PHOTOEMISSION STUDY OF CO$_2$
ADSORBED ON K/Cu(110). ANALYSIS
OF ADSORBATE INDUCED STRUCTURES

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(Received November 13, 1998)

Using photoemission spectroscopy, adsorption and reaction of CO$_2$ on potassium modified Cu(110) were studied. In agreement with published results of thermally programmed desorption, apart from carbonate and carbon monoxide as the disproportionation reaction products, a linear CO$_2$ molecule and a bent active CO$_2$($-$) species were identified. The reaction paths are independent on the potassium precoverage but the number of CO$_3$ molecules increases with the number of potassium adatoms. The presence of the CO$_2$($-$), stable up to 200 K, suitable for the reactivity of the interface in respect of the methanol synthesis, could be confirmed in the complex valence band spectra by occurrence of the characteristic peak at binding energy of 6.8 eV.

PACS numbers: 79.60.Jv, 33.60.–q, 82.80.Pv

1. Introduction

Investigations of CO$_2$ adsorption on alkali modified copper surfaces using surface sensitive spectroscopies are interesting in the field of catalysis. It is known that in the methanol synthesis of CO,CO$_2$/H$_2$ mixture over the copper supported on zinc oxide catalyst, CO$_2$ is the main source of methanol. Consequently, the question of CO$_2$ applying as a reactant in hydrocarbons synthesis motivates such study on well-defined surfaces.

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Adsorption and reaction of CO$_2$ on alkali modified (or not) various metal surfaces were studied by photoelectron spectroscopy, thermally programmed desorption (TPD) and changes in work function ($\Delta\Phi$) [1-12]. It was shown that the adsorption of CO$_2$ and the attendant processes are substrate and face specified. Two basic species are detected on the surface: an undistorted CO$_2$ linear species of physisorbed state and a bent CO$_2^-$ anionic species of chemisorbed state. The relative concentration of the physisorbed species can be varied by changing the background CO$_2$ pressure, the surface temperature and photon or electron irradiation.

Although CO$_2$ does not adsorb on Cu(110) surface at temperatures above 110 K, the presence of preadsorbed potassium, even in small amounts, extremely increases the sticking coefficient of CO$_2$. TPD of CO$_2$ adsorbed at 110 K on the K/Cu(110) interface shows the peaks whose intensities and positions depend on the potassium coverage [6]. High intensity 44 a.m.u. peak appears at 135 K and corresponds to the physisorbed state. Relatively smaller peak at temperature range of 195–200 K corresponds to CO$_2$ chemisorbed state. High temperature 44 a.m.u. region consists of a broad feature around 430 K for small K coverages which develop into two high intensity peaks, depending on the potassium coverage, at temperature intervals of 475–500 K and 525–550 K for higher K coverages [9]. The different states of CO$_2$ are characterized basing on the energy positions and peak intensities of C 1s and O 1s core lines [6]. Both physisorbed CO$_2$ and chemisorbed anion CO$_2^-$ are detected at 110 K. The chemisorbed species decomposes onto CO$_3$ and CO with CO desorbing at 210 K.

Inspection of the valence band region of the CO$_2$/K/Cu(110) interface recorded in photoelectron spectroscopy using synchrotron radiation (PSSR) shows on the presence of different forms of adsorbed CO$_2$, adsorbed CO and chemisorbed CO$_3$. The spectra obtained with exciting photon energy of 125 eV, due to the presence of two Cu 3d satellites at binding energies (relative to the Fermi level) of 14.3 and 11.6 eV, could not be easily decomposed into its components [7]. The aim of this paper is to present new description of the levels in the valence band obtained in PSSR with the help of low energy electron diffraction (LEED) and $\Delta\Phi$ results. The incident photon energy was chosen as 40 eV to reduce the satellites intensity less than 1% of the 3d emission intensity [13] and increase ionization cross-sections of peaks induced by adsorbed molecules. Identification of the species as a physisorbed CO$_2$ and an ionic, bent CO$_2^-$ was done by means of multi-component spectra analysis. The results of the present investigations show more definitively assignment of the spectra of the CO$_2$/K/Cu(110) interface.

2. Experimental

The experiments were performed in a VG CLAM-2 electron spectrometer on the SX700 beam line at the Aarhus synchrotron radiation source ASTRID [14]. The pressure of residual gases in the experimental chamber was below $1.33 \times 10^{-8}$ Pa during measurements. The photoelectron spectra were measured for electron emission along the surface normal, typically with exciting photon energy of 40 eV. Due to the influence of synchrotron radiation on the stability of the adsorbate layer the period of accumulation of the data was reduced to obtain the
signal to noise ratio necessary for the analysis. The overall resolution was evaluated as 200 meV in the used photon energy. The binding energy, BE_F, is related to the Fermi energy, determined as the inflection point of the Fermi edge. The IBM PC processing software was elaborated by the Synchrotron Surface Group at the Aarhus University. Work function changes were determined from the shift of the low energy tail of the secondary electron peak with a sample bias of -9 V relative to the ground potential.

The Cu(110) monocrystal of dimension 10 x 10 x 2 mm^3 mounted to the manipulator holder through a tungsten wire (diameter of 0.5 mm) loop, could be cooled down to around 110 K and heated over 1000 K. The sample temperature was controlled by a chromel-alumel thermocouple fixed in a hole made at the upper edge of the sample. The surface of the crystal was cleaned by Argon ion bombardment followed by annealing to 950 K. The cleanliness of the initial and potassium predosed surface was checked by PSSR using higher photon energies in order to reach K and L shell electrons of the characteristic impurities (C, O, P, and S). Before adsorption the sample showed a sharp (1 x 1) LEED pattern with low background intensity. The adsorption temperature did not exceed the temperature giving rise to the adsorbate induced substrate reconstruction, i.e. for K/Cu(110) T(rec.) = 158 K [15].

Potassium was evaporated from a SAES zeolite source mounted approximately 5 cm away from the copper surface [16]. The quantity of deposited potassium was evaluated from the measured work function changes [17] and the density of the saturated potassium monolayer on Cu(110) is equal to n(K) = 3.70 x 10^{14} at./cm^2. The coverage, Θ_K, is expressed in terms of adsorbate monolayers, AML, i.e. one monolayer Θ_K = 1 AML corresponds to the mentioned density. It is easy to calculate that the saturated potassium overlayer expressed relative to the density of the substrate layer of atoms, SML, corresponds to the coverage of 0.34 SML.

CO_2 was admitted to the whole chamber via a dosing system, typically dose of 1 L (langmuir) corresponded to 20 s of 6.65 x 10^{-6} Pa. It is known that within a CO_2 pressure range of 10^{-6} - 10^{-4} Pa, CO_2 interacts with ion pumps as well as hot filaments loading to formation of CO and its preferential adsorption on the sample (e.g. [1]). The gas adsorption experiments were performed with extreme care; the dosing system was flushed repeatedly with CO_2 and the ion pump was closed during admission of CO_2. The filament of the ionization vacuum meter was switched off as quickly as possible, i.e. when the steady conditions of the pressure were attained. Upon CO_2 adsorption at low temperature used, no sharp LEED pattern was observed, indicating on disordered adlayer. However, the photoemission spectroscopy can provide information on the identity and bonding of an adsorbed species and fully characterize the interface. Closely related to the solid CO_2, the often used model [1] of the relative orientation of the linear CO_2 molecules within a two-dimensional layer is postulated. For this model of a T-shaped arrangement, with the distance between C and nearest O atom of a second molecule of 0.296 nm [8], the number of molecules that complete the hypothetical monolayer on Cu(110) is equal to the density in the “solid CO_2” layer, i.e. to n(CO_2) = 5.89 x 10^{14} molec./cm^2.
3. Results

Adsorption of CO$_2$ on the K/Cu(110) interface can be characterized mainly on the basis of presented results with potassium coverage corresponding to work function change ($\Delta \Phi$) before minimum ($\Theta_K < 0.5$ AML). Exposition of K/Cu(110) in CO$_2$ increased the work function monotonically with saturation starting above 5 L of dose. For example, for the potassium adsorbed Cu(110) with the $\Delta \Phi$ decrease of $-2.84$ eV ($\Theta_K = 0.45$ AML), the followed adsorption of CO$_2$ increased $\Delta \Phi$ of $+1.48$ eV relative to the K-predosed surface. The secondary emission, measured as the area under the secondary peak, increased approximately 6 times after 0.45 AML K adsorption and then decreased 3.5 times after exposition in CO$_2$.

The 0–20 eV BE$_F$ range of the valence band spectrum of the K/Cu(110) interface consists of the broad $s-p$ band near the Fermi level, the Cu 3d band complex between 2–5 eV, whose shape and relative intensity depends on the angular arrangement of the experiment and energy of the photon beam, and finally the K 3p level at 18.2 eV. Because of the low cross-section for the K 4s level excitation (with BE$_F = 0.4$ eV) there was no evidence of this contribution to the total PSSR spectrum. During adsorption of CO$_2$ on the 0.42 AML K/Cu(110) interface the shift of the K 3p peak position towards lower BE$_F$ of $-0.5$ eV at saturation was observed. No change in the full width at half maximum (FWHM) equal to 0.90 eV was detected. At saturation with CO$_2$, the intensity of the K 3p line, represented by the area under the peak, increased about twice.

The photoemission spectrum of the CO$_2$/K/Cu(110) interface obtained at $T(\text{ads}) = 125$ K is shown in Fig. 1. The Cu(110) sample with potassium coverage of $\Theta_K = 0.38$ AML was exposed to 10 L of CO$_2$. The energy distribution curve, apart from the Cu $s-p$ with Cu 3d bands and the K 3p level, contains several series of overlapping peaks in the region of 5–16 eV BE$_F$. Heating the interface to 230 K, i.e. to the temperature greater than CO$_2$(phys.) desorption (135 K), K-induced substrate reconstruction (158 K), CO$_2$(—) desorption (195–200 K) and CO desorption (210 K), decidedly simplifies the BE$_F$ region leaving three distinct features (Fig. 2). Three peaks of BE$_F$ of 6.0, 9.5, and 11.8 eV were assigned to the $1e''/4e'$, $1a2''/3e'$ and 4a1 orbitals of carbonate, CO$_3$, respectively. Therefore, the 5–16 eV spectrum of carbonate is characterized by three features with the one at 9.5 eV of the highest amplitude (Table). It is worth noting that after CO$_2$(phys.) desorption and heating over $T(\text{rec.})$, apart from the sharpening of the peaks, no changes were registered. Such behaviour indicates on the ordering process on the interface which accompanies substrate reconstruction.

Inspection of the energy distribution curve of Fig. 1 shows two dominating maxima at BE$_F$ of around 12 and 9.6 eV. The first one could be attributed only to the strongest line of CO$_2$ i.e. to the 4r orbital (Table). The second maximum corresponds to the highest line of CO$_3$, namely to the $1a2''/3e'$ joint orbitals. The BE$_F$ of the 4a1 orbital of CO$_3$ is very close to that one of the 4$\sigma$ orbital of CO, leading to overlap between peaks of two species presented on the interface under investigation. After linear background subtraction from the region of 5–16 eV BE$_F$ of the spectrum, two triplets consisting of the Gaussian peaks were fitted to the experimental points. The relative amplitudes of the lines in the groups,
Fig. 1. Decomposition of the photoemission spectrum of the 10 L CO2/0.38 AML K/Cu(110) interface (not smoothed data) obtained at $T = 125$ K. The analysis order of the data is as follows. First, after linear background subtraction, the CO ($1\pi/5\sigma$, $4\sigma$, $4\sigma$-satellite) and CO$_2$($-$) orbitals ($1e''/4e'$, $1a2''/3e'$, $4a1$) fitted to the data are subtracted. The resulting difference spectrum shows evidence of two sets of peaks which corresponds to the CO$_2$ ($1\pi_3$, $1\pi_0/3\sigma_0$, $4\sigma_0$) and CO$_2$($-$) orbitals ($1a2/4b2$, $5a1/1b1/3b2$, $4a1$). For clarity, only the background and the individual components resulting from the best fit procedure are shown as the solid lines.

Fig. 2. The valence band spectrum of the CO$_2$/K/Cu(110) interface obtained by deposition of 0.42 AML K and dosing 12 L of CO$_2$ at $T(\text{ads.}) = 125$ K followed by heating to 230 K (not smoothed data). Three well defined features at BE$_F$ of 6.0, 9.5, and 11.8 eV correspond to the CO$_3$ peaks of the $1e''/4e'$, $1a2''/3e'$, and $4a1$ orbital, respectively.
Parameters of orbitals determined as the best fit of Gaussian lines to the data from different interfaces. The intensity \( I \) is related to the peak amplitude \( A \) and the FWHM by the equation \( I = 1.062 \times A \times \text{FWHM} \). Binding energy and FWHM is expressed in eV and \( A \) in arbitrary units, the same in given group of peaks.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Orbital</th>
<th>( \text{BE}_F )</th>
<th>FWHM</th>
<th>( A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2/K/\text{Cu}(110) )</td>
<td>( \text{CO}_3 ; 1e''/4e' )</td>
<td>6.00</td>
<td>0.92</td>
<td>0.175</td>
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<tr>
<td>adsorbed at 125 K and</td>
<td>( \text{CO}_3 ; 1a2''/3e' )</td>
<td>9.50</td>
<td>1.04</td>
<td>0.255</td>
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<td>heated to 230 K, this work</td>
<td>( \text{CO}_3 ; 4a1 )</td>
<td>11.8</td>
<td>0.60</td>
<td>0.095</td>
</tr>
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<td>( \text{CO}/\text{K}/\text{Cu}(110) )</td>
<td>( \text{CO} ; 1\pi/5\sigma )</td>
<td>8.70</td>
<td>1.80</td>
<td>0.178</td>
</tr>
<tr>
<td>adsorbed at 118 K [17]</td>
<td>( \text{CO} ; 4\sigma )</td>
<td>11.8</td>
<td>1.20</td>
<td>0.512</td>
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<tr>
<td></td>
<td>( \text{CO} ; 4\sigma\text{-satellite} )</td>
<td>13.5</td>
<td>1.80</td>
<td>0.158</td>
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<td>( \text{CO}_2/K/\text{Cu}(110) )</td>
<td>( \text{CO} ; 1\pi/5\sigma )</td>
<td>8.90</td>
<td>1.60</td>
<td>0.078</td>
</tr>
<tr>
<td>adsorbed at 125 K, this work</td>
<td>( \text{CO} ; 4\sigma )</td>
<td>11.9</td>
<td>1.20</td>
<td>0.220</td>
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<tr>
<td></td>
<td>( \text{CO} ; 4\sigma\text{-satellite} )</td>
<td>13.5</td>
<td>1.70</td>
<td>0.059</td>
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<tr>
<td></td>
<td>( \text{CO}_3 ; 1e''/4e' )</td>
<td>5.95</td>
<td>0.92</td>
<td>0.135</td>
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<tr>
<td></td>
<td>( \text{CO} ; 1a2''/3e' )</td>
<td>9.64</td>
<td>1.04</td>
<td>0.200</td>
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<tr>
<td></td>
<td>( \text{CO}_3 ; 4a1 )</td>
<td>12.0</td>
<td>0.70</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>( \text{CO}_2 ; 1\pi_G )</td>
<td>8.50</td>
<td>0.70</td>
<td>0.088</td>
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<tr>
<td></td>
<td>( \text{CO}_2 ; 1\pi_U/3\sigma_U )</td>
<td>12.9</td>
<td>0.88</td>
<td>0.146</td>
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<td>( \text{CO}_2 ; 4\sigma_G )</td>
<td>14.8</td>
<td>1.54</td>
<td>0.040</td>
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<td></td>
<td>( \text{CO}_2^- ; 1a2/4b2 )</td>
<td>6.8</td>
<td>0.80</td>
<td>0.0217</td>
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<td></td>
<td>( \text{CO}_2^- ; 5a1/1b1/3b2 )</td>
<td>9.1</td>
<td>0.50</td>
<td>0.0512</td>
</tr>
<tr>
<td></td>
<td>( \text{CO}_2^- ; 4a1 )</td>
<td>11.0</td>
<td>0.96</td>
<td>0.0857</td>
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their FWHM's and \( \text{BE}_F \)'s positions were fixed and/or restricted to the narrow interval of values according to the determined quantities indicated in the upper part of Table. After subtraction of the peaks corresponding to the CO and \( \text{CO}_3 \) orbitals, the difference spectrum showed the presence of further six features, which could be fitted by six Gaussian functions. Three of them at \( \text{BE}_F \) of 8.5, 12.9, and 14.8 eV represent the \( \text{CO}_2 \) orbitals, i.e. the \( 1\pi_G \), \( 1\pi_U/3\sigma_U \) and \( 4\sigma_G \), respectively. Remaining ones at \( \text{BE}_F \) of 6.8, 9.1, and 11.0 eV were assigned as corresponding to the \( \text{CO}_2^- \) orbitals, namely to the \( 1a2/4b2 \), \( 5a1/1b1/3b2 \) and \( 4a1 \), respectively. The results of the synthesis are shown as the solid lines in Fig. 1 and collected in Table. For clarity, the groups of peaks of different species are depicted separately on the graph once again. Despite of the above synthesis seems to be arduous and time consuming, it is believed that it provides univocally determined results. The procedure which was adopted to the complicated valence band bases on the parameters well established from the simple, reference spectra.

The photoemission spectra of the \( \text{CO}_2/K/\text{Cu}(110) \) interface for different \( \Theta_K \) show qualitatively the same reaction paths. However, with increasing K coverage
the yield of the disproportionation increases which is observed in Fig. 3. Intensities of both: the $1e''/4e'$ and $1a_2''/3e'$ orbitals of CO$_3$ increase with $\Theta_K$. Evaluated amplitude of the $1e''/4e'$ orbital, as depicted in the inset in Fig. 3, follows a sigmoidal curve with $\Theta_K$, saturating at higher potassium coverages. Thus, the number of produced CO$_3$ molecules could be correlated with the length of the K-islands edges (not the interior of the islands) on Cu(110).

4. Discussion

The increase in work function during dosing of CO$_2$ indicates on a charge transfer from the K/Cu(110) substrate to adsorbing molecules. Although CO and carbonate species appears at temperature of adsorption, here $\Delta \Phi$ increases more than for CO adsorption alone [17]. Thus, it is evidence of the formation of negatively charged CO$_2$(−), which agrees well with published increase of $\Delta \Phi$ on the K/Fe(film) influenced by a carbon dioxide anionic species [3]. While the chemisorbed species increases work function, the physisorbed linear CO$_2$ molecules can decrease it again.

Existence of mentioned anionic carbon dioxide molecule is unambiguously confirmed by the PSSR. The energy distribution curve shows the presence of the CO, CO$_3$, CO$_2$ and CO$_2$(−) species on the CO$_2$/K/Cu(110) interface at temperature of adsorption. However, there is no indication of CO$_2$ dissociation to adsorbed CO and O, i.e. no oxygen orbitals were found. Such behaviour is opposite to finding on a stepped Cu(332) [5]. It means that the carbonate is created by the reaction of disproportionation in which anionic carbon dioxide takes part. While the undistorted CO$_2$ molecule forms a linear CO$_2$–metal bond, the anionic species has a bent geometry with the angle between the C–O bonds of around 135°. In the
interaction with the metallic substrate they can exhibit three modes of coordination: (a) a pure carbon coordination (symmetrical upward) or (b) a pure oxygen bidentate coordination (symmetrical downward) or (c) a mixed carbon–oxygen coordination (asymmetrical). Theoretical calculations showed that (b) and (c) lead to more stable arrangements than (a) [8]. It is likely that CO$_2$ molecules adsorbing near the coadsorbed K atom on the Cu(110) surface react to surface carbonate through intermediate (b) and (c) configuration. This is supported by the fact that the carbonate species is readily formed on other surfaces by reaction of CO$_2$ with an oxygen precovered surface. The (c) coordination is accompanied by an elongation of the C–O bond distance of atoms directly involved in the interaction with the substrate. The reaction of disproportionation is favored if the binding energy for adsorbed oxygen is smaller than the energy gained by the formation of a surface carbonate. The (a) geometry relative to the substrate is less stable and has tendency to interact with neutral CO$_2$ e.g. to form stable anionic dimer moiety. Thus, in consequence the CO$_2$($-$) anion can be solvated by other neutral CO$_2$. The chemisorbed CO$_2$($-$) was stable on the interface up to 200 K and above this temperature it desorbed, i.e. when the temperature rises to 200 K, the CO$_2$($-$) peaks vanish with no further increase in the amplitude of the CO$_3$ peaks.

It is known that molecular fragments can take up particular, well-defined orientations relative to the substrate. For example, the (1 x 2) surface structure was observed on the CO$_3$/Ag(110) interface [18, 19]. The adsorption geometry of the ad-molecule is that the carbonate is bounded to Ag mainly through the oxygen atoms. Assuming the same structure for the CO$_3$/Cu(110) interface, i.e. the (1 x 2) surface with a missing row reconstruction, the number of carbonate molecules that complete a monolayer is $n$(CO$_3$) = $5.43 \times 10^{14}$ molec./cm$^2$. Taking into account the densities of different species on Cu(110) it can be assumed that each CO$_2$ molecule occupies 1.08 adsorption sites of CO$_3$ or 0.68 adsorption sites of CO. Thus, the reaction of disproportionation reduces the total gas coverage of the surface, e.g. from 100% to 88% for all CO$_2$ molecules reacting. In such a case, during reaction without desorption of any species, there is no origin of blocking mechanism to the formation of the CO$_3$+CO complex due to geometrical dimensions of the molecules. However, the disproportionation reaction takes place at 125 K, i.e. the dynamical process takes place during adsorption. Finally, the number of CO$_3$ molecules depends only on the number of edge K adatoms, i.e. only on the $\Theta_K$.

5. Conclusions

1. The PSSR provides a clear distinction between CO$_2$ and CO$_2$(−) bent species. The characteristic features of the CO, CO$_3$, CO$_2$ and CO$_2$(−) at BE$_F$ of 11.9, 9.5, 12.9, and 6.8 eV, respectively, can be indicative in establishing of the components by rough inspection of the complex valence band spectrum.

2. The surface reactions (formation of CO$_2$(−), disproportionation) proceed at the adsorption temperature, i.e. 125 K, on the CO$_2$/K/Cu(110) interface. Solved CO$_2$(−) species does not follow disproportionation to CO$_3$ with increase in temperature. The CO$_2$(−) readily reacts with coadsorbed hydrogen
to form formate on K/Cu(110) [20, 21]. Thus, reactivity of the interface in aspect of methanol synthesis is dependent on the ability of creation of the stable bending CO$_2$(-) molecules among adsorbing CO$_2$.

**Acknowledgments**

We gratefully acknowledge the support by the Danish Research Council through the Center for Surface Reactivity and through the Grant for Synchrotron Radiation Research.

**References**