Creating model systems for catalysis with mass-selected nanoparticles: Characterization and properties

This PhD thesis reports research on the fundamental properties of nanoscale catalysts related to energy conversion processes. These processes and the connected materials will hopefully become more and more important in our future as humanity is shifting to renewable energy sources, but already today plenty of industrial heterogeneous catalysts are based on nanoparticles and their properties. The chapters in this thesis contain research on different processes and give examples of the possibilities of nanoscale catalyst materials. Because of the wide range of processes and materials involved, a brief summary of the included projects is given individually. If we were to switch to renewable energy sources, utilizing sunlight would be an obvious choice. With the use of a suitable photoabsorber and catalysts, sunlight can be directly used to drive the water splitting process generating O₂ in the oxygen evolution reaction (OER) and H₂ in the hydrogen evolution reaction (HER). It is well known that platinum is the best catalyst for the HER, but its scarcity and cost hinders its large scale use. However, in case of a photoelectrocatalytic water splitting process the rate of HER is limited by the amount of sunlight reaching the photoabsorber, therefore the question arises: how much platinum is actually needed to utilize sunlight? In order to investigate this, we produced silicon photocathodes with different mass loadings of 5 nm mass-selected platinum nanoparticles between 1000 ng/cm² down to 10 ng/cm² and investigated their behaviour. The results showed that even the cathodes with the lowest loadings (10 ng/cm²) have significant catalytic activity, while this loading cannot be detected with X-ray photoelectron spectroscopy (XPS). This means that in non-noble HER catalyst research more sensitive methods than XPS have to be used to ensure truly platinum free electrodes. Based on our results by accepting an overpotential of approx. 50 mV to achieve a current density of 10 mA/cm², which is comparable to the best non-noble HER catalysts, platinum seems feasible and scalable on the TW scale as electrocatalysts for the OER. The exact mechanism and active sites in case of these catalysts are still under debate, and by investigating well-defined model systems further insights can be gained. We studied the OER activity of mass-selected NiFe nanoparticles as a function of their size in 1 M KOH electrolyte. Particles with a diameter of 5.4 nm proved to be the most active in the investigated size range (3.9-8.4 nm). The data shows that the 5.4 nm nanoparticles are among the most active non-noble alkaline OER electrocatalysts on a turnover frequency basis. We also explored the effect of particle proximity on the OER activity of the particles. It seems that as the particles are getting closer to each other their activity decreases. This could be the result of mass transport limitations and it is under further investigation. Creating well-defined and clean model systems also allowed us to investigate the stability of the NiFe particles during OER. With samples having only a 100 ng of NiFe nanoparticles on their surface, no significant decline of activity was found throughout a 1000 h chronoamperometry at 1.6 V vs. the reversible hydrogen electrode (RHE) in 1 M KOH electrolyte showing the stability of the catalyst. Apart from (photo)electrochemical reactions, nanoparticles play a very important role in different heterogeneous catalytic reactions where the reactants are in the gas phase. In order to investigate some of these reactions we created model systems utilizing the silicon μ-reactors developed earlier at DTU Physics. Unfortunately, because of practical issues with the temperature measurement and control in case of the μ-reactors, the catalytic activity data for both projects included here are compromised, but there are still conclusions which can be drawn. We investigated the size dependent activity of NiFe nanoparticles in the methanation reaction, where methane is created from CO and H₂. The particles proved to be active and produce methane at low pressures and relatively low temperatures. Another reaction investigated was CO oxidation with AuTi bimetallic mass-selected nanoparticles. This is to explore the possibility of utilizing gold as a nanocatalyst. Nanometer sized gold is active for multiple reactions, but gold particles tend to sinter rapidly. It seems possible to stabilize gold particles by alloying them with a different metal, for example titanium. Our results showed that titanium does not cover all gold atom completely even when the alloy particles are heated in an oxidizing environment and TEM results show that the alloying is indeed stabilizing the particles.

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