

Modification of NiO(111) surfaces by hydroxylation and carbonate formation

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NiO is used as main or co-catalyst in heterogeneous catalysis. H₂O, CO and CO₂ are commonly present at catalytic reactions and strongly interact with NiO surfaces. It is observed that they block surface sites or alter the surface structure by hydroxylation and carbonate formation and thereby poison the catalyst.

In our study of the response of NiO to these gas phases we focused on the polar NiO(111) surface. The bulk-truncated structures are intrinsically unstable and especially susceptible to reactions with adsorbates. We performed spin-polarized GGA+U calculations for possible reconstructions of NiO(111) in contact with water, hydroxyl groups and protons or CO and CO₂. A thermodynamic formalism was applied to deduce phase diagrams of the energetically most stable surface structures depending on temperature and pressure conditions.

The O-H phase diagram is dominated by a fully hydroxylated (1x1)-OH surface at ambient and low temperature UHV conditions and an adsorbate free (2x2)-O-octopolar structure after high temperature annealing [1]. A transformation between these two stable phases includes not only the adsorption or desorption of water molecules but also the diffusion of Ni and O surface atoms. NEB calculations for reaction barriers of subprocesses of this phase transformation explain the experimentally observed high thermal stability of surface hydroxylation.

The interaction of CO and CO₂ with NiO(111) leads to the formation of tridentate carbonate complexes including O surface atoms which are interconnected by Ni surface atoms. Again, the molecules strongly alter the surface configuration. A transition path between adsorbate covered and adsorbate free surface structures has to involve a mass transport of Ni and O surface atoms. As expected from our theoretical results, a high thermal stability of carbonates is observed in experiment.

We showed that the adsorption of small molecules on NiO(111) alters the surface considerably. These modifications have to be considered when modeling catalytic reactions.

[1] C. Ebensperger and B. Meyer, *Physica Status Solidi B*, **2011**, 248, 2229-2241