Photolysis of the CO_2 + K/Au(111) System[†]

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Photoinduced activation of CO_2 was investigated on a K-dosed Au(111) surface. The methods used were work function measurements, high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy. Illumination of CO_2 adsorbed on a clean Au(111) surface with a 65 W Hg arc lamp produced no HREEL spectral signals indicative of the formation of CO_2^-. As was revealed in a previous paper (Farkas and Solymosi, *J. Phys. Chem. C* **2009,** *113,* 19930), potassium adatoms induce the formation of negatively charged CO_2 on Au(111). Illumination of the CO_2 + K/Au(111) system enhanced (i) the electron transfer from K-dosed Au to CO_2, (ii) the amount of strongly adsorbed CO_2, (iii) the formation of CO, and (iv) the intensity of the vibration loss of the asymmetric stretch of CO_2^-. It is assumed that the photoelectrons play a role in the photolysis of the CO_2 + K coadsorbed layer.

1. Introduction

Activation of the stable CO_2 molecule and its conversion into valuable compounds are of a great challenge for the catalysis.[1–3] Our laboratory became interested in this subject quite early studying first the hydrogenation of CO_2,[4,5] the CH_4 + CO_2 reaction,[6,7] the photolysis of H_2O + CO_2,[8] and the surface chemistry of CO_2 on various metal single crystal surfaces.[9] The easiest way to activate the CO_2 molecule is to donate an electron into the anti bonding π orbital of CO_2, and to produce a more reactive negatively charged CO_2.[9,10] Due to the high work function of metals, the electron transfer between metals and CO_2 is extremely limited. The probability of the dissociative chemisorption of CO_2 on Rh(111) at room temperature and at low pressure was calculated to be of the order of 10^{-11}–10^{-15}.[11,12] However, potassium due to its electron-donation character can reduce the work function of the metals and induce the activation of CO_2. This was first demonstrated on a K-dosed Pd(100) surface,[13,14] followed by extensive studies on Rh(111),[15–17] Pt(111),[18,19] Pd(111),[20,21] Ru(0001),[22–24] Ag(111),[25] Co(1010),[26] Mo_2C/Mo(100),[27] Cu(110), and Cu(115).[28,29] Further enhancement of the electron transfer to CO_2 can be achieved by the illumination of adsorbed CO_2, as was first demonstrated on the Rh(111) surface.[30] In the present paper, an account is given on the photolysis of the CO_2 + K/Au(111) system. Recently, we reported that the potassium promoted the formation of CO_2^- on Au(111) single crystal, which was converted into carbonate species at higher temperatures.[31] The formation of carbonate was also observed on the clean Au(111) surface in the reaction of preadsorbed CO_2 with an O atomic beam.[32,33] Carbonate was also identified by soft X-ray photoelectron spectroscopy by adsorbing CO_2 on the O/Au(111) surface at 90–100 K.[34] It exhibited a very low stability decomposing by 125 K. Extended exposure of the beam resulted in the enhanced decomposition of surface carbonate.[34]

2. Experimental Section

The experimental details have been described in our previous paper.[31] All measurements were performed in a UHV chamber equipped with facilities for Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), and temperature-programmed desorption (TPD). The UV light source was a focused 100 W Hg lamp; we worked at 65 W. The light passed through a high-purity silica window into the vacuum chamber. The incident angle was 45° off the sample normal. The temperature rise of the sample during irradiation did not exceed 3–5 K. Work function changes, based on the secondary electron energy threshold, were measured with the same electron gun and analyzer used in AES. The HREEL spectrometer (LK, ELS 3000) has a resolution of 20–40 cm^{-1} (fwhm). The count rates in the elastic peak were typically in the range of 1×10^4 to 1×10^5 counts-per-second (cps). All spectra reported were recorded with a primary beam energy of 6.5 eV and at an incident angle of 60° with respect to the surface normal in the specular direction. The Au(111) crystal was secured to a Mo plate, which was connected via a copper block directly to a liquid nitrogen reservoir. The sample was heated with a tungsten spiral situated at the back of the sample from 100 to 900–1000 K. Its temperature was monitored by a chromel–alumel thermocouple pressed firmly into a hole drilled into the side of a crystal and was controlled with a feedback circuit to provide a linear heating rate of ca. 2 K/s. The dosing temperature was ∼100–110 K unless otherwise noted. The Au(111) crystal used in this work was a product of MaTeck GmbH, purity 99.999%. Initially, the sample was cleaned by cycled heating, which was followed by cycles of argon-ion bombardment and annealing at 850–1000 K for several minutes. CO_2 was a product of Linde, 99.995%. A commercial SAES getter source was used to deposit potassium metal onto the Au surface, which was situated 3 cm from the sample. The getter was resistively heated. The deposition of the potassium was done at ∼110 K. The onset of potassium desorption from the second adlayer (T_p = 370 K) was accepted as an indication of the completion of a monolayer denoted by Θ_K = 1.0 ML.

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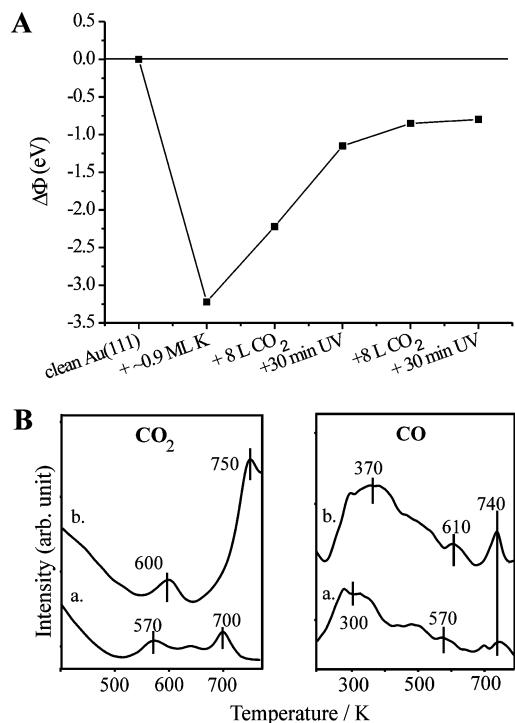
A

B

Figure 1. Changes in the work function of Au(111) following the deposition of potassium, adsorption of CO$_2$, and illumination of the coadsorbed layer at 110 K (A). Postirradiation TPD spectra of the CO$_2$ + K/Au(111) system at Θ_K = O.9 (B): (a) no irradiation; (b) irradiation for 120 min at 110 K.
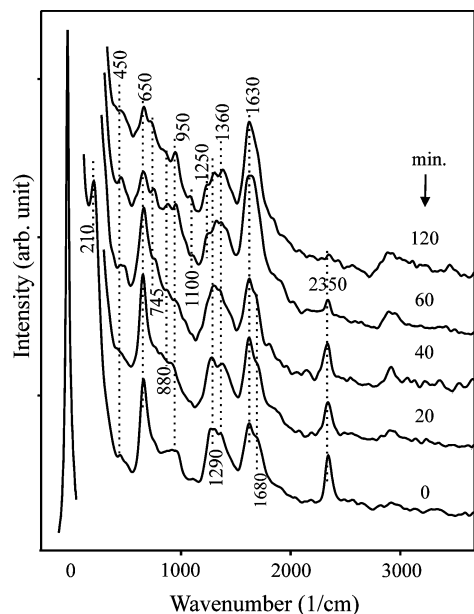

Figure 2. Effect of illumination time on the HREEL spectra of the CO$_2$ + K/Au(111) system at 110 K. Θ_K = 0.5 ML.
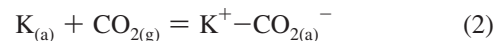
3. Results and Discussion

In Figure 1A, the work function changes of Au(111) are presented following K deposition, CO$_2$ adsorption, and illumination. Potassium lowers the work function of the Au(111) maximum by ~3.2 eV, indicating a considerable charge transfer from potassium to Au(111). This value was attained at Θ_K = 0.75−0.9 ML; further increase of K coverage exerted no influence on the work function of Au(111). Adsorption of CO$_2$ on K-dosed Au(111) at 110 K leads to an increase in the work function of the sample by about ~2.0 eV. When the coadsorbed

CO$_2$ + K layer on Au(111) at Θ_K = 0.9 ML was irradiated, the work function further increased by about 1.05 eV. Exposing this surface to CO$_2$ again caused a slight enhancement of about 0.5 eV. Further illumination for 30 min led only to ~0.2 eV increase. These features suggest that the charge transfer from K/Au to CO$_2$

$$K^{\delta+}/Au^{\delta-} + CO_2 = K^{\delta+}/Au-CO_{2(a)}{}^{\delta-} \qquad (1)$$
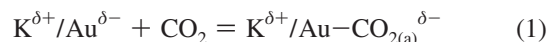
or directly from metallic potassium

$$K_{(a)} + CO_{2(g)} = K^+-CO_{2(a)}{}^- \qquad (2)$$

in dark is limited, and the illumination induces further electron transfer from the sample to neutrally adsorbed CO$_2$. The fact that the repeated adsorption of CO$_2$ and subsequent illumination exerted only a slight positive influence suggests that the above processes are almost completed.

TPD spectra for the unirradiated and irradiated CO$_2$ + K coadsorbed layer are presented in Figure 1B. Whereas CO$_2$ adsorbs only weakly and nondissociatively on the clean Au(111) surface (T_p = 124 K), potassium induces the formation of new adsorption states. The peak temperatures depends on the K coverage and on the CO$_2$ exposure.[31] In the present case, the desorption of CO$_2$ from an unirradiated adsorbed layer is characterized by T_p = 570 and 700 K and that of CO with T_p = ~300, 570, and 740 K. These features can be explained by the disproportionation of CO$_{2(a)}{}^-$ into stable carbonate

$$2CO_{2(a)}{}^- = CO_{3(a)}{}^{2-} + CO_{(a)} \qquad (3)$$
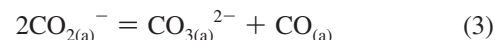
and by its decomposition at high temperatures

$$CO_{3(a)}{}^{2-} = CO_{2(g)} + O_{(a)}{}^{2-} \qquad (4)$$
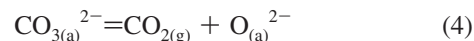
The direct dissociation of the activated CO$_2$

$$CO_{2(a)}{}^- = CO_{(a)} + O_{(a)}{}^- \qquad (5)$$
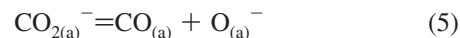
can also be taken into account.

As shown in Figure 1B, the photolysis of the CO$_2$ + K coadsorbed layer enhanced the desorption of CO$_2$ in the range 500−790 K and somewhat shifted the T_p values to higher temperature. The results are in harmony with the conclusions drawn from work function measurements; namely, the irradiation promotes the formation of negatively charged CO$_2$, and as a result, the extent of the subsequent reactions of activated CO$_2$ is increased (eqs 3−5). Note that the desorption of O$_2$ was not detected by TPD measurement similarly to other CO$_2$ + K/metal systems. The possible reason is that the adsorbed oxygen is also stabilized by potassium on the metal surfaces; as a result, it is released only at high temperatures, 900−1000 K.[35]

The effect of illumination on the activation of CO$_2$ clearly appeared in the HREEL spectra of the coadsorbed layer. Adsorption of CO$_2$ on clean Au(111) at ~100 K produces no signals in the HREEL spectrum, and no CO$_2$ losses were detected following the illumination of the adsorbed layer. This can be explained by the assumption that, similarly to Rh(111),[15−17] CO$_2$ is lying down on the Au(111) surface. The presence of potassium, however, induced the appearance of several losses
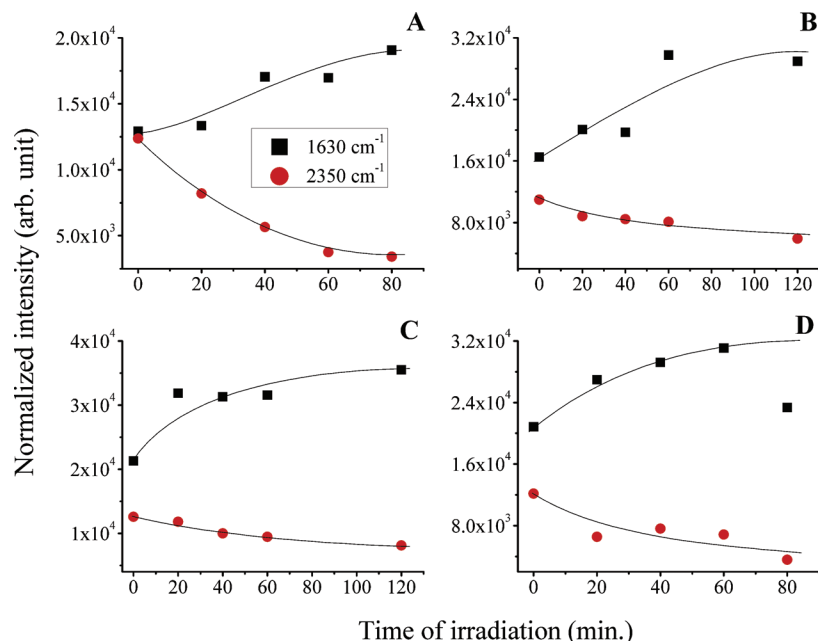
Figure 3. Changes of the normalized intensities of the vibration losses at 1630 and 2350 cm^{-1} at different Θ_K values as a function of irradiation time at 110 K: (A) $\Theta_K = 0.2$ ML; (B) $\Theta_K = 0.5$ ML; (C) $\Theta_K = 1.0$ ML; (D) $\Theta_K = 1.5$ ML.

at 650, 950, 1290, 1360, 1630, 1680, and 2350 cm^{-1} (Figure 2). Taking into account that the interaction of CO_2 with K-dosed metals and even with potassium results in the formation of several surface compounds (see above), there is no unambiguous interpretation of these vibrations. It is generally accepted, however, that the loss feature at $1620-1630$ cm^{-1} is due to the asymmetric stretching mode of the negatively charged CO_2, and the shoulder at 1680 cm^{-1} is very likely due to adsorbed CO formed in the dissociation of activated CO_2. Interestingly, losses at ~650, ~1290, and ~2350 cm^{-1}, which are characteristic for weakly bonded, nonactivated CO_2, also developed in the spectrum of the K-dosed Au surface. Its presence can be explained by a coupling between neutral and charged $CO_{2(a)}$ to give the $(CO_2)_nCO_2^-$ surface compound, which was also detected on other K-dosed metals.[30]

The spectra presented in Figure 2 show that the illumination of the CO_2 + K coadsorbed layer on Au(111) markedly enhances the intensity of the loss feature at 1630 cm^{-1}. At the same time, the vibrations of neutrally bonded CO_2 at 650 and 2350 cm^{-1} gradually attenuated very likely due to its photoinduced transformation into $CO_{2(a)}^-$. Similar results were obtained at all K coverages. This process is clearly demonstrated by the intensity changes of the losses at 1630 and 2350 cm^{-1} at different Θ_K values, which also shows that the largest intensity increase of the 1630 cm^{-1} loss occurred at $\Theta_K = 0.5$ ML (Figure 3).

In regard to the mechanism of excitation, we can assume the following: (i) direct optical excitation of the adsorbate/substrate complex, (ii) optical excitation of the substrate to generate photoelectrons above the vacuum level, and (iii) optical excitation of the substrate to produce hot electrons below the vacuum level. From the study of the wavelength dependence in the case of the CO_2 + K/Rh(111) system, we came to the conclusion that photoelectrons are responsible for the formation of CO_2^-. As the behavior of CO_2 + K/Au(111) resembles very much that of the CO_2 + K/Rh(111) system,[30] we assume that the same mechanism of the photolysis operates in the present case, too.

4. Conclusions

Illumination of adsorbed CO_2 on the clean Au(111) surface at 110 K did not result in the formation of negatively charged CO_2 species. Work function measurements, however, indicated that the photolysis of adsorbed CO_2 on K-dosed Au(111) promoted the transformation of weakly adsorbed CO_2 into CO_2^- species. This was also exhibited by the significant increase in the intensity of loss feature at 1630 cm^{-1} due to negatively charged CO_2, and in the amount of stabilized CO_2 and CO released only at high temperature.

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