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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.

Keywords: Catalytic ammonia oxidation; Platinum; Surface morphology; Restructuring; Faceting; SEM

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 ($C_2H_4^*$, O_2H^*). 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 PtO_2. 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 (NH_3, O_2) 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 $Pt_{90}Rh_{10}$ 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 $PtO_2{}^+$ 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 PtO_2 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/Al_2O_3, 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):

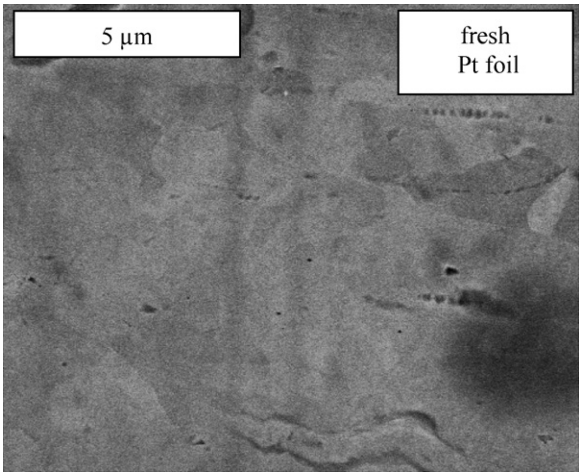

Fig. 1. SEM of fresh Pt foil catalyst, as supplied by Alfa Aesar.