COMMENT

Comment on: Interaction of carbon dioxide with clean and oxygenated Cu(110) surfaces, by T. Schneider and W. Hirschwald

Received 24 August 1992

A recent paper by T. Schneider et al. [1] claims that nearly 100% of the adsorbed CO_2 dosed at 85 K to clean Cu(110) dissociates during subsequent heating to give CO gas in a peak at 215 K, and adsorbed oxygen (O_a). This would require a very low activation energy for the dissociation of adsorbed CO_2 (<10 kcal/mol), since the CO_2 itself desorbs below 160 K. This is clearly contradictory to measurements of the activation energy for the dissociative adsorption of CO_2 on clean Cu(110) [2] and Cu(100) [3], which are around 16–22 kcal/mol. (From the adsorbed state, the barrier should be even higher than these values by an amount equal to the heat of adsorption of CO_2, or ≈ 6 kcal/mol [3].) These latter, much higher values are also consistent with the barrier predicted from the known heat of adsorption of oxygen and the activation energy for the reverse process: $CO + O_a \rightarrow CO_2$ [2,3]. We wish to point out here possible experimental complications that could easily have led the authors of [1] to have falsely concluded that CO_2 dissociation was occurring.

First, it is very important to realize that the maximum amount of dissociation they claim to have observed corresponded to only 6% of a monolayer, which only equals 6.5×10^{13} molecules cm^{-2} (or less by a factor of two, depending upon their definition of a monolayer). This was achieved after a 5 L dose of CO_2, for a total exposure of 1.5×10^{15} molecules cm^{-2}. Thus, an impurity of CO in the CO_2 of only 4% (or 2%) would have been sufficient to explain all of the CO observed in subsequent thermal desorption. The authors to some extent addressed this issue by using ^{18}O-labelled CO_2. However, if a CO impurity were produced by CO_2 dissociation on the walls of the storage vessel, the gas-handling system, or the UHV chamber, the CO impurity would also have been ^{18}O-labelled. In our experience, such a dissociation reaction is always seen in UHV systems containing titanium sublimation pumps or ion pumps, unless extreme precautions are followed. Unfortunately, no statement was made by the authors concerning the purity of their reagents, or their purity in the vacuum chamber. This CO desorption signal was also the only data presented in the paper to support CO_2 dissociation. The authors did state that "The oxygen built up during the course of CO_2 adsorption sequences was followed by AES," but no other details were given about the magnitude of the observed signals. Of course electrons can induce dissociation, so the authors turned off the electron gun during dosing. However, they apparently left the ion gauge filament on to measure exposures. This can also aid dissociation. To avoid this in similar experiments at 110 K, where we saw no CO desorption from Cu(110) after 350 L of CO_2 [2,4], we used a directed gas doser whose flow rate could be maintained without using an ion gauge. The same type of doser was used in similar experiments on Cu(100) at 79 K, where no dissociation was seen when the ion gauge was turned off during the dose [3].

The authors of [1] pointed out this discrepancy between our results, and attributed it to the fact that we had used a sample temperature of 110 K, while they used 85 K. According to them, this is a critical difference, since the CO_2 desorption peak is at 100 K, just between these temperatures [1]. However, since molecular sticking coefficients are known not to be strong functions of temperature, there must have been many monolayers of CO_2 molecules which adsorbed and redesorbed without dissociation during our 350 L exposure at 110 K. (Here, we have used data from refs. [1,3] to estimate that the sticking coefficient is about 0.1 to 0.5.) It would require a very dramatic decrease by a factor of 1000 in the molecular sticking coefficient between 85 and 110 K to explain the differences between these data in this way. Such differences are never observed, to our knowledge. (By sticking coefficient, we mean the probability that a molecule that strikes the clean surface becomes accommodated on the surface, irrespective of whether it thermally desorbs after a short residence time on the surface.) Alternatively, these data could be interpreted by a kinetic model wherein the activation energy for the dissociation of adsorbed CO_2 is far below its activation energy for desorption (≈ 6 kcal/mol). This would contradict the very large barrier seen in other experiments on Cu single crystals (≈ 22–28 kcal/mol, see above and refs. [2,3]). It would also be completely inconsistent with the known barrier for the reverse reaction ($CO + O_a \rightarrow CO_2$) [2,3]. Furthermore, even when dosed at 79 K, CO_2 desorbs without dissociation from Cu(100) [3].

A curious aspect of the results in ref. [1] is the fact that the CO desorption peak area continued to increase proportional to the CO_2 exposure between 2.5 and 5.0 L, whereas the CO_2 peak area only increased by 25%. This behavior would be understandable if the CO resulted from impurity in the CO_2, or from ion gauge effects on the gas phase CO_2. It seems, however, rather contradictory to the authors' model, in that they also observe that preadsorbed oxygen largely reduces the amount of the CO desorption seen after CO_2 exposures. Unfortunately, exposures beyond 5 L were not studied to see just where these trends lead at coverages of CO and oxygen beyond the few percent of a monolayer level. Certainly, the coverage of oxygen would have been much easier to quantify for correlation with the CO signal, and the influence of surface impurities would have been easier to rule out, if higher exposures had been studied.

References

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