Combined Study of Ionic Processes on Surfaces: Photoelectric and Photocatalytic Effects

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Introduction

Challenge:
• molecular reaction pathways in photocatalytic and photoelectric processes remain unclear
• previously published mechanisms seem to explain only individual cases under certain selected conditions
• reaction mechanisms are required
determination of the presence and the role of reagent ions, like for example \( O_2^- \), is necessary
differentiation between surface bound and gas phase ions and reactions, respectively

Background

CAPECI

Use of the photoelectric effect at atmospheric pressure
UV-light interaction with metal surfaces yields low energy electrons
electron capture forms negative ions
superoxide, \( O_2^- \), represents main reagent ion when oxygen is present

Photoemissive measurements:
• radiation is directed through a quartz window onto the sample material
• adjustable acceleration voltage is applied to the probe plate
distance between probe and detector plate is variable
detector plate is connected to the electrometer to measure ion/photo current
chamber background pressure is adjustable down to \( 10^{-10} \) mbar
chamber is pressurized with \( O_2 \) or synthetic air to vary gas phase conditions

Experimental Setup

Probe plate carrying target material; adjustable acceleration voltage
Pump

Dependences of the Photoelectric Yield

Laser power

Acceleration voltage (AV)

Pressure

Light: The signal intensity strongly depends on the pressure. The photovoltaic increase yields with decreasing pressure. Additionally, the signals become narrower.

Surprisingly, the photoemissive measurements do not show any significant differences between air or nitrogen being present in the chamber. Previous investigations revealed a strong dependency of the oxygen ratio for photoemissive as well as photocatalytic effects. For CAPECI-MS the presence of oxygen is necessary. In contrast, the used commercial photocatalytic dispersion paint (TiO\(_2\)) shows photocatalytic activity even in an oxygen-free atmosphere, which is traced back to the fact that water and/or oxygen is adsorbed on the surface (see figure 1).

Conclusions

Photocatalytic measurements:
• VUV irradiation (185 nm) leads to generation of gas phase negative ions when aluminium as well as TiO\(_2\) dispersion paint is used as photocatalystic material
• measured ion distributions are consistent with previous CAPECI-MS measurements
• photocatalytic conversion of NO is observed using the TiO\(_2\)-dispersion paint at 390 nm
• NUV irradiation (390 nm) does not generate any gas phase ions detectable by the MS

Photoemissive measurements:
• dependencies of the photoelectric yield on the acceleration voltage and the pressure are as expected
• at elevated pressures no photoelectric yield without applying acceleration voltage
• variation of laser power shows a surprisingly low dependency of the photo current
• no significant difference between air or nitrogen, most probably caused by gas impurities
• used materials do not show significant differences in their photoemissive properties

Outlook:
• presented results are pre-examinations, further MS-experiments will follow
• use of light source which is tunable in energy and power (e.g. OPOs)
• further investigations on gas phase dependencies (water vapor, noble gases, compounds with high electron affinities e.g. SF\(_6\))
• differentiation between photo and ion currents

Methods

Experimental Setup:
- MS: Esquire 6000 QIT, Bruker Daltonic
- Photoelectro: custom designed flow tube type reactor (Fig. 2)
- Photoemissive: Sto Photoanode (TiO\(_2\)); monocrystalline ZnO; Cu; Al
- Radiation sources: ATL Atlas Kr*; excimer laser (248nm); NUV-Diode (390 nm); low pressure mercury lamp (Penflay) 185/254 nm
- Measurement chamber: custom designed chamber with detector and target plate (Fig. 3)
- Ion Current measurements: Keithley 662 electrometer;
- Tektroxx oscilloscope
- NO\(_x\) monitor: NO/LAPF instrument
- Pump: Pfeiffer Vakuum TurboDrag Pump

Literature


Acknowledgement

Financial support by BMBF/13N9194 (Haus, Germany) is gratefully acknowledged.