Interaction of NO with alumina supported palladium model catalysts

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The interaction of NO with a well-defined supported Pd model catalyst has been investigated, employing a combination of IR reflection absorption spectroscopy (IRAS) and molecular beam methods. The model catalyst is based on an ordered Al₂O₃ film, grown on NiAl(110) and has been characterized in detail with respect to its geometric and electronic structure previously. In a first step the interaction of NO with the pure Al₂O₃ model support is studied. It is observed that NO slowly decomposes at low surface temperature (100 K), resulting in the formation of a variety of $N_x O_y$ surface species. The decomposition process involves strong structural transformations of the Al₂O₃ film and is initiated at oxide defect sites. The adsorption of NO on the Pd/Al₂O₃ model system is explored systematically as a function of surface coverage and temperature. For NO adsorption on the Pd particles, characteristic absorption bands are identified by comparison with single crystal data, which are indicative of particle-specific sites such as edges and other defects. At 300 K and above NO dissociation occurs on the Pd particles, whereas the low-temperature decomposition channel on the alumina support is found to be strongly suppressed in the presence of the Pd particles. Finally, co-adsorption of NO with oxygen- and CO-precovered Pd particles is investigated. Preadsorbed oxygen results in the formation of a mixed adsorbate layer with an enhanced NO population of on-top sites on the particles. NO adsorption on a CO layer, on the other hand, gives rise to a compression of the CO layer and an enhanced population of on-top sites by CO.

1. Introduction

Most heterogeneous catalysts are characterized by a complex surface structure and composition, which is optimized empirically in order to maximize activity and selectivity for the reaction of interest. In the case of supported catalysts, the reaction mechanism and kinetics is often found to depend sensitively on factors such as the particle size, particle structure, the support and the presence or absence of promoters and poisons. Although this type of effects have been discussed for a long time (see *e.g.* ref. 1), their molecular origins could be identified in very few cases only (*e.g.* see refs. 2 and 3 and references therein). This lack of thorough understanding arises as a result of two factors: first, a structural characterization of real catalysts on a molecular basis proves to be difficult, and secondly, sufficiently detailed experimental data on the surface kinetics is not available in most cases.

In order to overcome these problems, we follow a twofold approach: We employ model catalysts,^{4,5} which provide a reduced level of complexity and can be easily investigated using a variety of surface science techniques.^{2,3,6–8} In this work, we use a well-defined Pd/Al₂O₃ model catalyst, which was characterized in detail previously,^{6,9,10} and we will fall back on these studies for information on its geometric and electronic structure.

With the aim of correlating structural information with detailed data on the adsorption behavior and reaction kinetics, we employ molecular beam techniques^{11–13} combined with *in-situ* vibrational spectroscopy. From this type of combined experiment, detailed insight into qualitative and quantitative aspects of reactions on complex catalyst surfaces can be derived, as we have recently demonstrated for several reaction systems (see *e.g.* refs. 14–17).

In the work reported here, we focus on the adsorption, dissociation and reduction of NO. Recently, the catalytic reduction of NO_x has attracted considerable attention in environmental catalysis due to the fact that modern lean-burn engines produce oxygen-rich exhaust gas conditions, under which conventional three-way catalysts may not operate efficiently.¹⁸ As a result, alternative reduction pathways involving e.g. hydrocarbons and nitrogen storage mechanisms have been considered (see e.g. refs. 19-21). Scientifically, these attempts introduce several new aspects to the fundamental work in this field. On the one hand, the origin of size and structure dependent effects and their relation to the kinetics is of pivotal importance. Here, the use of supported Pd catalysts has been suggested in addition to the more traditional Rd and Pt based systems (see e.g. refs. 22-24 and references therein). Surface science experiments on the origin of structure dependent reactivity effects have been performed both on Pd single crystals²⁵⁻³⁰ and on supported Pd model catalysts.^{31,32} As a second aspect, the interaction of NO_x with oxide supports becomes incre-asingly important, ^{20,33,34} but has received little attention in fundamental studies yet.

In the current work, we utilize molecular beam methods and *in-situ* IRAS (IR reflection absorption spectroscopy) in order to address these questions. We investigate the mechanism and kinetics of NO adsorption and reaction on the well-defined Pd/Al₂O₃ model system described above. In this paper, we summarize experimental results on the adsorption and decomposition of NO with the pristine Al₂O₃ model support as well as adsorption and co-adsorption of NO on the Pd model catalyst. The work is intended to serve as a basis for the interpretation of kinetic studies on the NO dissociation and reduction, which will be published elsewhere.^{35,36}

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2. Experimental

All experiments were performed in a UHV molecular beam apparatus at the Fritz-Haber-Institute (Berlin) which allows up to three beams to be crossed on the sample surface.³⁷ Two molecular beams are generated by doubly differentially pumped effusive sources and one beam is prepared from a supersonic expansion. The NO beams (NO: Messer Griesheim, 99.5%; ¹⁴NO: Messer Griesheim, >99.5%; ¹⁵NO: Linde, >99 atom% ¹⁵N) were further purified by cold traps before use. For experiments involving large exposures, effusive beams with a typical beam intensity of 2.8×10^{14} molecules cm⁻² s⁻¹ were employed. For experiments at low NO exposures, on the other hand, a supersonic NO beam was used, which by means of a mechanical chopper was attenuated to a flux of typically 9.5 \times 10^{12} molecules cm⁻² s⁻¹. Residual gas spectra were recorded with an automated quadrupole mass spectrometer system (ABB Extrel). IR spectra were acquired using a vacuum FT-IR spectrometer (Bruker IFS 66v/S) at a spectral resolution of 2 cm⁻¹. In most cases the spectra were recorded simultaneously with the gas exposure.

The alumina film was prepared by sputtering and annealing of a NiAl(110) single crystal, followed by an oxidation and annealing procedure, the details of which are given elsewhere.³⁸ Cleanliness and quality of the oxide film were checked via LEED (Low Energy Electron Diffraction) and AES (Auger Electron Spectroscopy). Before the experiment, Pd (>99.9%) was deposited by evaporation from a rod using a commercial evaporator (Focus, EFM 3) based on electron bombardment (Pd coverage: 2.7×10^{15} cm⁻², sample temperature: 300 K). The evaporator flux was calibrated by a quartz microbalance prior to use. In order to avoid damage by ion bombardment, the sample was biased during Pd evaporation. Unless stated otherwise, the Pd particles were stabilized after preparation by extended exposure to oxygen $(2.7 \times 10^{14} \text{ molecules cm}^{-2})$ s^{-1} , 2400 s, sample temperature 495 K) and followed by surface oxygen removal by CO titration^{9,10} and temperatureprogrammed desorption of CO.

3. Results and discussion

3.1. Structure of the Al_2O_3 model support and the Pd model catalyst

Before we discuss NO adsorption, we briefly summarize the previous results on the structure of the $Al_2O_3/NiAl(110)$ model support and the Pd particles on $Al_2O_3/NiAl(110)$ used in this study. More detailed structural information as well as data on adsorption properties can be found elsewhere.^{6,9,38} A scanning tunneling microscopy (STM) image of the alumina film is displayed in Fig. 1(a). The film is well-ordered and atomically flat. An important aspect for the current study concerns the defect structure of the film, which has been investigated in great detail.^{6,38} Apart from steps on the NiAl substrate, the most important defect structures are oxide domain boundaries, which appear as bright lines in Fig. 1(a) as well as point defects. For details we refer to the literature.

The oxide defects play a pivotal role for the growth of metal particles, since they tend to act as preferential nucleation centers. In Fig. 1(b) STM images of the Pd particles on the NiAl substrate are displayed. The aggregates preferentially nucleate at oxide domain boundaries and other defects. For the specific system considered in this work, the three dimensional Pd particles are characterized by an average size of 5.5 nm and contain about 3000 Pd atoms each. The majority of particles exhibits the morphology of well-shaped crystallites. These crystallites grow in (111) orientation and are predominantly terminated by (111) facets. Additionally, a small fraction of (100) facets is exposed. For the given preparation conditions



Fig. 1 (a) STM image of the Al₂O₃ film on NiAl(110) (1000 nm × 1000 nm), from ref. 88 (b) STM image of the Pd particles, grown on the Al₂O₃ film on NiAl(110) (300 nm × 300 nm). The inset shows a differentiated close-up (20 nm × 20 nm), from ref. 9 (c) Schematic representation of the Pd crystallites.

the particle density was $1.0 \ (\pm 0.2) \ \times \ 10^{12} \ \text{cm}^{-2}$. About 20% of the support surface is covered by Pd particles. For experiments requiring elevated temperatures the system has to be stabilized by oxygen treatment at elevated temperatures followed by oxygen removal by CO titration and thermal removal of adsorbed CO. Details concerning the experimental procedure have been published previously.^{9,10} Note that neither the particle shape nor density are affected by this procedure, but the oxide substrate is modified. Unless stated otherwise, all systems have been subject to this treatment prior to use.

3.2. NO interaction with the pristine Al₂O₃ model support

In the first step we investigate the interaction of NO with the pristine $Al_2O_3/NiAl(110)$ by *in-situ* IRAS during exposure to a molecular beam of NO (see Fig. 2). Here, we restrict ourselves to a brief description. A more detailed analysis can be found elsewhere.³⁹

At 100 K, a rather complex behavior is observed (see Fig. 2(a)): A relatively large NO exposure of approximately 22×10^{15} molecules cm⁻² (approximately 60 L; 1 L (Langmuir) = 10^{-6} Torr s corresponds to 3.7×10^{14} NO molecules cm⁻² at



Fig. 2 (a) IR spectra acquired during exposure of the pristine Al_2O_3 film on NiAl(110) to a molecular beam of NO at a sample temperature of 100 K; (c) the same experiment as in (a) but performed at a sample temperature of 300 K.

300 K) is required before first indications of a weak absorption band (3) around 1620 cm^{-1} appear. LEED (Low Energy Electron Diffraction) studies in the same region of exposures reveal that, simultaneously with the appearance of the IR signal, the characteristic LEED pattern of the oxide film vanishes (see also ref. 40). With increasing exposure, the band slowly grows in intensity, before at even higher NO doses $(1 \times 10^{17} \text{ molecules cm}^{-2}, 270 \text{ L})$ a second band (2) emerges around 1690 cm⁻¹, which finally dominates the spectrum. Subsequently, peaks become visible at 1880 cm⁻¹ (1) and 1304 (4) at NO doses exceeding 2×10^{17} molecules cm⁻² cm^{-1} (540 L) and finally a weak band at 1260 cm^{-1} (5) around 5×10^{17} molecules cm⁻² (1400 L). Up to the maximum NO dose used in this experiment $(10^{18} \text{ molecules cm}^{-2}, 2800 \text{ L})$ all bands with the exception of feature (3) grow in intensity continuously.

In contrast to the spectra at 100 K, a rather inert behavior is found for NO exposure at 300 K (Fig. 2(b)). Only at NO doses exceeding 10^{18} molecules cm⁻² (2800 L) a very weak and narrow band is observed at 1604 cm⁻¹.

The observations described above can be interpreted on the basis of previous work on NO adsorption on different oxide⁴¹⁻⁴³ and metal surfaces (see refs. 43–51 and references therein). In addition to the work under UHV conditions, IR experiments at ambient pressures have been performed on bare alumina⁵²⁻⁵⁴ and on mixed oxides^{33,34} (see ref. 55 for a recent review).

Based on this work, we tentatively assign the absorption band (3) at 1620 cm^{-1} to a strongly bound nitrogen–oxo surface species (see ref. 39 for a detailed discussion). Typically, bands in this region are assigned to surface nitrates, nitro or nitrito species.⁵⁵ The slow adsorption kinetics and simultaneous loss of the oxide LEED pattern (see also ref. 40) indicates that the adsorption process is facilitated by a structural change of the oxide surface, possibly also involving some redox process. Preferential sites at which such a restructuring process might be initiated are the various types of line and point defects on the oxide film (see section 3.1). The NO adsorption behavior on the Pd modified alumina film as described in section 3.3 supports this hypothesis.

The band (2) at 1690 cm⁻¹ is assigned to a second nitrogenoxo species, which is only formed after substantial surface reconstruction, *i.e.* at a sufficiently high density of the first NO species at 1620 cm⁻¹. The appearance of the feature (2) is followed by an emerging high-frequency absorption band (1) at 1880 cm⁻¹. Absorption features in this frequency range have previously been assigned to the formation of NO dimers^{47,48,50} and asymmetric dimers. Analogous to this interpretation, we tentatively assign band (1) at 1880 cm⁻¹ to a dimer-like NO species adsorbed on the NO derived species (1690 cm⁻¹).

On many surfaces, NO dimers decompose *via* formation of N₂O and oxygen.^{46,48–50} It is noteworthy, that this reaction can occur at cryogenic temperatures both on metal⁴⁸ and on oxide surfaces.⁵⁶ Typically, N₂O can be identified *via* two characteristic bands in the region of 1250–1320 and 2230–2270 cm^{-1.48,50} Thus, the bands (4) and (5) appearing in the low-frequency region may contain a contribution from adsorbed N₂O. However, no indication of absorption bands in the N₂O high-frequency region are observed, suggesting that N₂O, if formed during exposure, rapidly desorbs under the reaction conditions applied (compare *e.g.* ref. 50).

Another point to be taken into account is that NO decomposition and N₂O desorption necessarily result in the accumulation of surface oxygen. In the presence of reactive oxygen species, NO could be converted to various higher oxidized species such as *e.g.* surface nitrites and nitrates. Several types of such nitrogen and oxygen containing entities have been suggested, (see *e.g.*, refs. 33,34,52,53,55 and references therein), typically give rise to a variety of bands in the frequency range between 1000 and 1600 cm⁻¹. Features (4) and (5) and possibly also the broadening of band (1) can be tentatively assigned to the formation of such nitrogen–oxo surface species.

Finally, it should be noted that at 300 K almost no indications can be detected for a similar surface chemistry as observed at 100 K. Up to the highest NO doses, the surface remains practically inert. A possible reason for this effect is the weak initial adsorption of NO, which results in rapid desorption and thus prevents a restructuring similar as in the lowtemperature case. Consequently, the following steps involving dimer formation and decomposition are inhibited as well.

3.3. NO adsorption on the Pd model catalyst

The adsorption of NO on the Pd particles supported on $Al_2O_3/NiAl(110)$ is discussed in two steps. First, a comparison is made between the interaction of NO with the pristine alumina film on the one hand and the Pd covered film on the other. In the second part, we analyze the coverage and temperature dependence of NO adsorption on the Pd particles in detail.

In Fig. 3, IR spectra of Al₂O₃/NiAl(110) and Pd/Al₂O₃/ NiAl(110) (not stabilized, see section 3.1) are shown, which were recorded at different NO doses during exposure to a NO beam at a sample temperature of 100 K. The range of NO doses corresponds to the series of spectra displayed in Fig. 2(a). For the pristine alumina film, we find the characteristic absorption bands at 1880, 1690, 1630, 1304 and 1260 cm⁻¹, indicating the different steps of NO adsorption and decomposition as discussed in the previous section. In the case of the Pd covered sample a completely different behavior is observed. Whereas at NO exposures up to 11×10^{15} molecules cm^{-2} (30 L) no absorption signals are observed on the pristine alumina film, the spectrum of the Pd covered system has already reached its full integral absorption level. Three principal spectral regions are identified with bands at 1750 cm^{-1} (I), 1620 cm^{-1} (II) and 1542 cm^{-1} (III). The absorption features



Fig. 3 Comparison of IR spectra acquired during exposure of the pristine Al_2O_3 film (gray traces) and the Al_2O_3 film partially covered by Pd particles (black traces, not stabilized by oxygen treatment, see text) to a molecular beam of NO at a sample temperature of 100 K ((a)–(d): different NO doses).

are subject to a very slow change affecting mainly the dominating absorption band at 1750 cm^{-1} , which develops a highfrequency shoulder at 1775 cm^{-1} . Most importantly, however, the most characteristic bands for NO decomposition on the alumina film remain absent. Only at the highest coverage, a weak feature at 1690 cm⁻¹ appears, which coincides with the band observed on the pristine alumina film.

The rapid saturation of the absorption bands for NO adsorbed on Pd is expected for NO chemisorption on the metal surface, which in contrast to nitrogen–oxo compound formation on the alumina, proceeds with a high sticking coefficient and without an appreciable activation barrier. Thus, we can immediately attribute all bands observed at low exposure $(11 \times 10^{15} \text{ molecules cm}^{-2}, \text{ Fig. 3(a)})$ to a molecular NO species on the Pd particles. A detailed assignment of the features is given below, together with their coverage and temperature dependencies.

Comparing the NO spectra on the Pd covered and Pd free support, the most surprising observation is the absence of all bands which are characteristic for the surface restructuring and NO decomposition process. The only indication for a beginning slow restructuring of the oxide support at the highest NO exposure is a weak feature at 1690 cm^{-1} , which could be a signature of a minor amount of NO reacting with the oxide substrate. This observed inertness of the oxide suggests that the corresponding low-temperature dissociation channel is strongly inhibited on the Pd covered film. A possible explanation for this difference would be that the reaction with the support, involving redox processes and restructuring of the oxide film, may require specific defect sites, at which the process is initiated (see also ref. 39). From growth studies (see section 3.1) it is known that the Pd particles preferentially nucleate at antiphase domain boundaries of the film, thus efficiently covering these sites. We conclude that specific sites at these domain boundaries are responsible for the low-temperature NO decomposition pathway and their blocking by metal deposition leads to the observed inertness. Currently, a lowtemperature STM study is in progress, which may reveal additional information on the local atomic structure of the oxide domain boundaries and the corresponding NO dissociation sites (see ref. 57 for first results).

The origin of the slow change in the absorption band (I) at 1750 cm^{-1} , which is assigned to NO adsorbed at on-top sites on the Pd particles (see below), remains unclear. There are two possible explanations for the fact that the band develops a high-frequency shoulder. First, the new band at 1775 cm⁻ may be due to the presence of a surface contamination. A possible candidate would be co-adsorbed oxygen, which e.g. might be produced via NO decomposition on the support. This appears unlikely, however, as the shoulder emerges well before first indications for NO derived species on the support (1690 cm^{-1}) are detected. Moreover, we investigate oxygen coadsorption in section 3.4 and show that not only the on-top NO band is blue-shifted in the presence of co-adsorbed oxygen but other absorption features as well. In the view of these findings it appears improbable that co-adsorbed oxygen is the source of the slow spectral change in the on-top region. An alternative explanation would be the slow formation of a high-coverage adsorbate structure. Due to the low mobility within the adsorbate layer and the low sticking coefficient at high coverage this structure may develop only slowly and at high NO doses.

The development of the IR spectra at low NO exposure is displayed in Fig. 4(a), and the corresponding integral intensities in the different spectral regions are shown in Fig. 4(b). The spectra were recorded during admission of a low intensity molecular beam of NO to the stabilized $Pd/Al_2O_3/NiAl(110)$ model catalyst (see section 3.1). Note that the highest NO dose in Fig. 4 corresponds to the lowest dose in Fig. 3. Minor differences between the corresponding spectra may be due to the



Fig. 4 (a) IR spectra acquired during exposure of the Pd particles supported on the Al_2O_3 film on NiAl(110) (stabilized by oxygen treatment, see text) to a molecular beam of NO at a sample temperature of 100 K; (b) Integral absorption of the different IR bands in the three frequency regions indicated in (a).

stabilization procedure applied in case of the experiment in Fig. 4.

In the low coverage limit a band (III) at 1525 cm⁻¹ is observed. At NO exposures around 8×10^{13} molecules cm⁻² (0.2 L), a second absorption band (II) around 1640 cm⁻¹ appears, and subsequently, at exposures around 2×10^{14} molecules cm⁻² (0.5 L) a sharp band (I) at 1735 cm⁻¹ emerges, which dominates the spectrum at higher coverage. With increasing NO dose, all bands shift to slightly higher energy and bands (II) and (III) develop low-frequency shoulders (1620 and 1548 cm⁻¹), dominating over the higher frequency features at higher exposure.

A comparison of analogous spectra is shown in Fig. 5 as a function of the sample temperature in the range between 100 and 300 K and for two representative NO doses $(2.6 \times 10^{14}$ molecules cm⁻² or 0.7 L and 4.8×10^{15} molecules cm⁻² or 13 L). Whereas qualitatively the same features are observed in all cases, the intensity of the bands strongly depends on the sample temperature. In region (I), the absorption band at 1750 cm⁻¹ strongly decreases for temperatures above 140 K. We note, however, that a weak band at 1734 cm⁻¹ remains even at a sample temperature of 300 K. In general, the bands in region II (1655–1660 and 1625–1630 cm⁻¹) and III (1570 and 1546–1552 cm⁻¹) are not attenuated, but rather gain intensity with increasing adsorption temperature. At 300 K and for an exposure of 4.8×10^{15} molecules cm⁻² (13 L), four absorption signals are observed at 1734, 1655, 1630 and 1546 cm⁻¹.

On the basis of the discussion above, all bands in Fig. 4 can be assigned to NO adsorption on the Pd particles themselves. Further insight into the origin of the different features can be obtained from previous work on Pd single crystals. In TPD studies on Pd(111), three main desorption features were observed at 257, 285 and 510 K.^{58,59} The high-temperature desorption is connected to a disordered adsorbate phase at a NO coverage of up to $\theta = 0.33.^{59,60}$ Vibrational studies of NO adsorption in this temperature range have been preformed by Ramsier *et al.*,^{25,26} who observed at 373 K a single band



Fig. 5 IR spectra acquired during exposure of the Pd particles supported on the Al_2O_3 film on NiAl(110) (stabilized by oxygen treatment, see text) to a molecular beam of NO at different sample temperatures; (a) at low NO exposure; (b) at high NO exposure.

shifting from 1540 to 1590 cm^{-1} with increasing coverage, and Bertolo *et al.*^{59,60} who found after NO saturation at 300 K a single band at 1589 cm^{-1} . Under UHV conditions, higher coverages can be obtained at lower surface temperature only. Here, several ordered adsorbate structures have been indentified: An ordered $c(2 \times 4)$ phase gives rise to an absorption band around 1610 to 1620 cm⁻¹ at $\theta = 0.50$,^{59–62} and at the highest coverage ($\theta = 0.75$) at 100 K a (2 × 2) structure is observed which is characterized by bands at 1589–1600 and 1735-1750 cm⁻¹.^{25,59-61} In an intermediate coverage region ($\theta = 0.625$) between these phases, an ordered (8 × 2) antiphase domain boundary structure was reported (1590, 1615, 1736, 1744 cm⁻¹).⁶² The local sites occupied by NO in these adsorbate structures have recently been investigated theoretically.63-65 It was concluded that NO occupies fcc hollow sites at low coverage, a mixture of fcc and hcp sites at $\theta = 0.50$, and on-top sites in addition to the mixture of fcc and hcp sites at $\theta = 0.75$. The misassignments of sites, which in older studies arose from the interpretation of vibrational spectra on the basis of nitrosyl compounds, have recently been reviewed by Brown and King.⁵

On Pd(100), the vibrational spectra of adsorbed NO have been investigated by Nyberg and Uvdal.⁶⁶ At elevated temperature (420 K) a p(4 × 2) superstructure is formed, which corresponds to a coverage of $\theta = 0.25$ and a vibrational spectum showing a single signal at 1492 cm⁻¹. At temperatures of 400 K and below a second band at 1653 cm⁻¹ emerges and at 250 K ($\theta = 0.50$) a ($2\sqrt{2} \times 2\sqrt{2}$)R45° superstructure is obtained, which is finally characterized by a single band at 1678 cm⁻¹. The saturation coverage at 80 K was estimated as $\theta = 0.65$.⁶⁷ In a similar manner as for Pd(111), the site occupation was reinterpreted recently, concluding that fourfold hollow sites are occupied in the case of the low coverage structure ($\theta = 0.25$ –0.30), whereas at higher coverage ($\theta = 0.50$) NO adsorbs on bridge sites.⁶⁸

In addition to the close-packed single crystal planes, adsorption on open and stepped Pd surfaces is of high relevance for the present case of NO adsorption on supported particles. An extensive comparative study was performed by Ramsier *et al.* on Pd(112) and Pd(111).^{25,26} Briefly it was observed that upon adsorption on Pd(112) at 373 K, an additional band appears in the spectral region between 1655 and 1670 cm⁻¹, which is assigned to NO adsorption at edge sites. Similar results were recently obtained by Nakamura *et al.* in a comparative investigation on Pd(111), Pd(100) and Pd(311).⁶⁹

On the basis of these results we can assign the bands in region (III) between 1525 and 1580 cm⁻¹ to NO adsorbed on hollow sites, predominately on Pd(111) facets. Indications for NO on fourfold hollow sites of (100) facets are extremely weak (*i.e.* a faint low energy shoulder is observed for the band at 1546 cm⁻¹ for NO exposure at 300 K). These findings are consistent with the particle morphology discussed in section 3.1. A possible origin of the observed splitting into two peaks could be related to the formation of NO structures with different local surrounding, either due to the formation of adsorbate phases of different density or due to an interaction with NO adsorbed at particle defects.

In contrast to the spectral region (III), strong deviations from the single crystal behavior are observed in regions (I) and (II). First, we find that the peak at 1734 cm⁻¹, which is characteristic for NO adsorbed in on-top geometry, is preserved up to 300 K. As discussed above, this is in sharp contrast to the single crystal behavior, both on Pd(111) and Pd(100). Consequently, we tentatively assign the red-shifted band remaining at 1734 cm⁻¹ to on-top NO adsorbed with an enhanced binding energy at particle defect sites such as *e.g.* edges and corners.

The most drastic deviation from NO on Pd(111), however, is found in the spectral region (II). On Pd(111) a band at 1620 cm⁻¹ is observed only at coverages exceeding $\theta = 0.50$, which, however, are not reached at 300 K in UHV. Under similar conditions on the supported Pd particles, on the other hand, a strong band at 1630 cm^{-1} is observed with a shoulder at 1655 cm⁻¹. There are two possible origins of these absorption features. First, the band may be due to NO adsorption at defect sites such as particle edges or steps. This assignment is corroborated by the fact that similar bands between 1639 and 1674 cm⁻¹ prevail on stepped Pd(112) and Pd(311) surfaces up to elevated temperatures.^{25,26,69} Moreover, an enhanced binding energy at steps was verified by theoretical calculations.⁷⁰ In addition to the edge sites, a contribution due to (100) facets is possible, which would typically give rise to an absorption band around 1630 to 1680 cm⁻¹, present up to room temperature and above.^{66,69} Taking into account the morphology of the particles and the small fraction of (100) facets (see section 3.1), however, the band can hardly be attributed to (100) facets only. In addition, the large tilting angle of the (100) facets leads to a suppression of the IR absorption as a result of the metal surface selection rule (MSSR), which, due to the small thickness of the oxide film, also applies to the present model surface.⁷¹ Thus we assign the bands in region (II) (1625-1660 cm⁻¹) predominately to NO adsorbed at defect sites such as particle edges and other defects such as e.g. steps on the particle facets. In addition, a small contribution due to (100) facets is possible.

As a final remark it should be noted that the relative intensities of the NO bands do not reflect the relative concentrations of the corresponding species. In particular, the on-top signal at 1750 cm^{-1} strongly dominates the spectrum at higher coverage (see Fig. 4(b)), although a majority of NO is expected to

remain adsorbed at higher coordinated sites (according to the behavior on $Pd(111)^{63,64}$). There are several possible reasons for this effect including e.g. differences of the dynamic dipole moment as a function of the local adsorption geometry and coupling to the metal, different molecular orientation in combination with the MSSR discussed above and intensity transfer between neighboring bands due to dipole coupling (see e.g. ref. 72). A clear indication of such intensity borrowing is found in Fig. 4(b), where we observe that as soon as the on-top band at the highest frequency emerges, the bands in the region (II) are strongly attenuated. The bands in region (III), for which the difference in stretching frequency is larger, are subject to a weaker loss in intensity. However, it should again be noted that other effects such as the electronic coupling might also change as a function of coverage and, therefore, a quantitative understanding of the IRAS intensities would require a detailed theoretical analysis.

In order to further investigate the different absorption features for NO adsorbed on the Pd model catalyst, we have performed isotope exchange experiments involving ¹⁴NO and isotopic labeled ¹⁵NO. A characteristic experiment is displayed in Fig. 6. At a temperature of 185 K, the stabilized model surface was initially exposed to dose of 2×10^{16} molecules cm⁻² (50 L) of ¹⁴NO using a beam flux of 2.8×10^{14} molecules cm⁻² s⁻¹, before switching to a ¹⁵NO beam of equal intensity. IR spectra were continuously recorded in order to monitor the exchange of adsorbed NO.

After initial exposure to ¹⁴NO, the observed bands at 1749, 1675, 1620 and 1545 cm⁻¹ qualitatively correspond to those discussed in connection with Figs. 4 and 5. Upon switching



Fig. 6 Isotopic exchange experiment using molecular beams of ¹⁴NO and ¹⁵NO, respectively. The spectra were acquired during exposure of the Pd particles supported on the Al₂O₃ film on NiAl(110) (stabilized by oxygen treatment, see text) to NO: The topmost spectrum (left) and upper spectrum (right) were measured during ¹⁴NO exposure at a dose of 2×10^{16} cm⁻², the other spectra were taken after switching to ¹⁵NO at doses up to 33×10^{16} cm⁻² (bottom spectrum on the left and lower spectrum on the right).

to ¹⁵NO, slow changes are observed in the spectral regions (I) and (II). Isotopically shifted peaks appear at 1710, 1695, 1645 and 1590 cm⁻¹ in addition to the above mentioned features. Only a weak attenuation, but no shifted band is observed in the absorption signal in region (III) at 1545 cm⁻¹.

The observed isotopic shifts agree with the expected values (see e.g. refs. 47 and 48). It is noteworthy that two shifted bands appear in the on-top region (1710 and 1695 cm^{-1}). This observation corroborates the above hypothesis that in addition to the regular on-top sites on Pd(111) facets appearing at higher frequency there is a second type of on-top site available, which is characterized by a lower NO stretching frequency and an enhanced binding energy. Similar to the on-top NO, the NO species giving rise to the bands in region (II) are subject to an isotopic exchange at 185 K, although more precise conclusions on the kinetics of the exchange are precluded by the width of the overlapping bands. Finally, it should be noted that no indication is detected for an isotopically exchanged species derived from NO in region (III). This observation indicates a slower exchange of the most strongly bound species at hollow sites.

3.4. Co-adsorption of NO on the oxygen precoved Pd model catalyst

After investigating the adsorption of pure NO on the Pd/ $Al_2O_3/NiAl(110)$ model catalyst, we now explore the effect of co-adsorbed oxygen and CO. Both gases have been shown to interact weakly with the model support (after stabilization by oxygen treatment, see section 3.1). Thus we focus on co-adsorption effects on the Pd particles, investigated in the regime of low NO exposure.

For the case of oxygen co-adsorption, a corresponding set of experiments is displayed in Fig. 7. The sample was predosed with $O_2~(8~\times~10^{16}~molecules~cm^{-2},~230~L)$ at 300 K. Subsequently, the surface was exposed to NO at a temperature of 100 K. The IR spectra taken during exposure are shown in Fig. 7 in comparison to the corresponding spectra acquired on the oxygen-free sample. Strong changes are observed with respect to both the intensity ratios and the frequency of all NO induced bands. In the low NO coverage limit (NO exposure $0.3-1.2 \times 10^{14}$ molecules cm⁻², 0.1-0.3 L) three bands appear on the oxygen precovered sample around 1565, 1660 and 1750 cm⁻¹. With increasing coverage, all bands shift slightly to higher frequency. With respect to the oxygen-free surface all absorption features exhibit a pronounced blue-shift of approximately 30 to 40 cm⁻¹. In addition, the highfrequency band in region (I) at 1752-1783 cm⁻¹ already appears at lowest NO coverages, whereas the corresponding peak on the clean Pd model catalyst is found at much higher exposure only (compare Fig. 4b). Finally, it should be noted that the high-frequency band (I) develops a pronounced low-frequency shoulder at high NO doses.

Unfortunately, no vibrational studies of NO and oxygen co-adsorption on Pd(111) under ultrahigh vacuum conditions are available as a possible reference for the present work. On Pd(100), Nyberg and Uvdal observed a blue-shift of bridge bonded NO of approximately 20-30 cm⁻¹ on Pd(100) $p(2 \times 2)O.^{73}$ A similar effect was reported in a study on Ni(111) in which the oxygen induced blue-shift for NO adsorbed in higher coordinated sites was additionally connected with a strong occupation of on-top sites, which are not populated on clean Ni(111).⁷⁴ The blue-shift was interpreted in terms of a strengthening of the N-O bond due to the electronegative oxygen co-adsorbate, reducing the NO $2\pi^*$ electron density. Co-adsorption of oxygen and NO on Pd(112) was investigated by means of temperatureprogrammed desorption (TPD) by Ramsier et al.75 It was found that preadsorbed oxygen reduces the NO uptake above room temperature and - in accordance with the above



Fig. 7 Comparison of IR spectra acquired during exposure of the pristine Pd particles (gray traces) on $Al_2O_3/NiAl(110)$ (stabilized by oxygen treatment, see text) and oxygen precovered Pd particles (black traces) to a molecular beam of NO (a–f: different NO doses) at a sample temperature of 100 K.

study — leads to a shift of the desorption signal to lower temperature, *i.e.* a weakening of the Pd–NO bond.

In the present work, the conditions were chosen such that a saturation coverage of oxygen at a surface temperature of 300 K was obtained. On Pd(111), saturation under these conditions occurs at $\theta = 0.25$, corresponding to a p(2 × 2) superstructure (see *e.g.* refs. 76 and 77 and references therein). In this structure, one of eight hollow sites is occupied by oxygen and three quarters of all Pd surface atoms are directly coordinated to oxygen, leading to a strongly modified electronic structure.

The experimental findings can be interpreted on the basis of this information. In the limit of low NO coverage, the band at 1565 cm⁻¹ (region III) can be assigned to NO adsorbed on hollow sites, which are predominately located on (111) facets. The pronounced blue shift is related to the electronic influence of direct oxygen coordination to the Pd atoms of the binding site and indicates the formation of a mixed adsorbate layer. The simultaneous appearance of the on-top (region I) and hollow (region III) NO signal in the low coverage limit points towards similar binding energies for both sites. Assuming that the adsorbate structure on the particle facets is similar to Pd(111) $p(2 \times 2)O$, this may be due to the fact that one quarter of the Pd surface atoms is not directly coordinated to oxygen and, consequently, the binding properties are expected to be affected to a lesser extent. This assumption is consistent with the observed reduced blue shift of the band in the on-top region (I) at lower exposure (1750–1760 cm⁻¹) with respect to the clean surface (1740–1750 cm⁻¹). The exact origin of the blue-shift of the on-top band at higher exposure (to 1780 cm⁻¹) and the slow development of the low-frequency shoulder is not clear. A possible explanation would be a slow rearrangement of the oxygen adsorbate layer as has been observed in the case of Pd(100).⁷³

Another observation is related to the bands in region (II) between 1600 and 1700 cm⁻¹. In addition to the blue shift observed at higher exposure, adsorption appears to be suppressed at these sites in the low coverage limit. These finding are connected to the fact that the bands in region (II) are mainly related to particle edges and defects (see section 3.3). In a recent STM study on the same Pd model catalyst⁷⁸ as well as in a TR-IRAS study published elsewhere,³⁵ it was demonstrated that there is a particularly strong interaction of oxygen with such defect and edge sites. This enhanced interaction with oxygen may be the origin of the suppressed adsorption of NO.

3.5. Co-adsorption of NO on the CO precovered Pd model catalyst

A summary of the co-adsorption experiments of NO on the CO precovered model catalyst is given in Fig. 8. The sample was saturated by exposure to CO at 300 K (CO exposure: 8.7×10^{15} molecules cm⁻² or 23 L). Subsequently, IR spectra were acquired as a function of NO exposure at a sample temperature of 100 K (Fig. 8(a)-(f)). The IR spectrum of pure CO, which in Fig. 8 is displayed for comparison (gray traces), is characterized by a strong band at 1952 cm⁻¹ with a broad low-frequency shoulder stretching down to approximately 1800 cm⁻¹. In addition, two weak bands are observed at 2072 and 2090 cm⁻¹. Upon NO exposure, all parts of the CO spectrum are subject to strong changes. First, a pronounced increase in intensity is observed for the feature at 2090 cm⁻¹. Secondly, the band at 1952 cm⁻¹ undergoes a successive blue shift of up to 30 cm⁻¹ with increasing NO exposure and, finally, the integral absorption in the low-frequency region increases, developing a pronounced maximum at 1880 cm⁻¹. In the NO region, a weak on-top NO band around 1740 cm⁻¹ appears, however, NO bands in the lower frequency range cannot be identified unambiguously.

Co-adsorption of CO and NO on Pd(111) single crystals has been investigated both experimentally⁷⁹ and theoretically.^{65,80} Employing IRAS, Xu *et al.* observed the formation of mixed adsorbate layers, with NO occupying hollow sites at high sample temperature and switching to on-top sites at low temperature.⁷⁹ In the CO region at low temperature, features around 1900 and 1970 cm⁻¹ were found for Pd(111) and Pd(100), respectively, and the authors interpreted CO–NO co-adsorption on supported Pd particles on the basis of these data.

In the present experiments, CO adsorption is performed at 300 K in order to establish a well defined partial CO coverage on the particles. On Pd(111) at 300 K, a maximum coverage of approximately $\theta = 0.5$ is obtained under UHV conditions (see *e.g.* refs. 81–83), whereas at 100 K the saturation coverage corresponds to a $(2 \times 2) - 3$ CO structure at $\theta = 0.75$.^{84,85} The assignment of the different bands of CO on the Pd model catalyst has been discussed in detail recently (see ref. 86 and references therein). Briefly, absorption features in the region between 1950 and 1980 cm⁻¹ were assigned to bridge bonded CO adsorbed at particle edges and steps, possibly with an



Fig. 8 Comparison of IR spectra acquired after saturation of the Pd particles on $Al_2O_3/NiAl(110)$ (stabilized by oxygen treatment, see text) by CO (at 300 K) and after subsequent exposure to a molecular beam of NO (black traces) at a sample temperature of 100 K ((a)–(f): different NO doses).

additional small contribution from (100) facets. The broad features at lower frequency are assigned to CO adsorbed at hollow sites, primarily on (111) facets. The bands at 2072 and 2090 cm⁻¹ are due to on-top CO, with the lower frequency signal most likely being related to a more strongly bound species at specific defect sites.

The pronounced blue-shift of the CO edge and defect peak from 1952 to a value of 1970 to 1980 cm⁻¹ upon NO coadsorption is similar to what is found upon simple compression of the adsorbate layer by increasing the CO coverage.⁸⁷ Moreover, it has to be pointed out that the enhanced absorption in the region around 1880 cm⁻¹ is not necessarily due to an enhanced occupation of hollow sites on particle facets, but most probably a consequence of the decreasing intensity transfer to the bands at higher energy with increasing difference in resonance frequency (see section 3.3).

Focusing on the NO region, no clear indication of NO induced bands can be identified at low NO dose. However, the absence of the characteristic strong band in the on-top region points to an initial occupation of higher coordinated sites by NO. Only at higher exposures, a band at 1740 cm⁻¹ appears indicating additional occupation of on-top sites. This behavior is consistent with the Pd(111) single crystal results discussed above,⁷⁹ for which on-top NO was observed at low temperature and high coverage only. The red shift of the on-top NO signal in comparison to adsorption on the clean

Pd particles (see Fig. 4(a)) can be attributed to a reduced dipole coupling in the diluted NO layer as well as to a preferential occupation of defect sites.

The most prominent change in the CO spectrum, however, is observed in the on-top CO region. The strong increase in the band intensity at 2089 cm⁻¹ indicates a partial change of the adsorption sites of CO from higher coordinated sites to ontop positions. A similar behavior has not yet been reported on single crystal surfaces. A possible explanation for this effect is related to the presence of defects and steps, which-in comparison with the low index Pd single crystal planes-have been shown to exhibit a drastically enhanced tendency for binding CO in on-top geometry^{6,87} and thus may facilitate the CO site change as a function of NO coverage.

4. Conclusions

We have studied the adsorption and reaction of NO on a wellordered Al_2O_3 film on NiAl(110) as well as the adsorption of NO and co-adsorption with CO and oxygen on nanometersized Pd crystallites on $Al_2O_3/NiAl(110)$. Previously, the Pd particles have been characterized in detail with respect to their structural properties. Experimentally, a combination of timeresolved IRAS and molecular beam methods was applied.

• On the pristine Al_2O_3 film at 100 K, NO undergoes a slow decomposition process. This process is initiated at oxide defects and involves a strong structural transformation of the oxide film. Two types of nitrogen–oxo species are formed successively, one of which permits the formation of an asymmetric NO dimer-like structure. Decomposition of the dimer occurs, presumably *via* N₂O formation. The active oxygen species produced in this step facilitates slow formation of higher oxidized nitrogen surface species at high NO doses.

• After growth of the Pd particles on $Al_2O_3/NiAl(110)$, the decomposition pathway observed on the pristine Al_2O_3 film is found to be strongly inhibited. This is due to the fact that Pd efficiently blocks the defect sites on the support at which the decomposition process is initiated.

• NO adsorption on the Pd particles was studied in a temperature range between 100 and 300 K. Significant differences are observed in the IR spectra of adsorbed NO in comparison to single crystal reference data. The corresponding vibrational features can be assigned to NO adsorbed at specific defect sites such as particle edges and allow a spectroscopic identification of such sites on supported particles. Isotopic exchange experiments were performed in order to identify different sites and probe the exchange of NO with the gas phase.

• Co-adsorption of NO on oxygen precovered Pd particles results in a strong modification of the adsorption behavior. Adsorption at on-top sites becomes energetically equivalent to adsorption at hollow positions on facets. NO adsorption at particle defects is found to be strongly inhibited due to the enhanced interaction of oxygen with particle edges and other defects. All vibrational bands are significantly blueshifted due to the electronic influence of co-adsorbed oxygen.

• Co-adsorption of NO on CO-precovered Pd particles results in a compression of the CO layer and a partial change of adsorption sites. Most of the CO remains adsorbed in bridge-bonded coordination at particle edges and in hollow coordination at (111) facets, but with increasing NO coverage a fraction of the CO moves to on-top sites. At low coverage NO is adsorbed at higher coordinated sites, whereas at higher coverage on-top sites are occupied.

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