

Experimental Report

Scientific background:

Several decades of widespread catalytic technology has resulted in high-tech three-way catalysts (TWC) for the clean-up of automotive exhaust gases. This material comprises a mix of highly relevant metal and support components that are able to efficiently remove CO and NO. Recently, several groups have shown that metal oxide overlayers on nanoparticles or metal oxides are more active than the metal surfaces itself for the CO oxidation reaction [1].

For NO reduction, there is strong support from surface science as well as computational studies for the position that metallic Rh catalyzes NO dissociation: *e.g.* the barrier to dissociate NO over Rh(100) is only 38 kJ/mol. Given the evidence for the importance of Rh-oxide for CO oxidation, we speculated that if the active phase of Rh under TWC conditions is oxidic it should also be able to catalyze NO reduction. Accordingly, we employed experimental and computational methods to find support for our hypothesis. In short, we have found similar size dependence between NO reduction and CO oxidation, while *ab initio* thermodynamics revealed that under both reaction conditions small Rh-oxide particles are more stable than Rh metal particles. These results suggest that the reactions proceed with highest rate on Rh-oxide clusters in close interaction with ceria. Our DFT calculations strongly indicated that H-assisted NO dissociation is favourable over direct NO dissociation.

We intended with the proposed measurements to identify the active phase and possible changes in the Rh-based catalyts under TWC conditions. Operando X-ray absorption spectroscopy is a very suitable technique to resolve it.

Experimental:

This XAS study was essential to obtain information on the oxidation state of Rh in supported Rh nanoparticle catalyts. More conventional techniques such as XPS of spent catalyts cannot conclusively resolve this issue, because metals can become oxidized by ceria under high vacuum conditions. The results will be combined with those of experimental and computational methods.

Experiments:

We performed X-ray absorption spectroscopy measurements at the Rh K edge with our homebuilt in situ gas-phase cells. Two types of experiments were carried out at the required high-level of safety:

- (i) Spectra were taken after reduction to study the structure of Rh nanoparticles before reaction;
- (ii) Spectra were taken at various temperatures under gas mixtures of NO+H₂, NO+CO and NO+CO+H₂O to study the possible changes of the Rh nanoparticles supported on different (nanostructured) ceria during reaction.

Results obtained and their significance in the respective field of research:

The preliminary analysis of the XANES/EXAFS results show that:

- a) Small Rh particles are more oxidic than larger ones in an NO+H₂ atmosphere and that the oxidation state is almost independent of the H₂/NO ratio;
- b) Small Rh particles are more oxidic (and active) in NO+H₂ at higher temperatures, so that we infer that the active phase is indeed oxidic under NO reduction conditions;
- c) The oxidation state of small Rh particles changes with H₂/NO ratio. It does not follow the trend of lower activity with lower ratio, but rather trends with the changes in selectivity;
- d) Small Rh particles dispersed on CeO₂-polyhedra are more oxidic (and active) than those on CeO₂-nanorod in NO+H₂ (independent of the H₂/NO ratio). The ones embedded in the CeO₂ matrix are also oxidic but somewhat less active than small particles on CeO₂-nanorod. The latter observation suggests that the embedded particles are less accessible to the reactants;
- e) Small Rh particles are more oxidic than larger ones in the NO+CO(+H₂O) reaction. There is no clear effect of H₂O on the oxidation state;
- f) Small particles are more oxidic (and active) than larger ones in N₂O decomposition. The co-feed of H₂, reduces the small particles (as well as the activity).

Scientific prospect:

The initial results do not fully support our hypothesis, that the oxidation state determines the activity of TWC catalysts. It rather indicates that the interface between the particles and the support is more effective for smaller particles. In addition, corrugation of the CeO₂ support likely plays an important role as well. Further data analysis (structural change determination) and a more indepth study of the correlations between the many XAS results and kinetic measurements and computational methods should provide us with a clear understanding of the influence of oxidation state and particle size on activity and selectivity in TWC conditions. We wish to publish the results in a high-ranked journal within the next half year.

References:

[1] J. Singh et al. *Angew. Chem.* 120 (2008) 9400; T. Schalow et al. *Angew. Chem. Int. Ed.* 45 (2006) 3693; H. Over et al. *Science* 287 (2000) 1474; H. Over et al. *Catal. Today* 145 (2009) 236; M.E. Grass et al. *Angew. Chem. Int. Ed.* 47 (2008) 8893; D.A.J.M. Ligthart et al. *Angew. Chem. Int. Ed.* 50 (2011) 5306; W. Song et al. *Chem. Commun.* 49 (2013) 3851.