Catalysis Letters 3 (1989) 179–190

MECHANISM OF THE AMMONIA FORMATION FROM NO-H_2. A MODEL STUDY WITH Pt-Rh ALLOY SINGLE CRYSTAL SURFACES

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Received 22 May 1989; accepted 3 July 1989

Platinum-rhodium alloy, crystal surfaces, ammonia formation on Pt-Rh

The reduction of NO by H_2 was studied over three different Pt-Rh single crystal surfaces, i.e. Pt-Rh(111), (410) and (100). The adsorption and dissociation of NO was studied by HREELS, LEED, XPS, AES and TDS. It was found that the dissociation of NO and its reaction with H_2 is very surface structure sensitive. The selectivity towards nitrogen and the dissociation activity increases in the same order, i.e. Pt-Rh(111) < (100) < 410). Nitrogen atoms were easily hydrogenated at 400 K in hydrogen to NH_x ($x = 1$ or 2) on the surface. A model is proposed in which the selectivity of the $NO - H_2$ reaction over Pt-Rh surfaces is determined by the relative amounts of hydrogen, NO and nitrogen adatoms on the surface.

1. Introduction

There is considerable interest in the catalytic reduction of NO over Pt-Rh surfaces [1–4], since these metals are the active components of the three-way catalyst utilized to control the emissions from automotive exhaust gases. Reduction of nitric oxide by hydrogen can produce a variety of N-containing reaction products such as N_2, NH_3 and N_2O. More information is needed on the factors determining the selectivity of the catalyst. Moreover, it is important to know how the selectivity can be influenced because ammonia formation is undesired.

Two important problems were tackled in this study: The influence of the surface structure on the selectivity and the mechanism of the NH_3 formation reaction. For this purpose the NO-H_2 reactions have been studied on three Pt-Rh alloy single crystal surfaces at a total pressure of 6 Torr. The surfaces studied were the (111), (100) and (410) surfaces of a $Pt_{0.25}$-$Rh_{0.75}$ single crystal. In addition to the selectivity study, HREELS experiments were performed in order to elucidate the reaction intermediates and the mechanism of the NH_3 formation.

2. Experimental

A $Pt_{0.25}$–$Rh_{0.75}$ single crystal (Metal Crystals and Oxides Ltd, Cambridge, U.K.) was oriented by means of Laue back reflection within 1.0 degree of the desired direction, spark eroded and mechanically polished down to 0.25 μm grain size using standard techniques. The samples were spotwelded onto a Ta filament and could be heated up to 1700 K by Joule heating. The temperature was measured by means of either a Pt/$Pt_{0.90}$-$Rh_{0.10}$ or a chromel/alumel thermocouple spotwelded to the side of the crystal. The experiments were carried out in all metal UHV systems with base pressures $< 2 \cdot 10^{-10}$ Torr. "High-Pressure" (6 Torr) experiments were done in a small reactor separated from the UHV chamber. When the reaction was stopped and the reactor pumped down to 10^{-7} Torr, the sample was transferred to the UHV chamber for AES, HREELS or LEED analysis. Details of this system are given elsewhere [5]. All systems were equipped with a CMA and a quadrupole mass spectrometer. The samples were cleaned by cycles of argon ion bombardment, oxidation and high temperature annealing. The samples were equilibrated at 1100 K. The surfaces of the $Pt_{0.25}$-$Rh_{0.75}$ crystal prepared in this way contain about 50% Pt as described by van Delft et al. [6,7].

3. Results

3.1. CHEMISORPTION OF NO ON Pt-Rh (410), (100) and (111) AS STUDIED BY TDS

In fig. 1 desorption spectra of NO adsorbed on the Pt-Rh (100), (111) and (410) surfaces are shown. Desorption of NO was monitored during the desorption scan by following $m = 30$ amu, whereas $m = 28$ amu and $m = 14$ amu yielded information about N_2 desorption due to dissociatively adsorbed NO. Desorption of oxygen is not shown but occurs around 1000 K. N_2O formation has never been observed during the desorption experiments. In the case of the Pt-Rh (111) and (410) surfaces the N_2 desorption spectra are composed of two peaks, a lower temperature β_1 peak, and a β_2 peak at higher temperature. The β_1 peak is usually assigned to reaction of NO_{ads} and N_{ads}, leading to N_2 which is released into the gasphase and an oxygen atom left on the surface. The β_2 peak which is not observed for pure Pt [8–11] is assigned to the combination of two N adatoms [12–14]. The position of the peaks, especially that of β_2 depends on the surface structure and surface composition. Van Delft [6] showed that the β_2 peak is more pronounced on Rh-rich surfaces. This effect is probably related to the higher concentration of N adatoms on these surfaces. In the case of Pt-Rh(111) the β_1 peak appears slightly below 500 K and the β_2 peak appears around 600 K. For the Pt-Rh(410) surface of the β_2 peak is centered around 700 K, while the peak is larger than for Pt-Rh(111). These differences demonstrate that the strength of the

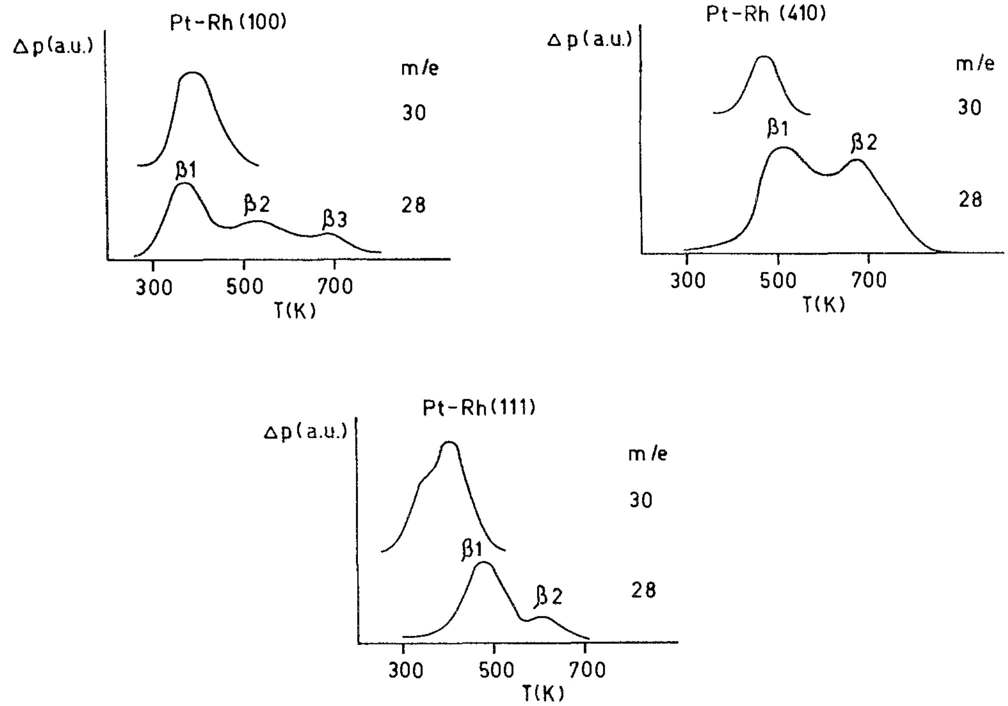

Fig. 1. TDS spectra for a NO adsorbed at 350 K on the Pt-Rh(111), (100) and (410) surfaces. The exposures yielded a saturated NO layer.

metal nitrogen bond is surface structure sensitive and that it is weaker for the Pt-Rh (111) surface than for the other two surfaces. The N_2 desorption spectrum of Pt-Rh(100) shows three desorption states β_1, β_2 and β_3 which were also observed on the pure Rh(100) surface [15]. On Rh(100) Ho and White [15] assigned the β_1 peak to combination of N adatoms which still have an interaction with oxygen atoms. The β_2 and β_3 peaks which lie around 550 and 700 K, respectively, are assigned to N adatom combination. Thus, compared with the Pt-Rh(111) and (410) surfaces a split β_2 desorption state is observed for the (100) surface. The dissociation activity of the three surfaces increases in the order (111) < (100) < (410). This is also the order of the maximum metal-nitrogen bond strength as suggested by the N_2 desorption spectra.

3.2. DISSOCIATION OF NO STUDIED WITH XPS

With XPS the oxygen and nitrogen (1s) binding energies can be used to distinguish oxygen and nitrogen present in molecularly adsorbed NO from oxygen adatoms and nitrogen adatoms on the surface at a given temperature. According to the relative intensities of the N adatom signal and the nitrogen

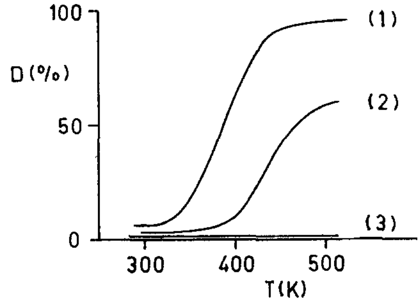

Fig. 2. The dissociation percentage according to XPS, %D_s, as a function of the temperature for Pt-Rh(111) and Pt-Rh(410). (1) Pt-Rh(410) (2) Pt-Rh(111) Pt surface concentration 20–30% (3) Pt-Rh(111), Pt surface concentration 60–70%

signal from molecularly adsorbed NO the dissociation percentage can be calculated using;

$$\%D_s = [(N)/((N) + (NO))] \cdot 100\%.$$

The results for the Pt-Rh(111) and (410) alloy surfaces as measured following an exposure of 20 L at 300 K are shown in fig. 2. Details can be found in [16]. The (100) surface was not studied with XPS. No NO bondbreaking is observed on the Pt-Rh(111) surface when the Pt surface concentration is high. The Rh-rich (111) alloy surface, on the other hand, shows a dissociation percentage of around 50%, when the sample is heated up to 500 K. For Pt-Rh(410) the dissociation is almost complete at 400 K, independent of the surface composition of the alloy. Hence, the activity for NO bondbreaking is very sensitive to the surface structure. For surfaces that are not very active in NO bondbreaking, the activity also depends on the surface composition. The activity for NO bond scission increases in the order Pt-rich(111) < Rh-rich(111) < Pt-rich(410) $\Leftarrow$ Rh-rich(410) [16].

3.3. ADSORPTION OF NO STUDIED WITH AES

In fig. 3, the Auger (N_{380} eV) and (O_{510} eV) signal intensities in the presence of a flow of $5 \cdot 10^{-7}$ Torr NO are given for a Pt-rich and a Rh-rich, Pt-Rh(410) surface as a function of temperature [17]. When the temperature of the sample is increased the nitrogen signal intensity decreases because of desorption of NO or N_2 and the oxygen signal intensity increases because of NO dissociation. There is a marked difference between Pt-rich and Rh-rich alloy surfaces. The nitrogen signal intensity on a Pt-rich surface is reduced to zero at 580 K. On a Rh-rich surface, however, a much higher temperature is needed to reduce the nitrogen signal intensity to zero, i.e. 680 K. At temperatures higher than 520 K the residence time of a NO molecule will be low on Pt-Rh alloy surfaces because of the high desorption rate at these temperatures. At temperatures above 500 K, the desorption temperature of NO, the measured nitrogen signal intensity will,

Fig. 3a.

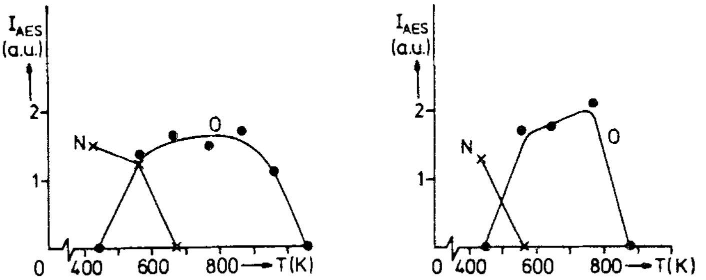

Fig. 3b.

Fig. 3. Auger (N_{380} eV) and (O_{510} eV) signal intensities in a flow of $5 \cdot 10^{-7}$ Torr NO as a function of the temperature for a) Pt-Rh(410), Pt surface concentration 60–70% b) Pt-Rh(410), Pt surface concentration 20–30%.

therefore, predominantly be caused by atomic nitrogen on the surface. Hence, it is clear that the metal-nitrogen bond strength must be higher in the case of Rh-rich alloy surfaces, as is shown by the higher temperature to remove the nitrogen completely from the surface for Rh-rich alloy surfaces [18].

3.4. NO-H_2 REACTION OVER Pt-Rh(111), (100) AND (410) ALLOY SURFACES

NO:H_2 = 1:5; The NO-H_2 reaction was carried out in a batch reactor at a total pressure of 6 Torr, with a NO-H_2 ratio of 1 : 5. The temperature was kept constant and the reaction products were followed in time by leaking a small amount of the reaction mixture into the mass analysis chamber. The main products are N_2, NH_3, H_2O and a small amount of N_2O, as shown in fig. 4. The relative amounts of reaction products at a NO conversion of 10% are presented in table 1. The initial reaction product observed for the (100) and (410) surfaces was N_2. The formation of NH_3 showed in all cases an induction period, which was temperature dependent. The nature of this induction period is unclear at this moment. It might be caused by adsorption of ammonia on the reactor walls in the initial stage of the reaction. It could also be caused by an intrinsic property of the reaction mechanism.

The selectivity of the NO-H_2 reaction varies drastically for the three surfaces studied. On the Pt-Rh(111) surface no N_2 formation has been observed. The Pt-Rh(410) surface, on the other hand, shows the highest selectivity towards N_2. The N_2/NH_3 ratio increases in the order (111) < (100) < (410). It should be

Table 1

Pt-Rh surface	N_2/NH_3 ratio
(111)	0
(100)	1.4
(410)	3

The relative amounts of N_2 and NH_3 at a total NO conversion of 10% are given for the three surfaces studied.

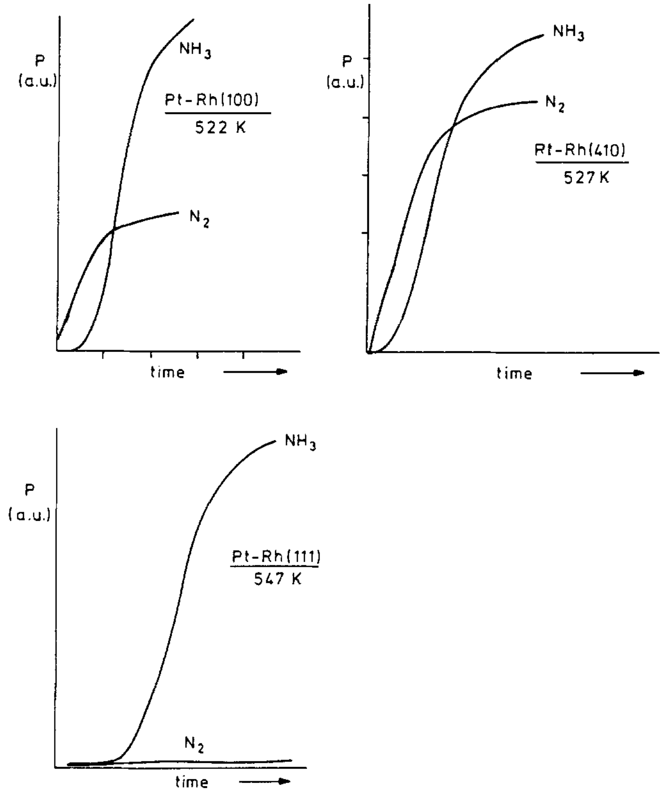

Fig. 4. The product (N_2, NH_3) formation given as a function of time at a constant temperature for the Pt-Rh(111), (100) and (410) surfaces.

noted that the contribution of the edges whose surface area is about 10% of the total surface area may not be neglected. However, the observed trend is clear. No additional information could be obtained concerning the reaction product N_2O, because the N_2O concentration was very low under these experimental conditions.

3.5. LOW PRESSURE NO-H_2 REACTION OVER Pt-Rh(100) STUDIED WITH HREELS

The NO-H_2 reaction was carried out at 500 K, with a total pressure of $6 \cdot 10^{-7}$ Torr and a NO : H_2 ratio of 1 : 5. After evacuating the reaction chamber and cooling down to 400 K the sample was analysed using HREELS. The samples were equilibrated in ultrahigh vacuum for 5 minutes at 1100 K which results in a $Pt_{0.50}$-$Rh_{0.50}$ surface. The HREELS results are presented in fig. 5a. The loss spectra taken directly after the reaction was stopped, show a weak intensity feature around 3200 cm^{-1}, indicating that a small amount of NH_x is present on the surface. No nitric oxide vibration is observed under these conditions. A small energy loss feature is observed around 480 cm^{-1}, a frequency that points to a

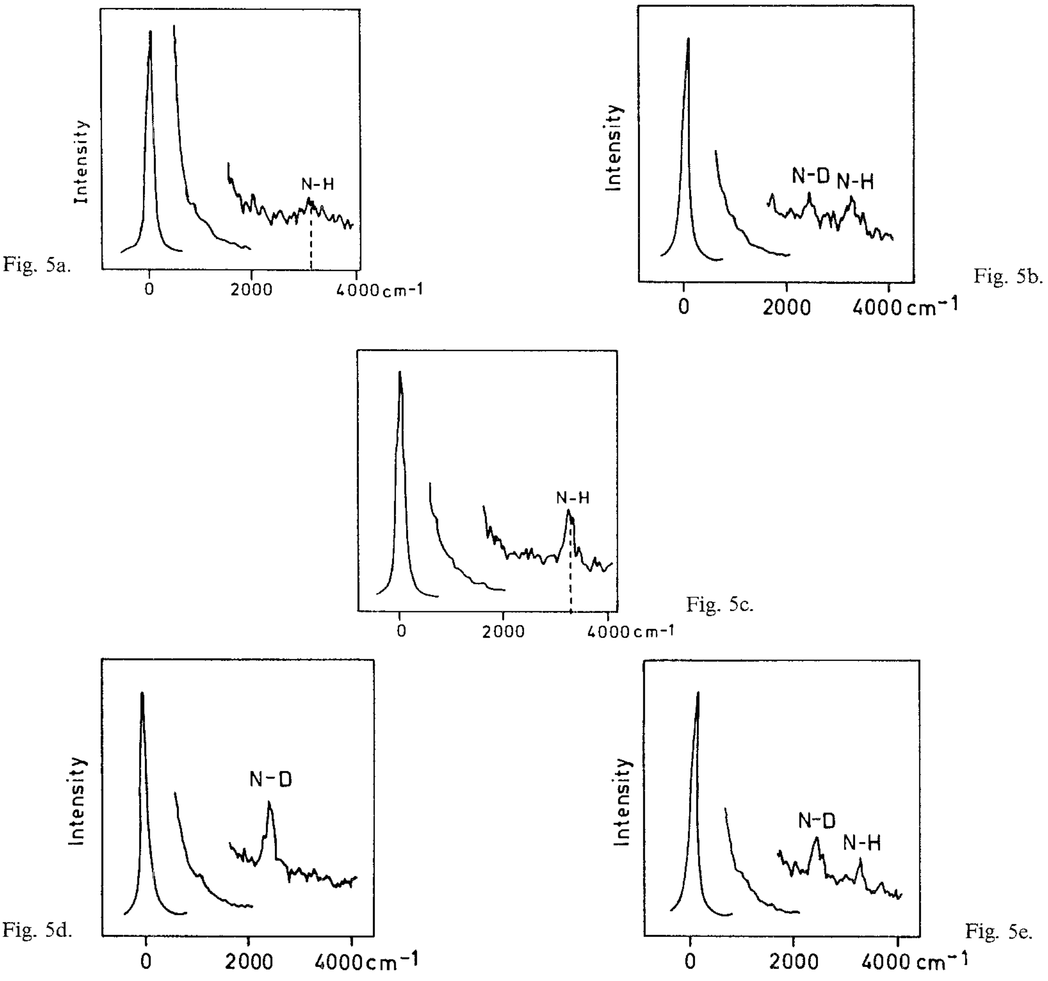

Fig. 5. a) HREELS spectrum for a Pt-Rh(100) surface taken directly after a NO-H_2 reaction at a total pressure of $6 \cdot 10^{-7}$ Torr and a NO-H_2 ratio of 1 : 5. The reaction chamber was evacuated and the surface was exposed to b) $H_2(1 \cdot 10^{-7}$ Torr)/$D_2(1 \cdot 10^{-7}$ Torr) mixture at 400 K. c) $H_2(1 \cdot 10^{-7}$ Torr) at 400 K. d) D_2 $(1 \cdot 10^{-7}$ Torr) at 400 K. e) $H_2(1 \cdot 10^{-7}$ Torr)/$D_2(1 \cdot 10^{-7}$ Torr) at 400 K.

metal-nitrogen vibration. AES analysis showed only the N_{380} eV signal intensity, no O_{510} eV signal intensity was observed. The next step was to expose the surface to a H_2, D_2 or a H_2/D_2 atmosphere at 400 K. HREELS spectra were recorded in situ, i.e. in the presence of H_2 or D_2. The results are given in figs. 5b–5e. Loss features are observed around 2400 cm^{-1} and 3200 cm^{-1}, frequencies which are assigned to N-D and N-H stretch vibrations, respectively. Evacuation of H_2, D_2 or H_2/D_2 results in a decrease of the observed N-H, N-D and N-H/N-D vibration intensities, respectively. From these results it is clear that atomic nitrogen present on the surface after the NO-H_2 reaction can easily react with H_2, D_2 or H_2/D to a NH_x, ND_x or NH_x/ND_x species at 400 K. Evacuation results in a decrease of the loss feature belonging to NH_x, ND_x or NH_x/ND_x, respectively, showing that the (de)hydrogenation/(de)deuteration reaction can proceed in both directions.

4. Discussion

The selective reduction of NO towards N_2 rather than to NH_3 or N_2O is one of the most important problems to be considered in the removal of NO_x from automotive exhaust gases. Pt and Rh are the active components of the present generation of the three-way catalyst formulation [1]. Despite the widespread use of the three-way catalysts little is known about the mechanisms that determine the selectivity. The nature and distribution of the various adsorption complexes and the competition among the adsorption complexes will largely determine the selectivity.

It is known that Rh exhibits excellent activity for the selective reduction of NO towards N_2 [1]. Pt, on the other hand, is more selective in the reduction of NO towards NH_3 under net-reducing conditions [18]. The fundamental reason for the high selectivity of Rh catalysts towards N_2 has not been established. Shelef [18] suggested that the selectivity towards nitrogen is determined by the probability of pairing-up of N-atoms. In the case of Ru, which is known to be the most selective metal in reducing NO towards N_2 [19], it has been suggested that the high selectivity may be caused by the formation of large separated islands of nitrogen and oxygen adatoms [20], facilitating the combination of adjacent nitrogen adatoms. Obuchi et al. [21,22], found that during the NO-H_2 reaction over Pd or Rh atomic nitrogen was deposited on the surface. The relative concentration of the N adatoms and the metal-nitrogen bond strength could play a key role in determining the selectivity of the NO-H_2 reaction. A full understanding of the processes which determine the selectivity should include a detailed description of the mechanisms of N_2 and NH_3 formation. It is well established that N_2 is formed by reaction of adsorbed nitrogen with either adsorbed nitrogen or adsorbed nitric oxide. However, the mechanism by which NH_3 is formed, is unclear. Bell [23] proposed that atomic nitrogen is hydrogenated to a NH_x species, which finally yields ammonia. Direct hydrogenation of molecularly adsorbed NO is also a possible mechanism. The fact that metals like Pt or Pd, which are not very active in NO bond scission give rise to high NH_3 production is consistent with such a mechanism.

The influence of the surface structure on the selectivity is described in the present paper. The adsorption of NO at low pressure, and the NO-H_2 reactions at a total pressure of 6 Torr were studied on three Pt-Rh single crystal surfaces. The selectivity of the NO-H_2 reaction varies drastically with the surface structure. The N_2/NH_3 ratio increases in the following order $(111) < (100) < (410)$. This is the same order as we found for the NO bond scisson activity, on the basis of XPS and TDS studies. TDS results also show that the surface composition has a significant influence on the desorption spectra and the NO dissociation.

The observed effect of the surface structure on the selectivity is consistent with the mechanism of which NH_3 is formed via direct NO hydrogenation. However, the HREELS results obtained on Pt-Rh(100) after the NO-H_2 reaction indicate that the surface is covered with atomic nitrogen mainly and a small amount of NH_x. This atomic nitrogen is easily hydrogenated to a NH_x species at 400 K. The absence of molecularly adsorbed NO proves that the NH_x species were formed by the following reaction;

$$N_{ads} + xH_{ads} \rightarrow NH_{x\,ads}$$

These results make it unlikely that the major pathway of ammonia formation proceeds via direct hydrogenation of molecularly adsorbed NO. If the formation of ammonia is considered to proceed through NO dissociation, the relevant reactions in the reduction of NO by H_2 can be summarized in the following scheme;

$$NO_{(g)} \rightarrow NO_{ads} \tag{1}$$

$$NO_{ads} \rightarrow N_{ads} + O_{ads} \tag{2}$$

$$H_{2(g)} \rightarrow 2H_{ads} \tag{3}$$

$$N_{ads} + N_{ads} \rightarrow N_{2(g)} \tag{4}$$

$$N_{ads} + H_{ads} \rightarrow NH_{ads} \tag{5}$$

$$NH_{ads} + H_{ads} \rightarrow NH_{2ads} \tag{6}$$

$$NH_{2ads} + H_{ads} \rightarrow NH_{3ads} \tag{7}$$

$$NH_{3ads} \rightarrow NH_{3(g)} \tag{8}$$

$$O_{ads} + 2H_{ads} \rightarrow H_2O_{(g)} \tag{9}$$

$$NO_{ads} + O_{ads} \rightarrow NO_{2(g)} \tag{10}$$

$$NO_{ads} + N_{ads} \rightarrow N_2O_{(g)} \tag{11}$$

$$NO_{ads} + N_{ads} \rightarrow N_{2(g)} + O_{ads}. \tag{12}$$

The simultaneous presence of NO and H_2 in the gas phase may result in a complex set of reactions that can occur simultaneously on the surface of the catalyst. From our XPS and TDS measurements it is clear that reactions 2 and 4 depend strongly on the surface composition. Moreover, reaction 2 is usually found to be the rate determining step in most NO reactions. Therefore, the structure and composition of the Pt-Rh alloy catalysts should affect the nature of the reaction. The Pt-Rh(410) and (100) surfaces which show a higher activity for NO bond scisson than the Pt-Rh(111) surface should give rise to a high nitrogen concentration on the surface, which favors N_2 formation via reaction step 4. For surfaces with a low atomic nitrogen concentration, reaction step 4 becomes less probable and other reaction pathways now determine the selectivity of the reaction. The concentration of hydrogen is expected not to vary drastically with surface structure and surface composition on group VIII metals [24]. With high partial hydrogen pressures reaction steps 5 through 7 seems to dominate, leading to relatively high ammonia formation on surfaces with a low activity for NO bond scisson. The selectivity towards nitrogen of catalysts which have a high activity for NO bond scission can be understood in this way.

Other possible reactions that should be discussed are the decomposition of ammonia and the reaction of ammonia with NO. It is known that the rates of ammonia decomposition over Pt are in the order, polycrystalline > (210) > (111) > (100) [25]. The decomposition is strongly inhibited by hydrogen. The order in hydrogen pressure is $(-3/2)$. Under our experimental conditions, however, the hydrogen pressure exceeds the ammonia pressure, especially in the beginning of the reaction where the NH_3/H_2 ratio is < 0.01.

During a study of the catalytic reduction of NO with ammonia over a stepped platinum single crystal surface [26], it was found that the reaction rate was inhibited by excess of nitric oxide. Under our experimental conditions the NH_3/NO ratio is < 0.05 in the beginning of the reaction. The NO-NH_3 reaction is completely suppressed under these conditions [24]. Hence, it is likely that the reduction of NO with ammonia or decomposition of ammonia will play a significant role under our experimental conditions. It can also be excluded that NH_3 is formed via molecular N_2 since both Pt and Rh cannot break the N-N bond and are not active in the synthesis of NH_3 from N_2 and H_2.

5. In conclusion

The selectivity of the NO-H_2 reaction seems to be determined by the relative concentrations of nitrogen, hydrogen and NO on the surface. It is shown that atomic nitrogen can be easily hydrogenated to a NH_x species at 400 K, which is most likely the reaction intermediate towards NH_3.

Acknowledgements

The authors acknowledge the Ministry of Economic Affairs of the Netherlands for financial support. Het Bureau Buitenland of the Leiden University and the Japan-Netherlands Institute (Tokyo) for all the arrangements done to enable J. Siera to carry out part of the research described in this paper.

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