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The NO– H_2 reaction over Pd(111)

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Abstract

The NO-H₂ reaction over Pd(111) was studied at NO pressures in the 1×10^{-7} mbar pressure regime and at temperatures between 300 and 750 K. The H₂/NO ratio was varied from 1 to 54. Hysteresis phenomena in the rate of NH₃ and H₂O formation were observed in a heating-cooling cycle and can be attributed to atomic hydrogen absorbed in the bulk. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

To meet the stringent exhaust emission regulations most cars are equipped with a so-called threeway catalyst [1,2]. For a long time a catalyst based on platinum and rhodium was used to simultaneously oxidise the CO and unburned hydrocarbons and reduce the NO_x. However, in 1992, 85% of the total world supply of rhodium and 43% of platinum were used for automobile catalysts [3]. Therefore, interest in the development of a palladium-only catalyst, and, due to the unique capability of rhodium to reduce NO, a Pd/Rh catalyst has grown. Not only is palladium less scarce and, hence, more economically attractive, it also has favourable oxidation activity at low temperatures and a high thermal stability. A major drawback of palladium in the past has been its high sensitivity to lead and sulfur poisoning. However, due to improved boundary conditions,

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such as the composition of the fuel and the advanced catalyst design, this disadvantage can now be satisfactorily overcome [3,4].

To obtain a more fundamental knowledge regarding the processes that take place in automotive catalysis, a number of surface science studies have been dedicated to the CO–O₂ and CO–NO reactions over palladium (see, for example, [5–15]). However, only a few papers exist on the NO–H₂ reaction, mainly concentrated on the Pd(100) surface [15–19].

In this paper we describe a study concerning the NO-H₂ reaction over Pd(111) single-crystal surface. It represents a part of more a extended research programme, with the main objective of understanding non-linear processes on various precious metal surfaces. Non-linear phenomena, such as oscillations, spatio temporal pattern formation and hysteresis phenomena, have already been observed by our group for the NO-H₂ reaction over Pt(100), Rh(111), stepped rhodium surfaces consisting of (111) terraces, Ru(0001), Ir(100), Ir(110) and stepped iridium surfaces with (100)

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terraces and (110) steps [20-23]. To our knowledge, only oscillations in the rate of CO oxidation over Pd(110) surface have been reported so far, in addition to explosive reactions in NO and CO coadsorption experiments over the three low-index planes of palladium [5-8,11].

2. Experimental

The measurements were performed in a standard ultrahigh vacuum (UHV) system equipped with facilities for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and a differentially pumped (60 l s⁻¹) quadrupole mass spectrometer. The base pressure of the system was always less than 5×10^{-10} mbar.

The palladium sample was cut from a singlecrystal palladium rod by spark erosion and polished within 1° of the desired direction. The crystal was spotwelded to a tantalum support and could be heated resistively up to 1600 K. The temperature was measured with a Pt–Pt/Rh thermocouple, which was spotwelded to the back of the crystal. The crystal was cleaned by repetitive cycles of oxygen treatment, Ar^+ -ion sputtering and flashing in UHV to 1600 K. The surface cleanliness and structure were checked by AES and LEED.

During the reactions the NO and H₂ pressures were kept constant while the system was pumped by a turbomolecular pump. Prior to the measurements the NO pressure was stabilised for more than 1 h and only the second and subsequent heat and cool cycles for each H₂/NO ratio were recorded. In this way the hysteresis phenomena proved to be reproducible. The crystal was turned in front of a small opening which gave access to a small chamber containing the mass spectrometer (MS) to increase the sensitivity and to minimise the contributions of the edges of the crystal. For NH₃, 16 amu was followed instead of 17 amu to decrease the contribution of the cracking product of H_2O (OH). The cracking pattern of N_2O was estimated to be 100% at 44 amu 30% at 30 amu and 10% at 28 amu.

The AES measurements were performed using a single-pass cylindrical mirror analyser with an incident electron energy of 2.0 kV. To check the influence of the electron beam on the reaction, a heat and cool cycle was performed directly after the AES measurements and the MS intensities were compared with previous measurements.

High-purity NO (99.5%) and H₂ (99.999%) gases were used without further purification. The pressure readings were corrected for the ionisation efficiencies of the ion gauge using relative sensitivities for NO and H₂ to N₂ of 1.3 and 0.46, respectively.

3. Results

To create a basis for the study of the NO– H_2 reaction, the interaction of NO with Pd(111) was studied first. Fig. 1 shows the thermal desorption (TD) spectra of NO adsorbed at 300 K. NO desorbs in a single peak, which shifts from 508 K for low NO coverages to 488 K for the saturation coverage. Small amounts of N₂ and N₂O, estimated as less than 5% at saturation, desorb around 495 K. Remarkably, the quantity of N₂ and N₂O that was formed did not change with increasing NO coverage. The minor amounts of oxygen atoms were removed by flash annealing to 1600 K as was confirmed by AES [30].



Fig. 1. TD spectra of NO (m/e=30), N₂ (m/e=28) and N₂O (m/e=44) after dosing various amounts of NO at 300 K. The heating rate is 5 K s⁻¹.

The NO-H₂ reaction over Pd(111) was studied in the temperature regime between 300 and 750 K at NO pressures ranging from 7.7×10^{-8} to 7.7×10^{-7} mbar and H₂/NO ratios varying from 1 to 54. The primary reaction products were N₂, NH₃, H₂O and small amounts of N₂O.

A typical example of the product formation during a heating-cooling cycle in the reaction mixture is shown in Fig. 2 for a H_2/NO ratio of 2.8. The consumption of NO starts around 470 K and leads to the formation of N₂, NH₃, H₂O and minor amounts of N₂O. Around 550 K the NO conversion and the formation of H₂O and NH₃ start to decrease, whereas the rate of N₂ formation is still increasing and reaches its maximum around 620 K. Around 750 K the surface has become completely inactive with respect to the NO conversion.

Upon cooling the NO conversion increases immediately and reaches it maximum around 540 K, and, simultaneously, the rates of N_2 and H_2O formation begin to increase. A minor amount of N_2O starts to be formed around 670 K. Accompanied by the increase in the rate of NH_3 formation, the N_2 formation rate starts to decrease



Fig. 2. The rates of NO conversion and N₂O, NH₃, H₂O and N₂ formation during a heating–cooling cycle at an NO pressure of 7.7×10^{-7} mbar and an H₂/NO ratio of 2.8. The heating and cooling rate is 1.6 K s⁻¹.

around 620 K, while the NH_3 and H_2O partial pressures reach their maximum when the temperature is further lowered to 530 K. Around 400 K the NO can no longer dissociate on the surface and the reaction is stopped.

As can be seen from Fig. 2, between roughly 470 K and 600 K small hysteresis phenomena in the rate of H_2O and NH_3 formation occur during the heating–cooling cycle for the NO– H_2 reaction over Pd(111). Note that the gradual increase of the background pressures of H_2O and NO is caused by the slow pumping rate of these gases.

To examine the influence of the H_2/NO ratio on the product formation, a series of heating– cooling cycles were performed with increasing H_2 pressure. Fig. 3 shows the results for the heating branch. No hysteresis phenomena in the N_2 and N_2O formation rate were observed for the ratios studied. The rates of NH_3 and H_2O formation were always more pronounced on the cooling branch and shifted to slightly lower temperatures with respect to the heating branch.

From Fig. 3 it is clear that the onset of the main N₂ formation shifts from around 450 K at $H_2/NO = 1$ to ca. 600 K at $H_2/NO = 54$. In addition to the aforementioned N₂ maximum, a low-temperature maximum is observed which becomes more pronounced at higher H₂ pressures. Precisely in between the maxima in the rate of N₂ formation, a peak in the NH₃ formation is observed which shifts to higher temperatures upon increasing the H₂/NO ratio.

The results in Fig. 3 were used to quantitatively compare the reaction orders in H₂ for the formation of N₂, NH₃ and N₂O. For that purpose, the slopes of the ln [product] versus $\ln[p(H_2)]$ plots were determined at a temperature at which all products were formed simultaneously, i.e., at 567 K. The pressures of the product gases were corrected for the background pressures of these gases at zero catalytic activity.

The dependence of the three nitrogen-containing reaction products on the H₂ pressure is shown in Fig. 4. The order in H₂ of the N₂ formation becomes strongly negative at H₂/NO ratios over 14, whereas the order for NH₃ formation is positive, but becomes less so at H₂/NO ratios over 2.8. The order in H₂ of the N₂O formation was



Fig. 3. The rates of N_2 , NH_3 and N_2O formation during the heating branch of a heating–cooling cycle at an NO pressure of 7.7×10^{-7} mbar and H_2/NO ratios of 1, 2.8, 5.6, 14, 25 and 54. The H_2/NO ratio increases in the direction of the arrows. The heating rate is 1.6 K s⁻¹.



Fig. 4. A schematic representation of the reaction orders in H_2 at 567 K for the formation of N_2 , NH_3 and N_2O at various H_2/NO ratios, based on the results of Fig. 3. The NO pressure was 7.7×10^{-7} mbar.

slightly negative over the whole range of measured H_2/NO ratios.

For a better understanding of the observed phenomena, AES measurements were performed during the heating-cooling cycle. In this way some knowledge on the nitrogen species present on the surface during the reaction may be obtained. The N_{381 eV} peak-to-peak height was measured and normalised against the Pd_{279 eV} peak to exclude the influence of a fluctuating electron beam. The results are shown in Fig. 5 for the heatingcooling cycle at $p(NO)=1.5 \times 10^{-7}$ mbar and H₂/NO=28. The O_{510 eV} signal remained very low during the heating–cooling cycle, indicating that O_{ads} is removed by hydrogen as soon as it is formed. NO_{ads} is not visible at this energy due to shielding.

At room temperature a $N_{381 eV}$ signal is measured whose intensity gradually diminishes upon heating the surface. Around 520 K, N_2 starts to leave the surface and at 560 K the $N_{381 eV}$ peak has completely vanished. On the cooling branch the decrease in the rate of N_2 formation, which starts around 600 K, was accompanied by an increase in the rate of NH₃ formation. In addition, the $N_{381 eV}$ signal starts to increase around 560 K,



Fig. 5. The N_{381 eV}/Pd_{279 eV} AES signal ratios in addition to the NH₃ and N₂ formation rates at an NO pressure of 1.5×10^{-7} mbar and an H₂/NO ratio of 28. The solid symbols represent the heating branch and the open symbols represent the cooling branch.

thus deviating from the heating branch. The rate of NH_3 formation reaches its maximum around 500 K. At the same temperature the growth of the $N_{381 eV}$ signal starts to level. Around 410 K the $N_{381 eV}$ signal collides again with the one of the heating branch.

No indication of any oscillatory behaviour was found under the conditions studied.

4. Discussion

The interaction of NO with Pd(111) has previously been investigated by several authors [24– 32]. From these studies it was concluded that NO is molecularly adsorbed in the temperature range between 100 and 373 K. Upon heating only minor dissociation takes place, presumably at active sites like steps or kinks. The N_{ads} recombines with N_{ads} or NO_{ads} to form N_2 or N_2O , respectively [25,30,31]. Since the amount of N_2 and N_2O desorbing from the surface in this study proved to be independent of the NO coverage, we conclude that the dissociation can be mainly attributed to the presence of some more active sites.

In the temperature regime above 370 K, NO desorbs in one single peak [26,28,29]. Although the peak temperature shifts to lower temperatures upon increasing the NO coverage, the desorption of NO can be considered as a first-order process, the temperature shift being caused by a coveragedependent activation energy for desorption [24,25,28,30]. Using this assumption, the activation energy for desorption and the pre-exponential factor in the low coverage limit were calculated by the Chan-Aris-Weinberg method [33]. A value of 100 kJ mol⁻¹ was found with a pre-exponential factor of $1 \times 10^{9.6}$ s⁻¹, which is within the range of the values calculated by Ramsier et al. [30] who found pre-exponential factors ranging from 10¹⁷ to 10^8 s^{-1} and activation energies of ca 180 to 90 kJ mol⁻¹ depending on the NO coverage. According to these authors, strong repulsive interactions between the adsorbed NO molecules lower the kinetic parameters at higher NO coverages. Therefore, it is likely that the highest value of the activation energy reported by Ramsier et al. was determined at a lower NO coverage in comparison with the lowest exposure of Figure 1. The difference may also be partly attributed to a higher concentration of defect sites or to the presence of residual O_{ads} on the crystal used in this study. This is supported by the results of Schmick et al. [25] who found values for the activation energy of desorption ranging from ca 146 to 71 kJ mol⁻¹ on a stepped Pd(111) surface exhibiting average terrace widths of 16 atoms that was pre-exposed to 0.75 L O₂.

Clearly, the high desorption temperature and low dissociation probability of NO influence the rate of the NO-H₂ reaction at low temperatures. As can be seen in Fig. 2, no reaction takes place until some NO molecules desorb from the surface around 500 K. The creation of vacant sites allows NO to dissociate into N_{ads} and O_{ads}. Subsequently, N₂ is formed in addition to the formation of N₂O, via N_{ads}+NO_{ads}→N₂O(g). The formation of intermediate NO dimers, which was suggested for Pd(100) [34] and Pd(111) [25], was excluded for Pd(111) on the basis of more recent high-energy electron energy-loss spectroscopy (HREELS) results [28]. The formed O_{ads} immediately reacts with two hydrogen atoms to form H₂O(g) [15]. The origin of the atomic hydrogen will be discussed later.

Below the desorption temperature of NO, the major pathways to N_2 formation over precious metal surfaces are either the recombination of two adsorbed nitrogen atoms, or a disproportionation reaction between adsorbed NO and N [35]. Both reactions were used to describe the N_2 formation over platinum, rhodium and platinum–rhodium alloy surfaces [36–46], although in recent studies on Rh(111) and Rh(100) the latter reaction path was excluded [45,46]. The presence of a low-temperature N_2 peak in the TD spectrum shown in Fig. 1, which coincides with the NO desorption peak, might suggest that the disproportionation reaction may play a minor role over Pd(111).

Further heating of the Pd(111) surface in the reaction mixture leads to the formation of NH₃. As can be seen in Figs. 3 and 4, the formation of N_2 and NH₃ are competitive processes in the temperature regime between 500 and 700 K for the highest H_2/NO ratios and between 500 and 600 K for lower ratios. The rate of NH₃ formation shows a positive order in the H_2 pressure. The higher positive order at low H_2/NO ratios is caused by the temperature shift of the maximum in the rate of NH₃ formation towards T = 567 K. The order in H₂ for the N₂ formation is slightly negative and becomes very negative when increasing amounts of NH₃ start to be formed. Due to the removal of $N_{ads}\xspace$ by H, the formation of N₂O is also negatively influenced by an increase in the H_2 pressure.

For $H_2/NO = 2.8$, the formation of N_2 becomes more favourable above 560 K. According to the TDS results of Fig. 1, only minor amounts of molecular NO are present on the surface at this temperature. As a consequence, the formation of N_2O is becoming negligible and the only way to N_2 formation is by the recombination of N_{ads} atoms. In addition, the rate of NO consumption starts to decrease. This can be understood if one considers the low tendency of NO to dissociate on Pd(111). In other words, the residence time of NO on the surface is simply to short to dissociate at temperatures above its desorption temperature.

On lowering the temperature, the NO consumption rate increases again, resulting in the formation of N_2 and H_2O . Around 660 K the temperature is low enough to allow NO_{ads} to react with N_{ads} to form N_2O . At a slightly lower temperature NH_3 also starts to be formed.

To understand the hysteresis in the hydrogencontaining species, knowledge on the interaction between H_2 and Pd(111) is indispensable. Over the years a lot of research has been performed on this subject [47-54]. From these studies it was concluded that hydrogen adsorbs dissociatively on Pd(111) and can penetrate into the subsurface region already at 90 K. At temperatures above 350 K diffusion from the subsurface to the bulk can take place. Furthermore, it was found that in the H₂O formation the reaction between O_{ads} and H from the bulk is preferred over the reaction of O_{ads} with H adsorbed on the surface [19,55]. Therefore, the rate of H₂O formation is dominated by the transport of atomic hydrogen between the bulk and the surface. The presence of major amounts of O_{ads} can slow down the diffusion rate and, hence, the rate of H₂O formation [55].

Using this information the increased rate of NH₃ and H₂O formation on the cooling branch with respect to the heating branch can be understood as follows. On the heating branch the amount of bulk H is limited due to the low temperature, which does not support bulk diffusion, in combination with a high surface coverage of NO and possibly some O_{ads} that hinders the dissociative hydrogen adsorption. On the beginning of the cooling branch, however, both the temperature and the abundance of vacant sites promote the diffusion of atomic hydrogen into the bulk. Since H_2O is mainly formed by the reaction of O_{ads} with bulk H, an increased supply of bulk H will lead to a higher reaction rate. Most likely, the same reaction path holds for the formation of NH₃. Moreover, the fast removal of N_{ads} and O_{ads} creates vacant sites that promote the dissociative adsorption of NO and, hence, increase the total reaction rate.

The presence of bulk H also explains the formation of NH_3 already at H_2/NO ratios as low as 1 (Fig. 3).

As can be seen in Fig. 5, a nitrogen-containing species is built up on the surface during the NH₃ formation on the cooling branch. Unfortunately, using conventional AES, no distinction can be made between N, NH_x and NO. However, since NH₃ is the only reaction product under these conditions and the formation of NH_{2'ads} is considered to be the rate-determining step in the NH₃ formation, this species can probably be assigned to NH_{ads} in combination with molecular NO [15]. This indicates that the dissociation of NO is faster than the rate of NH₃ formation under these conditions.

The nitrogen-containing species on the cooling branch at temperatures lower than 420 K and the nitrogen-containing species on the heating branch of Fig. 5 are primarily connected to NO_{ads} , because now the dissociation rate of NO is rather slow.

5. Conclusions

After adsorption at 300 K, NO desorbs in one single peak from the Pd(111) surface, with an activation energy of desorption of 100 kJ mol^{-1} and a pre-exponential factor of $1 \times 10^{9.6} \text{ s}^{-1}$. Only minor amounts of N₂ and N₂O were formed during temperature-programmed desorption.

During the NO– H_2 reaction over Pd(111), three nitrogen-containing products were observed: N_2 , NH₃ and N₂O.

Hysteresis phenomena in the rate of NH_3 and H_2O formation were observed during a heatingcooling cycle in the reaction mixture. The cooling branch showed a higher activity for the formation of hydrogen-containing species than the heating branch, probably due to the bigger supply of atomic hydrogen dissolved in the bulk. Both H_2O and NH_3 are considered to be formed by the reaction between bulk H and O_{ads} , respectively, with N_{ads} . No hysteresis phenomena were observed in the rate of N_2 formation.

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