Surface-structure dependencies in catalytic reactions

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Summary

Heterogeneous catalysis is very important for industrial applications and the environment. It is known that precious metals, such as Pd and Pt, can be good catalyst materials for various reactions. However, these metals are expensive and their catalytic action is not yet completely understood. In the search for better and cheaper materials, more fundamental knowledge is necessary. We use ultra-high vacuum techniques and well-ordered Pd and Pt single crystals to further investigate the oxygen dissociation process and the interaction of water with deuterated surfaces.

The breaking of the oxygen-oxygen bond of O_2 is a crucial step in various oxidation reactions, for example in the CO oxidation reaction in the three-way catalytic converter. In chapter 3, we have studied the oxygen dissociation process in the zero-coverage regime on Pd(100) as function of incident energy, surface temperature and incident angle. We have compared our data to those previously obtained by other groups. The Pd(100) surface shows a very high oxygen reactivity. Two mechanisms play a role in sticking and dissociation of O_2. At high incident energy, O_2 molecules dissociate directly on the Pd(100) surface. At low incident energy, O_2 dissociates via an indirect pathway. We suggest a dynamical precursor that accounts for the indirect process and steering causes the absolute reactivity. The barrier to dissociation on this surface is very low. The other low-Miller-index surfaces show different dynamics. On Pd(111), a sequential physisorption and molecular chemisorption precursor mechanism was suggested for low incident energy. At high energies, the molecules directly adsorb in the molecular chemisorption well, but no direct dissociation was observed. The molecular state is stable on Pd(111), where it is not on Pd(100) (in the zero-coverage limit). The very attractive molecular chemisorption precursor state leads to dissociation on Pd(110) at low energies. At

high incident energy, a direct dissociation pathway opens.

In chapter 4, we investigate the oxygen adsorption and desorption processes on Pd(100) further. The sticking probability over time and the obtained maximum coverage are dependent on incident energy and surface temperature. The King and Wells traces indicate that the dissociation process is temperature independent for the first few seconds of the experiment. After some time the trace of 100 K remains higher than the 400 K trace for all energies. Additional oxygen molecules can adsorb on the patches of oxygen atoms. This is also confirmed by the subsequent TPD spectra. Dosing at a temperature between 100 and 150 K results in an additional molecular desorption peak (the δ-peak). During the temperature ramp, part of the oxygen molecules desorb, the other part still dissociates and desorbs recombinatively at a higher temperature in a sharp and narrow peak (the γ-peak). This leads to a relatively high surface coverage with respect to the high temperature experiments. At temperatures between 200 and 600 K and at low incident energy, the γ-peak is absent. This peak increases with increasing energy and temperature. A combination of high energy and temperature or dosing at a very low surface temperature results in higher oxygen coverage on the Pd(100) surface.

In chapter 5, oxygen adsorption and dissociation on Pt(553) was studied in a similar way as described for Pd(100). The data is compared to literature data from Pt(533), Pt{110}(1x2), and Pt(111). At low incident energy, all stepped surfaces show a similar reactivity. This reactivity is higher than on the flat Pt(111) surface. The exact arrangement of the atoms that form the corrugation of the surface does not play a role here. At high incident energy, Pt(533) and Pt(553) are still more reactive than Pt(111), however, in this regime the dissociation dynamics do depend on step type. The sticking probability is higher on the surface with the (100) steps than the one with (110) steps. On Pt(111), it was suggested that oxygen dissociation proceeds via an indirect process via the physisorbed state to the molecularly chemisorbed state at low energy. At high energy, the molecules can access the molecular chemisorbed state directly. The processes on Pt(533) are described to be be the same as on Pt(111), with an additional pathway to dissociation. At low energy, the steps provide an additional path to direct chemisorption and increase the conversion of the physisorbed state to the molecular chemisorbed state. At high energy, oxygen molecules can dissociate directly via an activated pathway. For Pt(553), we suggest that parallel sticking mechanisms indeed occur, but we expect that the molecular sticking at steps at low energy is a non-activated process.

At high energy, the indirect mechanisms are replaced by activated direct sticking at the (111) terraces. TPD experiments show the presence of a molecular state on the (111) terraces and the (110) steps. Oxygen desorption from the (100) step type surface occurs at a higher temperature than the surface with (110) steps. The difference in the processes of Pt(553) and Pt(533) is due to a variation in the effective lowering of the barrier to dissociation from the molecularly adsorbed states into the atomic states.

The co-adsorption of water and deuterium on Pt is a relevant process for e.g. fuel cells, where both types of molecules are present on the surface. In chapter 6, we study the interaction of water with D-precovered Pt surfaces with the (100) step type and varying width of the (111) terraces by temperature programmed desorption. Water TPD spectra from the bare surfaces show a desorption peak from the step sites, the terrace sites and the multilayer. The (100) steps bind water more strongly than the (111) terraces. The water stabilization is annihilated by pre-adsorbing deuterium to the steps. At the same time, the water on the (111) terraces is stabilized, as on Pt(111). The stabilization reverses when the (111) terraces are also precovered with deuterium. The completely precovered Pt surfaces with (100) steps and terraces (up to 8 atom wide) become completely hydrophobic. Water desorption occurs in a single desorption peak in the region where the water multilayer usually desorbs and the exchange between H (from water) and D (from deuterium) atoms decreases. On these stepped surfaces with (100) steps, water forms amorphous solid water clusters near the step sites and does no longer spread over the surface as the Pt(111) and P(553) surfaces. Defect sites play a role in the delicate balance between intermolecular forces. The adsorption energy governs hydrophilic or hydrophobic behavior. The influence of steps on the adsorption of water on nanostructured Pt has a very long-ranged character which is non-linear with step density. The steps break the ability of terrace-bound water to properly form hydrogen bonds.

The future plans are presented in chapter 7. The combination of double molecular beam experiments and the use of curved single crystals is the next challenge to obtain even more knowledge on complex processes occurring in real heterogeneously catalyzed reactions.