Abstract

It is well known in literature that for many metal-catalyzed reactions the support influences the catalytic properties of the metal particles. It has also been observed that the electronic properties of the supported Pt particles depend on the acid/base properties of the support. However, the nature of this interaction between metal and support is poorly understood. The goal of the research described in this thesis was to understand the nature of the metal-support interaction and to relate the support-induced changes in catalytic properties to the changes in electronic properties. The work in this thesis has provided important insights in finding answers to these questions.

Chapter 2 aims at understanding which processes take place during the pretreatment of Pt(NH$_3$)$_4$(NO$_3$)$_2$ impregnated on SiO$_2$. The ultimate goal was (i) to understand how a certain metal particle size and particle size distribution is obtained and (ii) based upon these insights to prepare a supported metal catalyst with a narrow particle size distribution. Using the combination of mass spectrometry, in situ QEXAFS, HRTEM and hydrogen chemisorption, the reactions taking place during different pretreatments of the catalyst precursor [Pt$^{2+}$(NH$_3$)$_4$(NO$_3$)$_2$ impregnated on a high surface area SiO$_2$ ($400$ m$^2$/g)] were elucidated.

In Chapter 3, the attention was focused on using a catalytic test reaction, the exchange of hydrogen for deuterium (H/D exchange) in cyclopentane (CP). The H/D exchange of CP is a promising test reaction for studying support effects in heterogeneously metal catalyzed reactions. In order to employ this test reaction, a full understanding of the H/D exchange mechanism is essential. In this chapter, a kinetic model that adequately describes the observed activity and orders in CP and D$_2$ is developed. To understand the observed selectivities a Monte-Carlo model is developed which accurately simulates the observed exchange patterns and reveals the relative contributions of four competitive intermediates.

In Chapter 4 the H/D exchange of cyclopentane was measured for Pt catalysts with supports of various acidity. The activities of the various catalysts show a compensation effect, which is directly correlated to the contribution of the various exchange mechanisms that proceed via different intermediates. The contribution of each intermediate depends on the electronic properties of the Pt particles, which in turn depend on the support acidity. This shows that the compensation effect is caused by support induced changes in the adsorption modes of cyclopentane.

A long-standing problem in the research of hydrogen chemisorption on supported Pt catalysts is the unclarity about the difference in nature of the Pt-H bonding for weakly and strongly bonded hydrogen. Based on Pt-Pt EXAFS and a newly developed XANES analysis of the Pt L$_2$ and L$_3$ edges it is shown in chapter 5 that both types of hydrogen are truly chemisorbed species.

In chapter 6, hydrogen chemisorption position on supported Pt catalysts was again studied utilizing Pt L$_3$ XANES data. It is found for Pt on basic supports that H is adsorbed in the Pt 3-fold hollow sites near cluster edges at high temperatures, whereas in the case of acidic supports, the H appears to adsorb at the Pt cluster edge atop sites. This difference in adsorption site is supported by density functional theory (DFT).

One of the changes in the electronic properties going from small metal particles to bulk metal is the change in conductivity: bulk metal is a conductor, small particles are insulators. In chapter 7, using XAFS it a very strong support effect on the metal-insulator transition with cluster size in supported Pt clusters is found. Pt particles with basic supports show metallic
screening for sizes as small as 6Å, while in contrast, Pt with acidic supports does not show metallic behavior below 10Å.

In chapter 8 it is shown that increased support alkalinity induces an increased whiteline intensity of the Pt L₂ and L₃ X-ray absorption edges. DFT shows that the origin of this support effect is due to a rehybridization of the Pt valence band, caused by the Madelung potential. The metal-support interaction consists of three additional effects: the Madelung potential of the support polarizes the Pt particles, the complete valence band is shifted to higher energies for basic supports and the bonding between metal and support is strong as long as the support is non-inert.

The changes in the electronic properties of the supported metal particles were connected to the chemisorption of reactants in chapter 9, where the influence of the acid/base properties of the support on the adsorption of H and CHₓ (x=2,3) on supported Pt particles is investigated using DFT. The Pt-H bond strength is strongly affected by changes in the support acidity while the difference for the Pt-CHₓ bond strength is much smaller. Due to the stronger Pt-H bond on basic supports, the H coverage with strongly bonded hydrogen on Pt particles with a basic support is higher than on acidic supports.

The support induced changes in hydrogenolysis reactions of alkanes can be explained to a large extent by support induced changes in the Pt-H bond strength and hydrogen adsorption site on Pt. This can easily explain the well-known compensation effect found in the kinetics of the hydrogenolysis of alkanes catalyzed by supported metal catalysts.