Focusing Effect of Coadsorbed CO on the Spatial Distribution of H₂ Flow Desorbed from Iridium

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Abstract—Angular distributions of H_2 desorbing from the surface of polycrystalline iridium are studied by temperature-programmed desorption with spatial resolution. The presence of coadsorbed CO strongly affects the spatial distribution of the desorption flow (SDDF) of H_2. In the absence of CO, SDDF of H_2 is described by the Knudsen law. If H_2 desorbs from the layer of coadsorbed CO and H_2, SDDF of hydrogen concentrates along the normal to the sample surface. A model is proposed to explain this phenomenon.

INTRODUCTION

The spatial distribution of the desorption (SDDF) flow of hydrogen from metal surfaces was considered for many surfaces [1–14]: Pd [1, 7], Fe [1, 12, 13], Ni [2–4, 6, 9], Pt [5, 10, 14], and Cu [8]. In most cases, these data refer to single-crystalline surfaces.

Half of the studies [1, 3, 4, 6–8, 12] employed the transparent membrane method based on hydrogen ability to dissolve in the metal bulk and diffuse at high temperatures. The stationary flow of hydrogen obtained on the vacuum side of a metallic membrane is rather intensive. Therefore, the method rapidly became very popular. However, Comsa and David [8] showed that, when penetration membranes are used, chemisorbed hydrogen atoms can recombine with subsurface hydrogen atoms.

Two other methods use purely surface processes: temperature-programmed desorption (TPD) of adsorbed hydrogen [9, 11–13] and H/D exchange in the flow of H_2 and D_2 from molecular beam onto the surface [2, 5, 10, 14].

SDDFs observed in all cited papers concentrate along the normal to the sample surfaces. They can be described by the Van Willigen equation [1] within the limits of the experimental error:

$$I/I_0 = [(\varepsilon + \cos^2\varphi)\exp(-\varepsilon\tan^2\varphi)]/[(\varepsilon + 1)\cos\varphi]. \quad (1)$$

This equation was derived on the basis of microscopic reversibility principle. I_0 and I are the intensities of desorption flows along the normal to the surface and at the angle φ, $\varepsilon = E_a/RT$, and E_a is the activation energy of adsorption.

The Van Willigen equation transforms into the Knudsen equation at $\varepsilon = 0$,

$$I/I_0 = \cos\varphi, \quad (2)$$

which is applicable to nonactivated desorption and condensation.

To describe SDDF, a simple empirical formula is often used,

$$I/I_0 = \cos^n\varphi, \quad (3)$$

which rather accurately approximates equation (1) at $n = 2\varepsilon + 1$ [15].

Kurz and Hudson [12, 13] showed for the H_2, D_2/Fe system that the values of E_a obtained by the approximation of apparent SDDF with equation (1) quantitatively agree with adsorption activation energies calculated from kinetic data and isosteric adsorption heats.

The activation energies calculated using this model for the metals that dissociatively adsorb hydrogen (Pt, Pd, Ni, and Fe) are rather low (≤16 kJ/mol), and this supports the Van Willigen model. Moreover, when the metal surface was thoroughly cleaned from S, Si, and C traces, as it was done for Ni [4] and Pd [7], SDDF of hydrogen followed the Knudsen law; that is, $E_a = 0$. We cannot exclude that the values $E_a = 4–16$ kJ/mol obtained for hydrogen on Pt [5, 10, 14], Ni [2, 3, 6, 9], and Fe [12, 13] were also due to the presence of impurities on the surface. For the H_2/Cu system, which is a classical example of activated chemisorption, the Van Willigen equation gives a value of the activation energy of 40 kJ/mol [8].

In general, little is known about the effect of impurities on SDDF of gases [7, 8, 16]. These effects have been studied for the surface impurities like K, C, Si, and S, but the effects of one gas on SDDF of another have not been studied.

In this work, we found that the presence of CO on the surface of polycrystalline iridium focuses SDDF of hydrogen along the normal to the sample surface.
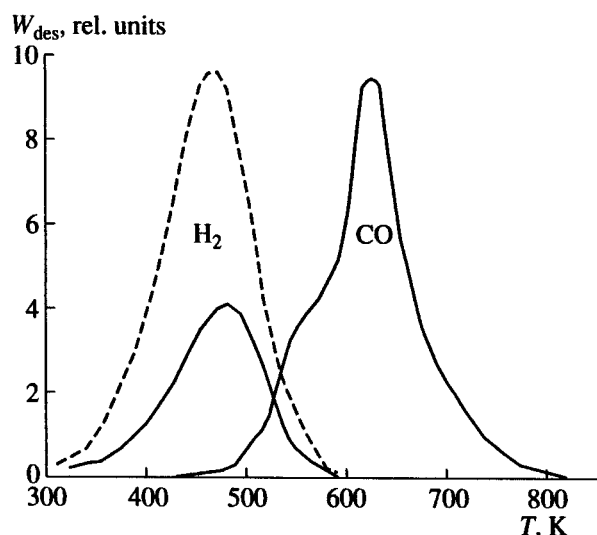
Fig. 1. TPD spectra of H_2 and CO obtained after adsorption of these gases to saturation ($\theta_H : \theta_{CO} \approx 1$) and the TPD spectrum of H_2 after its individual adsorption (shown with a dashed line). The rate of heating is 50 K/s.
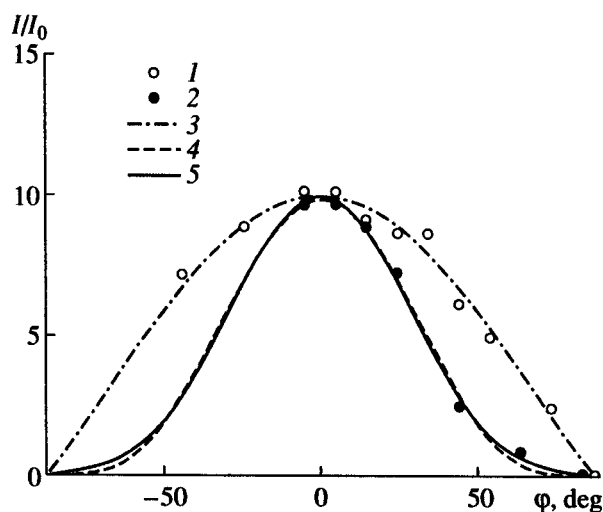

Fig. 2. SDDF of H_2 obtained after adsorption of (*1*) pure hydrogen and (2) H_2 + CO mixture and their approximation by equations (3) with (*3*) $n = 1.1$ and (*4*) $n = 3.5$ and equation (5) with (*5*) $n = 4.0$ and $a = 0.1$.

EXPERIMENTAL

Experiments were performed in ultrahigh vacuum setup with a maximal pressure of residual gases of 5×10^{-10} torr. The setup was equipped with a mass spectrometer. The technique of TPD/TPR studies with spatial resolution was reported in detail in [15, 17].

A sample (10×4 mm) was prepared from 0.05-mm-thick iridium foil and fixed in a manipulator, which enabled sample rotation to any angle with respect to the direction of the entrance slot of the mass spectrometer. A sample was heated with electric current. The temperature was measured with a Pt/Pt–Rh thermocouple.

Pure hydrogen or an H_2 + CO mixture (5 : 1) was adsorbed at room temperature upon the saturation of the front side of a sample from an effusion molecular beam formed with a capillary. Upon the adsorption of the mixture with the above-mentioned composition, the surface coverages with H (θ_H) and CO (θ_{CO}) were about the same. Then, the sample was heated in a programmed mode and TPD spectra were recorded at different angles of sample rotation. This enabled the determination of the intensity of desorbing flow depending on the angle at which particles escape from the surface.

RESULTS

Figure 1 shows TPD spectra of H_2 and CO obtained after the adsorption of these gases to saturation and the TPD spectrum of H_2 after its individual adsorption (the dashed line). The TPD spectrum of H_2 has only one peak with a temperature T_{max} corresponding to the maximum of 450–470 K. The form of TPD spectrum of CO points to the presence of at least two forms with T_{max} of

~550 and 610 K. The second form is present in larger amounts.

The activation energy of desorption E_d was estimated from the Redhead equation [18],

$$E_d = 25RT_{max}, \qquad (4)$$

which gave the following values of activation energies of H_2 and CO (two forms) desorption: 90, 110, and 120 kJ/mol.

Figure 2 shows the results of SDDF measurements for H_2 obtained after the adsorption of pure hydrogen and the H_2 + CO mixture. These are the dependences of TPD peaks on the angle φ between the sample surface normal and the direction of desorbing molecules.

SDDFs for CO/Ir were measured earlier [19] and described for both CO forms by the Knudsen law.

Figure 2 shows that, upon the adsorption of pure hydrogen, SDDF of H_2 is close to Knudsenian. During desorption from the mixed H_2 + CO layer, SDDF of H_2 is sharper. The presence of CO adsorbed on the iridium surface focuses the flow of desorbing H_2 and concentrates it along the surface normal.

This dependence was approximated by equation (3) and by the superposition of equations (2) and (3),

$$I/I_0 = (1 - a)\cos^n\varphi + a\cos\varphi, \qquad (5)$$

which describes the experimental data more accurately than (3). In the first case, we obtained $n = 3.5 \pm 0.3$. In the second case, we obtained $n = 4.0 \pm 0.3$ and $a = 0.10 \pm 0.05$.

The value of a in equation (5) determines the contribution of molecules desorbing according to the Knudsen law and escaping from the surface along the normal

to the surface. Their fraction b in the general flow can be calculated by the simple formula [20]

$$b = a(1 + n)/[2 + (n - 1)a], \qquad (6)$$

from which we have $b = 0.2 \pm 0.1$.

DISCUSSION

The effect of surface impurities on SDDF of gases is poorly studied. The Van Willigen model provides the formal explanation of these effects (see equation (1)), according to which sharpness of the spatial distribution is determined by the value of the chemisorption activation energy E_a of gas on a surface. The activation energy may strongly depend on the type and concentration of impurities. In this case, a change in the activation energy of desorption E_d and the corresponding shift in the TPD maximum was expectable, but this was not seen in the experiments.

To explain this effect, we propose the following model. The surface of our polycrystalline iridium sample largely consists of close-packed Ir(111) planes. As shown by Savchenko [21], CO adsorption on Ir(111) reconstructs the surface to form the $\sqrt{3} \times \sqrt{3}$ structure (see Fig. 3). This structure of adsorbed CO layer has enough free sites for the dissociative chemisorption of the equivalent amount of hydrogen molecules. Because the main form of CO starts to desorb after virtually complete H_2 desorption, we assume that the structure of CO layer remains virtually unchanged during H_2 desorption.

The recombination of hydrogen atoms probably occurs upon the migration of one of the atoms into the cell occupied by the other atom. As can be seen from Fig. 3, three CO molecules squeeze a hydrogen molecule, preventing it from diffusion along the surface and leaving it only one degree of freedom along the normal to the surface. Thus, the desorption flow of hydrogen from the iridium surface focuses along the normal.

Probably, on the perfect Ir(111), the focusing effect of CO on H_2 desorption should be more pronounced than in our experiments. Our value n obtained for polycrystalline surface may be underestimated [22] because of surface roughness leading to a scatter of the desorption flow relatively to the average surface normal. Roughness should lead to SDDF broadening as compared to SDDF for the perfect surface.

We can explain the fact that SDDF of hydrogen in the presence of coadsorbed CO is described by equation (5) and has a sharp and Knudsenian components.

One possible explanation is that, at surface coverages by hydrogen atoms and CO molecules used in this work, only a fraction of H_2 formed (70–90%) is focused by CO molecules. Other H_2 molecules (10–30%) desorb according to the Knudsen law as in the absence of CO.

Another explanation can be based on the precursor state model [23], according to which some fraction of
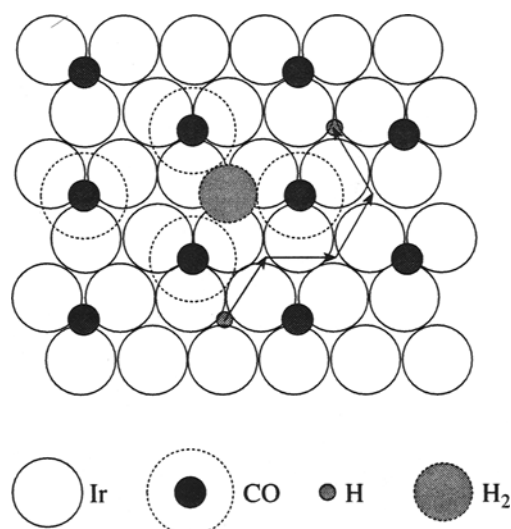
Fig. 3. The structure of Ir(111)–($\sqrt{3} \times \sqrt{3}$)CO, possible transformations of adsorbed hydrogen, and the directions of its migration (arrows). The dashed line shows the effective sizes of CO and H_2 molecules calculated from the kinetic diameters of collisions and bond lengths in these molecules.

molecules may desorb via a weakly adsorbed state (physical adsorption or condensation). It is reasonable to assume that the desorption from this state is Knudsenian.

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