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The Catalytic Chemistry of Nitric Oxide

II. Reduction of Nitric Oxide Over Noble Metal Catalysts

THADDEUS P. KOBYLINSKI AND BRIAN W. TAYLOR

Process Research Division, Gulf Research & Development Company,
Pittsburgh, Pennsylvania 15230

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The reduction of NO with H_2, CO, and an equimolar mixture of H_2/CO over supported Pt, Pd, Rh, and Ru catalysts has been studied. The activity sequence of the catalyst tested was Pd > Pt > Rh > Ru when H_2 was used as the reducing agent. When CO or a CO/H_2 mixture was used, this activity sequence was reversed. It has been found that CO inhibits NO reduction strongly over Pt and Pd but to a lesser extent over Rh. Over the Ru catalyst the presence of CO accelerates the reaction. The reduction of NO in the presence of Pt and Pd gave NH_3 as a major reaction product. Rh and especially Ru catalysts were selective toward N_2 formation. The material balance obtained for the Ru catalyst indicates that most of the NO reacts with H_2 even if CO is present. Comparative runs indicated that NH_3 decomposition is not responsible for the high selectivity toward N_2 observed with Ru and Rh catalysts. A reaction mechanism, not involving the ammonia decomposition step, is proposed.

INTRODUCTION

As a result of the present day concern with environment quality, the purification of automobile exhaust gases has been the subject of many investigations in both industrial and academic communities (*1*). The catalytic conversion of nitric oxide, one of the noxious components of exhaust gases, has provided one of the most important scientific challenges of the past decade.

The most practical and convenient method of removing NO is by catalytic reduction with CO or H_2, both of which are present in ample amounts in the exhaust gases. In practical systems, where NO, CO, H_2, and H_2O are simultaneously present, the following reactions may occur:

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad (1)$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \quad (2)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \quad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (4)$$

$$2NO + H_2 \rightarrow N_2O + H_2O \quad (5)$$

The latter reaction takes place at temperatures below 220°C. While the products of both reactions (1) and (2) are environmentally acceptable, the formation of ammonia by reaction 3 creates a major problem. In the dual converter approach for complete purification of auto exhaust (*2*), any ammonia produced in the reduction stage is reoxidized to NO in the second stage, thereby decreasing the overall effectiveness of the system. Although the formation of NH_3 from the reaction of NO with H_2 has long been recognized, it was largely overlooked during the early work in exhaust gas purification.

All of the common commercially available catalysts, which had been used for CO and hydrocarbon oxidation, produced large quantities of NH_3 during NO reduction in an exhaust gas environment. The extent of NH_3 formation over certain noble metals during the reduction of NO with H_2 has been recently noted (*3*). However, little information exists concerning the competitive reduction of NO with mixtures of CO and H_2 in the presence of these catalysts. Although it has been reported recently (*4*) that NH_3 decomposition is an important step in the selective reduction of NO to nitrogen, it is not completely clear whether this is true in the presence of the noble metal catalysts.

A study was undertaken to determine the relative importance of reactions (1), (2), and (3) in a competitive CO/H_2 reaction system. Further, the effectiveness of the catalysts for NH_3 decomposition and especially the effect of CO on this reaction, was investigated. The results of this study are reported herein.

EXPERIMENTAL METHODS

Materials

All gases for the experiments were supplied by Air Products & Chemicals, Inc. (Ar, 99.998%; H_2, 99.995%; NO 99.5%; CO, 99.6%; NH_3, 99.99%). They were used without further purification.

Catalyst Preparation

Alumina spheres (1/16 in. diam) were supplied by Universal Oil Products Company with a pore volume of 0.82 cc/g and average pore diameter of 85 Å. These were impregnated with aqueous solutions of chemically pure, palladium chloride, chloroplatinic acid, rhodium trichloride, or ruthenium trichloride. The concentrations of the respective solutions were adjusted to give 0.05–0.5 wt% metal on the finished catalyst. The impregnated spheres were dried at 120°C and calcined at 500°C for 6 hr in air. The total surface area of the finished catalyst was approximately 190 m^2/g. Catalyst was reduced in flowing hydrogen for 1 hr at 460°C prior to use.

Experimental Procedure and Analysis

The apparatus, experimental procedure and analysis were described in the first paper of this series (*5*).

RESULTS AND DISCUSSION

Reduction of NO with CO and H_2

The relative activity of a series of catalysts used to study the reduction of NO with a given reducing component, has been expressed in terms of percent NO conversion versus catalyst bed temperature at a constant flow rate. Figure 1 shows activity data obtained for the reduction of NO with H_2 over four supported noble metal catalysts. By arbitrarily choosing the temperature of 50% NO conversion (T_{50}) as an activity indicator, the relative activity sequence was Pd > Pt > Rh > Ru. It was noted that the activity of noble metal catalysts for the NO–H_2 reaction was significantly higher than that of base metals. Even in the case of Ru, the least active catalyst of the series, T_{50} was 238°C compared to 432°C for supported Fe_2O_3 or Cr_2O_3 under similar conditions. (5).

Similar data are shown in Fig. 2 for the reduction of NO with CO. In this case, each catalyst was exposed for 1 hr to 2% CO in argon at 460°C after the initial H_2 reduction and prior to the NO reduction runs. The activity sequence was the reverse of that for the NO/H_2 reaction: Ru > Rh > Pd > Pt. This reversal of activity order depending upon the reducing agent employed means that for Pt, Pd, and Rh, the reaction NO with H_2 is faster than NO with CO under the above conditions. However, ruthenium differs in that NO reduction with CO is faster than with H_2 within the temperature range used. This behavior is similar to that observed with base metals and suggests that of the catalysts studied, Ru is the "least noble." The observation that CO adsorbs more strongly than either O_2 or NO on Pt and Pd surfaces (*6–8*) may explain why the reversal of activity occurs.

Of greater significance to practical applications is the catalytic activity for NO reduction in the presence of mixtures of CO and H_2. Figure 3 indicates that an equimolar CO/H_2 mixture behaves in a similar manner to CO alone. The reason for this is apparent from Table 1, which summarizes Figs. 1–3, and compares the values of T_{50}. It is clear that addition of

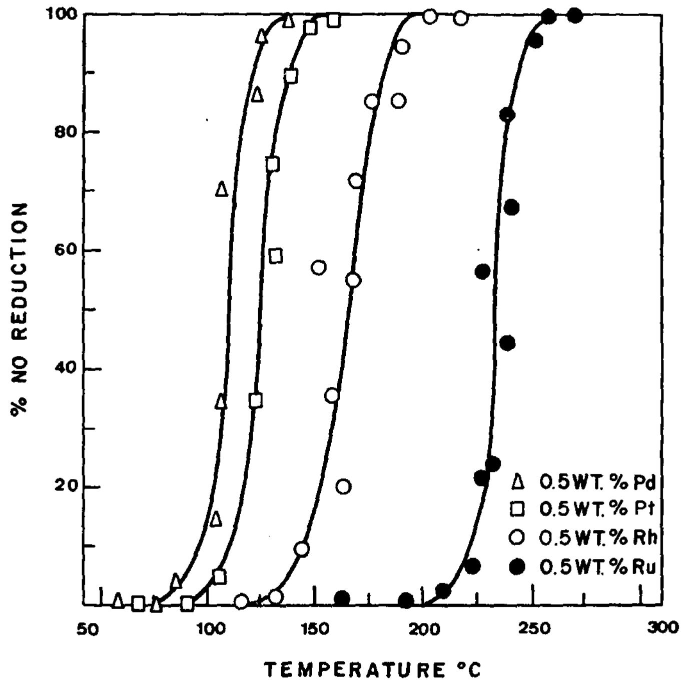

FIG. 1. Relative activity curves for reduction of NO with H_2 over supported noble metals. Reaction conditions: 0.5% NO, 2.0% H_2, 97.5% Ar, 24,000 GHSV.

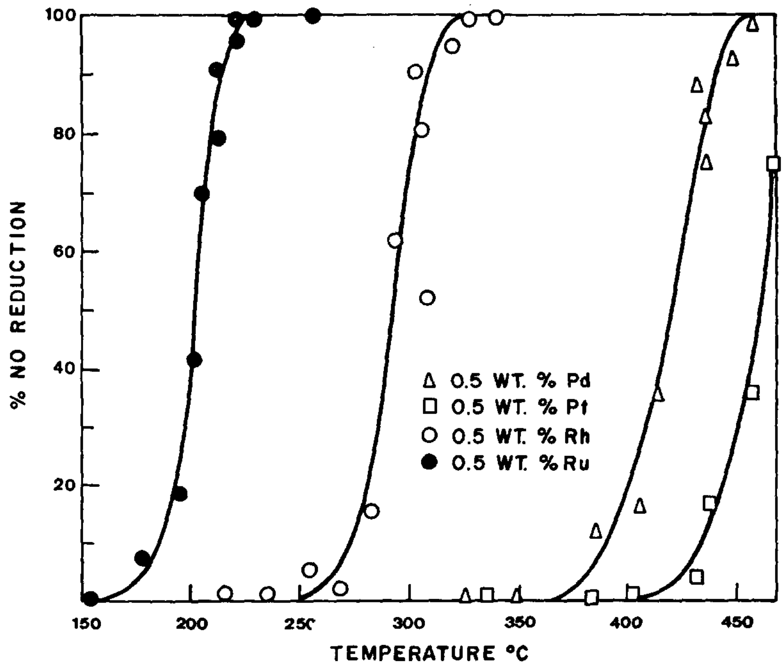

FIG. 2. Relative activity curves for reduction of NO with CO over supported noble metals. Reaction conditions: 0.5% NO, 2.0% CO, 97.5% Ar, 24,000 GHSV.

TABLE 1
TEMPERATURE OF 50% NO REDUCTION WITH H_2, CO OR CO/H_2 AS A REDUCING AGENT (°C)

Catalysts	H_2	CO	CO-H_2
Pt	121	471	398
Pd	106	431	330
Rh	163	296	275
Ru	237	205	210

CO to the NO/H_2 system strongly inhibits reduction over the Pt and Pd catalysts. In the case of Rh, CO inhibition is less pronounced, T_{50} being raised from 163°C to 276°C. Since the NO/CO reaction was faster than NO/H_2 over the Ru catalyst, it was expected that the $NO/H_2/CO$ system would show a similar rate to the NO/CO reaction.

In a system where CO and H_2 are competing for NO, three possible processes can take place:

a. The NO/H_2 reaction is a primary process, e.g., over Pt, Pd, and Rh catalysts, where the NO/H_2 reaction rate is fast.

b. Simultaneous participation of H_2 and CO, e.g., over Ru, where the inhibiting effect of CO is small.

c. Preferential reaction between NO and CO with only limited participation in the reaction by H_2.

Table 2 shows the mass spectral analysis of the reaction products obtained from the $NO/CO/H_2$ system over the Pt, Pd, Rh, and Ru catalysts. H_2O and H_2 were not analyzed, and the concentration of NH_3 in the reactor outlet was verified by chemical analysis. The material balance was calculated for the nitrogen containing compounds from the equation:

$$[\text{mole\% NO unconverted} + \text{mole\% NH}_3 \text{ formed} + 2(\text{mole\% N}_2 \text{ formed})]/(\text{mole\% NO in feed})^{-1} \times 100.$$

It was always within 2.5% of the theoretical value. The data in column 10 are based on the NH_3 analysis, and were calculated from

$$(\text{mole\% NH}_3 \text{ formed}/\text{mole\% NO converted}) \times 100.$$

Columns 11 and 12 show the extent of NO participation in reaction with both CO and H_2. The values in column 11 were calculated from

$$(\text{mole\% CO}_2 \text{ formed}/\text{mole\% NO converted}) \times 100,$$

and those in column 12 by difference. Since N_2 can be formed via both the NO + CO and NO + H_2 reactions, the percent N_2 resulting from the NO/CO reaction was

TABLE 2
PRODUCT DISTRIBUTION IN MOLE% AND NO CONVERSION AS A FUNCTION OF REACTION TYPE FOR THE REDUCTION OF NO WITH H_2/CO MIXTURE[a]

(1) Catalyst	(2) Temp (°C)	(3) NO (%)	(4) NH_3 (%)[b]	(5) N_2 (%)	(6) CO_2 (%)	(7) CO (%)	(8) NO conversion (%)	(9) NO → N_2 (%)	(10) NO → NH_3 (%)[c]	(11) NO + CO (%)[b]	(12) NO + H_2 (%)	(13) N_2 from NO + CO (%)[d]
Pt	515	0.09	1.09	0.15	0.12	4.35	94	22.7	77.3	8.5	91.5	40.0
Pd	515	0.09	1.05	0.17	0.13	4.38	94	25.6	74.4	9.2	90.8	38.2
Rh	482	0	0.50	0.52	0.30	4.16	100	66.7	33.3	20.0	80.0	28.8
Ru	432	0	0.12	0.70	0.43	4.00	100	92.0	8.0	28.6	71.4	30.7

[a] Reaction conditions: 0.5 wt% of each metal on support, flow rate, 24,000 GHSV. Feed composition, mole%: NO, 1.5; CO, 4.5; H_2, 4.5; Ar, 89.5.

[b] Amount of NH_3 was verified with the chemical analysis.

[c] NH_3 decomposition was insignificant under the reaction conditions.

[d] Assuming that H_2O formed in the NO reduction does not undergo significant water shift reaction.

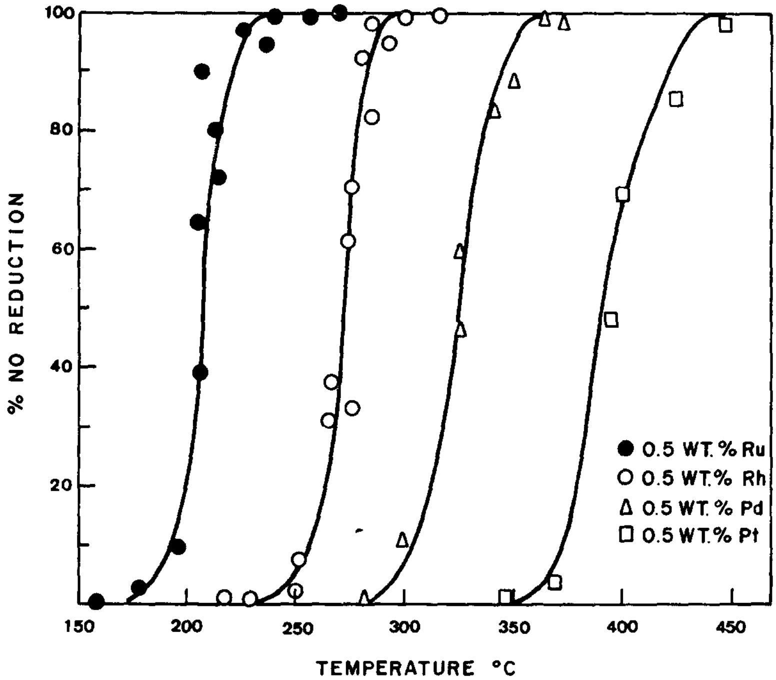

FIG. 3. Relative activity curves for reduction of NO with a CO/H_2 mixture over supported noble metals. Reaction conditions: 0.5% NO, 2.0% H_2, 2.0% CO, 95.5% Ar, 24,000 GHSV.

estimated. These data are shown in column 13, and were calculated from:

$$[\text{mole\% } CO_2 \text{ formed}/2(\text{mole\% } N_2 \text{ formed})] \times 100.$$

Product distributions obtained after the reaction over Pt and Pd are very similar, and, as reported by others (*3*), most of the NO is converted to NH_3 (77.3% over Pt and 74.4% over Pd). The Rh and Ru catalysts show much lower amounts of NH_3 formed, 33.3% and 8%, respectively.

As was expected, H_2 reacts preferentially with NO over both Pt and Pd, and as established from the amount of CO_2 formed, only about 9% of the NO was reduced by CO under the reaction conditions employed. Participation of CO in the NO reduction was higher for both Rh and Ru catalysts, being estimated to be 20% and 28%, respectively. However, even in the case of Ru where CO participation is the highest among the metals tested, H_2 is still the predominant reducing agent (71% of NO is reduced by H_2). The data presented in Table 2 indicate that process 'a,' where the H_2 reacts preferentially in the competitive system, completely dominates over Pt and Pd, and is still the major pathway in case of Rh and Ru. For Ru in particular, CO participation was much less than expected from a comparison of the T_{50} values for NO/CO and NO/H_2 shown in Table 1. It should be noted, however, that the reaction temperatures for the results in Table 2 are significantly higher than in Table 1. It is conceivable that the NO/H_2 reaction may become faster than the NO/CO at the higher temperatures.

The values in columns 11, 12, and 13 of Table 2 are subject to the assumption that the H_2O produced in the NO + H_2 reaction does not react subsequently with CO to any significant extent. However, if the water gas shift reaction indeed occurs, then the values in columns 11 and 13 will be lower and the H_2 participation in NO reduction in the competitive system will be even higher than estimated in Table 2. The data clearly indicate that under practical temperature conditions, process, 'a,' is the dominant reaction pathway even over the Ru catalyst. The increased participation of the NO/CO reaction can only partially explain the low NH_3 formation of the Ru catalyst. Of the N_2 formed during the reaction, it is interesting to note that the amount resulting from the NO/CO reaction is relatively independent of the catalyst, as shown in column 13. For the Ru catalyst, some 70% of the total N_2 produced results either directly or indirectly from the NO/H_2 reaction. Mechanistic schemes which can explain these results are discussed in a later section.

Ammonia Formation and Decomposition

It is known that supported Rh and Ru catalysts are among the most active for decomposition of ammonia into its elements (*9*). In the reduction of NO with H_2 or CO/H_2 mixtures, the selectivity towards NH_3 formation is lower over Rh and Ru catalysts than over other noble metal catalysts. A study was undertaken to determine whether these properties are directly related to each other.

Figure 4 shows reduction of NO with H_2 over both Rh and Ru catalysts as a function of temperature. On the same graph the mole% selectivity of reduction to NH_3 as a function of temperature is also shown. Even at relatively low temperatures, selectivity to NH_3 over the 0.5 wt% Ru catalyst never exceeds 14%. The 0.5 wt% Rh catalyst is somewhat similar in behavior to Pt and Pd at lower temperatures, where selectivity to NH_3 is 59%. However, as the temperature increases to the region of 540°C, NH_3 formation essentially ceases. This is in direct contrast to the behavior of Pt and Pd catalysts, where significant NH_3 formation is observed up to temperatures as high as 760°C.

If a mixture of CO and H_2 is used as the reducing agent, then a slight increase in NH_3 formation is observed at lower temperatures over both catalysts. These results are shown by the broken line in Fig. 4. This is in contrast to what might be expected, since if CO enters the reaction, the role of the NO/H_2 reaction (and consequently the likelihood of NH_3 forma-

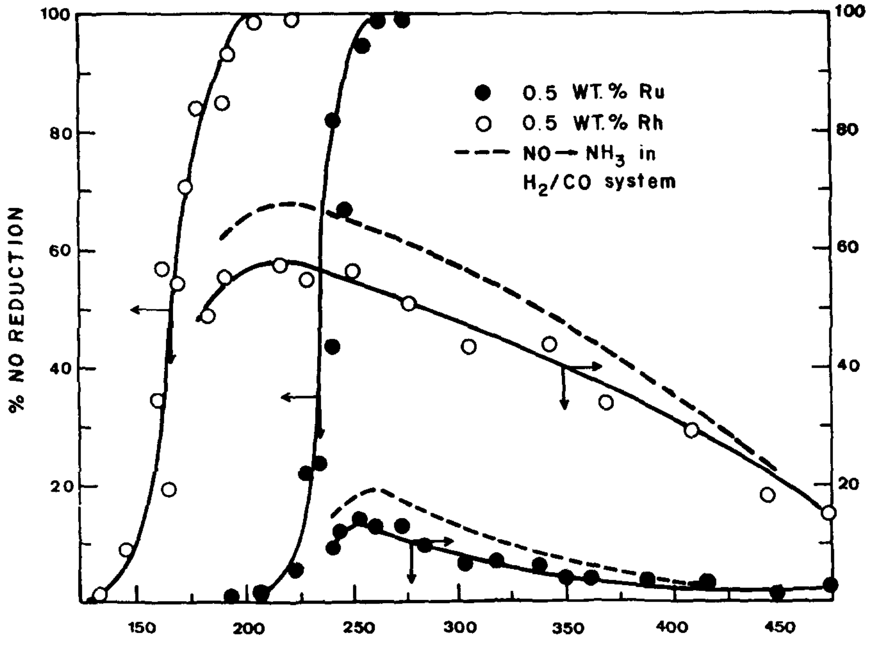

FIG. 4. Effect of reaction temperature on conversion of NO to NH_3. Reaction conditions: Solid line: 0.5% NO, 2.0% H_2, 97.5% Ar. Broken line: 0.5% NO, 2.0% CO, 2.0% H_2, 95.5% Ar, 24,000 GHSV.

tion) should diminish. This effect was also noted by Shelef (*3*). He attributed the observation to the fact adsorbed CO molecules decrease the opportunity for the occurrence of adjacent adsorbed NO molecules, the latter being necessary for N_2 rather than NH_3 formation. Although this is a plausible explanation, it is conceivable that the presence of CO could serve to inhibit either NH_3 decomposition or the reaction of NO with NH_3, both of which may be effective for removal of NH_3 from the system.

An attempt to establish the importance of NH_3 decomposition and to determine whether CO does inhibit this reaction is shown in Fig. 5. Streams of 1% NH_3 in argon, and 1% NH_3 + 2% CO in argon were passed over the Rh and Ru catalysts. It is clear that Ru is a more active NH_3 decomposition catalyst than Rh. This is consistent with the observation that NH_3 formation during reduction of NO with H_2 is lower over Ru than Rh catalysts. Furthermore, it is clear that the presence of CO has an inhibiting effect on the NH_3 decomposition, since the 50% decomposition temperature over Ru is raised from 315 to 416°C in the presence of CO. This could account for the increased NH_3 formation when NO is reduced by H_2/CO mixtures rather than H_2 alone.

However, a careful comparison of the data in Figs. 4 and 5 indicates that NH_3 decomposition is probably not an important reaction contributing to the low overall NH_3 formation over both Ru and Rh catalysts. Figure 4 shows that over Ru, 10% NH_3 was produced at 288°C in the NO/H_2 system. However, at the same temperature, using a 1% NH_3 in argon mixture, only 31% NH_3 decomposition occurred. This discrepancy is even wider when CO is present in the reaction system, where 15% NH_3 was formed at 288°C, and only 16% was decomposed under similar conditions. Similar observations can be made for the Rh catalyst.

A further indication that NH_3 decomposition is not a significant step in the

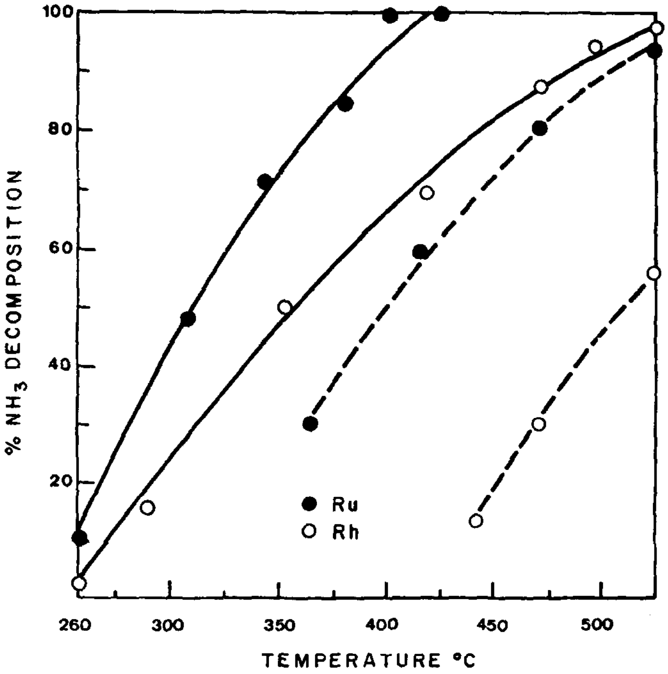

FIG. 5. Effect of temperature and CO on the decomposition of NH_3 over Ru and Rh catalysts. Reaction conditions: Solid line: 1% NH_3, 99% Ar. Broken line: 1% NH_3, 2% CO, 99% Ar, 24,000 GHSV. Catalyst: 0.5% wt% Ru or Rh.

overall reaction scheme is exmplified by the data in Fig. 6. The catalyst used in this case contained only 0.05 wt% Ru, and was prepared by a procedure which leads to a more highly dispersed metal of smaller crystallite size. It is clear that the rate of the $NO/CO/H_2$ reaction is similar to that for the catalyst containing 0.5% Ru; however, the rate of NH_3 decomposition is significantly lower. Nevertheless, it is important to note that NO conversion to NH_3 is not markedly greater over the 0.05% Ru catalyst than over the 0.5% catalyst.

Although it is evident from Table 2 that those catalysts which are most active for NH_3 decomposition form the least NH_3 in the reduction of NO in the presence of H_2, it is our contention that NH_3 decomposition is not responsible for this.

Mechanism of the Reaction

In the reduction of NO with mixtures containing CO and H_2, the following set of reactions may occur simultaneously:

$$2NO + 2CO \rightarrow 2CO_2 + N_2 \quad (1)$$
$$2NO + 2H_2 \rightarrow 2H_2O + N_2 \quad (2)$$
$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \quad (3)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad (4)$$
$$2NH_3 \rightarrow N_2 + 3H_2 \quad (6)$$
$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (7)$$

It is clear that for Pt and Pd catalysts, reaction 3 is the most important over a wide temperature range. With Rh and Ru catalysts, which produce appreciably less NH_3, the reaction sequence is less certain. For reduction of NO with H_2 over the Ru catalyst, several possibilities can account for the final product distribution. In the simplest case, reaction (2) may be the major path, with reaction (3) occurring to a limited extent under those conditions where some NH_3 is produced. The combination of reactions (3) and (6) also produces the net effect of reaction (2). Here, NH_3 is merely a reaction intermediate, being decomposed to its elements at a rate similar to that at which it is

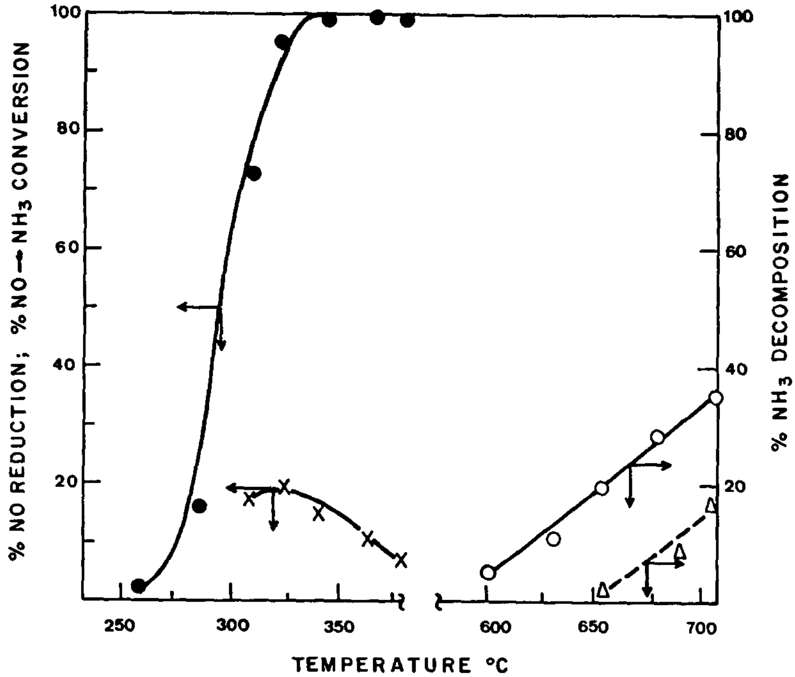

FIG. 6. Effect of temperature of the conversion of NO to NH_3 and the decomposition of NH_3 over a 0.05 wt% Ru on γ-Al_2O_3 catalyst. Reaction conditions: (× and ●) 0.5% NO, 2.0% CO, 2.0% H_2, 95.5% Ar. (○) 0.5% NH_3, 2.0% H_2, 97.5% Ar. (△) 0.5% NH_3, 2.0% H_2, 2.0% CO, 99.5% Ar. 24,000 GHSV.

formed. Although this is plausible, the data shown in Figs. 4–6 suggest that it is not a likely major reaction path.

A third scheme which also satisfies experimental observations involves reactions (3) and (7). If reaction (7) is fast compared with (3), then the NH_3 produced in (3) will be consumed immediately by reaction (7). The relative rates of these reactions have not been measured, so that the feasibility of the scheme cannot be assessed. In any event, even if such a scheme were feasible, the presently available data do not distinguish between reaction (2) or the combination of (3) and (7) as the major route for N_2 formation.

The observation that the presence of CO in the reaction mixture actually leads to an increase of NH_3 in the final product, points to the (3–7) reaction path. If (2) were the dominant reaction, with small amounts of NH_3 forming via (3), then the presence of CO should not effect an increase in NH_3 formation. However, if overall NH_3 formation is controlled by reaction (7), then inhibition of this reaction by CO (which might be expected) would lead to increased NH_3 formation.

The product distribution in Table 2 shows that for reduction of NO with a CO/H_2 mixture, the part played by CO varies significantly from Ru to Pt. With the Ru catalyst, using an equimolar CO/H_2 mixture, 30% of the NO reduction occurs by reaction with CO, whereas for Pt, this accounts for only 8.5% NO reduction. The predominant participation of H_2 in NO reduction in the competitive system, where both CO and H_2 are present, is in apparent contradiction with the data reported in Table 1 for the Ru catalyst. As shown in Table 1 the rate of NO/H_2 reaction was apparently lower than that for the NO/CO system. The reason for this discrepancy is not clear at present although one possible explanation has been proposed. However, it is also plausible that NO reduction with CO over the Ru catalyst, which is the least noble in its catalytic properties, is inhibited by H_2O. This would be consistent with observations reported previously (*3*) for base metal oxide catalysts.

In summary, Ru catalysts are unique among the noble metals, for not only do they produce very small amounts of NH_3 in the NO/H_2 reaction, but in the $NO/CO/H_2$ system significant participation by CO occurs. These properties serve to make Ru a desirable catalyst for control of NO_x in automotive exhaust gases.

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