Catalysis Letters 10 (1991) 335–342

The NO-H_2 reaction over Pt(100) Oscillatory behaviour of activity and selectivity

J. Siera [1], P. Cobden [1], K. Tanaka [2] and B.E. Nieuwenhuys [1,]*

[1] *Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
[2] *The Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppong, Minato-Ku, Tokyo 106, Japan*

Received 17 July 1991; accepted 23 July 1991

The NO-H_2 reaction has been studied over a Pt(100) single crystal surface as a function of temperature and partial pressures of the reactants. The activity as well as the selectivity, shows oscillatory behaviour under isothermal conditions from 420 K to 520 K. The oscillations observed for the formation rates of N_2 and NH_3 are out of phase with those found for the formation rate of N_2O. These observations are in line with recently proposed mechanisms for the formation of N_2, NH_3 and N_2O.

Keywords: NO-H_2 reaction; oscillating selectivities; Pt(100)

1. Introduction

The major reactions of NO conversion to nitrogen in the automotive catalytic converter are [1–4]:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2.$$

However, NO can also react to the undesired N_2O and NH_3. The overall reactions are

$$2NO + H_2 \rightarrow N_2O + H_2O$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$$

$$2NO + CO \rightarrow N_2O + CO_2.$$

The selectivity of Pt to promote NO reduction to N_2 rather than NH_3 is poor, especially at low temperature [5]. In previous work [6] it was reported that the dissociation of NO and its reaction with hydrogen is very sensitive to the surface

---

* To whom correspondence should be addressed.

structure. A model was proposed for the factors determining the selectivity of the NO-H_2 reaction. The relative concentrations of NO, N and H adsorbed on the surface are the key-factors determining the selectivity [6,7].

In this paper a study is described of the NO-H_2 reaction over a pure Pt(100) single crystal surface as a function of temperature and NO-H_2 partial pressures, with emphasis on the self-sustained oscillations in the reaction rate.

The clean Pt(100) surface is reconstructed to the (5 × 20) surface structure [8,9]. However, a (5 × 20) → (1 × 1) transformation is induced by adsorption of NO [10–13]. The oscillatory behaviour of CO-O_2 [14,15] and CO-NO [15,16] reaction rates has been associated with this surface reconstruction. The aim of this paper is to find conditions where the NO-H_2 reaction rate displays oscillatory behaviour. Special attention was paid to the selectivity of the NO-H_2 reaction under these conditions. To the best of our knowledge, this is the first report of observed isothermal oscillations in the selectivity of a catalytic reaction.

2. Experimental

The experiments were performed in a UHV-system equiped with AES, a quadrupole mass spectrometer (QMS) and LEED. The temperature of the Pt sample could be controlled to within 0.2 K of the desired reaction temperature. The QMS was controlled by a microcomputer enabling a maximum rate of 400 measurements per minute. The data were stored on disk for analysis in a later stage. The (100) surface was oriented and cut from a single crystalline Pt rod, and polished to within 0.5° of the (100) direction by using standard metallographic techniques. The sample was mounted by spotwelding to a Ta support and could be heated resistively up to 1700 K. Its temperature was measured by a Pt-Rh/Pt thermocouple spotwelded to the edges of the crystal. The surface of the crystal was cleaned in situ by Ar-ion sputtering, oxidation and high temperature annealing cycles.

The NO and H_2 gases were admitted through variable leak valves. Nitric oxide (99.99% NO) and H_2 (99.995% H_2) were used without further purification. The purity of each reagent was verified with in situ mass spectrometry. The reactions were performed by using the UHV chamber as a flow reactor which was pumped by a turbomolecular pump. The Pt sample was placed in front of a small slit which gave access to the QMS. The QMS itself was differentially pumped by a 8 l/s ion pump allowing sensitive and fast analysis. This set-up also ensures that contributions of the crystal edges are negligible small.

3.1. RESULTS

A typical recorder trace of the variation of the partial pressure of N_2 observed during the NO-H_2 reaction is shown in fig. 1. The partial pressures are

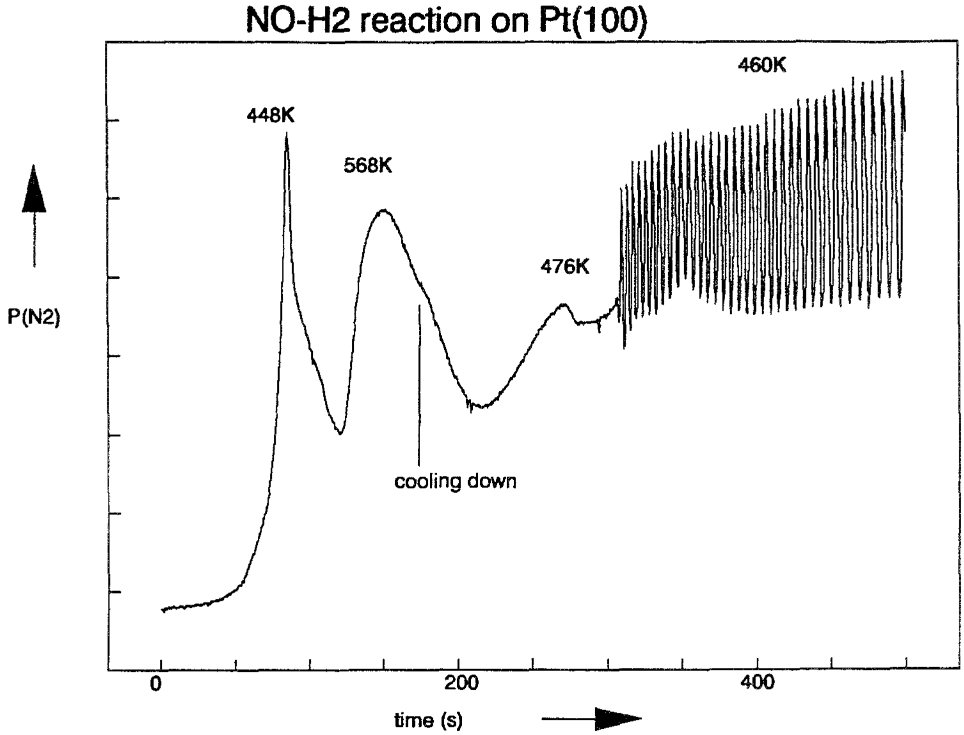

Fig. 1. Variation of the N_2 partial pressure during the NO-H_2 reaction as a function of time, at the indicated temperatures. $P(NO) = 3 * 10^{-6}$ mbar and $P(H_2) = 3 * 10^{-6}$ mbar.

$3 \cdot 10^{-6}$ mbar for each reactant. The crystal is heated slowly to about 600 K and cooled down afterwards to 460 K, where its temperature is held constant. During the heating procedure a sudden jump in N_2 production is observed around 450 K. This phenomenon is often described in terms of a surface explosion. Surface explosions have also been reported for the NO-H_2 reaction under TPD conditions in ultra high vacuum by Schmidth [17] et al. Recently, Ertl [18,19] et al. discussed this feature for the CO-NO reaction. During cooling oscillations occur in the temperature range 430–500 K. Once the oscillations have started the temperature of the crystal is kept constant. The temperature where the oscillations start depends on the total pressure. At higher total pressures the start of the oscillations occurs at higher temperatures. Long sustained oscillations, up to several hours, were observed.

A typical trace of the variation of the N_2 partial pressure as a function of time under oscillatory conditions is shown in fig. 2. The conditions are similar to those described in fig. 1. However, in the latter case a longer time was used for stabilization.

The selectivity of the NO-H_2 reaction performed under isothermal conditions at various NO/H_2 pressure ratios is shown in fig. 3. The partial pressures of N_2, NH_3 and N_2O are plotted versus time. The NO-H_2 partial pressure ratio is

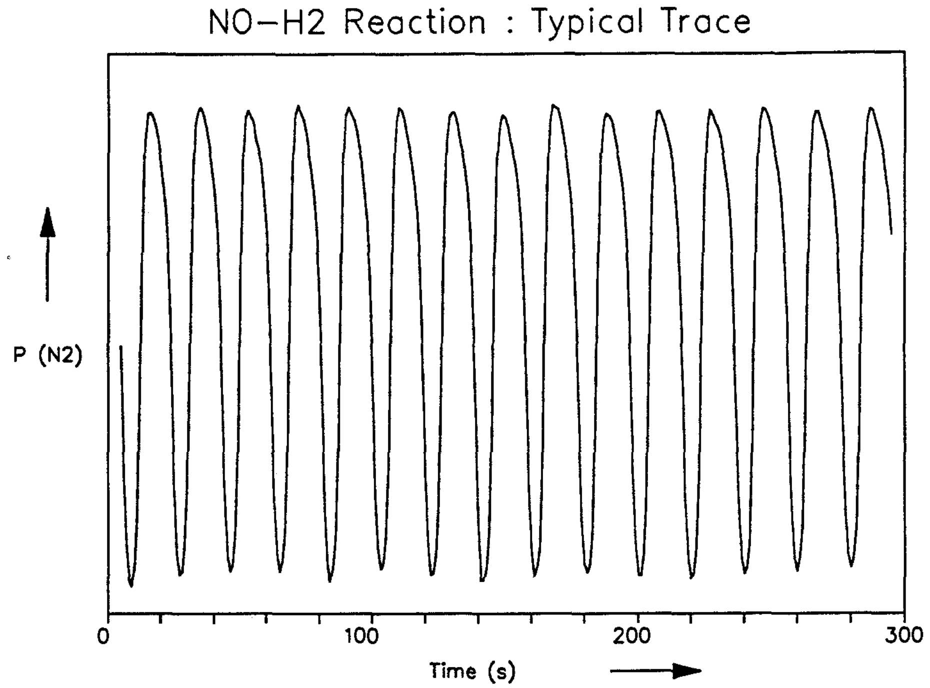

Fig. 2. Variation of the N_2 partial pressure during the NO-H_2 reaction as a function of time, $T = 460$ K, $P(NO) = 3 * 10^{-6}$ mbar and $P(H_2) = 3 * 10^{-6}$ mbar.

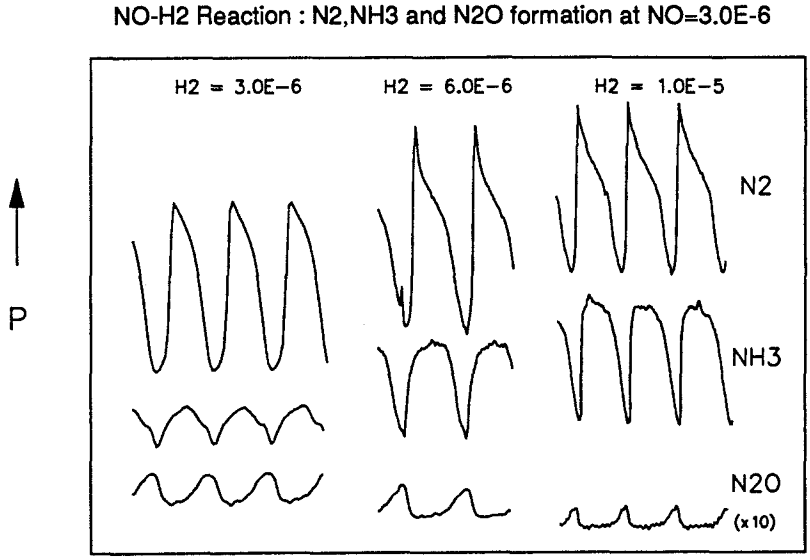

Fig. 3. Variation of the N_2, NH_3 and N_2O partial pressures during the NO-H_2 reaction as a function of time, $T = 460$ K. The partial pressures of NO and H_2 are indicated in the figure.

varied from 1 to 0.3. Increasing the hydrogen partial pressure only slightly increases the N_2 formation. However, the formation of NH_3 and N_2O are strongly affected by variation of the H_2 pressure. The formation rates of N_2, N_2O and NH_3 oscillate in time. Moreover, a high rate of N_2 formation is accompanied by a high rate of NH_3 formation. The production rates of N_2 and NH_3 are in phase. However, careful analysis revealed that the selectivity of the NO-H_2 reaction shows oscillatory behaviour. The selectivity of the reaction towards NH_3 changes from 70% at the high formation branch to 85% at the low formation branch using a NO/H_2 ratio of unity. The partial pressure of NO, which is not plotted in fig. 3, is out of phase with the formation rates of N_2 and NH_3. The formation rate of N_2O is out of phase with that of N_2 and NH_3, and decreases with increasing H_2 pressure. These results indicate that the formation of N_2O is competing with the formation of N_2 and NH_3.

4. Discussion

The adsorption of NO on Pt(100) has gained considerable attention [10–13]. It is well established that the clean Pt(100) is unstable in the (1 × 1) phase and transforms to the energetically more favourable (5 × 20) phase [8,9]. This surface is often regarded as a hexagonal structure because of its resemblance to the F.C.C.(111) surface which has hexagonal symmetry. However, NO lifts the reconstruction and the (1 × 1) phase returns [10–13]. Small amounts of adsorbates are sufficient to make the (1 × 1) phase energetically more favourable. The potential energy changes for NO adsorption on the two surfaces are schematically shown in fig. 4. On Pt(100)-(1 × 1) the activation energy for NO dissociation is relatively small and dissociation will occur, provided that empty sites (vacancies) are available [21]. Dissociation on the hex phase is negligibly small [20] due to the high activation energy required.

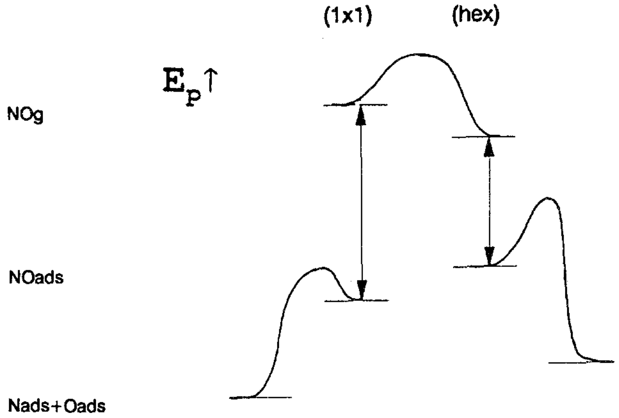

Fig. 4. A schematical representation of the potential energy changes for NO adsorption on the two surfaces.

Several mechanisms have been discussed to describe the phenomenon of oscillations in heterogeneous catalysed reactions [15]. According to Ertl the two main mechanisms for the occurrence of isothermal kinetic oscillations for CO-O_2 and CO-NO over Pt under low pressure conditions are [15]:

I. Autocatalytic surface reaction.

II. Adsorbate driven structural transformation.

Ertl [15] describes that the second mechanism applies to the CO-O_2 reaction over Pt(100) and (110) and the first one prevails for the CO-NO reaction over Pt(100), at least at low temperatures. Both mechanisms can in principle also be applied to the NO-H_2 reaction over Pt(100). The dissociation of NO plays a central role in the CO-NO reaction (mechanism I). The same arguments can be used for the NO-H_2 reaction over Pt(100). The nature of the course of the processes according to mechanism I will then be as follows:

1) At first the total NO coverage is high and dissociation of NO is inhibited due to a lack of vacancies.

2) A surface explosion occurs once a vacancy is created via NO desorption or reaction between $2H_{ads} + O_{ads}$. The rate constant for NO desorption does in fact depend on the coverage.

3) Oxygen is built up on the surface, i.e. the $O_{ads} + 2H_{ads}$ reaction is not very efficient due to a low H_{ads} coverage under the experimental conditions used. At a critical coverage the NO dissociation will be inhibited again.

4) The NO coverage will increase and after consumption of O_{ads} the initial situation is reached again. At high oxygen coverage the removal of O_{ads} and its replacement with NO from the gas phase will not lead to further reaction because the coverage of NO is low. In this model the surface reconstruction is not necessarily needed to explain the observed oscillations.

Mechanism II will proceed through steps 1 and 2, already described for mechanism I. However, steps 3 and 4 are slightly different:

3) The NO surface coverage drops below the critical value which is needed to keep the (1×1) phase stable. The surface will reconstruct back to the hex phase, which is not active in NO dissociation and, hence, the reaction rate decreases.

4) The NO coverage will increase and lift the surface reconstruction and restore the (1×1) phase.

Several refinements of the two mechanisms may be considered. For example, adsorbed NO molecules may form islands with a local coverage of 0.5 [18]. In these islands the dissociation of NO is inhibited due to a lack of vacancies. (point 1). It could be that both mechanisms apply to the NO-H_2 reaction over Pt(100). Mechanism I might be favoured at low temperature and high NO-H_2 ratios, whereas mechanism II may need higher temperature and H_2 rich conditions.

The results shown in fig. 1. can be rationalized as follows. Around 430 K NO starts to desorb slowly from the Pt(100)-(1 × 1) surface. Vacancies are created and a neighbouring NO molecule is able to dissociate. N_2 is formed, desorbs immediately and new vacancies are created. As a result, the N_2 production grows exponentially. The surface coverage of NO drops below the critical value for keeping the (1 × 1) structure stable and switches to the hex phase. During cooling, NO starts to adsorb around 470 K and the (1 × 1) phase is stabilized. The N_2-production rises sharply at this temperature. When the temperature is kept constant, the oscillations start, as shown in fig. 1.

In figs 2 and 3 the NH_3, N_2 and N_2O formation rates are shown versus time under the specified conditions. In a recent paper the mechanisms of the various nitric oxide reduction reactions were discussed. The main conclusions emerging from this study [7] are:

[A] N_2 can be formed by combination of two N adatoms in a wide temperature range (350–1300 K) provided that sufficient N adatoms are available.

{B] Below 600 K the main contribution to N_2 is via $NO_{ads} + N_{ads} \rightarrow N_2 + O_{ads}$. At higher temperatures the dominant mechanism is $2N_{ads} \rightarrow N_2$.

[C] N_2O and NH_3 are formed via $N_{ads} + NO_{ads} \rightarrow N_2O$, and $N_{ads} + 3H_{ads} \rightarrow NH_3$. The decomposition of N_2O may be determined by the availability of a vacancy. In the abscence of a vacancy N_2O desorbs, whereas it decomposes into N_2 and O_{ads} in the presence of a vacancy.

[D] The selectivities to N_2, NH_3 and N_2O are determined by the relative concentrations of NO_{ads}, N_{ads} and H_{ads}.

In the present study increasing the H_2 pressure results in an increasing NH_3 and N_2, and decreasing N_2O formation. The N_2 and NH_3 formation rates are in phase. A large number of vacancies (step 2), will result in a rapid NO dissociation and, as a consequence, the N_{ads} concentration increases. The formation of N_2 via 2 $N_{ads} \rightarrow N_2$, or $NO + N \rightarrow N_2 + O_{ads}$ and NH_3 via $N_{ads} + 3H_{ads}$ will increase. N_2 formation via $NO_{ads} + N_{ads} \rightarrow N_2 + O_{ads}$ requires a vacancy to decompose the N_2O intermediate. The NH_3 formation requires a high H_{ads} concentration, combined with N_{ads}. The adsorption of H_2 may require also one or more vacancies. This explains that N_2 and NH_3 formation will be in phase with each other. However, the selectivity towards NH_3 oscillates between 70% at the high activity branch to 85% at the low activity branch.

A very interesting observation is that the N_2O formation is out of phase with the N_2 and NH_3 formation rates. N_2O is formed via $N_{ads} + NO_{ads} \rightarrow N_2O$ [7]. The availability of a vacancy may determine whether N_2O is released into the gas phase or decomposed into N_2 and O_{ads}, as discussed above. In steps 1/4 of mechanisms I and II the number of available vacancies will be small. The N_2O_{ads} intermediate will leave the surface without decomposing into $N_{2,g}$ and O_{ads}. However, in step 2 vacancies are being created and the decomposition of N_2O_{ads} into N_2 and O_{ads} will increase. The model as described here explains the fact that the formation of N_2O is out of phase with that of N_2 and NH_3.

5. Conclusions

The NO/H_2 reaction displays clear oscillatory behaviour. The selectivity as well as the activity oscillates in time under isothermal conditions. More especially, the oscillatory behaviour of N_2, NH_3 and N_2O formation depends on the experimental conditions used. N_2O formation is out of phase with the formations of N_2 and NH_3. These observations are in agreement with recently proposed models for the mechanisms of N_2, NH_3 and N_2O formation [7].

References

[1] K.C. Taylor, in: *Automotive Catalytic Converters* (Springer, Berlin, 1984).

[2] W.C. Egelhoff Jr., in: *Chemical Physics of Solid Surfaces and Heterogeneous Catalysis,* Vol 4, ch. 9, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982).

[3] M. Shelef, Catal. Rev. Sci. Eng. 11 (1975) 1.

[4] R.M. Wolf, J. Siera, F.C.M.J.M. van Delft and B.E. Nieuwenhuys, Faray. Disc., Chem. Soc. 87 (1989) 275.

[5] M. Shelef and H.S. Ghandi, Ind. Eng. Chem. Prod. Res. Develop. 8, 4 (1972) 393.

[6] J. Siera, B.E. Nieuwenhuys, H. Hirano, T. Yamada and K.I. Tanaka, Catal. Lett. 3 (1989) 179.

[7] H. Hirano, T. Yamada, K.I. Tanaka, J. Siera, P. Cobden and B.E. Nieuwenhuys, Surf. Sci., submitted.

[8] S. Hagstrom, H.B. Lyon and G.A. Somorjai, Phys. Rev. Lett. 15 (1965) 491.

[9] M.A. van Hove, R.J. Koestner, P.C. Stair, J.P. Biberian, L.L. Kesmodel, I. Bartos and G.A. Somorjai, Surf. Sci. 103 (1981) 189.

[10] H.P. Bonzel and G. Pirurg, Surf. Sci. 62 (1977) 45.

[11] E. Ritter, R.J. Behm, G. Pötschke and J. Wintterlin, Surf. Sci. 181 (1987) 403.

[12] P. Gardner, M. Tushaus, R. Martin and A.M. Bradshaw, Surf. Sci. 240 (1990) 112.

[13] K. Mase and Y. Murata, Surf. Sci. 242 (1991) 132.

[14] G. Ertl, P.R. Norton and J. Rustig, Phys. Rev. Lett. 49 (1982) 177.

[15] G. Ertl, Adv. Catal. 37 (1990) 213.

[16] S.B. Schwartz and L.D. Schmidt, Surf. Sci. 206 (1988) 169.

[17] M.W. Lesley and L.D. Schmidt, Surf. Sci. 155 (1985) 215.

[18] Th. Fink, J-P. Dath, M.R. Bassett, R. Imbihl and G. Ertl, Vacuum 41, 1–3 (1990) 301.

[19] Th. Fink, J-P. Dath, M.R. Bassett, R. Imbihl and G. Ertl, Surf. Sci. 245 (1991) 96.

[20] J.M. Gohndrone and R.I. Masel, Surf. Sci. 209 (1989) 44.

[21] R.M. Wolf, J.W. Bakker and B.E. Nieuwenhuys, Surf. Sci. 246 (1991) 135.