CO Adsorption on the O-saturated Ag/Pt(110) Composite Surface: Direct Observation of the Diffusion of Adsorbed CO from Strongly Bound Pt Sites to Weakly Bound Ag Sites

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In our work, photoemission electron microscopy (PEEM) was employed to real-time and in situ study CO adsorption on the O-saturated Ag/Pt(110) composite surface. Coupling occurred between adjacent surfaces with different activities for CO + O_{ad} reaction, in which adsorbed CO was directly observed to migrate from strongly bound Pt sites to weakly bound Ag sites in the form of reaction−diffusion wave. Our results imply that surface species may migrate not only from weakly bound sites to strongly bound sites (enthalpy favorable process) but also from strongly bound sites to weakly bound sites (enthalpy unfavorable process) during heterogeneous catalysis reactions.

Introduction

Diffusion of surface species is one of the most fascinating phenomena associated with solid surfaces. For heterogeneous catalysis reactions, the migration of surface species between metals and supports/metals is defined as spillover, which has been widely investigated and plays a crucial role in many heterogeneous catalysis processes.[1−3] In the spillover of surface species between metals, surface species usually migrate from the weakly bound metal surface to the strongly bound metal surface (enthalpy favorable process). For example, Masai et al. found that the high affinity of Sn for O results in the migration of adsorbed O from Rh and Ru to neighboring Sn during the oxidation of CO by NO and O_2 over Rh−Sn and Ru−Sn alloys supported on γ-Al_2O_3.[4] Furthermore, because of the lack of direct methods to observe the diffusion of surface species on the catalyst surfaces during heterogeneous catalysis reactions, the experimental evidence for spillover mostly come from the direct observations of the rate and selectivity of a reaction in the presence of additives or at different temperatures, which generally requires postulating a mechanism for the reaction.

In this paper, we fabricated a Ag/Pt(110) composite surface as the model catalyst and employed photoemission electron microscopy (PEEM) to real-time and in situ study CO adsorption on the O-covered Ag/Pt(110) composite surface. The diffusion of adsorbed CO from strongly bound Pt surface to weakly bound Ag surface was directly observed by PEEM in the form of reaction−diffusion wave. To our knowledge, it is the first direct evidence for the migration of surface species from strongly bound sites to weakly bound sites on the catalyst surfaces, which is an enthalpy unfavorable process.

Experimental Section

Our experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with PEEM, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and mass spectroscopy. The base pressure was 5.0×10^{-10} mbar. The Pt(110) surface was cleaned by repeated cycles of oxidation and Ar^+ sputtering and annealing until AES detected no contaminants and LEED gave a sharp Pt(110)−(1 × 2) pattern. The fresh Ag/Pt(110) composite surface was prepared by directly depositing high-purity silver on the clean Pt(110) surface with a mask in the front so that only part of the Pt(110) surface was covered by silver film. Because our experiments were performed at 480 K, the as-prepared composite surface was annealed at 500 K to acquire a stable surface under experimental conditions. As reported in our previous paper,[5] the Ag/Pt(110) composite surface for experiments consists of three regions, namely, Pt(110) surface, AgPt interface, which was formed during the annealing process, and Ag-covered surface. The experimental results of CO adsorption and oxygen adsorption on the clean surface indicate that the active sites on Pt(110) surface, AgPt interface, and Ag-covered surface are Pt atoms, Pt atoms, and Ag atoms, respectively.[5]

The main experimental results here were acquired with PEEM. PEEM is a surface technique developed around the 1990s.[6] It is based on the principle that the photoelectron yield depends sensitively on the local work function when the metal surface is illuminated by photons whose energy is just above the threshold for the photoelectron excitation.[7] PEEM can monitor slight work function changes with high-image contrast. The bright area and dark area in the PEEM image correspond to the surface with low work function and high work function, respectively. PEEM possesses both lateral resolution ($\approx$0.2 μm) and temporal resolution ($\approx$20 ms), which enable PEEM to real time and in situ observe the kinetic processes on metal surfaces following local work function changes over mesoscopic surfaces, such as adsorption/desorption, reaction, and diffusion.[8−10]

Results and Discussions

The clean Ag/Pt(110) composite surface was first exposed to oxygen ($P_{O2} = 4.0 \times 10^{-4}$ mbar) at 480 K till the brightness of PEEM images did not change. The work functions of Pt(110) surface, AgPt interface, and Ag surface increased monotonically upon oxygen adsorption, indicating that only surface oxygen

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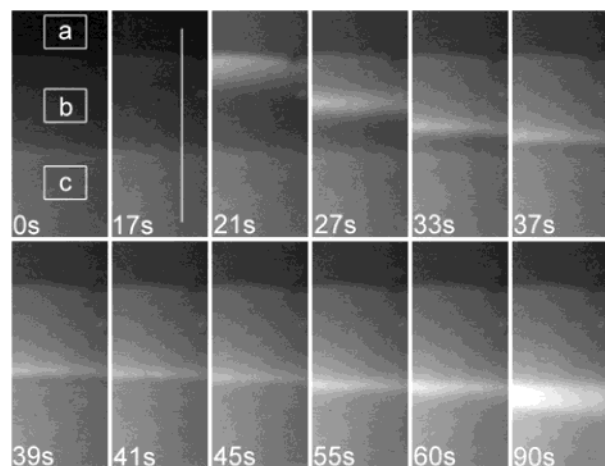§ Max-Planck-Society.

Figure 1. Series of PEEM images during CO adsorption on the O-saturated Ag/Pt(110) composite surface. $P_{CO} = 5.0 \times 10^{-7}$mbar, T = 480K. Image size: 9 μm × 20 μm.
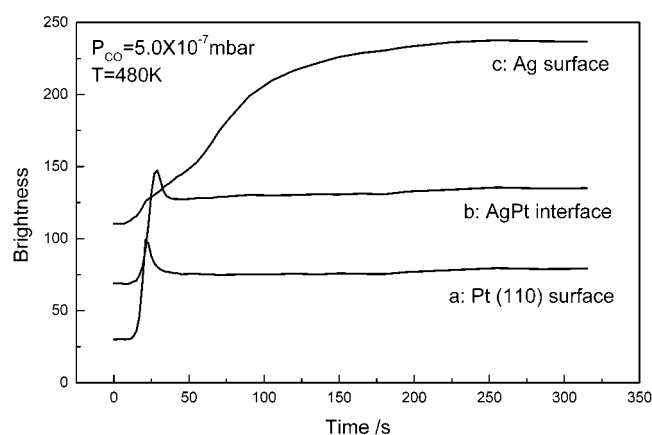

Figure 2. Brightness profiles of areas a, b, and c indicated in Figure 1.

Figure 3. Brightness profiles of the line indicated in Figure 1 at different times: (a) 0 s; (b) 17 s; (c) 21 s; (d) 27 s; (e) 33 s; (f) 37 s; (g) 39 s; (h) 41 s; (i) 45 s; (j) 55 s; (k) 60 s; (l) 90 s.

adatoms existed on all areas because the formation of surface oxide or subsurface oxygen species will lower the work function of metal surfaces.[5] The O-saturated surface was then exposed to CO ($P_{CO} = 5.0 \times 10^{-7}$mbar) at 480K. Figure 1 presents a series of PEEM images upon CO adsorption on the O-saturated Ag/Pt(110) composite surface, in which the indicated rectangular areas a, b, and c correspond to O-saturated Pt(110) surface, AgPt interface, and Ag surface, respectively. The corresponding brightness profiles of areas a, b, and c during the CO adsorption process are shown in Figure 2.

For CO adsorption on the O-saturated Ag/Pt(110) composite surface, mainly two processes might change the local work function of surfaces. One is the "cleaning-off" of precovered O_{ads} through CO + O_{ads} reaction, which lowers the local work function and creates a clean surface; the other is the succeeding adsorption of CO on the clean surface, which increases the local work function. The competition between these two processes governs the brightness profiles of the PEEM images for each area. CO oxidation on both Pt surface and Ag surface follows Langmuir−Hinshelwood (LH) mechanism.[11] Therefore, CO adsorption on Pt surface and Ag surface is the first step for CO + O_{ads} reaction in our case. As reported, CO can easily adsorb on Pt(110) at RT but can only reversibly adsorb on the Ag sites of Ag/Pt(111) above 150 K.[12,13] The difference between the activities of Pt sites and Ag sites for CO + O_{ads} reaction and CO adsorption results in the various brightness profiles of Pt(110) surface, AgPt interface, and Ag surface, as depicted in Figure 2. For O-saturated Pt(110) surface (area a), its brightness
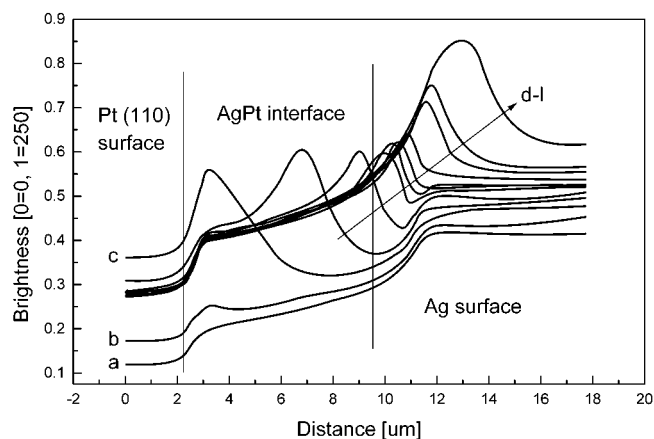
first increases sharply followed by a fast decreasing after experiencing a brightness peak, and then the Pt(110) surface is soon saturated with CO_{ads}. It can be roughly assumed that the Pt(110) surface is dominated by CO + O_{ads} reaction before the brightness peak and by CO adsorption on the clean surface after the brightness peak. The PEEM image of CO-saturated Pt(110) is brighter than that of O-saturated Pt(110) because the work function increase induced by CO saturation was about 0.4−0.6 eV lower than that induced by oxygen saturation for Pt(110).[14,15] The brightness profile of area b is similar to that of area a because the active sites for CO adsorption on AgPt interface were identical with those on Pt(110). However, the coexistence with Ag seems to decrease a little the activity of Pt sites on AgPt interface, as indicated by Figure 2. For area c, its active sites are silver, so the brightness profile of area c is quite different from those of areas a and b. The initial slow brightness increase of area c indicates that CO + O_{ads} reaction on O-saturated Ag surface proceeds very slowly. Therefore, from Figure 2, it can be clearly concluded that the CO + O_{ads} reaction and the succeeding CO adsorption proceed much faster on Pt sites than on Ag sites.

The different activities for CO + O_{ads} reaction on Pt sites and Ag sites result in great concentration gradients of CO_{ads} among areas a, b, and c. As shown in Figure 2, the CO coverage on area c can be considered as zero while areas a and b are saturated with CO_{ads}. The great concentration gradient can induce the migration of CO_{ads} between adjacent surfaces. As depicted in Figure 1, a reaction−diffusion wave initiating from the boundary between Pt(110) surface and AgPt interface was imaged to move across the AgPt interface and Ag surface by PEEM during CO adsorption on the O-saturated Ag/Pt(110) composite surface. The propagation of the chemical wave on the surface can be shown clearly by calculating the brightness profile along the line indicated in Figure 1 at different times; the result is shown in Figure 3. The CO adsorption proceeds homogeneously on the O-saturated Pt(110) surface, while a brightness peak appears on the AgPt interface and moves across the AgPt interface and the Ag surface. The brightness peak in Figure 3 corresponds to the CO_{ads} + O_{ads} reaction front, which possesses the lowest coverage of CO_{ads} and O_{ads}, and therefore is a minimum local work function. The propagation of the reaction front can be attributed to the local coupling between the CO_{ads} diffusion and the reaction between the diffusing CO_{ads} and the preadsorbed O_{ads} on the surface.

The formation of the chemical wave can be described as the following (taking Ag surface as the example): because of the

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CO_{ads} concentration gradient between AgPt interface and Ag surface, CO_{ads} diffuse from AgPt interface to the adjacent O-covered Ag surface and react with O_{ads}, thus creating a clean Ag domain; CO can adsorb or CO_{ads} can migrate from AgPt interface onto the clean Ag domain, which results in the CO-covered Ag domain; then CO_{ads} on the CO-covered Ag domain can react with O_{ads} on the adjacent O-covered Ag domain, resulting in the clean Ag domain again. The concentration gradient of CO_{ads} on Ag surface will decrease with the prolonging of CO + O_{ads} reaction on Ag surface and finally will not sustain the diffusion of CO_{ads}. Therefore, the chemical wave on Ag surface triggered from the boundary between AgPt interface and Ag surface will die out within certain a distance. Beyond this distance, the CO + O_{ads} reaction proceeds homogeneously on the O-saturated Ag surface.

The observations of the chemical wave on AgPt interface and Ag surface indicate the occurrence of reaction coupling between adjacent Pt surface, AgPt interface, and Ag surface through CO_{ads} diffusion upon CO + O_{ads} reaction on the Ag/Pt(110) composite surface. Reaction coupling between adjacent surfaces have been directly observed by PEEM on Pt polycrystalline and Pd polycrystalline during CO oxidation and hydrogen oxidation, in which surface species were imaged to diffuse between adjacent crystal planes with different activities.[16−18] In our case, reaction coupling between Pt(110) surface and AgPt interface occurs through the diffusion of CO_{ads} between Pt sites with different activities. However, the observed reaction coupling between adjacent AgPt interface and Ag surface, in which CO_{ads} diffuses from Pt sites to Ag sites, has not been reported before. As we know, CO_{ads} is much more stable on the Pt surface than on the Ag surface; therefore, our results indicate that under certain reaction conditions, surface species can migrate from the strongly bound sites to the weakly bound sites, which is an enthalpy unfavorable process.

In the thermodynamic view, migration of surface species is due to the chemical potential gradient between different surface sites, to which both enthalpy (bond strength) and concentration gradient of the migrating species contribute. The migration of CO_{ads} from Pt sites to Ag sites does not occur during CO adsorption on the clean Ag/Pt(110) composite surface, though a concentration gradient of CO_{ads} also exists between AgPt surface and Ag surface because of their different activities for CO adsorption.[5] Therefore, CO + O_{ads} reaction plays a key role in the occurrence of such a coupling between Pt sites and Ag sites during CO adsorption on the O-saturated Ag/Pt(110) composite surface, that is, the different activities of Pt sites and Ag sites for CO + O_{ads} reaction can produce the CO_{ad} concentration gradient that is large enough to drive CO_{ads} migrate from strongly bound Pt surface to weakly bound Ag surface.

In the kinetic view, this kind of reaction coupling between adjacent surfaces will exert a great influence on the reaction kinetics of the surface involved. As depicted in Figure 3, on the O-covered AgPt interface and Ag surface, CO + O_{ads} reaction proceeds much faster where the chemical wave propagates across because of the participation of diffusing CO_{ads} in the reaction. The different reaction kinetics between CO + O_{ads} reaction on Ag surfaces with and without reaction coupling can be described by the following formulas:

on Ag surface with reaction coupling:

$$r = -\frac{d\theta_O}{dt} = k_1\theta_O P_{CO} + k_2\theta_O\theta_{CO}(\text{diff})$$

on Ag surface without reaction coupling:

$$r = -\frac{d\theta_O}{dt} = k_1\theta_O P_{CO}$$

k_1 and k_2 represent the rate constant for O_{ads} on Ag surface reacting with CO in gas phase and CO_{ads} diffusing from adjacent Pt sites, respectively.

Conclusions

In summary, reaction coupling occurs between adjacent Pt(110) surface, AgPt interface, and Ag surface during CO adsorption on the O-saturated Ag/Pt(110) composite surface because of their different activities. Coupled with CO_{ads} + O_{ads} reaction, CO_{ads} is imaged to diffuse not only between Pt sites with different activities but also from strongly bound Pt sites to weakly bound Ag sites. This kind of reaction coupling between adjacent active sites during heterogeneous catalysis has a great influence on the reaction kinetics of the surface involved and may provide an alternative explanation for the synergistic effect of bimetal catalysts except the electronic effect and the ensemble effect.[19]

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