POISONING EFFECT OF CARBON MONOXIDE ON THE DESORPTION PROCESS OF HYDROGEN FROM PALLADIUM

H. Sakai, T. Nakajima, N. Yoshida and S. Kishimoto

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan

The desorption of H_2 from clean and CO-poisoned Pd wires was studied by a temperature programmed desorption technique. Poisoning effect of CO on H_2 desorption process can be accounted for in terms of blockage of the surface sites for the recombination of H atoms.

Десорбция H_2 с чистой палладиевой проволоки и, отравленной СО, была исследована методом температурно-программированной десорбции. Отравляющий эффект СО на процесс десорбции H_2 вызван, вероятно, блокированием поверхностных центров, на которых происходит рекомбинация атомов водорода.

It is well known that at low temperatures ($< 100 \,^\circ$C) the absorption rates of H_2 by Pd are very sensitive to the presence of impurities on the surface /1/. These results suggest that the steps on the surface, e.g. dissociation of H_2, may be responsible for the absorption process. It is expected that a similar situation exists in the case of the desorption process of H_2. However, few data from this point of view have been reported up to the present /2, 3/. CO is one of the best known inhibitors for catalytic hydrogenation reactions. Conrad et al. /4/, studying the coadsorption of H_2 and CO on Pd, have found that CO may displace preadsorbed H_2 completely from the surface, whereas no displacement of adsorbed CO by H_2 takes place. The purpose of this work was to clarify the effect of CO on the desorption process of H_2 from the Pd-H system by a temperature programmed desorption technique (TPD).

EXPERIMENTAL

Experiments were performed in an UHV system (base pressure 10^{-9} Torr). A Pd wire ($>99.9\%$ pure) 0.02 cm in diameter and 50 cm in length was used. The specimen was welded to metal leads in the reaction cell and connected to a bridge circuit. Cleaning and activation of the Pd surface were carried out by the following oxidation-reduction cycles: (1) first outgassed at 800 °C in vacuum for several hours, (2) heated in O_2 (1 Torr) at 200 °C for 1 h, (3) pumped, then H_2 (1 Torr) for 1 h at 300 °C, and (4) pumped to 10^{-9} Torr. It has been confirmed by different investigators that the electrical resistance in the α-phase of Pd-H system is proportional to the H concentration /5, 6/. Therefore, the specimen was exposed to H_2 (1 Torr) in a limited time at room temperature and then the amount of dissolved H was determined by measuring the resistance change (accuracy $\pm 10^{-4}$ Ω). All the experiments were carried out using specimens in the range of α-phase (atomic ratio, H/Pd = 0.0006–0.005). Following the absorption, the cell was rapidly cooled to −196 °C and pumped out and than TPD was commenced with a heating rate of 0.2 °C/sec. The temperature of the specimen was measured by a thermocouple which was in contact with the specimen. The changes in the partial pressure due to desorbing gases were recorded with a B—A gauge and a mass filter simultaneously. Surface poisoning was made by exposure of the H containing specimens to CO at different pressures (10^{-3}—10^{-4} Torr) at room temperature. The gases (H_2, O_2 and CO) of high purity were obtained from the Takachiho Co. and used without further purification.

RESULTS AND DISCUSSION

Desorption of H_2 from clean surfaces. Figure 1 shows typical TPD curves for the specimens with H/Pd = 0.0006–0.005. The desorption always commenced at the same temperature, about −180 °C. Only a single peak can be detected and the position of peak maximum shifts to lower temperatures with the increase of H content. This temperature shift and the symmetric shape of the spectra suggest that the desorption obeys second-order kinetics /7, 8/. Therefore, the data were analyzed in term of the equation

$$E_d/RT_m^2 = (n_o \nu/\beta) \exp(-E_d/RT_m),$$

where ν is the preexponential factor, E_d the activation energy of desorption, n_o initial H concentration, β heating rate and T_m the temperature at which the desorp-
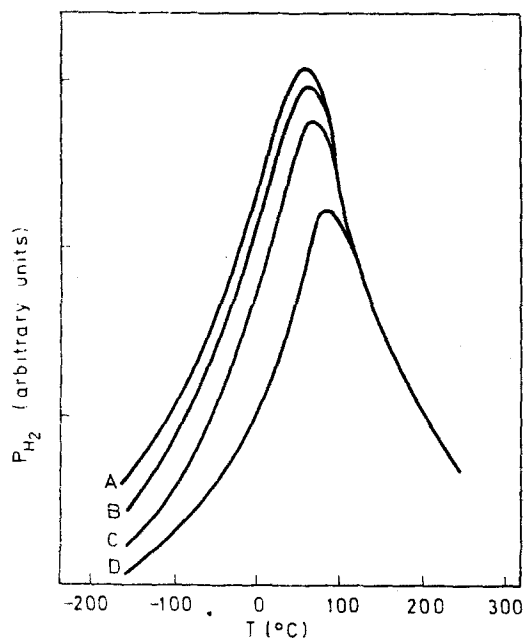
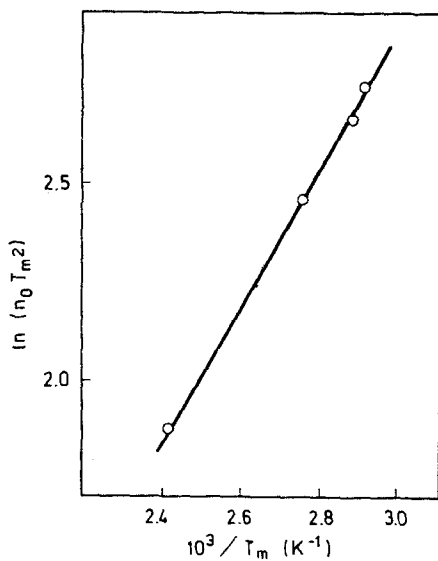Fig. 1. TPD spectra of H_2 from Pd with different H contents. H/Pd, (A) 0.005, (B) 0.004, (C) 0.0024, (D) 0.0006
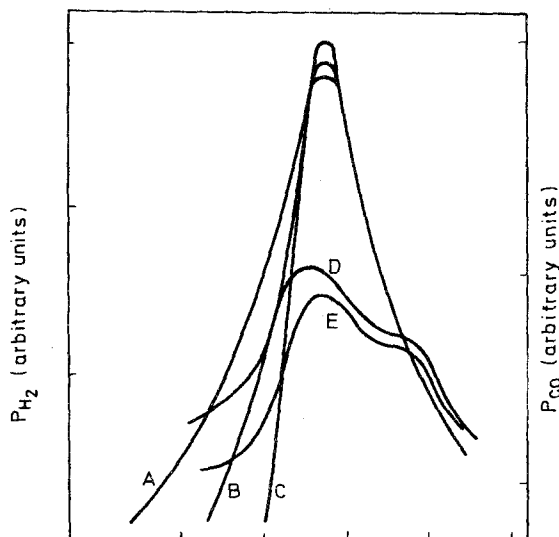

Fig. 2. Plot of $\ln(n_o \cdot T_m^2)$ vs. $1/T_m$

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Fig. 3. Effect of CO poisoning on TPD spectra of H_2 for the specimens with H/Pd = 0.0025.
(A) without poisoning; dose pressure of CO, (B) 3×10^{-4} Torr, (C) 1.5×10^{-3} Torr.
Curves (D) and (E) show the desorption of CO from specimens (B) and (C)

tion rate is maximum. Figure 2 shows that the desorption is well represented by second-order kinetics with an E_d of 15.5 kcal. An E_d value of 11.5 kcal was found by Auer and Grabke /6/, using thin foils of the α-phase. It was suggested by them that this value is equal to the sum of the heat of dissolution of H_2 (4.7 kcal) and the activation energy of absorption (6.8 kcal). Bucur et al. /9, 10/ also obtained a second-order rate law and E_d of 20.5 kcal on thin films under isothermal desorption conditions. These results suggest that the rate-controlling step of the desorption undoubtedly occurs at the surface. The discrepancy of E_d is difficult to explain but it may presumably result from the different type of specimens and the different methods of investigation used.

Desorption of H2 from CO-poisoned surfaces. Figure 3 shows TPD spectra obtained from CO-poisoned specimens (H/Pd = 0.0025). It is seen that the initiation temperatures of H_2 desorption (T_d) are shifted to 0 °C with increase of CO dose pressure, whereas T_m (about 70 °C) is almost unaffected. A relation between T_d and the dose pressure of CO is given in Fig. 4. In Fig. 3, CO desorption patterns are similar to those found by Stephan et al. /11/ and these peaks can be attributed to chemisorbed CO. It is clear that the rates of H_2 desorption rapidly increase with removal of prechemisorbed CO, that is, the surface steps in the desorp-
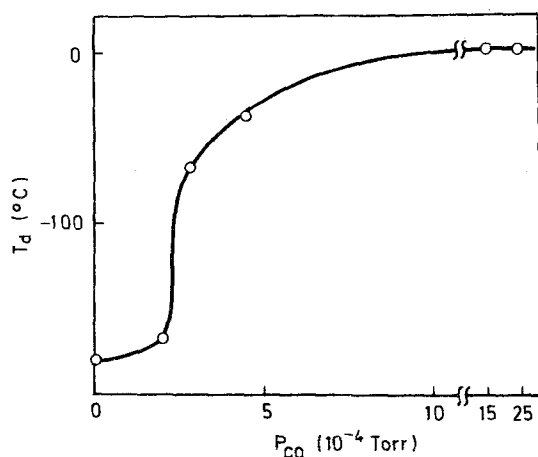
Fig. 4. Change in the initiation temperature (T_d) of H_2 desorption as a function of CO dose pressure

tion process are strongly inhibited by the presence of CO. During thermal desorption, only desorption of H_2 and CO were observed and no reaction products were found. This fact is in agreement with the results of Conrad et al. /4/ observed in the case of mixed adsorbed layers on single crystal planes of Pd. Further, it was observed that T_m was independent of the amount of dissolved H in the range $H/Pd = 0.0025-0.006$. At present, we have no satisfactory explanation for the mechanism of H_2 desorption from poisoned surfaces, but observations suggest that the interaction between H and CO at the surface must be weak and the chemisorbed CO merely blocks up the available sites for H recombination.

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