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PII: S0039-6028(18)30626-5
DOI: <https://doi.org/10.1016/j.susc.2018.08.028>
Reference: SUSC 21328



To appear in: *Surface Science*

Received date: 22 July 2018
Accepted date: 30 August 2018

Please cite this article as: Hao Li , Christoph Rameshan , Andrey V. Bukhtiyarov , Igor P. Prosvirin , Valerii I. Bukhtiyarov , Günther Rupprechter , CO₂ activation on ultrathin ZrO₂ film by H₂O co-adsorption: In situ NAP-XPS and IRAS studies, *Surface Science* (2018), doi: <https://doi.org/10.1016/j.susc.2018.08.028>

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Highlights

- Ultrathin ZrO_2 trilayer as model oxide surface
- Pristine surface shows no interaction with CO_2
- Co-adsorption of H_2O activates ZrO_2 for CO_2 adsorption
- adsorbed carbonaceous species identified as formate, dioxymethylene and formaldehyde
- potential methanol activation route on oxide-supported metal catalysts

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FunOx Special Issue

CO₂ activation on ultrathin ZrO₂ film by H₂O co-adsorption:
In situ NAP-XPS and IRAS studies

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Abstract

Utilizing CO₂ as sustainable carbon source requires its activation by catalytically active oxides on which CO₂ can form different surface bound carbonaceous species. This may be promoted or even enabled by surface hydroxyl groups. We have investigated the interaction of CO₂ with a ZrO₂ model surface, i.e. a O-Zr-O trilayer grown on Pt₃Zr(0001), in the absence and presence of H₂O, employing *in situ* near ambient (atmospheric) pressure X-ray photoemission spectroscopy (NAP-XPS) and infrared reflection absorption spectroscopy (IRAS). Whereas room temperature exposure to pure CO₂ up to 3×10⁻² mbar did not induce any interaction with the ZrO₂ model surface, co-adsorption of CO₂ + H₂O resulted in the formation of various carbonaceous surface species. Apparently, in the presence of humidity (surface hydroxylation) CO₂ was activated on ZrO₂ at near ambient pressures. Combining NAP-XPS and IRAS allowed identifying the surface species, which were, formate, dioxymethylene, formaldehyde and carbon. These species may be intermediates of upconverting CO₂ to methanol and highlight the ability of ZrO₂ as active support.

Key Words: ZrO₂ ultrathin film, CO₂ activation, H₂O co-adsorption, formate, formaldehyde, dioxymethylene

1. Introduction

Increasing greenhouse gas emissions and decreasing fossil energy resources have stimulated interest in developing environmentally clean and safe processes of maintaining or even

expanding our energy infrastructure. The utilization of CO₂ as carbon source is attractive both from an environmental and economical perspective [1], but due to the stable nature of CO₂, its efficient activation by suitable catalysts is required [2]. In this context, the co-adsorption of water has been reported to enhance adsorption/activation of CO₂ on oxide surfaces [3], e.g. on ZrO₂ [4] or Fe₂O₃ [5].

Various materials are currently used as catalysts for converting CO₂ to fuels or chemicals. For example, CO₂ is utilized for methanol synthesis [6], with adsorption/activation of CO₂ (also together with H₂O) on ZnO [4, 7] or Cu/Cu₂O [8] surfaces. For photocatalytic CO₂ activation, different modifications of TiO₂ are mainly used (also for H₂O co-adsorption studies), due to their stability, low cost, and nontoxicity [9, 10]. Defects play a central role for CO₂ adsorption on titania, as shown for brookite [9]. The activation of CO₂ was also investigated on several other oxide surfaces, such as γ -Al₂O₃, β -Ga₂O₃, or In₂O₃ [1].

Another way of activating CO₂ is via dry reforming of methane (DRM) [11, 12], when CH₄ and CO₂ react on Ni or Pt particles supported by zirconia [13-15]. During DRM, the carbon formed via CH₄ dissociation reacts with activated CO₂ to CO (although exact reaction pathways are still debated). The CO₂ activation can occur on ZrO₂ or on the metal/oxide interfacial sites [16, 17]. Technical ZrO₂ powder supports can activate CO₂ by forming carbonates with basic anionic sites, or by forming formate with hydroxyl groups [16]. However, the microscopic mechanisms of the ZrO₂ function need to be better understood. Herein, we apply a surface science approach, systematically studying the interaction of CO₂ with an ultrathin ZrO₂ (trilayer) film [18, 19], as well as with a hydroxylated ultrathin ZrO₂ film. It is shown that co-adsorbed water is essential for activating CO₂ by forming surface adsorbed formaldehyde, dioxymethylene and formate that may be intermediates of methanol synthesis on metal/oxide catalysts.

2. Experimental

Laboratory measurements (temperature programmed desorption, TPD and infrared reflection absorption spectroscopy, IRAS) were performed in a custom-built UHV chamber that was described in detail elsewhere (Vienna) [20-23]. In short, the preparation chamber is equipped with a differentially-pumped quadrupole mass spectrometer (MKS eVison+), a low energy electron diffraction (LEED) optics (SPECS ERLEED 1000-A), and a standard X-ray source (SPECS XR 50, with AlK α and MgK α anode) combined with a SPECS EA 150 PHOIBOS hemispherical analyzer. The UHV-compatible high pressure cell ("Rupprechter design") [22-24] is connected to a Fourier transform IR spectrometer (Bruker Vertex 60v) and a ZnSe

photoelastic modulator operating at 34 kHz. A sample single crystal can be heated resistively via tungsten wires, forming a cage around the edge of the crystal. Temperature is measured by a K-type thermocouple spot-welded to the side of the sample.

In order to prepare the model ZrO₂ trilayer film, a Pt₃Zr(0001) single crystal was cleaned by successive steps of sputtering (8×10^{-6} mbar of Ar, 2 kV) at room temperature (20 min), annealing in UHV at 1173 K (10 min), sputtering (20 min) during cooling from 673 to 373 K, and finally annealing in UHV at 1173 K (10 min). After cleaning, the Pt₃Zr(0001) single crystal was exposed to 1×10^{-7} mbar of O₂ at 673 K for 30 min, followed by annealing in UHV 1073 K for 20 min, to obtain the ZrO₂ trilayer film. This follows the recipe described in earlier work [18, 19]. The structure and homogeneity of the film was confirmed by X-ray photoemission spectroscopy (XPS), TPD and LEED.

TPD spectra were collected with the differentially-pumped quadrupole mass spectrometer, and temperature ramping was controlled by a Eurotherm 3216 PID, with a heating rate of 60 K/min [18]. For IRAS experiments, CO₂, D₂O, HCOOH and HCHO were dosed via leak valves, and spectra were collected at grazing incidence with a liquid nitrogen-cooled MCT detector. All spectra were obtained by averaging 2048 interferograms with spectral resolutions of 4 cm⁻¹. For purifying the water from gaseous impurities, a repeated freeze-pump-thaw cycle was applied: cooling down by liquid nitrogen, followed by pumping to $\sim 10^{-6}$ mbar, and warming up.

The *in-situ* NAP-XPS experiments were performed in a second UHV chamber (Novosibirsk), equipped with a VG ESCALAB High Pressure photoelectron spectrometer with a conventional X-ray source with a double Al/Mg anode [25-29]. The spectrometer consists of three main chambers (an analyzer chamber and two preparation chambers), each one pumped by a separate diffusion pump, providing background pressure better than 5×10^{-10} mbar. A special gas cell incorporated into the analyzer chamber allows to measure photoelectron spectra at a pressure up to 0.1 mbar. Due to the short distance between (hot) X-ray anode and sample, the lowest temperature is 343 K. The spectrometer was calibrated using the Au4f_{7/2} (84.0 eV), Ag3d_{5/2} (368.3 eV) and Cu2p_{3/2} (932.7 eV) peaks from metallic gold, silver and copper foils.

The spectra were fitted with XPSPEAK, using Shirley background subtraction and mixed Gaussian–Lorentzian (GL) peak shapes for the Zr, C, and O components. The Zr 3d region was fitted with doublets, restricted by equal FWHM, fixed doublet separation of 2.4 eV (spin orbit splitting) and an area ratio of 2:3 [18]. The assignment of the signals to Zr-clusters and Zr-film was based on previous studies by Li et al. [18].

Possible beam damage or beam-induced surface modifications were examined prior to the actual *in situ* experiments. This was achieved by measuring different positions (spots) on the sample surface (in equilibrium gas pressure) upon using different beam exposure times [30, 31]. Based on the comparison of the results, which indicated no differences for different exposure times, X-ray beam damage could be excluded.

The pressure of the reactants in the high-pressure cell was measured using an absolute pressure sensor (Baratron MKS-121A). A quadrupole mass spectrometer (MS) QME-220 (Pfeiffer, Germany) with differential pumping was used to determine the purity of incoming gases and to analyze the gas phase composition above the sample. Dosing of CO₂ was carried out via a high-precision mass flow controller (Horiba, SEC-Z512MGX). Water was introduced into the cell using a standard leak valve.

3. Results and discussion

3.1. CO₂ TPD

To examine the adsorption properties of the ZrO₂ trilayer film, we have acquired CO₂ TPD spectra. CO₂ typically adsorbs weakly on various oxide surfaces, as revealed previously by TPD. For example, on SrTiO₃(100) the main desorption peak was at 132 K, growing in intensity upon increasing exposure, up to saturation at 1 L [32]. On a ZnO(0001) surface low exposures (<0.75 L) resulted in a peak at 180 K, whereas higher exposures produced a second desorption feature at 125 K. The first was assigned to CO₂ more strongly adsorbed on defect sites, whereas the second was attributed to CO₂ weakly adsorbed on pristine (terrace) sites [33, 34].

Such weakly bonded CO₂ was also observed on the current ultrathin ZrO₂ film. Figure 1 displays TPD spectra of a CO₂ exposure series at 90 K. At 0.2 L dose, a single desorption feature was observed at 117 K, with the intensity increasing at higher (0.5 and 1 L) exposure. Further increase to 1 and 2 L CO₂ did not change the desorption signal, indicating saturation. At all exposures the desorption maximum remained at 117 K, which was assigned to CO₂ likely physisorbed on the ultrathin ZrO₂ (trilayer) film. The adsorption energy was estimated by applying the Redhead equation [35] (desorption maximum 117 K), using a pre-exponential factor for desorption of 10^{13} s^{-1} , yielding a desorption energy of $E_{des} \approx 0.3 \text{ eV}$, which is typical for E_{des} of weakly adsorbed CO₂ (0.3-0.5 eV) on oxides [34]. Multilayer adsorption was not observed, as the desorption temperature of multilayer CO₂ is expected to be below 90 K (e.g. at 85 K for TiO₂ [36]).

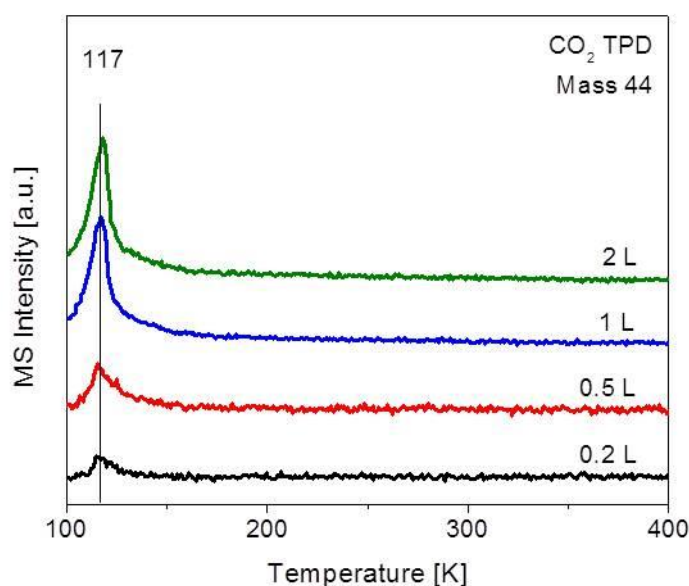


Figure 1: CO_2 -TPD spectra of ultrathin ZrO_2 trilayer film showing a desorption feature at 117 K (surface exposed to 0.2 L, 0.5 L, 1 L and 2 L CO_2 at 90 K). Heating rate was 1 K/s.

3.2. Synchrotron *in situ* NAP-XPS of CO_2 adsorption

The TPD results clearly indicated a weak interaction of CO_2 with the ZrO_2 trilayer film under UHV conditions. In order to examine the interaction at catalytically more relevant conditions, pressure-dependent adsorption experiments were performed from 1×10^{-6} to 1×10^{-1} mbar at room temperature. Zr 3d and C 1s core level signals were examined simultaneously by synchrotron-based *in situ* XPS, as summarized in figure 2 a,b.

The bottom spectra correspond to the clean pristine ZrO_2 trilayer film after preparation (characteristic Zr 3d signals and featureless C 1s region). As revealed by a previous XPS/STM/DFT study, the Zr 3d spectra (figure 2a) showed two prominent features, originating from the ZrO_2 ultrathin film (180.8 eV) and from ZrO_2 clusters (182.4 eV) [15, 18]. The small component (purple) at 179.6 eV is due to (alloyed) Zr of the Pt_3Zr substrate [18]. When the oxide was exposed to up to 1×10^{-3} mbar CO_2 at room temperature, no changes were detected. However, when the CO_2 pressure was increased to 1×10^{-1} mbar, a new Zr 3d species appeared at 181.8 eV (termed Zr_x) and C 1s indicated various C-related surface species (figure 2b).

The total intensity of the Zr 3d signal was dampened in 1×10^{-1} mbar CO_2 because of photoelectron attenuation by the gas phase and the carbonaceous adsorbate layer.

Nevertheless, also the intensity ratios changed. For example, the $Zr_{\text{film}}/Zr_{\text{substrate}}$ ratio of 12.3 for pristine oxide decreased to 7.6 in 1×10^{-1} mbar CO_2 because part of the ultrathin ZrO_2 film was converted to the new unknown Zr_x species. According to literature, features at 284.6 eV are typically assigned to adventitious carbon [37] and those at 285.5 and 286.5 eV may be attributed to different H_xC-O ($x=0-3$) species [38, 39]. The signal at 289.5 eV is characteristic of $O-C=O$, and possible candidates are carboxyls, formates and carbonates [40-44].

The low TPD-derived weak binding energy between CO_2 and ZrO_2 explains the absent interaction in the XPS spectra up to 1×10^{-3} mbar, but not the strong changes at 0.1 mbar. For elevated pressure experiments one must be cautious, however, about possible impurities [21]. In the current case, co-adsorption of water traces may have activated CO_2 and stimulated the formation of different surface carbon species. This was the motivation for an in-depth study of CO_2 and H_2O co-adsorption on the ZrO_2 trilayer film at partial pressures in the mbar range, as discussed below.

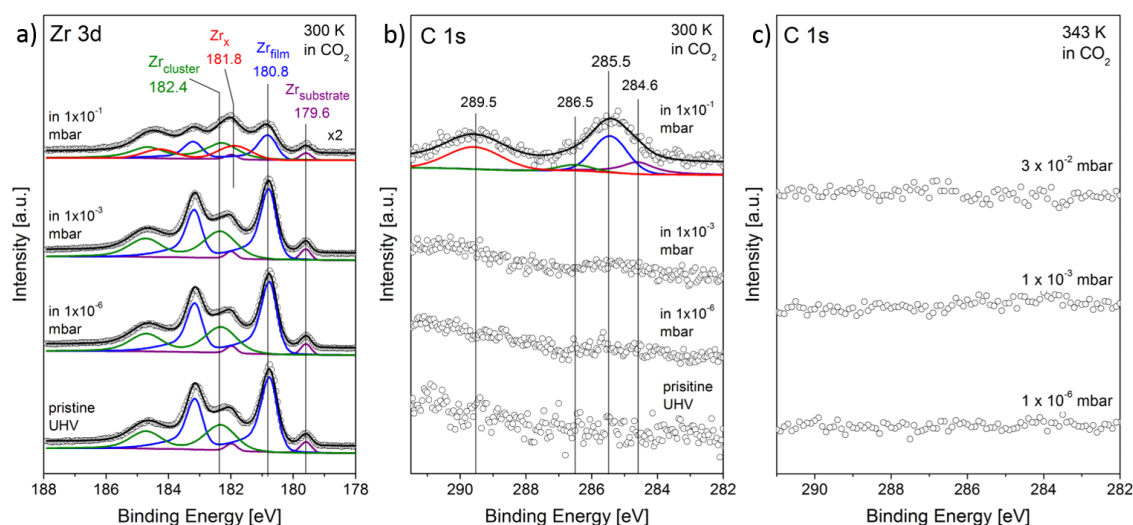


Figure 2: Zr 3d (a) and C 1s (b) synchrotron NAP-XPS spectra of the pristine ZrO_2 trilayer film in UHV and at the indicated CO_2 pressures. All spectra were recorded at 300 K for a photoelectron kinetic energy of ≈ 140 eV. Lab-based C 1s (c) NAP-XPS spectra of pristine ZrO_2 trilayer film at the indicated CO_2 pressures (all spectra were taken at 343 K with Al $K\alpha$)

3.3. Lab based *in situ* NAP-XPS of CO_2 adsorption and $CO_2 + H_2O$ co-adsorption

Two sets of experiments were performed at the Boreskov Institute of Catalysis, using the *in situ* cell of the NAP-XPS setup. First, the interaction of pure CO₂ with the ZrO₂ ultrathin film surface was re-examined, ensuring that no trace amounts of water were present in the gas feed. A maximum pressure of 3×10^{-2} mbar was used to obtain a sufficient signal/noise ratio for reasonable acquisition times (about 30 to 45 min). The XPS spectra in figure 2c confirm that upon exposure to pure CO₂ (up to 3×10^{-2} mbar at 343 K) no C-related species were present on the surface.

Second, a fresh ultrathin ZrO₂ film was prepared and exposed to different partial pressures and ratios of CO₂ and H₂O (5 mixtures), monitored by *in situ* NAP-XPS (figure 3). Already for the 1st mixture of 1×10^{-6} mbar CO₂ and 1×10^{-6} mbar H₂O, the C1s spectrum revealed two species at 284.4 and 286.4 eV. As mentioned, the former is due to adventitious carbon [37], and the latter to H_xC-O species [38, 39]. When the H₂O pressure was increased to 3×10^{-4} mbar (2nd mixture, CO₂ still 1×10^{-6} mbar), no significant change was registered. In the next step the CO₂ pressure was increased to 7×10^{-4} mbar (3rd mixture, H₂O 3×10^{-4} mbar) and a new C1s signal at 285.5 eV appeared (i.e. possibly another H_xC-O species) [45]. When the CO₂ pressure was further increased to 3×10^{-2} mbar (4th mixture, H₂O remained 3×10^{-4} mbar), an additional signal at 288.3 eV was observed (probably resulting from a O-C=O species) [40-42, 44]. A final increase of the H₂O pressure to 3×10^{-3} mbar (5th mixture, CO₂ 3×10^{-2} mbar) did not induce significant changes (apart from slightly increasing the H_xC-O species). Apparently, the co-adsorption of H₂O and CO₂ produced various surface carbonaceous species.

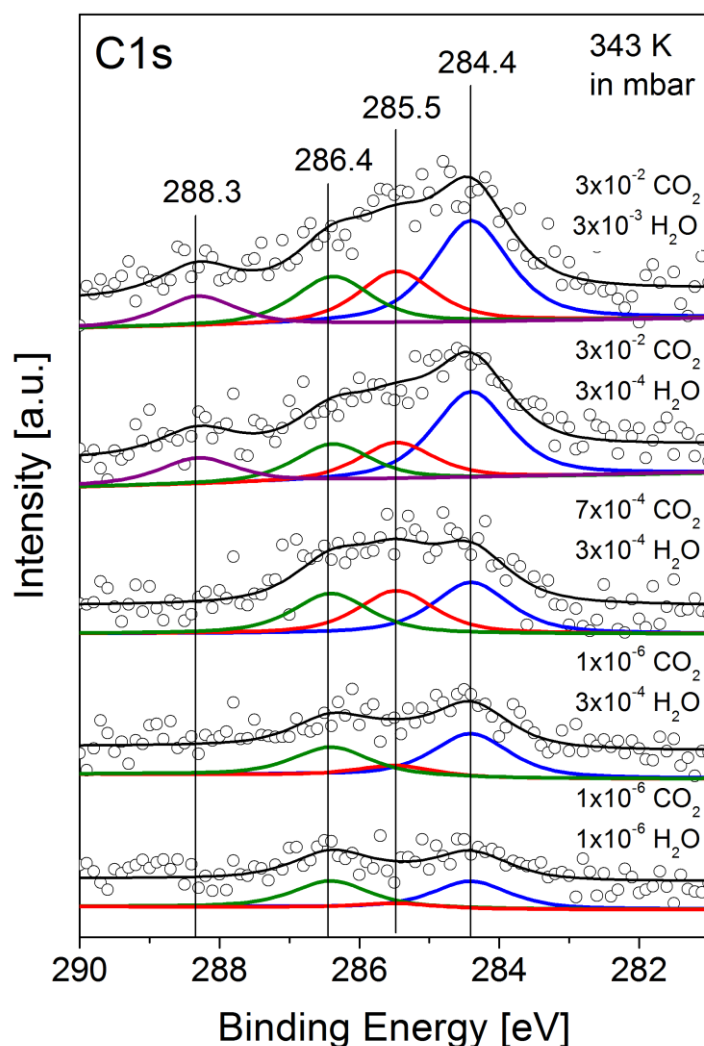


Figure 3: Lab-based NAP-XPS C 1s spectra of the pristine ZrO_2 trilayer film at various CO_2 and H_2O partial pressures. All spectra were taken at 343 K with Al K α .

The Zr 3d region was monitored simultaneously, as shown in figure 4. For the highest CO_2 and H_2O pressure (3×10^{-2} mbar CO_2 and 3×10^{-3} mbar H_2O), a new Zr_x species appeared at a binding energy of 181.7 eV. This was in accordance with the previous synchrotron spectra (figure 2a) showing a similar Zr_x species. As mentioned, the change in Zr 3d may be attributed to a partial conversion of Zr_{film} to new Zr_x species.

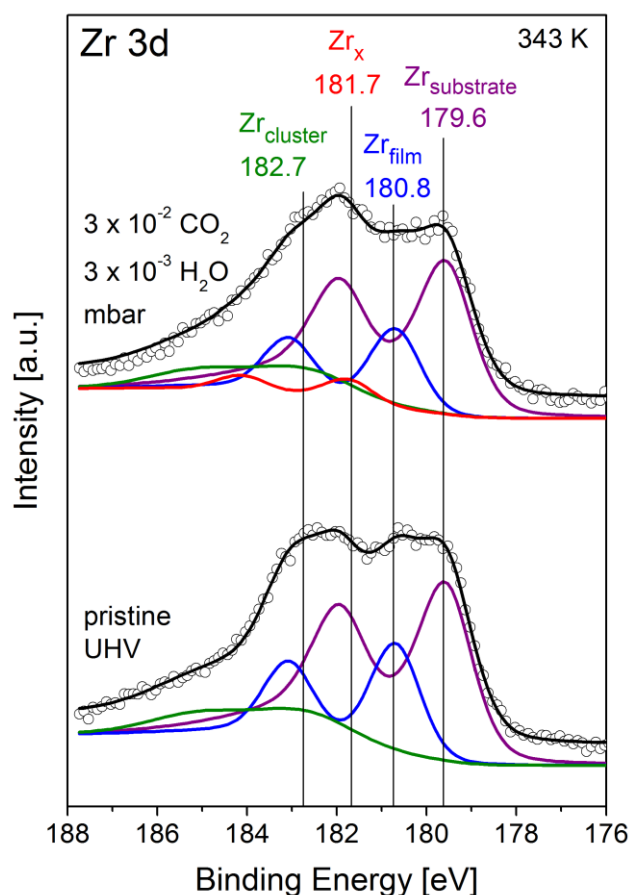


Figure 4: Lab-based NAP-XPS Zr 3d spectra of pristine ZrO_2 trilayer film measured in UHV and upon exposure to 3×10^{-2} mbar CO_2 and 3×10^{-3} mbar H_2O . In $\text{CO}_2/\text{H}_2\text{O}$ a new Zr_x species appeared at 181.7 eV. All spectra were taken at 343 K with Al K α .

Clearly, the surface sensitivity (i.e. information depth) was much higher (lower) for the synchrotron measurements (~ 140 eV kinetic energy; IMFP of about 0.6 nm) than for laboratory *in situ* XPS (~ 1300 eV kinetic energy; IMFP of about 2 nm). Apparently, the $\text{Zr}_{\text{substrate}}$ signal is much stronger for the Boreskov setup. However, the ratio of Zr_x to Zr_{film} is nearly the same for both setups.

In a next step, we have investigated the thermal stability of the C-related surface species formed in 3×10^{-2} mbar CO_2 and 3×10^{-3} mbar H_2O at 343 K. As shown in figure 5, the O-C=O species at 288.6 eV fully disappeared when the sample was heated to 423 K. The signal intensity of the $\text{H}_x\text{C-O}$ species (285.5 and 286.4 eV) decreased at 423 K but almost completely vanished at 523 K. At 523 K, only the surface carbon at 284.4 eV remained. After

the heating series, the sample was cooled in $\text{H}_2\text{O} + \text{CO}_2$ back to 343 K, leading to the re-appearance of the surface $\text{H}_x\text{C-O}$ and O-C=O species. The final step was removal of the gas phase at 343 K, showing that the surface species were stable upon evacuation (with slightly decreased intensity).

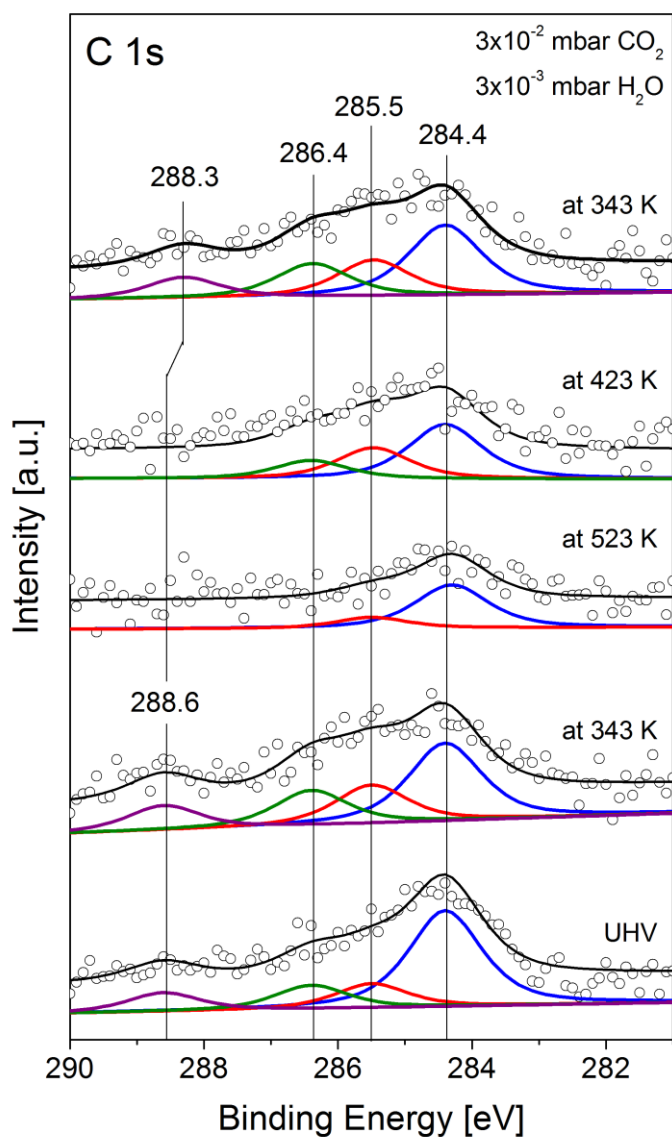


Figure 5: Lab-based NAP-XPS C 1s spectra of trilayer ZrO_2 in 3×10^{-2} mbar CO_2 and 3×10^{-3} mbar H_2O at different temperatures and after evacuation. First, the surface was heated stepwise to 523 K, followed by cooling down in the same gas environment. The lowest spectra was acquired after evacuation in UHV. All spectra taken with Al K α .

In summary, *in situ* XPS indicated that (pure) CO₂ did not interact with the ultrathin ZrO₂ film at 343 K, as expected from TPD. However, co-dosing of CO₂ and H₂O induced the formation of surface species with C 1s binding energies of 284.4 eV (carbon), 285.5 and 286.4 eV (different H_xC-O species, likely candidates are formaldehyde and dioxymethylene) and 288.3 to 288.6 eV (O-C=O species, possibly formate). Beside the already discussed oxide surfaces, similar findings were also obtained by XPS for co-adsorption on metal surfaces, e.g. for Al(110) [44, 45]. Furthermore, the interaction of CO₂ and H₂O at elevated pressure led to formation of a new unknown Zr_x species.

3.4. IRAS of HCOOH and HCHO adsorption on ZrO₂

In order to validate or improve the interpretation of the XPS results of H_xC-O and O-C=O species, IRAS spectra of formic acid (HCOOH) or formaldehyde (HCHO) adsorbed on the ZrO₂ trilayer film were acquired (both serving as reference substances). The expected vibrational bands include stretching and deformation modes of CH, CH₂, O-C-O and C=O. Figure 6a displays the IRAS spectrum of adsorbed HCOOH at 343 K. In 1×10⁻⁶ mbar HCOOH, two absorption bands at 1593 and 1395 cm⁻¹ were detected, indicating the typical wavenumber splitting (~200 cm⁻¹) of ν(OCO) of (bridge bonded) bidentate formate (HCOO) [46]. Thus, the 1593 cm⁻¹ band is assigned to ν_{as}(OCO) and the 1395 cm⁻¹ band is assigned to ν_s(OCO). The δ(CH) signal was not observed because its absorption band (~1360 – 1390 cm⁻¹) overlaps with ν_s(OCO) [48].

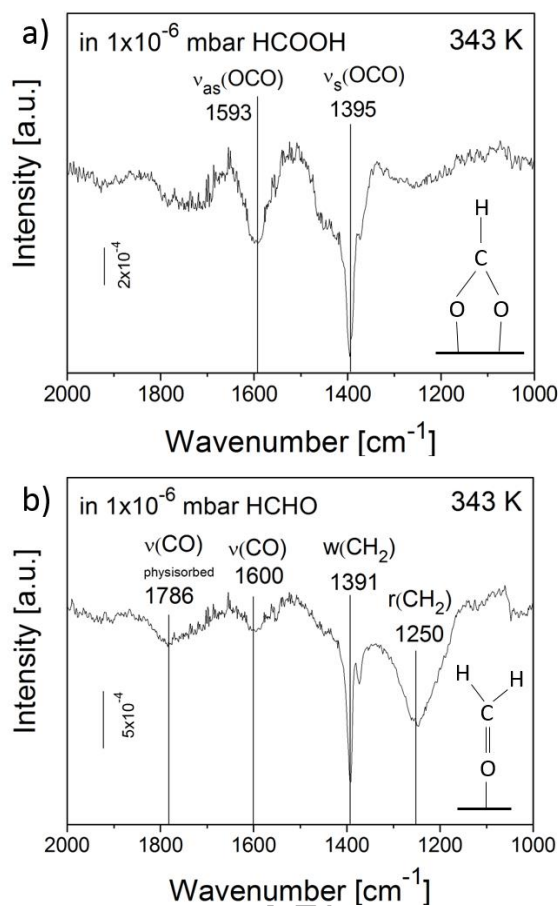


Figure 6: IRAS spectrum of a) HCOOH and b) HCHO adsorption on the ZrO₂ thin film, taken in 1 × 10⁻⁶ mbar at 343 K.

In analogy, figure 6b shows the IRAS spectrum of HCHO adsorption on the ZrO₂ trilayer film. In 1 × 10⁻⁶ mbar HCHO, absorption bands were observed at 1786, 1600, 1391 and 1250 cm⁻¹. Referring to literature, they can be assigned to ν(C=O) modes of physisorbed HCHO and ν(C=O), ω(CH₂), ρ(CH₂) modes of chemisorbed HCHO, respectively [48, 49]. The ν(C=O) mode is red-shifted relative to the value reported for solid formaldehyde (1740 cm⁻¹), indicating that the chemisorbed HCHO molecule binds to the cationic Zr site through O [49].

3.5. IRAS of CO₂ and H₂O co-adsorption on ZrO₂

Figure 7 collects the IRAS spectra acquired during CO₂ and H₂O co-adsorption at pressure conditions identical to those of the *in situ* NAP-XPS measurements. Exposure to (pure) CO₂ did not produce any signals, analogous to NAP-XPS (cf. Figure 2c).

When the ZrO₂ thin film was exposed to 1 × 10⁻⁶ mbar CO₂ and 1 × 10⁻⁶ mbar H₂O, a band at 1265 cm⁻¹ was observed, which can be assigned to the ρ(CH₂) mode. At a H₂O partial

pressure of 3×10^{-4} mbar, the intensity of the $\rho(\text{CH}_2)$ mode increased and additional features were detected at 1383 and 1455 cm^{-1} , typical of $\omega(\text{CH}_2)$ and $\delta(\text{CH}_2)$ [48]. However, the band at 1383 cm^{-1} may also be related to $\nu_s(\text{OCO})$ of formate. The weak signal at $\sim 1600 \text{ cm}^{-1}$ can be attributed to $\nu(\text{CO})$ of formaldehyde and/or $\nu_{as}(\text{OCO})$ of formate.

Upon increasing the CO_2 pressure to 7×10^{-4} mbar (3×10^{-4} mbar H_2O), no significant change was registered by IRAS. Finally, when the pressure of CO_2 and H_2O were increased to 3×10^{-2} mbar and 3×10^{-3} mbar, respectively, strong absorption bands appeared at 1735 and 1290 cm^{-1} , which can be assigned to $\nu(\text{C=O})$ and $\nu(\text{C-OH})$ vibrational modes of COOH [50].

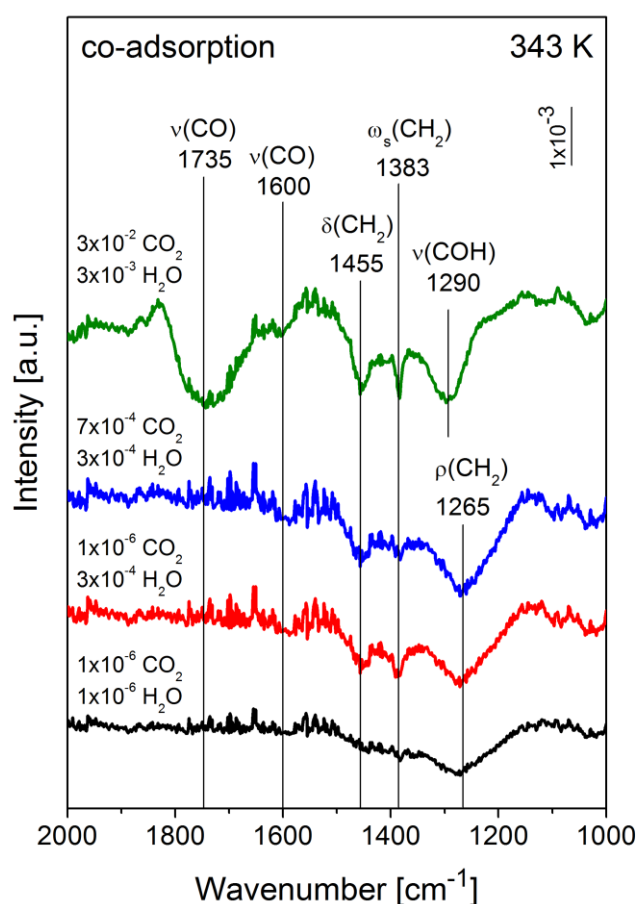


Figure 7: In situ IRAS spectra of different CO_2 and H_2O mixtures on ultrathin ZrO_2 at 343 K (spectrum at the highest pressure measured after evacuation).

3.6. Schematics of CO_2 and H_2O co-adsorption and reaction on ZrO_2

Based on the results discussed so far, it is quite clear that (pure) CO_2 did not interact with the well-ordered ZrO_2 trilayer surface under the applied experimental conditions (UHV to

elevated pressures around/above room temperature). In contrast, in the presence of water, reactive CO_2 adsorption took place and different adsorbed carbonaceous species were spectroscopically observed. This is in line with previous studies of tetragonal and monoclinic ZrO_2 powders, for which CO_2 adsorption was reported in the presence of surface hydroxyl groups [3, 17]. Similarly, the CO_2 adsorption energy on TiO_2 increased when adsorbed water was present [10].

Combining data from *in situ* NAP-XPS and IRAS, the observed $\text{H}_x\text{C-O}$ and O-C=O surface species could be assigned. The detected C 1s signals at 285.5, 286.4 and 288.3 eV were assigned to formaldehyde, dioxymethylene and formate, respectively [42]. The results show that the presence of water did not only activate CO_2 adsorption on ZrO_2 trilayer film, but even more the activated CO_2 reacted with surface hydrogen/hydroxyl groups (from H_2O) and formed adsorbed species such as formate, dioxomethylene and formaldehyde, see figure 8. Reaction of adsorbed CO_2 with surface hydroxyl groups to formate species was reported previously for ZrO_2 and ZnO powders. This step is particularly important for methanol synthesis from CO_2 [4, 51].

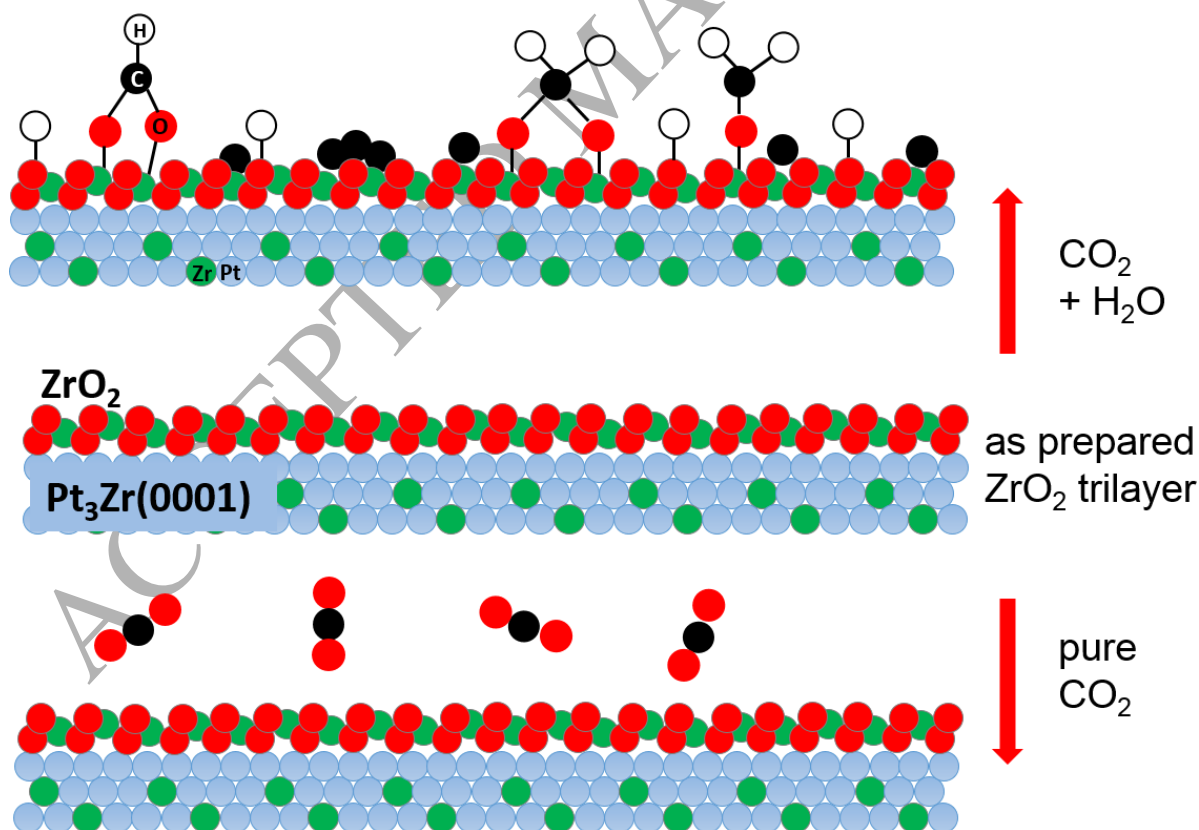


Figure 8: Scheme illustrating CO_2 and $\text{CO}_2 + \text{H}_2\text{O}$ exposure of the ZrO_2 trilayer surface (grown on $\text{Pt}_3\text{Zr}(0001)$). Upon co-adsorption different surface carbonaceous species were formed.

In addition, the spectroscopic results revealed that during these processes part of the Zr^{4+} of the ZrO_2 trilayer film was transformed into a new Zr_x species, which is currently unknown (but is likely related to film restructuring). For its identification, and a more detailed characterization of the adsorption sites and geometry of the different carbonaceous species, theoretical calculations are currently performed.

4. Conclusions

CO_2 adsorbed only weakly on ultrathin ZrO_2 trilayer film in UHV and desorbed already at 117 K (E_{des} about 0.3 eV). Even at low mbar pressures, (pure) CO_2 did not adsorb/interact with the ZrO_2 surface at 343 K. However, CO_2 was activated by the presence of H_2O and adsorbed forming different adsorbed carbonaceous species. *In-situ* NAP-XPS in the 10^{-2} mbar range revealed the formation of $\text{H}_x\text{C-O}$ and O-C=O species, upon exposing the ultrathin ZrO_2 film to a mixed feed of CO_2 and H_2O . During this process, Zr^{4+} of the ultrathin ZrO_2 film was partially converted into an unknown Zr_x species, likely related to film restructuring. IRAS spectra of adsorbed reference molecules (HCOOH and HCHO) enabled the assignment of the adsorbed species, identifying adsorbed formate, dioxymethylene and formaldehyde. Accordingly, in the presence of water (i.e. hydroxyl groups) CO_2 could be activated and adsorbed on the ZrO_2 surface forming different surface intermediates. Similar activation processes may be important in the context of methanol synthesis on oxide-supported metal catalysts.

Acknowledgements

This work was supported by the Austrian Science Fund (FWF) through project SFB “FOXSI” F4502. The BIC team thanks budget project No. AAAA-A17-117041710078-1 for Boreskov Institute of Catalysis. We thank MAXLAB for providing beamtime (proposal 20140032) and the SPECIES beamline staff for support.

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Graphical abstract

