Insight into the Nature of Active Species of Pt/Al₂O₃ Catalysts for low Temperature NH₃ Oxidation

Dmitry A. Svintsitskiy, Lidiya S. Kibis, Andrey I. Stadnichenko, Elena M. Slavinskaya, Anatoly V. Romanenko, Elizaveta A. Fedorova, Olga A. Stonkus, Dmitry E. Doronkin, V. Marchuk, Anna Zimina, Maria Casapu, Jan-Dierk Grunwaldt, and Andrei I. Boronin

Two series of Pt/γ-Al₂O₃ catalysts for low temperature NH₃ oxidation were prepared using Pt(NO₃)₃ and H₂PtCl₆ precursors. Using both precursors results in the formation of small Pt particles (d < 1.5 nm), however, Cl-containing Pt precursors give a higher fraction of highly dispersed Pt species. Such species show high stability against thermal or H₂ treatment probably due to the presence of a substantial amount of chlorine on the surface. Treatment of the samples prepared from Pt(NO₃)₃ with H₂ leads to the formation of metallic Pt nanoparticles accompanied by the improvement of catalytic activity in NH₃ oxidation at T < 200 °C. The main products of ammonia oxidation at temperatures below 250 °C were molecular nitrogen and nitrous oxide with the N₂ selectivity reaching 80%. Operating XANES/EXAFS revealed that even after H₂ pretreatment at least 40% of Pt surface remains in oxidized state under reaction conditions resulting in the appearance of N₂O as a by-product.

1. Introduction

The strict environmental protection regulations are currently applied to control the toxic emissions from refineries, power plants, and vehicles. Exhausts of many industrial processes such as nitric acid production, biomass and coal gasification, the regeneration of fluid cracking catalysts (FCC), and selective catalytic reduction (SCR) of NOₓ by NH₃ contain ammonia which has a harmful effect on human health and environment. Global NH₃ emission from industry was estimated to be about 220 thousand tons per year. In addition to this, the emerging use of ammonia as an energy carrier for various mobile energy sources and transportation also requires solving the NH₃ emission problem preferably via its catalytic transformation to molecular nitrogen.

The catalyst for selective ammonia oxidation is an essential component of NH₃-SCR diesel engine systems for NOₓ removal. In these systems NH₃ is generated onboard from aqueous urea solution. For higher NOₓ removal efficiency excess of ammonia is dosed resulting in its slip in the exhaust. To remove NH₃ before it reaches the environment the Ammonia Slip Catalyst (ASC) is additionally installed. The state-of-the-art ASC systems include a combination of an ammonia oxidation (AMOX) catalyst (usually, Pt/Al₂O₃) and a SCR catalyst in a dual-layer architecture, where a part of ammonia is oxidized over the Pt catalyst to N₂ and NOₓ, which is further transformed to N₂ over the SCR catalyst layer. The dual-layer ASC systems have been extensively studied in the last decade. Nevertheless, there is still strong debate on the full understanding of the system, which is required, for example, for the development of the kinetic models, optimization of the catalyst architecture and addressing catalyst deactivation. In addition, further knowledge is necessary to increase the activity of AMOX catalysts to full NH₃ conversion below 250 °C. Among different supported noble metal catalysts, Pt-based systems are considered to be the most active for NH₃ oxidation. However, using Pt-based catalysts requires increasing N₂ selectivity by minimizing the formation of undesired N₂O. Despite many data about NH₃ oxidation to NOₓ over single- and polycrystalline platinum surfaces, Pt gauzes or sponges as well as supported platinum
catalysts,\textsuperscript{2,22–25} the structure-activity relationships for Pt-based systems for selective NH\textsubscript{3} oxidation to N\textsubscript{2} are still under discussion and require further systematic fundamental studies.

The ASCs operate under excess of O\textsubscript{2}, which has a great impact on the oxidation state of the active component. Over supported Pt catalysts the main issue to be considered is the relationship between the oxidation state of platinum and its particle size, as they are directly related.\textsuperscript{22} Smaller Pt particles are readily oxidized\textsuperscript{22,29} and the reducibility of PtO\textsubscript{X} species is found to be enhanced with the decrease of particle size.\textsuperscript{25,30} It was proposed that metallic Pt is significantly more active for NH\textsubscript{3} oxidation than oxidized platinum,\textsuperscript{26–28} which does not provide sites for O\textsubscript{2} dissociation.\textsuperscript{31} Due to low resistance to oxidation small Pt nanoparticles are, therefore, considered less active in NH\textsubscript{3} oxidation than larger ones.\textsuperscript{25,27,29} The selectivity towards various N-containing products seems to be also governed by Pt particle size and oxidation state.\textsuperscript{22,25} The deactivation of platinum is discussed to be caused not only by the noble metal oxidation but also by the accumulation of N-containing surface species, especially at low temperatures.\textsuperscript{26,28} Hence, one way to obtain efficient NH\textsubscript{3} oxidation catalysts is to carefully select the Pt precursor\textsuperscript{22,23} and the drying/pretreatment procedure,\textsuperscript{25–30} since they can influence the size and state of Pt particles. However, the number and nature of active sites are ultimately affected by the changes in reaction conditions.\textsuperscript{21,28,34,37} Thus, it is mandatory to establish structure-activity correlations directly during catalyst application to avoid conditions. The rapid development of in situ/operando techniques, which are extensively applied in heterogeneous catalysis nowadays, can provide such an opportunity.\textsuperscript{38–40}

This work presents a systematic study of Pt/Al\textsubscript{2}O\textsubscript{3} catalysts for low temperature NH\textsubscript{3} oxidation. The size of Pt particles and their oxidation state were varied depending on the Pt precursor and the applied calcination and/or reductive treatment. The outcome of the operando X-ray absorption near edge structure (XANES) study allowed us to shed light on the average oxidation state of Pt during the NH\textsubscript{3} oxidation reaction. It was shown that the improvement of catalytic properties at low temperature correlates with the Pt reduction. At higher temperatures, reoxidation of Pt surface takes place leading to the NO\textsubscript{3} formation.

2. Results

2.1. Effect of the Pt Precursor

2.1.1. Catalytic Properties

The catalytic properties of the air-calcined and reduced Pt-N-400 and Pt-Cl-400 catalysts in the NH\textsubscript{3} oxidation reaction are presented in Figure 1. Such catalysts were prepared using N- and Cl-containing Pt precursors, respectively (see Experimental section for details).

All studied catalysts were characterized by the evident consumption/storage of NH\textsubscript{3} from the reaction mixture at room temperature. It resulted in the NH\textsubscript{3} desorption from the catalyst surface at the beginning of heating. Therefore, negative values of NH\textsubscript{3} conversion were observed until the amount of oxidized NH\textsubscript{3} started to exceed the amount of desorbed ammonia. In case of the Pt-N-400 sample the temperature of 50% conversion of NH\textsubscript{3} (T\textsubscript{50}) was ca. 230 °C, while the reduction in hydrogen at 250 °C or 600 °C caused the shift of NH\textsubscript{3} conversion curve towards lower temperature reaching the T\textsubscript{50} value of ~ 170 °C (Figure 1a). Previously, a similar shift was also observed for Pt/Al\textsubscript{2}O\textsubscript{3} catalytic systems in terms of NH\textsubscript{3} oxidation.\textsuperscript{5,24} Note that no significant differences in catalytic properties of the Pt-N-400-250H and the Pt-N-400-600H were observed.

Below 250 °C the main products of NH\textsubscript{3} oxidation over Pt/Al\textsubscript{2}O\textsubscript{3} catalysts were N\textsubscript{2} and N\textsubscript{2}O. NO and NO\textsubscript{2} appeared in the effluent gas mixture only at temperatures above 250 °C while the N\textsubscript{2} and N\textsubscript{2}O concentrations evidently decreased. This distribution of N-containing products depending on the reaction temperature is typical for the Pt-based catalysts.\textsuperscript{41,42} The onset of NH\textsubscript{3} conversion for all studied catalysts coincided in temperature with the simultaneous appearance of N\textsubscript{2} and N\textsubscript{2}O. It indicates that the same active sites were responsible for N\textsubscript{2} and N\textsubscript{2}O formation over Pt/Al\textsubscript{2}O\textsubscript{3} surface, possibly, as a result of interaction between N\textsubscript{ads} and NO\textsubscript{ads} species on metallic platinum. \textsuperscript{25,22} Reduction of the Pt-N-400 in H\textsubscript{2} at 250 °C resulted in the clear activation of the catalyst in the temperature range from 150 to 200 °C. It was accompanied by the appearance of an additional peak on the N\textsubscript{2}O concentration curve (maximum near 180 °C, Figure 1e) with the simultaneous growth of N\textsubscript{2} contribution below 200 °C. Therefore, it confirms the metallic nature of sites for N\textsubscript{2}/N\textsubscript{2}O formation. Also, note that in the H\textsubscript{2} treatment of the Pt-N-400 sample the decrease in NO/NO\textsubscript{2} ratio above 360 °C. It might be due to the change in the average Pt particle size.\textsuperscript{21}

In the case of the Pt-Cl-400 catalyst the T\textsubscript{50} value of 215 °C was similar to that of the Pt-N-400. Reduction of the Pt-Cl-400 in H\textsubscript{2} at 250 °C did not shift the NH\textsubscript{3} conversion curve and only a slight decrease of the T\textsubscript{50} value was observed after H\textsubscript{2} reduction at 600 °C (Figure 1b). The N\textsubscript{2}, N\textsubscript{2}O, NO, and NO\textsubscript{2} concentration curves were rather similar to the as-prepared and reduced Pt-Cl-400 catalysts (Figures 1d and 1f). It indicates that the H\textsubscript{2} treatment of the Pt-Cl-400 sample did not significantly modify its catalytic properties in contrast to the Pt-N-400 catalyst.

2.1.2. Structural Characterization

X-ray diffraction (XRD) data for the Pt-N and Pt-Cl samples are given in Figure 2. The X-ray diffraction patterns of the pristine Pt-N-400 and Pt-Cl-400 catalysts show only reflections stemming from the of γ-Al\textsubscript{2}O\textsubscript{3} phase (ICDD PDF-2 # 29-0063). The difference curves of the X-ray patterns of the Al\textsubscript{2}O\textsubscript{3} support and Pt-containing samples are given in Figure S1 (cf. Supporting Information). Reduction of the Pt-N-400 with H\textsubscript{2} results in the appearance of small reflections from metallic Pt. Reduction at 600 °C leads to the increase of the Pt particle size. The average size of Pt\textsuperscript{0} crystallites determined by the Rietveld method was 1.7 and 3.1 nm for the Pt-N-400-250H and Pt-N-400-600H...
samples, respectively. In the case of the Pt-Cl-400 system no reflections from Pt were observed in the XRD patterns even after H₂ reduction at 600 °C. Hence, all Pt-Cl samples contain platinum in a highly dispersed state.

Transmission electron microscopy (TEM) data is in good agreement with the XRD results. The pristine Pt-N-400 sample contains small Pt particles with an average size of ~1.3 nm (Figure 3e). The reduction of Pt-N-400 results in the sintering of Pt particles with a bimodal size distribution with maxima around 1.5–3 nm (Figure S2). Reduction at 600 °C results in further increase of the particle size up to 1.5–3 nm (Figure S2).

Transmission electron microscopy (TEM) data is in good agreement with the XRD results. The pristine Pt-N-400 sample contains small Pt particles with an average size of ~1.3 nm (Figure 3e). The reduction of Pt-N-400 results in the sintering of Pt particles with a bimodal size distribution with maxima around 1.5–3 nm (Figure S2). Reduction at 600 °C results in further increase of the particle size up to 1.5–3 nm (Figure S2).

2.1.3. X-ray Spectroscopic Investigations

Figure 5 presents the X-ray photoelectron spectra (XPS) of the Pt-N (a) and Pt-Cl (b) samples. Pt4f spectra can be approximated with two doublet components. For the Pt-N-400 sample the binding energies (E_b) of Pt4f⁷/₂ peaks are 72.2 eV and 74.3 eV. These components can be related to the oxidized species such as Pt⁺⁻/Pt²⁺ and Pt⁴⁺, respectively. For the Pt-Cl-400 sample the E_b(Pt4f½) value for Pt⁺⁻ like component is a bit higher – 74.9 eV. It can be related to the presence of Cl-containing Pt compounds, including oxychlorides PtOClₓ. The peak at E_b (Pt4f½) = 72.2–72.3 eV can also originate from atomically dispersed Pt species. Thus, XPS points to the formation of...
oxidized and/or highly dispersed Pt species in the Pt-N-400 and Pt-Cl-400 samples. The spectrum of the Pt-N-400-250H sample treated with H₂ shows a peak at E₀(Pt4f_{7/2}) = 71.1 eV, typical for bulk Pt. A slight decrease of the ratio of Pt and Al atomic concentrations (Pt₄/Al₆) from 1.9% to 1.6% is observed upon reduction of the Pt-N-400 sample confirming the sintering of the Pt particles (quantitative XPS data for all samples are given in Supporting Information, Table S1). The second Pt4f doublet is shifted to lower E₀(Pt4f_{7/2}) = 73.1 eV close to Pt(OH)₂ and/or PtO species. Hence, the treatment of the Pt-N-400 sample with H₂ results in substantial Pt reduction. In the case of the Pt-Cl-400-250H the main Pt4f_{7/2} peak has E₀(Pt4f_{7/2}) about 71.9 eV. The increase of the binding energy compared to the value typical for bulk metallic platinum points to the formation of very small metallic (Pt⁰) or partially charged (Pt⁺) species. The Pt₄/Al₆ ratio remains about 1.1% for the Pt-Cl-400 and the Pt-Cl-400-250H samples. Based on the XRD and TEM data, we can conclude that the H₂ treatment of the Pt-Cl-400 sample results in a minor reduction of Pt species without a substantial increase of the particle size. The analysis of the surface composition shows a quite significant amount of chlorine in the Pt-Cl samples (see Table S1). Only a slight decrease of the Cl₆/Al₆ ratio from 3.7% to 3.3% is observed upon H₂ treatment of the Pt-Cl-400 sample at 250 °C. The corresponding Cl2p spectra are given in Figure S3. Based on all experimental data, the strong influence of chlorine on the tolerance of Pt species towards reduction and sintering can be reliably concluded. This conclusion is in good agreement with the previous studies on the effect of chloride on the properties of Pt/Al₂O₃ catalysts.

Figure 6 shows (a) XANES and (b) Fourier transformed (FT) extended X-ray absorption fine structure (EXAFS) spectra for the Pt-N and Pt-Cl samples. Intensity of the first peak above the Pt L₃ absorption edge (so-called “white line”, the region marked grey in Figure 6a) is proportional to the density of unoccupied d-states and is often used to estimate oxidation state of Pt⁴⁺ by comparing to the reference spectra for PtO₂ and metallic platinum. The intensity of the white line in the Pt-N-400 XANES spectrum is slightly higher than in the PtO₂ reference spectrum which confirms fully oxidized Pt species. Reduction at 250 °C leads to a significant decrease in the white line intensity in the case of the Pt-N-400-250H. Further H₂ treatment at 600 °C leads to even lower white line intensity due to, possibly, sintering of Pt particles and lower availability of Pt surface for interaction with O₂ from the air (note that in this case the reported measurements were performed ex situ).

At the same time, the observed inconsistency between the Pt-N-400 and PtO₂ XANES spectra, probably due to the different coordination environment around Pt atoms, limits reliable quantification since PtO₂ cannot be used in this case as a good reference for XANES analysis. For this reason, the corresponding EXAFS spectra were also analyzed (Figure 6b).

To further evaluate the structure and quantify the average oxidation state of the Pt sites EXAFS spectra were fitted to a model containing Pt⁰–O and Pt–Pt coordination shells from PtO₂ and the first Pt–Pt coordination shell from metallic Pt (fcc). The average oxidation state of Pt is defined from an average coordination number (CN) in the Pt–O first shell (where CN = 6 corresponds to Pt⁴⁺). The fitting results reported in Table 1 confirm full oxidation of the Pt-N-400 and allow using it as a Pt⁴⁺ reference for linear combination analysis of XANES spectra. The FT EXAFS spectrum of Pt-N-400-250H allows identifying the formation of Pt nanoparticles (backscattering on Pt–Pt shell at an uncorrected distance between 2 and 3 Å) while the Pt-Cl samples are largely oxidized and no significant Pt–Pt interaction corresponding to metallic Pt can be identified. Furthermore, both O and Cl nearest neighbors were required to achieve a good EXAFS fit of the Pt-Cl samples (Figure S4, Table S2). The reduction of Pt-Cl-400 sample results in a decrease in the number of chlorine nearest neighbors and an increase of oxygen backscattering.
Figure 3. HAADF-STEM and TEM data for (a,b) Pt-N-400 and (c,d) Pt-N-400-250H samples. Particle size distribution for (e) Pt-N-400 and (f) Pt-N-400-250H samples with total number of particles near 100–150.

Figure 4. HAADF-STEM data for (a,b) Pt-Cl-400 and (c,d) Pt-Cl-400-250H samples. The particle size distribution for (e) Pt-Cl-400 and (f) Pt-Cl-400-250H samples with total number of particles near 100–150.

Table 1. A summary of average Pt oxidation states and coordination environments determined from XANES and EXAFS spectra.

| Catalyst       | Pt oxidation state | Pt–O [Cl] distance [Å] | CN | Pt–Pt [metallic] distance [Å] | CN | Pt–O [Cl] | Pt–Pt [metallic] | ρ [%] |
|----------------|--------------------|-------------------------|----|-------------------------------|----|----------|-----------------|------|
| Pt-N-400       | +4 ± 0.7[a]        | 1.99 ± 0.01 (O)         | 6.0 ± 1.0 (O) | n.a                          | n.a | 2.1 ± 2.0   | 9.2 ± 1.7       | 0.8  |
| Pt-N-400-250H  | +1.01 ± 0.7[a]     | 1.97 ± 0.02 (O)         | 1.9 ± 0.5 (O) | 2.74 ± 0.02                   | 6.0 ± 2.3 | 4.2 ± 4.3 (O) | 7.0 ± 2.1       | 1.6  |
| Pt-Cl-400      | –                  | 2.00 (O)                | 3.0 ± 0.5 (O) | n.a                          | n.a | 9.8 ± 3.7 (Pt) |                 |      |
| Pt-Cl-400-250H | –                  | 2.27 ± 0.06 (Cl)        | 2.3 ± 3.0 (Cl) | n.a                          | n.a | 7.0 ± 10.8  | 10.3 ± 5.4      | 4.3  |

[a] Determined by linear combination analysis (LCA) of XANES spectra using Pt-N-400 and Pt foil spectra as references for Pt⁺ and Pt⁰ respectively in the range 11545–11595 eV. In lieu of Pt oxychloride reference spectra, LCA of Pt-Cl samples was not performed.
2.2. Activation of Pt-Cl Catalysts by High-Temperature Treatment

2.2.1. Catalytic Properties

Figure 7 presents the catalytic data for NH$_3$ oxidation over the Pt-Cl catalysts calcined at different temperatures, namely: Pt-Cl-400, Pt-Cl-600, and Pt-Cl-800 catalysts. In contrast to H$_2$ reduction at 600°C, calcination in air at elevated temperature resulted in the improvement of catalytic activity accompanied by a shift of the NH$_3$ conversion curve towards lower temperatures – to 190°C and 170°C for the Pt-Cl-600 and Pt-Cl-800 catalysts, respectively. In the case of the Pt-Cl-800 sample an additional peak appeared on the N$_2$O concentration curve in the range 150–200°C indicating the formation of additional active sites for NH$_3$ oxidation to N$_2$/N$_2$O. It is known that calcination at temperature above 600°C causes decomposition of oxidized Pt species to metallic Pt particles.[52,53] Based on the literature data, we can propose that calcination of our samples at 800°C should result in the decomposition of PtO, metallic Pt and H$_2$PtCl$_6$ reference samples. The k-range of EXAFS of 2.5-10.5 Å$^{-1}$. 

Figure 5. Pt4f spectra for (a) Pt-N samples: (1) Pt-N-400, (2) Pt-N-400-250H; (b) Pt-Cl samples: (1) Pt-Cl-400, (2) Pt-Cl-400-250H. Blue-and red-colored peaks corresponds to metallic and oxidized platinum, respectively.

Figure 6. (a) Ex situ XANES (grey field marks the “white line” peak) and (b) FT EXAFS (uncorrected for the phase shift) spectra of Pt-N-400, Pt-N-400-250H, Pt-Cl-400, Pt-Cl-400-250H, and data for PtO, metallic Pt and H$_2$PtCl$_6$ reference samples. The k-range of EXAFS of 2.5-10.5 Å$^{-1}$. 

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA
2.2.2. Structural Characterization

XRD patterns for the Pt-Cl samples calcined at T ≥ 600 °C show the reflections stemming from metallic Pt (Figure 8). The average size of Pt\textsuperscript{0} particles is about 18 and 50 nm for the Pt-Cl-600 and Pt-Cl-800 samples, respectively. Note that in the case of the Pt-Cl-600 the amount of crystalline Pt\textsuperscript{0} particles is small in contrast to the Pt-Cl-800 sample.

TEM data also show the gradual increase of the particle size with calcination of the Pt-Cl sample at higher temperatures (Figure 9). For the Pt-Cl-600 sample Pt particles with size of about 0.7 nm and no highly dispersed Pt species can be detected (Figure 9c). In the case of the Pt-Cl-800 sample only large particles with size about 30–200 nm can be seen without the presence of highly dispersed Pt species. Hence, calcination of the Pt-Cl catalyst at 600 °C does not cause significant Pt sintering. The major part of platinum remains in a dispersed state.

2.2.3. X-ray Photoelectron Spectroscopy

Two doublet components with $E_b$(Pt4f\textsuperscript{7/2}) at 72.1 and 74.8 eV corresponding to Pt\textsuperscript{δ+}/Pt\textsuperscript{2+} and Pt\textsuperscript{4+} species can be observed in the Pt4f spectrum of the Pt-Cl-600 sample (Figure 10). Thus, calcination of the Pt-Cl sample at 600 °C does not substantially change the oxidation state of platinum. Note, that the surface amount of chlorine is still high for the Pt-Cl-600 sample reaching Cl/Al ratio of 1.9 % (Figure S3). However, for the Pt-Cl-800 sample a substantial reduction of platinum is observed. The $E_b$(Pt4f\textsuperscript{7/2}) of the main peak is 71.3 eV which is close to the bulk metallic platinum, and its contribution is about 80 % of the overall Pt4f signal intensity. So, air-calcination at 800 °C results in the substantial reduction and sintering of Pt species. However, a decrease of the Pt surface concentration is observed upon calcination at 800 °C. The Pt/Al ratio decreases to ~ 0.5 % for the Pt-Cl-800 sample due to the sintering of Pt particles. Also, calcination at 800 °C leads to a substantial decrease of surface Cl concentration (Figure S3) indicating again the significant role of Cl for the preservation of platinum in the highly dispersed state.\(^{[32,54]}\) For the Pt nitrate-derived samples, calcination already at 600 °C caused decomposition of oxidized Pt species and sintering of the Pt nanoparticles.\(^{[55]}\)

2.3. Operando XANES under NH\textsubscript{3}+O\textsubscript{2} Conditions

In order to analyze the role of Pt state in catalytic NH\textsubscript{3} oxidation, the catalytic experiments were complemented by operando XANES. Figure 11 reports average oxidation state of Pt (probed in the first quarter near the inlet of the catalyst bed) as well as the simultaneously recorded catalytic data (conversion of NH\textsubscript{3} and yields of N\textsubscript{2}, N\textsubscript{2}O, and NO\textsubscript{x}) for the Pt-N-400 and Pt-N-400-250H catalysts during the first and second heating in the NH\textsubscript{3}+O\textsubscript{2} mixture. The absolute error of Pt oxidation state values determined by linear combination analysis with Pt and PtO\textsubscript{2}...
references can reach 10% while the fits relative to the first and
the last spectrum have relative error values of less than 2%, and
thus the reported trends are rather precise.

It should be noted that there are some differences in the
onset temperature, \( T_{50} \) values, and product yields if we compare
results of catalytic tests in a plug flow lab reactor and the plug
flow microreactor used during the operando XANES experi-
ments. These differences might be explained by the different
conditions of the experiments: reactor configurations, gas
hourly space velocity, temperature ramp rate, sample loading,
etc. Hence, a direct comparison of the catalytic data is not
possible. However, the catalytic profiles detected during
operando XANES are helpful for the correlation of the average
oxidation state of Pt with the NH\(_3\) conversion and for deriving
qualitative trends in the reaction product yields.

When comparing the first and the second heating light-off
of the Pt-N-400 catalyst, the average oxidation state of Pt
changes drastically from approx. +3.75 to less than +2. At the
same time, the NH\(_3\) conversion curve is only slightly (<20°C)
shifted to lower temperatures and the selectivity trends are not
significantly influenced.

Pretreatment of the Pt-N-400 with H\(_2\) results in a pro-
nounced increase of NH\(_3\) conversion at temperatures below
250°C, in a good agreement with the catalytic data obtained in
the laboratory test bench (plug flow reactor, Figure 1). The
reductive pretreatment causes the decrease of the average Pt
oxidation state down to +1.2 with its variation in +0.7–+1.2
range during heating under NH\(_3\)+O\(_2\) conditions. The prere-
duced Pt-N-400-250H catalyst is characterized by Pt reduction at
intermediate temperatures (corresponding to offset of NH\(_3\)
conversion) and a slight increase in the Pt oxidation state at
higher temperatures (Figure 11c,d). A similar but less pro-
nounced trend is observed for the second heating of the Pt-N-
400 sample in the reaction mixture (Figure 11b). This may be a

Figure 9. HAADF-STEM and HRTEM data for (a,b) Pt-Cl-600 and (d-f) Pt-Cl-800 samples. Particle size distribution for the (c) Pt-Cl-600 sample with the total
number of particles near 150.

Figure 10. Pt4f spectra for (1) Pt-Cl-600, (2) Pt-Cl-800 samples. Blue-and red-
colored peaks correspond to metallic and oxidized platinum, respectively.
sign of surface-oxidized Pt nanoparticles being reduced by NH$_3$ during the reaction onset with further chemisorption of oxygen at higher temperatures. Due to the high NH$_3$ conversion at high temperature, the NH$_3$ concentration in the gas phase is not sufficient to remove surface oxygen causing Pt oxidation. Similar behavior of Pt NPs was observed in CO oxidation.\[56\] The lowest value of Pt oxidation state in the case of the Pt-N-400-250H catalyst $\sim +0.7\pm 0.8$ corresponds to the reaction temperature of 180–250°C. After this treatment NH$_3$ conversion reaches ca. 100\% and only N$_2$ and N$_2$O appear as reaction products. It indicates that reduced Pt species are mainly responsible for low temperature NH$_3$ oxidation. Furthermore, we can observe that the steady-state value of the average Pt oxidation state is close to $+0.9\pm 0.2$. In the case of Pt-N-400 catalyst, this value was not reached during the first and the second heating-cooling cycles due to the low rate of Pt oxidation/reduction.\[57,58\]

During the operando XANES study the N$_2$, N$_2$O, and NO$_x$ formation trends were similar for the Pt-N-400 and Pt-400-250H catalysts and, hence, independent on the average oxidation state of Pt. The only difference is in the light-off temperature. Also, the NO$_x$ contribution at high temperatures is slightly larger in the case of catalyst with more reduced Pt (Figure 11c,d). This agrees well with the catalytic data obtained in the plug flow reactor (Figure 1). Hence the overall rate of NH$_3$ oxidation is probably related to Pt oxidation state, which should be completely metallic to reach the highest catalytic activity. However, the steady-state Pt oxidation state which can be reached in the presence of O$_2$ excess in the reaction mixture for the NPs of 1–2 nm is only $\sim 0.7\pm 0.8$. The remaining oxygen coverage on Pt surface leads to the appearance of N$_2$O in addition to N$_2$ at temperatures $<250$°C. Note that the Pt reoxidation under the reaction conditions above 250°C (Figure 11) is accompanied by the decrease of the selectivity towards N$_2$ formation and an increase in NO$_x$ formation.
3. Discussion

Two Pt/Al₂O₃ systems were thoroughly investigated by a systematic variation of the pretreatment and the combination of physicochemical techniques (XRD, XPS, operando XANES/EXAFS, TEM) to unravel the relationship between Pt state, particle size and catalytic properties in NH₃ oxidation. The two sets of Pt/Al₂O₃ catalysts were prepared by incipient wetness impregnation using Pt(NO₃)₄ and H₂PtCl₆ precursors.

Calcination in air and reduction with H₂ at different temperatures were applied to control the oxidation state and particle size of Pt. Pristine Pt/Al₂O₃ catalysts calcined at 400 °C comprised of highly dispersed and deeply oxidized (Figure 5, Table 1) Pt nanoparticles with an average size less than 2 nm. Such particles exhibit significant catalytic activity in NH₃ oxidation only above 200 °C with the formation of N₂/N₂O (at T < 250 °C) and N₂/N₂O/NO/NO₂ (at T > 250 °C) reaction products (Figure 1). H₂ treatment of Pt/Al₂O₃ prepared from the Pt(NO₃)₄ precursor results in (1) the significant reduction of Pt (Table 1), (2) the appearance of bimodal particle size distribution with maxima at ~1 and ~2 nm (Figure 3), and (3) the enhancement of the NH₃ oxidation activity at temperature below 200 °C. Such an enhancement is accompanied by the evident widening of the temperature window of N₂/N₂O formation by 50–60 °C (Figure 1). The improvement of the catalytic activity in NH₃ oxidation for pre-reduced catalysts is well-known for Ag- and Pt-based systems owing to the generation of metallic species, which facilitate the adsorption and dissociation of NH₃ in the presence of O₂. H₂ treatment at high temperature (600 °C) results in the increase of average Pt particle size (up to ~3 nm) without significant changes in the catalytic properties. It indicates that Pt oxidation state is of primary importance for NH₃ oxidation while the effect of Pt particle size is only related to the stabilization of metallic platinum under O₂-rich conditions. [17,28,62]

In the case of Pt/Al₂O₃ catalysts prepared from H₂PtCl₆ precursor the treatment with H₂ does not improve the catalytic activity at T < 200 °C due to the stabilization of highly dispersed (<1 nm, Figure 4) and oxidized Pt clusters (Table 1). It might be related to the residual Cl on the catalyst surface (Table S1). From the XPS data presented in Figure 5b, the presence of PtO₂Clₓ with Eₜ(Pt4fₓ₋₁) > 74.5 eV was revealed in the pristine samples as well as catalysts after the H₂ treatment. Platinum oxychlorides PtO₂Clₓ interact stronger with alumina surface than PtO₂ species resulting in the stabilization of highly dispersed particles. [83] Additionally, the presence of Cl might be responsible for the redispersion of Pt particles at high temperatures. [32] The influence of Cl on the catalytic properties of Pt/Al₂O₃ was discussed in terms of CH₄ oxidation [30,63] and the decrease of catalytic activity for Cl-containing Pt/Al₂O₃ catalysts was suggested to be a result of the preservation of oxidized Pt state hindering CH₄ adsorption. Similarly, oxidation of Pt might have a negative effect on the adsorption of NH₃. The ammonia adsorption followed by its activation by adsorbed oxygen is considered as the rate-determining step of catalytic NH₃ oxidation over platinum at low temperatures. [52,65] EXAFS data confirm the presence of Cl and O neighbors in the first coordination shell of Pt, which explains the significantly higher Pt oxidation state in the reduced Pt/Al₂O₃ catalysts in contrast to Cl-free samples (Table 1). Therefore, Cl-containing Pt/Al₂O₃ catalysts are not active in NH₃ oxidation below 200 °C due to the preservation of oxidized Pt species, which are unable to absorb and activate ammonia. Only calcination at 600–800 °C causes the removal of Cl from Pt/Al₂O₃ (Table S1) resulting in the appearance of large PtO nanoparticles with improved catalytic activity in NH₃ oxidation at T < 200 °C (Figure 7). Finally, the residual Cl might also influence the acidity of catalyst surface resulting in the modification of the catalytic properties. [63,64] In the present study Cl-containing and Cl-free Pt/Al₂O₃ catalysts were characterized by similar amount and strength of acidic sites adsorbing NH₃ at T > 150 °C (cf. Supporting Information), i.e. temperature at which the NH₃ conversion was observed (Figures 1 and 5). Hence, it can be suggested that the modification of the surface acidity for Pt/Al₂O₃ by Cl has a negligible effect on catalytic NH₃ oxidation.

The treatment of the Cl-free Pt/Al₂O₃ samples with H₂ causes a significant enhancement of its catalytic activity in NH₃ oxidation (Figure 1a) while the consequent heating-cooling cycles in NH₃+O₂ mixture up to 400 °C have a little effect on its performance (Figure 11). According to the operando XANES data, the H₂ treatment results in the decrease of average Pt oxidation state, which, then, varies between +0.7–+1.2 under NH₃+O₂ conditions (Figure 11). Based on the TEM, XPS and XANES data we can speculate on the ratio of metallic and oxidized Pt atoms on the surface of the Pt-N-400-250H sample vs. bulk species. Taking into account the Pt particle size distribution, which is the same before and after catalytic measurements, [28] the fraction of surface Pt atoms for this sample can be estimated to be ~62% (cf. Supporting Information). As indicated by the XPS data only Pt⁰ and Pt²⁺ oxidized species are present on the surface of this sample (Figure 5a). Therefore, oxidation of all surface Pt atoms (~62%) to Pt³⁺ state would give the average Pt oxidation state ~+1.25 rather close to value initially observed for this sample by XANES (Figure 11). It indicates that the interaction of pre-reduced Pt particles with oxygen leads to nearly complete oxidation of their surface, in good agreement with previously published data. [52] During catalysis in NH₃+O₂ mixture at T < 250 °C the decrease of the average Pt oxidation state down to ~+0.7 is observed. Note that this value might be related to the contribution of both Pt²⁺ and Pt³⁺ surface species. According to the literature data, the stoichiometry of the surface PtO₂ structures upon heating in O₂ depends on the Pt particle size with x value changing from 1 to 2 when particle size decreases below 2 nm. [85] Taking into account the size distribution of Pt particles for the Pt-N-400-250H sample we can estimate the maximal Pt oxidation state assuming that initial Pt⁰ nanoparticles are oxidized to PtO₂ structures. The integration of the particle size distribution function with the corresponding limits (cf. Supporting Information) gives the maximal Pt oxidation state in the case of Pt-N-400-250H catalyst close to ~+2.9. Thus, the minimal value of Pt oxidation state observed during catalysis (~+0.7) corresponds to oxidation of ~25% of all Pt atoms or ~40% of Pt surface. Based on the obtained results we can conclude that for the Pt/
Al₂O₃ samples containing 1–2 nm Pt particles at least 40% of surface Pt atoms would be oxidized under NH₃ oxidation conditions irrespective to the pretreatment procedure.

In accordance with the previously proposed mechanism of NH₃ oxidation over platinum, the appearance of N₂O as a reaction product is inevitable in the presence of O₂ excess even at low temperatures due to high degree of Pt oxidation. It was claimed that deactivation of Pt/Al₂O₃ in the catalytic NH₃ oxidation occurs at temperatures below 130 °C due to the accumulation of NH₃ species on the Pt surface while adsorbed oxygen species cause deactivation at higher temperatures. The presented operando XANES data demonstrate that in the case of highly dispersed Pt particles the stabilization of PtOₓ species on the platinum surface takes place in the whole temperature range of interest up to 400 °C (Figure 11). Similar behavior was established during mathematical simulations of Pt-based diesel oxidation catalysts under lean conditions.57,66

The surface coverage of PtOₓ was found to vary from 0.3 to 0.8 depending on the reaction temperature. The lowest PtOₓ coverage corresponded to the highest catalytic activity which can be reached below 200 °C due to Pt reduction or above 400 °C as a result of PtOₓ decomposition.57 In the case of NH₃ oxidation the best catalytic performance is attributed to metallic Pt species providing sites for NH₃ and O₂ adsorption followed by ammonia activation.5,27,41 Therefore, the degree of Pt surface oxidation should be controlled to tune the catalytic properties of Pt-based systems in NH₃ oxidation including selectivity to desired reaction products.22,25

The most appropriate way to control Pt oxidation is a variation of Pt particle size. Larger Pt particles tend to be less oxidized while smaller PtOₓ structures require higher temperatures to be reduced to Pt0.26,67 The optimal Pt particle size for low temperature NH₃ oxidation was discussed to be in the range from 2–4 to 20 nm.26,27 In the present work no significant difference in the NH₃ oxidation rate is found for Pt/Al₂O₃ catalysts with the average Pt particle size more than 2 nm (Figures 1 and 7). The highest oxidation rate is reached already for the preduced 1–2 nm Pt particles. However, the N₂ selectivity for such particles does not exceed 60–70% (Figures 1 and 11) due to the presence of at least 40% of the oxidized Pt species on the noble metal particle surface under reaction conditions. To enhance the N₂ selectivity the steady-state oxygen concentration on Pt surface under reaction conditions has to be decreased. Therefore, the stabilization of Pt particle size above 2 nm with narrow size distribution should be considered as a subject for further research with the aim to improve the catalytic properties of Pt-based catalysts in selective NH₃ oxidation at low temperatures.

4. Conclusions

Platinum supported on Al₂O₃ is considered as the most appropriate system for selective NH₃ oxidation among various ammonia slip catalytic systems. In this work Pt/Al₂O₃ catalysts prepared by impregnation using Pt(NO₃)₄ and H₂PtCl₆ precursors were investigated by ex situ and operando spectroscopy to establish a relationship between the Pt oxidation state, the particle size and the catalytic properties in NH₃ oxidation. In the presence of O₂ excess in the reaction mixture the main products of NH₃ oxidation were N₂ and N₂O below 250 °C, while NO and NO₂ appeared at higher temperatures. It was shown that the nature of the Pt-containing precursor has a strong impact on the size of the obtained Pt nanoparticles as well as on their redox properties. The presence of residual Cl on the catalyst surface provided enhanced tolerance towards sintering and reduction of Pt during calcination and H₂ treatment, respectively. The preservation of highly dispersed oxidized Pt nanoparticles due to residual Cl was proposed to be responsible for the low catalytic activity in NH₃ oxidation below 200 °C. Using a Cl-free Pt precursor during the synthesis of Pt/Al₂O₃ catalysts allowed stabilizing 1–2 nm Pt particles. The reduction of such particles with H₂ leads to the formation of metallic Pt species with improved catalytic activity in NH₃ oxidation at T < 200 °C. Operando XANES study revealed the variation of the average Pt oxidation state depending on the reaction temperature during catalytic NH₃ oxidation. It was found that the highest N₂ selectivity is observed in the temperature range corresponding to the most reduced Pt surface. However, a substantial part of Pt surface remains in oxidized form as PtOₓ under NH₃ + O₂ conditions limiting the N₂ selectivity. To further tune the catalytic properties of Pt/Al₂O₃ catalysts in NH₃ oxidation optimization of Pt particle size is required. The size of Pt particles should be large enough to prevent oxidation under reaction conditions with O₂ excess, while the upper limit of Pt particle size is defined by the requirement to efficiently use the expensive active component of the catalysts.

Experimental Section

Sample Preparation

Boehmite AlO(OH) (Pura Al2O₃, Merck, Germany) was calcined in static air at 750 °C for 4 h (heating ramp 5 °C/min with intermediate calcination at 300 °C for 1 h) to obtain γ-Al₂O₃ support. The specific surface area of the prepared alumina as determined by BET was 174 m²/g. 2 wt.% Pt was deposited by incipient wetness impregnation with aqueous solutions of Pt(NO₃)₄ or H₂PtCl₆. Then the samples were dried for 16 h at room temperature followed by heating to 60 °C for 1 h and further to 120 °C for 2 h. Finally, the catalysts were calcined in air at 400, 600 or 800 °C for 4 h. Some samples were additionally reduced in H₂ flow at 250 or 600 °C for 2 h. Samples are designated depending on the Pt precursor (N stands for the nitrate and Cl – for chloride) and pretreatment conditions. For instance, the designation “Pt-N-400-250H” corresponds to a Pt/Al₂O₃ sample prepared from Pt(NO₃)₄, calcined in air at 400 °C followed by the reduction in H₂ at 250 °C.

X-ray Diffraction

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 diffractometer (Germany) using a CuKα radiation, and a Ni filter in the reflected beam path to remove the CuKβ component. The primary slit was 0.1°, the receiving one was 2.2°, the aperture of the Soller slits in the primary and reflected beams was 2.5°. The diffraction intensities were measured using an
one-dimensional LynxEye detector with an angular range of 2.0° on a 2θ scale. XRD patterns were collected in the 2θ range 15–90° with a 0.05° step and acquisition time of 5 s. ICDD PDF-2 powder database was used for the analysis of the crystalline phases. The structure refinement and profile analysis were carried out with the TOPAS software package. The X-ray diffraction patterns for Pt/Al₂O₃ samples were refined as a set of reflections from γ-Al₂O₃ with fixed parameters (defined from a measurement of the pristine support) and metallic platinum using the Rietveld method. To estimate the instrumental broadening crystalline Si powder was used as a reference. The mean crystallite size was calculated using the LVol-IB method.

Transmission Electron Microscopy

The data were collected on a JEM-2200FS electron microscope (JEOL Ltd., Japan) with an accelerating voltage of 200 kV to obtain high-resolution TEM and STEM HAADF images with a spatial resolution of 1 Å. Images of crystal lattices obtained by high-resolution transmission electron microscopy were analyzed by the Fourier method. The samples were dispersed in ethanol ultrasonically and deposited by sputtering the ethanol dispersion on 3 mm copper grids covered with a carbon film. The particle size distribution was determined from the TEM data using ImageJ software.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) were measured on an ES300 spectrometer (KRATOS, UK) using MgKα source (1253.6 eV). The Au4f, Cu2p, and C1s core-level spectra of gold and copper foils with binding energy (E_b) at 84.0 eV and 932.7 eV were used for the spectrometer calibration. The maximum of the Al2p line set at 74.5 eV was used as an internal standard for calibration of the experimental spectra. Pt4f spectra were analyzed after the subtraction of the Al2p signal. The Al2p, Pt4f, C1s, O1s, Cl2p core level spectra were used for the analysis of surface composition and chemical state of the elements. Surface concentrations of the elements were estimated based on the intensity of the corresponding core-level spectra with consideration of atomic sensitivity factors. Curve fitting was performed with a combination of Gaussian and Lorentzian functions after Shirley background subtraction. Spectra were processed using the XPS-Calc program tested previously on a number of catalytic systems.

X-ray Absorption near Edge spectra and X-ray Absorption Fine Structure

X-ray absorption near edge structure (XANES) spectra at Pt L₃ absorption edge were recorded ex situ at the SUL-X beamline of the KIT synchrotron radiation source (Karlsruhe, Germany) in transmission mode. Catalyst samples were measured as powders packed in Kapton tubes (d = 1.6 mm). The spectra were corrected for the energy shift using a spectrum of Pt foil measured simultaneously and then normalized using the Athena program from the IFEFFIT software package. The average Pt oxidation state was determined from an average number of oxygen atoms in the first coordination shell of Pt as obtained during the analysis of extended X-ray absorption fine structure (EXAFS). For this purpose EXAFS spectra were background-subtracted, k²-weighted and Fourier-transformed in the k-range 2.5–10.5 Å⁻¹ and multiplied by a Hanning window with sill size of 1 Å⁻¹. The amplitude reduction factor S⁰₂ = 0.96 was obtained by fitting PtO₂ (Alfa Aesar, 99.95%) reference spectrum to a structural model reported in the Inorganic Crystal Structure Database (ICSD, CC = 4415). The fits were performed using Artemis by a least square method in R-space between 1.0 and 2.5 Å in the case of a single O shell and between 1.0 and 3.6 Å when fitting O and Pt (metallic) shells. Coordination numbers, interatomic distances, energy shift (E₀) and mean square deviation of interatomic distances (σ²) were refined during the fitting. The absolute misfit between theory and experiment was expressed by p.

For the operando experiments the catalysts (approx. 5 mg, pressed and sieved to 100–200 μm grains) were placed in situ micro-reactors (quartz capillary, 1.5 mm diameter, 20 μm wall thickness, Hilgenberg GmbH) heated by a hot air blower. X-rays probed the first 1 mm of catalyst near the inlet of the catalyst bed. Gases were dosed using mass flow controllers and the outlet gas was analyzed using an MKS MultiGas 2030 FTIR gas analyzer. The concentration of the produced N₂ was not measured directly but determined as a difference between the reacted NH₃ and produced NO, N₂O, and N₂O taking into account the number of N atoms in each of these species. The total gas flow was 70 cm³/min and the Gas Hourly Space Velocity (GHSV) = 630 000 h⁻¹. As-prepared catalysts were heated twice in flow of 890 ppm NH₃ and 10 vol.% O₂ (He and N₂ mixture as balance) from 50 °C to 400 °C (ramp to setpoint 5 °C/min, cooling down between heating in the same gas feed). Pt-N-400 and Pt-N-400-250H were measured at P64 beamline of the PETRA III synchrotron (DESY, Hamburg, Germany) operating in the QEXAFS mode. The average Pt oxidation state was determined by a linear combination analysis (LCA) of the XANES spectra using internal references from QEXAFS datasets in a fitting range of 11544–11594 eV using JAQ software. To translate the relative fractions obtained from the QEXAFS analysis to the oxidation state of Pt the internal reference spectra were exported and evaluated using LCA with Pt foil and PtO₂ reference spectra in Athena.

Catalytic Measurements

The catalytic measurements were carried out using an automatic setup equipped with a plug flow quartz reactor (ID = 9 mm), FTIR spectrometer (I1801, MIDAC corp., USA) and a gas chromatograph (Crystal 2000 M, CHROMATEC). The catalyst weight was 0.145 g. The catalytic measurements were performed using the Athena program from the IFEFFIT software package. The average Pt oxidation state was calculated as (C₇/C₈) × 100, where C₇ = inlet NH₃ concentration and C₈ = outlet NH₃ concentration. The product selectivity (S) was calculated as n/2nₓ, where nₓ = the concentration of the product reaction (N₂, N₂O, NO, or N₂O₂).
Acknowledgments

The work was supported by Helmholtz – Russian Science Foundation Joint Research Groups grant #18-43-06201 from 03.09.2018 (RSF)/HRSF-0046 from 01.09.2018 (HGF). We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provided beamtime. Parts of this research were carried out at PETRA III and we would like to thank Dr. Edmund Welter, Dr. Wolfgang Caliebe, and Dr. Vadim Murzin for assistance in using beamlines P64 and P65. In addition, we thank the Institute for Beam Physics and Technology (IBPT) for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA) at KIT (Karlsruhe, Germany), in particular Dr. Jörg Göttlicher and Dr. Ralph Steininger for their help and technical support during experiments at SUL-X beamline of the Institute for Photon Science and Synchrotron Radiation (IPS).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: ammonia slip catalyst · NH3 · operando spectroscopy · Pt/Al2O3 · platinum

[1] A. Walker, Top. Catal. 2016, 59, 695–707.
[2] T. Johnson, SAE Int. J. Engines 2016, 9, 1258–1275.
[3] R. Kruehnet, M. Baerens, Chem. Eng. J. 2008, 137, 361–375.
[4] R. Burch, W. M. Southward, Catal. J. 2000, 195, 227–226.
[5] B. Bahrami, V. G. Komvokis, M. S. Ziebarth, O. S. Alexeev, M. D. Amiridis, Appl. Catal. B 2013, 130, 25–35.
[6] R. Zhang, N. Liu, Z. Lei, B. Chem. Rev. Chem. 2016, 116, 3658–3721.
[7] H. Wu, Z. Ma, Z. Lin, H. Song, Y. Yan, Y. Shi, Nanomaterials 2019, 9, 388.
[8] A. De Marco, C. Proietti, A. Anav, L. Ciancarella, I. D’ella, S. Fares, M. F. Fornasier, L. Fusaro, M. Guatieri, F. Manes, Environ. Int. 2019, 125, 320–333.
[9] Y. Pan, S. Tian, D. Liu, Y. Fang, X. Zhu, Q. Zhang, B. Zheng, G. Michalski, Y. Wang, Environ. Sci. Technol. 2016, 50, 8049–8056.
[10] L. Chmielarz, M. Jabłońska, RSC Adv. 2015, 5, 43408–43431.
[11] D. Chakrabarty, H. N. Petersen, C. Elkjær, A. Cagulada, T. Johannessen, Appl. Catal. B 2017, 214, 861–870.
[12] S. Z. Andersen, V. Colic, S. Yang, J. A. Schwachle, A. C. Nielander, J. M. Enenkel, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, H. W. P. Carvalho, B. Mutz, T. Bligaard, M. J. Hoffmann, J.-D. Grunwaldt, Surf. Sci. 2019, 457–473.
[13] O. B. Bel’skaya, R. K. Karymova, D. I. Kochubei, V. K. Duplyakin, Kinet. Catal. 2008, 49, 729–736.
[14] R. M. Mironenko, O. B. Belskaya, V. P. Talsi, T. Gulyaeva, M. O. Lazurkin, A. I. Nizovskiy, V. I. Bukhtiyarov, A. V. Lavrenov, V. A. Likholobov, Appl. Catal. A 2014, 469, 472–482.
[15] E. Ogel, M. Caiaupi, D. E. Dornonik, R. Popescu, H. Störmer, C. Mechler, G. Marzun, S. Barciowsk, M. Türk, J.-D. Grunwaldt, J. Phys. Chem. C 2019, 123, 5343–5446.
[16] A. C. M. Van den Broek, J. Van Grondelle, R. A. Van Santen, Catal. Lett. 1998, 55, 79–82.
[17] G. Golffison, L. R. Wallenberg, A. Anderssen, J. Catal. 2005, 230, 1–13.
[18] A. Boubnov, S. Dahl, E. Johnson, A. P. Molina, S. B. Simonsen, F. M. Cano, S. Helveg, L. J. Lemus-Yegres, J.-D. Grunwaldt, Appl. Catal. B 2012, 115, 315–325.
[19] A. Chakrabarti, M. E. Ford, D. Gregory, H. Lu, C. J. Keturakis, S. Lwin, Y. Zhang, Z. Yang, M. Zhu, M. A. Baahes, Catal. Today 2017, 283, 27–53.
[20] F. Wang, J. Jiang, B. Wang, Catalysts 2019, 9, 477.
[21] G. Novell-Leruth, J. M. Ricart, J. Pérez-Ramírez, J. Phys. Chem. B 2008, 112, 13554–13562.
[22] J. Schaffler, V. A. Kondratenko, N. Steinfeldt, M. Sebek, E. V. Kondratenko, J. Catal. 2013, 301, 210–216.
[23] M. Peuchht, H. P. Bonzel, Surf. Sci. 1984, 145, 239–259.
[24] Z. R. Ismagilov, S. A. Yashnik, A. N. Startsev, A. I. Stadnichenko, V. V. Kriventsova, S. Kazetlan, D. Guillaume, M. Mkakke, J. A. Mouljin, Catal. Today 2009, 144, 235–250.
[25] D. A. Svintsitskii, L. B. Isi, A. I. Stadnichenko, S. V. Koczew, V. I. Kibis, A. I. Boronin, ChemPhysChem 2015, 16, 3318–3324.
[26] A. V. Kalinkin, M. Y. Smirnov, A. I. Nizovskiy, V. I. Bukhtiyarov, J. Electron Spectrosc. Relat. Phenom. 2010, 177, 15–18.
[27] Y. T. Kim, K. Ohshima, K. Higashime, T. Uruga, M. Takata, H. Suematsu, T. Mitani, Angew. Chem. Int. Ed. 2006, 45, 407–411; Angew. Chem. 2006, 118, 421–425.
[28] I. V. Vovk, A. V. Kalinkin, M. Y. Smirnov, L. O. Klembovskiy, V. I. Bukhtiyarov, J. Phys. Chem. C 2017, 121, 17297–17304.
[29] J. E. Drawdy, G. B. Hoflund, S. D. Gardner, E. Yngvadottir, D. R. Schryer, Surf. Interface Anal. 2019, 16, 369–374.
[30] F. J. Gracia, E. E. Wolf, T. J. Miller, A. J. Kropf, Stud. Surf. Sci. Catal. 2001, 139, 471–478.
[31] T. I. Hyde, P. W. Ash, D. A. Boyd, G. Randlshofer, K. Rothenbacher, G. Sankar, Platinum Met. Rev. 2011, 55, 233–245.
[32] G.-W. Jiang, K. Rajeshwara, J. Electrochem. Soc. 1987, 134, 1830–1835.
[33] C. Szikhely, L. Keerthana, I. Prabha, Johnson Matthey Tech. Rev. 2009, 63, 122–133.
[34] A. Boubnov, A. Gänzler, S. Conrad, M. Casapu, J.-D. Grunwaldt, Top. Catal. 2013, 56, 333–338.
[35] D. A. Svintsitskii, L. S. Kibis, A. I. Stadnichenko, E. M. Slavinskaya, A. S. Zaguzin, A. V. Romanenko, A. A. Derevyannikova, O. A. Stonkus, A. I. Boronin, in AIP Conf. Proc., 2002, p. 20008.
[36] A. M. Gänzler, M. Casapu, A. Boubnov, O. Müller, S. Conrad, H. Lichtenberg, R. Frahm, J.-D. Grunwaldt, J. Catal. 2015, 328, 216–224.
[37] A. Arjavapaa, P. Koči, Chem. Eng. Sci. 2017, 138, 181–187.
[38] L. Olsson, H. Karlsson, Catal. Today 2009, 147, 12–15.
[39] L. Zhang, H. He, J. Catal. 2009, 268, 18–25.
[40] J. Gang, B. G. Anderson, J. Van Grondelle, R. A. Van Santen, Appl. Catal. B 2003, 40, 101–110.
[61] D. P. Sobczyk, A. M. De Jong, E. J. M. Hensen, R. A. Van Santen, J. Catal. 2003, 219, 156–166.
[62] R. W. McCabe, C. Wong, H. S. Woo, J. Catal. 1988, 114, 354–367.
[63] E. Marceau, H. Lauron-Pemot, M. Che, J. Catal. 2001, 197, 394–405.
[64] P. Berteau, B. Delmon, Catal. Today 1989, 5, 121–137.
[65] C.-B. Wang, C.-T. Yeh, J. Catal. 1998, 178, 450.
[66] A. Arvajová, P. Kočí, V. Schmeißer, M. Weibel, Appl. Catal. B 2016, 181, 644–650.
[67] N. Seriani, Z. Jia, W. Pompe, L. C. Ciacchi, Phys. Rev. B 2007, 76, 1–10.
[68] TOPAS, version 4.2., Bruker AXS Inc., Madison, Wisconsin, USA.
[69] M. D. Abramoff, P. J. Magalhaes, J. S. Ram, Biophotonics Int. 2004, 11, 36–42.
[70] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corp, Eden Prairie, Minnesota, USA, 1992.
[71] L. S. Kibis, D. A. Svintsitskiy, T. Y. Kardash, E. M. Slavinskaya, E. Y. Gotovtseva, V. A. Svetlichnyi, A. I. Boronin, Appl. Catal. A 2019, 570, 51–61.
[72] E. D. Grayfer, L. S. Kibis, A. I. Stadnichenko, O. Y. Vilkov, A. I. Boronin, E. M. Slavinskaya, O. A. Stonkis, V. E. Fedorov, Carbon N. Y. 2015, 89, 290–299.
[73] D. A. Svintsitskiy, E. M. Slavinskaya, T. Y. Kardash, V. I. Avdeev, B. V. Senkovskiy, S. V. Koscheev, A. I. Boronin, Appl. Catal. A 2016, 510, 64–73.
[74] B. Ravel, M. Newville, J. Synchrotron Radiat. 2005, 12, 537–541.
[75] J.-D. Grunwaldt, N. Van Vegten, A. Balzer, Chem. Commun. 2007, 4635–4637.
[76] D. E. Doronkin, H. Lichtenberg, J.-D. Grunwaldt, in XAFS Tech. Catal. Nanomater. Surfaces, 2016, pp. 75–89.
[77] B. Bornmann, J. Kläs, O. Müller, D. Lützenkirchen-Hecht, R. Frahm, AIP Conf. Proc. 2019, 2054, 40008.

Manuscript received: September 11, 2019
Revised manuscript received: October 15, 2019
Accepted manuscript online: October 15, 2019
Version of record online: November 26, 2019