Surface Chemistry

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CO_2 Activation by ZnO through the Formation of an Unusual Tridentate Surface Carbonate**

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The activation of CO_2 is one of the most important topics in catalysis.[1] For example, one of the simple Zn–enzyme-catalyzed processes, the hydration of CO_2 by carbonic anhydrase, has led to extensive mechanistic and theoretical studies of the interaction of CO_2 with Zn–OH.[2–5] Also, in heterogeneous catalysis, a detailed understanding of the surface chemistry of CO_2 is an important issue; interest in this topic ranges from developing new processes for an emplacement of this greenhouse gas to the synthesis of methanol from syngas ($CO/CO_2/H_2$) over Cu/ZnO catalysts.[6] Numerous studies have been reported on CO_2 adsorption on clean metal surfaces, where frequently activation is found to occur via the formation of a bent $CO_2^{\delta-}$ species.[7–9] For oxide surfaces much less information is available. This deficit is in part due to the poor electric conductivity of many oxides which severely complicates the application of electron-based spectroscopic methods. In particular, there is a lack of information concerning molecular vibrations from high-resolution electron energy loss spectroscopy (HREELS). The application of HREELS on oxide surfaces is—in addition to the electric conductivity problem—severely limited by the presence of intense substrate lattice excitations (Fuchs–Kliewer phonons[10]) which obscure the relatively weak vibrational modes of adsorbed species.

Herein we present the results of a systematic multi-technique experimental and theoretical study on the interaction of CO_2 with the mixed-terminated ZnO($10\bar{1}0$) surface. In contrast to other oxides, ZnO is sufficiently conductive that electron-based methods can be applied without significant difficulties. The results from HREELS, thermal desorption spectroscopy (TDS), low-energy electron diffraction (LEED), He-atom scattering (HAS), and X-ray photoelectron spectroscopy (XPS) reveal a complicated scenario, comprising the presence of two different ordered phases. By employing accurate periodic density-functional theory (DFT) and wave-function-based quantum-chemical cluster calculations it could be shown that the previously proposed bidentate bonding of CO_2 to this ZnO surface[11] has to be revised. Exposure to CO_2 leads—even at temperatures below 100 K—to the formation of an unusual tridentate carbonate species with the two O atoms of the CO_2 molecule being almost equivalently bound to two different Zn surface atoms.

In a first set of experiments, the phase diagram of CO_2 adlayers on this ZnO substrate was determined using HAS. This technique uses neutral He atoms with thermal energy so charging problems are avoided. HAS is a highly sensitive surface-analysis method,[12–14] and has been successfully used to determine the phase diagram of H_2O on the same surface.[15] The HAS data show that exposure of the sample to very small amounts of CO_2 in two steps (first with 4 L at 260 K and then 8 L at 120 K; exposures are given in units of langmuir ($1\,L = 1.33 \times 10^{-6}$ mbar s)) results in the formation of a well-ordered (2×1) phase (Figure 1 b; the arrows indicate half-order diffraction peaks). Upon saturation with CO_2 the (2×1) structure disappears and a (1×1) phase forms. The data in Figure 1 c were recorded for a nearly saturated (1×1) phase, in which a small concentration of residual (2×1) patches gives rise to weak and broad half-order diffraction peaks. The (2×1) periodicity is also seen in LEED data whereas the LEED pattern for the saturated (1×1) phase could not be distinguished from that for the clean surface. A simplified phase diagram of CO_2 on the mixed-terminated ZnO is shown in Figure 2.

Measurements using TDS show three desorption peaks at 325, 200, and 125 K indicating the presence of three different adsorbate states referred to as α, β, and γ (Figure 3). The TDS

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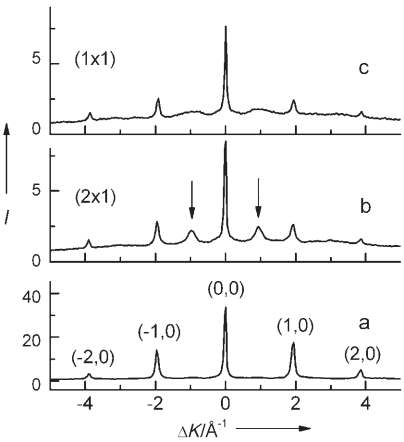

Figure 1. He-atom angular distributions measured along the [$\bar{1}2\bar{1}0$] azimuth at an incident-beam wave vector of 7.8 Å^{-1} for the clean ZnO(10$\bar{1}$0) surface (curve a), after low exposure to CO_2 (curve b; see text), and after saturation with CO_2 (curve c).

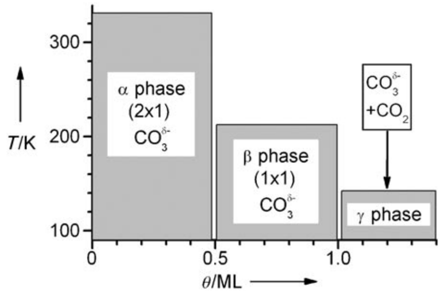

Figure 2. Schematic phase diagram of CO_2 on ZnO(10$\bar{1}$0).

data also reveal that the transformation of the β into the α phase is accompanied by the desorption of about 0.5 monolayers (ML) of CO_2; this is shown by the integrated areas of the β and α peaks being nearly identical. Furthermore, after desorption of the β state, the LEED data clearly demonstrate the transformation from a (1 × 1) to a (2 × 1) phase. Two small TDS peaks are observed at about 240 and 295 K, which are tentatively attributed to the interaction of CO_2 with surface defects.

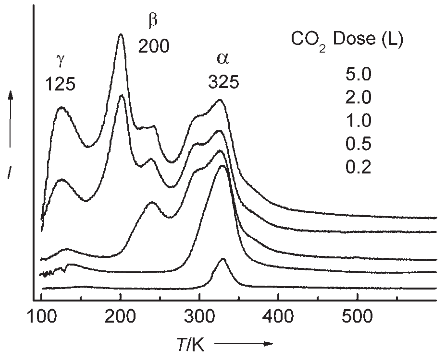

Figure 3. TDS data of CO_2 for various CO_2 exposures on ZnO(10$\bar{1}$0) at 95 K. The heating rate was 1 K s^{-1}.

An unambiguous identification of the surface CO_2-containing species is provided by vibrational spectroscopy. The HREELS data recorded after exposing the clean ZnO-(10$\bar{1}$0) surface to various amounts of CO_2 at 95 K are shown in Figure 4. Figure 4 a is the raw spectrum which is dominated by the intense primary phonon mode at 549 cm^{-1} and its multiple excitations.[16–19] After Fourier deconvolution, the multiple phonons are almost completely removed and new peaks arising from CO_2 adsorption appear (Figure 4 b–d). Interestingly, the vibrational spectra for the α and β states are very similar. The HREELS data in Figure 4 show frequencies typical for carbonate species:[20,21] an out-of-plane deformation mode $\pi(CO_3)$ at 839 cm^{-1} and the three C–O stretching modes at 994, 1340, and 1615 cm^{-1}. To unambiguously identify the vibrations arising from $CO_3^{\delta-}$ species, measurements were carried out by exposing ZnO(10$\bar{1}$0) to 5 L of the isotopologue $C^{18}O_2$ at 95 K. The corresponding HREEL spectrum shows bands at 831, 976, 1311 and 1601 cm^{-1}, which exhibit the expected isotopic shifts for a $C^{18}O_2{}^{16}O^{\delta-}$ carbonate ion.

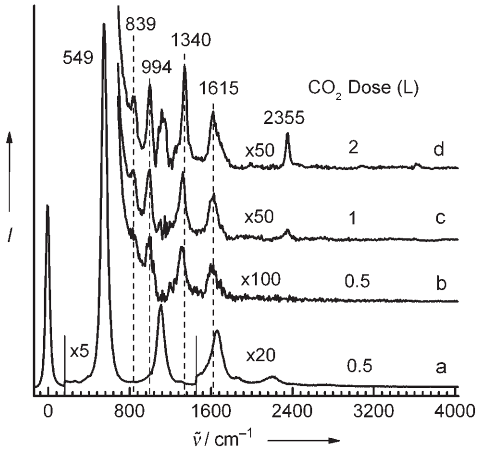

Figure 4. HREELS data recorded after adsorption of CO_2 on ZnO-(10$\bar{1}$0) at 95 K. Curve a is the raw spectrum which is dominated by the intense Fuchs–Kliewer phonons; the Fourier-deconvoluted spectra are shown in curves b–d. In curve d, the phonon at 1113 cm^{-1} is not completely removed by the Fourier deconvolution. The spectra were recorded at a surface temperature of 95 K in specular-reflection geometry with an incidence angle of 55° and with a primary energy of 10 eV.

After exposure of the ZnO(10$\bar{1}$0) surface to $C^{18}O_2$ at 95 K the desorption of $C^{18}O^{16}O$ is detected from the α and β states by TDS, but not from the γ state. This result indicates an isotope exchange with the substrate, directly demonstrating the presence of a rather strong bond between CO_2 and the ZnO(10$\bar{1}$0) surface. After saturation of the α and β states a new phase is formed (γ state; Figure 3) containing only weakly bound CO_2 species. The desorption peak at 125 K in the TDS and the peak at 2355 cm^{-1} in the HREELS data (Figure 4) are characteristic for additionally, weakly physisorbed linear CO_2.

At first sight the presence of the two phases, α and β, each with a different periodicity seems to point towards a thermally activated chemisorbate formation. This explanation, however, is at variance with the data from vibrational spectroscopy obtained after annealing the sample: no new peaks appear, indicating that the molecular species constituting the different phases must be identical or at least very similar.

To resolve the atomic structure of the adsorbed CO_2 molecules, extensive ab initio DFT calculations in a periodic slab setup were carried out (for details see ref. [22]). Many different CO_2 binding geometries at coverages ranging from isolated molecules to full monolayers were investigated. Interestingly, only one stable adsorption configuration for CO_2 molecules could be found, which is basically the same for all CO_2 coverages. The most stable CO_2 adsorbate structure is not a bidentate carbonate ion as suggested by Davis et al.,[11] but a tridentate configuration where the C atom binds to a surface O atom, and both O atoms of the CO_2 molecule interact with the neighboring Zn atoms. The Zn–O bond lengths are only slightly larger than in bulk ZnO (Figure 5a,b). The calculated bond lengths and bond angles are indicated in Figure 5b. As a consequence of the carbonate-ion formation, the Zn–O bond length of the surface dimer beneath the carbonate ion is elongated from 1.98 to 2.15 Å with respect to the bare surface. This change is accompanied by large relaxations of the positions of the surface O and Zn atoms. The energy needed for these relaxations is compensated, to a large extent, by the energy gained from forming two additional Zn–O bonds, so that the binding energy of the tridentate species is, in fact, comparable to that of monodentate carbonate species, for example, on $RuO_2(110)$.[20,21]

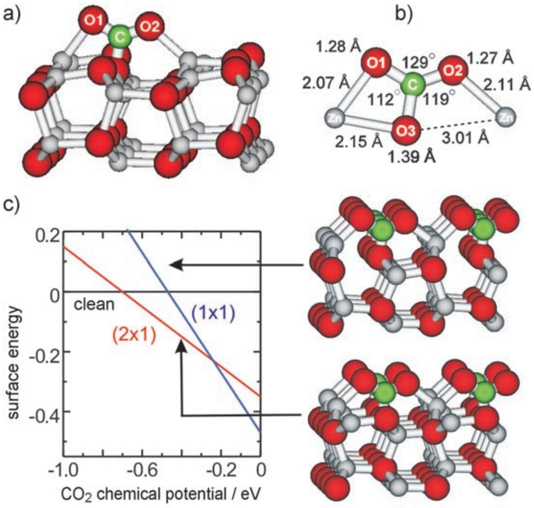

Figure 5. a, b) Side view of the atomic structure of an isolated carbonate ion on ZnO(10$\bar{1}$0) formed upon CO_2 adsorption. c) Relative thermodynamic stability of the half- and full-monolayer CO_2 coverage.

The same CO_2 adsorption geometry was also found in the quantum-chemical cluster calculations. An analysis of the charge distribution and of the O1s core levels reveals a significant charge transfer to the O atoms of the adsorbed CO_2 molecule and confirms that a negatively charged carbonate ion is indeed formed upon CO_2 adsorption. The charge transfer and the equivalence of the adsorbate O atoms were confirmed by XPS measurements of the O1s core-level shifts, which show a uniform separation of 1.8 eV between the O1s core signals of the ZnO substrate and the carbonate ion.

The thermodynamic stability of the adsorbate layers has been obtained by converting the calculated CO_2 adsorption energies for the different coverages into changes in the ZnO surface energy (for details see ref. [23]). Temperature and pressure conditions are represented by the CO_2 chemical potential. Two stable adsorbate phases are found (Figure 5c): at high CO_2 chemical potential (low temperature, high pressure) there is a full (1 × 1) monolayer with a binding energy of 0.47 eV per CO_2 molecule and at medium chemical potential (increasing temperature, lower pressure) a half monolayer with (2 × 1) structure and a binding energy of 0.70 eV per CO_2 molecule. The calculated vibrational frequencies (in harmonic approximation) for the two phases are summarized in Table 1. The good agreement with the experimental values confirms the presence of an unusual tridentate carbonate species on the ZnO(10$\bar{1}$0) surface and the formation of two different ordered phases that are dependent on temperature and pressure.

Table 1: Experimental and calculated vibrational frequencies [cm^{-1}] of the tridentate carbonate ion formed on ZnO(10$\bar{1}$0).

		$\pi(CO_3)$	$\nu(CO)$	$\nu_s(OCO)$	$\nu_{as}(OCO)$
Experiment	0.5 ML	839	994	1323	1609
	1 ML	839	994	1340	1617
Calculation	0.5 ML	795	953	1291	1562
	1 ML	802	932	1299	1624

In summary, we are able to conclude that the rather special geometry of Zn cations and O anions on the mixed-terminated ZnO (10$\bar{1}$0) surface makes an activation of CO_2 possible even at temperatures as low as 90 K. An unusual tridentate carbonate species is formed, which is strongly bound to the surface by three covalent bonds involving the C atom and both O atoms of the adsorbed CO_2 molecule. In addition to a close packed (1 × 1) phase, in which there is significant repulsion between the carbonate species, an open (2 × 1) structure is also formed in which there is a much lower degree of repulsion between the carbonate moieties. It will be interesting to explore whether reactions can be induced between the activated species of CO_2, which is the most important greenhouse gas and the C source for methanol synthesis over Cu/ZnO catalysts, and other small molecules adsorbed on the free sites of the open (2 × 1) carbonate adlayer.

Experimental Section

The HREELS, TDS, and LEED experiments were carried out in an ultra-high vacuum (UHV) apparatus consisting of two chambers separated by a valve. The base pressure was 2×10^{-11} mbar. The upper chamber is equipped with an argon-ion sputtering gun, a LEED optic, and a quadrupole mass spectrometer used to perform TDS experiments. The lower chamber houses a HREEL spectrometer (Delta 0.5, SPECS, Germany) with a straight-through energy resolution of

1 meV. The HAS experiments were carried out with an UHV molecular beam system that was described in detail in ref. [14].

In all experiments the ZnO($10\bar{1}0$) sample was cleaned by repeated cycles of sputtering (1 keV Ar^+, 30 min) and annealing in O_2 (1×10^{-6} mbar, 850 K, 2 min) and in UHV (850 K, 5 min). Typically, about two sputtering cycles with annealing in UHV were followed by one cycle with annealing in O_2. After about 20 preparation cycles the XP spectra showed no C-containing species (contamination level < 0.05 ML). For the clean surfaces typical (1×1) diffraction patterns were recorded as reported elsewhere.[15,18] Exposure of the sample to CO_2 was carried out by backfilling the UHV chamber through a leak valve. Exposures are given in units of langmuir ($1\ L = 1.33\times10^{-6}$ mbar s).

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[1] S. Schenk, J. Notni, U. Köhn, K. Wermann, E. Anders, *Dalton Trans.* **2006**, 4191 – 4206.
[2] M. Rombach, H. Brombacher, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **2002**, 153 – 159.
[3] D. Schröder, H. Schwarz, S. Schenk, E. Anders, *Angew. Chem.* **2003**, *115*, 5241 – 5244; *Angew. Chem. Int. Ed.* **2003**, *42*, 5087 – 5090.
[4] M. J. Loferer, C. S. Tautermann, H. H. Loeffler, K. R. Liedl, *J. Am. Chem. Soc.* **2003**, *125*, 8921 – 8927.
[5] A. Bottoni, C. Z. Lanza, G. P. Miscione, D. Spinelli, *J. Am. Chem. Soc.* **2004**, *126*, 1542 – 1550.
[6] a) J. M. Thomas, W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, **1997**; b) C. Wöll, *Prog. Surf. Sci.* **2007**, *82*, 55 – 120.
[7] F. Solymosi, *J. Mol. Catal.* **1991**, *65*, 337 – 358.
[8] H.-J. Freund, M. W. Roberts, *Surf. Sci. Rep.* **1996**, *25*, 225 – 273.
[9] G. Heß, C. Baumgartner, H. Froitzheim, *Phys. Rev. B* **2001**, *63*, 165416.
[10] R. Fuchs, K. L. Kliewer, *Phys. Rev. [Sect.] A* **1965**, *140*, 2076 – 2088.
[11] R. Davis, J. F. Walsh, C. A. Muryn, G. Thornton, V. R. Dhanak, K. C. Prince, *Surf. Sci. Lett.* **1993**, *298*, L196 – L202.
[12] C. Wöll, *J. Phys. Condens. Matter* **2004**, *16*, 2981 – 2994.
[13] F. Traeger, *ChemPhysChem* **2006**, *7*, 1006 – 1013.
[14] T. Becker, M. Kunat, C. Boas, U. Burghaus, C. Wöll, *J. Chem. Phys.* **2000**, *113*, 6334 – 6343.
[15] B. Meyer, D. Marx, O. Dulub, U. Diebold, M. Kunat, D. Langenberg, C. Wöll, *Angew. Chem.* **2004**, *116*, 6809 – 6814; *Angew. Chem. Int. Ed.* **2004**, *43*, 6641 – 6645.
[16] H. Ibach, *Phys. Rev. Lett.* **1970**, *24*, 1416 – 1419.
[17] S. Crook, H. Dhariwal, G. Thornton, *Surf. Sci.* **1997**, *382*, 19 – 25.
[18] Y. Wang, B. Meyer, X. Yin, M. Kunat, D. Langenberg, F. Traeger, A. Birkner, C. Wöll, *Phys. Rev. Lett.* **2005**, *95*, 266104.
[19] Y. Wang, M. Muhler, C. Wöll, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1521 – 1524.
[20] A. Lafosse, Y. Wang, K. Jacobi, *J. Chem. Phys.* **2002**, *117*, 2823 – 2831.
[21] Y. Wang, A. Lafosse, K. Jacobi, *J. Phys. Chem. B* **2002**, *106*, 5476 – 5482.
[22] B. Meyer, D. Marx, *Phys. Rev. B* **2003**, *67*, 035403.
[23] B. Meyer, H. Rabaa, D. Marx, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1513 – 1520.