CHEMISTRY LETTERS, pp. 1429-1432, 1986.

Hydrogen Adsorption on N-Modified Ni(755) Surface. Evidence of a Molecular "Precursor" State

Hisakazu NOZOYE

Basic Research Division, National Chemical Laboratory for Industry, Higashi 1-1, Yatabe, Tsukuba, Ibaraki 305

Hydrogen adsorption experiments were performed on N-modified Ni(755) surfaces. Sticking probabilities for hydrogen on the surfaces were determined by the analysis of temperature programmed desorption spectra. It is found that the adsorption of hydrogen proceeds through a molecular "precursor" state.

Stepped surfaces, that have high-Miller-index faces of single crystals of metals, are a good model of real catalysts. And many investigations have shown that step and kink sites show enhanced activities in some kinds of reactions or chemisorptions.[1,2] Under real conditions of catalytic reactions these sites may be occupied by ad-atoms and enhanced activities of the sites might be masked out. But there were few reports in which step or kink sites were modified by ad-atoms and studied the effects of these modifications to chemical reactions or chemisorptions.

Hydrogen adsorption on Ni single crystal surfaces is extensively studied.[3-9] But these studies are restricted to low-Miller-index surfaces. There are few investigations about adsorption of hydrogen on high-Miller-index surfaces. The initial sticking coefficients for hydrogen on Ni(111) and Ni(110) are 0.05 and 0.96 respectively.[5] This means that chemisorption behaviors of hydrogen for these surfaces are completely different. The reason for this difference is that the adsorption of hydrogen is activated for Ni(111) while that for Ni(110) has no noticeable barrier for adsorption.[8] We showed that step sites of Ni(755) surface can be selectively modified with nitrogen atoms.[10] This paper reports the difference of the sticking coefficients for hydrogen on different Ni crystal faces and the role of steps on hydrogen adsorption.

The experiments were performed in a stainless-steel UHV system with a turbo-

molecular pump (base pressure 1.3×10^{-8} Pa) equipped with a double pass CMA analyzer, a quadrupole mass spectrometer, 4-grid LEED optics and an ion gun. A Ni(755) crystal was in a form of disc (ca. 8 mm x 1 mm) and heated resistively by passing current through 0.3 mm tantalum-wires spot welded along the edges of the crystal. The temperature of the crystal was monitored by a chromel-alumel thermocouple spot welded to the edge of the crystal. For temperature programmed desorption measurements (TPD), the temperature of the crystal was raised from 123 K to 573 K with a heating rate of 15 K/s by a programmed power supply. The stepped Ni(755) surface was ascertained by LEED. Atomic nitrogen can adsorb on Ni surfaces easily by the activation of nitrogen molecules.[11] The activation of gaseous nitrogen was performed by operation of the electron bombardment ion gun at an accelaration voltage of 500 eV and emission current of 30 mA in high-purity nitrogen gas at 1.3×10^{-3} Pa. The amount of adsorbed nitrogen was regulated by the irradiation period and the exact amount of nitrogen was determined by the ratio of N 380 eV to Ni 716 eV Auger intensity. The Auger peak intensity ratio of 0.1 corresponds to the completion of selective adsorption along step sites (we defined this amount as P) and the ratio of 0.5 corresponds to the full monolayer coverage of nitrogen on the surface. Hydrogen was introduced to the surface using a molecular beam doser collimated with a glass micro-capillary array. Clean or N-modified

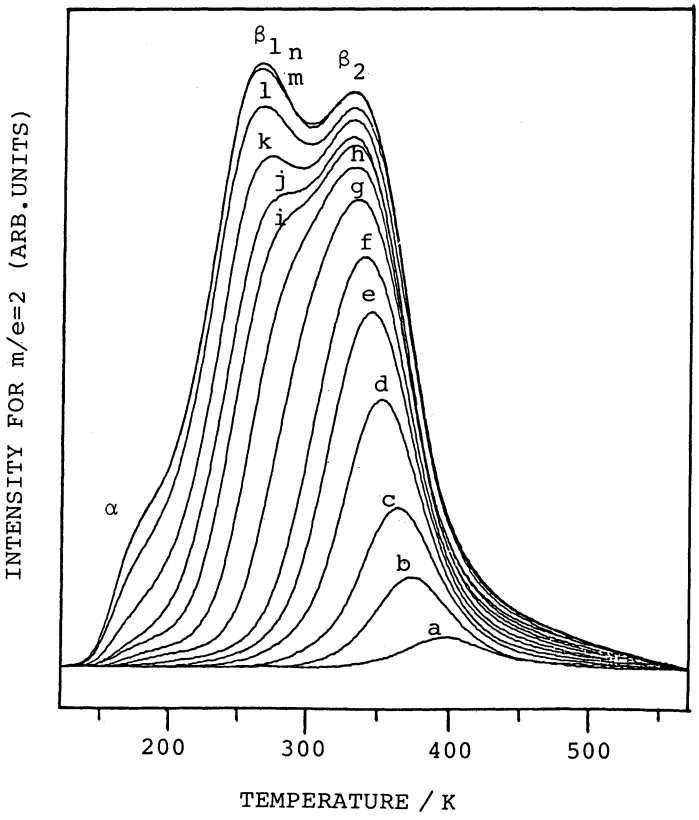

Fig.1. TPD spectra for H_2 on N-modified Ni(755) after adsorption at 123 K and $N_{380}/Ni_{716}=0.02$. Hydrogen exposure(L) a:0.03, b:0.08, c:0.15, d:0.30, e:0.45, f:0.60, g:0.91, h:1.21, i:1.51, j:1.81, k:2.42, l:4.84, m:19.4, n:38.7.

surface of the Ni(755) was exposed to hydrogen molecular beam to predetermined doses. Then the surface was positioned to face directly into the mass spectrometer ionizer. TPD spectra were measured for the mass number of m/e=2. TPD spectra for a N-modified surface are shown in Fig.1. The TPD spectra for hydrogen are similar to the previously reported one.[5] For low hydrogen doses β_2 peak appeared around 400 K and when the doses of hydrogen increased further it shifted to lower temperature, and β_1 peak and α peak appeared around 260 K and 180 K, respectively. The sticking coefficient of hydrogen is shown in Fig.2. The most characteristic feature is the existence of plateau when the amount of the preadsorbed nitrogen is below P. For the clean surface the sticking coefficient is constant up to hydrogen coverage of 0.24. The lengths of the plateau decrease in proportion to the amount of the preadsorbed nitrogen. When the step sites are completely occupied by preadsorbed nitrogen the plateau disappears. The initial sticking coefficient on the clean surface is 0.41 and when the amount of preadsorbed nitrogen increases it decreases steeply. At P the ennanced initial sticking coefficient on Ni(755) is completely suppressed. The initial sticking coefficient is 0.15 at P. This value can be compared with 0.05 for Ni(111). The difference between the two values can be explained by the difference of the number of defects which inevitably exist on any real surfaces.

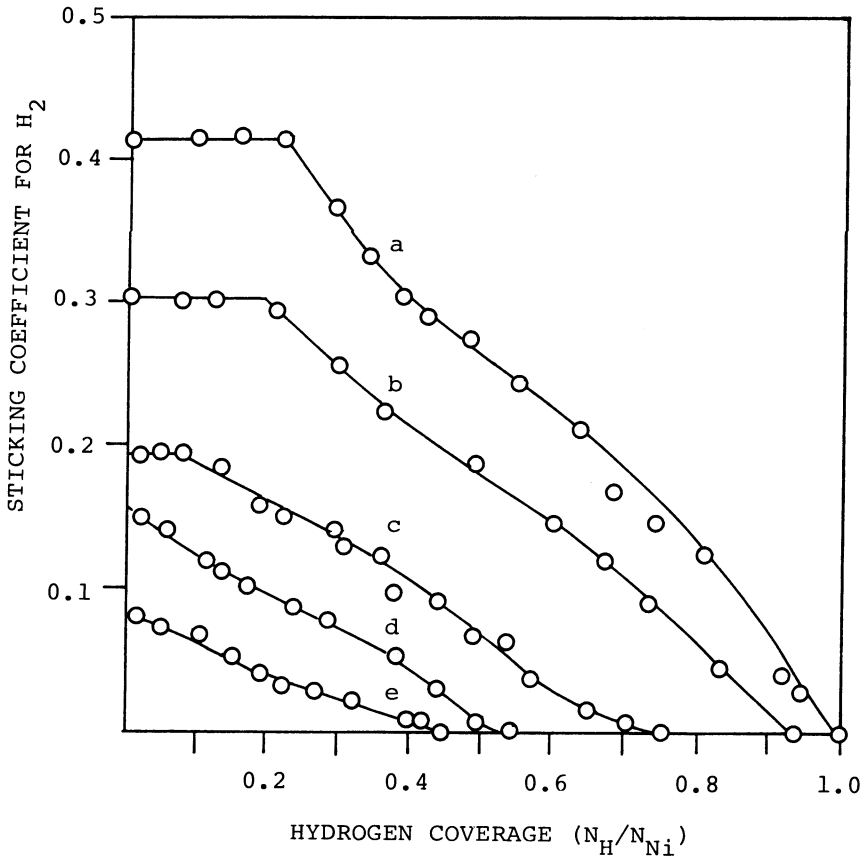

Fig.2. Sticking coefficient for H_2 on N-modified Ni(755) surfaces at 123 K. The amount of preadsorbed nitrogen (N_{380}/Ni_{716}); a:0, b:0.02, c:0.05, d:0.1, e:0.16.

The enhanced

initial sticking probability clearly indicates that step sites promote the dissociative adsorption of hydrogen. If all of hydrogen molecules which impinge on the step sites can adsorb on the sites, the initial sticking probability for clean surface is 0.34. This value is smaller than the observed value. This fact suggests that the adsorption of hydrogen through intermediate trapping in a molecular precursor state contributes to the initial sticking probability. The existence of the plateau indicates that hydrogen adsorbed along step sites does not mask out the high activity as long as there are vacant step sites. On the other hand nitrogen atoms that adsorbed along step sites mask out the high activity of step sites. The high probability of the bond breaking at step sites can be explained by the similarity between the structures of the step sites of Ni(755) and that of Ni(110). There are no noticeable activation barrier for dissociative chemisorption on Ni(110), while this is of the order of about 0.1 eV for Ni(111).[8] This difference of activation barriers explains the difference of sticking coefficients.

We thank Dr. Kazuo Someno for helpful discussions.

References

1) G.A.Somorjai, "Chemistry in Two Dimmensions," Cornell University Press. Ithaca and London.

2) H.Wagner, "Physical and Chemical Properties of Stepped Surfaces," in "Solid Surface Physics," Springer-Verlag, Berlin, Heidelberg and New York (1978), p.151.

3) K.Christmann, O.Schober, G.Ertl, and M.Neumann, J.Chem.Phys., 60, 4528 (1973).

4) K.Christmann, R.J.Behm, G.Ertl, M.A.Van Hove, and W.H.M.Weinberg, J.Chem.Phys., 70, 4168 (1979).

5) A.Winkler and K.D.Rendulic, Suf. Sci., 118, 19 (1982).

6) K.D.Rendulic and A.Winkler, J.Chem.Phys., 79, 5151 (1983).

7) K.Christmann, V.Penka, R.J.Behm, F.Chehab, and G.Ertl, Solid State Commun., 51, 487 (1984).

8) H.J.Robota, W.Vielhaber, M.C.Lin, J.Segner, and G.Ertl, Surf. Sci., 155, 101 (1985).

9) K.Christmann, F.Chehab, V.Penka, and G.Ertl, Surf. Sci., 152/153, 356 (1985).

10) H.Nozoye, Surf. Sci., 169, L362 (1986).

11) E.Roman and R.Riwan, Surf. Sci., 118, 682 (1982).

(Received May 26, 1986)