

Pd(110) 단결정에서의 CO와 H₂의 상호작용에 대한 압력과 온도의 영향

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The effects of pressure and temperature on the interaction of CO and H₂ on Pd(110)

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Introduction

Coadsorption of CO and H₂ on Pd single crystal and polycrystalline surfaces has been previously studied by various techniques. On the basis of these results, the following phenomena have been observed; displacement of the adsorbed hydrogen by CO and further blocking of the surface sites for hydrogen adsorption, hydrogen penetration into the bulk induced by adsorbed CO, and segregation of CO and H islands on the surface. However, the mechanism of the transition between surface and bulk hydrogen induced by coadsorbed CO is still unclear. It has been noticed recently that the gas pressure as well as the sample temperature plays a very important role on the behavior of adsorbates. It is therefore of particular interest to study the interaction of CO and hydrogen in a relatively high pressure at low temperature.

Experimental

The experiments were performed in a conventional UHV chamber equipped with a quadruple mass spectrometer(QMS) for temperature program desorption(TPD). The exposure pressure of hydrogen is in the range of 10^{-7} - 10^{-6} Torr. The Pd(110) sample was cleaned by cycles of argon ion sputtering, oxygen oxidation and annealing. Sample temperature was monitored by a chromel-alumel thermocouple spot-welded to the rear face of the sample. High purity gases of H₂ and CO were introduced into the chamber through leak valves without further purification. Detail of this part was described elsewhere[1].

Results and discussion

Five types of experiments were carried out to probe the interaction of CO and hydrogen on Pd(110).

1. H₂ / Pd(110)

The H₂ thermal desorption spectra obtained after several different exposures at 200 K are shown in fig. 1. A single desorption peak, whose temperature is shifted from 330 K at low coverage to 270 K at high coverage is observed. We assign this peak to the β states which result from the recombination of chemisorbed atomic hydrogen on the surface. Fig. 1 also shows a small lift in the high temperature side with increasing hydrogen exposures which are assigned to dissolved hydrogen in the bulk. Note that large exposures make the further shift of β -H peak to lower temperature arising from the stronger repulsive interaction between the adsorbates.

Pre-exposure to 5 L CO and post-exposure to hydrogen cause drastic change of the H₂ TPD spectra as shown in fig. 2. A new peak at 370 K increases in its intensity with increasing H₂ exposures. A shoulder also appears at near 270 K which is approximately equal in peak temperature as shown in fig. 1. Total amount of H₂ desorbed in all the TPD spectra reported in this paper are shown in fig. 3. It has to be noted that the total amount of H₂ desorbed in fig. 2 at the same hydrogen exposure is nearly a half of that of H₂ desorbed in the experiment of H₂ / Pd(110).

According to the literature, the peak appeared at high temperature in fig. 2 is assigned to the hydrogen penetrating into the bulk. The shoulders appeared below 300 K, on the other hand, indicate the existence of adsorbed hydrogen on the surface.

The observation of adsorbed hydrogen on high CO covered surface is the most interesting result reported in this paper. Though few papers reported the interaction of CO and H₂ on Pd(110) surface, Behm et al [2] found that adsorbed CO not only block Pd surface sites for hydrogen, but also inhibit the hydrogen passage through the surface into the bulk. On Pd(111), Kok [3] reported that high CO coverage prevent any adsorption of hydrogen at 220 K. Our TPD results present evidences of adsorbed and dissolved hydrogen in considerable amounts on a surface presaturated with CO. Although no obvious change in peak shapes has been observed in the CO TPD spectra, the decrease in its amount is noticeable when the pressure of hydrogen is increased to 10⁻⁶ Torr, suggesting the displacement of adsorbed CO by hydrogen.

3. CO+H₂ / Pd(110) and H₂ / CO / Pd(110)

Fig. 4 shows the H₂ TPD spectra obtained by exposing Pd(110) to the mixture of CO and H₂ at 200K. Preadsorption of H₂ at various exposures followed by a fixed CO exposure yields similar spectra. Being compared with fig. 2, the high temperature peak was shifted to low temperature side nearly by 10 K. The ratio of area of shoulder to that of the peak is decreased sharply, whereas the total amount of hydrogen desorbed is largely increased. It is also noted that a small amount of preadsorbed hydrogen still remains on the surface which can be removed by further exposing to CO. This implies that these surface sites occupied by remained adsorbed hydrogen are somewhat CO unfavorable. Therefore the competition between CO and hydrogen on these weak bound sites would be probably part of the reason for the appearance or remains of adsorbed hydrogen whose amount strongly depends on the exposure pressures of CO and H₂. Though we can not clarify the exactly adsorption sites of hydrogen in this work, in a common view, the easily replaced chemisorbed CO are always those weakly bound on the surface.

The formation of CO-H complex has been proposed by some authors to explain the high temperature peak of hydrogen in the presence of CO. Though any kind of CO-H complex can not be traced in our TPD experiments, as a matter of fact, the assumption of CO-H surface complex at least on Pd(111) and Pd(110) has been argued and rejected by some authors, whereas a trapping mechanism which suggests that hydrogen can be trapped during the growth of islands of adsorbed CO and are further pushed below the surface by changing the polarization state of hydrogen atoms is more reasonable. However, this trapping mechanism can not explain our observation that hydrogen can adsorb and/or penetrate into bulk on a surface without free sites (both CO and hydrogen compete on the same surface sites). We therefore suggest that an intermediate of CO-H which precedes the dissolution of hydrogen is present on the surface during the coadsorption of CO and hydrogen.

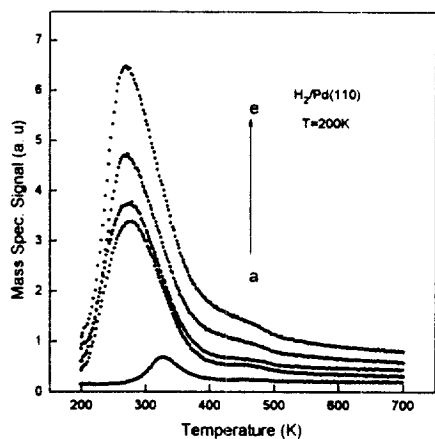


Fig. 1. H_2 TPD spectra after Pd(110) surface is exposed to hydrogen at 200 K. The pressures and exposures are (a) background; (b) 2.1×10^{-7} Torr, 25 L, (c) 2.1×10^{-7} , 63; (d) 1.0×10^{-6} , 120 and (e) 1.0×10^{-6} , 300.

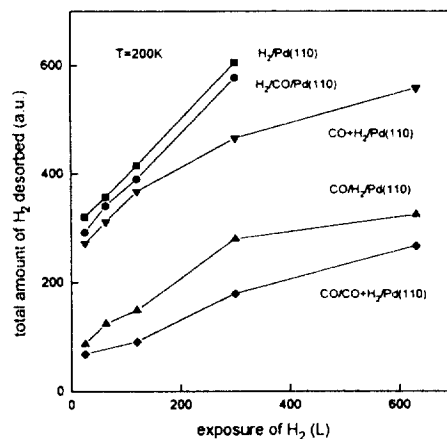


Fig. 3. Total amount of H_2 desorbed in the H_2 TPD spectra obtained under various exposure conditions.

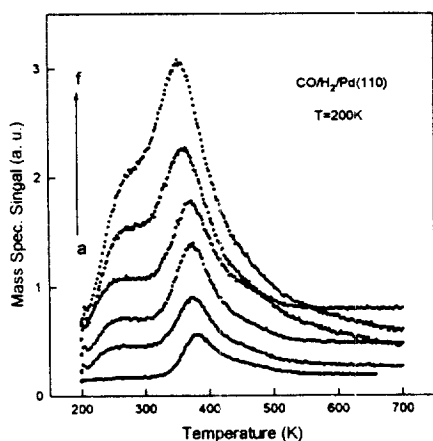


Fig. 2. H_2 TPD spectra from Pd(110) initially saturated with CO (5 L) and exposed to hydrogen at 200 K. The pressures and exposures are (a) in 5 L CO; (b) 2.1×10^{-7} Torr, 25 L; (c) 2.1×10^{-7} , 63, (d) 1.0×10^{-6} , 120; (e) 2.1×10^{-5} , 630 and (f) 2.1×10^{-6} , 1260.

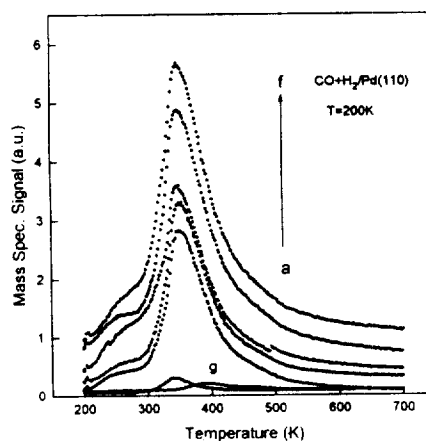


Fig. 4. H_2 TPD spectra after Pd (110) surface exposed to (CO+ H_2) mixture. The CO partial pressure is 5×10^{-8} Torr. The partial pressures and exposures of hydrogen are (a) background; (b) 2.1×10^{-7} Torr, 25 L; (c) 2.2×10^{-7} , 63, (d) 1.0×10^{-6} , 120; (e) 1.0×10^{-6} , 300; (f) 2.1×10^{-6} , 630 and (g) in 5 L CO.

Recently a concerted adsorption and desorption mechanism based on the delocalized chemisorption model which was used to explain the exchange reaction between gaseous and surface CO molecules on transition metals has been suggested by Guo et al. [4]. This mechanism may be applied to explain the dissolution of hydrogen in the presence of CO. When gaseous hydrogen molecule(s) or its precursor(s) strikes the effective vacancy ($1/\alpha - 1$), where α is the saturation coverage at this temperature, i.e., the average neighborhood around each adsorbed CO, it can either desorb the preadsorbed CO (this can only happen at very high pressure) or jump back into gas phase (when strikes straight on the head of adsorbed CO) or simultaneously form some kind of CO-H complex by coadsorbed on the same surface site with CO. This complex is quickly decomposed by pressing the hydrogen atom(s) into the bulk only because CO is bound much more stronger than hydrogen. According to this mechanism, the adsorption of hydrogen, and the formation and decomposition of the intermediate of CO-H is a concerted process. High pressure enhances the probability of hydrogen to desorb the adsorbed CO, while at medium pressures the probability to form a unstable surface complex is encouraged.

4. CO / CO+H₂ / Pd(110)

Pd(110) presaturated with CO was exposed to the mixture of CO and H₂ at different CO/H₂ ratios. The TPD spectra show that both the total amount of H₂ desorbed and the intensity of shoulders sharply decreases even if compared with those obtained in CO / H₂ / Pd(110) experiment. As shown in fig. 3, the order according to the total amount of hydrogen desorbed is as follows: H₂ / Pd(110) > H₂ / CO / Pd(110) > CO+H₂ / Pd(110) > CO / H₂ / Pd(110) > CO / CO+H₂ / Pd(110). This can also be explained by this concerted mechanism.

Conclusions

The following results has been obtained:

- (1) Hydrogen starts to desorb adsorbed CO when its pressure is in the range of 10^{-6} Torr.
- (2) The adsorption of hydrogen is the rate limiting step during its dissolution. The formation and decomposition of CO-H complex is too fast to be trapped on the surface.
- (3) Hydrogen coexists with CO on the surface by locating on some weakly bound sites and can be induced to penetrate into the bulk by further exposing to CO.
- (4) Further penetration of dissolved hydrogen into deep bulk has an energy barrier that cannot be overcome at low temperatures.

References

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