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# The Catalytic Reduction of Nitric Oxide over Supported Ruthenium Catalysts

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The activity of supported ruthenium catalysts for reducing NO to $N_2$ in an exhaust-like feedstream has been examined in laboratory experiments. The rate and temperature of NO removal is largely dependent on the NO inlet concentration and independent of the concentration of reducing agents in the system. The selectivity for nitrogen formation, however, is dependent on the concentration of the reducing agents CO and $H_2$ as well as the concentration of NO. No evidence was found for an ammonia intermediate in the conversion of nitric oxide to elemental nitrogen over ruthenium. The high selectivity of ruthenium for the NO to $N_2$ conversion is explained and compared with the behavior of platinum and palladium catalysts.

## INTRODUCTION

Earlier papers from our laboratory have noted the role of ammonia as an intermediate in the catalytic reduction of nitric oxide in feedstreams similar to automotive exhaust (*1*, *2*). Supported ruthenium catalysts have exhibited high selectivity for the formation of nitrogen rather than ammonia. Low ammonia formation is a very desirable property for automotive emission control catalysts (*2*–*4*). This paper reports additional studies of the product distribution obtained in the reduction of nitric oxide over ruthenium catalysts. The influences of catalyst support, catalyst pretreatment, space velocity, and reactant concentration in reducing exhaust-like atmospheres are examined. In addition, nitric oxide reduction over supported platinum, palladium, and ruthenium catalysts are compared with respect to the role of CO, $H_2$, and water vapor.

## EXPERIMENTAL

The ruthenium catalysts were prepared by impregnation of either eighth-inch silica–alumina spheres (Harshaw AL-1602) or eighth-inch alumina spheres (Kaiser KC/SAF) with an aqueous solution of ruthenium trichloride ($RuCl_3 \cdot 1$–$3H_2O$, Alfa Inorganics). The platinum and palladium catalysts were prepared by impregnating the alumina spheres with aqueous solutions of chloroplatinic acid (10% solution $H_2PtCl_6 \cdot 6H_2O$, Matheson, Coleman, and Bell) or palladium chloride (5% solution $PdCl_2$, Matheson, Coleman, and Bell). The catalysts were dried in air at 25°C and then calcined in air at 620°C for 4 hr (G.H.S.V. = 500 $hr^{-1}$). The composition and surface area of the catalysts used in this study are listed in Table 1.

The catalyst treatment with $H_2SO_4$ involved soaking the supported ruthenium catalyst in a 3.6 *M* solution of the acid, then calcining the catalyst at 620°C in air for 4 hr to remove excess sulfur oxides. The $SO_2$ treatment consisted of passing pure $SO_2$ over the catalyst (G.H.S.V. = 2000 $hr^{-1}$) for 1 hr at 250°C followed by treatment with air for 1 hr at 250°C.

The catalytic reactor and gas handling and analysis techniques have been described before (*1*). A catalyst charge of 15 cc gave a bed depth of 5 cm. The gas hourly space velocity was generally 38,000 $hr^{-1}$. The feedstream referred to as the

TABLE 1
Catalysts

| Catalyst | Catalyst composition (wt % metal) | | BET Surface Area ($m^2/g$) |
|---|---|---|---|
| | Calculated | Analysis | |
| Ru-$SiO_2$-$Al_2O_3$ | 0.1 | 0.081 | 205 |
| Ru-$Al_2O_3$ | 0.1 | 0.081 | 185 |
| Ru-$Al_2O_3$ | 1.0 | — | 180 |
| Pt-$Al_2O_3$ | 0.3 | 0.31 | 178 |
| Pd-$Al_2O_3$ | 0.3 | 0.30 | 195 |

standard feedstream contained 0.10% NO, 1.0% CO, 0.3% $H_2$, 10% $CO_2$, and 10% $H_2O$ in a nitrogen atmosphere. All the data points represent steady state conversion and were taken at descending temperatures. The catalysts were reduced in the standard feedstream at 650°C before use unless otherwise specified.

## Results and Discussion

### *"Reduced" and "Oxygen Treated" Ruthenium Catalysts*

In previous work in this laboratory (*2*) we found a change in performance after treatment of the ruthenium catalyst with excess oxygen. Subsequent work however has revealed that the dual state behavior of this Ru-$Al_2O_3$ catalyst disappears after the catalyst is exposed to engine exhaust for a short time (2 hr). Experiments showed that treatment of the catalysts with $H_2SO_4$ or $SO_2$ also eliminated the dual state behavior and only the activity profile characteristic of the "reduced" state could be obtained. The reversible dual state behavior probably involves ruthenium oxidation and reduction. It is also probable that ruthenium can remain partially oxidized even in the reducing atmosphere of the standard feedstream (*5*). Apparently the sulfur (from $H_2SO_4$, $SO_2$ or the engine exhaust) interacts with the ruthenium and affects its oxidation. In any case, subsequent experiments were carried out with reduced ruthenium catalysts since this apparently represents the normal state for these catalysts.

### *Ruthenium Loading and Support Effects*

The results in Fig. 1 were obtained for a 0.1% Ru-$SiO_2$-$Al_2O_3$ catalyst that had been reduced at 650°C in the standard feedstream. The nitric oxide was only partially converted to ammonia and the small change in the CO level with temperature indicated that the water gas shift reaction did not proceed extensively. The product distribution shown in Fig. 1 was also obtained when a 1.0% Ru-$Al_2O_3$ catalyst was used and is similar to the results obtained earlier for a 0.1% Ru-$Al_2O_3$ catalyst (*2*). Thus, neither the ruthenium loading nor the catalyst support affected the products formed with the "reduced" catalyst.

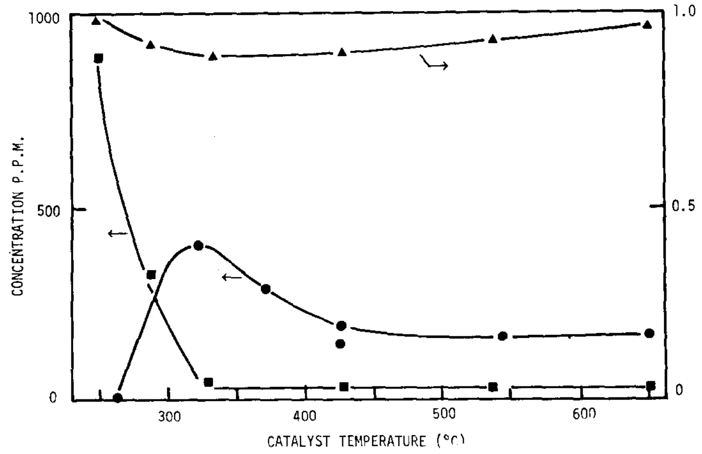

Fig. 1. Nitric oxide reduction and ammonia formation over the reduced 0.1% Ru-$SiO_2$-$Al_2O_3$ catalyst. Species: ■ NO, ● $NH_3$, ▲ CO. Standard feedstream; 38,000 $hr^{-1}$ space velocity.

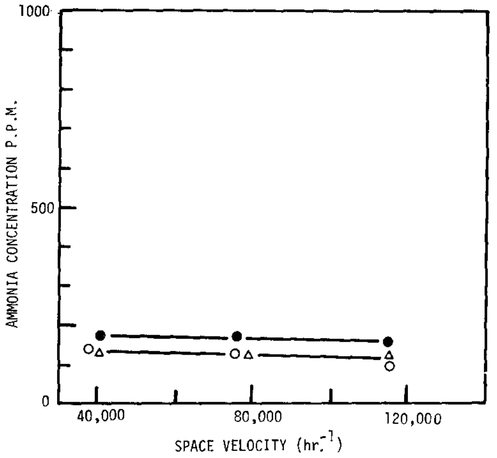

Fig. 2. The effect of space velocity on ammonia formation over the 0.1% Ru-$SiO_2$-$Al_2O_3$ catalyst: ● 370°C, △ 425°C, ○ 540°C. Standard feedstream.

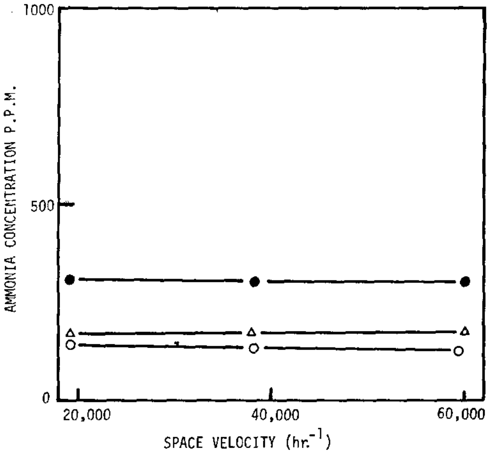

Fig. 3. The effect of space velocity on ammonia formation over the 0.1% Ru-$Al_2O_3$ catalyst: ● 370°C, △ 425°C, ○ 540°C. Standard feedstream.

### *Space Velocity Effects*

The conversion of NO to $N_2$ was found for another series of catalysts to proceed through ammonia as an intermediate (*2*). Since the ruthenium catalysts showed the highest activity for ammonia decomposition, it was inferred that the mechanism for ruthenium was similar (*2*). However, when space velocity was varied from 38,000 hr$^{-1}$ to 114,000 hr$^{-1}$, no change in the product distribution was observed over Ru-$SiO_2$-$Al_2O_3$ (Fig. 2). Similarly, no change in the product distribution was observed over Ru-$Al_2O_3$ when the space velocity was varied from 18,000 hr$^{-1}$ to 60,000 hr$^{-1}$ (Fig. 3). These results suggest that the formation and decomposition of ammonia is not a major path from NO to $N_2$ over ruthenium.

### *Reactant Concentration Effects*

The concentration effects of various reactants in the feedstream were examined in order to assess the role of each in the NO reduction reaction.

The effect of NO concentration on the reaction is shown in Fig. 4. The NO inlet concentration was varied from 500 to 2000 ppm in these experiments while the other constituents of the standard feedstream were held constant. At low temperature ($<$300°C), NO tends to inhibit its own removal. The self inhibiting effect of NO indicates a strong interaction of NO with ruthenium. Apparently NO competes quite effectively with CO and $H_2$ for the surface sites. The reaction approaches first order at the higher temperature which suggests a mass transfer limited process. NO concentration also influences the product distribution. These product studies, summarized in Fig. 5, show that the $NH_3/N_2$ product ratio tends to decrease steadily with increasing NO concentration.

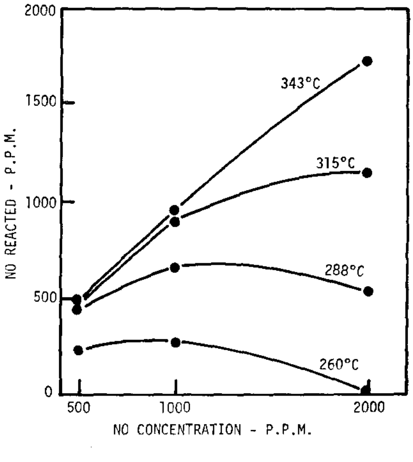

Fig. 4. The effect of NO concentration at various temperatures. Feedstream: variable NO, 1.0% CO, 0.3% $H_2$, 10% $CO_2$, 10% $H_2O$, and the balance $N_2$; 38,000 hr$^{-1}$ space velocity. Catalyst: 0.1% Ru-$SiO_2$-$Al_2O_3$.

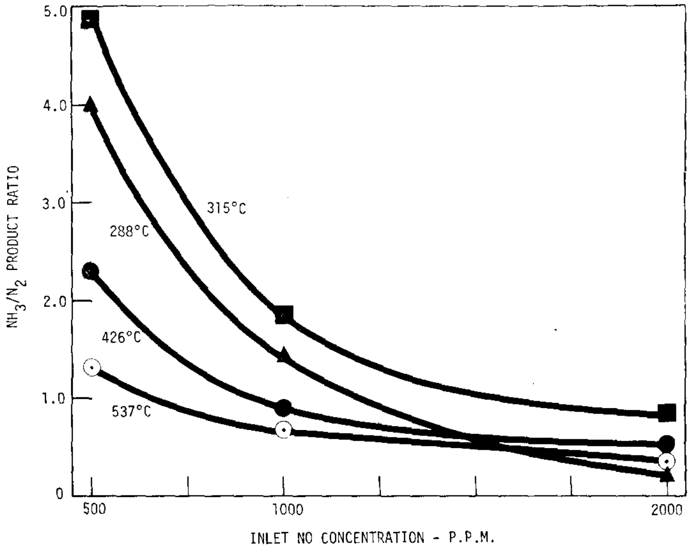

FIG. 5. The selectivity for nitrogen formation at various temperatures. Feedstream: variable NO, 1.0% CO, 0.3% $H_2$, 10% $CO_2$, 10% $H_2O$, and the balance $N_2$; 38,000 $hr^{-1}$ space velocity. Catalyst: 0.1% Ru-$SiO_2$-$Al_2O_3$.

Experimental data were also obtained for variations of CO concentration from 0.5% to 1.5%. In contrast to the NO results, the CO concentration has little effect on the rate of NO removal as shown by the conversion-temperature data in Fig. 6. However, CO concentration does have a rather large effect on the $NH_3/N_2$ product ratio. These data are replotted in Fig. 7 and show that higher CO concentrations tend to favor formation of ammonia rather than $N_2$. As a matter of fact, it is possible to convert over half the NO to $NH_3$ over ruthenium at high CO concentration (1.5%).

The elimination of CO altogether has a significant and interesting effect on both the rate and the product distribution. The temperature of NO removal is shifted to higher temperature (by 50°C) when CO is removed from the standard feedstream. In addition very little $NH_3$ is formed (70

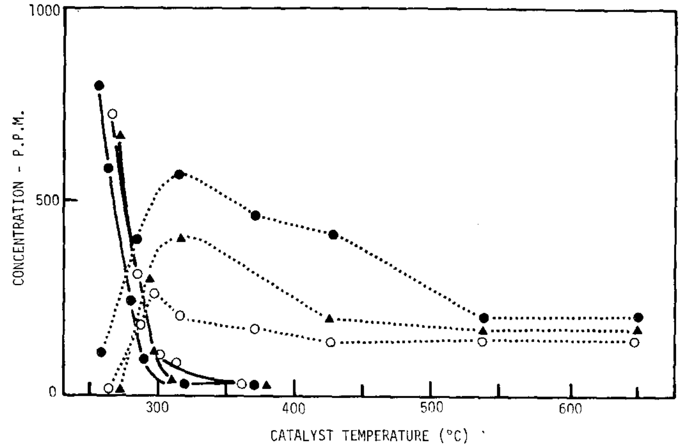

FIG. 6. The effect of carbon monoxide concentration: — NO; - - - $NH_3$; ⊙ 0.5% CO; ▲ 1.0% CO; ● 1.5% CO. Feedstream: variable CO, 0.1% NO, 0.3% $H_2$, 10% $CO_2$, 10% $H_2O$, and the balance $N_2$; 38,000 $hr^{-1}$ space velocity.

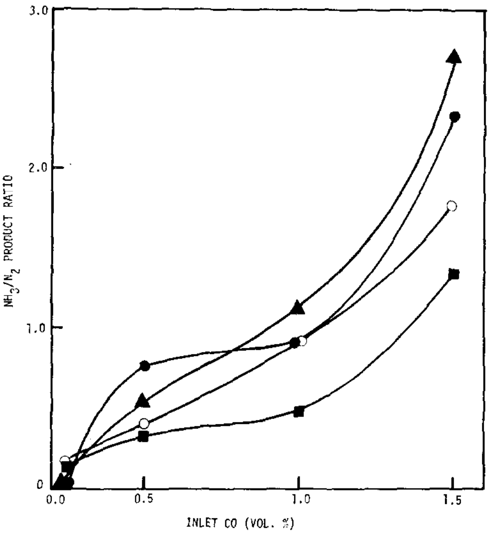

FIG. 7. The selectivity for nitrogen formation: ● 288°C; ▲ 315°C; ⊙ 371°C; ■ 426°C. Feedstream: variable CO, 0.1% NO, 0.3% $H_2$, 10% $CO_2$, 10% $H_2O$, and the balance $N_2$; 38,000 $hr^{-1}$ space velocity. Catalyst: 0.1% Ru-$SiO_2$-$Al_2O_3$.

ppm maximum) in this case, in spite of the fact that hydrogen is the only reducing agent.

The effect of inlet hydrogen on the reduction of nitric oxide was also examined for the 0.1% Ru-$SiO_2$-$Al_2O_3$ catalyst (Fig. 8). Variation of the hydrogen inlet concentration between 0 and 1.5% does not influence the temperature of NO removal. In addition, the product ammonia/nitrogen ratio at low temperature (<315°C) was the same even if $H_2$ was not present in the feedstream. Since the reaction is forced to obtain its hydrogen from CO and water in this latter case, the extent of ammonia formation is primarily influenced by CO rather than added hydrogen. The catalyst shows a slight increase in the CO conversion in this temperature region (cf. 10% at 325°C in Fig. 8). Incidentally, no CO reacted over the "reduced" ruthenium catalyst (i.e., no water gas shift reaction) when NO was omitted from the feedstream. This result suggests that the observed CO removed represents reaction with NO alone. At higher temperature (>425°C) where nitric oxide removal is complete, ammonia formation becomes dependent on inlet hydrogen concentration.

The simple fact that nitrogen formation involves the interaction of two surface nitrogen species can be used to rationalize most of the product distribution results, particularly at low temperature. Thus, as Shelef (*3*) suggests, increasing the NO concentration tends to increase surface N species, the probability for N-species pairing, and thus the formation of $N_2$. Apparently, CO competes for these same sites and thus tends to promote the formation of $NH_3$ which does not require the

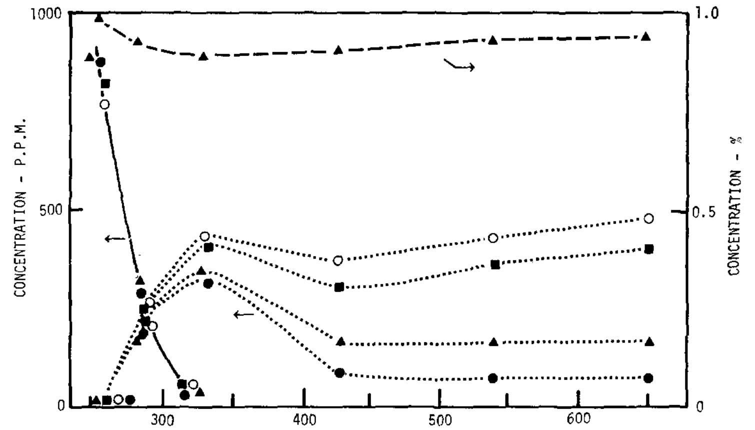

FIG. 8. The effect of $H_2$ concentration on nitric oxide reduction: — NO; - - - $NH_3$; - · - · CO; ● 0.% $H_2$; ▲ 0.3% $H_2$; ■ 1.0% $H_2$; ⊙ 1.5% $H_2$. Feedstream: variable $H_2$, 0.1% NO, 1.0% CO, 10% $CO_2$, 10% $H_2O$, and the balance $N_2$; 38,000 $hr^{-1}$ space velocity.

interaction of two surface N species. Superimposed on these effects is the apparent efficiency of CO and water for forming ammonia. This latter effect was observed earlier for other catalyst systems (*1*) and attributed to the water gas shift reaction. The "reduced" ruthenium catalyst, however, does not promote the shift reaction. Perhaps a more appropriate explanation is provided by the recent infrared studies of Unland (*6*) which involve an isocyanate (–NCO) intermediate for $NH_3$ formation. Such a mechanism is also compatible with the observed CO concentration effects below 425°C.

These complex interactions are only important over a limited temperature range. At higher temperature these effects apparently do not operate. Above 425°C (with the standard feedstream) the product distribution appears to reflect the competition between the reactions:

$$5/2H_2 + NO \rightarrow NH_3 + H_2O$$
$$CO + NO \rightarrow CO_2 + 1/2N_2.$$

The various concentration data (especially Fig. 8) and the space-velocity data (Figs. 2 and 3) are consistent with this interpretation and indicate that the rates of these two reactions are really quite comparable in this temperature range. Fortunately, the concentration excess of CO over $H_2$ in engine exhaust favors $N_2$ formation in that important application.

### *Comparison of Noble Metals*

Alumina supported ruthenium, platinum, and palladium catalysts were compared for the CO–NO reaction, the $H_2$–NO reaction and the CO–$H_2$–NO reaction. These data are summarized in Table 2. The $H_2$–NO reaction takes place at a remarkably low temperature over both the platinum and the palladium catalysts. However, when CO is added to the feed, the $H_2$–NO reaction is very strongly inhibited. It is also noteworthy that both platinum and palladium yield fairly large quantities of nitrous oxide, $N_2O$.

The low temperature $H_2$–NO reaction and the concomitant $N_2O$ formation do not occur for the ruthenium catalyst. In contrast to the other two catalysts, the CO–NO reaction is actually faster than the $H_2$–NO reaction over ruthenium.

TABLE 2

COMPARISON OF CO–NO, $H_2$–NO, AND $H_2$–CO–NO REACTION FOR VARIOUS NOBLE METAL CATALYSTS[a]

| | Temperature (°C) for 50% NO removal | | |
|---|---|---|---|
| Catalyst | $H_2$–NO | CO–NO | CO–$H_2$–NO |
| 0.3% Pt-$Al_2O_3$ | 70°C | 300°C | 305°C |
| 0.3% Pd-$Al_2O_3$ | 60°C | 300°C | 300°C |
| 0.1% Ru-$Al_2O_3$ | 320°C | 290°C | 270°C |

[a] Feedstream: 0–0.3% $H_2$, 0–1.0% CO, 0.1% NO and balance $N_2$ G.H.S.V. = 38,000.

The absence of the low temperature $H_2$–NO reaction over ruthenium probably results from the very strong chemisoption of NO on ruthenium. This is consistent with the inhibiting effect of NO on its own removal (Fig. 4) and the unique stability of NO–Ru compounds in homogeneous chemistry (*7*). The results are also consistent with the chemisorption studies of McKee (*8*) who found that CO is much more strongly adsorbed than $H_2$ on platinum and palladium but not on ruthenium. Thus, it is not surprising that CO interferes with the $H_2$–NO reaction over platinum but not over ruthenium. The behavior of the palladium catalyst is very similar to that of the platinum catalyst in these experiments which is consistent with McKee's results also.

As far as product distribution is concerned, CO probably monopolizes the platinum and palladium sites at low temperature. This severely limits the occurrence of adjacent N-species and thereby promotes the formation of ammonia over these catalysts. At high temperature where adsorption effects are minimized, the very fast $H_2$–NO reaction (forming primarily ammonia) is the dominant reaction over the platinum and palladium catalysts.

The low ammonia yield over ruthenium is primarily a result of the strong NO chemisorption since this tends to increase the probability of adjacent N-species under all conditions. However, it is apparent that reduction of nitric oxide over the ruthenium catalysts is very delicately balanced such that a slight shift either in relative chemisorption strength or in gas concentration can have a major effect on product distribution.

## SUMMARY

Space-velocity studies indicate that ammonia is not an important intermediate in the conversion of NO to $N_2$ over ruthenium catalysts.

Increasing the NO concentration tends to decrease both the rate of NO removal and the extent of ammonia formation. Increasing CO and $H_2$ concentrations do not affect the rate of NO removal but both tend to increase ammonia formation. CO tends to affect $NH_3$ formation at low temperature (below 425°C), while hydrogen tends to increase ammonia formation above 425°C.

The primary difference between the noble metal catalysts is that CO strongly inhibits NO reduction over platinum and palladium, but not over ruthenium. These results are consistent with chemisorption studies and provide an explanation for the efficient conversion of nitric oxide to elemental nitrogen over ruthenium catalysts.

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