

Chapter 6

Conclusions

The objective of this thesis was to investigate heterogeneous catalytic model systems from UHV conditions up to elevated pressure (and temperature) applying PM-IRAS spectroscopy. This peculiar vibrational technique was mainly applied to study Pd(111) model singly crystals, but further efforts were also spent to demonstrate the applicability of PM-IRAS spectroscopy to investigate a more complex model catalyst, Pd nanoparticles deposited on a thin alumina film. The PM-IRAS technique is therefore an excellent *in situ* vibrational spectroscopy to investigate the interaction between gas and metal interfaces both under UHV and under high pressure, providing great versatility in the spectral range of acquisition, straightforward data analysis and (relatively) low experimental cost.

Beside PM-IRAS, other surface science techniques working under UHV have been employed, such as XPS, LEED, and room temperature STM. During high pressure reactions, the catalytic behaviour of Pd model catalysts has been followed by GC as well.

CO

PM-IRAS has been successfully applied to investigate the adsorption of CO on Pd model catalyst surfaces from UHV up to elevated pressures. PM-IRAS measurements on the CO/Pd(111) system are in good agreement with previous SFG data and confirmed that results obtained under UHV hold also under higher pressure, (i.e. no surface reconstruction or high pressure induced species have been observed under “technical” conditions). PM-

IRAS can also be applied to study three-dimensional model catalysts, and initial results of CO adsorption on alumina supported Pd nanoparticles have been reported.

Methanol

Methanol adsorption, decomposition and oxidation on Pd(111) and Pd/Al₂O₃/NiAl(110) were investigated under UHV and higher pressure in a wide temperature range between 100 K and 550 K. A combined XPS and PM-IRAS study reported that these two Pd model catalysts have similar behavior under the same conditions. Under UHV, desorption of methanol dominated, while under higher pressure and temperature considerable amounts of carbon deposit through methanolic C-O bond scission was observed. Methanol oxidation reaction at high pressure and temperature was followed by PM-IRAS and GC, which reported similar activity for Pd(111) and alumina supported Pd clusters. Carbon residual were detected on both surfaces by post-reaction XPS, but the oxidation state of the catalyst surfaces was different after the high pressure reaction. XPS measurements suggested that Pd(111) remained *metallic*, while Pd nanoparticles became *partially oxidized*.

Ethylene and Butadiene

Ethylene adsorption on Pd(111) under UHV and under high pressure was followed by PM-IRAS and its different adsorption geometries have been spectroscopically detected. PM-IRAS gas phase spectra showed that Pd(111) is an active catalyst for ethylene hydrogenation to ethane under elevated pressure. Under reaction conditions it was not possible to detect any ethylene or ethylene-derived species by PM-IRAS.

High pressure selective 1,3-butadiene hydrogenation at 300 K on Pd(111) was followed by IRAS and these results are in good agreement with former kinetic studies using GC. Post-reaction XPS showed only a small amount of carbon deposit, suggesting that deactivation due to carbonaceous species may be of minor importance under the reaction conditions used. XPS measurements in UHV showed that butadiene decomposition (dehydrogenation) on Pd(111) occurred only above 500 K.

Suggestions

It has been shown in this work that the PM-IRAS technique is not limited to study model single crystal surfaces and simple probe molecules. The applicability of PM-IRAS to different heterogeneous catalytic systems in a wide pressure range is of great usefulness to narrow the *materials* and *pressure gaps* existing between surface science and real catalysis. Nevertheless, more efforts have to be spent in order to improve and enrich studies of metal supported catalysts under relevant conditions.