THE EFFECT OF BORON IMPURITY ON THE ADSORPTION AND DISSOCIATION OF CO_2 ON Rh SURFACES

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No dissociation of CO_2 was observed up to 300 K on clean Rh(111) and Rh foil surfaces. However, when boron impurity segregated to the surface of Rh foil, dissociation of CO_2 occurred, as indicated by electron energy loss and thermal desorption spectroscopy.

There is great controversy in the literature concerning the adsorption and dissociation of CO_2 on Rh single-crystal surfaces, as well as on supported Rh [1]. Recently, Somorjai et al. [2,3] demonstrated by means of HREELS and thermal desorption methods that CO_2 chemisorbs and dissociates on various surfaces of Rh at 300 K. The calculation of Weinberg [4], however, showed that the probability of dissociative adsorption of CO_2 at low pressures (of order 10^{-6} Torr) and at 300 K is of the order of 10^{-15}. Dubois and Somorjai [5] criticized the calculation of Weinberg, stating that it was based on oversimplification using incorrect kinetic and thermodynamic parameters.

The primary aim of this Letter is to show how the boron impurity that is common for Rh can influence the adsorption and dissociation of CO_2; this may shed new light on the abovementioned controversy.

The methods applied included LEED, Auger electron, electron energy loss (in the electronic range) and thermal desorption spectroscopy. We used two different Rh samples, a Rh(111) disk-shape crystal (6 × 1 mm, Material Research Co., 99.99% purity) and a polycrystalline Rh foil (10 × 10 mm and 0.127 mm thick, Hicol Co., 99.9% purity). The cleaning procedure of these samples was the same as described in our previous papers [6–8]. It consisted of cycles of argon ion bombardment (typically 600 eV, 1×10^{-6} Torr Ar, 300 K, 3 μA for 10–30 min), and annealing at 1270 K for some minutes. Note that no oxygen treatment was used in this work. The Auger electron spectrum of Rh(111) showed no other signals as Rh after this cleaning procedure. The purity of the Rh foil was lower than that of Rh(111). The major contaminants were B, P, S and C. The P, C and S were easily removed, but the elimination of B required several cleaning cycles. The final thermal treatment in this case was performed at 700 K. CO_2 was introduced into the chamber through a stainless-steel capillary with a diameter of 0.8 mm. The Rh sample was positioned about 0.5 cm in front of the effusion hole.

The adsorption of CO_2 on clean Rh(111) was first investigated by EEL spectroscopy. This method was found to be particularly sensitive for determination of the surface decomposition of organic compounds by following the development of an intense loss at 13–13.5 eV due to chemisorbed CO [6–10]. Fig. 1 shows the EEL spectra of the Rh(111) surface exposed to 45 L CO_2 at the pressure of $\approx 1 \times 10^{-7}$ Torr around the sample at 110 K. The adsorption of CO_2 produced only one new loss at 14 eV. This loss could easily be eliminated by heating the sample to 265 K, without any new loss appearing in the EEL spectrum. Parallel TD measurements showed a significant desorption of CO_2 (T_p = 244 and 170 K), but no formation of CO was detected.

Exposure of a clean Rh(111) surface to CO_2 up to 180 L at the pressure $\approx 3 \times 10^{-7}$ Torr around the sample and 300 K produced no observable change in the LEED, Auger electron and EEL spectra. In agreement with this, no desorbing products were detected

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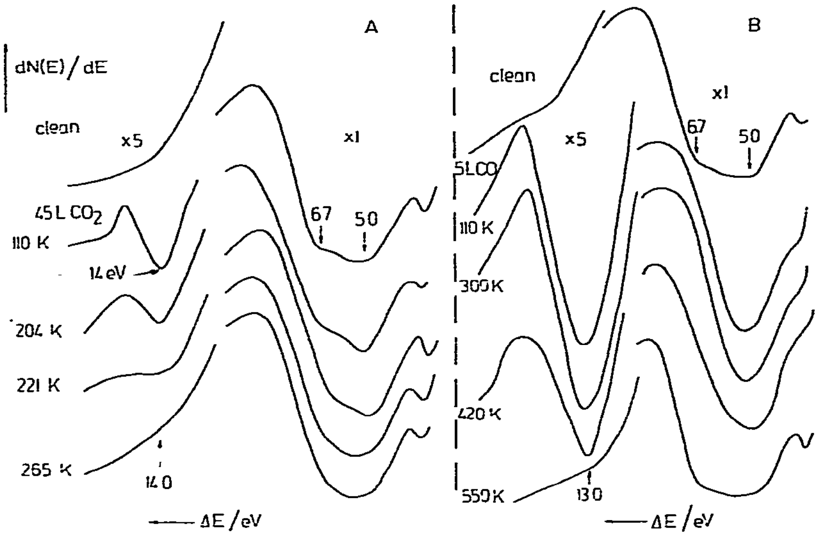

Fig. 1. Electron energy loss spectra of Rh(111) surface following CO_2 (A) and CO (B) adsorption at 110 K and after heating the sample to different temperatures.

by subsequent thermal desorption measurements. These results support the theoretical calculation of Weinberg [4] on the adsorption of CO_2 on Rh surfaces.

Adsorption of CO on Rh(111) under the same condition yielded a strong loss at 13.0 eV and apparently intensified the Rh loss at 5.2 eV (fig. 1). The 13.0 eV loss due to adsorbed CO was observed on a number of metal surfaces and was assigned to a $(1\pi{-}5\sigma)$ to $2\pi^*$ type intramolecular electronic excitation [6–10]. This loss is thermally very stable and its intensity started to decrease only above 350–400 K in harmony with the characteristics for CO desorption. Attempts to segregate boron impurity on the surface of Rh(111) crystal were unsuccessful.

The experiments were repeated *on Rh foil.* When the intensity of the boron Auger signal at 178 eV was reduced to a lowest level for Auger spectroscopy (the B_{178}/Rh_{302} Auger intensity ratio was less than 0.003) we obtained the same picture as in the case of Rh(111) surface. There was no indication of CO_2 dissociation either following the warming up to the adsorbed layer from 95 to 300 K, or adsorbing CO_2 on Rh foil at 300 K (fig. 2). However, when the sample was annealed at ≈1000 K for about 1 min, which led to a segregation of small amounts of boron (the B_{178}/Rh_{302} Auger intensity ratio was 0.036), the subsequent adsorption of CO_2 on this surface produced an intense CO loss at 13.0 eV in the EEL spectrum of Rh (fig. 2).

In addition a weak loss developed at 9.4 eV. As this loss feature was also observed on the EEL spectrum following O_2 adsorption on Rh contaminated with boron at 300 K, but never on clean Rh surfaces [11], the 9.4 eV loss is attributed to the formation of boron oxide. We note here that a stable oxide-like species has been identified by vibration EEL spectroscopy in the interaction of oxygen with low-level boron impurities at the surface of Rh crystal [12]. Due to its high dipole moment, this surface species gave much more intense vibration losses at 750 and 1500 cm^{-1} than chemisorbed oxygen on Rh, i.e. Rh–O, at 530 cm^{-1}. The boron oxide at the surface was found to be stable to heating above 1100 K in vacuum [12].

When the level of boron impurity was enhanced by extended thermal treatment at ≈1000 K to yield a B_{178}/Rh_{302} Auger intensity ratio of 0.067, the extent of CO_2 dissociation was increased as indicated by the more intense losses at 13.0 and 9.4 eV (fig. 2).

The effect of boron impurity on the dissociation of CO_2 on Rh was exhibited in the thermal desorption data. Whereas on boron-free Rh foil there was no observable CO desorption after CO_2 adsorption at

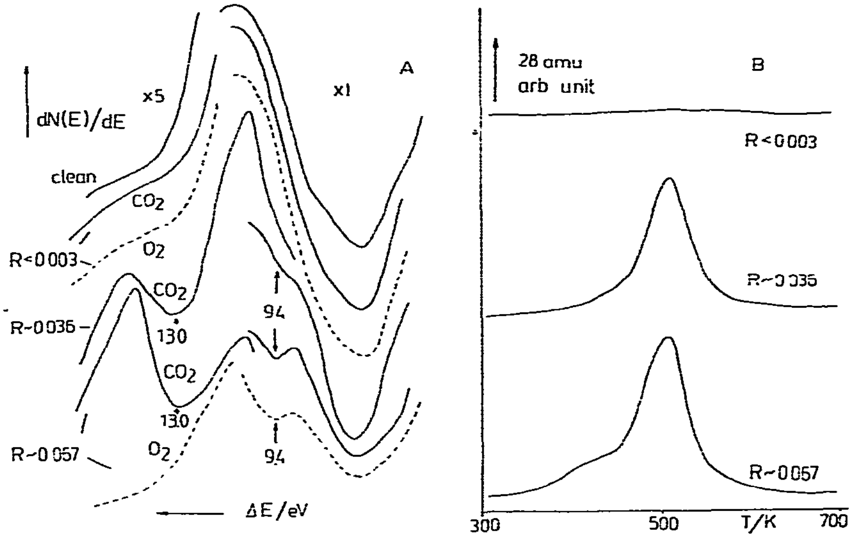

Fig. 2. Effects of impurity boron on the electron energy loss spectra of Rh foil following CO_2 (24 L) adsorption at 300 K and on the subsequent thermal desorption spectra. The pressure around the Rh sample was $\approx 1 \times 10^{-7}$ Torr. R = Auger intensity ratio of B_{178}/Rh_{302}. For comparison some EEL spectra following O_2 (1 L) adsorption at 300 K (– – –) are also shown.

300 K (at the abovementioned pressures and exposure), in the presence of boron impurity significant desorption of CO was registered with peak maximum, $T_p \approx 502$–488 K (fig. 2).

In conclusion, we can state that under the conditions applied in this work CO_2 does not appear to dissociate either on clean Rh(111) or on Rh foil surfaces. The presence of boron impurity, however, exerted a dramatic influence on the reactivity of Rh surface and caused the dissociation of CO_2. A possible reason of this effect is the formation of a stable boron oxide species. A similar influence of boron impurity has recently been experienced in the surface reactions of N-containing compounds (such as HNCO, C_2N_2, N atoms) on Rh surfaces [6,13]. The formation of a stable boron nitride surface compound markedly influenced the associative desorption of nitrogen and CN radicals, and also resulted in an enhanced dissociation of adsorbed CN groups [13]. All these results illustrate the important role of low-level impurities in the surface reaction. This is a feature to which appropriate attention and consideration should be paid in the evaluation of the experimental data.

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