CHEMISTRY LETTERS, pp. 537-540, 1981.

THE EFFECTS OF SULPHUR IN A PALLADIUM SURFACE ON THE ADSORPTION AND DECOMPOSITION OF FORMIC ACID

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Ultraviolet photoelectron spectra indicate that formic acid is adsorbed as formate ion on not only clean, but sulphur segregated Pd surface with saturated amounts. The rate of formic acid decomposition stayed unchanged in the presence of surface sulphur.

It has been long fascinated research works to study the catalytic decomposition of formic acid from various reasons; the reactant and its reaction products are simple molecules, and secondly, its reaction products are associated with the catalytic selectivity, producing different decomposition products over different catalysts.[1] The dehydrogenation reaction($HCOOH \longrightarrow H_2 + CO_2$) is considered to be major reaction path on metal catalysts. Hirota et al.,[2] and Sachtler and Fahrenfort[3] found formate on silica supported Ni catalyst by infrared spectroscopy during the decomposition. In particular, the latter authors proposed a mechanism that the formic acid decomposes through formate ion and that the catalytic activity is directly correlated with the heats of formation of their formates, giving a volcano shape.[3] Pd is one of the best catalysts for the decomposition of formic acid because its formate stability(heat of metal formate is moderate value such as 3.3×10^2 KJ/mol.[3]), is such that neither the formation nor the decomposition of the formate intermediate will severely limit the reaction rate. The stability of surface formate may be affected by the presence of sulphur on the surface which acts as poison for various catalytic reactions. The effects of surface sulphur on the catalytic activity may also be associated with those on the electronic state of the catalyst surface, which can be examined by various electron spectroscopic techniques.[4,5] From these points of view, the adsorption and decomposition of formic acid were studied on the Pd surface where sulphur had been segregated to various extents by means of Auger electron spectroscopy(AES), ultraviolet photoelectron spectroscopy(UPS) and mass spectrometry(MS).

AES, UPS and MS spectra were obtained with a combined system and examined the same sample in the same vacuum chamber.[6,7] A quadrupole mass spectrometer, which was attached to the sample chamber, analysed the residual gas, estimated the amount of adsorbed gas by flash desorption and examined reaction kinetics. The sample

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employed was a polycrystalline Pd foil(0.02x3x20 mm^3, its purity was higher than 99.9 %) and was spot welded to the sample holder. The temperature of the sample was regulated by resistive heating and was measured by a Pt-Pt/Rh 13 % thermocouple, which was spot welded on the back side of the sample. The purity of formic acid which was used for the experiments, was about 99 %(WAKO Pure Chemical Industries, Ltd.). The base pressure of the sample chamber for AES, UPS and MS measurements was 9.3×10^{-6} Pa. Gases were introduced into the sample chamber through a bakable variable leak valve.

The Pd sample was treated at 673 K by several Langmuirs(1 Langmuir=1×10^{-6} Torr·sec) of O_2 and was evacuated and flashed to 1000 K under vacuum for a few seconds. The surface subjected to such treatments several times was proved to be clean by AES and UPS. He (I) UPS of clean Pd surface gave only Pd 4d band, located at 0 ∿ 4 eV binding energy(Fig. 1(a)-(i)). When the Pd sample was heated to 773 K under vacuum, sulphur was segregated onto the surface by AES and UPS. The concentration of sulphur on the Pd surface was estimated by AES. The ratio K(=S($L_{2,3}M_{2,3}M_{2,3}$: 150 eV) peak/Pd($M_{4,5}N_{4,5}N_{4,5}$: 330 eV) peak) was used as a measure of the relative concentration of sulphur, where peak intensities refer to the areas of both S(150 eV) and Pd(330 eV) peaks. The coverage of sulphur(θs) was estimated by the inhibition of CO adsorption on Pd.[4] K=0.0 corresponds to θs=0.0 and K=0.75 to θs=1.0. UPS of Fig. 1(b)-(i) shows a peak at 5.5 eV which is assigned to S 3p.[8] UPS and XPS measurements have indicated that the electron was transferred from Pd to sulphur and sulphur was negatively charged, especially in its lower coverages.[5]

When the Pd surface was proved to be clean by AES and UPS, formic acid (6.7×10^{-4} Pa) was introduced onto clean Pd surface at 298 K. Three peaks appeared at binding energies of 5.0, 8.0 and 10.0 eV by UPS(Fig. 1(a)-(iii)). If we compare the results with the adsorption of formic acid on Ni, Cu and Au studied by Joyner and Roberts,[9] UPS of formic acid on Pd at 298 K is similar to that on Ni at 295 K. It is generally accepted that formic acid is adsorbed as formate ion on Ni at room temperature.[10] Their peak intensities did not decrease by evacuating formic acid at 298 K. Therefore, formic acid was irreversibly adsorbed as formate ion on Pd at 298 K. On heating up the Pd sample to 423 K after evacuating formic acid, these three peaks disappeared and Pd surface became clean by AES and UPS. At the same time, CO_2(mass number=44) was desorbed in the gas phase by MS. CO(mass number=28) was not desorbed in the gas phase in this treatment. The decomposition of formic acid was studied on clean Pd surface at 423 K in the presence of formic acid (6.7×10^{-4} Pa) by MS. The result shows that the dehydrogenation reaction proceeded on clean Pd surface under steady state condition(Fig. 2).

The adsorption of formic acid was also examined in a similar manner on the Pd surface where sulphur was segregated to various extents. When formic acid(6.7×10^{-4} Pa) was introduced onto sulphur segregated Pd surface to various extents(K=0.23, 0.45, 0.59 and 0.75) at 298 K, three peaks appeared at binding energies of 5.0, 8.0 and 10.0 eV by UPS. The binding energies of three peaks and the amount of adsorbed formate which was estimated by the peak area of three peaks in UPS were the same as those on clean Pd(Fig. 1(b)). The decomposition of formic acid was also examined

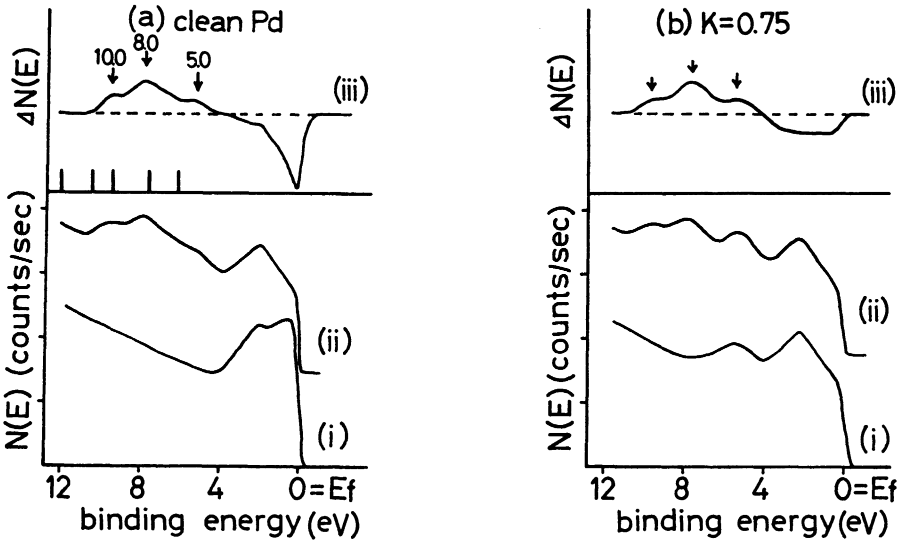

Fig. 1. UPS(He I=21.2 eV) for HCOOH adsorbed on clean and sulphur segregated Pd at 298 K. P_{HCOOH}=6.7x10^{-4} Pa. (a) (i) clean Pd, (ii) HCOOH adsorbed on clean Pd and (iii) differential spectrum; =(ii)-(i). (b) (i) sulphur segregated Pd(K[a]=0.75), (ii) HCOOH adsorbed on sulphur segregated Pd and (iii) differential spectrum; =(ii)-(i).

a) K is the ratio of the intensity of S($L_{2,3}M_{2,3}M_{2,3}$) Auger peak at 150 eV to that of Pd($M_{4,5}N_{4,5}N_{4,5}$) Auger peak at 330 eV.

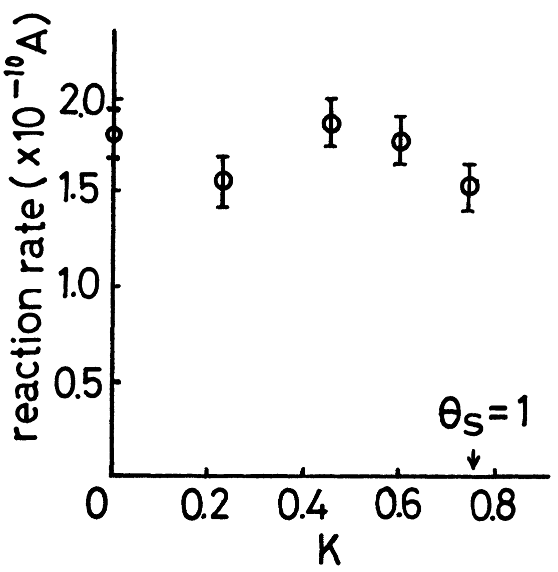

Fig. 2. Effects of surface sulphur on the decomposition of HCOOH at 423 K. P_{HCOOH}=6.7x10^{-4} Pa. The reaction rate under steady state condition(back ground is subtracted) is plotted according to K(the ratio of the intensity of S(150 eV) Auger peak to that of Pd(330 eV) Auger peak.

under steady state condition by MS at 423 K in the presence of formic acid (6.7×10^{-4} Pa) on the Pd surface where sulphur was segregated to various extents (K=0.23, 0.45, 0.59 and 0.75). The dehydrogenation reaction proceeded on sulphur segregated Pd surface. The rate of CO_2 formation on sulphur segregated Pd with various amounts under steady state condition is shown in Fig. 2. It is of great interest to note that the activity of decomposition of formic acid did not change, and that the effects of surface sulphur on the activity of adsorption and decomposition of formic acid were different from those on the adsorption of CO, the adsorption and decomposition of NO as previously reported.4)

It is concluded that formate ion would be adsorbed on Pd, and the decomposition of formate ion would control the overall rate, and that the stability of formate ion on the surface was not markedly changed by sulphur on the surface.

It has been demonstrated by means of UPS that the presence of sulphur on the Pd surface considerably change the electronic state of the surface, the electron on the Pd surface being localized at surface sulphur.5) Such drastic change in the electronic state still affects neither the catalytic activity nor its selectivity for the decomposition of formic acid.

Acknowledgement: The authors wish to express their gratitude to Dr. Mitsuyuki Soma for helpful discussions and a critical reading of the manuscript, and to Mr. Kunio Suzuki for valuable assistance in the experiments.

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(Received January 14, 1981)