SUPPORTING INFORMATION

A Mechanistic Study of Methanol Decomposition and Oxidation on Pt(111)

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To determine the coverage (θ) of platinum surface by different carbon-containing species (like C, CO, HCOO), we used the method based on a comparison of the C*1s* peak intensity normalized to the Pt*4f* peak intensity with that obtained at a reference point. As the reference point, the relative intensity of the C*1s* spectrum of the Pt(111) surface obtained *in situ* under 2×10^{-3} mbar *CO* at 320 K was used. According to the published data,[1] under these conditions, a saturated *CO* coverage near 0.62 ML is formed (1 ML equals the density of Pt atoms in the (111) plane; 1.5×10^{15} atom/cm^2).

Since the coverage of carbon-containing species during the methanol decomposition and oxidation is low (θ is about 1 ML), it is possible to ignore the XPS signal attenuation in the adsorbate layer. Accordingly, the calculations were carried out using the Fadley's equation[2] derived specially for the case of a semi-infinite substrate with a non-attenuating overlayer at fractional monolayer coverage. The Fadley's overlayer/substrate ratio is as follows:

$$\frac{N_l(\alpha)}{N_k(\alpha)} = \frac{\Omega_0(E_l)\cdot A_0(E_l)\cdot D_0(E_l)\cdot s'\cdot \dfrac{d\sigma_l}{d\Omega}\cdot d}{\Omega_0(E_k)\cdot A_0(E_k)\cdot D_0(E_k)\cdot s\cdot \dfrac{d\sigma_k}{d\Omega}\cdot \Lambda_e(E_k)\cdot \sin\alpha} \qquad \text{(S1)}$$

where $N_l(\alpha)$ and $N_k(\alpha)$ are photoelectron peak intensities measured at a fixed take off angle α; the peak *k* is from substrate; the peak *l* is from overlayer; Ω_0 is an effective solid angle; A_0 is an effective specimen area; D_0 is an instrument detection efficiency; s' is the mean surface density of atoms, in which the peak *l* originates; s is the mean surface density of the substrate; $\frac{d\sigma}{d\Omega}$ is the differential photoelectric cross-section; d is the mean separation between layers of density s in the substrate; $\Lambda_e(E_k)$ is an attenuation length in the substrate.

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The value s'/s is identically equal to the fractional monolayer coverage of the adsorbed species in which peak l originates. Correspondingly, the coverage of platinum surface by different carbon-containing species can be obtained by transformation of the equation (S1):

$$\theta = \frac{N_l(\alpha)\cdot\Omega_0(E_k)\cdot A_0(E_k)\cdot D_0(E_k)\cdot\dfrac{d\sigma_k}{d\Omega}\cdot\Lambda_e(E_k)\cdot\sin\alpha}{N_k(\alpha)\cdot\Omega_0(E_l)\cdot A_0(E_l)\cdot D_0(E_l)\cdot\dfrac{d\sigma_l}{d\Omega}\cdot d} = K\cdot\frac{N_l(\alpha)}{N_k(\alpha)} \qquad \text{(S2)}$$

where $N_l(\alpha)/N_k(\alpha) = \int C1s \Big/ \int Pt4f$ calculated for each components in the C*1s* spectrum. To determine the constant K, we used the reference point, that is saturated *CO* coverage observed on Pt(111) under 2×10^{-3} mbar *CO* at 320 K. It was shown previously[1] that the coverage is approximately equal 0.62 $\pm$ 0.02 *ML* under these conditions.

It should be noted that taking into account the XPS signal attenuation in the adsorbate overlayer leads to a change of calculated θ values in the range $\pm$2 % only.

[1] Ertl, G.; Neumann, M.; Streit, K. M. Chemisorption of CO on the Pt(111) Surface. *Surf. Sci.* **1977**, *64*, 393–410.

[2] Fadley, C. S. Basic Concepts of X-ray Photoelectron Spectroscopy. *Electron Spectroscopy: Theory, Techniques and Applications*. **1978**, *2*, 2–156.