

Ammonia oxidation on Pt(410)

C.J. Weststrate^{a,*}, J.W. Bakker^a, E.D.L. Rienks^a, C.P. Vinod^{a,b}, A.V. Matveev^c, V.V. Gorodetskii^c,
B.E. Nieuwenhuys^{a,b}

^a *Leids Instituut voor Chemisch Onderzoek, Universiteit Leiden, P.O. Box 9502, Einsteinweg 55, 2333 CC Leiden, The Netherlands*

^b *Technische Universiteit Eindhoven, Schuit Institute of Catalysis, P.O. Box 5600 MB, Eindhoven, The Netherlands*

^c *Boskov Institute of Catalysis, Russian Academy of Sciences, Novosibirsk 630090, Russia*

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Abstract

The adsorption of both O₂ and NH₃ on Pt(410) was studied using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Molecular NH₃ desorbed from Pt(410) between 100 and 450 K, and dissociation was not observed. Radiation (X-rays, electrons) induced NH_{3ad} dissociation, and as a result several dissociation products (NH_{2ad}, NH_{ad}, and N_{ad}) were observed in the N 1s core-level spectrum. NH_{ad} is a rather stable dissociation product that starts to dehydrogenate above 350 K. The N_{ad} and H_{ad} formed in this process desorbed on formation (as N₂ and H₂). Both molecular and dissociative O₂ adsorption were observed after the surface was exposed to O₂(g) at 100 K. Molecularly adsorbed O₂ desorbed below 200 K, whereas atomic oxygen desorbed (as O₂) between 600 and 900 K, in two distinct desorption peaks. In the O 1s core-level spectrum, both molecular O₂ and two different types of O_{ad} were distinguished. NH_{3ad} dissociation was observed on an oxygen-presaturated surface. The NH_{3ad} oxy-dehydrogenation started at 150 K. NO_{ad} and NO(g) were also observed, but only during experiments in which an excess of O_{ad} was available. NO_{ad} desorbed/decomposed between 400 and 500 K. For the steady-state ammonia oxidation reaction, N₂ and H₂O were the major products at low temperatures, whereas the selectivity toward NO and H₂O changed at higher temperatures. This selectivity change can be attributed to changes in surface composition.

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1. Introduction

Catalytic ammonia oxidation is an important process in the chemical industry. It is used on a large scale to produce nitric oxide, a precursor for nitric acid. The catalyst of choice for this process is an alloy of Pt and Rh. A number of surface science studies have been performed to unravel the surface chemistry of NH₃ on Pt surfaces in both the absence and presence of co-adsorbed oxygen [1–3].

The surface chemistry of ammonia on a metal surface is complex, involving several different surface species. Adsorption and decomposition of NH₃ can in principle lead to five different species: NH_{3ad}, NH_{2ad}, NH_{ad}, N_{ad}, and H_{ad}. In the

presence of oxygen, several other species can be involved in the surface chemistry, including O_{ad}, OH_{ad}, H₂O_{ad}, and NO_{ad}. The complexity of the surface chemistry is reflected in the gas-phase product selectivity during catalytic NH₃ oxidation. Different gaseous products, including N₂, NO, and N₂O, can be formed. The selectivity depends on the type of catalyst, its surface structure, and the experimental conditions, such as reactant pressures, NH₃/O₂ ratio, and catalyst temperature.

It has been found that ammonia decomposition does not take place on Pt surfaces at temperatures below 400 K. Some NH₃ decomposition has been observed *above* the NH₃ desorption temperature; in that case, stepped surfaces were found to be more active than “smooth” surfaces [1,4,5]. On several metals, including Pt, Ag, Ir, and Cu, the presence of oxygen has been found to enhance NH₃ dissociation [3,6–11].

In this paper we present the results obtained for ammonia oxidation on a Pt(410) surface, which consists of {100} terraces

* Corresponding author.

E-mail address: c.weststrate@chem.leidenuniv.nl (C.J. Weststrate).

and {110} steps. Faceting of the surface was observed, resulting in the formation of larger {100} terraces on which a (5 × 20) reconstruction occurred. A more detailed discussion concerning the actual surface structure of our Pt(410) sample has been provided previously [12].

XPS was used to study the nature and concentration of surface species, and the gas-phase reaction products were detected by quadrupole mass spectrometry (QMS). The aim of our experiments was to obtain fundamental insights into surface processes, which can help elucidate the reaction pathways involved in catalytic ammonia oxidation. Based on our previous studies, we also can compare the NH₃ chemistry on Pt(410) with that on (previously studied) Ir surfaces [9,13–16].

2. Experimental

The thermal desorption studies were performed using the experimental setup in Leiden, which has been described in more detail elsewhere [12]. High-energy resolution fast XPS measurements [17,18] were performed on the SuperESCA beamline of ELETTRA, the synchrotron radiation facility in Trieste, Italy. The vacuum system, with a base pressure of $\sim 1 \times 10^{-10}$ mbar, is equipped with a sputter ion gun for sample cleaning, a mass spectrometer, and LEED optics. Details about the sample used in this study and the cleaning procedure can be found elsewhere [12].

The N 1s spectra were measured with a photon energy of 496 eV, and the O 1s spectra were measured with a photon energy of 650 eV. Temperature-programmed XPS (TP-XPS) measurements [19] were performed at a heating rate of 0.25 K s⁻¹. The different core level regions were measured in a separate experiment; that is, either O 1s or N 1s could be measured during an experiment. The XPS spectra were evaluated after a linear background was subtracted by fitting the peaks with a Doniach–Šunjić function convoluted with a Gaussian function [20].

Core-level binding energies of the different species were measured with respect to the Fermi level. The position of the Fermi edge was determined using an photon energy of 110 eV. In recent experiments, we found that the position of the Fermi level should be measured using the photon energy used for the actual measurements as well, because the calibration of the photon energy was not very accurate (e.g., when the excitation energy was set to 650 eV, the *actual* energy was ~ 647 eV). As a result of the approach used here (i.e., measuring the Fermi edge with a different photon energy than for the actual measurements), the reported *absolute* binding energies (BEs) can exhibit a (constant) shift with respect to literature values. Therefore, the Δ BEs between different species instead of *absolute* BEs should be used for comparison with literature data. This issue affected only the comparison with literature data; the position of the different species remained constant throughout the experiments. The N 1s and O 1s signals were normalized using the intensities obtained for a saturated NO layer at 100 K (which was arbitrarily set to 1).

Both Sun et al. [21] and Schwaner et al. [22] found that adsorbed NH₃ decomposed when exposed to a beam of (~ 50 eV) electrons. In the experimental setup used for the thermal de-

sorption experiments, radiation damage due to electrons from the QMS filaments (~ 70 eV) can be excluded, because the QMS was situated in a separate compartment, with only a small hole connecting it to the main chamber (where the crystal was located). In this setup, the likelihood of electrons generated by the QMS filaments reaching the sample surface is very low. During the XPS measurements, NH_{3ad} dissociation was induced by the intense radiation (either X-rays or ~ 100 eV photoelectrons). This is described in more detail in Section 3.1.

3. Results

3.1. NH₃ surface chemistry

Thermal desorption spectra obtained after exposure to NH₃ at 100 K are shown in Fig. 1a. Ammonia bonded directly to the surface (through the nitrogen atom) desorbed molecularly between 200 and 450 K. After an NH₃ exposure of ~ 3 L, a new desorption feature appeared, with a desorption maximum at around 175 K. In line with literature assignments, this peak can be attributed to desorption of a second NH₃ layer that was hydrogen-bonded to the first, chemisorbed layer [5,13,23–26]. Even higher exposures led to the formation of NH₃ multilayers that desorbed at around 120 K [5,27]. The observed peaks are very similar to the desorption spectra observed for other Pt surfaces, and the presence of steps seemed to have little effect on the desorption spectra. N₂ or H₂ desorption was not observed, indicating that NH₃ dissociation did not take place on the clean surface.

Fig. 2a shows one of the N 1s core-level spectra obtained during XPS experiments of an adsorbed NH₃/NH_{xad} layer. It also shows the fitting components used to deconvolute the spectra. The BEs of all of the fitting components used to evaluate the XPS data are summarized in Table 1. Fig. 2b shows a series of spectra taken during heating of an adsorbed NH₃/NH_{xad} layer in vacuum. Ammonia was dosed at 175 K, to avoid formation of the NH₃ double layer. During the uptake (not shown), initially only molecular ammonia was observed (at 400 eV). However, the intense radiation (either X-rays or the resulting ~ 100 -eV photoelectrons) induced dissociation of the adsorbed NH₃, and another peak developed at 398.3 eV, assigned to NH_{ad}. We suggest that another small peak was present at 399.1 eV, which is assigned to NH_{2ad} on the basis of its BE. This peak was never clearly resolved, and the concentration of this species was low. Heating of the dissociated NH_{xad} layer (Figs. 1c and 2b) resulted in the formation of an additional (small) peak at 397.4 eV, assigned to N_{ad}. This assignment is in line with literature data [8,13,21] in which the Δ BE among various NH_{xad} species was reported to be ~ 1 eV on several different metal surfaces. The same BE component was observed after NO dissociation on this surface [12]. Fig. 1c shows the results obtained after evaluation of the data shown in Fig. 2b using the components shown in panel (a). NH_{3ad} desorbed between 175 and 400 K, and NH_{2ad} decomposed (into NH_{ad} and H_{ad}) between 175 and 250 K. NH_{ad} decomposition was observed above 350 K. As a result, a small amount of N_{ad} that desorbed almost immediately on formation (as N₂) was observed.

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