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THE REDUCTION OF NITRIC OXIDE BY HYDROGEN OVER Pt, Rh AND Pt-Rh SINGLE CRYSTAL SURFACES

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ABSTRACT

The reduction of NO by hydrogen has been studied over $Pt_{0.25}$ - $Rh_{0.75}$ (100), (111), (410), Rh(100) and Pt(100) single crystal surfaces in the 10 mbar range. The surfaces were analysed using AES and LEED. Both the activity expressed as conversion after a constant reaction time and selectivity depend strongly on the surface structure and composition. The activity for the (100) surfaces decreases in the order Pt(100) ≥ Pt-Rh(100) > Rh(100). The activity of pure Rh is drastically enhanced by alloying with 25% Pt. The selectivity towards N_2 for the (100) surfaces decreases in the order Rh(100) > Pt-Rh(100) > Pt(100) at a temperature of 575K and Rh(100) > Pt(100) > Pt-Rh(100) at 520K . The activity for the alloy surfaces decreases in the order Pt-Rh(100) > Pt-Rh(410) > Pt-Rh(111), and the selectivity towards N_2 formation decreases in the order Pt-Rh(410) > Pt-Rh(100) > Pt-Rh(111), at 520K and 575K. The differences in selectivity and activity can be understood on the basis of the relative concentrations of N, NO and H on the various surfaces.

INTRODUCTION

The catalytic reduction of NO by hydrogen is of great importance for the emission control of automotive exhaust gases [1]. Reduction of NO with H_2 may produce several N-containing products such as N_2, NH_3 and N_2O. The formation of NH_3 and N_2O is undesired and catalysts favouring N_2 as a major reaction product are required. The noble metals Rh and Ru are very efficient for this purpose [1]. Metals like Pt and Pd, on the other hand, favour under certain conditions the reaction pathway which leads to the formation of NH_3 in large quantities [1]. More information is needed on the factors determining the large differences in the selectivity of the $NO-H_2$ reaction over different metals and surfaces structures. Previously, it was

found that the selectivity may be determined by the relative concentrations of NO, N and H distributed over the catalyst surface [2,3]. Nitrogen adatoms formed on a Pt-Rh(100) [3,4] or a Rh(100) [5] surface are easily hydrogenated at 400-450K, resulting in the formation of NH_{ads}. Dinitrogen can be formed in a large temperature range provided that sufficient N atoms are available. Below 600K, the main contribution to the formation of N_2 over the Pt-Rh(100) surface occurs via the reaction $NO_{ads} + N_{ads} \rightarrow N_2 + O_{ads}$. In this work, the reduction of NO by hydrogen was studied over the (111), (100) and (410) surfaces of a $Pt_{0.25}$-$Rh_{0.75}$ single crystal and the pure Pt(100) and Rh(100) single crystal surfaces. The purpose of this paper is to establish the effects of the surface structure and alloying on the kinetics and selectivity of the NO-H_2 reaction. A comparison between pure Pt(100) and Rh(100) on the one hand, and Pt-Rh(100) on the other, provides the information needed to understand the effect of alloying.

Kinetic results
     In fig.1 the formation rates of NH_3, N_2 and N_2O over the Pt(100) surface are shown versus reaction time at two selected temperatures, 520K and 575K.
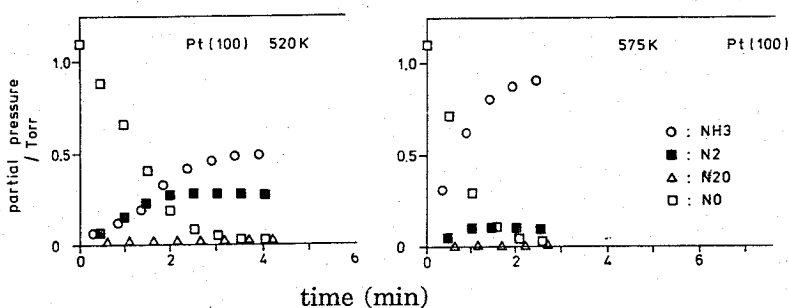

Figure 1 Formation of N_2, NH_3 and N_2O over Pt(100) (1x1).

The reaction was performed in a batch reactor at a total pressure of 6 mbar with a NO/H_2 ratio of 1 to 5. For details, concerning the experimental equipment we refer to previous papers [2-4]. The NO consumption indicates that the reaction of NO with H_2 proceeds relatively easy at both temperatures. Nitric oxide is converted into N_2 and NH_3 in comparable amounts at 520K. On the other hand, more NH_3 is formed at 575K. The formation of N_2O was below the limit of detection at both temperatures. The formation rates of N_2, NH_3 and N_2O over Rh(100), under identical conditions as described for Pt(100), are shown in fig.2. The conversion of nitric oxide over the Rh(100) surface proceeds much slower than over the Pt(100) surface. The reaction is very slow at 520K and the detection of products is difficult. Although formed in minor concentrations N_2 was the only reaction product detected. At 575K, the conversion of nitric oxide has increased drastically and detection of products is easily accomplished. The main product is still N_2, although the contribution of N_2O is significant. The formation of NH_3 was below the limit of detection, even at high conversions of nitric oxide. At 575K, total NO conversion is reached after 20 min. of reaction time.

The results obtained on Pt-Rh(100) are shown in fig.3. The reduction of nitric oxide by hydrogen proceeds relatively easy at 520K and 575K. The activity of this surface is only slightly smaller than that of the Pt(100)
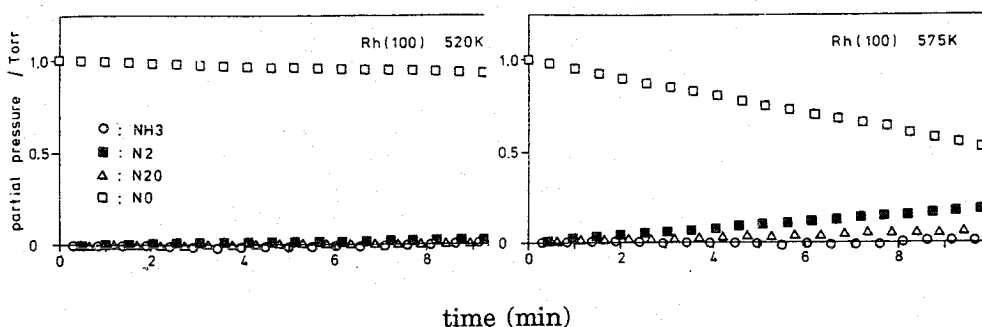
Figure 2
Formation of N_2, NH_3 and N_2O over Rh(100).
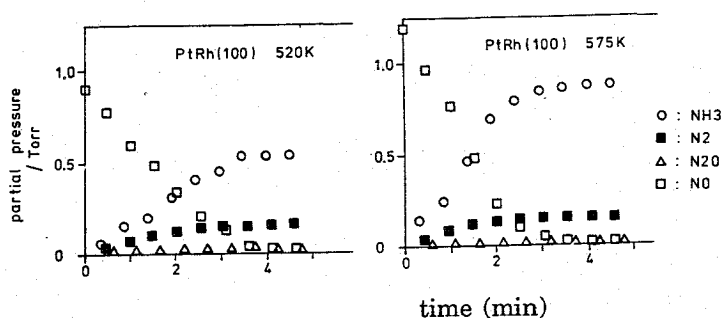
Figure 3
Formation of N_2, NH_3 and N_2O over Pt-Rh(100).

surface. N_2 and NH_3 are the products which are formed in detectable concentrations. A remarkable observation is that that the selectivity towards N_2 at 520K is higher over the Pt(100) surface than over the Pt-Rh(100) surface. Although Rh(100) has the higher selectivity towards N_2, alloying Pt(100) with Rh, lowers the selectivity towards N_2. These differences in selectivity towards N_2 are small but reversed at 575K.

The results obtained on Pt-Rh(111) are shown in fig.4. The only reaction product formed over this surface is NH_3, and the formation rates of N_2 and N_2O are below the limit of detection at 520K and 575K, even after long periods of reaction time. The conversion of NO is relatively slow compared with the Pt(100) and Pt-Rh(100) surfaces. The reaction rate increases rapidly when the temperature is raised to 575K. Total NO conversion at this temperature is reached after 5 min. Fig.5 shows the results obtained over the Pt-Rh(410) surface. The reaction products formed are N_2 and NH_3. The NO conversion is slower than over the Pt(100) and Pt-Rh(100) surfaces but

higher than over the Pt-Rh(111) surface. The selectivity towards N_2 is relatively high, a higher selectivity towards N_2 is only observed over the Rh(100) surface.
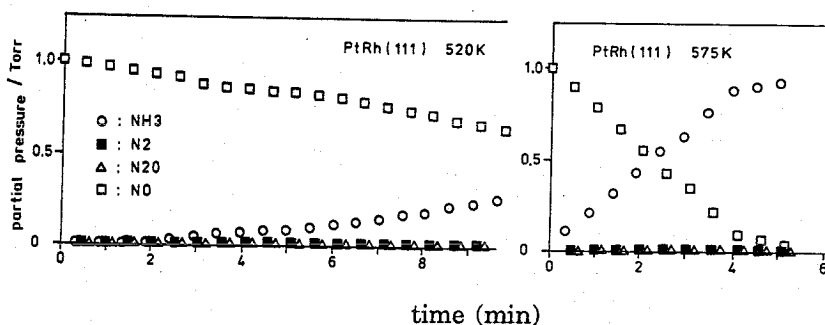
Figure 4
Formation of N_2, NH_3 and N_2O over Pt-Rh(111).
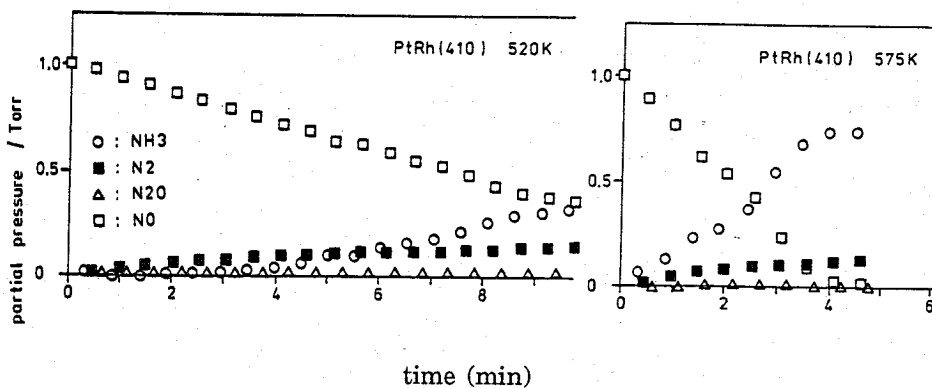
Figure 5
Formation of N_2, NH_3 and N_2O over Pt-Rh(410).

The results for the selectivity and activity expressed as conversion after a constant reaction time of the NO-H_2 reaction for the various surfaces are summarised in fig's 6 and 7, respectively. The selectivities towards N_2 determined at a total NO conversion of 10% are shown in fig.'s 6a and 6b for 520 and 575K, respectively. Large differences exist in the selectivities towards N_2 for the various surfaces. It ranges from 0% over the Pt-Rh(111) surface to 100% over Rh(100) at 520K. The conversion after 3 minutes of reaction time varies from 5% over the Rh(100) surface to 90% over the Pt(100) surface at 520K. It should be noted that the activity for all the surfaces shown in fig. 7 are expressed as conversion measured after 3 minutes of reaction time.
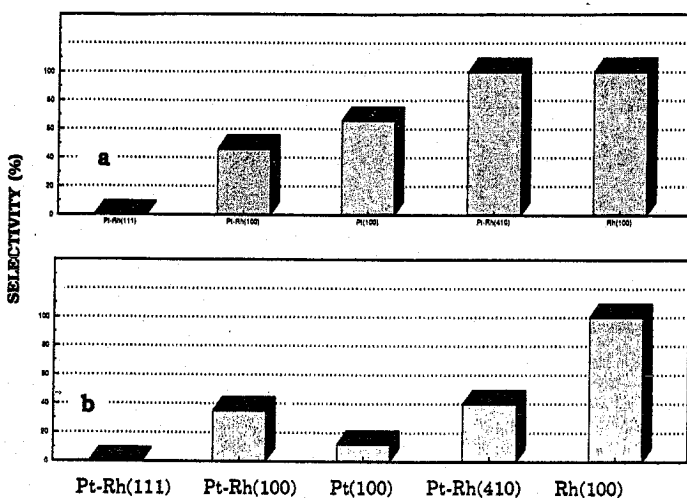
Figure 6
The selectivity of the NO-H_2 reaction towards N_2 determined at a total conversion of 10% at a) 520K and b) 575K.
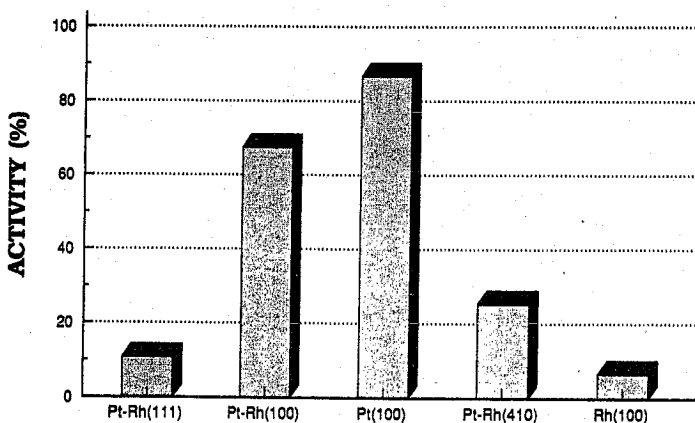
Figure 7
The NO conversion after 3 minutes of reaction time at 520K.

Spectroscopic results - After the reaction was stopped, the reactor was evacuated and the sample was transferred to the UHV chamber for spectroscopic analysis by AES and LEED. It should be noted that the information concerning the physical and chemical state of the surfaces is obtained after the reaction was stopped and the surface composition and structure may not be the same as under the reaction conditions. However, as will be shown further on, the AES and LEED results provide useful additional information which may lead to a better understanding of the processes taking place on the various surfaces.

AES - The N_{380eV} and O_{510eV} AES signal intensities normalised by the proper

metal AES transistion are shown in table I, for the various surfaces. The nitrogen signal may be due to either NO, N or NHx adsorbed on the surface and no distinction between these species by means of low resolution AES is possible. The cross-section for an Auger process of an oxygen atom bound to nitrogen is small.

LEED - C(2x2) surface structures were observed after the NO-H$_2$ reaction over the Pt-Rh(100) and Rh(100) surfaces. No ordered LEED patterns are observed for Pt(100) and Pt-Rh(111). For these surfaces diffuse (1x1) surface structures were found. A (2x1) surface structure was observed for the Pt-Rh(410) surface.

Surface	N/Rh[a]	O/Rh[a]
Pt-Rh(111)	0.057	0.006
Pt(100)	0.013[b]	0.0055[b]
Pt-Rh(100)	0.038	0.055
Pt-Rh(410)	0.065	0.035
Rh(410)	0.045	0.012

Table I
The reduction of nitric oxide by hydrogen over Pt, Rh and Pt-Rh single crystal surfaces.
a: Rh 302 eV
b: Pt 64 eV

DISCUSSION

The NO-H$_2$ reduction consists of a set of several reactions which may occur simultaneously on the catalyst surface [2-4]. The main reactions are displayed below.

$$NO_{(g)} + [] \rightarrow NO_{ads} \qquad (1)$$
$$NO_{ads} + [] \rightarrow N_{ads} + O_{ads} \qquad (2)$$
$$H_{2(g)} + [] \rightarrow 2H_{ads} \qquad (3)$$
$$N_{ads} + 3H_{ads} \rightarrow NH_{3(g)} + [] \qquad (4)$$
$$O_{ads} + 2H_{ads} \rightarrow H_2O_{(g)} + [] \qquad (5)$$
$$N_{ads} + N_{ads} \rightarrow N_{2(g)} + [] \qquad (6)$$
$$NO_{ads} + N_{ads} \rightarrow N_{2(g)} + O_{ads} + [] \qquad (7)$$
$$NO_{ads} + N_{ads} \rightarrow N_2O_{(g)} + [] \qquad (8)$$
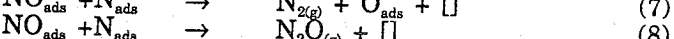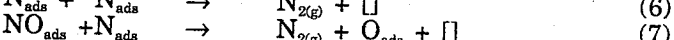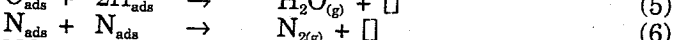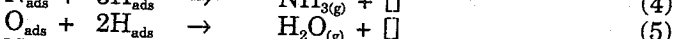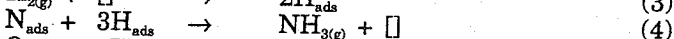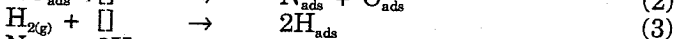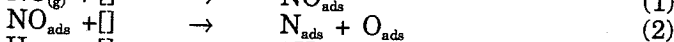
(where [] stands for surface vacancy or vacancies)

Each of these steps may have a different rate of reaction over the various surfaces. In the next section a brief description is given of the various steps according to the literature.

The adsorption of NO at room temperature (step 1) occurs with a high sticking probability on Pt and Rh surfaces. Several adsorbed complexes have been reported, including on top and bridged [6]. Usually, NO adsorbs with

the nitrogen end on the surface but lying down NO has also been reported. Also, NO adsorbed in a bent configuration has been suggested, although experimental confirmation of this type of adsorption complex is difficult. Adsorption of NO at low coverages on Rh surfaces occurs mainly on bridged sites, whereas on Pt on top adsorption is favoured. Dissociation of the NO molecule (step 2) is very sensitive to the surface structure and composition [7]. This is illustrated by the very low activity for bond scission on the Pt(111) surface and a high dissociation rate on the Pt(410) surface [8]. The high activity of NO bond scission on the Pt(410) surface may be due to an enhanced interaction of the oxygen atom at the step sites. Masel [8] suggested that the Pt(410) surface structure exhibits an electron orbital symmetry at the these sites which matches the symmetry of the antibonding orbitals of the NO molecule. This causes a strong weakening of the N-O bond strength and dissociation may occur. It is known that NO dissociation occurs more efficiently on Rh than on Pt surfaces [7]. The order in intrinsic activity for N-O bond breaking is Pt-Rh(410)> Rh(100) > Pt-Rh(100) > Pt(100) > Pt-Rh(111). However, it is well established that a number of free metal sites is needed before NO dissociation occurs [9].

The adsorption of the H_2 molecule (step 3) proceeds with a relatively low sticking probablity on Pt and Rh surfaces at 400-500K. The sticking probability of hydrogen depends on the surface structure. On the Pt(100) surface a higher sticking probability is measured than on the Pt(111) surface. The dissociation of the H_2 molecule proceeds very fast on group VIII metals at 400-500K [10].

On the Pt-Rh(100) [3,4] and Rh(100) [5] surfaces it was found that hydrogenation of N_{ads} (step 4) occurs at 400-450K. NH_{ads} was found as a major surface intermediate when N_{ads} was exposed to hydrogen. The formation of NH_3 via N_{ads} + $3H_{ads}$ was found at a temperature of 450K. The decomposition of NH_3 over Pt surfaces increases in the order (111)<(100)<(210) [11]. The NH_x surface intermediate may decompose before total hydrogenation has occurred. In fact, it was found that the formation of NH_{ads} on Pt-Rh(100) and Rh(100) in hydrogen is completely reversible and $NH_{ads} \rightarrow N_{ads} + 0.5 H_2$ occurs when hydrogen is pumped off [4]. The formation of H_2O (step 5) occurs through OH_{ads} intermediates and is a very fast process [10].

The combination of two N_{ads} adatoms (step 6) occurs in a wide temperature range [3]. This step also strongly depends on the surface structure and the metal being used. On Rh surfaces the metal-N bond is stronger than on the corresponding Pt surfaces. The metal-N bond strength increases in the order (111) < (100). In contrast to the Pt(100) surface where this step occurs almost instantaneously at the reaction temperatures considered, build-up of N_{ads} takes place on the Rh(100), Pt-Rh(100) and Pt-Rh(410) surfaces.

The NO_{ads} + N_{ads} reaction can give $N_{2(g)}$ + O_{ads} or $N_2O_{(g)}$ via steps 7 and 8, respectively. On Pt-Rh(100) it was found that step 7 is a main route through which $N_{2(g)}$ is formed in the temperature range below 600K [3]. At higher temperatures step 6 is the dominant mechanism for N_2 formation. Little is known about the specific contributions of steps 7 or 8 over Pt and Rh surfaces.

Based on the kinetic and spectroscopic results described in this paper a

model is proposed for the plane to plane variation of the selectivity and activity of the NO-H_2 reaction over the Pt,Rh and Pt-Rh alloy surfaces.

As shown in fig.6 the selectivity of the NO-H_2 reaction for N_2 varies between 0 and 100% after 10% NO conversion. The NO conversion after 3 min. of reaction time as displayed in fig 7 varies between 5 and 90%. A low conversion over Pt-Rh(111) is observed in combination with a high selectivity towards NH_3 ($\approx$100%). It is known that dissociation of NO is slow over the Pt-(111) surface, and that the behaviour of Pt-Rh alloy surfaces towards NO dissociation displays a Pt-like behaviour at high NO coverages. The high normalised N_{380eV} AES signal intensity on Pt-Rh(111) observed by AES is ,therefore, assigned to molecularly adsorbed NO. The Pt-Rh(111) surface will be covered mainly by NO under reaction conditions and the coverages of N_{ads} and O_{ads}, are small. This is also supported by the low normalised O_{510eV} signal intensity. Only NH_3 is formed as a product. The NH_3 molecule may be formed through process 4 as over Pt-Rh(100) or via an [NOH] intermediate. Gorodetskii [12], reported the formation of [NOH] on Pt. However, the [NOH] intermediate was found to be unstable at temperatures higher than 400K. The formation of NH_3 is favoured over the formation of N_2O or N_2. No ordered LEED structures were observed on Pt-Rh(111), indicating that the NO molecules do not form large ordered islands. Thus, for the Pt-Rh(111) surface it is assumed that step (2) occurs relatively slow, and the O_{ads} and N_{ads} react to H_2O and NH_3 through steps (5) and (4), respectively. N-N combination is unlikely due to the low concentration of N_{ads}. The formation of N_2 and N_2O is below the limit of detection, indicating that steps (7) and (8) do not take place at a detectable rate.

The conversion of NO over the Pt-Rh(100) surface after 3 min. reaction time at 520K is almost 70% and the selectivity towards N_2 is 32%. The normalised N_{380eV} AES signal intensity is 0.038 and for the O_{510eV} normalised signal intensity a value of 0.055 has been found. By EELS it was found that the N_{380eV} signal intensity is caused by nitrogen atoms [4]. This surface may be covered by a small amount of NO_{ads}, and a larger amount of O_{ads} and N_{ads}. Also H_{ads} which is not detectable by means of AES may be present on the surface. A c(2x2) surface structure is observed by means of LEED. Both O_{ads} and N_{ads} form a c(2x2) surface structure on the Pt-Rh(100) surface. However, the LEED pattern as observed after the NO-H_2 reaction resembles the pattern observed for the Pt-Rh c(2x2)-N surface structure. Islands of N adatoms may facilitate the formation of N_2 via step 6. The large O_{510eV} signal could be partly due to the formation of subsurface oxygen. Thus, for this surface NO dissociation occurs easily and the formation of N_2 through step 6 has increased. The high activity indicates that free sites remain available during the reaction. These sites probably consists of Pt atoms since the Rh atoms may be covered by N_{ads}.

Over Pt(100) the highest conversion was observed and the selectivity towards N_2 is 60% at 520K. The dissociation of NO over Pt(100) proceeds easily provided that vacancies are available. Since steps 4,5,6, and most likely also step 7 are fast these free sites remain available during the course of the reaction. This is supported by the low N_{380eV} and O_{510eV} signal intensities. The N_{380eV} signal intensity is partly due to the Pt_{382eV} peak. The Pt(100) surface exhibits a higher selectivity towards N_2, than the Pt-Rh(100) alloy surface at 520K. Pure Rh, however, has a higher selectivity towards N_2

than pure Pt. This may be explained by an effect of strongly bound nitrogen atoms on the rhodium atoms surrounding the platinum atoms. At 520K, the nitrogen atoms adsorbed on Rh sites are strongly bound to the surface and the formation of N_2 is slow. If an NO molecule dissociates on Pt sites, the nitrogen atoms may be surrounded by a matrix of strongly bound nitrogen atoms on Rh sites. The formation of N_2 will be slow at this temperature and the subsequent hydrogenation of this N-atom on the Pt-site can occur. On Pt(100), the nitrogen atom may recombine with NO, or N on other neighbouring Pt-sites forming N_2 or N_2O and N_2 respectively. The formation of NH_3 through $N_{ads} + H_{ads}$, over "isolated" Pt-sites is reduced. This explains the enhanced NH_3 production over the Pt-Rh(100) alloy surface at 520K in comparison with pure Pt(100). The high conversion of NO over the Pt-Rh(100) and Pt(100) surfaces is explained by the intrinsic high NO dissociation activity combined with the relatively low M-N bond strength on platinum which prevents that the reaction is inhibited by blocking of active sites by N_{ads}. At 575K, the selectivity towards N_2 over the Pt-Rh(100) surface is higher than over the Pt(100) surface. At this temperature the enhancement of the N_2 production over Pt-Rh(100) may be ascribed to N-N combination from sites containing few or more Rh atoms. The N_2 production over the Rh(100) surface is observed at 575K.

The selectivity towards N_2 and the activity over Pt-Rh(410) at 520K are 100% and 20%, respectively. The value for the selectivity towards N_2 is 40% at 575K. It is known that the dissociation of NO proceeds relatively easy on this surface and a high concentration of nitrogen is found by means of N_2 TDS. The nitrogen atoms adsorbed at the steps of the single crystal surface have an enhanced adsorption energy. The activity will decrease due to the higher number of metal sites which are occupied by strongly bound nitrogen. This is illustrated by the relatively low conversion of NO over the Pt-Rh(410) surface. The value for the normalised N_{380eV} signal intensity is 0.065, the largest found in this study. These nitrogen atoms are strongly bound to the step sites of the surface. At these sites an enhanced NH_x decomposition may also take place before total hydrogenation to NH_3 has occurred. The oxygen concentration on or near the surface layer is quite large as indicated by the normalised O_{510eV} signal intensity of 0.035. The LEED pattern after the reaction points to a (2x1) surface structure. The single crystal surface may facet under the reaction conditions. However, if this would be the case desorption of the adsorbates restores the structure characteristic of the f.c.c. (410) surface.

The selectivity towards N_2 has the highest value for the Rh(100) surface. However, the conversion of NO is low at temperatures below 600K, due to the high number of strongly bound nitrogen atoms. This is also reflected by the high value of the N_{380eV} AES signal intensity, 0.045. By EELS it was found that this signal is mainly caused by adsorbed nitrogen atoms. The accumulation of N adatoms during the NO-H_2 reaction at a total pressure of 2 x 10-7 mbar over a polycrystalline Rh surface was reported by Obuchi et al [13]. The high selectivity towards N_2 may be explained by the high number of nitrogen atoms on the surface. A c(2x2) surface structure was found by means of LEED. The relatively low O_{510eV} AES signal indicates that this structure consists mainly of N_{ads}. Therefore, it is believed that large islands of N_{ads} are formed during the reaction. This facilitates the

formation of N_2 via step 6. By EELS it was found that NH_{ads} can actually be formed on the Rh(100) surface [5]. However, NH_3 is not formed under the described reaction conditions. The low rate of NH_3 formation may be caused by a low H_{ads} concentration in the N_{ads} islands and the formation of NH_x species at the boundaries of these islands only. Also, an enhanced decomposition of NH_x could take place on Rh. The low activity of the NO/H_2 reaction at 520K is ascribed to the low number of free active sites available for reaction. Most of the metal atoms are blocked by nitrogen atoms, or NO molecules. At 575K, N_2O formation is observed, this indicates that even at this temperature the number of free sites must be relatively small. The N_2O intermediate will decompose into N_2 and O_{ads} if a sufficient number of vacancies is available. If these vacancies are absent, N_2O will desorb from the surface.

CONCLUSIONS

The activity and selectivity of the $NO-H_2$ reaction over Pt, Rh and Pt-Rh surfaces depends strongly on the metal and surfaces structure. The activity at 520K decreases in the order Pt(100) $\geq$ Pt-Rh(100) > Pt-Rh(410) > Pt-Rh(111) > Rh(100). The selectivity towards N_2 on the other hand decreases in the order Rh(100) > Pt-Rh(410) > Pt(100) > Pt-Rh(111). The selectivity towards N_2 ranges from 100% to 0%. The selectivity is determined by the relative concentrations of NO, N and N adsorbed on the various surfaces. A high selectivity towards N_2 is observed with relatively strong adsorbed nitrogen atoms on Rh(100) and Pt-Rh(410). However, the high selectivity towards N_2 is at the expense of the activity for the reaction.

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DISCUSSION

Q: Z. Schay (Hungary)
    1) Have you considered the dissociation of NO assisted by adsorbed hydrogen ?
    2) If H_a removes only oxygen, at low coverage NO adsorption and dissociation should occur and on hydrogen adsorption (following the NO adsorption) only water and no N_2 should be formed. Is this true ?

A: B. Nieuwenhuys and K. Tanaka
    1) From a thermodynamic point of view hydrogen could facilitate the dissociation of NO. However, we have not found any direct evidence for such an effect. All our experiments including TDS, XPS and FEM studies show that dissociation of NO starts at temperatures at which some of the adsorbed NO desorbs, creating vacant metal sites required for NO dissociation. In this stage hydrogen can also be adsorbed on the surface and it reacts with oxygen resulting in more vacancies and, hence, in faster dissociation and reaction. The observed reaction temperatures of hydrogen with NO adsorbed at low coverages do not differ significantly from the NO dissociation temperatures [1,2]. Therefore, hydrogen assisted NO dissociation does not seem to play an important role. However, at relatively high hydrogen pressures hydrogen seems to be able to displace some of the more weakly bound adsorbed NO and reaction starts at lower temperature [1]. This effect may also called "hydrogen assisted NO dissociation".
    2) Starting with a low NO precoverage, dissociation starts at a much lower temperature than on surfaces initially covered with a monolayer NO. On some Rh surfaces dissociation can already start below room temperature [1]. NO dissociation and interaction of NO with hydrogen have been studied in detail on a PtRh(100) surface using LEED, AES and EELS [2]. In the presence of NO at T > 350 K the (1x1) surface structure is slowly converted to an oxygen (3x1) surface structure due to NO dissociation and Rh surface segregation. In the presence of a NO + H_2 mixture the surface structure formed is the nitrogen c(2x2) showing again that hydrogen reacts more easily with oxygen than with nitrogen.

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[2]   H. Hirano, T. Yamada, K. I. Tanaka, J. Siera, B. E. Nieuwenhuys, *Surf. Sci.,* **222**, L804 (1989); *ibid* **262**, 97 (1992)

Q: R. W. Joyner (United Kingdom)
    Your conclusion that the selectivities are proportional to surface coverage are at first sight not surprising, since presumably you are dealing with Langmuir-Hinshelwood kinetics. But it suggests that the activations energies observed an those for desorption and not reaction. Do you agree and do you make different observations at higher temperatures ?

A: B. Nieuwenhuys and K. Tanaka
    Yes. The activities and the selectivities shown in the figure have been measured at relatively low temperatures (500-600 K), where for some of the surfaces the reaction rate may be controlled by desorption. An example is the Rh(100) surface. The intrinsic activity of the Rh(100) surface for NO dissociation and reaction is high. However in this low temperature range the activity found for this surface is very low due to nitrogen inhibition. As a result the order in activity and selectivity of the various surfaces examined are dependent on the temperature. An example can be found in Figure 6 showing that at 520 K the Pt-Rh(410) surface is more selective to N_2 formation than the Pt-Rh(100) whereas at 575 K the Pt-Rh(100) surface shows a better selectivity.

Q: J. H. Block (Germany)
    My question concerns the surface composition of the Pt-Rh alloy. Frequently chemisorption processes are combined with surface segregation of one of the alloy compounds. Is such a phenomenon observed ?

A: B. Nieuwenhuys and K. Tanaka

Yes. Pt-Rh alloy surfaces show a very dynamic behavior in adsorption and reaction. Under reducing conditions Pt surface segregation is observed. Under oxidizing conditions, Rh segregates to the surface. The O induced (O from O_2, or NO) Rh surface segregation can eventually lead to the separation of Rh-oxides. Under reducing conditions alloy formation takes again place.

Q: R. A. van Santen (The Netherlands)

The presentation focuses an the role of nitrogen. However it is well known that O_2 has a large negative effect on the rate of NO reduction. What information do you have on the role of oxygen in the reaction ?

A: B. Nieuwenhuys and K. Tanaka

It is right that Rh, Pt and Pt-Rh alloy catalysts are not selective towards the reduction of NO in the presence of oxygen. On the other hand our paper (see Table I and the text) suggests that there is no direct relation between the amount of oxygen (from NO) as found by AES and the activity/selectivity, while we did find a correlation between activity/selectivity and the N concentration. In our opinion this result is caused by the fact that the oxygen measured by AES is situated beneath the surface (subsurface O) and is not adsorbed on the surface. It should also be kept in mind that hydrogen-rich conditions were used in our experiments (H_2/NO ratio of 5/1), because it was the purpose of the study to examine the selectivity to NH_3, N_2 and NO formation.

Q: D. Chadwick (United Kingdom)

Your activities and selectivities are quoted after 3 minutes reaction time. For those cases with high N coverage, can you comment on the products observed from zero to 3 minutes reaction time ?

A: B. Nieuwenhuys and K. Tanaka

Due to space limitation we could not show the variation of the rates of formation of the various products with increasing reaction time. For the Pt-Rh(100) surface we have published these data in an earlier paper [3]. For Rh(100), the surface with a high N coverage, the only reaction product observed at 500-600 K from zero to 3 minutes is N_2. The order in conversion/selectivity for the various surfaces studied does not change going from zero to three minutes.

[3]   H. Hirano, T. Yamada, K. I. Tanaka, J. Siera, P. Cobden and B. E. Nieuwenhuys, *Surf. Sci.*, **262**, 97 (1992)

Q: G. B. Fisher (USA)

1) In actual automotive exhaust, among the gases present on the rich side of stoichiometry are NO, CO and H_2. Do you have any experiments which indicate how the NO-H_2 reaction completes with the NO-CO reaction on the Pt-Rh alloys ?

2) You have shown the trade-off between selectivity to N_2 formation and activity for the NO-H_2 reaction on several surfaces. Does it seem reasonable that this is most directly related to an inhibition of the H_2 dissociation step in the reaction in the presence of high N atom surface coverage which lead to good N_2 selectivity? I would seem reasonable from one point of view, since in 1988 [4] we found that high N atom coverage on Rh(111) dramatically inhibited dissociative O_2 adsorption. It would be very interesting to know the rate constant of H_2 dissociative chemisorption (and NO dissociation) as a function of N atom coverage on these alloys.

[4]   G. B. Fisher, et al., *Proc. of the 9th Int. Cong. on Catalysis* (Eds.: M. J. Phillips and M. Ternan), The Chemical Institute, Ottawa, p. 1355, (1988)

A: B. Nieuwenhuys and K. Tanaka

1) No. We have measured the NO + H_2 and NO + CO reactions over Pt-Rh alloys. However, we did not study the NO reduction in the presence of both CO and H_2. NO reduction with hydrogen is a much faster reaction than NO reduction with CO. In an atmosphere of CO, NO and H_2 the CO adsorption will compete with NO and hydrogen adsorption. Hence, we may expect CO inhibition of the reduction of NO by hydrogen at lower temperatures (T < 500 K).

2) The model that you propose: inhibition of hydrogen adsorption/dissociation by a high concentration of N adatoms seems reasonable to us. It is well documented in the literature that for dissociation of CO, NO and O_2 several adjacent free metal atoms are required. For hydrogen the available information is not that clear. In many papers it has been reported that H_2 dissociation requires an ensemble of free metal atoms. However, other papers suggest that hydrogen can also dissociate an isolated Pd or Pt atoms in the surface. We found that hydrogen can adsorb on Pt-Rh(100) or Rh(100) covered with an overlayer of N_{ads} to form NH_a [5]. Hence, we do not have a direct answer on the question to which extent H_2 dissociation is inhibited by a high concentration of N_{ads}. We agree that it would be interesting to know the rate constants of H_2 dissociative adsorption and NO dissociation as a function of N atom coverage.

[5]   K. I. Tanaka, T. Yamada, B. E. Nieuwenhuys, *Surf. Sci.*, **242**, 503 (1991)

Q: G. A. Sormorjai (USA)

Would it be advantageous to study alloy effects by depositing one monolayer of both alloy components on a third, neutral metal instead of one monolayer of one component on the single crystal of the other metal ?

A: B. Nieuwenhuys and K. Tanaka

In the studies described in our papers bulk Pt-Rh alloys have been used. In general, three different types of alloy surfaces can be prepared:

1) two dimensional alloys prepared by depositing component A on a substrate of component B:

2) by depositing of both components A and B on an inert substrate:

3) by using a bulk alloy A-B.

Each approach has its specific advantages and limitations. In 3) the bulk composition is well-defined and it is easy to study the large effect of the surface structure on adsorption and catalysis. For Pt-Rh alloys most of the work has been done with 3). Some limited information is available for surfaces prepared by 1) and 2) [6]. These results are in line with those reported for bulk single crystal surfaces of Pt-Rh.

[6]   L. D. Schmidt et al. and K. I. Tanaka et al., to be published