

Ammonia Oxidation Over Model Pd and PtRh catalysts

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The surface science approach to understand catalytic processes using Ultra High Vacuum (UHV) and well defined single crystal surfaces has provided useful information for many years on adsorption sites, dissociation processes, surface reactions, and surface structures involved in catalytic processes. However, industrial catalysts consist of a complex material system and operate under elevated temperatures and harsh gas environments, resulting in the so-called “pressure gap” and “material gap”. X-ray scattering and diffraction techniques under grazing incidence are powerful in situ tools to bridge these gaps, and can be applied to both nanoparticles and single crystal surface characterization under realistic conditions. A new environmental setup to try to bridge these gaps is now available at the SIXS beamline (Soleil).

As a case study, we will report on ammonia oxidation performed at a total pressure of 300 mbar. Industrially ammonia is the starting point for the production of nitrates, which are used in a broad range of fields from paints to fertilizers. The system is characterized by three competing reactions which are all of industrial interest. Therefore the possibility to select the desired reaction path is of high interest for the industry [1]. Industrial catalysts are based on PtRh alloys, however, Pd has been selected as one of the most active catalysts for this reaction [2-3]. A recent theoretical study [4] finds that the Pd metal is the most active phase for ammonia dehydrogenation, however no experimental evidence exists.

The present data concern Pd(100) and PtRh(100) single crystal surfaces as well as 6 nm Pd particles with the aim to establish a correlation between surface structure and reactivity.

The Pd data indicates that a change in the reaction products from nitrogen (N₂) to nitrogen oxide (NO) coincides with a decreasing signal from metallic Pd. This observation suggests that the ammonia is converted into N₂ on the metallic particles, while on oxidized particles it is preferentially converted into NO. Preliminary data from the PtRh(100) single crystal surface alloy instead demonstrate the presence of a thin tri-layer RhO₂ surface oxide on the surface despite a change from the production of N₂ to the production of NO. The reasons for these differences will be discussed.

1) G. Busca, L. Liett, G. Ramis, and F. Berti *Applied catalyst B* **18** (1998) 1.

2) N. I. Ilchenko *Russian Chem. Rev.* **45** (1976) 1119.

3) R. Q. Long and R. T. Yang, *Catalysis Letters* **78** (2002) 353.

4) Z. Jiang, Q. Pan, M. Li, T. Yan, and T. Fang *J. Appl. Surf. Sci.* **292** (2014) 494.