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Heterogeneous Catalysis

Tuning the Reactivity of Oxide Surfaces by Charge-Accepting Adsorbates[**]

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Dedicated to Süd-Chemie on the occasion of its 150th anniversary.

The surface-science approach to heterogeneous catalysis is based on well-controlled studies on model catalysts (usually single-crystal surfaces) under ultrahigh-vacuum (UHV) conditions.[1] These model systems make it possible to address specific problems on the atomic scale that are virtually impossible to solve with studies on polycrystalline catalyst powder samples. It is particularly important that the full strength of theory can be applied to such model systems, because a meaningful comparison between experiment and electronic structure calculations is only possible for substrates where the structure is well-defined.[2]

Herein, we demonstrate the strength of such a combined experimental and theoretical approach for ZnO surfaces by explaining the microscopic origins of an unexpected increase in CO binding energies upon preadsorption of CO_2. At present, it is tacitly assumed in most treatments that binding energies of individual molecules on oxides are not substantially affected by coadsorbates. Herein, we provide direct experimental evidence that substrate-mediated interactions between coadsorbates can significantly affect total binding energies on metals oxides and that these effects are present in both single crystals and powder samples. Accurate density functional theory (DFT) calculations explain this effect as a change in the Lewis acidity of metal cations exposed on an oxide surface when carbonates are formed on adjacent sites.

The present detailed analysis was triggered by the unexpected results of a study of ZnO powder samples under high-pressure conditions using static adsorption microcalorimetry and temperature-programmed desorption (TPD). Figure 1 shows the isotherms of CO adsorption on the CO_2-modified ZnO powder (Nanotek) and for a CO_2-free sample. Exposure of the latter to CO led to a very small uptake, whereas the amount of adsorbed CO was dramatically enhanced after modification of the ZnO surfaces by CO_2. Further experiments demonstrated that the adsorption of CO on the CO_2-preadsorbed sample is fully reversible at room temperature.

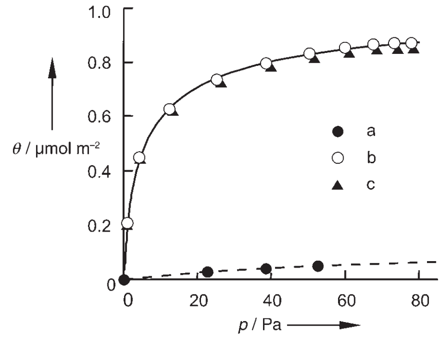

Figure 1. Isotherms of CO adsorption on a) CO_2-free ZnO powder (Nanotek); b) CO_2-modified ZnO powder, first adsorption; c) CO_2-modified ZnO powder, second adsorption after evacuation. The calculated curve for CO_2-modified ZnO is given by the solid line. All isotherms were obtained at room temperature. The coverage of preadsorbed CO_2 amounts to 0.5 monolayers (ML). According to the density of Zn^{2+} sites on the mixed-terminated ZnO(10$\bar{1}$0) surface, 1.0 ML corresponds to 9.8 $\mu mol\,m^{-2}$.

The initial heat of CO adsorption on CO_2-modified ZnO powders as derived from the microcalorimetry data was approximately 62 $kJ\,mol^{-1}$, which is much higher than that measured on CO_2-free samples (about 35 $kJ\,mol^{-1}$, Table 1). The adsorption energies of CO at higher coverages can be calculated by fitting the microcalorimetry and TPD data using a uniform energy distribution model on heterogeneous surfaces.[3,4] The corresponding results are presented in Table 1. The adsorption energy of CO varies between

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Table 1: Differential heats of adsorption ε [kJ mol^{-1}] of CO on CO$_2$-modified ZnO powders.

	θ_{CO} [μmol m^{-2}][a] 0.20	0.45	0.65	Microcalorimetry[b]	TPD[b]
ε	62	61	59	45–65	45–62

[a] Experimental values obtained from microcalorimetry. [b] Theoretical values calculated by fitting the microcalorimetry and TPD data based on a model with uniform energy distribution.[3,4]

45 kJ mol^{-1} (least active sites, ε_{min}) and 65 kJ mol^{-1} (most active sites, ε_{max}).

This increase in binding energy of CO on ZnO resulting from CO$_2$ preadsorption is rather surprising, as no previous findings of this type are known to us. Unraveling the microscopic origin of this unexpected behavior is very difficult for powder samples, since it is unknown which specific orientation of the ZnO powder particles is responsible. It is also possible that these effects are caused by defects, such as oxygen vacancies, which are presently believed to be the most active sites on ZnO surfaces.[5] Information about the type of facets responsible for this phenomenon is also required for electronic structure calculations, which in recent years have provided a very good description of adsorption phenomena on ZnO surfaces.[6–8]

For this reason we carried out a single-crystal study using standard surface-sensitive techniques for the mixed-terminated ZnO(10$\bar{1}$0) surface. This choice is based on the fact that detailed characterization of ZnO powders using X-ray diffraction (XRD) and transmission electron microscopy (TEM) have shown that polycrystalline nanoparticles are dominated by ZnO(10$\bar{1}$0) facets.[9] Furthermore, the CO$_2$ binding geometry on this particular ZnO surface is known in considerable detail from a previous study.[10]

The atomic structure of this mixed-terminated surface is shown in Figure 2a. The surface consists of Zn–O ion pairs that form characteristic rows along the crystallographic [1$\bar{2}$10] direction.[11] For each surface ion, the four-fold bulk coordination has been reduced to three-fold, so that the surface Zn and O ions act as Lewis acid and Lewis base sites, respectively.

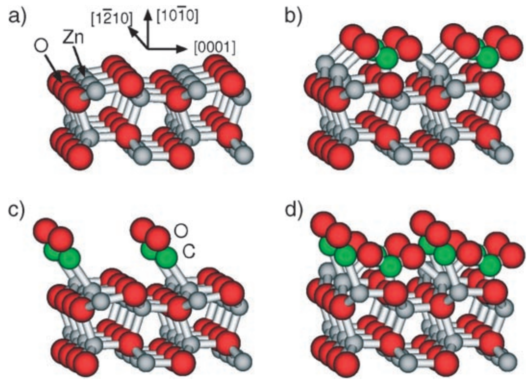

Figure 2. Side view of the atomic structures of differently modified ZnO(10$\bar{1}$0) surfaces: a) clean surface; b) surface with adsorbed CO$_2$ forming a tridentate carbonate species with a stable (2×1) structure; c) CO-adsorbed surface with an ordered (2×1) structure; d) CO and CO$_2$ coadsorption on the surface in which the CO is adsorbed on the free Zn sites of the open (2×1) carbonate adlayer. O red, Zn gray, C green.

The TPD spectrum of CO on the clean ZnO(10$\bar{1}$0) surface exhibited one desorption peak centered at 118 K (Figure 3a), revealing that CO is weakly bonded to the clean surface with a binding energy of 30.5 kJ mol^{-1}. This value is in very good agreement with the results of precise DFT calculations of 31 kJ mol^{-1} in the half-monolayer (ML) coverage limit,[8,12] and it is comparable to the CO adsorption energy of 26.9 kJ mol^{-1} observed on the polar Zn-terminated ZnO(0001) surface.[7] The total amount of adsorbed CO can be estimated by comparison of the integrated peak areas of CO and CO$_2$; a maximal coverage of 0.25 ML was achieved for CO adsorption at 100 K.

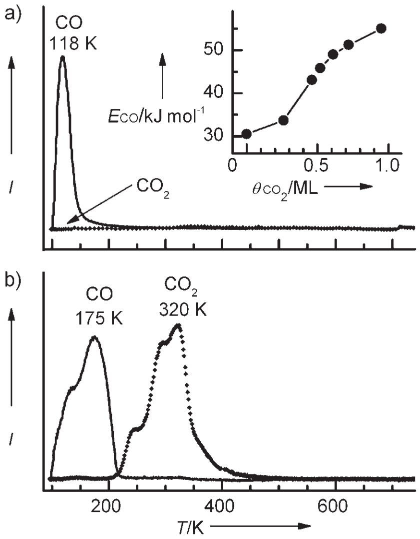

Figure 3. TPD data recorded for 2 L CO exposure at 100 K on a) clean ZnO(10$\bar{1}$0) surface; b) CO$_2$-modified ZnO(10$\bar{1}$0) surface prepared by exposure to 2 L CO$_2$ at 100 K and subsequent heating to 220 K. The heating rate was 1 K s^{-1}. The inset in (a) shows the binding energy of CO as a function of CO$_2$ preadsorption, obtained by assuming a prefactor of 10^{13} s^{-1}.

Interestingly, after modification of the clean ZnO(10$\bar{1}$0) surface by dosing 2 L CO$_2$ at 100 K and subsequent annealing to 220 K, the desorption peak of CO shifted to 175 K (Figure 3b), thus indicating a stronger interaction between CO and the modified surface. As shown in the inset of Figure 3a, the binding energy of CO increases significantly with increasing CO$_2$ precoverage, reaching a value of 55.2 kJ mol^{-1} when the surface is precovered by 0.95 ML CO$_2$. This finding is in excellent agreement with the coadsorption behavior of CO and CO$_2$ on ZnO powder samples.

A recent study showed that upon adsorption of CO$_2$ on the ZnO(10$\bar{1}$0) surface, CO$_2$ forms a very stable tridentate carbonate in which the C atom interacts with a surface O atom, and both O atoms of the CO$_2$ molecule form almost equivalent bonds to neighboring Zn atoms (Figure 2b).[10] Above 220 K, the carbonates form a (2 × 1) structure, leaving every second Zn surface site empty. It seems feasible that CO is adsorbed on the free Zn sites within this (2 × 1) structure

(Figure 2d). This speculation is supported by diffraction studies. After adsorption of CO at 100 K, the (2 × 1) diffraction peaks are still present in the data from low-energy electron diffraction (LEED). Furthermore, the integrated areas of CO and CO_2 desorption peaks are nearly identical, thus indicating that at saturation, 0.5 ML of CO is adsorbed on the CO_2-modified surface.

Data from high-resolution electron energy loss spectroscopy (HREELS) provide a deeper understanding of CO adsorption on the CO_2 modified surface. On the clean substrate,[8,13] the stretching mode of CO bound to a surface Zn ion is detected at 2192 cm^{-1}, whereas on the CO_2-pretreated ZnO($10\bar{1}0$) surface the frequency is found at 2200 cm^{-1} (Figure 4). This 8-cm^{-1} blue shift directly demonstrates the enhanced interaction of CO with CO_2-modified ZnO and strongly suggests that the Lewis acidity at the surface has changed upon CO_2 coadsorption. Enhanced Lewis acidity at Zn cations is expected to increase the 5σ donation from the CO molecule to the Zn surface ion. Because the 5σ orbital is weakly antibonding, enhanced electron donation strengthens the C–O bond and leads to a blue shift of the ν(CO) band. Simultaneously, this effect results in a stronger interaction of CO with Zn cations, thus causing an increase in the CO adsorption energy.

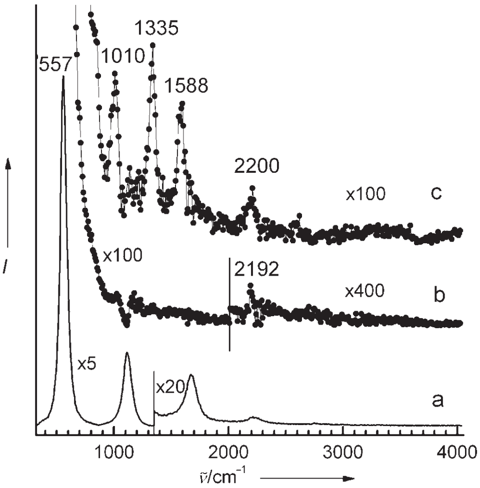

Figure 4. HREELS data recorded after adsorption of 2 L CO at 100 K on a) and b) clean ZnO($10\bar{1}0$) surface; c) CO_2-modified ZnO($10\bar{1}0$) surface prepared by exposure to 2 L CO_2 at 100 K and subsequent heating to 220 K. Curve (a) displays the raw spectrum, which is dominated by the intense Fuchs–Kliewer phonon at 557 cm^{-1} and its overtones.[14–16] The latter are successfully removed in curves (b) and (c) by Fourier deconvolution, thus allowing detection of the adsorbate-related peaks. Curve (c) exhibits additional bands at 1010, 1335, and 1588 cm^{-1} that arise from the tridenate carbonate species and are attributed to the different C–O stretching vibrations.[10] All spectra were recorded at 100 K in specular direction with an incidence angle of 55° and a primary energy of 10 eV.

For the most stable phase of preadsorbed CO_2 on ZnO($10\bar{1}0$), the (2 × 1) carbonate structure, an extensive search for the most stable binding geometry of CO molecules was performed using ab initio DFT calculations. As expected, binding of the CO molecules with the C atom attached to the free Zn sites between the carbonates was strongly favored (Figure 2d). The CO molecules adsorbed in a slightly more upright geometry than on the CO_2-free surface (the CO tilt angle with respect to the surface normal decreased from 26° to 18°), and the CO binding energy E_b increased from 31 kJ mol^{-1} to 50 kJ mol^{-1}. Simultaneously, the C–O bond length decreased by 0.5 %, and the CO vibration frequency (calculated in harmonic approximation) was blue-shifted by 6 cm^{-1}. All of these results are in excellent agreement with the experimental data obtained for the single crystals. A decomposition analysis of E_b revealed that the contributions from surface and adsorbate relaxations to the CO binding energy were smaller than 2 kJ mol^{-1} for the CO_2-free and the CO_2-precovered surfaces. Also, direct CO–CO_2 adsorbate interactions contributed less than 4 kJ mol^{-1} to E_b. Thus, the strong increase in CO binding energy can be attributed to a direct strengthening of the CO bond to the surface via electronic effects, which fully supports the notion of increased Lewis acidity of the surface Zn ions adjacent to preadsorbed CO_2 molecules.

Cooperative effects are also known to occur when NO_x is adsorbed on MgO(001).[17] However, these effects involve both electron transfer between two neighboring adsorbates and acid–base interactions with the oxide surface, thus leading to strong chemisorption to the MgO surface with additional lateral electrostatic stabilization.

In summary, CO is only very weakly bound to the Zn cations at the clean ZnO($10\bar{1}0$) surface. When the ZnO($10\bar{1}0$) surface is modified by exposure to CO_2 at room temperature, a surface matrix forms in which free Zn sites are embedded between tridentate carbonate species. The embedded Zn ions bind CO more strongly, as evidenced by the enhanced thermal stability and the blue shift of the C–O stretching frequency. DFT calculations clearly demonstrate that this unexpected effect results from an enhanced Lewis acidity of the embedded Zn sites caused by the carbonate species. The same enhancement of CO binding energies by CO_2 coadsorption is also observed for polycrystalline ZnO powders, as revealed by adsorption microcalorimetry. These findings demonstrate that substrate-mediated effects on oxides need to be considered and have important consequences for a deeper understanding of heterogeneous catalysis over oxides in the presence of charge-accepting coadsorbates.

Experimental Section

The HREELS, TDS, and LEED experiments on ZnO($10\bar{1}0$) single crystals were carried out in an UHV apparatus that has been described in detail previously.[18,19] The ZnO($10\bar{1}0$) sample was cleaned by repeated cycles of sputtering (1 keV Ar^+, 30 min) and annealing in oxygen (1×10^{-6} mbar, 850 K, 2 min). The surface cleanness was checked by LEED and HREELS. Exposures are given in units of Langmuir (1 L = 1.33×10^{-6} mbar s).

The studies on polycrystalline ZnO samples (Nanotek, with a specific surface area of 10 $m^2 g^{-1}$ and a grain size of 250–355 μm) were performed using static adsorption microcalorimetry and TPD. The microcalorimeter setup and the measurement procedures were introduced in previous work.[20,21] Briefly, the heat generated by adsorption is measured by a Tian–Calvet microcalorimeter, and the adsorbed amount is derived from the pressure change in the sample cells with calibrated volume. The ZnO sample was pretreated at 720 K in diluted oxygen (10% O_2 in Ar, purity: O_2 99.995%, Ar 99.999%) for 4 h to eliminate surface hydroxy groups and carbonates. The CO_2-modified ZnO sample was obtained in the microcalorimeter cell by exposing it to 1 kPa CO_2 (99.995%) at 303 K and subsequent evacuation overnight at the same temperature. The adsorption of CO (99.9995%) was achieved by successive dosing at 303 K; N_2 (99.9999%) was used as a non-adsorptive gas for pressure compensation. Repeated adsorption measurements were performed on CO_2-modified ZnO after desorbing CO in vacuum at room temperature overnight.

The TPD setup was described in detail previously.[22,23] The composition of effluent gas was monitored by a calibrated quadrupole mass spectrometer. The CO_2-modified ZnO sample was obtained as follows: ZnO (0.2 g) was pretreated at 720 K for 4 h, then exposed to 4% CO_2/He gas flow (10 NmL$\,$min^{-1}) at 303 K for 30 min and to He flow at 303 K for 1 h. The TPD measurement of CO was achieved by the following procedures: CO was preadsorbed at 300 K in a flowing mixture of 10% CO in He (10 NmL$\,$min^{-1}). Then the sample was cooled rapidly to 78 K in flowing CO/He, followed by purging with pure He for 10 min at 78 K. Afterwards, the sample was heated in He (10 NmL$\,$min^{-1}) with a heating rate of 5.2 K$\,$min^{-1} until all of the CO was desorbed.

The DFT calculations were carried out using periodic slabs with a thickness of six ZnO layers, Vanderbilt ultrasoft pseudopotentials, a plane-wave cut-off energy of 25 Ry, a (4,2,1) Monkhorst–Pack k-point mesh for the primitive surface unit cell and the PBE gradient-corrected exchange-correlation functional. The upper half of the slabs was fully relaxed, whereas the atoms in the lower half were kept at their bulk positions.

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