1 H, NH); IR (1 mM in CH_2Cl_2) 3459 (NH), 1733 (ester C=O), 1673 (amide C=O) cm^{-1}. EI MS *m/e*: 173.1045. Calcd for $C_6H_{11}NO_3$: 173.1052.

Variable-Temperature NMR Experiments. All amides used for preparation of CD_2Cl_2 solutions for variable-temperature ^1H NMR experiments were vacuum-desiccated in a heated drying pistol in the presence of P_2O_5 for several days before sample preparation. The CD_2Cl_2 was stirred with CaH_2 overnight and then distilled onto activated 4-Å molecular sieves under N_2 immediately before use. Syringes and NMR tubes were dried on a vacuum line at room temperature overnight. The samples were prepared in a glovebag (N_2) by dissolving a 5–20-mg portion of the dried amide in sufficient CD_2Cl_2 to make a 100 mM solution and then performing two serial 1:9 dilutions with CD_2Cl_2. The resulting 1 mM solution was placed in an NMR tube, freeze–pump–thaw degassed, and sealed under vacuum. Even with these precautions, the resulting samples typically contained 5–10 mM H_2O. CD_3CN NMR samples (10 mM) were prepared without special precautions. For samples prepared in 9:1 CCl_4/C_6D_6 (1 mM), the CCl_4 was dried by passage over a column of alumina.

Variable-temperature NMR measurements were performed on a Bruker AM-500 spectrometer. A microprogram was used to change temperature in fixed increments automatically, wait 15 min for temperature to stabilize, refine the Z and Z^2 shims, and then obtain a 128-scan spectrum. In one run, measurements were made in the range 193–273 or 253–303 K for CD_2Cl_2 or 253–323 K for CD_3CN. In these experiments, the first measurement was made at the lowest temperature, and then the temperature was increased in 10 K increments. At the top of the range, the temperature was dropped by 5 K and then by additional 10 K increments. For measurements in CD_2Cl_2, all chemical shifts were referenced to the signal for residual $CHDCl_2$, which was assumed to be 5.320 ppm *at all temperatures*. For measurements in CD_3CN, chemical shifts were referenced to residual CHD_2CN, at 1.950 ppm. From one run to another, amide proton chemical shift measurements at a given temperature were generally reproducible to within 0.05 ppm (with the same sample or an independently prepared sample). For thermodynamic analyses, nominal probe temperatures, read directly from the spectrometer console, were converted to actual temperatures by means of a calibration curve constructed with a chemical shift thermometer (0.03% concentrated HCl in MeOH).[36]

Variable-Temperature IR Experiments. Amides used for preparation of IR samples were vacuum-desiccated as described for NMR samples. CH_2Cl_2 solutions were prepared in a glovebag (N_2) by dissolving several milligrams of amide in solvent that had been distilled from CaH_2 under N_2 to yield 10–100 mM samples and performing serial dilutions to 1 mM. Acetonitrile samples (10 mM) were prepared from solvent stored over 3-Å molecular sieves. Baseline corrections were applied to obtain the spectra reproduced in Figures 1 and 2, but baseline corrections were *not* applied when quantitative analysis of the data was performed.

IR measurements were performed on a Nicolet 740 FT-IR instrument equipped with a TGS detector. A Specac variable-temperature cell P/N 21.500 equipped with CaF_2 windows and having a path length of 1.0 mm was used for variable-temperature experiments. Temperatures were maintained with various ice, dry ice, or liquid N_2 slush baths and were monitored with a platinum resistance thermometer attached directly to the cell. The cell temperature was allowed to stabilize for at least 20 min before measurements were obtained, and the cell temperature varied less than 1 °C during data acquisition. Spectra of 128 scans were obtained with 2-cm^{-1} resolution. Solvent subtraction was carried out by using reference spectra obtained at approximately the same temperatures as the sample spectra.

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Quasi-Equilibration of N(a) + $^1/_2H_2 \rightleftharpoons$ NH Established on c(2×2)-N of the Pd(100), Rh(100), and Pt–Rh(100) Surfaces during Hydrogenation of c(2×2)-N

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Abstract: Pd, Rh, and Pt are inert for the dissociative adsorption of N_2 and make no bulk nitrides, but we can prepare a nitrogen overlayer with the c(2×2) structure on Pd(100), Rh(100), and Pt–Rh(100) surfaces by the reaction of NO + $H_2 \rightarrow$ N(a) + H_2O. When the nitrogen overlayer denoted by c(2×2)-N was exposed to 10^{-6}–10^{-8} Torr of H_2 at around 400 K, a prominent energy loss peak appeared at 3200–3240 cm^{-1}. Pressure dependence of the in situ energy loss spectrum proved that a quasi-equilibration of N(a) + $^1/_2H_2 \rightleftharpoons$ NH is established on the Rh(100) surface at 400 K, but the c(2×2) LEED pattern changes little by being exposed to H_2. These results indicate that the NH species is prominently formed at the surroundings of the c(2×2)-N islands when the c(2×2)-N surface is exposed to H_2. The isotope effect on this quasi-equilibration was shown to be very small on the Rh(100) surface as well as on the Pd(100) and Pt–Rh(100) surfaces, which is in remarkable contrast to the large inverse isotope effect reported on the ammonia synthesis reaction.

Introduction

Pd, Rh, and Pt are inert for dissociative adsorption of N_2[1] so that they have no catalytic activity for ammonia synthesis reaction. Furthermore, these metals make no bulk nitrides.[2] On the other hand, these metals catalyze the reaction of NO_x with H_2 or CO. Provided that the NO molecule undergoes the following reactions on the metals surfaces, nitrogen intermediates should be formed on these metal surfaces during the reaction. Provided that re-

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(1) Cf: Hayward, D. O.; Trapnell, B. M. W. *Chemisorption*; Butterworths: London, 1964.

(2) Cf: Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; p 207.

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$$NO + H_2 \rightarrow N(a) + H_2O \quad (i)$$

$$N(a) \rightarrow \tfrac{1}{2}N_2 \quad (ii\text{-}a)$$

$$N(a) + \tfrac{3}{2}H_2 \rightarrow NH_3 \quad (ii\text{-}b)$$

$$N(a) + NO \rightarrow N_2 + O(a) \text{ or } N_2O \quad (ii\text{-}c)$$

action i proceeds rapidly but ii-a, ii-b, and ii-c are slow, the fugacity of the N(a) would be very high during the reaction. On the basis of this principle, we attempted to synthesize a surface nitride on Pd(100), Rh(100), Pt(100), and Pt-Rh(100) surfaces by performing the reaction of NO with H_2. We succeeded in getting a nitrogen overlayer with the c(2×2) structure on Pd(100), Rh(100), and Pt-Rh(100) surfaces[3-6] except on the Pt(100) surface. It is a noteworthy fact that the Pt enriched Pt-Rh(100) surface gives the c(2×2)-N overlayer although no nitrogen accumulation takes place on the Pt(100) surface.[5]

When the c(2×2)-N overlayer prepared on the Pd(100), Rh(100), and Pt-Rh(100) surfaces is exposed to H_2 pressure of 10^{-7} Torr at around 400 K, the hydrogenation of N(a), reaction ii-b, proceeds slowly.[3,4] The hydrogenation reaction of N(a) on these metal surfaces is a model reaction for the ammonia synthesis reaction, so we focussed on the intermediates of this model reaction. So far, adsorption of ammonia on single-crystal metals has been studied by spectroscopic methods,[7] but it should be realized that the adsorption of NH_3 could not discern the key intermediates as well as the mechanism of the ammonia synthesis reaction, and these will be discussed in this paper.

For this reason, the in situ spectroscopic study of the c(2×2)-N surface during the hydrogenation reaction is of crucial importance. To throw light on the mechanism and the reaction intermediates, a new dynamical spectroscopy using the in situ electron energy loss spectroscopy (EELS) was proposed.

Experimental Section

The experiments were carried out in a UHV chamber (base pressure less than 5×10^{-10} Torr) with an attached high-pressure reactor of small volume.[8] The UHV chamber is equipped with a LEED optics, an Auger electron spectrometer (AES), and a high-resolution electron energy loss spectrometer (HREELS). Single-crystal wafers (about 1-mm thickness) of Pd(100), Rh(100), and a Pt-Rh(100) alloy (Pt/Rh = 0.25/0.75 obtained from Metal Crystal Ltd., Cambridge) with an accuracy of ±1° of the (100) plane were finished by the mechanical polishing with a 0.25 μm diamond paste. The single-crystal disk was held by bridging between the two Ta rods and by bridging with two Ta wires of 0.25 mm diameter with a spot-welded crystal disk and was heated by a direct current through the Ta wires. The temperature was measured by a chromel-alumel thermocouple spot-welded on the edge of the crystal disk. The clean surface of Rh(100), Pt-Rh(100), and Pd(100) was obtained by cycles of Ar ion bombardment at room temperature, oxidation in O_2 of 10^{-7} Torr at about 900 K, and annealling at around 900 K. Reaction of NO with H_2 was performed on Pd(100), Rh(100), and Pt-Rh(100) at temperatures of 500–600 K in a high-pressure reactor. After several minutes of the reaction, the sample disk was flashed up to about 520 K in the UHV chamber to remove the adsorbed NO. By this procedure, a surface showing a clear c(2×2) LEED pattern with only N(a) by the AES analysis was obtained, which was denoted as c(2×2)-N.

In situ EELS study was performed by exposing the c(2×2)-N surface to H_2 or D pressure of 10^{-7}–10^{-8} Torr at the desired temperatures.

Results and Discussion

When a c(2×2)-N overlayer prepared on the Pd(100) surface is exposed to 10^{-7} Torr of H_2 pressure at around 400 K, an intense energy loss peak appears at about 3200 cm^{-1}, which is assignable to the N–H stretching vibration.[4] The same characteristic energy loss spectrum was observed when c(2×2)-N overlayer prepared on Rh(100) and Pt-Rh(100) was exposed to H_2 at 400 K. These results indicate the formation of NH_x species (NH and/or NH_2) by reacting the c(2×2)-N overlayer on Pd(100), Rh(100), and Pt-Rh(100) surfaces with H_2. Provided that such a consecutive hydrogenation mechanism as $N(a) \rightarrow NH \rightarrow NH_2 \rightarrow NH_3$ exists, observed NH_x species could be specified by the dynamical behavior of the spectrum during the reaction.

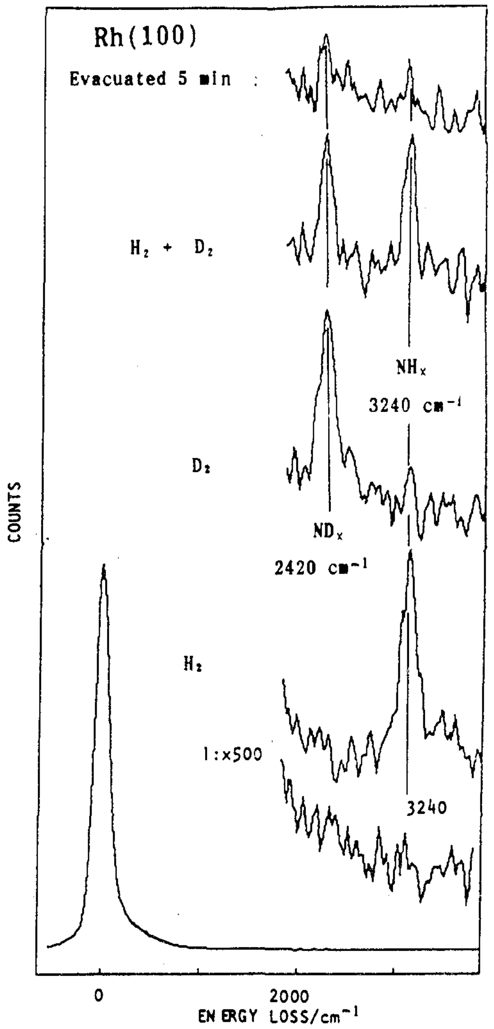

Figure 1. In situ energy loss spectrum of the c(2×2)-N/Rh(100) surface exposed to 10^{-7} Torr of H_2 and D_2 pressure on a 1:1 mixture of H_2 and D_2 at 400 K.

As shown in Figure 1, the c(2×2)-N of the Rh(100) surface exposed to H_2 at 400 K gives an intense energy loss peak at 3240 cm^{-1}. When ambient H_2 is replaced with D_2, the energy loss peak at 3240 cm^{-1} quickly disappeared and a new loss peak appeared at 2420 cm^{-1}, and these loss peaks almost disappeared by the evacuation for 5 min at 400 K. When the gas phase was changed to a 1:1 mixture of H_2 and D_2, the two peaks appeared in almost equal intensity, and the peak intensity at 3240 cm^{-1} changes reversibly depending on H_2 pressures at 400 K as shown in Figure 2a. Furthermore, it was also confirmed that the in situ energy loss peak at 3240 cm^{-1} in 10^{-7} Torr of H_2 pressure changes reversibly with the temperature as shown in Figure 3, that is, the amount of NH_x formed on the c(2×2)-N surface decreases with raising of the temperature and vice versa. It should be pointed out that the c(2×2) LEED pattern changes little by exposing the c(2×2)-N surface to H_2, and the hydrogenation of N(a) to NH_3 is rather slow at around 400 K, although the formatioin of NH_x is rapid and reversible on Rh(100) at 400 K. From these facts, we can conclude that a quasi-equilibration (1) is established at a limited part of the c(2×2)-N islands.

$$N(a) + xH \rightleftharpoons NH_x(a) \quad (1)$$

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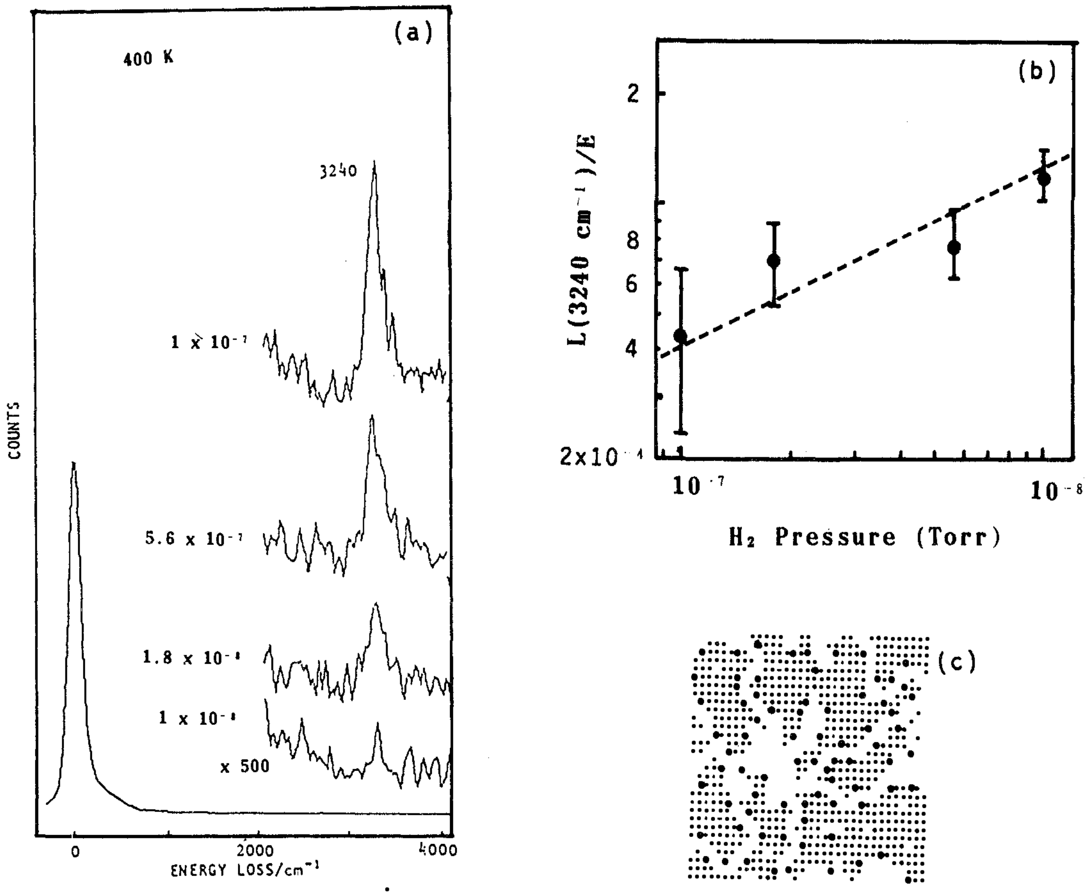

Figure 2. (a) In situ energy loss spectrum of the c(2×2)-N/Rh(100) surface at various H_2 pressures at 400 K. (b) Pressure dependence of peak intensity at 3240 cm^{-1}. Broken line corresponds to a half-order dependence on hydrogen pressure. (c) A fractal-like reaction model at the surroundings of c(2×2)-N islands. N atoms are indicated by small dots, and quasi-equilibrium NH species are shown by large dots.

In a previous paper,[3] it was shown that the decreasing rate of N(a) by the hydrogenation reaction is zero order with respect to the amount of N(a) on the Pd(100) surface. If the quasi-equilibration (1) could be established for the surroundings of the c(2×2)-N islands, the zero-order decrease of N(a) with respect to θ_N as observed on the Pd(100) surface[3] might suggest a fractal-like hydrogenation of NH_x at the surroundings of the c(2×2)-N islands, where the reaction proceeds at the surroundings of the c(2×2)-N islands as shown in Figure 2c, and, if this is the case, it is a new type of zero-order reaction.

The NH_x species in quasi-equiilibration reaction 1 are either NH or NH_2 species, which are described by the following equations

$$N(a) + H \rightleftharpoons NH(a) \qquad (NH) = K_1(N)(\theta_H) \qquad (2)$$

$$N(a) + 2H \rightleftharpoons NH_2(a) \qquad (NH_2) = K_2(N)(\theta_H)^2 \qquad (3)$$

where K_1 and K_2 are the equilibrium constants.

As the adsorption equilibrium is established for H_2 at around 400 K, the surface coverage of hydrogen (θ_H) is given by the following equation

$$\theta_H = K_H\sqrt{P_H}/(1 + K_H\sqrt{P_H}) = K_H\sqrt{P_H} \qquad \text{(iii-a)}$$

Consequently, the peak intensity (I) for N–H vibration will depend on H_2 pressures as described below

$$I = K_1[N][K_H\sqrt{P_H}] \qquad \text{for NH} \qquad \text{(iii-b)}$$

$$I = K_2[N][K_H\sqrt{P_H}]^2 \qquad \text{for NH}_2 \qquad \text{(iii-c)}$$

where P_H is hydrogen pressure. Accordingly, the loss peak will obey either a half order or the first order with respect to hydrogen pressures depending on NH or NH_2. As shown in Figure 2b, it is obvious that the intensity obeys a half order in H_2 pressures, that is, a quasi-equilibration (2) is established during the hydrogenation of the c(2×2)-N on the Rh(100) surface.

Consequently, the isotope effect for the formation of NH and ND in the quasi-equilibration (2) is an interesting subject. When c(2×2)-N of the Pd(100), Rh(100), and Pt-Rh(100) surfaces is exposed to a 1:1 mixture of H_2 and D_2, two peaks referred to as NH and ND appeared at around 3200 and 2400 cm^{-1} according to the following equations

$$N(a) + H(a) \rightleftharpoons NH \qquad (4)$$

$$N(a) + D(a) \rightleftharpoons ND \qquad (5)$$

The isotope effect for this equilibration is given by the following relation

$$K_{NH}/K_{ND} = [NH][N][\theta_D]/[ND][N][\theta_H]$$
$$= [NH][K_D\sqrt{P_D}]/[ND][K_H\sqrt{P_H}] \qquad \text{(iv)}$$

where K_{NH} and K_{ND} are the equilibrium constants in eqs 4 and 5. As shown in Figure 4, the peak for NH (3200 cm^{-1}) and the peak for ND (2400 cm^{-1}) have almost equal intensity on the surfaces of Pd(100), Rh(100), and Pt-Rh(100). Providing that the energy loss cross sections are almost equal for NH and ND, the same intensity of the energy loss peaks for NH and ND may indicate the formation of equal amounts of NH and ND on the surface. As the isotope effect on adsorption of H_2 and D_2 is very small,[9] $K_{NH}/K_{ND} = 1$ is derived from eq iv, that is, the isotope effect on the equilibration (2) is very small at around 400 K on the Pd(100), Rh(100), and Pt-Rh(100) surfaces. Such a small isotope effect on the equilibration of NH and ND in reactions 4 and 5 is analogous to the isotope effect on the adsorption of H_2 and D_2 on metals as well as on oxides, where the zero point energy difference between H_2 and D_2 (1.8 kcal/mol) is comparable to that of the newly formed bonds. Taking into account the fact that a rather small enthalpy change is expected for reactions 4 and 5 from the temperature dependence of the NH peak in Figure

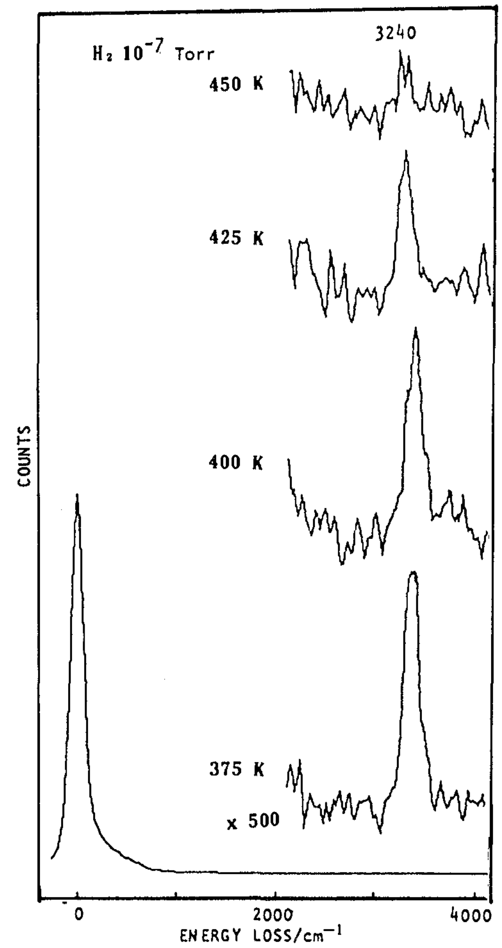

Figure 3. Temperature dependence of the peak at 3240 cm^{-1} in 10^{-7} Torr of H_2.

3, this argument may be applicable to the isotope effect on reactions 4 and 5.

$$\begin{array}{ll} N(a) + H(a) \rightleftharpoons NH(a) & \Delta H \\ \tfrac{1}{2}H_2 \rightleftharpoons H(a) & Q_H \\ \hline N(a) + \tfrac{1}{2}H_2 \rightleftharpoons NH(a) & \Delta H + Q_H \end{array}$$

$$d(NH)/dT = d/dT[K_1(N)(\theta_H)] = d[K_1K_H]/dT$$

From the temperature dependence of the energy loss peak at 3240 cm^{-1}, the enthalpy change ($\Delta H + Q_H$) was evaluated to be -9 ± 3 kcal/g-atom. We have no knowledge about the heat of adsorption of H_2 (Q_H) on the c(2×2)-N of the Rh(100) surface, but if we assume it to be about 12-13 kcal/g-atom, the value of ΔH will be less than several kcal/mol. If this is the case, the zero point energy difference between metal-H and metal-D may cancel out that of the N-H and N-D bonds.

It is worthy to note that the small isotope effect for K_{NH}/K_{ND} is in remarkable contrast to the unusually large inverse isotope effect observed on the ammonia synthesis reaction[10] as well as on the hydrogenation of N on a doubly promoted Fe catalyst,[11] where the formation of ND_3 is several times faster than that of NH_3 at 450-590 K. We should remember that the present experiments were performed at rather low hydrogen pressures (10^{-7} Torr) and that the consecutive hydrogenation of NH to NH_3 is slow. Thus, NH_3 pressure in the gas phase is almost zero during the reaction. Contrary to this, the ammonia synthesis experiments were carried out at higher pressures, and a certain pressure of ammonia is necessary to exist in the gas phase under a steady state of the reaction. As a result, the reverse process, $NH_3 \rightarrow NH_x \rightarrow N$, occurs on the catalyst surface. Consequently, relative partial pressure of ammonia in the gas phase, NH_3/ND_3, given by a dynamical balance, depends on the zero point energy difference between NH_3 and ND_3 (5.7 kcal/mol), which may be responsible for the large inverse isotope effect appearing on the hydrogenation of nitrogen on the Fe catalyst as Ozaki pointed out.[12]

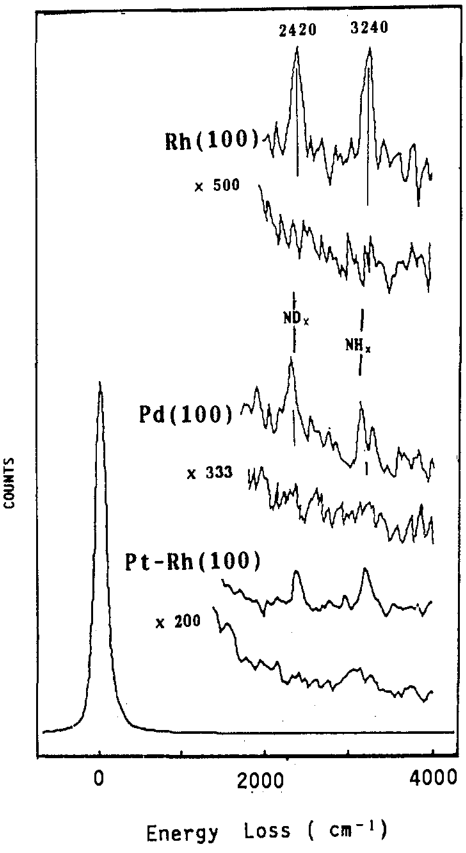

Figure 4. In situ spectrum of the c(2×2)-N surfaces exposed to a 1:1 mixture of H_2 and D_2. Spectrum was obtained at 375 K on Pd(100) and at 400 K on Rh(100)) and Pt-Rh(100) surfaces.

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