In situ investigations of the structure and CO oxidation activity of Pd/Al$_2$O$_3$

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Introduction

The catalytic oxidation of CO is of great practical importance and is e.g. used in commercial 3-way catalysts reducing automotive emissions. Depending on the reaction conditions different oxide species, e.g. chemisorbed oxygen, surface oxides or bulk oxide may be present on the surface. Despite several previous studies there are still open questions concerning the exact surface composition (which depends on the reaction conditions), the specific activity of the different phases, and their possible interplay [1].

The aim of this study is to investigate the oxidation of CO on a technical 2 wt.% Pd-Al$_2$O$_3$ catalyst under varying reaction conditions. In order to correlate the surface oxidation state with the catalytic activity in situ time resolved spectroscopy (FTIR and X-ray absorption) has been combined with simultaneous kinetic measurements by mass spectrometry and gas chromatography. Ex situ characterization was performed by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD).

Experimental

Palladium catalysts were synthesized by standard incipient wetness impregnation of alumina with Pd(NO$_3$)$_2$, followed by calcination in air. Before each experiment the catalyst was treated (in situ) in 1 bar hydrogen at 300$^\circ$C.

The adsorbates present under varying reaction conditions and reaction rates were investigated in an IR flow cell combining in situ FTIR spectroscopy and gas chromatography. The influence of the reaction conditions (ratio between carbon monoxide and oxygen, temperature) on the reaction rate and the structure of the catalyst was studied in a plug flow reactor combining in situ time resolved X- Ray Absorption Spectroscopy and mass spectrometry.

In addition, the reduced catalyst was partially and fully oxidized via different activation procedures and ex situ characterization methods (IR spectroscopy of adsorbed CO, HRTEM and XRD) were performed to further characterize the oxide phases present.

Results and discussion

A typical light- off behavior of the catalytic activity was observed at any ratio between carbon monoxide and oxygen. In the low activity regime the catalyst was fully reduced
and poisoned by CO. At a certain temperature a sudden increase of activity (ignition) occurred with the high catalytic activity being connected to a coexistence of metallic and partially oxidized palladium. In a narrow range of reaction conditions rate oscillations were observed.

Ex situ CO adsorption studies of the catalyst obtained after a mild oxidative activation procedure showed that partial oxidized palladium (which is present in the high activity regime) could be easily reduced by CO. This reduction takes place even at very low temperature (below 273 K) and CO partial pressure which indicates, that this substoichiometric oxide exhibited a significant activity for CO oxidation. In contrast, total oxidation to PdO led to a catalyst which showed no capacity for CO adsorption and was stable against reduction by CO even at high temperature. This may be the reason for its low catalytic activity in CO oxidation.

The contributions of the various surface phases, the underlying reaction mechanism and the dynamic changes will be discussed.

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**References**

