7. Summary and outlook

7.1 Summary

We have shown that the combination of vibrational spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and electron diffraction method (LEED) can provide a comprehensive investigation for the adsorption and reaction behaviors of gas molecules on oxide and metal deposited oxide surfaces. Furthermore, the theoretical work also plays an important role for getting the insight of the studied system.

Adsorption and reactions of a number of molecules (hydrogen, water, carbon monoxide, carbon dioxide, formaldehyde, formic acid and methanol) on clean and metal deposited oxide single crystal surfaces (ZnO and TiO$_2$) have been studied by high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED).

On the most stable surface of ZnO, ZnO(10$ar{1}$0), CO$_2$ adsorption is found to form an unusual tridentate carbonate species. Several ordered phases can be observed and are explained as the consequence of charge transfer between CO$_2$ and substrates. As the result of charge transfer, the Lewis acidity of surface Zn cations increases due to the formation of neighboring carbonate species after CO$_2$ adsorption, which essentially leads to an increase of adsorption ability of co-adsorbed CO molecules. With increasing the coverage of pre-covered CO$_2$ the binding energy of CO increases monotonically. However, the site-blocking effect also arises. A good balance of the binding energy and coverage of CO is achieved when the surface is pre-covered by half monolayer of CO$_2$, where the CO coverage reaches the maximum value of 0.5 ML.

H$_2$O adsorption on ZnO(10$ar{1}$0) at 100 K results in the formation of mono-, double- and multi-layer H$_2$O species, which are clearly identified by the different O-H stretching modes of H$_2$O with H-bonding. In the monolayer coverage regime it was further found that H$_2$O is partially dissociated forming a (2×1) superstructure along [11$ar{2}$0] direction. Surprisingly, the frequency of the ν(O-H) mode of H$_2$O monolayer
has a large red shift compared to the values in double- and multi-layer H$_2$O. This
findings reveals unusually strong hydrogen bonding interactions in monolayer H$_2$O to
both neighbouring absorbate molecules and the surface O atoms, which is responsible
for the partial dissociation of H$_2$O molecules on the perfect ZnO(10\bar{1}0) surface at
temperature as low as 100 K.
The interaction of formaldehyde (CH$_2$O) with TiO$_2$(110) surfaces was also
investigated. CH$_2$O adsorption on the perfect TiO$_2$(110) surface leads to the
polymerization production, paraformaldehyde, along Ti$_5$C rows. The binding energy of
the paraformaldehyde polymers to surface depends on the chain length. On defective
TiO$_2$(110) surfaces created by high temperature annealing and Ar$^+$ ion sputtering
methods, the adsorbed CH$_2$O is reduced to ethylene at oxygen vacancies. The
formation of ethylene results from the diffusion and recombination processes of the
adsorbate species, dioxy-methylene. The artificially sputtered surface can contain as
much as 40% of oxygen vacancies. The more reactive sites were found to be the
lattice oxygen vacancies created only by Ar$^+$ ion sputtering, where CH$_2$O is reduced to
ethylene even at temperatures as low as 150K.
For H adsorption on TiO$_2$(110) at room temperature, a maximum hydroxyl coverage
of 0.66 monolayer is achieved by exposing the clean surface to a large amount of
atomic hydrogen. Upon heating, the surface hydrogen species, instead of desorption,
undergoes a diffusion process into the TiO$_2$ bulk. This unusual behavior originates
from the lower activation barrier for diffusion of hydrogen into bulk compared to that
of recombinative desorption.

The existence of a hydrogen-free and unreconstructed polar ZnO(000\bar{1}) surface is still
under debate. We provided the experimental evidence for the stable surface structure
of ZnO(000\bar{1}) being either (3×1) reconstructed or (1×1) hydroxylated. The oxygen
vacancies on H-free ZnO(000\bar{1}) exhibit high catalytic activities toward a number of
chemical reactions. It was found that CO$_2$ is activated at surface oxygens on
ZnO(000\bar{1}) forming three different carbonate species: monodentate on surface oxygen,
bidentate carbonate species at single oxygen vacancies and tridentate carbonate at double oxygen vacancies.

The interaction of formic acid (HCOOH) with the clean, H-free ZnO(0001) surface leads to the formation of bidentate formate species at oxygen vacancies. The bidentate formate species undergo a geometry conversion to mono-dentate formate and further a dehydration process upon annealing to 500 K. Heating the sample to 550 K leads to a full decomposition of mono-dentate formate to H$_2$, CO and CO$_2$. The desorption of Zn atoms during the decomposition process is analyzed and proposed to reveal the presence of different oxygen vacancies.

Exposing the fully hydroxylated ZnO(0001) surface to atomic hydrogen leads to a significant broadening of the quasi-elastic peak in HREELS, which results from the existence of free charge carriers in the ZnO surface region. These free charge carriers are created by the thermal excitation of electrons from the donor level into the conduction band. The shallow donor states are created via diffusion of H atoms into the bulk. The analysis of the temperature dependence yields a shallow donor ionization energy of 25 ± 5 meV.

Cu deposition on ZnO(0001) surface leads to the formation of well-defined islands exposing Cu(111) facets. For the small clusters the partial oxidation of Cu$^0$ to Cu$^+$ was clearly identified by the characteristic C-O stretching frequencies. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the ZnO bulk. The doping of ZnO by Cu leads also to the formation of shallow donor states, from which the electrons can be thermally excited into the conduction band and, as a result, give rise to a plasmon-induced broadening of the quasi-elastic peak in HREELS. From the observed temperature dependence, the donor level ionization energy amounts to 20 meV, which reveals the low reaction barrier for the Cu-ZnO redox reaction. This unexpected doping effect of ZnO by Cu could have important consequences for its surface chemical activity and needs to be investigated systematically in future research.
7.2 Outlook

In this work, although much effort has been carried out to study the adsorption and reaction of gases on metal oxide surfaces, a deep understanding of metal substrate interaction, especially its effect on catalytic properties, is still scarce. Further studies, including new study methods, would be relevant.

Study contents:

(1) The study of adsorption on metal deposited substrate. This includes the growth mode, the chemical state of metal particles (films) and their effect on the catalytic properties. The presence of vacancies and pre-covered H₂O could also influence the mentioned properties.

(2) The doping of metal particles in oxide bulk leads to a change on electronic properties of the substrate, which can essentially change the charge distribution between adsorbates and substrates. As a result, the binding energy between adsorbates and substrates would be expected to increase to certain extent. This could be more prominent on powder sample since the dimension becomes smaller. A case study is the Cu doping effect on CO₂ adsorption properties that after Cu doping in ZnO the binding energy of CO₂ to ZnO increases. Combined techniques including HREELS, TDS, HAS and theoretical calculations are needed to get deep insight for this system.

Study methods:

(1) In this work, the analysis of TDS results seems too straightforward although more detailed information could be obtained from them. The combination of shape and quantitative analysis of TDS would make the study more comprehensive.

(2) The study from electronic and orbital point of view, which in many cases provides the original understanding for the reaction mechanism, could benefit the current study.

(3) The possible functional extending of HREEL spectrometer for study of electronic structure, which would enrich the current study contents.