this mean value corresponded to a reduced fraction of 0.25 in a zone about 20% from the entrance to the bed, and 0.45 for the rest of the bed. The ($NH_3 + H_2O$), then ($NH_3 + H_2 + H_2O$) reaction medium thus causes the reduction of the catalyst. Its steady state remains approximately the same from 400 to 600°C.

B. Ni Reduced Catalyst (14% wt Ni)

Figure 1 shows that above 350°C there is a stationary activity curve that is reversibly plotted by increasing or decreasing the temperature. The activation period either does not exist or is extremely brief. We can see that the stationary activity obtained with Ni is greater than with NiO. The stationary state of the catalyst has been characterized in the same way as previously. The mean reduced fraction is 0.66. X-Ray diffraction shows approximately 0.3 for the reduced fraction in the first 5% of the catalytic bed (sample taken at 450°C).

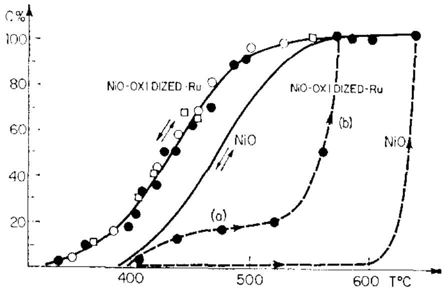

FIG. 3. Transient activity (a) and (b) and steady state activity (⇄) for NiO-oxidized Ru catalyst, three preparations of the same catalyst (●, ○, □). For comparison, the activity of NiO catalyst (Fig. 1) has been also plotted.

The preceding results thus confirm that, despite the presence of water, metallic nickel is the active phase, which explains the need for activation by reduction for the oxidized catalyst and not for the reduced catalyst.

II. RUTHENIUM BASED CATALYSTS (0.05% wt Ru)

With an oxidized catalyst (*oxidized Ru*), Fig. 2 shows that beginning at 370°C we find a stationary curve that is plotted in a reversible manner by increasing or decreasing the temperature. It can be seen that the activity observed is of the same magnitude as that discovered by Klimisch and Taylor (*6, 11*).

With a reduced catalyst (*reduced Ru*), Fig. 2 shows that the activity remains zero up to about 450°C (period a). Above that, conversion increases quickly to 100% at around 500°C (period b). Then the activity can be plotted on a single curve as a function of temperature, which corresponds to a much higher activity than the one obtained with the oxidized Ru catalyst. This experimental finding does not correspond to the one indicated by Klimisch and

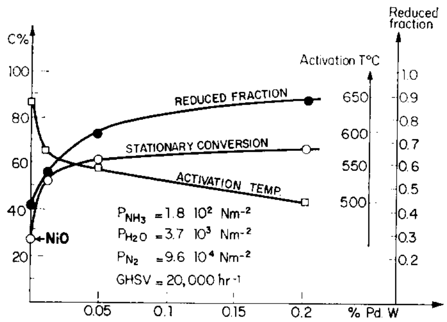

FIG. 4. Activation temperature, steady state conversion at 440°C, and steady state of the catalyst (mean reduced fraction), for NiO-oxidized Pd catalyst, vs Pd percentage.

Taylor (*6*), who observed a lower activity for the reduced species.

Instead of what was observed with nickel, it thus appears that it is the reduced form that requires an activation period. On the other hand, as with nickel, the reduced form is the most active, once stationary activity has been obtained.

III. NICKEL AND RUTHENIUM BASED CATALYSTS

Apart from a possible synergetic effect, we should expect an acceleration of NiO reducibility by the addition of ruthenium. Indeed, such an acceleration has been shown by the addition of other noble metals such as Pt and Pd (*13, 14*).

The results, shown in Fig. 3, concern an *NiO-oxidized Ru catalyst* containing 14% Ni and 0.05% wt Ru. As with the NiO catalyst, there is zero activity at low temperature. However, whereas for NiO the activity remains zero up to 600°C, a slight activity occurs for NiO-oxidized Ru between 400 and 530°C (period a) and then activity increases quickly to attain 100% at around 560°C (period b). The activity then remains at a stationary value which is quite similar to that of the catalyst Ni, and hence higher than that of the catalyst NiO. The three types of points correspond to three samples and illustrate the reproducibility of preparation. A TGA of the catalytic bed shows that the mean degree of reduction of nickel oxide from NiO-oxidized Ru is 0.66 (sample taken at 450°C).

A partial interpretation of these findings can be proposed. The domain of low activity (a), corresponds to the actual activity of ruthenium whose oxide is easy to reduce, and the clearly much lower value observed in Fig. 3 compared with Fig. 2 can probably be explained by the less good dispersion of ruthenium when it is deposited on alumina preimpregnated with NiO (this interpretation will be further confirmed by the performances of the NiO-oxidized Pd catalyst). The activation observed, beginning at 530°C instead of 600°C, results from the acceleration of reducibility caused by ruthenium. This effect will be further confirmed by additional TGA experiments.

IV. NICKEL AND PALLADIUM BASED CATALYSTS

It was interesting to confirm the acceleration of NiO reducibility by adding a metal such as palladium, which is known to be inactive with regard to the decomposition of ammonia. A prior experiment effectively confirmed the very weak activity of supported palladium. With an *NiO-oxidized Pd catalyst* (14% Ni and 0.05% Pd), the phenomena were quite similar to those observed with *NiO-oxidized Ru* (14% Ni and 0.05% Ru). The only difference lay in obtaining zero activity up to 530°C, after which the activity increased quickly. This result agrees with the very weak activity of metallic palladium and confirms the hypothesis according to which the activity corresponding to the (a) portion of the curve in Fig. 3 is attributed to reduced ruthenium.

To reveal clearly the effect of accelerating NiO reducibility by adding a noble metal, we used varying amounts of Pd, which has a simpler effect than Ru because of its own catalytic inactivity. Figure 4 shows that the increase in palladium concentration increased both the reducibility of nickel oxide (decrease in activation temperature) and the stationary level as well as the fraction of reduced nickel in the stationary state of the catalyst.

The enhancement of nickel oxide reduction by metals such as Ru or Pd was verified in a classical thermogravimetric experiment (*16*).

Mention should be made here of an experimental finding observed with all catalysts containing nickel which will be extremely useful for making a general interpretation of the experimental results. It has to do with the heterogeneity of the catalyst grains in the stationary state, as shown in Fig. 5. After the nitrogen quenching of a catalyst sample operating at 500°C, we observed that the grains located at the entrance of the catalytic bed invariably have nickel in the core (black color) and NiO (gray color) on the periphery (or at least were rich in Ni on the inside and rich in NiO on the outside). On the other hand, the grains located at the end of the catalytic bed mainly consist of reduced nickel, at least if ammonia conversion was sufficient.

V. General Interpretation

We will first consider all the catalysts containing nickel (NiO, Ni, NiO-oxidized Ru, NiO-oxidized Pd) and then the results obtained with ruthenium catalysts (oxidized Ru, reduced Ru).

A. Catalysts Containing Nickel

To discuss simultaneously the activation of the oxidized phases, the stationary activity, and the stationary state along the catalytic bed, three reactions are to be considered, only two of which are thermodynamically independent.

1. Catalytic ammonia decomposition.

$$NH_3 \rightleftarrows \tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,H_2. \qquad (1)$$

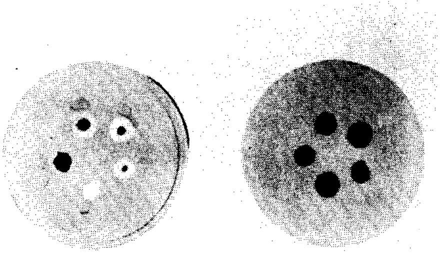

FIG. 5. Steady state of NiO catalyst grains depending on their position in the catalytic bed. Left: entrance of the reactor; right: end of the reactor.

2. The gas–solid reaction between NiO and NH_3, already investigated by some authors (15).

$$3\,NiO + 2\,NH_3 \rightarrow 3\,Ni + N_2 + 3\,H_2O. \qquad (2)$$

Thermodynamically, this reaction is almost complete for the temperatures used. Kinetically, it is slow at temperatures less than or equal to about 400°C.

3. The system of two reverse gas–solid reactions.

$$NiO + H_2 \underset{3\ \text{reverse}}{\overset{3\ \text{forward}}{\rightleftarrows}} Ni + H_2O. \qquad (3)$$

At thermodynamic equilibrium, this system obeys Eq. (4)

$$\frac{P_{H_2}}{P_{H_2O}} = K. \qquad (4)$$

In a diagram of coordinates (P_{H_2}/P_{H_2O}, temperature) the equilibrium curve in Fig. 6 separates the domains of existence of NiO and Ni.

Kinetically, both the Reactions (3) are faster than Reaction (2). Reaction (3 forward) is speeded up by adding metals such as Pt, Pd(*13, 14*) and Ru (results obtained here by TGA); we can assume that Reaction (2) is also accelerated by Pt, Pd, Ru. On the basis of these elements it is easy to recall the interpretation of phenomena concerning the activation period of the oxidized

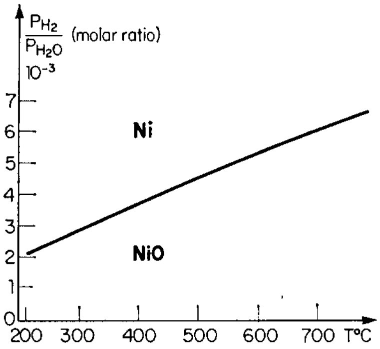

FIG. 6. P_{H_2}/P_{H_2O} value vs temperature for the equilibrium: $NiO + H_2 \rightleftarrows Ni + H_2O$.

phases. The more complex interpretation of the stationary state of the catalyst, as well as of the stationary activity, will then be taken up.

a. Oxidized Phase Activation. Period a observed for the different NiO based catalysts corresponds to the fact that this catalyst is inactive. For temperatures that are too low the rate of NiO reduction by NH_3 (Reaction 2) is too slow. NiO reduction by H_2 cannot occur because of the lack of hydrogen. When a temperature of 600°C is reached, reduction of the NiO phase by NH_3 becomes kinetically fairly fast and produces nickel which then catalyzes the NH_3 decomposition. The effect of Ru and Pd metals is to accelerate NiO reduction by NH_3 so that the activation temperature can be lowered. For catalysts previously reduced by H_2, it is logical to observe immediate activity on Ni species.

b. Interpretation of the stationary state of the catalyst. We will first attempt to interpret the phenomena observed with *NiO* and then with *NiO-oxidized Ru* or *NiO-oxidized Pd* after their activation. In each case we will begin by examining the stationary state of the catalyst at the entrance to the bed and then how it changes along the reactor.

a. Initial NiO catalyst. a1. Entrance to bed. The reaction atmosphere of the *homogeneous phase* is made up solely of NH_3, H_2O, and N_2. In particular, $P_{H_2} = 0$ at the entrance to the bed. Reaction (3 forward) cannot occur. Reaction (2) is too slow at low temperature. Hence the only reaction liable to occur is reoxidation, Reaction (3 reverse) of reduced Ni formed during activation, i.e., $Ni + H_2O \rightarrow NiO + H_2$. As a result, the initially activated catalyst, hence containing reduced Ni, should entirely return to the inactive NiO form. At this moment since no hydrogen is formed in the first sections of the catalytic bed, the subsequent sections should also return to the NiO state. However, this conclusion is contrary to experimental observations because, on the one hand, the stationary state of reduced nickel *persists* at the entrance to the bed (Fig. 5) and on the other hand, the NH_3 decomposition activity is not zero. We interpret these phenomena while considering that with the activated NiO catalyst (hence containing Ni) the catalytic decomposition of NH_3 *maintains* a hydrogen pressure *in the core* of the grain, which enables Reaction (3 forward) to take place. In the core of the grain, the P_{H_2}/P_{H_2O} ratio may thus attain a value corresponding to the Ni domain in Fig. 6. Of course, the hydrogen pressure decreases to a zero value from the core to the outside of the grain, and the equilibrium curve is thus crossed, bringing the outside of the grain into the NiO domain (Fig. 5).

a2. Evolution of the stationary state along the bed. This evolution results from the increase in hydrogen pressure along the bed. The core fraction of the grain in which the Ni domain is attained increases in proportion, and may reach the outside itself for a sufficient NH_3 conversion, after which the grain is totally reduced.

b. Initial NiO-oxidized Ru or NiO-oxidized Pd catalysts. For these catalysts, the same argument is applicable. However, enhancement of the reducibility of NiO by Ru or Pd enables a higher fraction of reduced Ni to be obtained at the end of activation. Consequently, the maintained production of H_2 in the core of the grain is higher, as is also the P_{H_2}/P_{H_2O} ratio at the center of the grain. Then, in the stationary state, the curve in Fig. 6 is crossed nearer the periphery for grains at the entrance to the catalytic bed, and grains become totally reduced nearer its beginning. Both forecasts correspond to experimental observation.

c. Correlation between activity and stationary state. The above results have shown a correlation between the overall activity and the mean reduced nickel fraction when the stationary state is attained. This correlation may be expressed quantitatively by plotting, for *all* nickel based catalysts, an isothermal line giving NH_3 conversion as a function of this mean Ni reduced fraction (Fig. 7). On this curve we have indicated the point corresponding to 100% Ni (*16*) which was obtained by operating with Ni in the absence of water vapor, with everything else being equal.

The curve obtained clearly reveals a quantitative correlation, but the raw relation obtained must be subjected to discussion and improvement. This will be done in Part II (*17*). We will simply remark here that the influence of the variation in crystallite size can be eliminated, to a first approximation, because chemisorption measurements have shown that, for the six catalysts in Fig. 7, the sizes of the crystallites were about 200 nm. Such measurements, concerning crystallites involving both NiO and Ni, have to be done, after reduction to Ni, under the mildest possible conditions (here at 400°C by H_2) to avoid sintering. A check of the absence of sintering results from the observation that the alternative reaction of oxidation and reduction of the catalyst up to 500°C does not change the chemisorption observed after the final reduction at 400°C.

It is rather surprising to note that the stationary state of the catalyst is different depending on whether the point of departure is NiO (0.41 mean reduced fraction) or Ni (0.66 mean reduced fraction). It might be supposed that this difference stems from the fact that the stationary states are not attained, but experiments carried on for 30 hr do not reveal any change. It is not excluded to suspect that different stationary states may exist, depending on whether the point of departure is activated NiO (hence partially reduced) or Ni (hence entirely reduced).

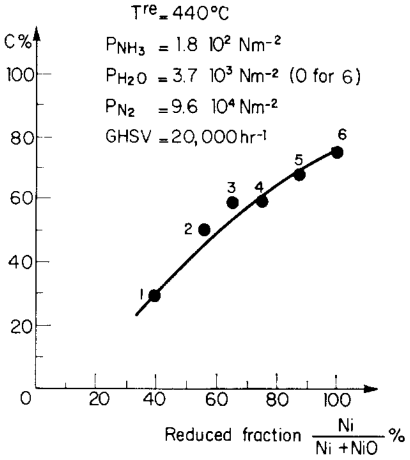

FIG. 7. Correlation between activity and mean reduced fraction, for different Ni catalysts: (1) NiO catalyst; (2) NiO-oxidized Pd (0.01%); (3) NiO-oxidized Ru (0.05%); (4) NiO-oxidized Pd (0.05%); (5) NiO-oxidized Pd (0.2%); (6) Ni catalyst operating without H_2O.

B. Ruthenium Based Catalysts

For such catalysts, considering the great reducibility of ruthenium oxides, it can be supposed that the stationary state is very close to the reduced state, either starting from an initial oxidized or reduced state. Now if we consider that the active phase is the reduced metal, the lower stationary activity observed with oxidized ruthenium should be due to an enlargement of the crystallites during the calcination steps in air. On the contrary, direct reduction should make it possible to maintain the greatly dispersed state obtained by exchange during the wetting stage. This hypothesis, which has not been experimentally checked (too small amounts of chemisorbed hydrogen), is based on a generally observed enhancement of the sintering of deposited

TABLE 1

Conversion Observed in the Stationary State for Various Initial Catalysts[a]

Initial catalyst	NiO	Ni	Ru		NiO–0.05% Oxidized Ru	NiO–0.05% Oxidized Pd
			Oxidized	Reduced		
NH_3 conversion (%)	7	30	5	60	25	25
%wt metal	14	14	0.05	0.05	14 (Ni)	14 (Ni)
ρ = conversion/% metal	0.5	2.1	100	1200	1.8	1.8

[a] $T = 400°C$; $P_{NH_3} = 1.8 \times 10^2$ N m^{-2}; $P_{H_2} = 3.7 \times 10^3$ N m^{-2}; $P_{N_2} = 9.6 \times 10^4$ N m^{-2}, GHSV = 20,000 hr^{-1}.

metal in an oxygen atmosphere, especially for Ru whose one oxide is volatile.

The need for activation with ruthenium reduced by H_2 might be interpreted by the need to obtain a *surface* structure that is favorable for the reaction. In other words, either the reduction by H_2 would allow inhibitors to subsist (such as Cl or H itself) that would be eliminated at a higher temperature in the presence of the reaction medium, or else, because of the demanding nature of the reaction, the surface structure produced by reduction with H_2 might be inactive. A reconstruction of the surface would be necessary and would be caused by the reaction environment (by NH_3). This latter hypothesis is suggested by various findings published on NH_3 synthesis by Brill and Kurzidim (*18*), who observed that Fe_3O_4 reduced by the reaction medium very quickly becomes active, whereas after reduction by H_2, an activation by the reaction medium proves necessary; other research by these authors bears out the reconstruction hypothesis.

It should be pointed out that this complex behavior of ruthenium catalysts was observed by Taylor *et al.* (*7*). We obtain activities that are quite similar to the ones they obtained with oxidized phases. But in our research, after activation by the reaction environment the reduced phase is much more active, while in the research of Taylor *et al.* it is much less active than the oxidized phase. Perhaps the weak activity of their reduced phases should be attributed to the use of a support with a larger surface area (250 m^2/g compared with our 10 m^2/g), which would make greater ruthenium dispersion possible and hence more interaction with the support. This interpretation has already been suggested by Taylor *et al.* themselves. The question arises whether activation of their reduced phases by the reaction medium at high temperature might not be liable to enhance their catalytic activity. We can note that the intervention of some Ru nitriding is in agreement with the reconstruction concept.

CONCLUSIONS

1. In the stationary state, the active species for the decomposition of ammonia is certainly the reduced metal, despite the presence of water vapor which probably mainly affects the oxidation–reduction state of metallic compounds. In the case of nickel in particular, this is demonstrated by the need of a reduction by the reaction medium (NH_3, H_2O) for a catalyst initially in the form of nickel oxide. On the other hand, activity is immediately observed for prereduced nickel. Likewise, a direct correlation appears between the stationary activity and the stationary reduced fraction of nickel. For an oxidized Ru catalyst, the activation by reduction is quite easy.

2. The need for activation by the reaction medium for a Ru based catalyst prereduced by hydrogen may be interpreted

by the need, under the influence of NH_3, to reconstruct the ruthenium surface reduced by H_2. This type of interpretation, associated with the intervention of metal–support interactions (with a large area support), may explain why other authors have found less activity for ruthenium prereduced by H_2 in comparison with oxidized ruthenium (*7*). With nickel reduced by H_2, the reconstruction phenomenon either does not intervene or is very fast.

3. The addition of small proportions of either active ruthenium or inactive palladium, for NH_3 decomposition, to an NiO species produces quite similar effects in enhancing the NiO reducibility.

4. In the stationary state, the activity of ruthenium is much greater than that of nickel, but the method of preparation is of considerable importance. These results are illustrated by the first four columns in Table 1 in which the findings are taken from Figs. 1, 2, 3, and 4.

A fundamental comparison between Ni and Ru catalytic species requires: (a) Characterization of activity by the reaction rate or kinetic parameters, rather than by conversion; and (b) knowledge of the number of surface metal atoms, so as to obtain the turnover number. However, the empirical ratio ρ = conversion/% metal shows the practical superiority of ruthenium (Table 1).

The importance of the preparation method is particularly sharp in the case of ruthenium. A catalyst prereduced by H_2 has, in the stationary state, a much greater activity than that of a catalyst calcined in air. This has been interpreted as the result of the enlargement of the oxidized Ru crystallites during the calcination.

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