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Morphology changes of Pt-foil catalyst induced by temperature-controlled ammonia oxidation near atmospheric pressure

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Abstract

Reaction-induced changes of the morphology of a Pt foil catalyst during ammonia oxidation were investigated in a temperature-controlled way for partial pressures of oxygen and ammonia around 4.5 and 3 kPa, respectively, and at temperatures between 20 and 700 °C. The presence of the feed mixture (ammonia and oxygen) was required to induce surface roughening. Moreover, the reaction temperature controlled the type of restructuring of the Pt surface, that is, either into rows of parallel facets where facet size increased with temperature, or as bulky microcrystals protruding from the surface. Surprisingly, reaction-induced surface faceting was already observed at 286 °C. Between 286 and 374 °C adsorbate-enhanced surface diffusion of Pt is suggested to account for the surface restructuring well below temperatures reported for significant Pt transport through the gas phase via volatile PtO_x.

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1. Introduction

Selective oxidation of ammonia on Pt-based alloy catalysts is the first step of the Ostwald process dominating the industrial production of nitric acid. The surface of the applied Pt catalysts is heavily reconstructed within hours and days during the reaction [1,2]. Since similar reaction-induced surface reconstructions have been reported also for the catalytic oxidation of hydrogen, ethane, and propane [3], the respective processes were summarized under the term of “catalytic etching”.

Depending on pressure, temperature, catalyst composition, and time of exposure to catalytic ammonia oxidation, the surface of Pt-based catalysts reconstructs into rows of facets and pits [4], and later on into bulky structures resembling the shape of cauliflowers [5–7]. Such extensive reconstruction of the surface of the industrially applied Pt–Rh alloy gauzes leads to loss of catalytic material, mechanical degradation, and finally to the collapse of the catalyst wires. Special gauzes

located downstream of the active package, usually made of palladium or Pd–Au alloys, can be applied to catch part of the platinum which is otherwise lost [8].

Catalytic etching of Pt catalysts during ammonia oxidation was not detected at pressures below 15 Pa even after extended periods of catalyst operation [9,10], an observation confirmed by our recent study on the influence of pressure on structural and catalytic properties of different platinum catalysts [11]. At higher reactant partial pressures (kPa range), the reconstruction of Pt surfaces has been studied during catalytic ammonia oxidation at temperatures above 600 °C on polycrystalline platinum in the shape of wires [4,6,7,12], gauzes [5,13,14], and spheres [15]. Evaporation of Pt-containing species, their transport in the gas phase, and subsequent decomposition and redeposition of Pt on the surface were suggested as key steps in the catalytic etching process [16,17]. Different transport mechanisms were proposed:

- (1) Phillips et al. [18–20] studied the oxidation of hydrogen and ethene on platinum catalysts, and proposed that Pt needs the aid of radicals to enter the gas phase (C₂H₄^{*}, O₂H^{*}). The radicals react homogeneously in the gas phase to form clusters, and finally fall back to the surface, producing the “cauliflower” structures.

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- (2) Lyubovsky and Barelko [7] studied etching phenomena during ammonia oxidation on Pt wires partly covered with gold to create (inactive) cold spots. Growth of microcrystals and some kind of “Pt wool” was observed on these spots. The authors suggested that a heterogeneous reaction at active centers induces local heat generation, causing rapid sublimation of Pt from the surface. The deposits were suggested to grow via a vapor-liquid-solid mechanism, where gas phase platinum is trapped by a liquid on colder parts of the surface.
- (3) McCabe et al. [21] proposed that platinum is transported from cracks and holes to the surface. Molecular oxygen diffuses into cavities, increasing oxygen activity locally, and forming PtO₂. While leaving the holes, most of this oxide decomposes at the surface, resulting in deposits around the cavities. Although this theory might be an explanation for etching of platinum wires, it does not offer a model for formation of “cauliflowers”. A phase diagram for the influence of temperature and reactant concentration (NH₃, O₂) on catalyst etching was reported by McCabe et al. [4] for the temperature range from 700 to 1400 °C.
- (4) Nilsen et al. [6] investigated recently thermal and catalytic etching on Pt and Pt₉₀Rh₁₀ wires in a flow reactor. During ammonia oxidation, formation of small nodules was detected, which later transformed into cauliflowers. *In situ* MS revealed Pt⁺, PtO⁺, and PtO₂⁺ species to be present in the gas phase. The proposed model suggested active centers for oxidation (preferably on dislocations ending at the surface), local generation of heat and evaporation of Pt species, and finally growth of protrusions from deposited Pt via a dendritic growth mechanism. Experiments that exposed Pt powder to pure oxygen atmosphere in combination with *in situ* MS confirmed PtO₂ as a major vapor species responsible for vapor phase transport of platinum [22].

Ammonia oxidation is a fast and highly exothermic reaction. Thus, previous studies of reaction-induced changes of the surface morphology of Pt were conducted in the ignited regime of ammonia oxidation, where the catalyst temperature is not controlled by the reactor oven, but results mostly from the heat generated in the reaction and its removal. Hence, composition and flow rate of the feed determined the catalyst temperature and imposed a minimum temperature of ca. 600 °C. Moreover, the catalytic reaction was limited by heat and mass transfer in the ignited regime, one possible reason why the cited studies did not report the changes in catalytic activity resulting from the morphological changes. Steep temperature and concentration gradients occur under such reaction conditions, making it difficult to establish the effect of the respective parameters on catalytic etching.

The aim of the present study was to elucidate the influence of temperature on the reconstruction of Pt catalysts induced by ammonia oxidation under temperature-controlled conditions, that is, at lower temperatures than previously accessible, and to observe the associated changes in catalytic activity.

Suitable tools to study the highly exothermic ammonia oxidation are microstructured reactors as proposed by Rebrov et al. [23,24] for supported Pt/Al₂O₃, and recently established by our group for catalytic investigations on polycrystalline Pt foils [11,25]. Applying the latter reactor that enabled temperature control in the reaction, product formation was recorded as a function of temperature and time. The Pt samples used as a catalyst for ammonia oxidation at temperatures between 286 and 700 °C were then characterized by electron microscopy. Based on the data, a relation is established between reaction temperature and the type and extent of changes of surface morphology, as well as the changes in overall catalytic activity.

2. Experimental

2.1. Catalyst

A thin Pt foil (purity 99.95%) supplied by Alfa Aesar (Ward Hill MA, USA) was used as a catalyst. The nominal thickness of the foil amounted to 4 μm. Scanning electron microscopy (SEM) images of the catalyst in the “as-supplied” state (Fig. 1) indicate a smooth surface with small scratches and holes, that is, minimal damage on the fresh samples.

2.2. Catalytic tests

Pt foils were applied as catalysts for ammonia oxidation using a microstructured quartz-reactor that assured temperature control. The reactor has been described earlier in detail [11,25]. It allowed measurements with minimal blank activity up to 700 °C, while the kinetic regime prevailed up to ca. 390 °C. Gas composition was continuously monitored downstream of the reactor using a QMS (Balzer Omnistar GCD 300).

The surface morphology of different Pt foil catalysts (Table 1) was studied by SEM after the reaction. To elucidate the influence of reaction temperature and time-on-stream on morphology changes, Pt foils were prepared by exposure to ammonia oxidation (a) at fixed temperatures (286, 330, 374 °C), and (b) temperature-programmed reaction (20–700 °C, 24 and 240 h, respectively):

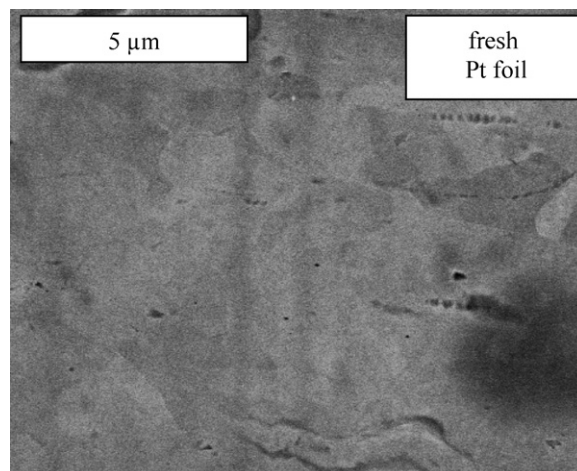


Fig. 1. SEM of fresh Pt foil catalyst, as supplied by Alfa Aesar.

- (a) Three Pt samples used in ammonia oxidation at constant temperatures of 286, 330, and 374 °C, respectively, were prepared applying the following procedure for a total period of time of about 30 h. Catalysts were initially exposed to a feed containing ammonia (3 kPa) and oxygen (4.5 kPa, balance Ar and Ne) of constant composition and temperature for about 12 h of initial time-on-stream. Thereafter, feed composition was varied at the same temperature between 1 and 6 kPa NH₃, 1 and 6 kPa O₂, adding 0 to 0.47 kPa NO, and 0 to 0.47 kPa N₂O.
- (b) Two Pt samples were exposed to temperature-programmed ammonia oxidation between 20 and 700 °C using a feed mixture (250 ml/min) containing ammonia (3 kPa) and oxygen (4.5 kPa, balance Ar + Ne). For one sample, overall activity was followed for 1 h at each temperature. The temperature ramp was repeated once, resulting in a total time-on-stream of about 24 h. The second sample was studied at each temperature level for about 12 h during the upramping of temperature, and for 4–12 h at each temperature level during downramping. Total time-on-stream for this catalyst amounted to 240 h (respective temperatures are indicated in Figs. 3 and 4).

2.3. Catalyst characterization

The surface morphology of Pt catalysts was studied by SEM. Images were recorded on a Hitachi-S4000 equipped with FEG (cold) in SE mode. An energy dispersive analyzer (DX 4, EDAX Inc.) equipped with Li-doped Si crystals was attached to the SEM for element analysis (EDX). Electron accelerating voltage for images and spectra was 15 kV. SEM images were acquired for different areas of each catalysts surface, exposed either to the catalytic reaction, or covered by the reactor wall.

3. Results

3.1. Overall catalytic activity

Results of catalytic tests are presented in the order of increasing reaction temperature, starting with experiments at constant temperature of 286, 330, and 374 °C, respectively, followed by temperature-programmed reaction up to 700 °C.

At constant temperatures of 286, 330, and 374 °C, fresh Pt catalysts were subject to initial activation at all temperatures. The respective relationship between oxygen conversion and time-on-stream is shown in Fig. 2. Since all three experiments were carried out at low temperatures and only moderate oxygen excess as compared to industrial practice, formation of N₂ prevailed, selectivity towards nitrogen being between 95 and 99%. Oxygen conversion increased with time-on-stream. The activation progressed faster during an initial period of 2–6 h (Fig. 2), and proceeded slowly thereafter. Moreover, the duration of the initial period of fast activation increased with reaction temperature.

Catalytic results of temperature-programmed ammonia oxidation between 20 and 700 °C are presented in Figs. 3

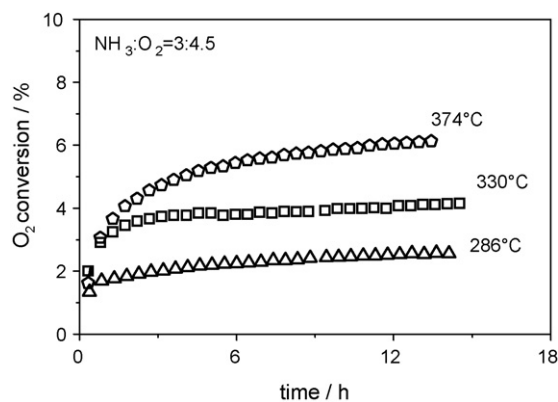


Fig. 2. Oxygen conversion *versus* time-on-stream in ammonia oxidation over fresh Pt foil at constant temperatures of 286, 330, and 374 °C (250 ml/min, 3% NH₃, 4.5% O₂, balance Ar + Ne).

and 4, respectively, as a plot of oxygen conversion *versus* temperature. The diagrams indicate a hysteresis behavior, where oxygen conversion increased after exposure to high temperature, that is, the Pt catalyst became more active. The activation as reflected by the hysteresis in Fig. 3a was permanent, and progressed further in a second temperature cycle (Fig. 3b). It should be pointed out that only a slight activation was observed during the second temperature cycle (symbols in Fig. 3b) as compared to the first cycle (dashed line in Fig. 3b), indicating that the initial activation in the first temperature cycle progressed significantly faster. Nevertheless, the catalyst became more active in the second cycle.

Hysteresis behavior was also observed in a 20 times slower cycle of temperature-programmed ammonia oxidation that required about 240 h for completion (Fig. 4). The hysteresis was more marked in this slow temperature cycle (Fig. 4, $t_{\text{exp}} = 240$ h) than in a faster temperature cycle (Fig. 3a, $t_{\text{exp}} = 12$ h), confirming that the extent of activation increases further with increasing time-on-stream.

The difference in overall activity between the heating and the cooling branches of the temperature cycles was only observable at temperatures below approximately 500 °C (Figs. 3 and 4). Two effects presumably contributed to this behavior: (i) limitation of mass-transfer of the fast reaction begins above ca. 390 °C, diminishing the observable effect of increased catalytic activity, and (ii) the time-on-stream between measurements at the same temperature in both branches of the hysteresis is significantly longer at lower temperatures, that is, activation should be further progressed.

3.2. Surface morphology

To elucidate reasons for the observed increase in conversion over the catalyst with time-on-stream in ammonia oxidation, the surface morphology of Pt foils was studied by SEM after exposure to elevated temperatures in absence and presence of the reactive feed. The results are presented first for the absence of feed gases (Section 3.2.1), thereafter for ammonia oxidation in the order of increasing temperature (<374 °C, Section 3.2.2; <700 °C, Section 3.2.3).

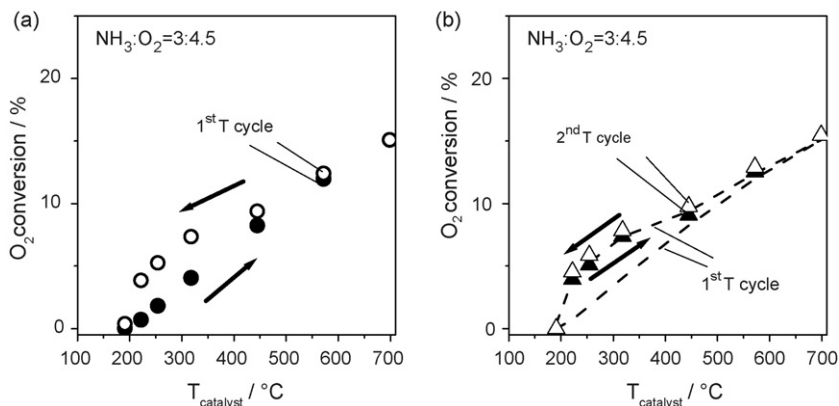


Fig. 3. Oxygen conversion *versus* temperature in TP ammonia oxidation in two consecutive temperature cycles ($t_{\text{cycle}} = 12$ h) over Pt foil (250 ml STP/min, 3% NH_3 , 4.5% O_2 , 1.5 mm Pt foil). (a) first temperature cycle (full circles: heating, open circles: cooling); (b) second temperature cycle (full symbols: heating, open symbols: cooling; dashed line: first cycle).

3.2.1. Pt foil after temperature treatments up to 700 °C in absence of reactive atmosphere

SEM micrographs of Pt foils treated for about 30 h at 374 °C are shown in Fig. 5a, and for a temperature-program of 20–700 °C for a total duration of 240 h in Fig. 5b, respectively. Both samples were covered by the quartz-plates of the reactor wall during the temperature treatment, and therefore not exposed to the reactive atmosphere of ammonia oxidation. Compared to the image of a fresh platinum foil (Fig. 1) the surface appears to be basically unchanged. Thus, the respective thermal treatments of Pt foil did not alter its surface morphology, and the process of thermal etching of platinum is concluded to be negligibly slow under the conditions of the present study.

3.2.2. Pt foil after catalytic ammonia oxidation at constant temperatures of 286–374 °C

The area of Pt foils being catalytically active in ammonia oxidation at constant temperature levels are shown in Fig. 6 for the reaction at 286 °C (Fig. 6a and b), 330 °C (Fig. 6c and d), and 374 °C (Fig. 6e and f). Already the sample catalyzing the

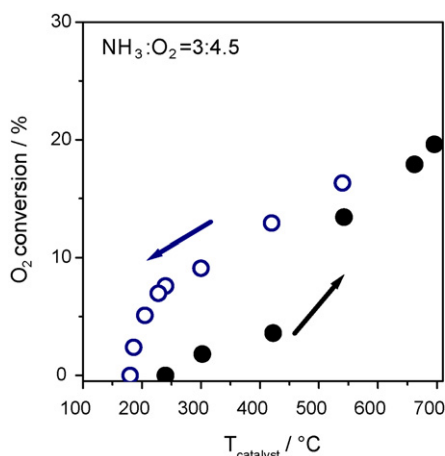


Fig. 4. Oxygen conversion *versus* temperature in TP ammonia oxidation ($t_{\text{exp}} = 240$ h) over fresh Pt foil; 250 ml STP/min, 3% NH_3 , 4.5% O_2 , 1.3 mm Pt foil full circles: heating open circles: cooling.

reaction at the lowest temperature of 286 °C expressed an altered morphology. Some areas appeared rougher after reaction, while others were not visibly changed (Fig. 6b). Roughening seems to have started from grain boundaries, perhaps due to a less ideal surface, and a locally increased defect concentration. The surface modifications exhibited the same orientation in neighboring areas.

At the higher reaction temperature of 330 °C etching of the catalyst surface occurred in wider areas (Fig. 6c and d), although some parts of the surface remained still unchanged in the SEM images. Moreover, the individual structures increased in size (Fig. 6b/d), and appeared as parallel rows of facets. The majority of facets formed at 330 °C were similar in size (Fig. 6d). Moreover, the facets locally possess the same orientation. However, different facet orientations existed along the foil sample (not shown).

The sample of Pt foil that was exposed to ammonia oxidation at 374 °C (Fig. 6e and f) featured a fully restructured and ordered surface, in contrast to platinum which had been used as catalyst at lower temperatures. The structures covered the complete surface (Fig. 6e), and were arranged in parallel rows of facets, each of them about 0.5 μm apart (Fig. 6f). Each row consisted of smaller shapes that resembled roofs, made up of flat planes and connected by sharply defined edges. The “roofs” look like welldefined single crystal faces, and are supposed to be thermodynamically stable low-index crystal planes. Some facets were penetrated by holes of a square shape, and less than 0.1 μm in diameter (Fig. 6f).

The same dominating orientation of the facets was observed over large (reaction-exposed parts of the) Pt sample, covering an area of at least 40 $\mu\text{m} \times 60 \mu\text{m}$. Only occasionally the order of parallel facets was locally disturbed, and the same type of facet rows appeared rotated by about 90° (left part of Fig. 6e), or sometimes 45°. The rotated facet rows terminated flat slabs of Pt of about 0.5 μm thickness (Fig. 6e).

3.2.3. Pt foil after temperature-programmed ammonia oxidation between 20 and 700 °C

SEM micrographs of the surface of Pt foils after catalysis in temperature cycles from 20 to 700 °C for a total duration

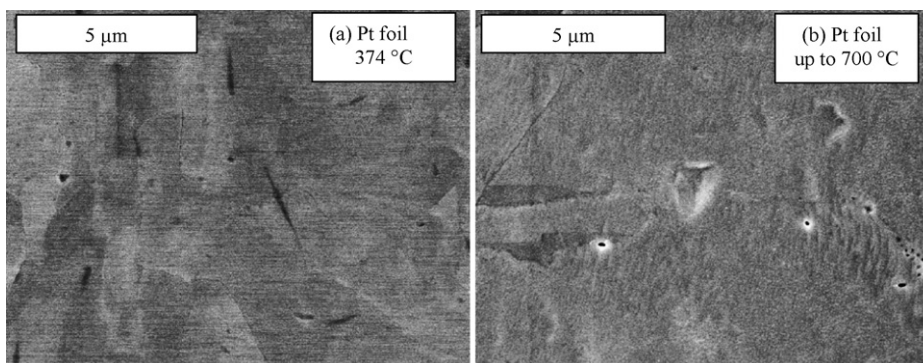


Fig. 5. SEM of platinum foil after exposure to reaction temperature, but not to the reactants of ammonia oxidation (surface of the Pt foil was protected from gases by plates of quartz glass). (a) at constant temperature of 374 °C for 30 h; (b) at 20–700 °C for a total of 240 h.

of 24 h and for 240 h are shown in Fig. 7a/b and in Fig. 7c/d, respectively. The conditions applied to the reaction exposure for 24 h (Fig. 7a,b) differed from the previous samples (Fig. 6) not so much in the exposure time (24 h vs. 30 h), but

most of all in the maximum temperature (700 °C vs. 286–330 °C).

After 24 h of time-on-stream the Pt surface featured somehow parallel rows of facets in some areas (Fig. 7a, right

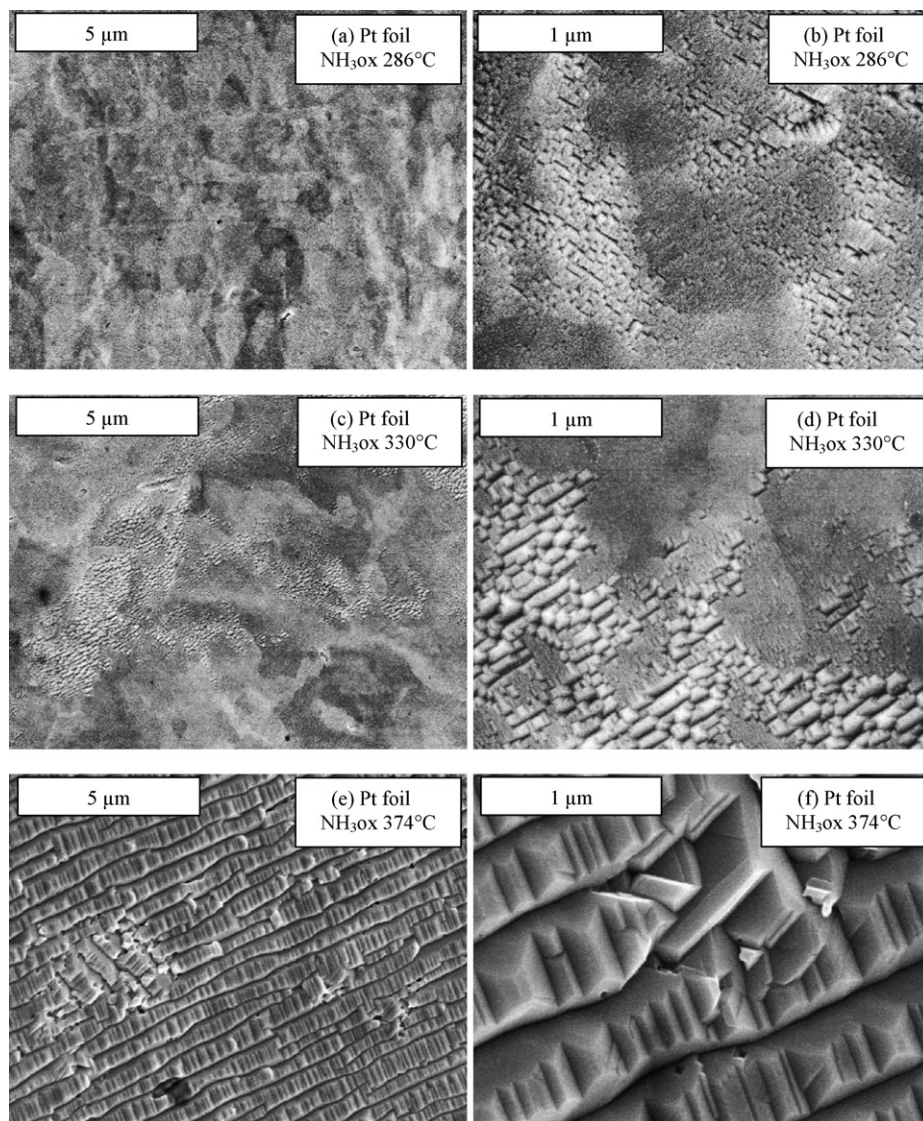


Fig. 6. SEM of platinum foil after ammonia oxidation at constant temperature: (a,b) 30 h at 286 °C; (c,d) 30 h at 330 °C; (e,f) 30 h at 374 °C.

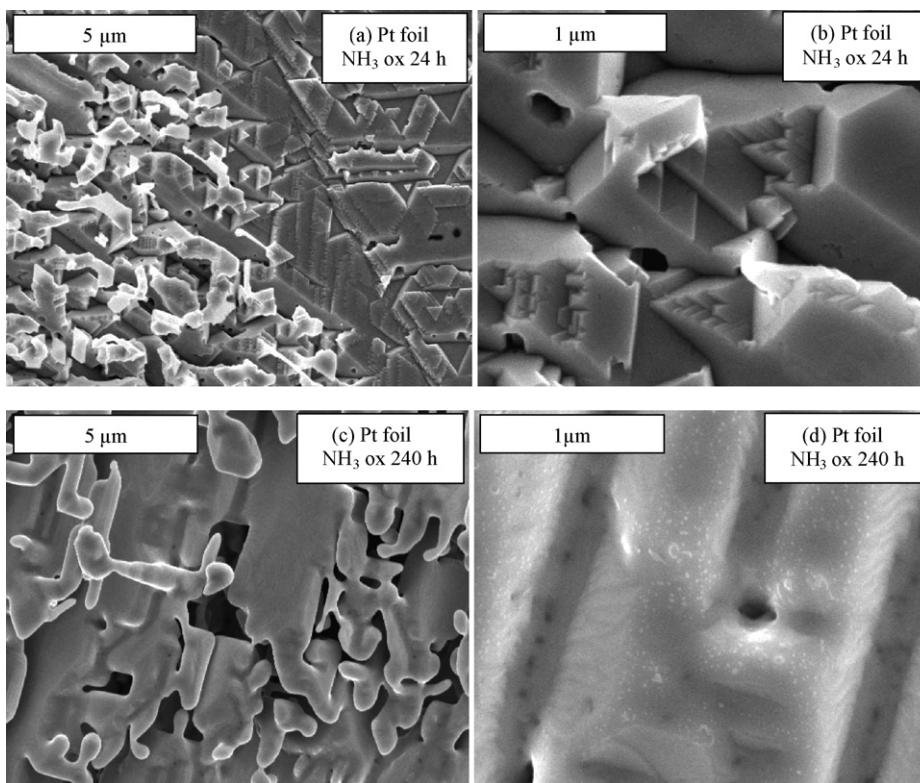


Fig. 7. SEM of platinum foil after temperature-programmed ammonia oxidation: (a,b) at 20–700 °C for a total of 24 h; (c,d) at 20–700 °C for a total of 240 h.

side), but the previously observed (Fig. 6) well-defined roof structures did not exist. Moreover, facet rows were about 2 μm wide, compared to less than 0.5 μm at 286 to 374 °C. In some areas (Fig. 7a, left side) the surface reconstructed into bulky and three-dimensional structures protruding from the surface. Furthermore, the formed facet rows were deep and undercut. Numerous holes penetrated the protrusions (Fig. 7b), and reached sizes similar to the dimensions of the crystals growing from the surface. Such crystals consisted of flat faces and sharp edges (Fig. 7b), but some of the sharp edges were faceted themselves. Compared to the low-temperature samples, the appearance of the Pt surface became rougher, disordered and porous.

The three-dimensional reconstruction of the Pt catalyst (Fig. 7b) progressed further in a period of 240 h of ammonia oxidation up to 700 °C (Fig. 7c and d), and resulted in loosely connected crystals (Fig. 7c). Instead of flat faces and straight edges, the protrusions looked smooth and rounded, where the

underlying shape of a wellformed crystals was only faintly visible (Fig. 7c). The crystals were several micrometers in size, and were connected to other crystals only via narrow bridges. Due to the porous surface morphology, and the small remaining connections between the Pt crystals, it is likely that heat conduction through the catalyst becomes severely obstructed, and local temperature gradients form due to the exothermic reaction.

4. Discussion

The reaction-induced changes of catalytic activity are discussed below (Section 4.1), followed by differences in observed surface morphologies (Section 4.2), and influences governing the surface restructuring (Section 4.3). Finally, the results are related to possible mechanisms of platinum transport (Section 4.4).

4.1. Reaction-induced changes of overall activity of the catalysts

Platinum foils became more active during catalytic ammonia oxidation under all investigated conditions, that is, during the reaction at constant temperatures of 286–374 °C (Fig. 2) as well as during temperature ramps to 700 °C (Figs. 3 and 4). Moreover, SEM images indicate that all of the activated catalysts developed a reconstructed surface during this activation process (Figs. 6 and 7), changing from a flat initial surface to different expressions of a roughened morphology. Hence, the presumably associated increase in

Table 1
List of Pt foil samples, used for ammonia oxidation and SEM characterization

Sample name	Description of sample treatment
Pt foil NH ₃ ox 286 °C	(a) Fresh Pt foil, ammonia oxidation, 286 °C, 30 h
Pt foil NH ₃ ox 330 °C	(a) Fresh Pt foil, ammonia oxidation, 330 °C, 30 h
Pt foil NH ₃ ox 374 °C	(a) Fresh Pt foil, ammonia oxidation, 374 °C, 30 h
Pt foil TP-NH ₃ ox 24 h	(b) Fresh Pt foil, H ₂ treated, ammonia oxidation, two temperature ramps 20–700–20 °C, total time 24 h
Pt foil TP-NH ₃ ox 240 h	(b) Fresh Pt foil, ammonia oxidation, one temperature ramp 20–700–20 °C, total time 240 h

the surface area of Pt catalysts is one effect that could account for the observed reaction-induced increase in overall catalytic activity. Nevertheless, etching of the Pt foils did not progress uniformly across the surface (Fig. 6b and d; Fig. 7a). It is therefore likely that the intrinsic activity of the Pt catalysts varied over the surface. Since the catalytic measurements of ammonia oxidation represented a sum of reactivity over the whole catalyst, local differences in activity could not be investigated.

Both, initial activation of the polycrystalline Pt catalyst as well as roughening of the Pt surface started at surprisingly low temperatures (286 °C) that were not accessible in previous studies of catalytic etching of platinum. Moreover, product formation in the catalytic ammonia oxidation (reactant partial pressures in the kPa range) started around 200 °C (Fig. 3). Thus, the temperature range, where possibly no significant reaction-induced restructuring of the platinum surface occurs is very narrow.

In contrast to earlier studies, the reaction-induced changes in the overall activity of polycrystalline Pt were investigated in the present work in a temperature-controlled way, and at oxygen conversions below 20%. Hence, direct evidence for a link between the activation of Pt with time-on-stream and faceting of the Pt surface was obtained for the first time, while previous reports [26] were limited to the discussion of selectivity and yield measured at full ammonia conversion in the ignited regime of the reaction.

4.2. Morphology of restructured Pt surfaces

The roughening of Pt catalysts due to ammonia oxidation was observed in different expressions, that is, rows of parallel facets (Fig. 6d and f), pits (Fig. 6f, Fig. 7b and d), and bulky crystals growing from the surface (Fig. 7b and c). Similar surface structures have been reported in literature such as facet rows [4,6,7,12,15], pits [4,12,15], and bulky crystals protruding from the surface [6,7,12]. In contrast, so-called “cauliflower” structures were reported for Pt gauzes after more than 330 h time-on-stream in ammonia oxidation [6,12,27], but not observed in the present study that was conducted at lower temperatures and time-on-stream.

Surface structures reported in literature differed from those in the present work in size, especially for Pt samples that were exposed to the lower reaction temperatures of 286 to 374 °C. While parallel rows of facets less than 0.1 μm apart from each other were formed in our experiments (Fig. 6b and d), the reported width of facet rows always exceeded 0.5 μm [4,6,7,12,15]. Moreover, also the assembly of facet rows from the sharply defined flat faces shown in Fig. 6f has not been reported yet to our knowledge. Such a difference can be ascribed to two reasons. First of all, the SEM images presented in this work are of higher resolution than shown by other authors. More importantly, temperature is a major parameter in the catalytic etching of Pt, and the present experiments were carried out at temperatures significantly below the 600 °C, which represented the lower temperature limit of earlier work on Pt spheres and wires.

As evidenced by several of the SEM images (Fig. 6b and d, Fig. 7a), ammonia oxidation did not roughen all areas of the Pt surface to the same extent. Literature reports agree with the finding that initial etching of the Pt surface is not uniform over the whole surface of polycrystalline Pt [4,12], but vary in the observation that whole grains were fully covered by similar facets [4] or etching started near grain boundaries [7,12]. The present data supports the view that etching of the Pt surface spreads from grain boundaries. Preferred restructuring near grain boundaries may result from a locally increased concentration of defects in such areas and disturbance of lattice regularity, which results in a variation of the corresponding reaction rates of the structure sensitive ammonia oxidation.

All SEM images of restructured Pt wires and spheres provided by other authors [4,6,7,12] featured different facet orientations in neighboring areas on the surface. In contrast, the studied Pt foil exhibited the same preferred facet orientation (Fig. 6e) over a range of at least 40 μm × 60 μm after ammonia oxidation at 374 °C (not shown). A definite explanation for the uniform faceting over such a large area cannot be given yet, since it is not known if the initial crystallite orientation on the fresh Pt foil was the same over the whole surface. It is suggested that the resulting facet orientation is either determined by a texture present in the fresh Pt sample from its manufacturing process, or from the flow direction of the feed mixture over the sample.

4.3. Influence of gas atmosphere, temperature, and time-on-stream on surface restructuring

Images of the surface after catalytic ammonia oxidation (Fig. 6e, Fig. 7c) were compared to those of samples that were exposed to the identical temperature treatment (Fig. 5a and b), but in the absence of any reactive gas atmosphere. While the latter samples resembled the surface of untreated Pt foil (Fig. 1), only the morphology of Pt exposed to the catalysis of ammonia oxidation became rough and restructured. Hence, the presence of reactive adsorbates on the surface is essential for restructuring of Pt catalysts between 286 and 700 °C. Therefore, the process of changing the surface morphology can be classified as “catalytic etching”, and not as thermal etching.

A comparison between SEM images of Pt samples that were applied in ammonia oxidation at different temperatures of 286, 330, and 374 °C for the same time-on-stream (Fig. 6b, d, and f), showed that in this temperature range similar shapes of facets formed on the surface. The size of facet rows clearly increased with temperature from less than 0.1 μm at 286 °C to about 0.5 μm at 374 °C (Fig. 6b, d, and f). Moreover, also the area that developed facets increased in this temperature range up to a fully faceted surface at 374 °C (Fig. 6b, d, and f). Hence, temperature is a major parameter that determines both facet size as well as surface coverage with facets in ammonia oxidation between 286 and 374 °C. In contrast to this present conclusion, previous work of McCabe et al. [4] reported only a “weak correlation” between facet size, which was between 0.5 and 3 μm, and temperature for experiments conducted at 700 to

1400 °C. As mentioned before, the differences may be attributed to better temperature control in the current reactor setup, and the fact that the present correlation was established for significantly lower reaction temperatures.

In contrast to the parallel rows of facets observed after reaction at 286 to 374 °C, where the faceted surface remained essentially flat (Fig. 6b, d, and f), bulky crystals of different shapes protruding from the surface formed in temperature-programmed ammonia oxidation up to 700 °C (Fig. 7b and c). Moreover, also the shape of the occasionally observed pits changed from straight-edged and square-shaped (Fig. 6f) towards a more rounded appearance (Fig. 7b and d). This variation in surface morphology occurred despite of the fact that the time of exposure to ammonia oxidation at 286–374 °C (30 h, Fig. 6) was comparable to that of one high-temperature sample (24 h, Fig. 7a and b). Hence, the shift from temperatures below 400 °C to about 700 °C resulted in a change of surface morphology towards bulky crystals and a porous surface appearance, that is, a completely different restructuring of Pt. Thus, temperature is of major importance over the whole studied temperature range of ammonia oxidation. Moreover, the essential differences in Pt structures formed below and above 400 °C also suggest a corresponding change in the dominating mechanism of Pt transport that is discussed in Section 4.4.

As concluded in Section 4.1, the initial activation of Pt at 286–374 °C progressed faster than at later stages (Fig. 2). Moreover, also in the temperature-programmed reaction up to 700 °C the activation was more marked in the initial first temperature cycle (Fig. 3a) than in the second cycle (Fig. 3b). The data suggest that the etching process slows down after reaching a more stable surface configuration during the initial time-on-stream.

To the best of our knowledge, rates of progressing activity changes of Pt during ammonia oxidation have not been reported in literature. Nevertheless, some authors presented SEM images of Pt wires after different times-on-stream under ignited (i.e. transfer-limited, full-conversion) conditions of the reaction. While Hannevold et al. [12] concluded that the size of facet rows and bulky crystals grows with time-on-stream, Lyubovsky and Barelko [7] observed a sequential two-step process where first facet rows are formed, and thereafter crystals grow from the surface. Since we did not image the Pt surface at different times, we cannot directly confirm or deny those previous reports. Nevertheless, catalyst activation progressed in two phases of fast initial, and slow further activation at 286–374 °C. However, this behavior cannot be explained by the two stages of surface roughening proposed by Lyuboski and Barelko, since only flat facets were observed on the surface at such temperatures (Fig. 6). More frequent SEM observations of the Pt surface during time-on-stream would be required to elucidate the kinetics of surface restructuring.

4.4. Mechanism of platinum transport

Based on the knowledge that Pt can be transported in oxygen atmosphere as volatile platinum oxide, and the fact that PtO_x

species were identified by MS to be present under conditions of ammonia oxidation at Pt wires at temperatures above 600 °C, the vapor of Pt oxide was previously concluded to be the major species responsible for platinum transport through the gas phase during ammonia oxidation [6,12,21,22]. Bulky crystals, and finally cauliflowers were assumed to grow upon oxide decomposition and Pt redeposition on the surface [6,12,22]. The same mechanism probably leads also to the growth of bulky crystals that were observed in the present study after temperature ramps to 700 °C (Fig. 7). Since we did not evaluate the gas phase species present over the catalyst *in situ*, further evidence on the presence of vapor of thermodynamically instable Pt oxides, and the temperatures at which they are formed, cannot be provided.

Reaction-induced reconstruction of the Pt surface occurred already at a temperature of 286 °C (Fig. 6b), a temperature significantly below the ca. 800 °C reported to be required for obtaining significant rates of PtO_x evaporation in oxygen atmosphere [16,28]. Hence, transport of Pt through the gas phase is unlikely to be an important transport mechanism below 400 °C. Moreover, the reconstructed Pt surface after ammonia oxidation at 286–374 °C developed into flat and ordered facets, but did not show any sign of the bulky microcrystals protruding from the surface at higher temperatures. Thus, a mechanism of Pt transport may be in operation different from that involving volatile PtO₂.

Since Pt reconstructed only in the presence of reactants (Figs. 6 and 7), but not during simple temperature treatments (Fig. 5), it is unlikely that surface or bulk diffusion of Pt atoms can account for the formation of facets. The required presence of the feed mixture containing oxygen and ammonia suggests that adsorbates provide Pt atoms with the mobility or driving force necessary for facet formation. As demonstrated by Horch et al. [29], hydrogen is a possible candidate that enhances the diffusion rate of Pt atoms on a Pt(1 1 0) surface up to 500 times at room temperature ($p_{\text{H}_2} = 7 \times 10^{-7}$ mbar) when monitored by STM, interpreted as lowering of the respective energy barrier. Moreover, also ammonia was reported to increase the surface mobility of step atoms on a Pt(4 4 3) surface in such a way that the straight step edges completely dissolved within 15 min at room temperature ($p_{\text{NH}_3} = 10^{-6}$ mbar) [30].

At the relatively high pressures ($p_{\text{NH}_3} = 3$ kPa) and low temperatures of the present work (286–374 °C) a significant coverage of the Pt surface with reaction intermediates of ammonia oxidation should be expected. It is therefore proposed that the restructuring, which was induced on the surface of Pt foil during ammonia oxidation between 286 and 374 °C (Fig. 6) is facilitated by the presence of adsorbates, that is, reaction intermediates of the ammonia oxidation. Such possible reaction intermediates can be adsorbed ammonia as well as other NH_x species [31]. An increase in reaction temperature would thus promote two opposing effects: on one hand higher temperatures accelerate diffusion rates on the surface, on the other hand adsorbate coverage decreases due to faster desorption, and the surface faceting would be hindered.

Summarizing the above discussion, temperature is suggested to be a major parameter controlling the reaction-induced

surface reconstruction of Pt under conditions of ammonia oxidation in various ways: via the kinetics of ammonia oxidation, temperature determines the adsorbate coverage of the surface, and hence a possible adsorbate-related mobility enhancement of Pt surface atoms. Moreover, temperature determines also the rate of formation of volatile Pt oxide, that is, the rate of Pt transport through the gas phase. By influencing the rates of both discussed ways of Pt transport, temperature is suggested to control which transport mechanism is dominant, and hence, if flat facets or protruding bulky crystals are formed.

5. Conclusions

The temperature-control in catalytic ammonia oxidation at reactant partial pressures of several kilopascals, established by the use of a microstructured reactor, allowed to investigate the influence of temperature and time on the reaction-induced changes of polycrystalline Pt and the related changes in overall catalytic activity. The surface of Pt foil restructured already at the surprisingly low temperature of 286 °C. This strong sensitivity of Pt catalysts towards the reaction environment emphasizes the need for thorough surface characterization in catalytic and kinetic studies of ammonia oxidation. Since facets significantly smaller than previously reported were observed, a sufficiently high resolution of electron microscopy images is required.

Temperature and time-on-stream were established as the major parameters that determine the morphology of Pt foil after ammonia oxidation, and led to changes in its surface structure throughout the studied temperature range of 286–700 °C. Moreover, comparing catalyst samples after thermal treatment with those exposed to the reaction confirmed, that for the present conditions etching of the Pt surface was induced only by a combination of reaction and elevated temperature.

The reaction temperature influenced the morphology of Pt catalyst in a characteristic way: at low temperature (286–374 °C) only flat facets were formed, while at higher temperatures (up to 700 °C) bulky structures grew from the previously flat surface. From the pronounced differences in formed Pt morphologies, and the fact that faceting started well below temperatures at which Pt is oxidized and evaporated at a significant rate, an additional mechanism different from the gas phase transport via volatile platinum oxide was suggested to be in operation between 286 and 374 °C. Adsorbate-enhanced surface diffusion was proposed as one possible mechanism of Pt transport.

Further studies are suggested to focus on elucidating the mechanism that governs platinum transport at temperatures below 400 °C, for example, DFT calculations or *in situ* microscopic investigations. The kinetics of morphology changes could be established by following the faceting *versus* time-on-stream for different temperatures and feed compositions. Moreover, relations between product selectivity in

ammonia oxidation and surface faceting need to be investigated by experiments carried out with feed mixtures of higher oxygen content, that is, under conditions of enhanced NO and N₂O formation.

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