

O 62: Surface chemical reactions II

Time: Friday 11:15–13:00

Location: SCH A01

O 62.1 Fri 11:15 SCH A01

In-situ investigation of sulfur oxidation on a stepped Pt surface — ●REGINE STREBER¹, CHRISTIAN PAPP¹, MICHAEL PETER ANDREAS LORENZ¹, ANDREAS BAYER¹, REINHARD DENECKE², and HANS-PETER STEINRÜCK¹ — ¹Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen — ²Willhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig

We studied the reaction of oxygen with preadsorbed sulfur on the stepped Pt(355) surface by in-situ high-resolution XPS applying synchrotron radiation at BESSY II. The reactivity strongly depends on surface temperature. At 250 K, dosing of molecular oxygen on the partially sulfur precovered surface leads to the coadsorption of atomic S and O, but almost no reaction, as concluded from the S 2p spectra. Upon heating this mixed layer to elevated temperatures, the subsequent formation of two new species is observed, which are assigned to SO₂ and SO₄. At 300 K, dosing of oxygen results in the partial formation of SO₂, while at 350 K a consecutive reaction to SO₄ occurs. To determine the kinetic parameters of these reactions, the oxidation has been studied at different temperatures. In addition, the influences of the initial sulfur precoverage and of the oxygen pressure have been investigated. This work was supported by BMBF (05 ES3XBA/5) and the DFG through the Cluster of Excellence "Engineering of Advanced Materials".

O 62.2 Fri 11:30 SCH A01

Structure Formation in Ultrathin V-Oxide films on Rh(111) under different Reaction Conditions — ●FLORIAN LOVIS, MARTIN HESSE, and RONALD IMBHL — Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr.3-3a, D-30167 Hannover, Germany

As a model system for vanadium-oxide based catalysts we prepared ultrathin vanadium oxide films on a Rh(111) surface. At 400°C 0.1 and 0.25 ML of vanadium were evaporated in oxygen with p(O₂)=2x10⁻⁷ mbar. After characterization with LEED and Auger electron spectroscopy the films were subjected to the O₂ + H₂ reaction using photoemission electron microscopy (PEEM). After evaporation a large variety of differently ordered Rh(111)/V/O phases were identified in LEED. The O₂ + H₂ reaction was studied in the 10⁻⁸ to 10⁻⁵ mbar range at temperatures between 400 and 500°C. With PEEM we observe that under reaction conditions the film is no longer homogeneous but reaction fronts and stationary Turing-like patterns develop. In the evaporated V-film we find partially ordered patterns consisting of large islands of about 0,05 mm diameter. These islands are very stable and change only very slowly after turning off the gases. Under different reaction conditions we find small islands of roughly 0,02 mm diameter which in contrast to the large islands are quite dynamic and vary in diameter depending on the reaction conditions. The patterns induced by the reaction are discussed in the context of the concept of reactive phase separation. It is suspected that the attraction between oxygen and vanadium is the driving force for the condensation process.

O 62.3 Fri 11:45 SCH A01

Non-adiabatic energy dissipation in metal homoepitaxy — ●ULRICH HAGEMANN, KORNELIA HUBA, DAVID KRUX, and HERMANN NIENHAUS — Experimental Physics, University of Duisburg-Essen, Germany

The growth of metal films releases energies of typically a few eV per metal atom. By now, the energy is believed to be dissipated adiabatically by direct excitation of phonons. We present data which give strong evidence for the creation of electron-hole pairs during Mg homoepitaxy, i.e., for a non-adiabatic dissipation channel. To detect the generated hot charge carriers, large-area ultrathin metal film Mg/p-Si(001) Schottky diodes were fabricated. The homogeneous Schottky barrier height was determined as 0.52 eV and the reverse current could be reduced to below 1 nA at low temperatures. During exposure of the diodes to a thermal Mg atom beam internal currents in the 100 pA range are observed. The currents can be attributed to two mechanisms: first the internal exoemission process (chemicurrent effect) due to non-adiabatic energy dissipation and second the photocurrent due to the infrared radiation of the evaporator. By varying the evaporator temperature and the Mg film thickness the two current contributions

can be distinguished. The chemicurrent during Mg homoepitaxy depends exponentially on the evaporation temperature yielding the Mg evaporation enthalpy of 1.3 eV. The strong exponential attenuation of the chemicurrent with increasing Mg film thickness further supports the concept of generation of ballistic charge carriers by the metal formation process.

O 62.4 Fri 12:00 SCH A01

State resolved measurements of photodesorbed NO from Ag (111) surface — ●DANIEL MULUGETA¹, KAZUO WATANABE¹, DIETRICH MENZEL^{1,2}, and HANS-JOACHIM FREUND¹ — ¹Fritz-Haber-Institute der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — ²Physik-Department E20, Technische Universität München, 85747 Garching

The distribution of energy over the various degrees of freedom of photodesorbed molecules contains important information about the dynamics of the desorption event. We have performed state resolved (translation, rotation, vibration) measurements of NO photodesorbed from (NO)₂ adsorbed on Ag (111) at 60 K by nanosecond laser pulses (2.3, 3.5 or 4.7 eV) by using (1+1) resonant multiphoton ionization (REMPI) via the A²Σ ← X²Π transition. Both thermal and non-thermal components are observed in state selective time of flight measurements. Rotational and vibration temperatures of about 430 K and 710 K, respectively, were found for NO photodesorbed with a velocity of about 960 m/s, regardless of the photon energy used. The translational energy distributions did not show major change with vibrational excitations. By contrast, the translational temperature showed a systematic increase with increasing rotational excitation. The results are interpreted in terms of an excitation-deexcitation mechanism via transient negative ions.

O 62.5 Fri 12:15 SCH A01

Direct photochemical formation of N₂ from NO dimers on cold Ag(111) — ●KI HYUN KIM¹, KAZUO WATANABE¹, DIETRICH MENZEL^{1,2}, and HANS-JOACHIM FREUND¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Technische Universität München, 85747 Garching, Germany

Direct photochemical formation of N₂ has been identified for the first time in photoreactions of (NO)₂ adsorbed on Ag(111) at ~ 30 K, induced by UV and visible light. Mass selected time-of-flight signals of N₂, N₂O, and NO formed from (NO)₂ on Ag(111) by irradiating with 2.3, 3.5 and 4.7 eV laser beams (Nd:YAG laser) were measured. The results show that the translational temperature of the N₂ formed from (NO)₂ on Ag(111) is ~ 5700 K, while those of photodesorbed N₂O and NO are ~ 1200 and 770 K, respectively, independent of incident photon energy. On the other hand the translational temperature of N₂ formed from adsorbed N₂O on Ag(111) is only ~ 1400 K, i.e. much lower than that of N₂ formed from (NO)₂.

We propose that the formation of fast N₂ from (NO)₂ on Ag(111) occurs via simultaneous cleavage of the two N-O bonds followed by the formation of an N-N triple bond of N₂, and can be regarded as mutual abstraction of the N atom from each nitrosyl in (NO)₂. The Ag surface reduces the N-N bond length of (NO)₂ to enable the formation of N₂ as well as of N₂O; furthermore, the equilibrium surface distance of (NO)₂ is considerably shorter than that of N₂ which leads to the latter's high kinetic energy.

O 62.6 Fri 12:30 SCH A01

Adsorption of Methanol on Ru(0001) — ●PAWEŁ GAZDZICKI and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, D-35032 Marburg, Germany

Infrared Absorption Spectroscopy was used to study the adsorption and reaction of methanol on Ru(0001). From the vibrational modes of the isotopes CH₃OH and CH₃OD clear evidence for intact adsorption at T = 80 K has been found. This finding contradicts previous studies which suggested an OH (OD) bond scission upon adsorption of methanol even at low temperatures as well as recombinative desorption at elevated T. Our conclusion is based on isotopic shifts of vibrational modes associated with the OH (OD) group of adsorbed CH₃OH and CH₃OD, respectively. The findings are corroborated by TPD experiments of CH₃OH with coadsorbed D on Ru(0001). While clearly showing desorption of CH₃OH, no desorption of CH₃OD caused by

the recombination of dissociated CH_3OH and D was observed. At low coverages (< 0.1 ML) we suggest the presence of isolated methanol molecules which begin to cluster with increasing density by building hydrogen bonds. This clustering was also observed after annealing a low coverage methanol layer up to 100-120 K. At temperatures $T = 170$ -200 K CH_3OH decomposes (O-H bond cleavage) to form an upright methoxy species (CH_3O). The final reaction products are CO and H which are formed at $T > 220$ K.

In comparison, CH_3OH adsorbed on pseudomorphic Cu/Ru(0001) produces the same species as on Ru(0001). Yet, the temperature range of the methoxy species is significantly larger, i.e. 200-300 K.

O 62.7 Fri 12:45 SCH A01

A new transferable method to calculate electronic excitations in adsorption on metal surfaces — •MATTHIAS TIMMER and PETER KRATZER — Fachbereich Physik - Theoretische Physik and Centre for Nanointegration (CeNIDE), Universitaet Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany

Non-adiabatic effects in adsorption on metal surfaces include the exci-

tation of electrons and holes, which can be observed as chemicurrents. We present a new quantitative method on the basis of ground-state density-functional theory (DFT) to calculate these excitation probabilities. The method uses first-order time-dependent perturbation theory, which is implemented using the evaluation of matrix elements between Kohn-Sham states of the rate of change of the Kohn-Sham potential between subsequent static DFT calculations. We can access the excitation spectra directly. The method is applied to adsorption of atomic hydrogen isotopes on-top the Al(111) surface. Results can explain the experimental data for noble metal surfaces; in particular the observed isotope effect in H versus D adsorption is described. Moreover, the results are in quantitative agreement with computationally expensive calculations of the full dynamics within time-dependent DFT, with the notable exception of effects due to spin dynamics.

The method presented is simple enough to be applied to a wide class of adsorbates and surfaces, while at the same time allowing us to extract system-specific information. It can be implemented with reasonable effort within existing DFT codes [1].

[1] <http://arXiv.org/abs/0810.5248>