TU Clausthal
Clausthal University of Technology

Interaction of Fe and Fe_2O_3 with H_2O and CO_2

O 59.98

Atom- und Molekülphysik an Oberflächen

Kai Volgmann[1], Anselm Hahn[1], Florian Voigts[1] und Wolfgang Maus-Friedrichs[1,2]

[1]Institut für Physik und Physikalische Technologien, TU Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany

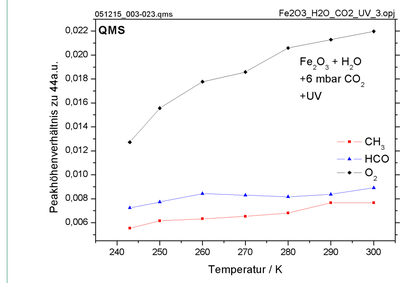
[2]Clausthaler Zentrum für Materialtechnik, TU Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany

Introduction

It has been found earlier that methane and formaldehyde can be produced through a photocatalytical process on a hematite surface with adsorbed water in a CO_2 atmosphere [1] (see figure below). To get an insight into the parameters of this surface reaction, basic investigations have been done on the interaction of Fe and Fe_2O_3 with molecular oxygen [2]. Metastable Induced Electron Spectrocopy (**MIES**), Ultraviolet Photoelectron Spectroscopy (**UPS**) and X-ray Photoelectron Spectroscopy (**XPS**) measurements revealed that a passivating oxide layer is formed and inhibits a further oxidation.

The scope of this work is to examine the interaction of Fe and Fe_2O_3 with water and CO_2. This is a further step towards a basic data set for ongoing research on the photocatalytical processes on hematite surfaces. Iron and Iron(III) oxide films are investigated by means of their interaction with H_2O and CO_2. These reactions have been studied with photoelectron spectroscopy. XPS is used to determine stoichiometry of the samples, while UPS and MIES are used to analyse the valence band region.

As a future step the photocatalytical process found in [1] will be investigated in detail. It is assumed that this photocatalytical process could be an alternate source for CH_4 and H_2CO in the Martian atmosphere. The work shown here is necesserary to built up an own data set for forthcoming measurements and correct interpretation of future work.

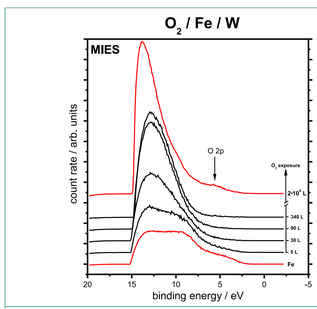


CH_4 formation on a hematite surface[1]

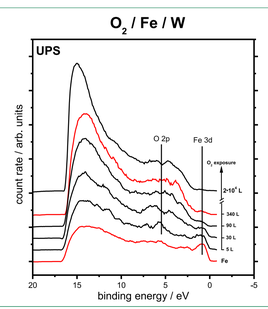
Preparation of Fe and Fe_2O_3 films

For preparation of clean **iron films**, an electron beam evaporator (EFM 3 by Omicron) filled with a rod of pure Fe (99.95 %, 2 mm diameter; Goodfellow) has been used. Typical flux was about 200 nA for an evaporation duration of 45 min resulting in a film thickness of about 10 nm.
Iron oxide films were prepared step by step applying a procedure proposed by Ranke and Weiss [3]. This was done at a sample temperature of 725 K. The resulting iron oxide film thickness is about 10 nm.

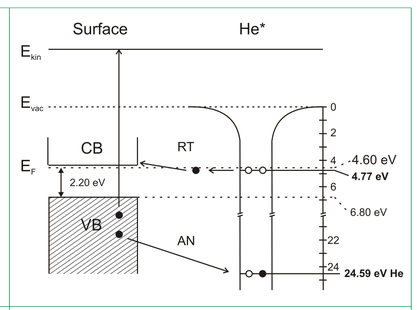
Experimental technique: MIES



(a) MIES[2]

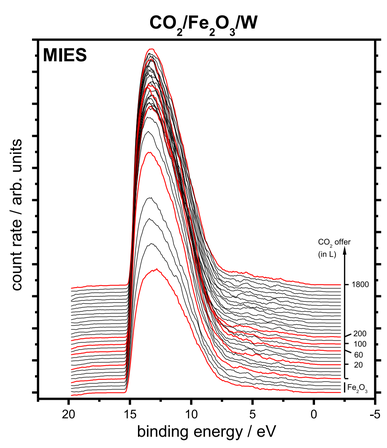


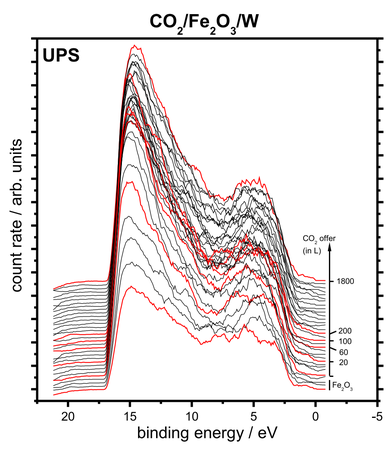
(b) UPS[2]



MIES AN process scheme[2]

CO_2 on Fe_2O_3 films



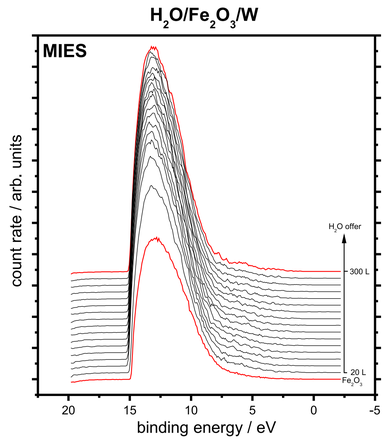


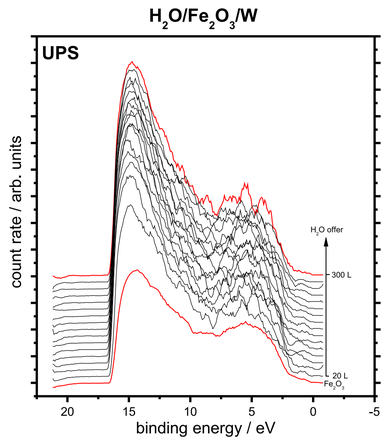
- After a CO_2 offer of 1800 L no spectral changes in MIES/UPS appear
- **Stoichiometry:**
  Fe 2p 33.4 at.%
  O 1s 66.6 at.%

  Fe^{2+} : Fe^{3+} = 0.06
  O 1s I : Fe^{3+} = 1.86
- XPS shows no C1s signal (not shown)
- O1s shows two contributions (530.8 eV, 532.5 eV) (not shown)

After an offer of $2.7 \cdot 10^9$ L CO_2 in our high pressure chamber MIES and UPS both show only an O 2p contribution. XPS shows no C1s signal and only an O 1s signal typical for iron oxide (not shown). Neither MIES/UPS nor XPS show any changes at the surface at moderate or high exposures of CO_2.

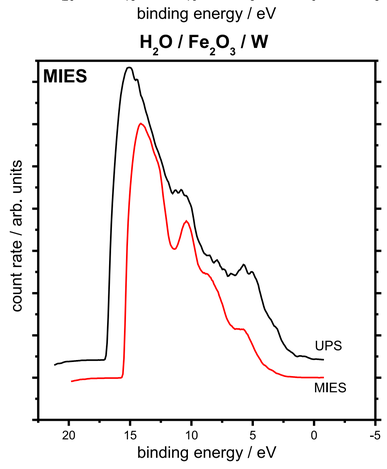
H_2O on Fe_2O_3 films

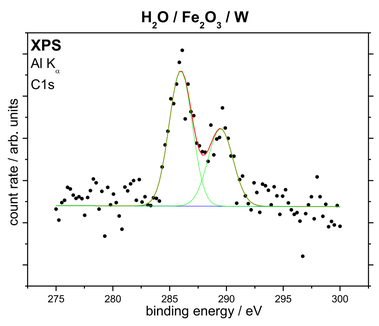




- After a H_2O offer of 300 L no spectral changes in MIES/UPS appear
- **Stoichiometry:**
  Fe 2p 36.9 at.%
  O 1s 63.1 at.%

  Fe^{2+} : Fe^{3+} = 0.18
  O 1s I : Fe^{3+} = 1.69
- O1s shows two contributions (531.0 eV, *533.0 eV*)

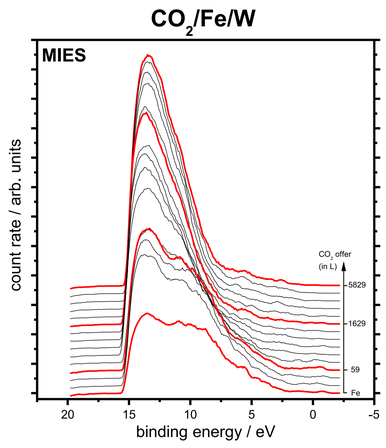


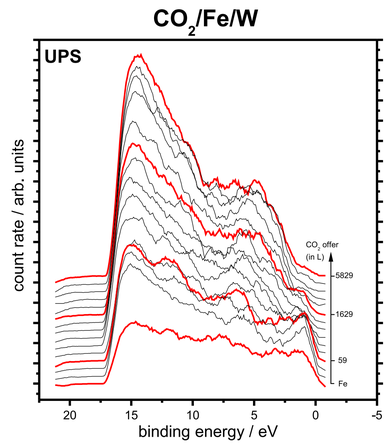


- Offering $2.7 \cdot 10^9$ L H_2O results in an irregular structure in MIES/UPS
- **Stoichiometry:**
  Fe 2p 29.1 at.%
  O 1s 70.4 at.%
  C 1s 0.5 at.%
  Fe^{2+} : Fe^{3+} = 0.32
  O 1s I : Fe^{3+} = 1.96
- XPS shows C1s signal due to contamination
- O1s shows two contributions (530.8 eV, 532.1 eV)

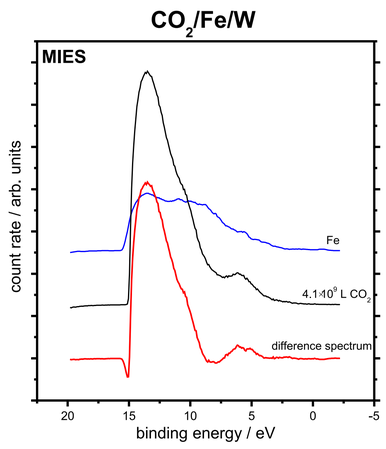
For moderate exposures of H_2O, MIES/UPS and XPS show primary an oxidation. At high exposures MIES/UPS show an unindentified structure, in XPS a C 1s contribution attributed to surface carbonate formation is observed.

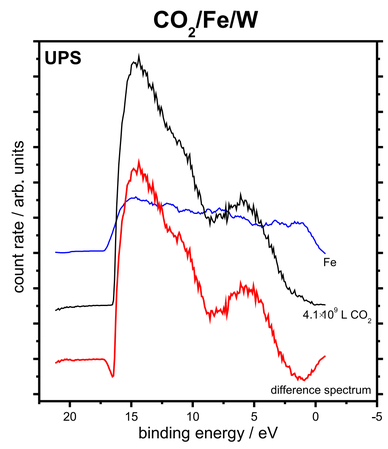
CO_2 on iron films



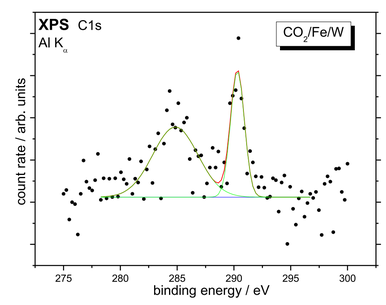


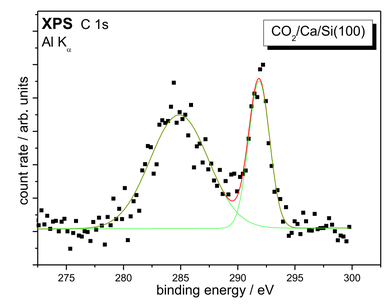
- After a CO_2 offer of 5829 L, MIES/UPS show the oxidation of iron
- **Stoichiometry:**
  Fe 2p 46.9 at.%
  O 1s 53.1 at.%
  Fe^{2+} : Fe^{3+} = 0.72
  O 1s I : Fe^{3+} = 1.91
  Fe^0 content: 35.6 %
- XPS shows no C1s signal (not shown)
- O1s shows two contributions (530.5 eV, 532.0 eV) (not shown)





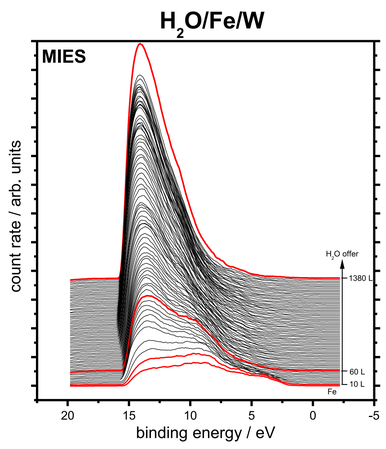
- After a CO_2 offer of $4.1 \cdot 10^9$ L MIES/UPS show no spectral changes
- **Stoichiometry:**
  Fe 2p 38.8 at.%
  O 1s 53.8 at.%
  C 1s 7.4 at.%
  Fe^{2+} : Fe^{3+} = 0.90
  O 1s I : Fe^{3+} = 2.13
  Fe^0 content: 33.0 %
- O1s shows two contributions (530.3 eV, 532.1 eV) (not shown)
- XPS shows C1s signal at 284.8 eV and 290.3 eV
- the second XPS C1s spectrum is a comparison to carbonate on calcium[4]

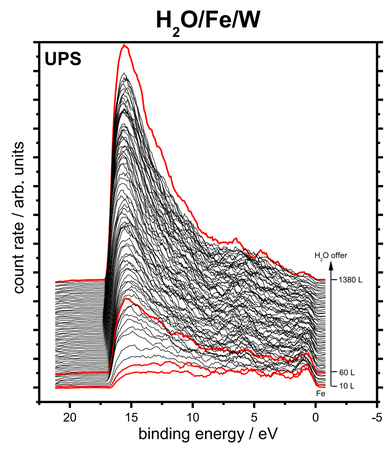




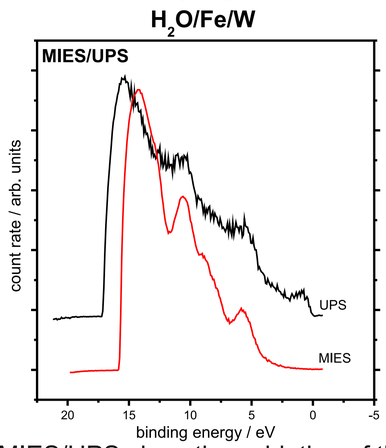
MIES/UPS show an oxidation of the iron film for moderate and high CO_2 offers. Only for high exposures, a C 1s signal is observed in XPS, which is comparable to carbonate formed on Ca.

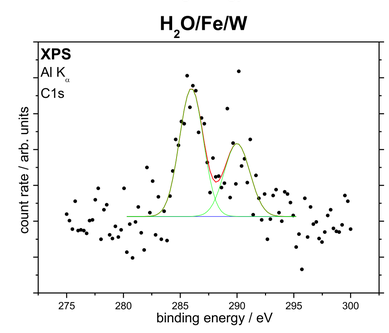
H_2O on iron films





- After a H_2O offer of 1380 L no spectral changes are observed in MIES/UPS
- **Stoichiometry:**
  Fe 2p 59.6 at.%
  O 1s 40.4 at.%
  Fe^{2+} : Fe^{3+} = 0.35
  O 1s I : Fe^{3+} = 1.42
  Fe^0 content: 46.3 %
- In XPS, the O1s shows two contributions (530.7 eV, 533.0 eV) (not shown)
- C1s signal not observed





- After a H_2O offer of $2.7 \cdot 10^9$ L unidentified structures in MIES/UPS appear
- **Stoichiometry:**
  Fe 2p 56.9 at.%
  O 1s 31.5 at.%
  C 1s 11.6 at.%
- In XPS, C1s shows two contributions (286.0 eV, 290.0 eV) due to contamination
- O1s shows four contributions (530.7 eV, 531.3 eV, 532.6 eV,

MIES/UPS show the oxidation of the iron film for moderate offer. At high H_2O exposure, MIES/UPS show an unidentified structure. A C1s signal is additionally observed in XPS.

Summary

- CO_2 and H_2O both show an oxidation of an iron film in MIES/UPS. An oxide layer may inhibit further reactions as can be seen for CO_2 offer. XPS shows two O1s contributions for both gases.
- On iron oxide films, the offer of CO_2 or H_2O does not lead to spectral changes in MIES/UPS. XPS shows for both gases only a O1s signal, in each case with two contributions.
- High exposures of CO_2 leads neither on iron nor on iron oxide to spectral changes in MIES/UPS. Only for iron, XPS shows a C1s signal similar to a signal found for carbonate on Ca.
- Water offer at high pressure (1 mbar for 60 min) leads to an irregular structure in MIES/UPS. XPS observes O1s and C1s signals. The latter is found due to contamination with CO_2 (approximately 5 %).

References

[1] B. Roos, D. Schwendt: *Extraterristische Chemie*, student research project, TU Clausthal 2006

[2] K.Volgmann, F. Voigts, W. Maus-Friedrichs: *The interaction of oxygen molecules with iron films studied with MIES, UPS and XPS*, Surface Science (2010), doi: **10.1016/j.susc.2010.02.018**, in press

[3] W. Weiss, W. Ranke, *Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers*, Surface Science **70** (2002), 1-151

[4] F. Voigts, F. Bebensee, S. Dahle, K. Volgmann, W. Maus-Friedrichs: *The adsorption of CO_2 and CO on Ca and CaO films studied with MIES, UPS and XPS*, Surface Science **603** (2009) 40-49