DISSOCIATION OF CO ON STEPPED/KINKED SURFACE AREAS OF A ROUNDED Pt CRYSTAL: I. CLEAN SURFACE

X.Q.D. LI and Ralf VANSELOW
Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, Wi. 53201, U.S.A.

Received 22 November 1988; accepted 10 January 1989

Work function measurements carried out by FEM on rounded, “FEM-clean” Pt crystals show that the dissociation of adsorbed CO occurs predominantly on kinked edges. The dissociation activity of a crystal area is proportional to its kink density.

The dissociation of carbon monoxide on platinum group metals plays an important role in several industrial catalytic processes. It seems, however, that not all parameters controlling this reaction have been investigated sufficiently. The effect of different surface structures on the dissociation process may serve as an example. In the case of platinum, for instance, it has been claimed that stepped/kinked surfaces do [1-4] or do not [5,6] promote the reaction. In the following, we shall report experimental results which show that on “clean”, rounded Pt crystals the dissociation is promoted predominantly by kinked edges.

The overall dissociation mechanism, e.g. [7-9]

\[
\begin{align*}
\text{CO(gas)} & \rightleftharpoons \text{CO(ad)} \quad (1a) \\
\text{CO(ad)} & \rightleftharpoons \text{C(ad)} + \text{O(ad)} \quad (1b) \\
\text{O(ad)} + \text{CO(ad)} & \rightarrow \text{CO}_2 \text{(gas)} \quad (1c)
\end{align*}
\]

suggests that each individual reaction step is accompanied by a work function change. Focussing on Pt, assuming saturation adsorption in step (1a), and making use of already known work function changes for oxygen/Pt [10-12], CO/Pt [11,13-15], and carbon/Pt [C(atomic): 16; C(graphite): 17,18], the following generalizing predictions can be made for the individual steps:

(1a) Adsorption of CO on the clean surface will lead to a relatively small work function increase ($\Delta\Phi = \text{pos.}$). Nieuwenhuys [13], who applied conditions similar to the ones described in the present paper, found an overall work function change of $\Delta\Phi = +0.4$ eV. (This value is in very good agreement with our results, which are quoted in section I.)

(1b) In cases, where adsorption experiments have been carried out on Pt under comparable conditions, it was found that the work function change caused
by oxygen [10–12] is about twice as large as that caused by CO [11,14,15]. Therefore, the replacement of CO(ad) by C(ad) and O(ad) will cause a work function increase (ΔΦ = pos.) which is higher than that obtained in step (1a). (Provided that the carbon exists in the atomic state. Which normally is the case below 870 K, see section (2)).

(1c) The reaction of O(ad) with CO(ad) and the desorption of the product CO₂ will not cause a return to the work function of the clean surface because there is atomic carbon, C(ad), left from step (1b). Our own measurements [16] indicate only very small work function increases (between about 0 and +0.1 eV), which are in agreement with the small electronegativity difference between C and Pt.

(2) There will be a significant work function decrease (ΔΦ = −1.6 eV [17,18]), however, if the temperature is high enough (T ≈ 870 K) so as to permit the short range migration of carbon atoms and the formation of two-dimensional graphite islands [17,19–21]:

\[ xC(ad) \rightarrow \text{graphite(ad).} \] (2)

(3) In areas where adsorption but not dissociation occurs, the adsorption will cause an initial work function increase according to step (1a). A gradual decrease to the value of the clean surface may be observed upon desorption:

\[ \text{CO(ad)} \rightarrow \text{CO(gas).} \] (3)

(4) The structure of the quenched, clean surface can be effected by annealing alone or by annealing in the presence of adsorbates. Therefore, even in case (3) one may not reach exactly the work function value of the original, clean surface after CO desorption has been completed, e.g. [22].

A field electron microscope (FEM) was used to determine the above indicated work function changes and, thereby, to study the related reactions. The investigated Pt sample was the apex crystal of a field emission needle, a rounded crystal (99.999% purity, Mat. Research Corp.) with flat equilibrium planes \{111\} and \{100\}. Such crystals have been used successfully to model larger catalytic particles (r = 3000 Å), e.g. [23,24].

A "FEM-clean" surface was obtained by extensive heating and flashing of the sample close to its melting point followed by rapid quenching to room temperature [25–27]. The residual gas pressure was in the 10⁻¹¹ Torr range. (A "FEM-clean" surface satisfies the strictest standards for "Auger-clean" surfaces [25–27]). Thereafter, the sample was exposed to CO (J.T. Baker, high purity research grade, 99.97%) for 2 min. at 8 * 10⁻⁷ Torr to achieve saturated adsorption. The gas pressure was then reduced again to 10⁻¹¹ Torr and the sample heated stepwise for 30 sec at increasing temperatures without applying the imaging field (to avoid field effects). After each heating step, the sample was rapidly quenched to room temperature, a FE-micrograph was taken and emission measurements were car-