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HREELS study of photo-induced formation of CO_2 anion radical on Rh(111) surface

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High-resolution electron loss spectroscopy revealed, probably for the first time, that the illumination of adsorbed CO_2 on K-promoted Rh(111) induces or enhances formation of the CO_2^- radical.

Keywords: Activation of CO_2; formation of CO_2^- anion; photolysis of adsorbed CO_2; photo-induced formation of CO_2^- anion; effects of potassium promoter; HREELS of adsorbed CO_2 on Rh(111)

1. Introduction

Production of the CO_2^- radical is an important step in the activation of CO_2, and in its catalytic reactions. Charge transfer to CO_2 results in a change in the linear structure to yield a bent form of CO_2, with a lengthening and hence a weakening of one or both C–O bonds [1–3]. CO_2^- is probably a key species in the photochemical reactions of CO_2, although its spectroscopic identification in surface photochemistry has not yet been achieved. The present paper gives an account of the photo-induced generation of CO_2^- on a K-dosed Rh(111) surface.

On carefully cleaned Pt metal surfaces, CO_2 adsorbs weakly and molecularly [1,2]. A dramatic change occurs in its bonding in the presence of alkali metal promoters; these donate an electron to CO_2 to produce CO_2^-, which dissociates even below 200 K. This was first demonstrated for the Pd(100) and Rh(111) surfaces [4]. It was also established that the nature of the interaction of CO_2 with a K-dosed Rh(111) surface depends on the K coverage. At low K coverage, where the K is mainly ionic, charge transfer to CO_2 may occur through the Rh atom. The CO_2^- formed readily dissociates to CO and O. Above a monolayer of K, where K is

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mainly metallic, a direct electronic interaction between CO_2 and K yields a relatively stable surface complex $K^{\delta+}$–$CO_2^{\delta-}$. This surface complex is transformed into a carbonate-like species and CO at high temperatures. These features were subsequently observed for several alkali metal-dosed metals too [5–10].

2. Experimental

The experiments described below were carried out in an ultra-high-vacuum (UHV) chamber with a base pressure of 4×10^{-10} Torr, equipped with facilities for Auger electron spectroscopy (AES), high-resolution electron loss spectroscopy (HREELS) and temperature programmed desorption spectroscopy (TPD). In HREELS, all spectra were taken with a beam energy of 5.0 eV and resolution of 10–12 mV full width at half-maximum. Impact and collection angles were 45° to the surface normal. Absolute intensity was in general 5×10^4–1×10^5 cps. The UV light source was a focussed 75 W Xe lamp. The light passed through a high purity sapphire window into the vacuum chamber. The incident angle was almost 0° off the sample normal. The sample can be cooled to 90 K and resistively heated to 1300 K. Sample cleaning is achieved by both Ar^+ sputtering and cycles of oxygen treatments (3×10^{-7} Torr of O_2, local pressure, for 10–30 min, with sample at 800–1200 K). We paid particular attention to the elimination of boron impurity (segregating from the bulk to the surface of the Rh crystal); it was demonstrated previously [11] that this greatly facilitates the dissociation of CO_2 on Rh(111). A commercial SAES getter alkali source was used to deposit potassium onto the Rh(111) surface situated 3 cm from the K source. AES measurements showed that a very small amount of oxygen ($R_O = O_{512}/Rh_{302} = 0.004$–$0.006$) was also unavoidably coadsorbed with K on Rh at 90 K. This amount remained practically the same at high K coverages. The K coverage was calibrated using LEED, AES and TPD yield, and was described elsewhere [4]. The CO_2 (Fluka) is 99% pure and was further purified by several freeze–pump–thaw cycles.

3. Results and discussion

First, the HREEL spectra for adsorbed CO_2 were determined with the complete exclusion of light. Adsorption of CO_2, at 10^{-9} Pa, on the Rh(111) surface at 90–300 K produced no observable loss features in the HREEL spectra. Weak losses at 650, 1320 and 2330 cm^{-1} were observed only at much higher pressure ($\sim 10^{-6}$ Pa). These vibrations are very near the corresponding gas-phase values (667, 1337 and 2349 cm^{-1}) [12] and are due to the bending mode, and the symmetric and asymmetric stretching vibrations of molecularly adsorbed CO_2. There was no indication of the dissociation of CO_2 under these conditions, even at 300 K, in harmony with previous findings that CO_2 adsorbs weakly and non-dissociatively on a carefully cleaned Rh(111) surface [11,13]. Illumination of the adsorbed layer at 90 K did not result in spectral features during the applied time, 120 min.

The situation was basically different in the presence of K adatoms. Without illumination, even at the lowest K coverage ($\Theta_K = 0.09$), weak loss features appeared in the spectrum. At $\Theta_K = 0.18$, losses were seen at 2350, 1490, 1128 and 640 cm^{-1}. A significant spectral change occurred at a monolayer of K, where a new loss feature appeared at 1610–1620 cm^{-1}. For a K multilayer, the loss at 1490 cm^{-1} was absent, but two other, quite intense features developed at 830 and 1320 cm^{-1}. At the same time, the loss at 1620 cm^{-1} became also intense. Fig. 1 shows the effect of K on the HREEL spectrum of adsorbed CO_2 at 90 K.

On the basis of previous HREELS measurements for CO_2 adsorbed on K-dosed Pt(111) and Pd(111) surfaces [2,8,9], the feature at 1610–1620 cm^{-1} is attributed to the asymmetric stretch, that at 1321 cm^{-1} to the symmetric stretch, and that at 830 cm^{-1} to the bending mode of the bent CO_2^- species. The loss features observed at 1490 and 1128 cm^{-1} at lower K coverages are associated with the vibrations of a carbonate-like species formed in the reaction of CO_2 with oxygen contamination during K deposition. Identical, but more intense losses were identified when the surface concentration of adsorbed oxygen was increased. Similar features were reported for the CO_2 + K/Pd(111) system [8]. Alternatively, these losses could be

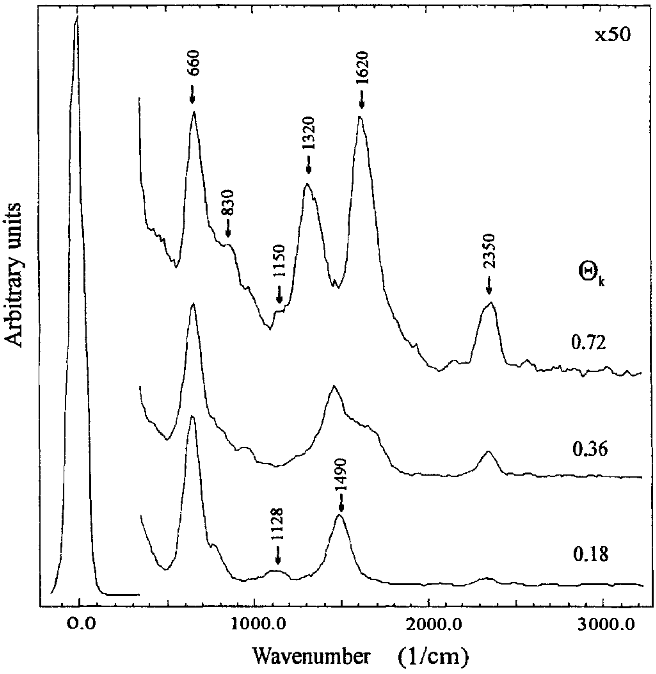

Fig. 1. Effects of potassium coverage on the HREEL spectra of adsorbed CO_2 (at saturation) on Rh(111) at 90 K.

attributed to the vibration of CO formed in the K-promoted dissociation of CO_2. This assumption, however, was not confirmed as adsorption of CO on the same K-dosed Rh(111) at 90 K gave loss features at different energies: 1765 cm^{-1} for $\Theta_K = 0.09$, 1750 cm^{-1} for $\Theta_K = 0.18$, 1605 cm^{-1} for $\Theta_K = 0.25$ and 1430 cm^{-1} for $\Theta_K = 0.36$. In the latter case, the intensity of the loss feature was very low. In harmony with previous experience on CO + K/metal systems [14–16], no CO adsorption was observed at 10^{-9} Pa on Rh(111) covered by a K multilayer.

The effect of illumination was first examined at $\Theta_K = 0.18$, where the work function of Rh(111) decreased from 4.98 to about 1.48 eV, which represents the minimum work function value for the K/Rh(111) system [4]. At this stage, the complete ionization of potassium occurred. Adsorption of CO_2 on this surface increased the work function of the system to 1.9 eV.

Spectra obtained as a function of the illumination time are presented in fig. 2. The intensities of the losses at 640 and 2340 cm^{-1}, characteristic of weakly adsorbed CO_2, gradually decreased. At the same time, a new loss feature developed

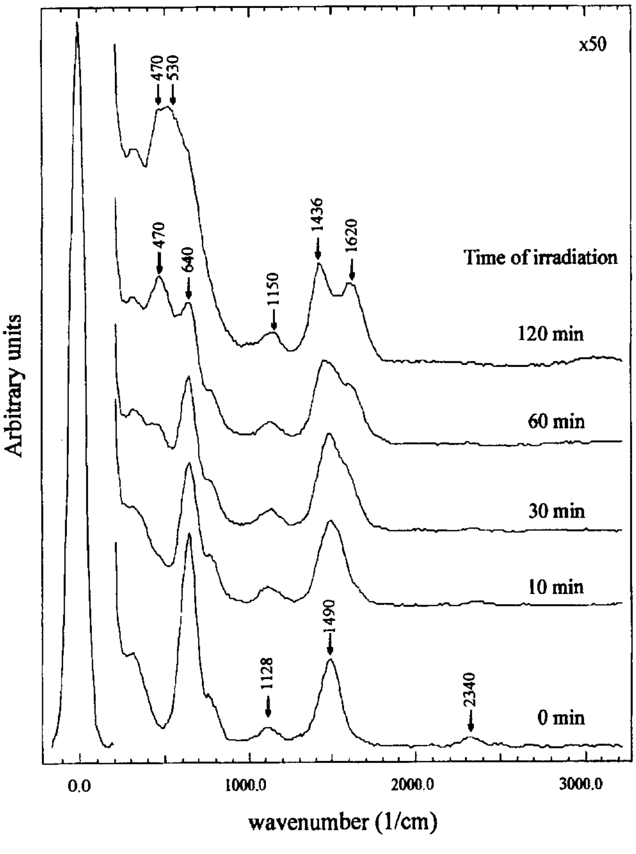

Fig. 2. Effects of illumination time on the HREEL spectra of adsorbed CO_2 on K-dosed Rh(111) surface at 90 K. $\Theta_K = 0.18$.

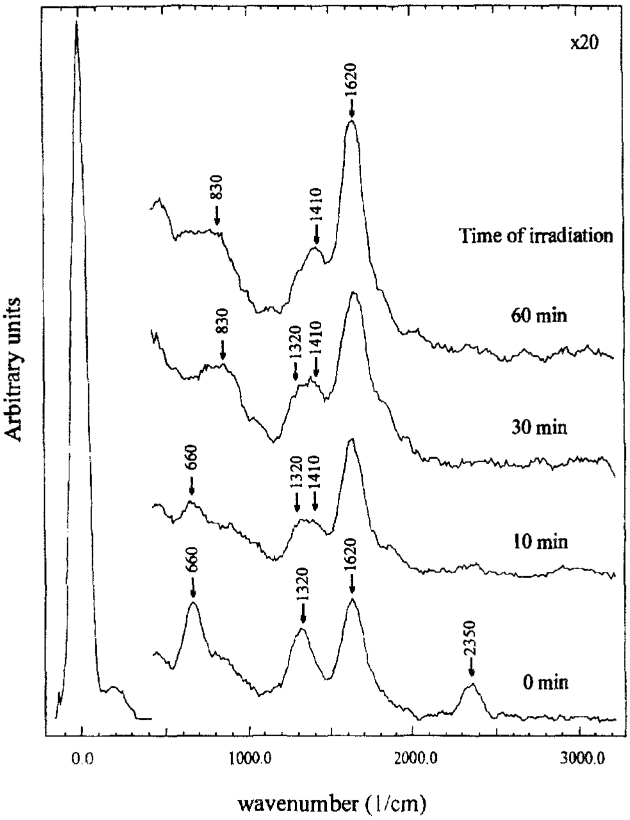

Fig. 3. Effects of illumination time on the HREEL spectra of adsorbed CO_2 on K-dosed Rh(111) surface at 90 K. $\Theta_K = 0.72$.

at 1620 cm^{-1} and the loss at 1490 cm^{-1} shifted to 1436 cm^{-1}. All these spectral changes suggest the transformation of weakly held CO_2 into a CO_2^- species. As a result of the extensive formation of more reactive CO_2^-, the amount of CO formed in its dissociation was increased, as was found by post-irradiation TPD.

Similar measurements were performed with a Rh(111) sample covered by a multilayer of K. The advantage of this high coverage is that the K is clearly in the metallic state, on which the adsorption of CO from the background is negligible. The work function of this system was 1.75 eV, which increased to 1.95 eV after saturation with CO_2. In this case, besides the losses of weakly held CO_2, loss features at 830, 1320 and 1620 cm^{-1}, very probably due to the species $K^{\delta+}$–$CO_2^{\delta-}$, were detected even following CO_2 adsorption on K/Rh(111) in the dark at 90 K. However, when the coadsorbed layer was illuminated at 90 K, the losses of weakly adsorbed CO_2 at 640 and 2350 cm^{-1} disappeared and at the same time the losses due to CO_2^-, particularly the 1620 cm^{-1} feature, gained in intensity.

Post-irradiation TPD measurements showed that the amount of CO and CO_2 desorbed at high temperatures clearly increased for an irradiated sample.

Conclusions. (i) Illumination of adsorbed CO_2 on a clean Rh(111) surface does not transform weakly held CO_2 into the CO_2^- species. (ii) On K-dosed Rh(111), however, illumination promotes charge transfer from the K/Rh(111) system to CO_2 and induces or enhances the formation of more reactive CO_2^- radical even at 90 K. (iii) As a result, the amounts of CO and/or carbonate produced by the reactions of CO_2^- at higher temperature are increased.

References

[1] H.J. Freund and R.P. Messmer, Surf. Sci. 1 (1986) 172.
[2] F. Solymosi, J. Mol. Catal. 65 (1991) 337.
[3] M.W. Roberts, Chem. Soc. Rev. 18 (1989) 451.
[4] A. Berkó and F. Solymosi, Surf. Sci. 201 (1986) L489; J. Catal. 104 (1986) 458;
F. Solymosi and L. Bugyi, J. Chem. Soc. Faraday Trans. I 83 (1987) 2015.
[5] J. Kiss, K. Révész and F. Solymosi, Surf. Sci. 207 (1988) 36.
[6] J.A. Rodriquez, W.D. Clendering and C.T. Campbell, J. Phys. Chem. 93 (1989) 5238.
[7] L. Bugyi, G. Klivényi and F. Solymosi, to be published.
[8] Z.M. Lin, Y. Zhou, F. Solymosi and J.M. White, J. Phys. Chem. 93 (1989) 4383;
Z.M. Lin, F. Solymosi and J.M. White, Surf. Sci. 248 (1991) 289.
[9] J. Wambach, G. Odörfer, H.J. Freund, H. Kuhlenbeck and M. Neumann, Surf. Sci. 209 (1989) 159;
S. Wohlrab, D. Ehrlich, J. Wambach, H. Kuhlenbeck and H.J. Freund, Surf. Sci. 220 (1989) 243.
[10] J. Paul and F.M. Hoffmann, Catal. Lett. 1 (1988) 445.
[11] F. Solymosi and J. Kiss, Surf. Sci. 17 (1985) 149.
[12] G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand–Reinhold, New York, 1945).
[13] W.H. Weinberg, Surf. Sci. 128 (1983) L224.
[14] H.P. Bonzel, Surf. Sci. Rept. 8 (1988) 43.
[15] J. Kiss, G. Klivényi, K. Revesz and F. Solymosi, Surf. Sci. 223 (1989) 551.
[16] A. Berko and F. Solymosi, J. Chem. Phys. 90 (1989) 2492.