

ABSTRACT

This thesis is focussed on the catalysis on thin film model systems consisting of a noble metal (Pt, Rh) and an oxidic support (SiO_2 , Al_2O_3 , CeO_2 , V_2O_5), and on their characterization by electron microscopy and related techniques (bright-and weak-beam dark field imaging, high-resolution imaging, electron diffraction and electron-energy loss spectroscopy). Special emphasis was placed on the structural and morphological changes developing under the influence of hydrogen at elevated temperatures, on (strong) metal-support interaction and on structure-activity correlations on the $\text{Rh}/\text{V}_2\text{O}_5$ catalysts.

Regular Pt particles in contact with different supports were subjected to reduction in hydrogen at different temperatures. Despite the chemical differences of the supports, similar results were obtained for Pt particles supported by SiO_2 , Al_2O_3 and CeO_2 under comparable experimental conditions. The formation of a Pt_3Me (Me=Si, Al, Ce) alloy phase has been observed on all systems. The proposed mechanism is connected to the special nature of our thin film system (epitaxially grown metal and support particles, intimate contact between them) and probably involves the formation of reduced support species, their penetration through the metal-oxide interface and the topotactic growth of the alloy on the former Pt particles. On the SiO_2 -based systems, melting and recrystallization phenomena are found to account for the formation of high-temperature (monoclinic Pt_3Si) and Pt-depleted phases ($\text{Pt}_{12}\text{Si}_5$). Studies on more real systems (impregnated Pt/SiO_2) yielded similar results ($\text{Pt}_{12}\text{Si}_5$ alloy formation), although at considerably higher temperatures.

Rh particles were also found to undergo a strong metal-support interaction on CeO_2 and V_2O_5 . Reductive treatments at elevated temperatures ($T \geq 773\text{K}$) most probably resulted in the formation of Rh_3Ce and Rh_3V_5 alloys accompanied by the formation of reduced CeO_x and VO_x species. Catalytic measurements of the CO hydrogenation revealed that the activity and the selectivity of the $\text{Rh}/\text{V}_2\text{O}_5$ system is strongly dependent on the reduction state. The activity was highest of the fully oxidized system ($\text{Rh}/\text{V}_2\text{O}_5$), and decreased constantly with increasing reduction temperature. This was tentatively explained by the partial coverage of the metal by reduced VO_x species and by alloying. At low CO partial pressures only small saturated hydrocarbons are present, but increasing the CO pressure favoured the formation of unsaturated products. Increasing the reduction temperature results in small saturated products, mainly methane is observed at 773K reduction temperature. Positive reaction orders with

respect to hydrogen and low CO partial pressures and negative orders with respect to CO at very high CO concentrations were measured, along with a relatively low activation energy. It was shown that considerable metal-support interaction exists between noble metals and classically-termed “non-reducible” oxides (SiO_2 and Al_2O_3) and that the special nature of the thin film model systems may give rise to unexpected interaction like alloying even at low reduction temperature, which in turn may be used to explain substantial changes in the catalytic activity.