Silver-alumina catalysts for lean NO_x reduction

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Introduction

Combustion in oxygen excess, as in diesel- and lean-burn engines, significantly improves the fuel-efficiency and thereby effectively reduces the CO_2 emissions. However, the lean environment obstructs the NO_x reduction ability of the three-way catalyst. One promising technique to reduce NO_x in oxygen excess is hydrocarbon-assisted selective catalytic reduction (HC-SCR). In particular, Ag supported on alumina has shown high activity for this reaction, see *e.g.* [1,2]. Although numerous experimental studies have clarified issues concerning this system, the state and structure of the Ag-alumina system, as well as the reaction mechanism, remain elusive.

This work presents an overview of our recent findings concerning lean NO_x reduction over silver-alumina with various types of reducing agents, including hydrocarbons, oxygenates and commercial biodiesel [3-11]. Furthermore, the structure and chemical state of the silver sites will be discussed in relation to the catalytic performance and reaction mechanisms.

Materials and Methods

The catalysts were prepared using a sol-gel method including freeze-drying [7], which results in small silver species uniformly distributed throughout the alumina matrix. The samples were thoroughly characterized using *e.g.* X-ray photoelectron and Ultraviolet-visible spectroscopy, and Transmission electron microscopy. The catalytic performance was investigated by temperature programmed extinction-ignition experiments using a continuous gas flow reactor and the evolution of surface species during reactant step-response experiments was studied *in-situ* by diffuse reflection Fourier transform infrared spectroscopy.

Results and Discussion

The results for lean NO_x reduction show that the type of reducing agent is crucial for the catalytic performance. For instance, the hydrocarbon chain length and degree of saturation as well as cyclic/aromatic content and presence of oxygen and OH-groups is important. The NO_x reduction is dependent on the partial oxidation of the hydrocarbon which, in turn, is dependent on the C–H (or C–C) bond strength, accessibility of π-electrons, molecular orientation and sticking probability of the hydrocarbon, *i.e.* the nature of the hydrocarbon. Furthermore, for the formation of surface species and likely also for the surface processes the hydrocarbon nature is vital. For example the formation of acetate, compared to formate, seems to be governed by a reactive hydrocarbon and a catalyst with more oxidizing sites, compared to formate formation (**Figure 1**).

However, the NO_x reduction over the silver-alumina catalyst is not only dependent on the nature of the reducing agent, but also on the silver loading and morphology. The calculated rates over low- and high-coordinated silver sites for NO_x reduction and HC oxidation show for instance that the overall reaction rate is a function of the nature of the reducing agent and the silver morphology. Thus, for rational catalyst design resulting in an optimal HC-SCR activity within a broad temperature range, these parameters need to be optimized.

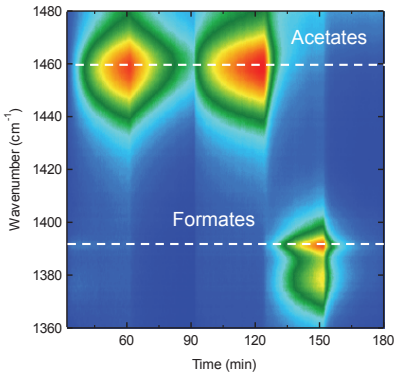

Figure 1. Evolution of surface acetate and formate species upon reactant step-response experiments over a silver-alumina catalyst.

Significance

These results provide novel understanding of the silver-alumina system, which can be used for tailored design of catalysts for emission control systems for alternative fuels.

References

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