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# Site blocking and CO/sulfur site exchange processes on stepped Pt surfaces

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## Abstract

The influence of preadsorbed sulfur on the adsorption of CO on Pt(355) and Pt(322) is investigated systematically for sulfur precoverages between 0.02 and 0.30 ML by *in situ* x-ray photoelectron spectroscopy of the C 1s and S 2p core levels. The two surfaces have the same nominal terrace width of 5 atomic rows, but different step orientation. For both, at low temperatures (130 and 150 K), S preferentially adsorbs at the steps and passivates them for CO adsorption. The required S precoverage is significantly smaller for Pt(322), because of the lower number of steps as a result of the S-induced double-step formation. Upon heating, population of step sites with CO occurs due to irreversible CO/S site exchange. At low S precoverages, the characteristic transition temperatures of 165 K for Pt(355) and 245 K for Pt(322) are significantly different, indicating a higher activation barrier for the CO/S site exchange process for Pt(322). For medium to high S precoverages the transition temperature stays unchanged for Pt(322) but increases for Pt(355). The observed behavior is attributed to a kinetic passivation of the steps by sulfur at low temperatures, which is lifted upon heating.

Dedicated to Professor Klaus Heinz on the occasion of his retirement.

## 1. Introduction

Defects often play a decisive role in catalysis. Many relevant heterogeneously catalyzed chemical reactions take place on small active particles, whose surface properties are governed by defects [1, 2]. This is mainly related to pronounced differences in the geometric and electronic structure of these defect sites as compared to flat surfaces of perfect single crystals, which are typically investigated in surface science. The resulting differences in the potential energy surfaces lead to changed bond strengths and, if existing, activation energies for adsorption. As adsorption is the starting point of any surface reaction, the understanding of this primary process is of particular importance for understanding surface reactions, in particular also on complex surfaces [1, 2].

Vicinal surfaces with a regular arrangement of monatomic steps are model systems to study such effects with various

surface science methods. In particular, CO adsorption on Pt single-crystal surfaces is very well suited for such investigations, due to the vast literature not only on flat surfaces (e.g. [3] and references therein) but also on stepped surfaces ([4] and references therein, [5–7]). Important parameters of such regularly stepped surfaces are the orientations of both terraces and steps, as well as the width of the terraces. Several systematic studies concerning the influence of terrace width and step orientation on CO adsorption on stepped Pt surfaces have been published. There is general agreement that CO adsorbed on step sites is more strongly bound than on terraces, as shown by temperature programmed desorption (TPD) and temperature programmed x-ray photoelectron spectroscopy (TPXPS) studies [4–8]; also there is no indication for CO dissociation under the particular experimental conditions. Other important aspects, which were investigated, are the distribution of CO on different adsorption sites at both terraces and steps [9–12] and the possible formation of ordered adsorbate structures [9, 13–17].

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Poisoning of active sites is a major issue in large scale applications of heterogeneously catalyzed reactions [18], but also of significant fundamental interest in understanding the underlying principles and mechanisms. One very efficient poison for catalysts is sulfur which occupies threefold hollow sites on Pt(111) [19–24]. TPD studies of CO adsorbed on Pt(111) showed that preadsorbed sulfur leads to a reduction of the total CO adsorption capacity and lowers the binding energy of CO [20, 21, 25, 26]. At a sulfur precoverage of  $\Theta_S = 0.25$  ML, S forms a  $(2 \times 2)$  overlayer structure, resulting in CO only bound at on-top sites with a maximum coverage of  $\Theta_{CO} = 0.25$  ML; for  $\Theta_S = 0.33$  ML, CO adsorption on Pt(111) is completely suppressed [20, 21]. XP spectra of S on Pt(111) showed a S 2p doublet with the  $2p_{3/2}$  peak at a binding energy of 162.2 eV at  $\Theta_S = 0.1$  ML, which shifts to lower binding energies by 0.2 eV when the S coverage is increased to  $\Theta_S = 0.3$  ML [19, 23]. Using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) it was observed that S can lead to faceting of stepped Pt surfaces [27–29]. TPD studies on stepped and also on polycrystalline Pt surfaces revealed a lower CO desorption temperature in the presence of S; the authors concluded that S blocks the defect sites for CO adsorption [30–32].

In the present study we present a systematic investigation of the influence of sulfur on the adsorption of CO at step sites on Pt surfaces with differently oriented steps. We have chosen this system, since the adsorption of CO on clean Pt(111) [3, 33], Pt(355) [4, 7] and Pt(322) [7] was examined recently in great detail by our group, which allows a direct comparison with effects observed for the S-covered stepped surfaces. In this contribution we want to examine the influence of preadsorbed sulfur on the adsorption of CO on two differently stepped platinum surfaces by *in situ* x-ray photoelectron spectroscopy (XPS), which allows site-resolving measurements during adsorption and during heating of the surface; the latter method is called temperature programmed XPS (TPXPS) [34]. Thereby, the temperature- and coverage-dependent occupation of adsorption sites can be studied, in particular also on stepped surfaces. A small portion of the results has been published in a previous publication [35]. For the present study a comprehensive dataset has been analyzed and all data have been reproduced, with only minor deviations from the previous study, which are within the denoted error bars.

## 2. Experimental details

The measurements were performed in a transportable apparatus (for details see [33]) at the BESSY II synchrotron radiation facility in Berlin, Germany, at beamline U49/2 PGM1. The chamber is equipped with a supersonic molecular beam set-up. The XP spectra were measured using an energy analyzer (Omicron EA 125 HR U7) that is mounted in the plane of the synchrotron ring, at an angle of  $50^\circ$  with respect to the incoming synchrotron radiation. C 1s spectra were collected with a total resolution of 200 meV at photon energy of 380 eV and a data acquisition time of 6 s per spectrum; the corresponding data for the S 2p spectra are 130 meV

(200 meV) at 260 eV (380 eV) and 8 s (6 s) per spectrum. The reproducibility of binding energy values within this study is  $\pm 0.03$  eV; the calibration of the absolute binding energy scale compared to other studies has an uncertainty of typically  $\pm 0.15$  eV. The Pt(322) and Pt(355) samples were oriented with their macroscopic surface normal pointing towards the electron analyzer and the monatomic steps perpendicular to the plane formed by the electron analyzer and incoming x-ray beam. Details of sample preparation and cleaning can be found in [7]. For some of the measurements a minor carbon contamination ( $< 0.03$  ML) was present on the surface; however, no significant influence of this contamination on the results presented below was found.

The Pt(355) and Pt(322) surfaces both have five atom rows wide (111) terraces with monatomic steps of different orientations, namely (111) and (100), respectively. Surface structure and adsorbate order were investigated using low energy electron diffraction (LEED). For the CO adsorption experiments the surfaces were exposed to a CO background pressure of  $1.5 \times 10^{-9}$  mbar, while XP spectra were recorded continuously. Sulfur was deposited via hydrogen sulfide adsorbed at  $\sim 130$  K, followed by heating to 700 K, which leads to the decomposition of  $H_2S$ , with hydrogen desorbing as  $H_2$  and S remaining on the surface [36]. The sulfur precoverages were calibrated by measuring S 2p spectra and comparing their intensities to those of a sulfur layer, exhibiting the  $p(2 \times 2)$  LEED pattern on the Pt(322) surface; this pattern was obtained by decomposition of a saturated  $H_2S$  layer and corresponds to a layer with a nominal coverage of 0.25 ML on the Pt(111) surface [36]. Since we only assume a comparable sulfur density at the steps and on the terraces in this approach, the error bars for the absolute S coverages denoted below are relatively large, i.e. 20–25%, but the relative error is expected to be low as in the case of CO (4%) [7].

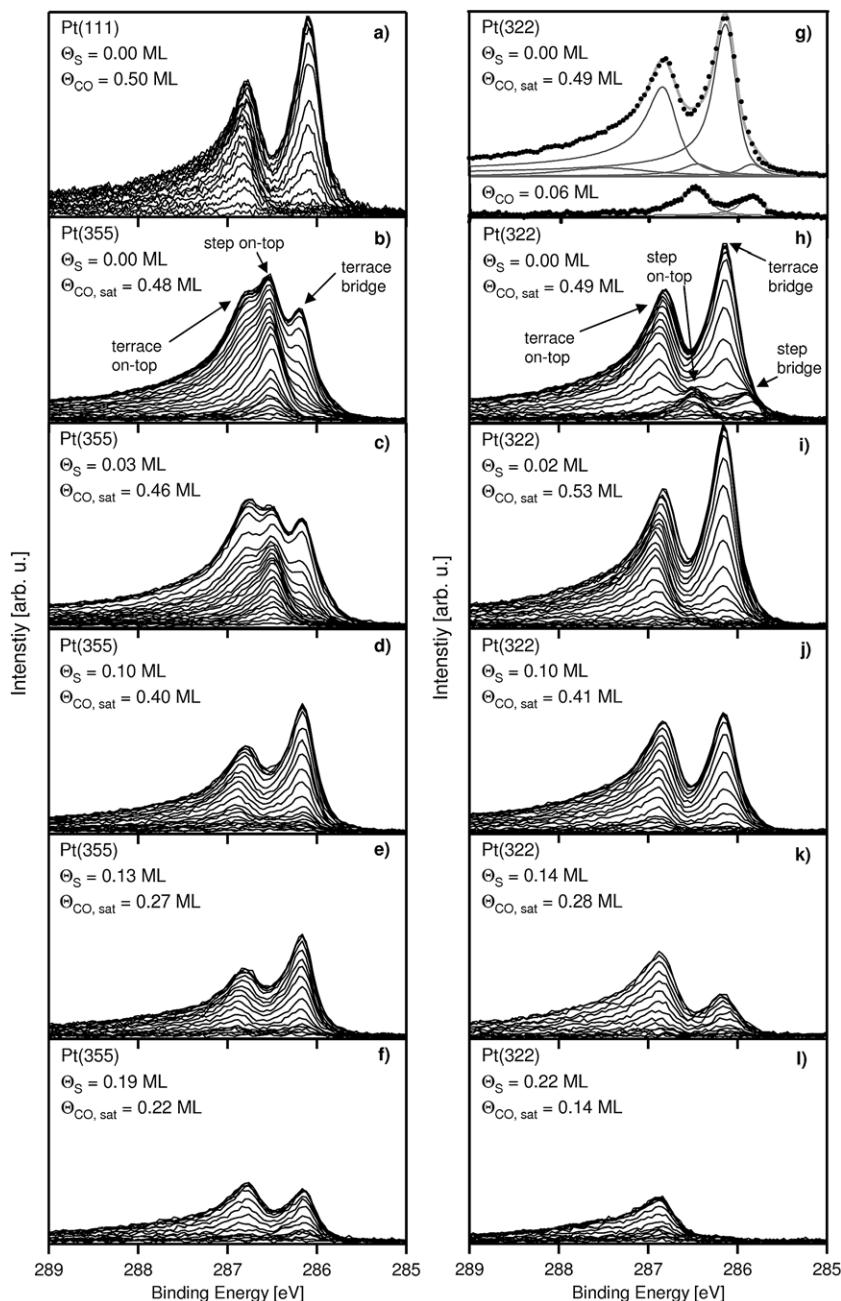
## 3. Results

### 3.1. Adsorption at low temperatures

To begin with we very briefly discuss the adsorption of CO on the clean Pt(111) surface at 110 K. In figure 1(a), the corresponding C 1s XP spectra are shown, which are collected successively while exposing the surface to  $1.5 \times 10^{-9}$  mbar CO. For  $\Theta_{CO} = 0.5$  ML (top spectrum), the two well-known contributions at 286.80 and 286.09 eV are observed, which are due to CO adsorbed at on-top and bridge sites, respectively ([3] and references therein). At low coverages, initially on-top sites and, at higher coverages, also bridge sites are populated [3].

For the clean Pt(355) surface, as shown in figure 1(b), CO first occupies step sites with a typical binding energy of 286.43 eV; subsequently, adsorption on the terraces is also observed, with a similar occupation sequence as on Pt(111), i.e. first adsorption at on-top sites (286.80 eV) and subsequently at bridge sites (286.09 eV), but somewhat less pronounced [4, 7].

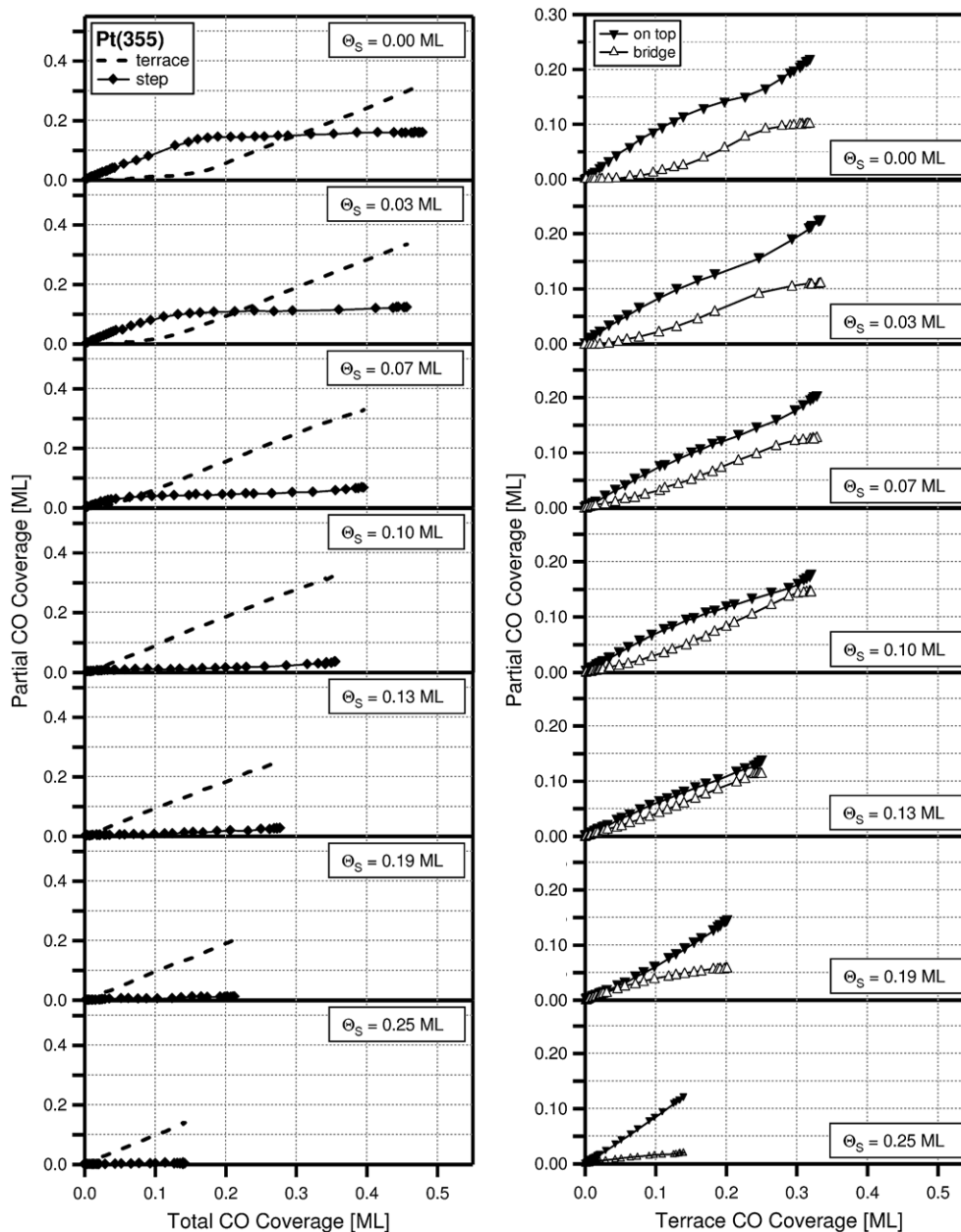
To systematically study the influence of sulfur, we investigated the adsorption of CO on Pt(355) at 130 K for sulfur precoverages ranging from  $\Theta_S = 0.03$  to 0.25 ML; note that  $\Theta_S \sim 0.11$  ML is estimated as step saturation coverage by



**Figure 1.** C 1s spectra collected continuously during exposing the surface to CO at a pressure of  $1.5 \times 10^{-9}$  mbar: (a) on Pt(111) at 110 K, (b)–(f) on Pt(355) at 130 K with increasing S precoverage (from top to bottom), as denoted; (g) two selected coverages on Pt(322) at 150 K along with the corresponding fits (see text); (h)–(l) on Pt(322) at 150 K, with increasing S precoverage (from top to bottom), as denoted. All spectra were recorded with a photon energy of 380 eV in normal emission geometry.

assuming that every second step site is occupied by S, yielding the same next-neighbor distance as found in the nominal  $p(2 \times 2)$  structure on Pt(111). No reconstruction of the Pt(355) surface was observed by LEED in the investigated coverage range. The C 1s XP spectra for different S precoverages, measured during exposure to CO, are shown in figures 1(c)–(f), respectively. Besides a general reduction of the CO saturation coverage, the C 1s signal from CO step sites decreases very rapidly with increasing S precoverage. In figure 2, the quantitative analysis of the Pt(355) spectra in figure 1 (and some additional precoverages) is depicted; in the left column

the partial coverages of CO step and terrace sites are plotted versus total CO coverage, whereas in the right column the partial coverage of terrace on-top and terrace bridge sites are shown as a function of terrace CO coverage. For  $\Theta_S = 0.03$  and 0.07 ML, CO step sites are still occupied first, but with significantly lower maximum coverages of  $\Theta_{CO,step} = 0.12$  and 0.07 ML, respectively, than the value of 0.16 ML for clean Pt(355). Starting at  $\Theta_S = 0.10$  ML the occupation of step sites with CO is completely suppressed at low CO coverage, due to passivation of step sites by S; only close to CO saturation are small amounts of CO found at step sites. The decrease of the



**Figure 2.** Partial CO coverages on Pt(355) for increasing S precoverages, as denoted: (left column): step and terrace sites as a function of total CO coverage; (right column): terrace on-top and terrace bridge sites as a function of total CO terrace coverage; data are derived from C 1s XP spectra in figures 1(b)–(f) and some additional spectra.

CO step contribution is accompanied by a reduction of the total CO saturation coverage, as is indicated by the corresponding values denoted in figure 1 and even more evident in the left column of figure 2, where the saturation value of the total CO coverage decreases from  $\Theta_{CO} = 0.48$  ML for clean Pt(355) to  $\Theta_{CO} = 0.14$  ML for  $\Theta_S = 0.25$  ML. The right column of figure 2 shows that the saturation coverage of terrace CO is nearly constant up to  $\Theta_S = 0.10$  ML and strongly decreases at higher S precoverages. This fits the picture that, up to  $\Theta_S = 0.10$  ML, S blocks only step sites and at higher S precoverages terrace sites are also blocked.

Adsorbed S also alters the distribution of CO at the terrace sites, as is evident from the right column of figure 2, where

the terrace on-top and bridge coverages are plotted versus the (total) CO terrace coverage. For clean Pt(355), CO initially adsorbs at terrace on-top sites, followed by the occupation of terrace bridge sites at higher coverage (for details see [4, 7]). A similar behavior is also seen here for  $\Theta_S$  up to  $\sim 0.10$  ML, albeit increasingly less pronounced. Although the saturation coverage of terrace CO is constant up to  $\Theta_S = 0.10$  ML, the relative amounts of CO adsorbed in on-top and bridge sites change. The saturation coverage of on-top CO is decreased, from  $\Theta_{CO,top} = 0.22$  ML for  $\Theta_S = 0.00$  ML to  $\Theta_{CO,top} = 0.18$  ML for  $\Theta_S = 0.10$  ML; simultaneously the bridge coverage is increased from  $\Theta_{CO,br} = 0.10$  to 0.15 ML. For  $\Theta_S = 0.13$  ML the total CO terrace coverage is significantly

reduced and the site preference of CO for on-top sites at low CO coverages has nearly vanished, i.e. the relative CO occupation of on-top and bridge sites on the terrace is nearly the same over the complete coverage range, with saturation values of  $\Theta_{\text{CO,top}} = 0.14$  and  $\Theta_{\text{CO,br}} = 0.12$  ML, respectively. For higher S precoverages of  $\Theta_S = 0.19$  and  $0.25$  ML, the total CO coverage is further reduced, with the saturation values for the CO on-top sites nearly unchanged ( $\Theta_{\text{CO,top}} = 0.14$  and  $0.12$  ML, respectively), but strongly reduced for the bridge sites ( $\Theta_{\text{CO,br}} = 0.06$  and  $0.02$  ML, respectively). Overall, the behavior at high S precoverages is in line with observations by Kiskinova *et al* for Pt(111), who found a reduction of CO adsorbed in bridge sites for increasing S precoverages, until for  $\Theta_S = 0.25$  ML only on-top sites are occupied ( $\Theta_{\text{CO,top}} = 0.25$  ML) [20, 21]. The smaller value of  $0.12$  ML for the saturation of on-top CO found on Pt(355) is attributed to the fact that the number of available on-top sites is smaller on the stepped surface and that on-top sites in the vicinity of the steps are energetically not favorable. The latter conclusion is derived from the fact that at low S precoverages the number of CO bridge sites increases at the expense of CO on-top sites (see above).

To investigate the influence of the step orientation, similar experiments were performed for Pt(322) for S precoverages between  $\Theta_S = 0.02$  and  $0.30$  ML. The CO adsorption temperature of  $150$  K was chosen as a compromise: on the one hand, on clean Pt(322) the step population increases with temperature [7] and, on the other hand, this temperature is still below the onset of CO/S site exchange processes (see below). Before we discuss the results, we want to mention an important difference to the Pt(355) surface, namely the formation of double steps upon S adsorption. This effect is known from other stepped Pt surfaces with (100) step orientation [28, 32]. Already at the lowest S precoverage of  $\Theta_S = 0.02$  ML, careful analysis of the LEED pattern reveals that the splitting of the substrate spots, which is observed for the clean Pt(322) surface, is halved upon S adsorption, indicating the formation of double steps; this reduces the number of steps by a factor of two and correspondingly increases the mean terrace width by a factor of two. Double-step formation is observed for all S precoverages and is neither lifted by CO adsorption at  $150$  K nor by heating to  $300$  K. Thus, from the resulting lower number of steps, one could expect that a lower S precoverage is sufficient to passivate the steps on Pt(322).

The C 1s spectra collected during CO exposure onto Pt(322) at different S precoverages are shown in figure 1 (right column); the corresponding quantitative analysis is depicted in figure 3, in which the CO step and terrace coverages are shown versus total CO coverage (left column) and the partial CO coverages of terrace on-top and bridge sites are plotted as a function of total CO terrace coverage (right column). On clean Pt(322), at low coverages, adsorption of CO leads to two step adsorption sites, namely step on-top and step bridge sites, at binding energies of  $286.43$  and  $285.83$  eV, respectively [7]. This is evident from figure 1(h), but also from figure 1(g), where two selected spectra for total CO coverages of  $\Theta_{\text{CO}} = 0.06$  and  $0.49$  ML are shown along with the corresponding fits used for the quantitative analysis in figure 3(a): at  $\Theta_{\text{CO}} =$

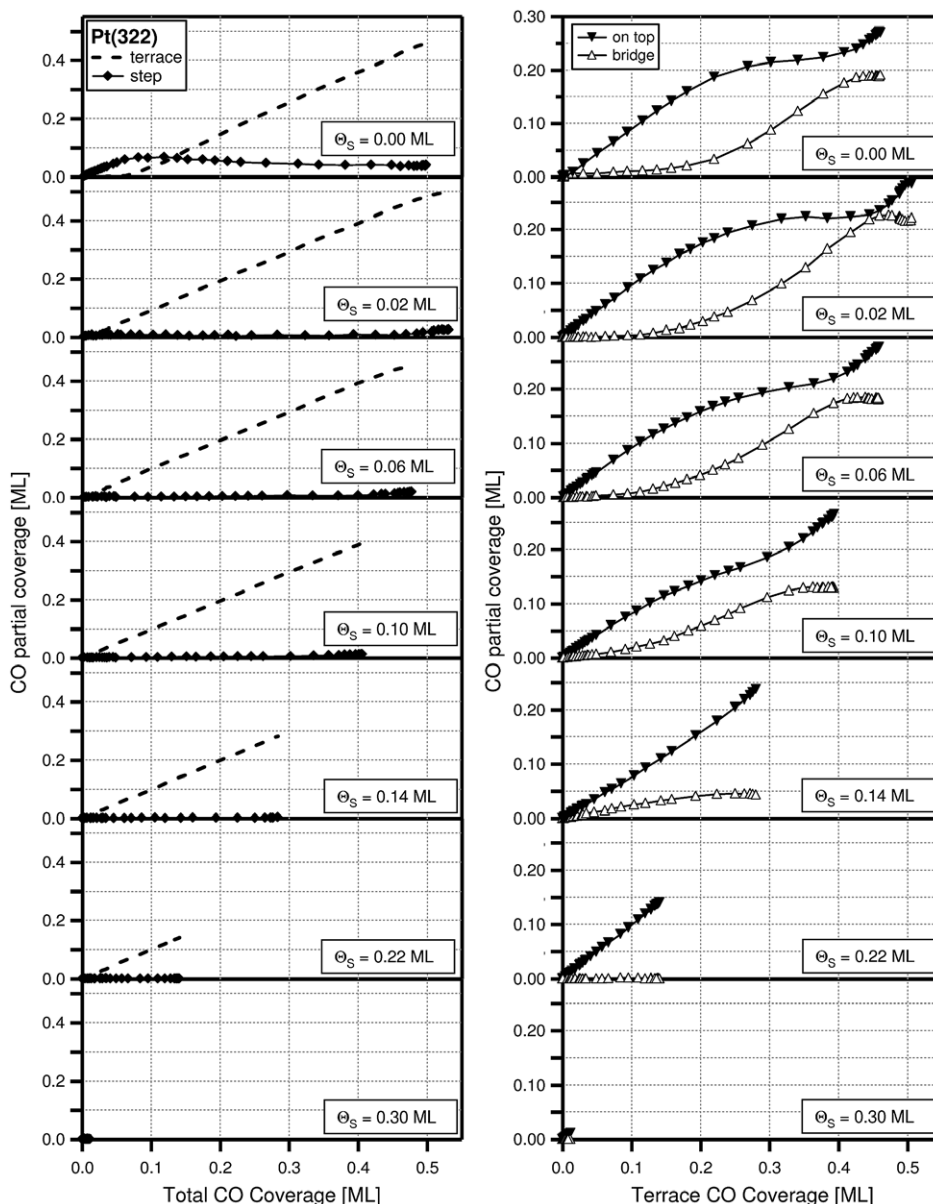
$0.06$  ML the two step peaks can be clearly identified. For the sake of clarity, we will treat these two step peaks together in the following, i.e. the coverage values for the step sites always represent the sum of step on-top and step bridge sites and are denoted as  $\Theta_{\text{CO,step}}$ . When the step sites are nearly saturated, CO also adsorbs at terrace sites. Interestingly, after an initial maximum coverage of step sites of  $\Theta_{\text{CO,step}} = 0.07$  ML, the step occupation decreases with increasing total CO coverage to a value of  $\Theta_{\text{CO,step}} = 0.04$  ML at saturation (for details see [3, 7]).

The preadsorption of  $\Theta_S = 0.02$  ML leads to a nearly complete suppression of CO at (both) step sites and nearly exclusive occupation of terrace sites—see spectra in figure 1(i); only at very high CO coverages is a minor population of CO step sites found (figure 3, left). One should note here that, in our previous study, we found a small, but not negligible, CO population of step sites at  $\Theta_S = 0.03$  ML [35], which probably indicates that the exact amount of S required to passivate the steps may be affected by minor contaminations such as carbon.

For  $\Theta_S = 0.02$  ML the total CO coverage of  $\Theta_{\text{CO}} = 0.53$  ML is higher than the value of  $0.49$  ML found on clean Pt(322). This is attributed to the formation of larger terraces on the reconstructed Pt(322) surface with double steps. From previous studies [7] it is known that the saturation coverage on Pt(111) is somewhat larger than on the stepped Pt(322) surface. Thus a higher CO coverage can be expected, if the terrace width is increased by double step formation. The observed suppression of CO adsorbed at steps already at this very low S precoverage shows that S very efficiently passivates the double steps. The complete suppression of CO step sites is also observed for higher S precoverages up to  $\Theta_S = 0.30$  ML. Above  $\Theta_S = 0.02$  ML, the total CO coverage continuously decreases with increasing S precoverage to  $\Theta_{\text{CO}} = 0.14$  ML at  $\Theta_S = 0.22$  ML and only  $\Theta_{\text{CO}} = 0.01$  ML at  $\Theta_S = 0.30$  ML (figure 3).

From the right column of figure 3, we can also derive a significant influence of the preadsorbed S on the relative population of terrace on-top and bridge sites by CO. For clean Pt(322) initially on-top sites are occupied and only at higher coverages does the occupation of bridge sites occur. The behavior is similar but not identical to the one found on Pt(111), where at a total coverage of  $0.50$  ML on-top and bridge sites are equally occupied [3, 7]. For  $\Theta_S = 0.02$  ML, the observed increased total CO coverage on Pt(322) also yields an increased terrace coverage and an identical population of on-top and bridge sites at  $\Theta_{\text{CO}} = 0.45$  ML. This observation is perfectly in line with the argument given above, namely that the size of the terraces increases by the S-induced double step formation; consequently the behavior found on the terraces is even more Pt(111)-like, yielding equal populations of on-top and bridge terrace sites (see [3, 7] and references therein). With increasing S precoverage, the occupation of bridge sites begins already at lower total CO coverages, but at the same time the maximum coverage of bridge sites is decreasing stronger than that of on-top sites. At  $\Theta_S = 0.22$  ML only CO terrace on-top sites are populated.

When comparing the behavior on the Pt(355) and Pt(322) surfaces with (111) and (100) steps, respectively, we can

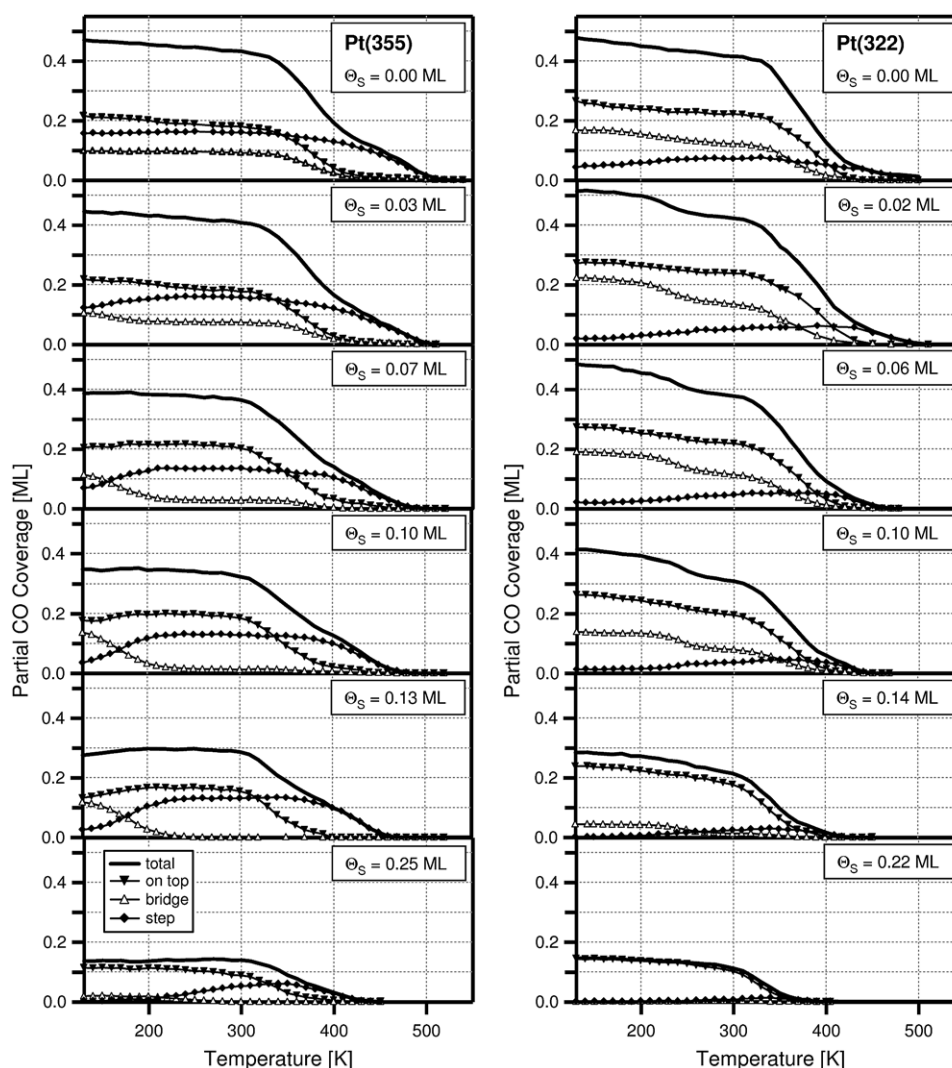


**Figure 3.** Partial CO coverages on Pt(322) for increasing S precoverages, as denoted: (left column): step and terrace sites as a function of total CO coverage; (right column): terrace on-top and terrace bridge sites as a function of total CO terrace coverage; data are derived from C 1s XP spectra in figures 1(h)–(l).

summarize the following similarities and differences. For both surfaces we find a decreasing CO step coverage, i.e. a blocking of CO adsorption at step sites, with increasing S precoverage. However, for Pt(322) significantly smaller amounts of S are sufficient for complete step passivation due to the S-induced formation of double steps. The quantitative analysis shows that, on the sulfur passivated surfaces, no CO is adsorbed at step sites, within the margins of error ( $\pm 0.02$  ML). Also, we find a decrease of the total CO coverage with increasing S precoverage; the only exception are very small S precoverages (0.02 ML) on Pt(322) where, due to the S-induced formation of larger terraces, a larger CO saturation coverage is achieved. For Pt(355) the saturation coverage of the CO terrace (on-top plus bridge) sites remains unchanged with increasing S precoverage until the steps are completely passivated (at  $\Theta_S \sim$

0.10 ML); the relative occupation of the two terrace sites changes, however. Furthermore, in the presence of S we observe a simultaneous occupation of terrace on-top and bridge sites by CO already at very low coverages. This behavior is not observed at low temperatures on the clean (111), (322) and (355) platinum surfaces [3, 4, 7]. Thus, the clear site preference observed on the clean flat and stepped surfaces is lifted. At high S precoverages for both surfaces a complete suppression of CO adsorption on terrace bridge sites is found, which is attributed to the site blocking by S at threefold hollow sites on the terraces. For Pt(322) this effect already occurs at lower S precoverages, since less S is required to passivate the double steps as compared to the single steps on Pt(355).

Sulfur-induced formation of double steps has been reported earlier [28, 32]; it was also observed by STM that



**Figure 4.** Partial and total CO coverages for increasing S precoverages (as denoted) as a function of temperature obtained by TPXPS during heating at a heating rate of  $0.5 \text{ K s}^{-1}$ : (left column): Pt(355); (right column): Pt(322).

this reconstruction could be lifted by extensive dosing of CO at 300 K [27, 29]. The fact that double steps are found only on Pt(322) but not on Pt(355) shows that the step orientation influences the stability towards reconstruction due to differences in local geometry and electronic properties. These properties are also responsible for differences reported for the CO step coverages of  $0.13 \pm 0.02$  and  $0.07 \pm 0.02$  ML for the clean Pt(355) and Pt(322) surfaces, respectively [4, 7]; note that the corresponding values in the present study are  $0.16 \pm 0.02$  and  $0.07 \pm 0.02$  ML, respectively; the slightly higher value for Pt(355) in this study, which is within the margin of error, might be attributed to a slightly different terrace width (due to repolishing of the crystal).

The experimental findings, namely the lowering of the step coverage of CO upon raising the sulfur precoverage, clearly show that sulfur is preferentially adsorbed at the step sites. This is not too surprising as sulfur is, in many respects, chemically similar to oxygen, which has been shown to adsorb at step sites [37, 38]. Furthermore, sulfur is known to bound at highly coordinated sites [24, 19–23, 36], e.g. threefold hollow sites on

Pt(111). Thus, the step sites, which allow a high coordination, are expected to be populated most likely by sulfur (see below).

The differences in the effect of sulfur for the different step orientations must be related to a different local bonding geometry of the sulfur atoms at the (111) and (100) oriented steps. This in turn could also influence the adsorption of CO on the terraces. In particular, the formation of ordered CO structures might be strongly affected when starting to occupy the sites from the steps. Furthermore, the excess S precoverage on the terraces also has to be taken into account, as S is expected to occupy threefold hollow sites, thereby probably blocking nearby CO terrace sites.

### 3.2. Thermal evolution

To gain further insight into the site blocking effects of sulfur, we performed temperature programmed XPS experiments in the C 1s region (spectra not shown) with a linear heating ramp of  $0.5 \text{ K s}^{-1}$ , after adsorbing CO on the S precovered surfaces to saturation. The quantitative analysis of the spectra is depicted in figure 4, where the partial coverages of step, terrace

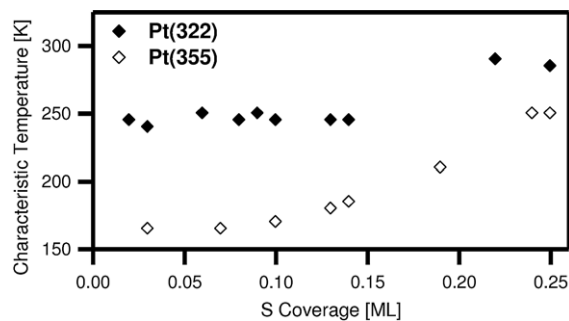


on-top and terrace bridge sites are plotted versus temperature. In addition the total CO coverage is also shown. The first data points for the individual datasets correspond to the last (rightmost) data points in figures 2 and 3.

We start with the thermal evolution on Pt(355), which is shown in the left column of figure 4. For the clean surface, upon heating to  $\sim 330$  K a slight decrease of the total CO coverage is observed, probably due to photon stimulated desorption induced by the highly intense synchrotron radiation (note that this effect is different for different datasets due to changes in the photon flux). Above 350 K a significant decrease of the total coverage occurs, which is attributed to thermal desorption of CO from both on-top and bridge terrace sites, and is completed at  $\sim 450$  K. In contrast, the occupation of step sites remains nearly constant up to  $\sim 400$  K and decreases thereafter to vanish at  $\sim 510$  K (for details see [4, 7]). The higher desorption temperature from the step sites is attributed to a higher binding energy at these sites. On the S precovered surfaces the behavior is quite different. We start with discussing the data for  $\Theta_S = 0.10$  ML, where we know from figure 2 that, after CO adsorption at 130 K, the occupation of step sites by CO is nearly completely suppressed and the terrace on-top and bridge CO contributions are similar ( $\Theta_{\text{CO,step}} = 0.04$  ML,  $\Theta_{\text{CO,top}} = 0.18$  ML and  $\Theta_{\text{CO,br}} = 0.14$  ML). Upon annealing, we find a population of step sites and a depletion of the terrace bridge sites, while the total coverages of CO and sulfur (data not shown) stay constant. At 170 K, the CO step coverage has increased by half of the maximum increment; this temperature is denoted as the characteristic temperature. The observed behavior clearly shows that the passivation of the step sites found upon adsorption at low temperatures is lifted upon heating. For  $\Theta_S = 0.10$  ML, this process is completed at 210 K, leading to CO only at step and terrace on-top sites, and not at terrace bridge sites. The CO step coverage of  $\Theta_{\text{CO,step}} = 0.13$  ML nearly equals the value of 0.17 ML found on the clean Pt(355) in the same temperature range.

Overall, the behavior for other S precoverages is similar. For  $\Theta_S = 0.03$  and 0.07 ML, where the amount of S is not sufficient to block all CO step sites, we find an increase of the CO step site population at the expense of CO terrace bridge sites. The characteristic temperature of 165 K for both S precoverages is slightly lower than the value of 170 K for  $\Theta_S = 0.10$  ML. The behavior for  $\Theta_S = 0.13$  ML is very similar to that at 0.10 ML, the major difference being a somewhat higher characteristic temperature of 180 K; the coverage dependence of the characteristic temperature is depicted in figure 5. For  $\Theta_S = 0.19$  (not shown in figure 4) and 0.25 ML again a population of step sites occurs; however, here not only at the expense of terrace bridge but also of terrace on-top sites. This effect is accompanied by a pronounced increase in the characteristic temperature to 210 and 250 K, respectively.

In addition to the increase of the characteristic temperature, two other trends are found with increasing S precoverage. The onset of the decrease of the total CO coverage, which mainly reflects CO desorption from terrace sites, is shifted to lower temperatures, from  $\sim 330$  K for the clean surface to 310 K at the highest S precoverage, with the biggest change



**Figure 5.** Characteristic temperature for S/CO site exchange on Pt(355) and Pt(322), as derived from the data in figure 4 and additional data (not shown), as a function of S precoverage.

already occurring up to  $\Theta_S = 0.07$  ML. Furthermore, the CO desorption temperature from step sites also continuously shifts to lower temperatures with increasing S precoverage. Note that during these temperature treatments no sulfur was desorbing, as concluded from the S 2p data (see below).

We now compare these results for Pt(355) with those for Pt(322), shown in the right column of figure 4. Overall we find a similar behavior: on clean Pt(322), above 330 K a significant decrease of the total coverage occurs, which is attributed to thermal desorption of CO from both on-top and bridge terrace sites, which is completed at  $\sim 430$  K. In contrast, the occupation of step sites,  $\Theta_{\text{CO,step}}$ , increases up to  $\sim 290$  K from 0.04 to 0.07 ML and decreases thereafter to vanish at  $\sim 500$  K (for details see [7]). The higher desorption temperature from the step sites is again attributed to a higher binding energy at these sites. With preadsorbed S, again a population of CO step sites is found upon heating, which coincides with a pronounced depopulation of terrace bridge sites (partly also due to desorption). The effect is not as clear-cut as on Pt(355), since the overall step population is smaller, the transition range is wider and since a slight increase of the step population with temperature already occurs on the clean surface (see above [7]).

In contrast to Pt(355), the characteristic temperature of  $\sim 245$  K is significantly higher at low coverages, but stays constant up to  $\Theta_S = 0.14$  ML, as is evident from figure 5. Only at  $\Theta_S \geq 0.22$  ML is a higher value of  $\sim 290$  K found. The population of step sites with CO is paralleled by a shift of the S atoms from the steps to the terraces, as will be shown below from the S 2p XP spectra, indicative of a CO/S site exchange also for Pt(322). Despite this site exchange, the reconstruction of the surface is not lifted, as is concluded from the unchanged LEED pattern at 300 K.

At low S precoverages the maximum CO step coverage obtained above the characteristic temperature slowly decreases with increasing S precoverage, from  $\Theta_{\text{CO,step}} = 0.07$  ML for clean Pt(322) to  $\Theta_{\text{CO,step}} = 0.06, 0.05, 0.04$  and 0.03 ML for  $\Theta_S = 0.02, 0.06, 0.10$  and 0.14 ML, respectively. For the latter two S precoverages this step coverage is roughly half of the value of  $0.07 \pm 0.02$  ML found for clean Pt(322). This is consistent with the fact that the surface is still reconstructed, in the investigated temperature range, with only half of the number of (double) steps as compared to the sulfur-free surface. The larger values of  $\Theta_{\text{CO,step}}$  for the smaller S

precoverages do not really fit in this picture and are not understood yet. A partial lifting of the reconstruction appears unlikely from the unchanged LEED pattern, but cannot be completely ruled out.

Similar to Pt(355) a decrease of the desorption temperature for all sites is found with increasing S precoverage: the temperature, where the signal of CO at step sites vanishes, decreases from 500 K on the clean surface to 440 K for  $\Theta_S = 0.10$  ML and 380 K for  $\Theta_S = 0.22$  ML. Also, the detailed inspection of the data in figure 4 shows that, for S precoverages from  $\Theta_S = 0.02$  to 0.10 ML on Pt(322), there is some desorption of CO at the temperature where the steps are populated; this is concluded from the decrease of the total CO coverage in the same temperature region.

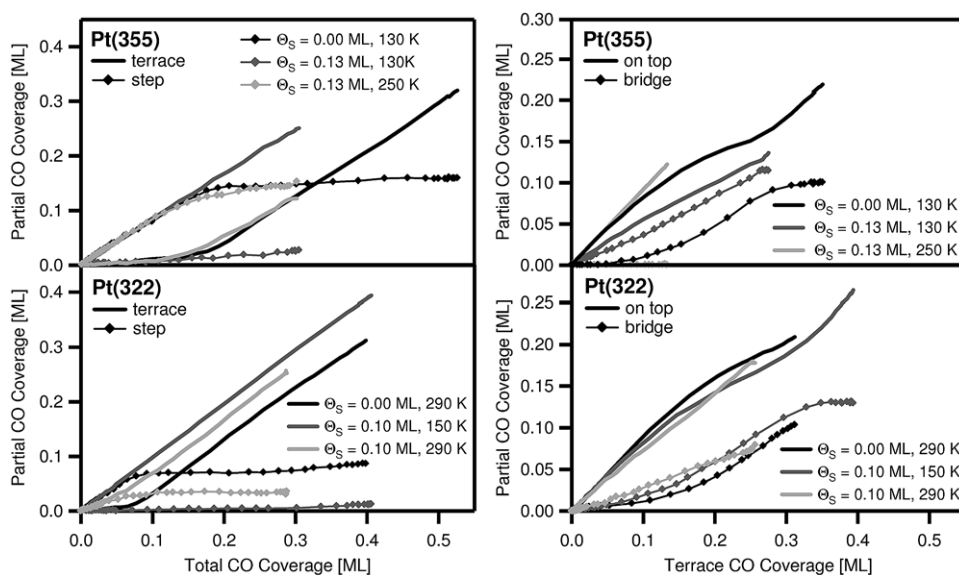
When comparing the thermal evolution on the two stepped surfaces, we again find similarities and differences. For both surfaces, site exchange of sulfur and CO occurs, but at different temperatures. The characteristic temperatures are significantly lower on Pt(355) than on Pt(322); for Pt(322) it is  $\sim 240$  K, independent of S precoverage up to  $\Theta_S = 0.14$  ML and thereafter increases to 290 K at  $\Theta_S = 0.25$  ML; for Pt(355) a value of 165 K is found at low precoverages, which starts to increase already at  $\Theta_S = 0.10$  ML up to a value of 245 K at  $\Theta_S = 0.25$  ML. It is important to note that the CO/S site exchange is an irreversible process: measurements at low temperature after heating the surface to above the characteristic temperature but below the onset of significant desorption of CO (not shown) still show that S is displaced from the steps. The fact that the passivation of CO adsorption sites at steps by sulfur is lifted irreversibly upon heating indicates that the passivation is a kinetic rather than a thermodynamic effect. Obviously, for both surfaces CO adsorption at the steps and S adsorption on the terraces are energetically favorable in the coadsorption situation. This means in a simplified picture that the effective energy difference  $\Delta E_{CO}$  between step and terrace sites for CO is larger than the corresponding energy difference for sulfur,  $\Delta E_S$  (note that lateral interactions in the pure and mixed phases are not taken into account). Upon heating to 700 K, i.e. after complete CO desorption, sulfur is again found at the step sites. If CO is dosed at low temperatures, the activation barrier to move the S atoms away from the steps is too high; it can only be overcome by providing thermal energy upon heating [35]. The fact that at low S precoverages the characteristic temperature of 165 K for Pt(355) is lower than the value of 245 K for Pt(322) indicates a lower activation barrier for the former. This might be related to the higher binding energy of sulfur at the fourfold (100) step sites on Pt(322) as compared to the threefold (111) step sites on Pt(355) and/or a stronger bond of CO at the steps on Pt(355) than on Pt(322). At higher S precoverages lateral interactions will also contribute significantly.

If we compare our results to those found for sulfur-precovered platinum surfaces by TPD [30–32], we also find a lowering of the desorption temperature with increasing S precoverage. However, our site-resolving spectroscopic results clearly demonstrate that this lowering cannot be attributed to a blocking of the step sites, as was done in the previous studies, but is due to a lowering of the binding energy of CO at the step sites, induced by S at terrace sites.

### 3.3. CO adsorption at higher temperatures

From the thermal evolution we deduce a CO/S site exchange process upon heating, which occurs at a characteristic temperature. In the course of this process, S atoms, which are initially adsorbed at step sites at low temperature, are replaced by CO due to energetic reasons. From this observation one can anticipate that, if the adsorption experiment at a given S precoverage is performed above this critical temperature, CO should directly adsorb at the step sites, i.e. the exchange process should occur immediately upon adsorption. To check that, we exposed the two surfaces, precovered with amounts of S sufficient to block all step sites at low temperature, to CO at temperatures above the characteristic temperature. The corresponding results for Pt(355), precovered with  $\Theta_S = 0.13$  ML, are shown in figure 6 (top) for CO exposures at 130 and 250 K along with the data for the clean surface at 130 K (the data for 250 K are not shown, since for the clean surface there is no significant temperature dependence [4, 7]). The data for  $\Theta_S = 0.13$  ML at 130 K show the behavior already seen in figure 2, i.e. complete blocking of CO step sites, in particular at low CO coverages, and only slight preferential occupation of terrace on-top sites as compared to terrace bridge sites; at saturation, the population of both is nearly the same. The behavior observed at 250 K is completely different, as expected. Now, at low coverages exclusively CO step sites are occupied and only after their saturation are terrace sites found; this overall behavior is very similar to that found on clean Pt(355). In particular, the absolute values for the step population are in nearly perfect agreement; the only difference is that a higher total CO saturation coverage is found on the clean surface, which is due to blocking of terrace sites by S atoms, which are shifted from step to terrace sites. Inspection of the relative site population on the terrace shows that only on-top sites are occupied; this is due to the fact that S preferentially blocks terrace bridge sites (see above).

For Pt(322) the chosen S precoverage is  $\Theta_S = 0.10$  ML and the adsorption temperatures are 150 and 290 K. The data are also shown in figure 6 (bottom), along with corresponding data for CO adsorption on clean Pt(322) at 290 K. At 150 K, no CO adsorption at step sites is found in the presence of S, as already seen in figure 3. At the higher temperature, here 290 K, starting from low coverages, CO step sites are also occupied (indicating immediate replacement of S from the steps) more or less simultaneously to the population of terrace sites. This behavior is different to that on clean Pt(322), which is also shown in figure 6 (bottom), on which only after saturation of step sites are terrace sites populated. The other major difference is that the step saturation coverage of  $\Theta_{CO,step} = 0.04$  ML on the S precovered surface amounts only to half the coverage of  $\Theta_{CO,step} = 0.08$  ML on the clean surface at 290 K. This is again attributed to the S-induced formation of double steps, leading to only half the number of available CO step adsorption sites. On the terrace, at 290 K, the preference for on-top sites at low CO coverages is less pronounced in the presence of S, similar to 150 K—see figure 3 (right column).



**Figure 6.** Partial CO step and terrace coverages as a function of total CO coverage for different adsorption temperatures: (top) on clean Pt(355) at 130 K and on Pt(355) precovered with  $\Theta_S = 0.13$  ML at 130 and 250 K; (bottom) on clean Pt(322) at 290 K and on Pt(322) precovered with  $\Theta_S = 0.10$  ML at 150 and 290 K.

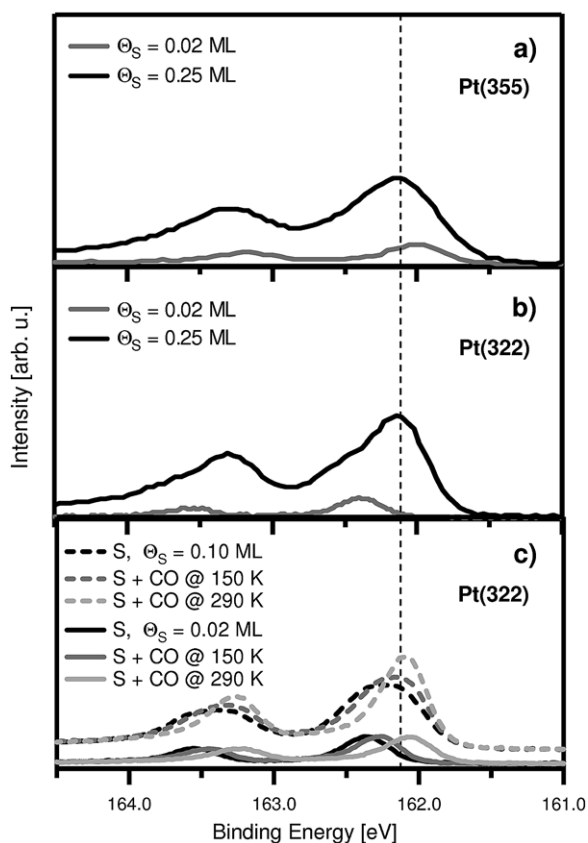
### 3.4. Analysis of S 2p spectra

To obtain further insight into the CO/S site exchange processes, we have also measured and analyzed S 2p spectra during CO adsorption and during heating. In the S 2p spectra each species has two components due to the spin-orbit split  $2p_{3/2}$  and  $2p_{1/2}$  lines, respectively. Their intensity ratio is  $\sim 2:1$  with a peak separation of  $1.18 \pm 0.03$  eV, independent of the chemical environment. Thus in the following only the more intense S  $2p_{3/2}$  peak is discussed. The corresponding spectra for Pt(355) and Pt(322) are shown for different S precoverages in figures 7(a) and (b), respectively. For  $\Theta_S = 0.02$  ML on Pt(355) a single S  $2p_{3/2}$  peak is observed at 161.96 eV, which is attributed to sulfur atoms adsorbed at the steps. For  $\Theta_S = 0.25$  ML the S  $2p_{3/2}$  peak is broadened and the maximum is found at 162.11 eV. The broadening is attributed to the fact that the S signal is now composed of two contributions, namely from S at step sites and S at terrace sites.

For Pt(322), the situation is similar: at  $\Theta_S = 0.02$  ML a single peak is seen in figure 7(b), now at a binding energy of 162.38 eV, which is assigned to S at step sites; for  $\Theta_S = 0.25$  ML a broader, but shifted peak is found at 162.15 eV, which is again attributed to a superposition of step and terrace sites. While the peak maxima for  $\Theta_S = 0.25$  ML, where the spectra are dominated by the signal from S at terrace sites, are found at very similar energies for both Pt(355) and Pt(322) (162.11 and 162.15 eV, respectively), we find shifts of the step S species in opposite directions, namely to lower binding energies ( $-0.15$  eV) for Pt(355) and to higher binding energies ( $+0.23$  eV) for Pt(322). The different signs of the shifts are attributed to differences in the initial and/or final states, due to the different local adsorption geometries, i.e. threefold and fourfold hollow sites, respectively. Without calculations of the complete photoemission event, no further interpretation can be given.

In figure 7(c) the influence of adsorbed CO and heating on the S 2p spectra is shown for  $\Theta_S = 0.02$  and 0.10 ML on Pt(322). For  $\Theta_S = 0.02$  ML, upon CO adsorption at 150 K, the S  $2p_{3/2}$  peak shifts to lower binding energy by  $-0.12$  eV, from 162.38 to 162.26 eV, which is attributed to lateral interactions between S at step sites and neighboring CO molecules. Upon adsorption and data collection at 290 K, a larger shift of  $-0.30$  eV is seen to 162.08 eV. This value is very similar to the position of predominantly terrace S (i.e. 162.15 eV, see above) for  $\Theta_S = 0.25$  ML and the peak is thus attributed to S at terrace sites, due to the above-mentioned CO/S site exchange processes upon heating; note that 290 K is well above the characteristic temperature of 245 K. The behavior found for  $\Theta_S = 0.10$  ML can be understood along the same lines and provides strong support for the above arguments. Prior to CO adsorption, a broad peak is found due to superposition of the signal from S at step and terrace sites. CO adsorption at 150 K leads again to a small shift of  $-0.08$  eV. Upon CO adsorption at 290 K, a pronounced narrowing of the S  $2p_{3/2}$  peak and a total shift of the maximum by  $-0.16$  eV to lower binding energy is found. This can be easily understood if one considers that, upon CO adsorption at 290 K, S moves away from the steps so that only one type of sites, namely exclusively threefold hollow terrace sites, are occupied, which leads to the narrow and shifted line. Similar observations are made for Pt(355), with the CO-induced shift at 130 K being smaller ( $-0.04$  eV) and the shift at 250 K ( $+0.08$  eV) having the opposite sign (data are not shown).

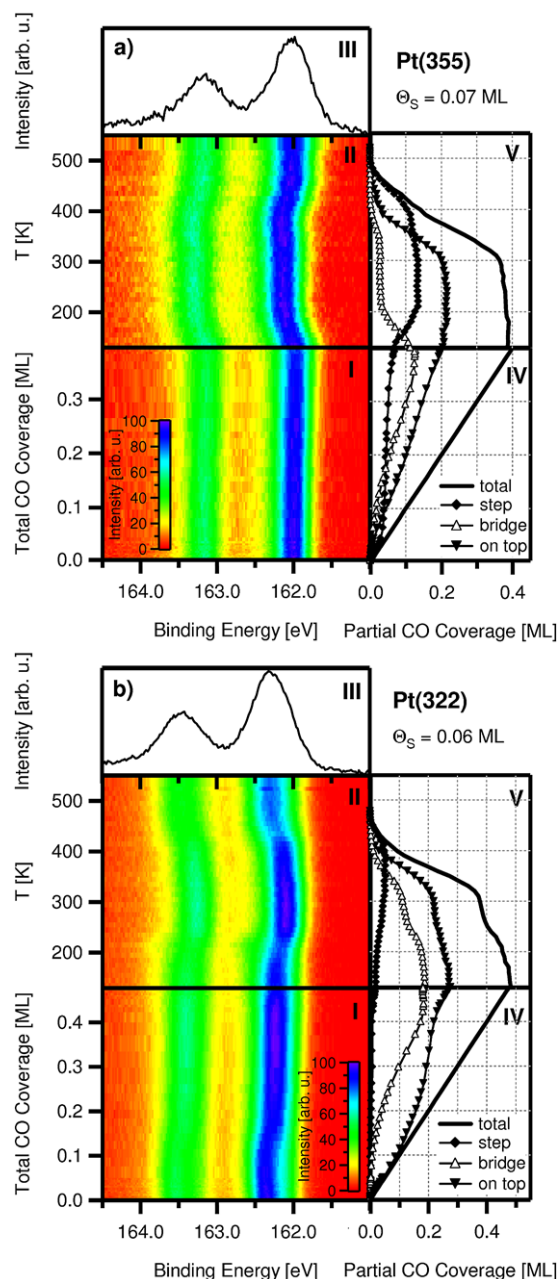
Based on this knowledge about the energetic position and line characteristics of the S peaks, they can be used as fingerprints to follow site occupation during CO adsorption and heating of the two surfaces precovered with S. An example of such an analysis is given in figures 8(a) and (b), where a series of S 2p spectra for S precovered Pt(355) and Pt(322) are shown in a density plot. In this type of plot the intensity of the peaks



**Figure 7.** S 2p spectra (a) for Pt(355) precovered with  $\Theta_S = 0.02$  and 0.25 ML; (b) for Pt(322) precovered with  $\Theta_S = 0.02$  and 0.25 ML; both collected with a photon energy of 380 eV; (c) Pt(322) precovered with  $\Theta_S = 0.02$  and 0.10 ML; after S deposition, CO exposure at 150 K and CO exposure at 290 K; collected with a photon energy of 260 eV. The vertical dashed line indicates the energetic position of S at terrace sites.

is shown in a color-coded (or grayscale) presentation such that intensive peaks appear blue (black) and the background red (white). For illustration, one ‘normal’ XP spectrum is shown at the top of each figure (panel III). In the lower part of each figure (panels I and IV), the total CO coverage increases from bottom to top, while in the upper part (panels II and V) the temperature increases from bottom to top. The position of the peak maxima of the S  $2p_{3/2}$  line and the occurring shifts can be easily identified from this presentation. To compare the positions of the S 2p lines with the site-specific CO coverages on the surface, the right part of the figure contains the quantitative analysis for the population of CO step, terrace on-top and terrace bridge sites upon adsorption (IV) and heating (V).

The data for Pt(355) precovered with  $\Theta_S = 0.07$  ML are shown in figure 8(a). Upon adsorption of CO at 130 K (panel I), only a minor shift to lower binding energy ( $-0.04$  eV, hardly seen in the figure) of the S  $2p_{3/2}$  peak is observed, indicating that the adsorption site of sulfur remains unchanged, i.e. S remains at the steps. Upon heating, at 165 K, parallel to the population of CO step sites (panel V of figure 8(a)) the  $2p_{3/2}$  peak shifts to higher binding energies by  $+0.16$  eV (panel II of figure 8(a)), i.e. to the position typical for S at terrace sites. At temperatures above 400 K, this shift is reversed and the  $2p_{3/2}$



**Figure 8.** (a) CO adsorption on Pt(355) precovered with 0.07 ML S; (b) CO adsorption on Pt(322) precovered with 0.06 ML S. (I) Grayscale density plots of S  $2p_{3/2}$  spectra during adsorption of CO and (II) subsequent heating of the surface at a linear heating rate of  $0.5 \text{ K s}^{-1}$ ; (III) last S  $2p_{3/2}$  spectrum of heating series in (II) at 550 K; (IV) partial and total CO coverages versus total CO coverage during adsorption and (V) during heating, as obtained from C 1s spectra. The intensity scales of (I) and (II) are shown as insets. (This figure is in colour only in the electronic version)

peak position shifts back by  $-0.12$  eV to the value before CO adsorption. This behavior is attributed to desorption of CO from the step sites and the reoccupation of steps by S.

The behavior found for Pt(322) precovered with  $\Theta_S = 0.06$  ML is shown in figure 8(b) and is quite similar to that found for Pt(355), with some small differences. The first is that, upon CO adsorption (panel I) at  $\Theta_{CO} \sim 0.10$  ML, a

small CO-induced shift of the  $2p_{3/2}$  peak by  $-0.06$  eV to lower binding energy is seen. Thereafter, up to CO saturation no further change occurs, again confirming that S remains at the step sites. Upon heating (figure 8(b), panel II), an additional larger shift of the  $2p_{3/2}$  peak by  $-0.14$  eV to lower binding energy parallels the CO/S site exchange process seen from the population of step sites by CO (figure 8(b), panel V). The shift occurs at a significantly higher temperature of 245 K than on Pt(355), in agreement with the results discussed above. Again, for temperatures above 400 K the  $2p_{3/2}$  peak shifts back, by  $+0.20$  eV, to the start value prior to CO adsorption; this is due to the fact that at these temperatures CO at step sites desorbs, allowing the S atoms to move back to the step sites.

Summarizing the results deduced from the S 2p spectra, we find that for both surfaces the  $2p_{3/2}$  binding energy allows us to differentiate between S adsorbed at step and terrace sites. This allows us to monitor the step occupation with S *in situ* as a function of CO coverage and temperature. The results obtained are in perfect agreement with the conclusions derived from the C 1s spectra, which allow monitoring the occupation of the step and terrace sites with CO. Finally, it is noteworthy to mention that the peak area of the S 2p peaks does not change during CO adsorption and also during heating in the temperature ranges discussed, indicating that the sulfur precoverages remain unchanged under the conditions of this study.

#### 4. Summary and conclusions

We have investigated the influence of preadsorbed sulfur on the adsorption and thermal evolution of CO on the stepped Pt(355) and Pt(322) surfaces. The two surfaces have a similar terrace width but different step orientation, namely (111) and (100), respectively. For a systematic investigation we have varied the sulfur precoverage,  $\Theta_S$ , from 0.02 to 0.30 ML. The data analysis is based on C 1s and S 2p spectra, measured with high resolution. The C 1s data directly allow us to determine the occupation of various CO adsorption sites, namely CO step, terrace on-top and terrace bridge sites. The S 2p data allow us to directly identify whether S is adsorbed at the step or at the terrace. As both measurements can be performed *in situ*, the site occupations are determined during adsorption and during heating.

At low temperatures, we observe a blocking of CO step sites by S for both surfaces. For Pt(355), a nearly complete blocking of step sites is found starting at  $\Theta_S = 0.10$  ML; up to this S precoverage the total CO coverage at the terraces remains unchanged. For higher S precoverages additional blocking of terrace bridge sites by S occurs, leading to a continuous decrease of the total CO terrace coverage. At  $\Theta_S = 0.25$  ML, CO exclusively occupies terrace on-top sites. For Pt(322) the amount of S necessary to block all CO step sites is significantly lower due to the lower number of steps, which results from S-induced double step formation. For higher S precoverages S again efficiently blocks CO terrace bridge sites. For both surfaces at intermediate S precoverage the strong preference of CO on-top sites at low terrace coverages is relaxed, i.e. bridge

sites are already occupied at low terrace coverages and not only after a significant population of on-top sites is achieved.

Upon heating the CO-covered surfaces a repopulation of the step sites with CO occurs on both surfaces, which is attributed to irreversible CO/S exchange processes. For Pt(355) the characteristic transition temperatures at low S precoverages up to  $\Theta_S \sim 0.10$  ML, i.e. the saturation of the steps with S, remain nearly constant at 165–170 K. At higher S precoverages, they continuously increase up to  $\sim 250$  K at  $\Theta_S = 0.25$  ML. For Pt(322) the characteristic temperature is significantly higher; at low S precoverages a value of  $\sim 245$  K is observed, which is constant up to  $\Theta_S = 0.14$  ML. At higher precoverages, it increases up to  $\sim 290$  K at  $\Theta_S = 0.25$  ML. Above the transition temperature, for Pt(355), finally the same CO step coverage as for the clean surface is obtained, whereas for Pt(322) only half the value of the clean surface is found for intermediate S precoverages. This behavior is attributed to the S-induced formation of double steps on Pt(322), which are stable in the investigated temperature range. From the irreversible lifting of the step passivation by sulfur upon heating for both surfaces we conclude that, under the experimental conditions applied, an occupation of step sites by CO is energetically favored over occupation with S, with the CO/S site exchange process being kinetically hindered at low temperatures. In a simplified picture and neglecting that lateral interactions in the pure and mixed phases are not taken into account this indicates that in the coadsorption situation the effective energy difference  $\Delta E_{CO}$  between step and terrace sites for CO is larger than the corresponding energy difference for sulfur,  $\Delta E_S$ .

These conclusions are supported by CO adsorption experiments for selected sulfur precoverages ( $\Theta_S = 0.13$  and  $0.10$  ML), performed above the transition temperatures, i.e. at 250 K for Pt(355) and 290 K for Pt(322). The corresponding data show that at these temperatures S immediately moves away from the step sites to terrace sites. The differences found for the two different step orientations are attributed to differences in the electronic structures and local adsorption sites.

Finally, our results also show that the S-induced lowering of the overall desorption temperature found by TPD cannot be attributed to a blocking of the step sites by S, as was proposed in the literature [30–32], but is due to a lowering of the binding energy of CO at step sites due to S at nearby terrace sites.

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