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Sulfur Oxidation

Sulfur Oxidation on Pt(355): It Is the Steps!**

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Platinum catalysts are frequently used in catalytic converters in cars[1–3] and also in oil refineries.[4–6] The catalysts' active sites are subject to deactivation through poisoning by sulfur (or sulfur oxides), which are common impurities in fuels.[1–8] These active sites are thought to be defects, such as step or kink sites, which are omnipresent on the surface of the highly dispersed catalyst nanoparticles. Adsorbed sulfur modifies the electronic properties of the catalyst surface, which leads to a decrease of chemical and catalytic activity.[9–11] The key step to regain catalyst activity is the removal of the sulfur atoms from the catalyst surface, for example by exposing it to molecular oxygen, thereby oxidizing the adsorbed sulfur, and then removing the resulting SO_x species from the surface. The mechanism, the chemical nature of the intermediates formed, and the specific role of defects in this process are unknown for the most part. This lack of insight is exists, because the relevant information can be obtained directly only by in situ methods, which allow a quantitative determination of the surface species or intermediates on the timescale of seconds. However, up to now there have been only very few studies for the direct measurement of kinetic parameters such as activation energies.[12,13] In most cases kinetic parameters are determined by temperature-programmed desorption (TPD), where only the desorbing species are detected. Since important reaction intermediates can thereby easily be missed, the correct determination of kinetic parameters can be hampered.

Herein we present the first in situ study of sulfur oxidation on a model catalyst surface, namely stepped Pt(355). We have clearly identified the steps as active sites and determined the activation energy directly. The Pt(355) surface has (111) terraces five atom rows wide, and monatomic steps with (111) orientation. The role of the steps is elucidated by comparison to data obtained on a flat Pt(111) surface. Using synchrotron radiation, we were able to measure high-resolution XP spectra in situ during adsorption and while heating the sample with short measuring times. Owing to the high resolution, different surface species could be identified and analyzed quantitatively and site selectively in a time-dependent fashion, also for very low adsorbate coverages.[14–17] This enabled us to investigate the oxidation of small amounts of sulfur with oxygen present on the surface in large excess, which simplifies the kinetic analysis and makes it possible to determine the activation energy of the rate-determining step.

The information on sulfur oxidation is rather limited in the literature. Early TPD studies[18,19] on Pt(111) yielded no information on surface intermediates, and consequently only an apparent activation energy was derived.[19] Theoretical calculations[20] indicate that at the oxygen saturation limit S is oxidized to SO_x ($x = 1$–4) and the total energy increases with x, but no information on the activation energy of the rate-limiting step is available. Furthermore, there are a number of studies on the adsorption of SO_2 on Pt surfaces, which serve as reference for the identification of reaction intermediates and partial reaction steps in the present study.[8,11,21–23]

The thermal evolution of a layer of coadsorbed sulfur and oxygen on Pt(355) provides a first overview of the relevant reaction steps. Figure 1a shows a series of S 2p spectra recorded before and after dosing of molecular oxygen at 250 K onto Pt(355) precovered with 0.020 monolayers (ML) of sulfur, and during subsequent heating of the coadsorbate layer. The spectrum in black (sulfur layer prior to exposure to oxygen) shows the S $2p_{3/2}$ and S $2p_{1/2}$ signals at 162.0 and 163.2 eV, respectively, with an intensity ratio of 2:1. As this ratio and the peak separation of these signals are identical for all sulfur species, only the stronger $2p_{3/2}$ signal will be discussed. The value of 162.0 eV is typical of S adsorbed at step sites on Pt(355).[17] The spectrum in orange, which was recorded after saturation of the surface with oxygen, shows the S $2p_{3/2}$ peak at 162.2 eV, which is typical for S at terrace sites.[17] The clearly discernable shift of 0.2 eV indicates that the S atoms were pushed away from the step to terrace sites by the O atoms, similar to a recent observation for the coadsorption of sulfur and carbon monoxide on Pt(355).[17]

When the sample is heated, the S 2p spectra in Figure 1a change dramatically. To visualize the thermal evolution more clearly, we have also plotted the data in a color-coded density plot in Figure 1b. For the quantitative analysis shown in Figure 1d, the spectra were fitted, with the energetic separation of the S $2p_{1/2}$ and $2p_{3/2}$ peaks fixed at 1.2 eV and their ratio set at 1:2 (see the Experimental Section). In Figure 1c a

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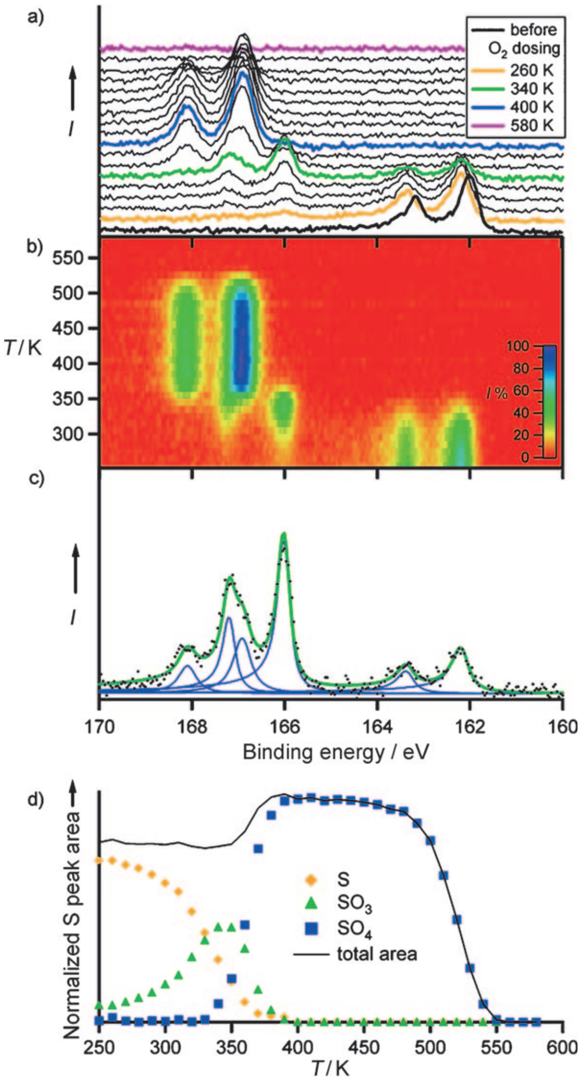

Figure 1. Thermal evolution of a sulfur layer (0.020 ML) with coadsorbed oxygen (0.31 ML) on Pt(355). a) Selected S 2p spectra collected at a photon energy of 260 eV and a measuring time of 10 s per spectrum. Black/orange spectrum: before/after dosing with 400 L oxygen at 250 K; other spectra: collected while the surface was heated at a constant rate of 0.5 K s^{-1}. b) Data of (a) in a color-coded density plot. c) Typical result of the fitting procedure (data for 350 K); the dots represent the measured spectrum, the thin blue lines correspond to the asymmetric peak profiles fitted to the individual peaks, and the green line is the sum of all. d) Quantitative analysis of the peak area of the individual species for the data shown in (a).

typical fitting result is shown. From Figure 1 b,d it is evident that above 260 K a new 2p$_{3/2}$ peak grows in at 166.0 eV at the expense of the peak at 162.2 eV; it reaches maximum intensity at ≈340 K (green spectrum in Figure 1 a) and thereafter decreases again. This signal is assigned to SO$_3$ by comparison to data from a detailed study of the adsorption and reaction of SO$_2$.[24] The peak separation of 3.8 eV relative to elemental S at terrace sites which we observe is significantly greater than the values of (2.4 ± 0.1) and (3.2 ± 0.1) eV found for two coexisting SO$_2$ species on Pt(111).[21,24] Simultaneous to the decrease of the SO$_3$ species at 350 K, a new doublet evolves with the S 2p$_{3/2}$ component at 166.9 eV; it reaches its maximum intensity at 400 K (blue spectrum in Figure 1 a), at which temperature SO$_3$ disappears, and it eventually starts to decrease above 500 K. Based on its peak separation of 4.7 eV relative to atomic S it is assigned to SO$_4$.[21,23] During the reaction step from SO$_3$ to SO$_4$ (i.e., between 340 and 390 K) the total coverage of sulfur species (solid line in Figure 1 d) seems to increase, but as no additional sulfur is adsorbed, the apparent increase is attributed to differences in photoelectron diffraction for SO$_3$ and SO$_4$ at the low kinetic energies (≈100 eV) of the photoelectrons used here.[25]

To determine the activation energy, we performed isothermal experiments in which we exposed the sulfur-precovered Pt(355) surface (0.020–0.035 ML of S) to a constant oxygen pressure of 6×10^{-7} mbar. Figure 2 a,b show the data at 300 and 350 K, respectively, with the corresponding quantitative analyses in Figure 2 c,d. At 300 K only the formation of SO$_3$ (S 2p$_{3/2}$ at 166.0 eV) is found, with no indication of SO$_4$ (166.9 eV). A closer look at the spectra (bottom of Figure 2 a) reveals that a shift in the S 2p$_{3/2}$ peak of atomic S (from 162.0 to 162.2 eV) is evident at 300 K, immediately after the start of oxygen dosing (see above); at 250 K the shift is seen after 40 s (not shown). This indicates that a higher temperature facilitates the site change of the preadsorbed S from the step to the terrace. The quantitative analysis in Figure 2 c shows that after an induction period of 50 s the formation of SO$_3$ accelerates and thereafter the amount of sulfur decreases exponentially.

At 350 K, the coverage of atomic S also decreases exponentially (after a significantly shorter induction period). As expected for the higher temperature, the decrease of S and the increase of SO$_3$ occur faster. After 100 s the onset of subsequent oxidation of SO$_3$ to SO$_4$ is observed. After 900 s the oxidation of S to SO$_4$ via SO$_3$ is almost complete.

Isothermal experiments were also performed at 250, 400, and 450 K. Note that the initial precoverages of sulfur varied between 0.020 and 0.035 ML, which does not, however, affect the data analysis and the conclusions derived. Figure 3 a shows the decrease of atomic S with time for the different temperatures. In all cases an exponential decrease is observed after an initial induction period. As expected, the S coverage decreases faster with increasing temperature. The logarithmic plots of the normalized S peak area versus time in Figure 3 b show straight lines for all temperatures, indicating that the reaction is pseudo first order with respect to sulfur. This is explained by the fact that after the initial induction period, the O coverage is much greater than the S coverage. During this induction period, the O coverage builds up on the surface and the observed behavior deviates from pseudo first order.

The slope of the fitted lines in Figure 3 b corresponds to the rate constant k. The plot of $\ln k$ versus T^{-1} in Figure 4 yields an activation energy of (34 ± 2) kJ mol^{-1} for the rate-determining step in the oxidation of S to SO$_3$ on Pt(355) at $\Theta_S = 0.020–0.035$ ML. The fact that no intermediate SO and SO$_2$ species are found indicates that the rate-determining step is the oxidation of S to SO. To verify that the reaction is indeed pseudo first order and that the activation energy does not depend on the pressure, we also performed experiments at an oxygen pressure of 2×10^{-6} mbar; those data (for $\Theta_S =$

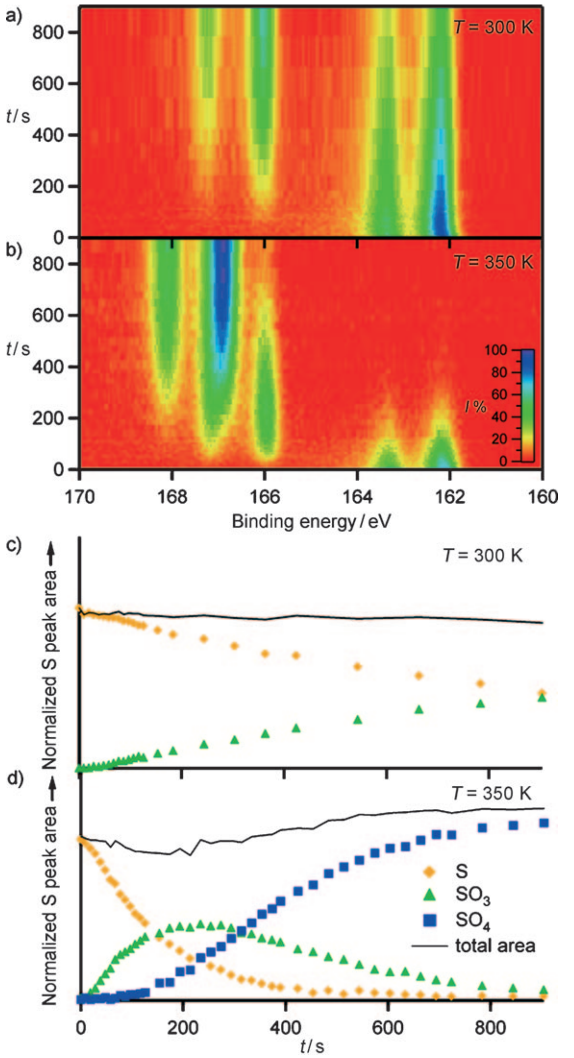

Figure 2. Isothermal oxidation of sulfur on Pt(355) at an oxygen pressure of 6×10^{-7} mbar. a) Color-coded density plot of the S 2p spectra collected at 300 K at an initial S coverage of 0.035 ML. b) Color-coded density plot of the S 2p spectra collected at 350 K at an initial S coverage of 0.020 ML. c),d) Normalized sulfur coverages vs. time as obtained from the quantitative analysis of the spectra in (a) and (b), respectively.

0.015–0.020 ML) are included in Figure 4 and yield the identical activation energy.

To elucidate the role of the steps in S oxidation we also studied the flat Pt(111) surface. Again we find pseudo-first-order reaction kinetics; however, the activation energy of (74 ± 4) kJ mol^{-1} for the oxidation on the flat surface (see data in Figure 4) is more than twice the value of reaction on the stepped surface.[26] The high activation energy on the flat surface demonstrates the importance of the steps in the oxidation process.

In conclusion we have studied the kinetics of the oxidation and removal of sulfur on stepped and flat Pt(111) surfaces by in situ high-resolution photoelectron spectroscopy. We identified SO_3 and SO_4 as reaction intermediates and determined the activation energy for the rate-limiting step for the oxidation of sulfur. The activation energy for the oxidation of S to SO on stepped Pt(355) is found to be less than half of the value of that on flat Pt(111), indicating the dominating role of steps and defects for the catalytic oxidation of sulfur. Since on the stepped surface S is pushed from the steps to the terrace by O, the catalytically active species on the Pt(355) surface must be oxygen at step sites. We believe that apart from the detailed insight in the role of steps in the particular surface reaction studied, the presented data represent a new level of insight in complex surface reactions in general.

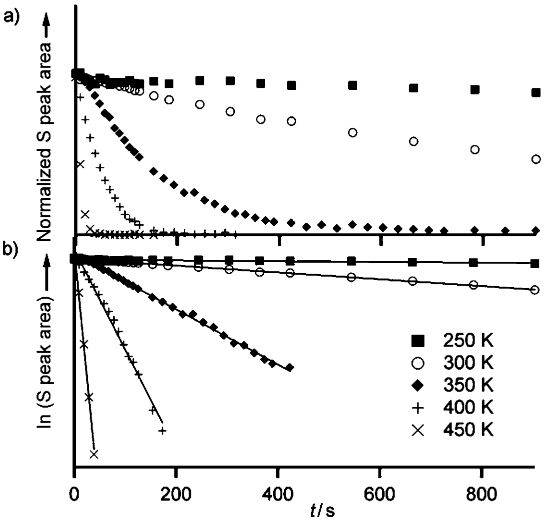

Figure 3. Linear (a) and logarithmic plot (b) of normalized sulfur coverage vs. time for sulfur oxidation on Pt(355) at various surface temperatures and at an oxygen pressure of 6×10^{-7} mbar. The initial S coverages for the different experiments are: 250 K: 0.020 ML, 300 K: 0.035 ML, 350 K: 0.020 ML, 400 K: 0.035 ML, 450 K: 0.030 ML.

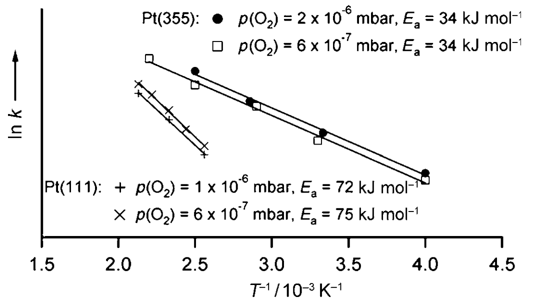

Figure 4. Arrhenius plot of the rate constants as determined from isothermal S oxidation experiments on Pt(355) and Pt(111) at different pressures (as noted). The data for Pt(355) at 6×10^{-7} mbar are derived from Figure 3. The activation energies for Pt(355) and Pt(111), derived from data at different pressures, are identical within the margin of error for each crystal.

Experimental Section

The experiments were performed at BESSY II in Berlin at beamline U49/2-PGM1, using a transportable ultra-high-vacuum apparatus.[27] The Pt surfaces were cleaned using standard procedures,[28] and the surface order was verified by low-energy electron diffraction. Sulfur was deposited via H_2S adsorbed at ≈130 K, followed by heating to 700 K, which leads to decomposition, with H_2 desorbing and S remaining on the surface. The S coverage was calibrated by comparison to the S 2p signal of a (2 × 2) superstructure on Pt(111).[29] No reconstruction of the Pt(355) surface was observed for $\Theta_S < 0.25$ ML.[17,30] Oxygen was dosed by means of a supersonic molecular beam with the nozzle at room temperature. The S 2p XP spectra were collected with a photon energy of 260 eV; for the quantitative analysis, first a straight line, fitted to the spectrum of the clean surface, was subtracted from all spectra. Thereafter, the positions and the areas of the different peaks were determined by fitting an asymmetric Doniach–Sunjic[31] profile convoluted with a Gaussian to each peak.

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[26] Note that the value of 54 kJ mol^{-1} reported by Köhler et al.[19] for Pt(111) is significantly smaller than the value found here. This is attributed to the fact that in their TPD study no intermediates could be identified and consequently the data analysis was probably incorrect.

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