Fundamental investigations of catalyst nanoparticles

Heterogeneous catalysis, the conversion of chemicals by the use of a suitable solid state catalyst, is a very important technology in modern society and it is involved in the production of up to 90% of all chemicals. Catalysis has in this way played a significant role in the technological and economic development in the 20th century. There is however a downside to this development and we are seeing significant pollution and pressure on resources. Catalysis therefore has an increasingly important role in limiting pollution and optimizing the use of resources. This development will depend on our fundamental understanding of catalytic processes and our ability to make use of that understanding.

This thesis presents fundamental studies of catalyst nanoparticles with particular focus on dynamic processes. Such studies often require atomic-scale characterization, because the catalytic conversion takes place on the molecular and atomic level.

Transmission electron microscopy (TEM) has the ability to image nanostructures with atomic resolution and reveal the atomic configuration of the important nanoparticle surfaces. In the present work, TEM has been used to study nanoparticles in situ at elevated temperature and with gas present in the microscope in order to recreate the conditions found in a chemical reactor. This is very important because we know that particles may change shape as their surfaces respond to a changing gas atmosphere. To obtain quantitative and credible information in situ, it is very important that we only study intrinsic structures and phenomena and not those that may be induced by the high energy electrons used to image the specimen. This requires careful consideration of the influence of the electron beam in order to understand, control and minimize that influence.

I present four different topics, each related to different aspects of nanoparticle dynamics and catalysis.

The first topic is the reduction of a homogeneous solid state precursor to form the catalytically active phase which is metal nanoparticles on an inert support. Here, we have reduced Cu phyllosilicate to Cu on silica and imaged the process in situ. The data obtained established the foundation for modeling work which revealed that the reduction proceeded by an autocatalytic route. Here, the initial nucleation of Cu is slow and the subsequent growth in size is fast because the Cu particles themselves catalyze further reduction.

The second topic treated the active state of a methanol synthesis catalyst. This work was performed by a parallel approach, where we investigated identically created nanoparticles both with TEM and X-ray photoelectron spectroscopy (XPS). The methanol synthesis catalyst is a complex high surface area Cu=ZnO=Al2O3 structure that is difficult to study by TEM. We therefore created size-selected CuZn alloy nanoparticles that were transformed by oxidation and reduction into Cu nanoparticles decorated with ZnO. This represents a simplified model system for the high surface area catalyst. The interplay between Cu and ZnO and the exact role of ZnO as a promoter for catalytic activity is not yet fully understood. Our work revealed that the surface of the reduced catalyst consists mainly of Cu decorated with well defined ZnO crystals. It was demonstrated by XPS that a fraction of the ZnO is reduced simultaneously with the Cu under H2 atmosphere, presumably forming a surface alloy in the Cu.

The third topic studied the sintering of Cu nanoparticles supported on silica. Sintering is the main deactivation mechanism for the methanol synthesis catalyst and so this topic is of great interest to the development of better catalysts. It was found that sintering proceeded via Ostwald ripening, i.e. the migration of atomic species between particles, with a net flow from small to larger particles resulting in an overall growth in particle size. The presence of CO increased the rate of sintering significantly and the presence of H2O slowed it down.

The fourth topic investigated the oxidation of CO on a Pt catalyst in the special case where the reaction displays temporal rate oscillations under fixed conditions. This is a well-known phenomenon, but the mechanism driving the oscillations on nanoparticles has hitherto been unknown. We used nanoreactor technology which allows for simultaneous TEM imaging and activity measurement, also referred to as an Operando experiment. With this we revealed that the shape of the Pt nanoparticles changed in phase with changes in global reaction rate. By the use of reactor modeling it was possible to show that the oscillations were possible due to the coupling between the self-poisoning nature of the CO oxidation reaction on Pt and gas flow and diffusion in the reactor. Our work showed that shape changes can drive global rate oscillations.

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