NO_x adsorption on Al_2O_3 and Ag/Al_2O_3 from first principles

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Introduction

Hydrocarbon (HC) assisted selective catalytic reduction (SCR) is an appealing technology for NO_x reduction in oxygen excess. In particular, a catalyst formulation with silver supported on alumina (Ag/Al_2O_3) has been measured to have high activity for this reaction [1,2]. Although numerous experimental studies have clarified issues concerning the Ag/Al_2O_3 catalyst, the nature of the active phase is still an open discussion [1,2]

Materials and Methods

The first-principles investigation is based on Density Functional Theory (DFT) calculations, as implemented in DACPO and CPMD.

Results and Discussion

In this contribution, we provide insights to the structure of active Ag clusters under reaction conditions relevant for HC-SCR using calculations and *ab initio* molecular dynamics simulations [3-5]. Three possible surface terminations, namely partially O-, Al- and OH-terminated surfaces, are considered. The adhesion energies of small Ag_n ($n \leq 4$) clusters supported on the different terminated Al_2O_3 are calculated as a function of cluster size. Furthermore, we calculate NO_x adsorption on all considered Ag clusters and different surface terminations. NO is found to adsorb weakly on the Ag_n clusters. In the case of O, NO_2 and NO_3, the adsorption process is initiated by a charge-transfer to the adsorbate. As a consequence, these reaction intermediates are strongly bound to the Ag_n clusters. This result supports the suggestion that reaction intermediates actually poison the catalyst [1]. However, the Ag monomer on partial O-terminated Al_2O_3 stands out as an interesting candidate for the active site for HC-SCR. In this case – which can be regarded as a model system for small Ag clusters incorporated in the Al_2O_3 matrix - the interaction of NO_2 with the surface is moderate, preventing catalyst poisoning. The results for the case with small Al_2O_3 supported Ag clusters is compared with our results for NO_x adsorption on Ag(111).

Owing to the porous nature of the Al_2O_3 support, it is possible that NO_x may be adsorbed in a configuration sketched in Figure 1, where NO_2 is adsorbed on Al_2O_3 supported by an Ag(111) slab. This represents the possibility of adsorption on Al_2O_3 in the presence of Ag in the neighboring pore. Our recent results [5] indicate that such configurations potentially can be of importance for HC-SCR on Ag/Al_2O_3.

The Figure shows results for the adsorption energy of NO_2 on $Al_2O_3(0001)$ supported on Ag(111) as a function of oxide thickness. For all studied thicknesses, the adsorption energy on the mixed oxide/metal system is higher than on the sole oxide. Enhanced adsorption energy is, moreover, calculated for Al_2O_3 in contact with small Ag_1-Ag_3 clusters located on the opposite side of the oxide film. Also in this case, the adsorption energy is strongly enhanced with a pronounced odd/even alternation as a function of cluster size. For the cluster case, we show by *ab initio* molecular dynamics that this stabilization mechanism is active also at elevated temperatures.

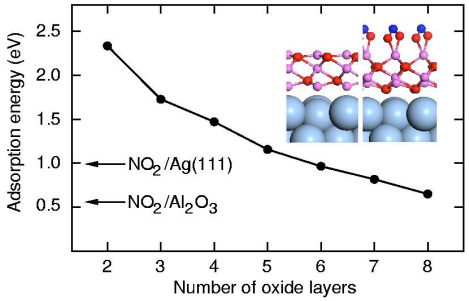

Figure 1. NO_2 adsorption energy as a function of Al_2O_3 layers. Adsorption energies for NO_2 on Ag(111) and unsupported Al_2O_3 are shown as references. Insets show the structure of $2Al_2O_3/Ag$ and $NO_2/2Al_2O_3/Ag$, respectively.

Our studies [5,6] show that the physical origin of the long-ranged mechanism is the concerted action of different contributions where a decisive component is a charged adsorbate; i) electrostatic interaction between the adsorbate and the polarized oxide and image charge in the metal, ii) direct chemical interaction between the adsorbate and the oxide and iii) modified oxide/metal interface. The general nature of the stabilization mechanism may, in fact, have implications for how oxide supports should be regarded in heterogeneous catalysis.

Significance

The HC-SCR is a promising technique to reduce NO_x in lean burn engines. The Ag/Al_2O_3 catalyst shows particularly high activity, however, the underling reason for this remains unclear. This work contributes with first-principles insights to questions, such as, the active phase and relevant reaction mechanisms.

References

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