Determination of site specific adsorption energies of CO on copper

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The binding energies of (isolated) CO molecules adsorbed at several atomic sites (terrace, step, kink) on a number of differently oriented copper surfaces have been measured by thermal desorption spectroscopy (TDS). In addition to the three low-indexed Cu surfaces several regular stepped and kinked single crystal surfaces have been employed. Using LEED measurements together with available data in the literature allowed identification of the various different CO adlayers and to assign the different TDS binding energies to the different adsorbate sites. For the close-packed surfaces binding energies between 47 kJ/mol (Cu(111)) and 51 kJ/mol (Cu(100)) were observed, which increased to 58 kJ/mol for CO molecules bound to step edges. Unexpectedly, for kink sites the same binding energy (to within 1 kJ/mol) as for step edges was observed. Moreover, a very similar binding energy of 58 kJ/mol was also measured for random defect sites on sputtered and on poly-crystalline substrates.

KEY WORDS: carbon monoxide; copper; adsorption; defects; kinks; steps

1. Introduction

Microkinetic modelling has demonstrated its ability to provide valuable contributions for a microscopic understanding of heterogeneous catalysis and is of practical relevance for an optimization of reactor performance [1,2]. The method represents an established approach to bridge the "pressure gap" between real catalysts operating typically at high pressure and model studies which are usually conducted under UHV conditions [3]. For an application of the method, however, detailed information about the elementary processes of the respective catalytic reaction and the identification of "active sites" are necessary [4–7]. Additionally, quantitative information on the relevant kinetic parameters (binding energies, desorption energies, sticking coefficients) is needed.

Most real catalysts consist of nm-sized (transition) metal particles dispersed on the surfaces of oxide particles [8]. As depicted schematically in figure 1 the surface of such small metal clusters consists of various micro-facets of different (low-indexed) orientation and numerous defects like steps or kinks. Evidently, the proportion of different atomic sites depends critically on the particle size and reveal a drastically increasing step density as the particle size decreases. For a microkinetic modeling of chemical reactions occurring at such particles it is therefore not sufficient to use information on the kinetic parameters obtained for low-indexed, flat single crystals but quantitative data for adsorption on step and kink sites (denoted by **s** and **k** in figure 1) is required. If this information is available, it can in turn be used to infer on the relative concentration of the different crystal faces and/or adsorption sites by comparing thermal desorption data recorded for real catalyst powders to the results of

the single crystal studies [9]. This information is rather important, since generally form and shape of the metal particles is not very well known.

A well suited approach to provide such information on binding energies at different adsorption sites is the use of stepped and kinked surfaces. These surfaces exhibit the type of adsorption sites of interest here but still allow an application of standard and well-established surface-analytical techniques, thus allowing for an unambiguous interpretation of the experimental data. The step and kink density of these so-called *vicinal* surfaces can be varied systematically by choosing appropriate orientations of the cutting plane relative to the next low-indexed surface plane. The geometry of the vicinal surfaces can be reliably characterized by, *e.g.*, electron diffraction (LEED) [10].

In the present study the binding energy of CO molecules at various specific adsorption sites on copper surfaces has
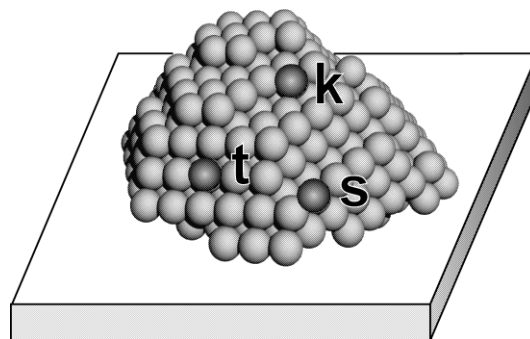

Figure 1. Schematic model of a metallic nano-particle on a support consisting of various surface terrace-facets (labeled by **t**) and a number of defects like step edges (**s**) and kinks (**k**) which are considered as catalytic "active sites". The minimization of the total free surface energy leads to a predominant formation of low-indexed terrace-facets (*i.e.*, (111) and (100) in case of copper).

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been measured by means of thermal desorption spectroscopy (TDS). The chemisorption of CO on copper surfaces is regarded as a prototype system of molecular adsorption on a transition metal surface and, as a result, has been extensively studied in the past. Surprisingly, however, no systematic data about site specific (*i.e.*, terrace, step, kink) binding energies are available so far. Moreover, in the literature quite different desorption temperatures have been reported, which vary, *e.g.*, in case of CO on Cu(110) between 200 and 225 K [11,12]. For a microkinetic modeling of the *water–gas shift* reaction [13,14],

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$
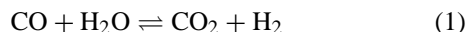
an important reaction also relevant for the methanol synthesis carried out over ZnO/Al$_2$O$_3$-supported Cu particles such information is, however, urgently needed [15–17]. Note, that for the adsorption of CO on such a catalyst only the Cu component is relevant [18].

In the present study systematic measurements were carried out for all low-index surfaces (*i.e.*, Cu(111), Cu(100) and Cu(110)) and for regular stepped and kinked surfaces (Cu(211), Cu(221) and Cu(532)) which allows a selective occupation of specific adsorption sites of different coordination by CO as checked by low-energy electron diffraction (LEED). The corresponding binding energies are further compared with those obtained for sputtered and polycrystalline surfaces.

2. Experimental

The present experiments were carried out with a multi-technique UHV surface analysis apparatus which has been described in detail elsewhere [19]. All copper samples were cleaned by a standard procedure involving Ar-sputtering and annealing. Their cleanliness was checked by photoelectron spectroscopy (XPS) and the structure was characterized by LEED. A detailed description of the preparation and characterization of the *vicinal* copper surfaces by LEED and STM has been reported in previous studies [20,21]. Carbon monoxide (purity 99.999%) was dosed through a leak valve at a pressure of less than 5×10^{-9} mbar. Simultaneous LEED measurements allowed for an identification of the various distinct CO superstructures. The thermal desorption spectra were recorded by a mass spectrometer employing a computer controlled linear heating ramp of 5 K/s with a root mean square deviation from the ideal linear increase of less than 0.05 K/s. The CO–Cu binding energy was obtained by applying the Redhead formula [22] with a pre-exponential factor of 10^{13} Hz. The temperature was measured by a thermocouple attached to the sample surface which had been carefully calibrated by the boiling point of liquid nitrogen and the desorption of alkane multilayers. In this way an experimental absolute temperature resolution of better than ±5 K is achieved corresponding to an uncertainty of ±1.4 kJ/mol in the binding energy.
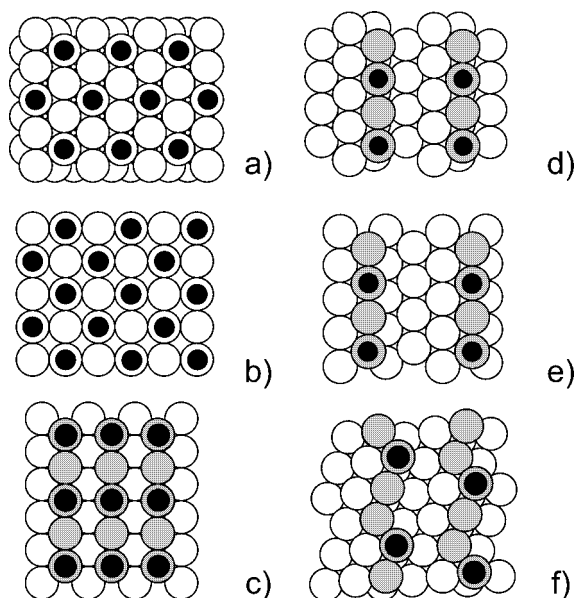

Figure 2. Top view of ball models of the single crystal surfaces. (a) Cu(111), (b) Cu(100), (c) Cu(110), (d) Cu(211), (e) Cu(221) and (f) Cu(532) together with the low-coverage CO superstructures. The light circles represent the copper atoms where the step edges are darkened, while the CO molecules are displayed as small black balls.

3. Results

All previous measurements have indicated that CO adsorbs at low coverage on copper surfaces at *on-top* sites with the carbon atom next to the substrate and with its molecular axis orientated normal to the surface [23]. As a result of the repulsive intermolecular interaction caused by the CO dipole moment dilute phases of isolated CO molecules are formed at low coverages [24]. At higher coverage compressed superstructures are observed where also *bridge* sites are occupied. Since the aim of this study was a determination of the binding energies of CO at *on-top* sites of different coordination the present TDS data were recorded for dilute phases well below the exposure required for the appearance of the first ordered structure. In this way further contributions arising from lateral interaction between adjacent molecules or different adsorption sites are largely excluded. Additional measurements were also carried out for saturated monolayers including also several compressed phases which will be reported elsewhere [25]. As shown exemplary in figure 3(a) additional desorption peaks associated with such compressed phases appear upon higher exposure whereas the initial low-coverage desorption peak remains almost unaffected.

To compare with previous studies and to provide a reference first the three low-index surfaces (*i.e.*, Cu(111), Cu(100) and Cu(110)) have been examined. On these surfaces CO forms well known ordered superstructures which are shown schematically in figure 2(a)–(c). While they start to appear at an exposure of about 1–2 L (1 Langmuir = 10^{-6} Torr s) as indicated by the LEED pattern, the present TDS measurements were recorded for dilute phases after an exposure of less than 0.3 L. A collection of typical TD spec-
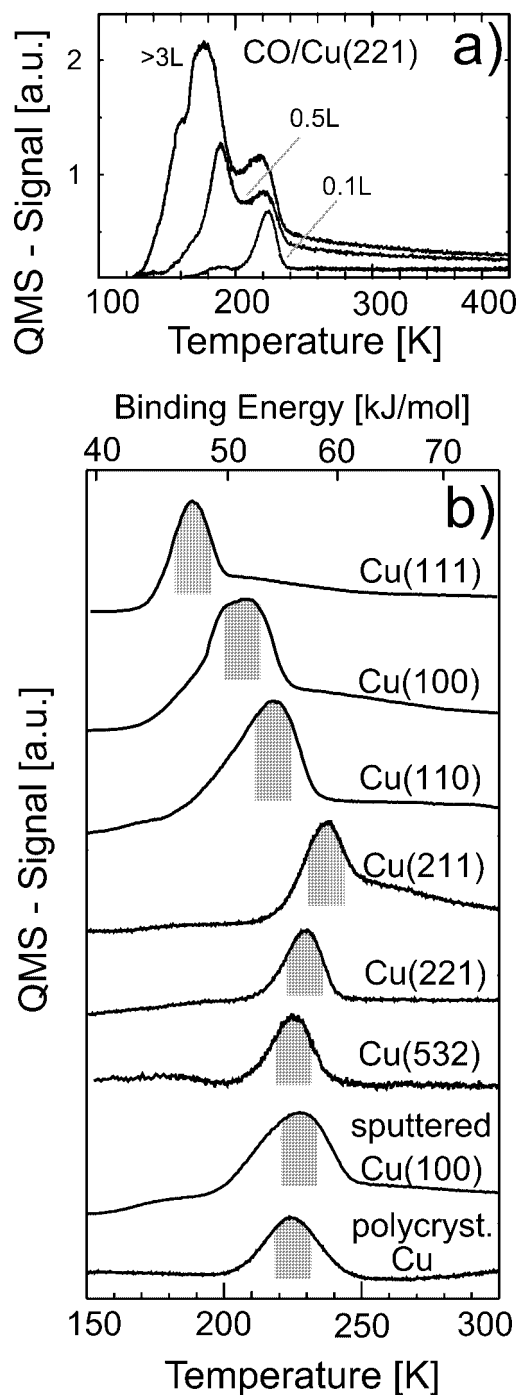
Figure 3. (a) Evolution of TD spectra with increasing CO exposure on Cu(221). (b) Summary of TD spectra of CO taken from dilute CO phases on the different copper surfaces. The grey lines underline the temperature of the desorption maximum where the width represents the experimental resolution. All measurements were recorded at a heating rate of 5 K/s.

Table 1
Summary of adsorption energies, E_b, of CO for different adsorption sites determined from TDS. The numbers of nearest substrate neighbors of the adsorption site, N_{NN}, is also included in the table.

Adsorption site	Surface	N_{NN}	E_b (kJ/mol)
Terrace	Cu(111)	9	47.3 ± 1.4
Terrace	Cu(100)	8	51.1 ± 1.4
Atomic row	Cu(110)	6	54.0 ± 1.4
Step edge	Cu(211)	7	58.4 ± 1.4
Step edge	Cu(221)	7	57.7 ± 1.4
Kink	Cu(532)	6	56.8 ± 1.4
Defects	Cu(100) sputtered	6–7	58.5 ± 1.4
Defects	Poly-crystalline	6–7	58.2 ± 1.4

Next the specific binding energy of CO at step edges was determined by employing a Cu(211) surface. As shown in previous low-temperature STM studies by Meyer *et al.* carbon monoxide adsorbs on this surface only at the step edges while no terrace sites are occupied [27]. The present low-coverage TDS data yielded a step edge related CO adsorption state with a binding energy of 57.9 kJ/mol. Almost the same binding energy was also obtained for the Cu(221) surface. Since the terraces on the latter surface are 38% longer than at Cu(211) the effect of the step separation on the binding energy is obviously negligible if the terraces are not too short as, *e.g.*, in the limit of the Cu(110).

Compared to step edge atoms kinks constitute as surface sites of next lower coordination. To study the adsorption on those sites we have chosen a Cu(532) surface as a representative for a periodically kinked surface. This particular surface is very similar to Cu(211) but instead of straight steps consists of regular kinked step edges, as shown in figure 2. The corresponding TDS measurements revealed an adsorption energy for isolated CO molecules of $E_b = 56.9$ kJ/mol. Within the error bars this value is identical to that obtained for step edge adsorption.

Further TDS measurements were also carried out for randomly distributed defects created by sputtering of a Cu(100) surface at low temperature (120 K) which yielded a binding energy of 58 kJ/mol. Finally, the same experiment was repeated for a poly-crystalline copper sample which had been cleaned in UHV by sputtering without any annealing. As displayed in figure 3(b), also for this sample a well defined desorption peak was observed from which an adsorption energy of 58 kJ/mol has been determined for isolated CO molecules.

All presently obtained binding energies are summarized in table 1 together with the coordination of the occupied substrate atoms.

4. Discussion

The TDS data for the low-index surfaces show the expected increase of CO binding energy with decreasing coordination, N_{NN}, of the substrate atom. Unexpectedly, however, for step edge adsorption sits on the (221) surface,

tra recorded for the various surfaces are summarized in figure 3(b). In close agreement with previous data [12,26][1] binding energies of $E_b = 47.3$, 51.1 and 54.0 kJ/mol were determined for the limit of isolated CO molecules adsorbed on Cu(111), Cu(100) and Cu(110), respectively.

[1] To our knowledge no TDS data have been reported so far for CO adsorbed on Cu(100).

where the coordination number of step edge atoms amounts to 7, the binding energy is not smaller than obtained for the Cu(110) surface ($N_{NN} = 6$), but larger. Table 1 shows similar behaviour for the other types of step and kink adsorpion sites.

This result demonstrates that simple geometric arguments based on coordination considerations alone can be misleading.

A comparison of the data for the sputtered Cu(100) films and the poly-crystalline substrates indicates that stepped surfaces indeed provide the type of defect-related adsorption sites present at disordered surfaces. A particular good agreement is observed with the data for the Cu(211) and Cu(221) surfaces.

In a previous study Waugh and coworkers have studied the morphology of the copper particles of an industrially used Cu/ZnO/Al$_2$O$_3$ methanol synthesis catalyst [28] using indirect information from IR spectroscopy and TDS. On the basis of the frequencies observed for the internal stretch mode of adsorbed CO they concluded a predominant presence of Cu(111), Cu(110) and Cu(211) microfacets [28,29]. In the corresponding TDS measurements (recorded for a heating rate of 5 K/min) they observed desorption peaks located at 269 and 275 K (which remained unassigned [28]) and a prominent desorption peak at 345 K ($\approx$95.4 kJ/mol) which was attributed to CO desorbing from Cu(211) facets. This value is at strong variance to the adsorption energy of about 58 kJ/mol obtained in the present study for Cu(211). For none of the Cu surfaces studied by us and others such a high binding energy for CO has been seen. The reason for this discrepancy is presently unknown; we speculate that readsorption processes occurring within the Cu/ZnO/Al$_2$O$_3$ powder may have to be considered. Moreover, we note that an identification of facets solely based on IR data is not unambiguous.[2]

To explain the adsorption of CO on transition metal surfaces frequently the Blyholder model [31] has been invoked. According to this model a charge transfer takes place from the molecular 5σ orbital into the metal d band. At the same time a back-donation occurs from the substrate into the 2π^* orbital. In a recent study Hammer *et al.* analyzed the adsorption of CO on various platinum surfaces theoretically in the framework of DFT calculations [32]. They found that the interaction of CO with platinum is dominated by the 2π^*–d coupling and that the position of the d-band center provides a quantitative measure of the electronic effects caused by the different surface structures.

Compared to the strong chemical interaction on Pt surfaces the Cu substrates studied here exhibit only a rather weak chemisorption. Since the d band of copper is com-

pletely filled only a small variation in the 2π^*–d coupling is expected for various adsorption sites and the resulting adsorption energy is a detailed balance of the different contributions. A recent detailed analysis of the different contributions to the CO binding to a Cu(100) surface revealed, that the repulsive interaction between the O atom and the metal surface electron density (mostly s states for Cu) plays an important role [33]. Since the electronic charge distribution at surface defects such as steps shows significant differences to that for flat terraces (so-called Smoluchowski effect [34]) the slightly reduced charge density at a step site could lead to a slight reduction in repulsion and thus to an increase of the CO binding energy, which could explain that the binding energy of CO at step sites, *e.g.*, for Cu(211) is anomalously high. Further theoretical work, however, is required to understand this unexpected behaviour in more detail.

In summary, the adsorption energies of isolated CO molecules at various well defined adsorption sites on copper have been determined from thermal desorption spectroscopy. By comparing data for low-indexed surfaces to results obtained for regular stepped and kinked single crystal substrates the binding to various different adsorption sites could be studied in a systematic fashion. The most striking result is that the expected inverse relation between coordination number of the adsorption site and the binding energy does not hold. For adsorption at surface defect sites such as steps or kinks we obtain binding energies which are systematically larger than for adsorption sites within perfect terraces with equal or smaller coordination number. For step sites an adsorption energy of 58 kJ/mol was found which compares well with binding energies seen for CO adsorbed on "real", *i.e.*, poly-crystalline surfaces. The latter result suggests that at least for CO interacting with Cu substrates stepped and kinked single crystal substrates (in particular Cu(211)) are a very good model for understanding adsorption on disordered and poly-crystalline surfaces.

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[2] The identification of micro-facets on catalytic copper particles was based on IR data of the internal stretch mode of adsorbed CO. In previous IR experiments for a number of differently oriented vicinal Cu substrates Pritchard *et al.* [30] observed only very small ($<$5 cm^{-1}) differences in those frequencies, thus making an identification of the CO adsorption site (or the presence of particular facets) on a real catalyst from the CO stretch frequency very difficult or impossible.

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