

ADSORPTION HISTORY DEPENDENCE OF THE STATE OF CHEMISORBED CO ON Fe(110)

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The chemisorption of CO on single crystals of Fe has been quite extensively studied. For instance, it has been found that the state of the chemisorbed CO depends on the surface structure of the substrate^[1,2], the temperature at which adsorption takes place^[3], as well as on the surface coverage of the adsorbed CO^[4]. In this communication we present the effect of adsorption history on the state of chemisorbed CO on Fe(110).

The experiments were performed on a VG ESCA-MK II system with a base pressure of 1.5×10^{-8} Pa. MgK_{α} radiation (1253.6 eV) and HeI resonance line (21.2 eV) were used for the XPS and UPS measurements respectively. The binding energies in the XPS are referred to the $Au4f_{7/2}$ level at 83.8 eV. The Fe (110) sample was mechanically polished to an optical finish with 0.05 μm alumina grit before use. A procedure described in the literature [5] was adopted to remove the various impurities present in the Fe(110) sample. The surface cleanliness of the sample after cleaning was verified by the Auger surface compositional analysis. The XPS C_{1s} peak area after background subtraction was used to measure the amount of CO adsorbed on the Fe(110) sample. CO with a purity better than 99.9% was used throughout the experiments.

Fig. 1 gives the XPS spectra of C_{1s} and O_{1s} for (a) CO adsorbed at 170 K, (b) CO adsorbed at 170 K and subsequently heated to room temperature, and (c) CO adsorbed at room temperature respectively. It is clearly seen that for the case of CO adsorbed at room temperature, a shoulder with a lower binding energy on both C_{1s} and O_{1s} spectra is present. These shoulders at 282.9 eV and 530.3 eV respectively

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are characteristic of the dissociated CO as described in the literature [6,7]. Whereas no shoulder appears in the spectra for the CO adsorbed at 170 K or the CO adsorbed at 170 K first and then subsequently heated to room temperature.

The different state of the chemisorbed CO involved in the adsorption at 170 K with subsequent heating to room temperature and the direct adsorption at room temperature is further substantiated by the UPS spectra taken for these systems. In Fig. 2 are shown the HeI UPS spectra of the chemisorbed CO on Fe(110) for (a) CO adsorbed at 170 K, (b) CO adsorbed at 170 K and subsequently heated to room temperature, and (c) CO adsorbed at room temperature directly. For the case of (c), the peaks due to dissociated CO at 3.7 and 5.3 eV below the Fermi level [7] are clearly seen on the spectrum in addition to those ascribed to the 4σ and $1\pi+5\sigma$ molecular orbitals of CO respectively as shown.

Thus, for the case of CO adsorbed at room temperature, part of the adsorbed CO has dissociated. Both molecularly and dissociatively adsorbed CO are present on the surface of Fe(110). But for the case of CO adsorbed at 170 K and subsequently warmed up to room temperature, the chemisorbed state of CO is exclusively molecular in nature.

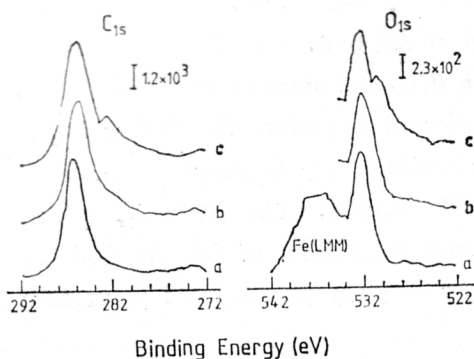


Fig.1 XPS C_{1s} and O_{1s} spectra for the CO/Fe(110) system with different adsorption history
On the left, C_{1s} spectra
a) CO adsorbed at 170 K, b) CO adsorbed at 170 K and subsequently heated to room temperature, c) CO adsorbed at room temperature.
On the right, O_{1s} spectra
a) CO adsorbed at 170 K, b) CO adsorbed at 170 K and subsequently heated to room temperature, c) CO adsorbed at room temperature

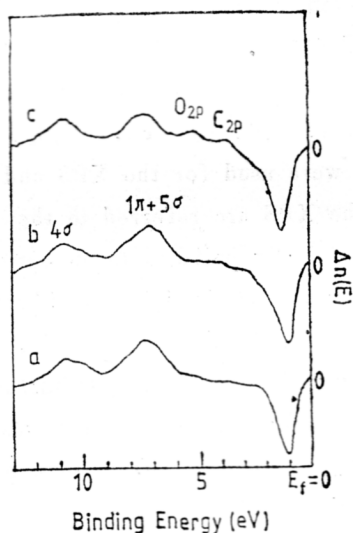


Fig.2 HeI UPS spectra for the CO/Fe(110) system with different adsorption history
a) CO adsorbed at 170 K, b) CO adsorbed at 170 K and subsequently heated to room temperature, c) CO adsorbed at room temperature

Another feature for the difference in the two adsorptions of CO on Fe(110) with different adsorption history is the difference in the amount adsorbed as shown in Fig. 3. The uptake of CO at saturation at the low temperature of 170 K is found to be higher than that at room temperature. This is expected as the molecularly adsorbed CO would not be restricted to a monolayer at this temperature. The interesting point is, however, when we raise the temperature from 170 K to room temperature with the desorption of a portion of the molecularly adsorbed CO, the amount of CO adsorbed on Fe(110) finally obtained is not the same as the amount of CO adsorbed directly at room temperature. The former is higher by $\sim 20\%$ than the latter as seen in Fig. 3. This lower amount of CO adsorbed in the direct adsorption at room temperature is certainly related to the dissociation of CO which has been observed. If we assume that the dissociation product of the atomic species of C occupies the same "long bridge" site on the surface of Fe(110) like the atomic species of O, which has been demonstrated by Gonzalez *et al.* [8], then each atomic species would be expected to hinder the adsorption of 2 molecules of CO in a distorted $p(1 \times 2)$ structure proposed by Erley [9] and schemetically shown in Fig. 4. In this structure each molecule of CO is adsorbed terminally on an Fe atom. Thus, the dissociation of 1 CO molecule would inactivate 4 sites for the molecular adsorption of CO on the surface of Fe(110). On this basis, the percentage of dissociated CO may be estimated from Fig. 3 to be about 25%. This is in good agreement with the value of the fraction of dissociated CO on Fe(110) at 300 K (ca. 22%) determined by TDS as reported in the literature [8].

It is thus seen that the difference in the state of the chemisorbed CO for the system of CO/Fe(110) with different adsorption history is exhibited in (a) the occurrence of dissociation of CO, approximately 25% of the total amount adsorbed, for the

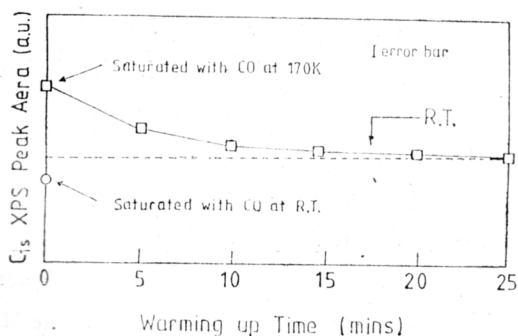


Fig.3 Adsorption of CO on Fe(110) surface with different adsorption history

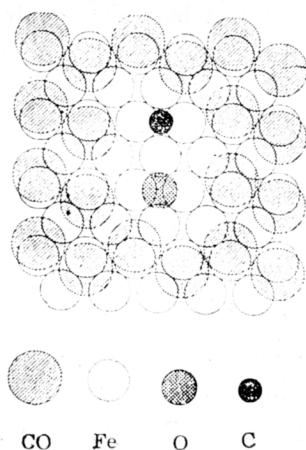


Fig.4 Schematic diagram for the blocking of adsorption sites on Fe(110) by the dissociated CO

case of direct adsorption at room temperature, and (b) the higher amount of CO adsorbed to the extent of $\sim 20\%$ with no dissociation of CO for the case of adsorbing CO at 170 K first and then subsequently heating to room temperature.

The absence of dissociation for the CO adsorbed at 170 K and subsequently heated to room temperature deserves further scrutiny. It has been found that the highly dispersed single Fe atoms on $\text{TiO}_2(110)$ can only adsorb CO weakly at room temperature^[10]. No dissociation of CO would be expected under such circumstances. It has been postulated that for that system the strong chemisorption of CO that leads to dissociation in the Fe/ $\text{TiO}_2(110)$ system would require an ensemble of neighboring Fe atoms acting synergetically. In our case of CO adsorbed at 170 K and subsequently heated to room temperature, the Fe(110) surface would be covered by a complete monolayer of CO at 170 K with a second layer of molecularly adsorbed CO on its top. Upon warming up to room temperature, however, the molecularly physisorbed CO of the second layer would be desorbed, but the first monolayer of the molecularly chemisorbed CO would still remain on the surface in full coverage. Although in this case neighboring Fe atoms are plentiful, but no neighboring FREE atoms of Fe are available on the surface. As a result, dissociation of CO still would not occur. This is complementary to the findings mentioned above [10], in which CO adsorbed on isolated single Fe atoms is only weakly chemisorbed, i.e., not capable to dissociate.

It is thus suggested that the dissociation of CO on the Fe(110) surface has two requirements to be met: (1) enough thermal energy to overcome the energy barrier for dissociation, this may be accomplished by raising the temperature of adsorption or reducing the height of the energy barrier for CO dissociation, and (2) neighboring FREE atoms of Fe at the adsorption site are available on the surface. For the two systems dealt with in this work, the adsorption of CO on Fe(110) at room temperature has met both the requirements, therefore dissociation of CO occurs at the initial stage of adsorption like the case reported for the system of CO/Fe(100)^[4]. For the case of adsorption of CO at 170 K first and then subsequently heated to room temperature, the dissociation of CO is although energetically favored, but structurally unrealizable. This appears to be the reason underlying the difference in the behavior for the two cases of CO adsorption on the same substrate under otherwise identical conditions, but with different adsorption history.

A considerable amount of data in the literature on the adsorption of CO on single crystal surfaces at room temperature was actually obtained by making the adsorption experiments at a low temperature (usually even lower than 170 K) and subsequently heating to room temperature. This mode of operation has been used with the tacit assumption that the state of the adsorbed species resulted therefrom would be the same as that obtained directly from the adsorption at room temperature. It is suggested that this assumption should be used with caution in the light of this study on the CO/Fe

(110) system with different adsorption history presented herein.

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Fe(110)面上CO化学吸附状态的吸附历史依赖关系

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摘要 Fe(110)面上直接在室温时吸附的CO同先在170K吸附然后升温到室温的CO吸附有所不同。前者有解离而后者无解离;另外,前者的饱和吸附量比后者低。这可以用前者发生了解离来解释。根据以上结果,提出了以下的设想,Fe(110)面上的CO解离除了需要足够的热能而外,还需要在表面的吸附位上有邻近的其它未被覆盖Fe原子的存在,即需要一定的表面结构。

关键词: Fe(110) CO化学吸附 光电子能谱