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A Study of NO Reduction by H_2 over an Alumina-Supported Ruthenium Catalyst

MINORU UCHIDA[1] AND ALEXIS T. BELL

Department of Chemical Engineering, University of California, Berkeley, California 94720

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INTRODUCTION

In contrast to other transition metal catalysts, Ru has the highest selectivity for the formation of N_2, rather than NH_3, during the reduction of NO by H_2 (*1–3*). To explain this observation, Shelef (*4*) has proposed that NH or NH_2 groups, formed by partial hydrogenation of adsorbed nitrogen atoms, rapidly annihilate each other, thereby precluding the formation of NH_3. Annihilation of NH_2 groups by reaction with adsorbed NO is also possible (*5*) but is not considered to be the main defixation path since this reaction is known to occur on the surface of Pt and Pd, catalysts which exhibit lower selectivities for N_2 than Ru. The present investigation was undertaken to further study the surface chemistry pertaining to the reduction of NO by H_2. The interactions of H_2, NO, and N_2 with Ru were investigated using temperature-programmed desorption (TPD) and the reduction of adsorbed NO by H_2 was investigated using temperature-programmed reaction (TPR).

EXPERIMENTAL

Apparatus

The apparatus used to perform temperature-programmed desorption and reaction experiments was identical to that described by Low and Bell (*6*). The central part of this apparatus is a quartz reactor tube in which the catalyst is supported on a quartz fritted disk. The reactor is heated by a programmable power supply which permits heating rates of up to 1°K/sec. Gas adsorption is carried out by passing either a pulse (0.7 cm^3 at STP) or a continuous flow of gas over the catalyst. The effluent from the reactor is analyzed by a quadrupole mass spectrometer connected to the reactor via a variable leak valve.

Materials

A 5% Ru/Al_2O_3 catalyst was prepared by impregnation of Alon C (Cabot Corp.) with a solution $RuCl_3$ (*6*). The resulting slurry was freeze-dried and then reduced in flowing H_2 for 2.5 hr at 673°K. The surface area of the reduced catalyst was established by H_2 chemisorption. At 373°K, 71 μmole of H_2 were adsorbed per gram of catalyst, leading to a calculated dispersion of 29%.

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[1] Current address: Chiyoda Chemical Company, 1580 Tsurumi-cho, Tsurumi-ku, Yokohama 230, Japan.

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Helium (99.998%) was purified of trace quantities of air and water by passage through a liquid nitrogen trap containing molecular sieves. Hydrogen (99.999%) was passed through an Engelhard Deoxo unit to convert traces of O_2 to water and then through a bed of molecular sieves cooled in liquid nitrogen. Nitric oxide (99.0%), nitrogen (99.999%), and oxygen (99.5%) were used without further purification.

Experimental Procedures

For each experiment a fresh 25-mg sample of the catalyst was reduced *in situ* in flowing H_2 at 673°K for 2 hr. Next, the gas was switched to He, and the H_2 in the reactor was eluted. The catalyst was then heated to 973°K at 1°K/sec to desorb any adsorbed H_2. Finally, the catalyst was cooled to 303°K in flowing He. In this state the catalyst was considered ready for gas adsorption. Details of the adsorption procedure for each adsorbate are described in the next section.

RESULTS AND DISCUSSION

Steady-State Reduction of NO

Prior to conducting TPD and TPR experiments, the steady-state activity and selectivity of the catalyst were investigated. A gas mixture containing 1.6% NO and 3.1% H_2 in He was passed over the catalyst at a total flow rate of 295 cm^3/min at STP. The composition of the products is shown in Fig. 1 as a function of the reaction temperature. Reduction of NO begins at about 520°K and proceeds rapidly to nearly 100% when the temperature is raised to 560°K. The major product is N_2 and only a small amount of NH_3 is observed. Nitrous oxide was also found in the products, but the concentration was even less than that of NH_3. These results are very similar to those reported by Kobylinski and Taylor (*2*), indicating that the catalyst prepared for this work has a high selectivity for the reduction of NO to N_2.

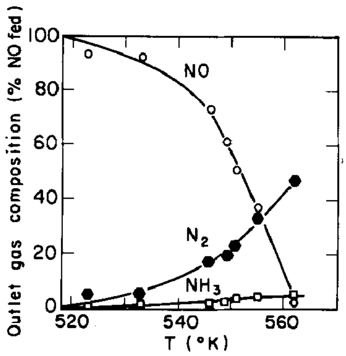

FIG. 1. Steady-state conversion of NO as a function of temperature.

Temperature-Programmed Desorption of H_2

To study the desorption of H_2, the catalyst was first exposed to 1 atm of H_2 at 373°K for 30 min. The catalyst was then cooled to 303°K in H_2 and the H_2 was eluted from the reactor with He. Figure 2 illustrates the TPD spectrum obtained. Two overlapping peaks are observed at 400 and 450°K, and a third, but smaller, peak is seen at 720°K.

The TPD spectrum shown in Fig. 2 is

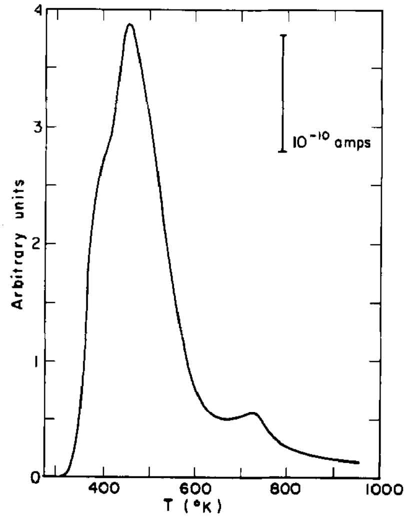

FIG. 2. TPD spectrum of H_2: Adsorption—continuous exposure to 1 atm of H_2 at 373°K for 30 min.

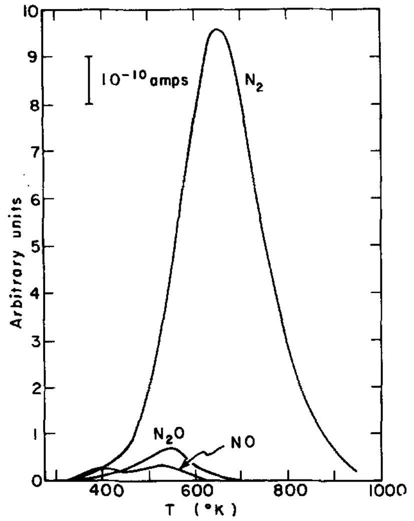

FIG. 3. TPD spectrum of NO: Adsorption—one pulse exposure at 303°K.

qualitatively similar to spectra reported by Babenkova *et al.* (*7*) for H_2 desorption from Ru black. Based upon the analysis of desorption kinetics reported by these authors, we would conclude that the low-temperature peaks correspond to the desorption of both molecularly and dissociatively bound H_2 while the small high-temperature peak is due to dissociatively bound H_2. In a study of the desorption of H_2 adsorbed on a Ru(10$\bar{1}$0) surface Goodman *et al.* (*8*) observed only a single low-temperature peak which obeyed first-order kinetics. Studies with coadsorbed H_2 and D_2 indicated, however, that chemisorption occurred in a dissociative fashion.

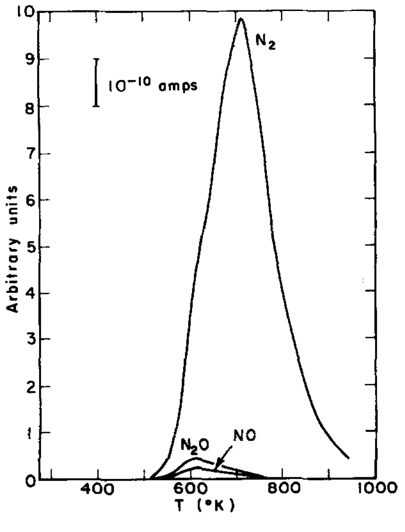

FIG. 4. TPD spectrum of NO: Adsorption—one pulse exposure at 523°K.

Temperature-Programmed Desorption of NO

Figures 3 and 4 illustrate TPD spectra obtained following NO adsorption by passage of a single pulse of the adsorbate over the catalyst. The adsorption temperature was 303°K for the results shown in Fig. 3 and 523°K for the results shown in Fig. 4. The major feature in both figures is a large N_2 peak, centered at 650°K in Fig. 3 and at 710°K in Fig. 4. Small NO and N_2O peaks are also observed in each figure. For adsorption at 303°K the NO signal consists of two peaks, appearing at 400 and 520°K. When the adsorption temperature is increased to 523°K, the low-temperature peak is no longer observed and the high-temperature peak shifts to 610°K. Only a single N_2O peak is observed at each adsorption temperature. This peak is centered at 550°K for NO adsorption at 303°K and at 600°K for NO adsorption at 523°K.

Most of the oxygen present in the adsorbed NO remains on the Ru surface following TPD. This is evidenced by the absence of any desorbed O_2 and the fact that desorbed NO and N_2O account for only about 10% of the oxygen in the adsorbed NO. To examine the effects of oxygen accumulation on the catalyst surface, experiments were carried out in which NO was sequentially adsorbed and desorbed, without reduction of the catalyst between cycles. The results of these experiments are shown in Fig. 5. The amounts of N_2 and N_2O formed decrease rapidly and in parallel as the number of adsorption–desorption cycles increases. Nearly identical curves are observed for NO adsorption temperatures of 303 and

523°K. By contrast, the amount of NO desorbed increases initially but then stays nearly constant with increasing numbers of cycles. The amount of NO desorbed is four times greater when NO adsorption occurs at 303°K than at 523°K.

The effect of the duration of exposure to NO prior to TPD is illustrated in Fig. 6. As the duration of exposure increases the N_2 peak progressively shifts to higher temperatures but the peak area remains roughly the same. The N_2O peak remains small in all cases and the only apparent change is a gradual shift in the peak position to higher temperatures. The NO peak grows extensively as the exposure time increases, and the shape of the NO peak changes. When the exposure time is short the low-temperature peak predominates, but as the exposure time increases the high-temperature peak grows more rapidly. Following the TPD of NO which had been adsorbed over a 30-min period, NO was again adsorbed on the now oxidized catalyst. A subsequent TPD spectrum showed only an NO peak identical to that seen in Fig. 6, but no peaks for either N_2 or N_2O.

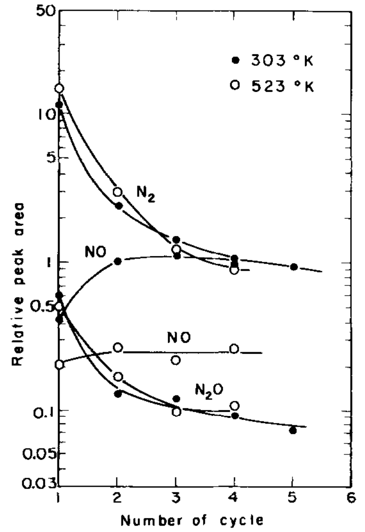

FIG. 5. Peak areas for NO, N_2, and N_2O as a function of the number of adsorption–desorption cycles: Adsorption—one pulse exposure at 303 or 523°K.

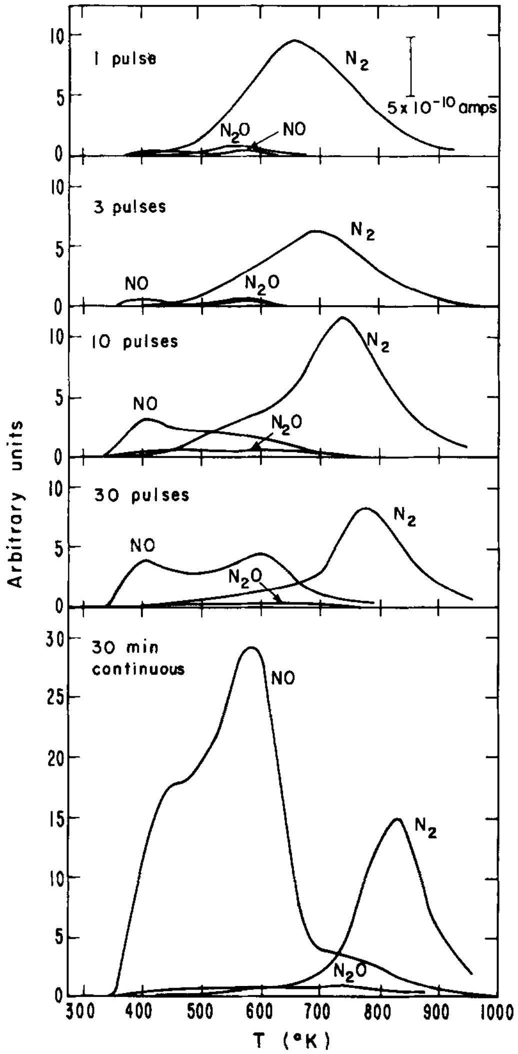

FIG. 6. Dependence of TPD spectra on the extent of NO exposure during adsorption at 303°K.

The results presented in Figs. 5 and 6 clearly demonstrate that the initial adsorption of NO is dissociative and that molecular adsorption of NO occurs only after a significant fraction of the sites available for dissociative adsorption have been occupied. In addition, it appears that molecular adsorption may be an activated process inasmuch as the spectra presented in Fig. 6 show that the amount of molecular NO desorbed increases with the extent of NO exposure during adsorption while the amount of N_2 desorbed, which is a measure of the extent of dissociative adsorption, remains about the same. The accumulation of oxygen on the Ru surface also inhibits dissociative adsorption as evidenced by the data shown in Fig. 5 and the fact that on a completely preoxidized surface only molecular NO adsorption occurs.

The observations reported here for NO adsorption on Ru/Al_2O_3 closely parallel those reported earlier by Ku *et al.* (*9*), Bonzel and Fischer (*10*), and Klein and Shih (*11*) for NO adsorption on a Ru $(10\bar{1}0)$ surface. In those studies it was noted that NO rapidly adsorbs into separate nitrogen and oxygen phases. Once the surface is saturated with dissociated NO, further NO adsorption occurs in a molecular state. The primary difference between the present work and the studies on Ru $(10\bar{1}0)$ surfaces in the number of NO and N_2 peaks observed during TPD. Thus, Ku *et al.* (*9*) reported only a single NO peak while Klein and Shih (*11*) found either two or three overlapping peaks, depending upon the adsorption temperature. Both groups of authors concur, however, that three well-resolved N_2 peaks are observed. The behavior of these peaks, referred to as β_1, β_2, and β_3, with increasing NO coverage is discussed below.

The present results are also consistent with infrared observations of Davydov and Bell (*12*). In that study it was observed that exposure of a Ru/SiO_2 catalyst to NO caused a gradual oxidation of the catalyst and a corresponding appearance of a band characteristic of NO adsorbed on an oxidized surface. Based upon a comparison of the vibrational frequency for adsorbed NO with the frequency for Ru nitrosyls it was concluded that molecularly adsorbed NO is positively charged.

The appearance of N_2 during the TPD of adsorbed NO results from the recombination of N-atoms formed via dissociative chemisorption of NO. The production of N_2 through the dissociation of molecularly adsorbed NO does not appear to occur extensively. The data illustrated in Fig. 5 show that the amount of N_2 formed is influenced to only a small degree by the amount of molecularly adsorbed NO. However, the activation energy for the formation of N_2 does appear to be affected by the extent of NO exposure during adsorption. Thus, as the exposure increases the peak position shifts to higher temperatures. This pattern is distinctly different from that observed for NO chemisorbed on a Ru $(10\bar{1}0)$ surface (*9, 11*). In those studies the β_2 peak shifted to lower temperatures and the position of the β_1 peak remained constant with increasing NO exposure. Furthermore, Ku *et al.* (*9*) observed that the desorption area and position of the β_2 peak were the same regardless of whether or not oxygen was present on the catalyst surface. The shift in N_2 peak position observed in the present studies cannot be fully explained. Possibly it may be associated with a progressive oxidation of the crystallites due to the use of high partial pressures of NO.

As was seen in Fig. 5 the yield of N_2O closely parallels the yield of N_2. This suggests that N_2O may be formed via the following reactions:

$$N_s + NO_s \rightarrow N_2O + 2S, \qquad (1)$$

$$2N_s + O_s \rightarrow N_2O + 3S. \qquad (2)$$

The correspondence between the formation of N_2O and the desorption of NO in Figs. 3 and 4 suggests that reaction (1) is the preferred route. This conclusion is further supported by the observation that reaction (1) is less endothermic than reaction (2).

It is important to recognize that the proposed mechanism for N_2O formation differs from that discussed by Otto and Shelef (*5*) and Shelef (*4*). These authors suggest that N_2O is formed via an HNO intermediate in a manner similar to that known to occur in flames. However, the formation of N_2O in the absence of H_2 on the catalyst surface as observed here argues against such an interpretation.

Temperature-Programmed Desorption of N_2

The adsorption of N_2 on a reduced Ru catalyst and its subsequent desorption were investigated using the following procedure. The catalyst was first exposed to 1 atm of N_2 at 373°K for 30 min and then cooled to 303°K in N_2. Subsequently the N_2 in the reactor was displaced with He and a TPD spectrum was recorded. As seen in Fig. 7, only a single N_2 peak is observed at 830°K. The position of this peak is nearly identical to the N_2 peak observed during the TPD of NO, following NO adsorption by continuous exposure for 30 min (see Fig. 6), but the peak shapes differ in two respects. First the peak in Fig. 7 is about five times smaller than in Fig. 6 and second, the peak in Fig. 7 lacks the long low-temperature tail of the peak appearing in Fig. 6.

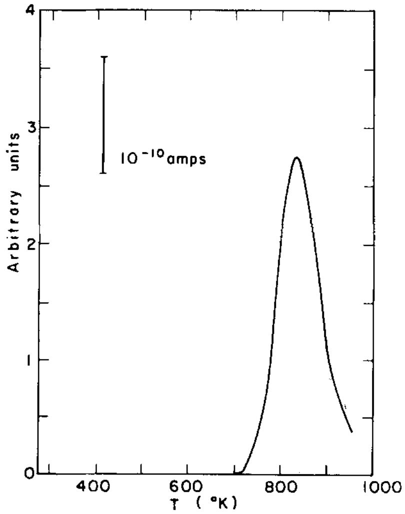

FIG. 7. TPD spectrum of N_2 adsorbed on reduced Ru: Adsorption—continuous exposure to 1 atm of N_2 at 373°K for 30 min.

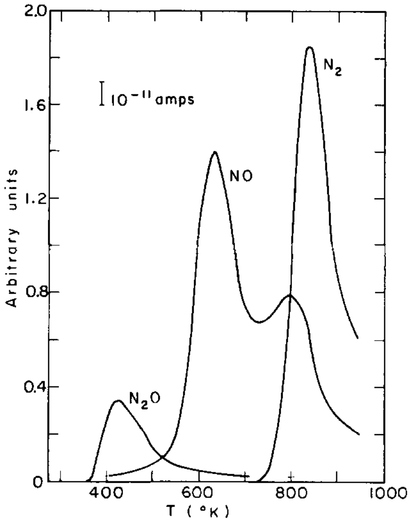

FIG. 8. TPD spectrum of N_2 adsorbed on Ru oxidized by NO: Adsorption—continuous exposure to 1 atm of N_2 at 373°K for 30 min.

The desorption of N_2 adsorbed on an oxidized surface was also investigated. Oxidation of Ru was carried out using either NO or O_2. The procedure when NO was used was as follows. Nitric oxide was first adsorbed at 303°K for 30 min. The catalyst was then heated to 973°K at a rate of 1°K/sec to bring about the desorption of nitrogen containing species. After cooling the catalyst to 303°K, it was again heated to 973°K in He to confirm the absence of NO, N_2, or N_2O on the catalyst surface. The catalyst was next cooled to 373°K and exposed to 1 atm of N_2 for 30 min. After the catalyst had been cooled to 303°K in N_2, the gas flow was switched to He and a TPD spectrum was recorded. The result is shown in Fig. 8. In addition to an N_2 peak at 830°K, NO and N_2O peaks are also observed. The N_2O peak is centered at 420°K and the NO peaks at 630 and 790°K. What is remarkable is that the amount of NO desorbed is greater than the amount of N_2 desorbed.

To further test whether NO and N_2O could be formed from adsorbed N_2, a catalyst sample was oxidized in O_2 at 1 atm

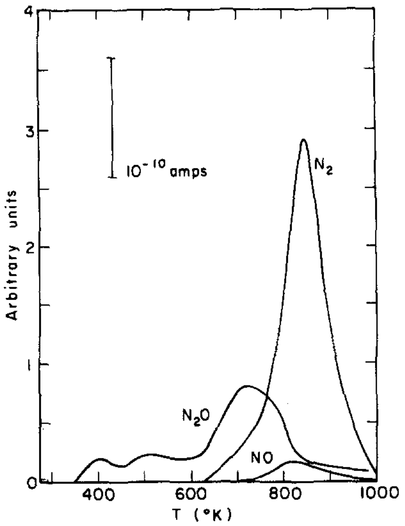

FIG. 9. TPD spectrum of N_2 adsorbed on Ru oxidized by O_2: Adsorption—continuous exposure to 1 atm of N_2 at 373°K for 30 min.

and 373°K for 30 min. The oxygen was then displaced by N_2, and N_2 adsorption was continued for 30 min. The catalyst was then cooled to 303°K and a TPD spectrum was taken. The resulting spectrum, shown in Fig. 9, again exhibits evidence of NO and N_2O formation. However, the amount of NO produced is significantly less than that observed in Fig. 8 and the NO peak occurs at a higher temperature (810°K). The N_2O signal in Fig. 9 is also different from that in Fig. 8, consisting of three overlapping peaks, the largest of which appears at 730°K.

The TPD spectrum observed here for N_2 desorption from reduced Ru is markedly different from that observed by Klein and Shih (*11*). In their study a Ru $(10\bar{1}1)$ surface was exposed to N_2 at 120°K. The subsequent desorption spectrum showed only a single low-temperature (160°K) peak which could be described by first-order desorption kinetics. Experiments with coadsorbed $^{14}N_2$ and $^{15}N_2$ failed to show any isotopic mixing during desorption. Based on this evidence, it was concluded that N_2 is weakly adsorbed in a molecular state on a Ru $(10\bar{1}0)$ surface.

Evidence for molecular adsorption of N_2 has also been reported for supported Ru. Lyutov and Borod'ko (*13*) reported that exposure of a Ru/SiO_2 catalyst to N_2 at 20°C led to the observation of an infrared band at 2240 cm^{-1} characteristic for molecular adsorption. The band position shifted to 2260 cm^{-1} when the $Ru–N_2$ complex was contacted with H_2 at -150°C.

The high-temperature N_2 peak observed in the present experiments and its similarity to the N_2 peak observed during the TPD of NO suggests that the N_2 peak arises from N-atom recombination. This would imply that N_2 chemisorption at elevated temperatures and pressures might be dissociative. The observation of NO during the TPD of N_2 adsorbed on an oxidized Ru surface also supports the idea of dissociative N_2 adsorption. The extent of NO formation is significantly dependent upon whether the catalyst was oxidized in NO or O_2. These differences may possibly be due to differences in the state of oxygen on the catalyst surface. Based upon a comparison of Figs. 8 and 9, one would conclude that the oxygen formed by oxidation in NO is more labile than that formed by oxidation in O_2.

The N_2O observed in Figs. 8 and 9 is presumably formed via reactions (1) and (2) discussed earlier. Here again differences in the manner of catalyst oxidation appear to influence the amount of N_2O formed.

Temperature-Programmed Reaction of NO with H_2

The reduction of adsorbed NO by H_2 was investigated using both reduced and oxidized catalyst samples. For the case of a reduced sample NO was adsorbed at 1 atm and 303°K for 30 min. Gas phase NO was then eluted with He. Following this a flow containing 20% H_2 in He was introduced, and the temperature of the catalyst was raised from 303 to 973°K at 1°K/sec. The TPR spectrum thus obtained is shown in Fig. 10. In contrast to the TPD spectrum of NO shown in Fig. 6, very little NO desorption is observed in Fig. 10. The positions and shapes of the two NO peaks are similar to those observed in Fig. 3 with the exception that the high-temperature peak exhibits a sharp cutoff at around 500°K.

Figure 10 shows four product peaks corresponding to N_2, N_2O, NH_3, and H_2O. The N_2 peak, centered at 500°K, is very narrow and intense and is characterized by a sharp cutoff on the high-temperature side of the peak. Both the peak position and shape are significantly different from those observed during the TPD of NO or N_2. Only a small N_2O peak is observed, which reaches a maximum at about the same temperature as the high-temperature NO peak and the N_2 peak. While the position of this peak is comparable to that of the N_2O peak seen in Fig. 3, the shape is different, the N_2O peak in Fig. 10 exhibiting a sharp cutoff at 500°K similar to that seen for the NO and N_2 peaks. The total amount of NH_3 produced is small but greater than the production of N_2O. The broadness of the NH_3 peak may be due to the interaction of NH_3, desorbed from the Ru surface, with the alumina support. Desorption of adsorbed NH_3 from the support might account for the observed high-temperature tail on the NH_3 peak. The H_2O signal shows two broad features, a peak centered at 490°K and a slowly rising band beginning around 600°K. Here again, it seems likely that the shape of the H_2O signal is affected by adsorption on and subsequent desorption from the support.

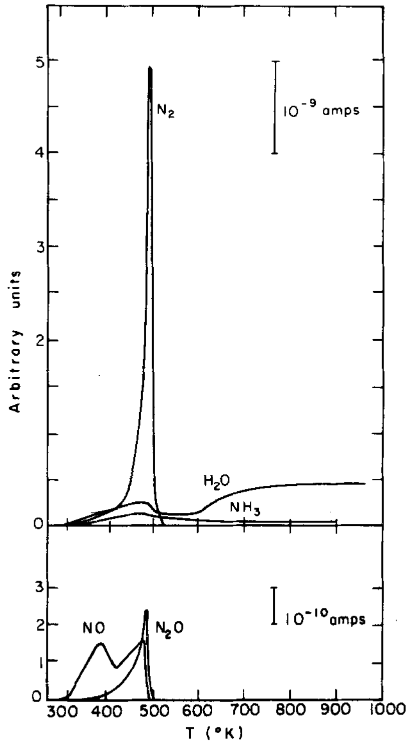

FIG. 10. TPR spectrum for the reaction of preadsorbed NO with H_2 on reduced Ru: Adsorption—continuous exposure to 1 atm of NO at 303°K for 30 min.

To study the TPR of NO on an oxidized Ru surface, the catalyst was first exposed to 1 atm of NO at 303°K for 30 min. Nitrogen, NO, and N_2O were then desorbed from the surface by heating the catalyst to 973°K at 1°K/sec. After cooling catalyst to 303°K, NO was adsorbed again. A TPR spectrum was then recorded while flowing a stream containing 20% H_2 in He. The results, shown in Fig. 11, are qualitatively similar to those seen in Fig. 10. The primary differences are that the NO, N_2O, and N_2 peaks are smaller for the case of the oxidized catalyst.

An experiment was also performed to determine how NO would interact with preadsorbed H_2. H_2 was adsorbed on a reduced catalyst at 373°K for 30 min, and the catalyst was cooled to 303°K in flowing H_2. The H_2 was then eluted from the reactor with He and a single pulse of NO was passed over the catalyst. The resulting TPR spectrum is shown in Fig. 12 and is seen to be quite similar to the TPD spectrum for NO adsorbed on a reduced Ru surface shown in Fig. 3. This result suggests that chemisorbed H_2 is rapidly displaced by NO at 303°K.

To further investigate the effect of H_2

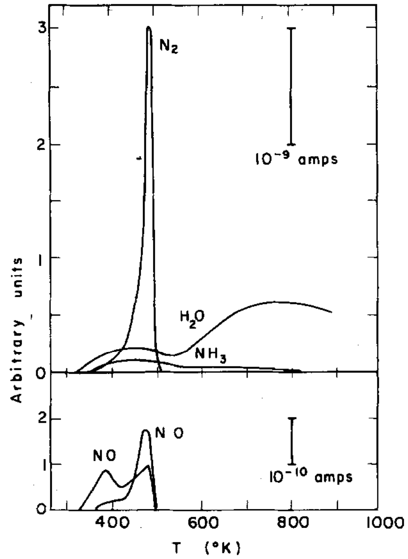

FIG. 11. TPR spectrum for the reaction of preadsorbed NO with H_2 on oxidized Ru: Adsorption—continuous exposure to 1 atm of NO at 303°K for 30 min.

on the desorption of N_2, the interaction of adsorbed N_2 with H_2 were explored using the TPR method. Nitrogen was adsorbed on a reduced catalyst at 373°C for 30 min. Next, the catalyst was cooled to 303°K in flowing N_2. The reactor was then flushed with He. Following this step a stream containing 20% H_2 in He was fed over the catalyst and the temperature was raised at 1°K/sec. Although both N_2 and NH_3 were monitored, only an N_2 peak was observed. The TPR spectrum is shown in Fig. 13. Two overlapping N_2 peaks are observed in the vicinity of 460°K. Comparison of the TPR spectrum with the TPD spectrum for N_2 shown in Fig. 7 shows that the N_2 peak is shifted downscale by 370°K when desorption occurs in the presence of H_2.

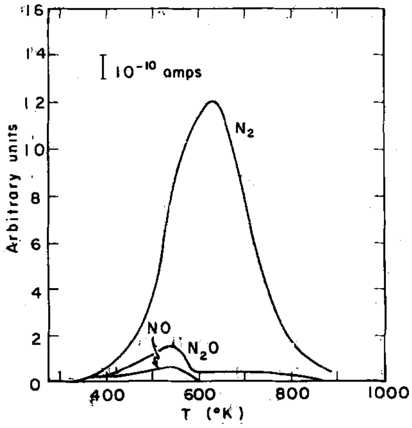

FIG. 12. TPR spectrum for reaction of coadsorbed NO and H_2: Adsorption—continuous exposure to 1 atm H_2 at 373°K for 30 min followed by one pulse exposure to NO at 303°K.

The TPR spectra shown in Figs. 10, 11, and 13 clearly indicate that the presence of H_2 in the gas phase greatly reduces the temperature at which N_2 is produced, relative to what is observed during the TPD of NO or N_2. Furthermore, the shape of the N_2 peak observed during the TPR of NO indicates that N_2 formation probably occurs by a process other than recombination of nitrogen atoms. An interpretation for these observations can be proposed by postulating that in the presence of H_2 partially hydrogenated nitrogen species are formed which react to produce N_2 by processes such as reactions (3) through (5).

$$2NH_s \rightarrow N_2 + H_2 + 2S, \quad (3)$$

$$N_s + NH_{2s} \rightarrow N_2 + H_2 + 2S, \quad (4)$$

$$2NH_{2s} \rightarrow N_2 + 2H_2 + 2S. \quad (5)$$

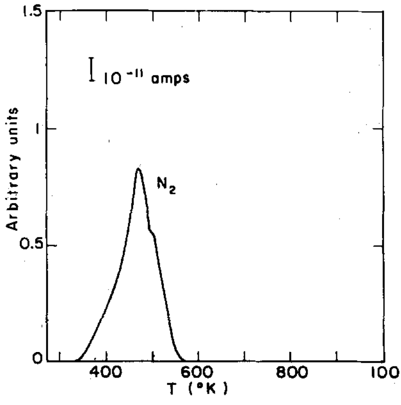

FIG. 13. TPR spectrum for the reaction of preadsorbed N_2 with H_2 on reduced Ru: Adsorption—continuous exposure to 1 atm N_2 at 373°K for 30 min.

Since each of these reactions is less endothermic than the direct recombination of adsorbed nitrogen atoms, it might be expected that the activation energies would also be less. This would be necessary to explain the lowering of the N_2-peak temperature in the presence of H_2.

While there is no direct evidence for the occurrence of reactions (3) through (5) during the reduction of NO by H_2, the work of Otto and Shelef (*5*) does provide some indirect evidence. Their investigation showed that the reduction of ^{14}NO by $^{15}NH_3$ yields $^{14}N^{15}N$ as the preferred N_2 product. The yield of $^{14}N_2$ was roughly three to five times less than that of $^{14}N^{15}N$ and only small amounts of $^{15}N_2$ were found. These observations were interpreted by postulating that the main path for N_2 formation is

$$^{15}NH_{2s} + {}^{14}NO_s \rightarrow {}^{14}N^{15}N + H_2O + 2S. \quad (6)$$

In a subsequent discussion of the results, Shelef (*4*) proposed that the appearance of $^{15}N_2$ might be due to reactions such as (3) and (5). Based upon their work with NH_3, Otto and Shelef suggested that NH_2 groups might also play an important role during the reduction of NO by H_2. Further support for this idea was later obtained by Davydov and Bell (*14*). Using infrared spectroscopy these authors were able to observe vibrations associated with surface ND_2 and ND_3 groups when preadsorbed NO was heated in the presence of D_2.

Reactions (7) through (9) illustrate a mechanism by which NH and NH_2 groups might be formed.

$$H_2 + 2S \rightleftarrows 2H_s, \quad (7)$$

$$H_s + N_s \rightarrow NH_s + S, \quad (8)$$

$$H_s + NH_s \rightarrow NH_{2s} + S. \quad (9)$$

The nitrogen atoms which participate in reaction 8 are presumably generated by dissociative chemisorption of NO or N_2. In the case of NO chemisorption on a preoxidized surface, a portion of the chemisorbed oxygen would first have to be removed by reaction with H_2 in order to create vacant sites at which NO could dissociate. Such an interpretation is consistent with the observation in Fig. 11 that the appearance of H_2O occurs at a significantly lower temperature than the appearance of N_2.

The shape of the N_2 peak observed during the TPR of NO can also be interpreted with the aid of reactions (3) through (9). The very narrow width of the peak and its nearly vertical cutoff at high temperatures are reminiscent of desorption proceeding by an autocatalytic mechanism (*15*). Such a process could occur in the present case if the rate of N_2 desorption were controlled by the rate of H_2 chemisorption (reaction (7)). Under such circumstances the rate of N_2 desorption would be proportional to the H_2 partial pressure and the void fraction of vacant sites. During a TPR experiment the partial pressure of H_2 remains constant but the void fraction of vacant sites increases and as a consequence the rate of H_2 chemisorption accelerates as the extent of N_2 desorption increases. The proposed interpretation also leads to the conclusion that the rate of N_2 desorption should fall to zero at the point at which the fractional coverage by nitrogen atoms become very small.

The reactions which control the relative rates of N_2 and NH_3 formation can now be discussed. Of the possible pathways to N_2 we propose that reaction (4) rather than (6) is dominant. To support this we recall that H_2 facilitates the formation of N_2 from NO as well as the desorption of chemisorbed nitrogen. Furthermore the TPR spectra for NO chemisorbed on reduced and oxidized Ru surfaces are nearly identical. This is important since in the former case both dissociated and molecular NO are present while in the latter case only molecular NO is present. The similarity in the spectra and the fact that NO dissociation is very rapid suggest that N_2 formation occurs via nitrogen atoms rather than adsorbed NO.

The formation of NH_3 can be described by reaction (10).

$$NH_{2s} + H_s \rightarrow NH_3 + 2S. \qquad (10)$$

If this is so, then the selectivity between N_2 and NH_3 would be dictated by the relative rates of reactions (4) and (10). Assuming that the rate coefficients for reactions (4) and (10) are not vastly different, as might be suggested by the fact that the first NH_3 peak coincides with the N_2 peaks in Figs. 10 and 11, we would conclude that product selectivity is controlled by the surface coverages of nitrogen and hydrogen atoms. The high selectivity of Ru for N_2 formation thus would have to be ascribed to a much higher surface coverage by nitrogen atoms than hydrogen atoms. This conclusion is consistent with the observation that dissociative chemisorption of NO on Ru is much more rapid than the chemisorption H_2 and that NO will displace adsorbed H_2. By contrast, on Pt, NO is first adsorbed into a molecular state (*16*), from which dissociative chemisorption occurs with an activation energy of 28 kcal/mole. A further characteristic of Pt is that the adsorption of H_2 is very rapid. As a result, one would expect the ratio of nitrogen to hydrogen atoms to be far less on Pt than on Ru and consequently the selectivity towards N_2 to be lower on the former metal, as is in fact observed (*1*).

Finally, we note that the presence of H_2 in the gas phase does not appear to influence the formation of N_2O. The initial shape of the N_2O peak seen during TPR is essentially the same as that appearing during TPD. The sharp high-temperature cutoff of the peak seen during TPR most likely reflects the sudden consumption of adsorbed nitrogen atoms via the N_2 formation process. These observations further support the idea proposed originally, that N_2O formation can occur without the interaction of NO with adsorbed H_2.

CONCLUSIONS

The present results suggest that the first step in the reduction of NO by H_2 is dissociative chemisorption of NO. Nitrogen appears to be formed via the reaction of adsorbed nitrogen atoms with NH_2 groups, which are also precursors to NH_3. The formation of NH_2 groups is assumed to occur via the partial hydrogenation of surface nitrogen atoms and appears to be rate limited by the slow chemisorption of H_2. The proposed mechanism thus suggests that the selectivity between N_2 and NH_3 is governed by the relative surface concentrations of nitrogen and hydrogen atoms. The high selectivity of Ru relative to other transition metals is ascribed to the rapid dissociative chemisorption of NO relative to the slow chemisorption of H_2. The appearance of N_2O in the products is due to the interaction of molecularly adsorbed NO with adsorbed nitrogen atoms, a process which also occurs in the absence of H_2.

A further conclusion of this study is that N_2 will slowly chemisorb on Ru. Desorption of the chemisorbed N_2 occurs at temperatures comparable to those observed during the formation of N_2 from chemisorbed NO, suggesting that the chemisorbed N_2 is present in a dissociative state. Further evidence supporting this comes from the observation of NO formation during the TPD of N_2 chemisorbed on an oxidized Ru surface.

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