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XPS STUDIES OF SURFACE NITROGEN DISSOCIATED FROM DINITROGEN ON RANEY RUTHENIUM

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Atomic nitrogen species on Raney-Ru was studied by means of XPS in connection with isotopic equilibration reaction. Binding energy of a main N 1s peak stable up to 673 K was 397.4 eV, which was assigned to be N(a). When the adsorbed nitrogen was heated from 673 K to 873 K under hydrogen atmosphere, the value shifted to 396.7 eV suggesting the formation of aluminum nitride.

Investigation of surface state of nitrogen species is important especially on the active catalyst for ammonia synthesis and isotopic equilibration of dinitrogen. XPS techniques have already been applied to an industrial ammonia catalyst1) and various transition metals.2-5) No such work, however, has been reported in connection with the activation of dinitrogen on Ru catalysts, which are the most effective for dissociation of dinitrogen.6-9) XPS measurement of nitrogen adsorbed on Ru at room temperature is usually difficult because of its low concentration. Raney-Ru can make this possible because of the high surface area and the stronger adsorption of nitrogen.10, 11) This catalyst is also worth studying in view of the extraordinary activeness for dinitrogen activation.9) Umbach et al. have already reported XPS data of surface nitrogen on Ru, however, the species is obtained by a dissociative adsorption of NO with the coexistence of dissociated oxygen.12) Egawa et al. have studied NH_3 decomposition on Ru single crystal by XPS techniques.13) Here we report for the first time XPS spectra of surface nitrogen obtained from dinitrogen on Ru catalyst.

Raney-Ru was prepared with a similar method to that reported previously except the use of leaching solution of KOH in stead of NaOH.11) The Al content in Raney-Ru after leaching was estimated to be about 10 wt% by measuring hydrogen evolution

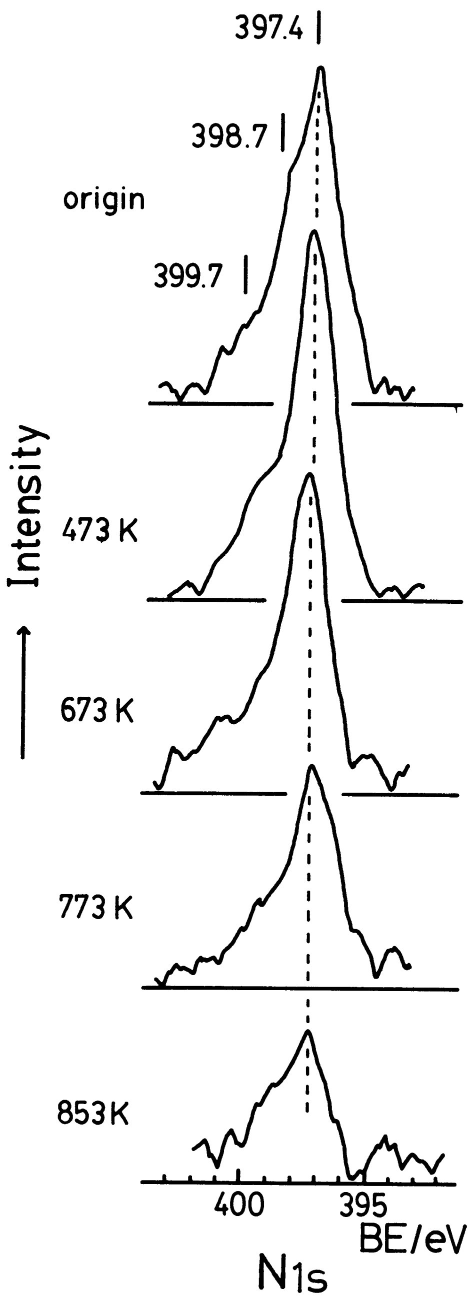

Fig. 1. Change of XPS spectra (N 1s) of adsorbed nitrogen on Raney-Ru during TPD. Dinitrogen was adsorbed at 623 K, and the sample was cooled to 298 K. TPD started from 298 K (origin) to the indicated temperature, and a part of the quenched sample was moved to XPS chamber. Spectra were recorded at 298 K.

during the leaching process.[11)] One gram of the sample with BET area of 98.4 m^2/g and with hydrogen chemisorption of 19.7 ml/g was used. N_2 adsorption onto Raney-Ru was carried out at 623 K for 40 h yielding N/Ru(total) atomic ratio of 0.126, under which condition N_2 dissociation reaction occurs effectively. During TPD (Temperature Programmed Desorption) or TPR (Temperature Programmed Reduction by hydrogen), the reaction chamber was quenched several times so that a part of the catalyst powder was moved into one of side-glass-arms attached to the reactor and the arm was sealed off. The powder was then mounted on an XPS sample holder in the argon chamber which was attached to the spectrometer. The spectra were recorded at room temperature by Shimadzu ESCA 750. All binding energies were corrected by the value of Au $4f_{7/2}$ (83.8 eV), and relative peak areas were calibrated against Ru $3p_{3/2}$ peak.

XPS spectra of nitrogen adsorbed on Raney-Ru during TPD are shown in Fig. 1. The spectrum shown as "origin" which was recorded after the N_2 adsorption is composed by a main peak at 397.4 eV and shoulders at 398.7 and 399.7 eV. The main peak intensity decreases above 773 K. Such intensity profiles with temperature correspond well with the previous TPD results obtained by a mass spectrometry,[10)] suggesting the main peak to be due to atomic nitrogens.

Changes of XPS spectra of adsorbed nitrogen on Raney-Ru during TPR are shown in Fig. 2. Similar peak to that in Fig. 1 was obtained at the beginning of TPR. However, at 873 K the peak did not decrease, but shifted from 397.4 to

396.7 eV.

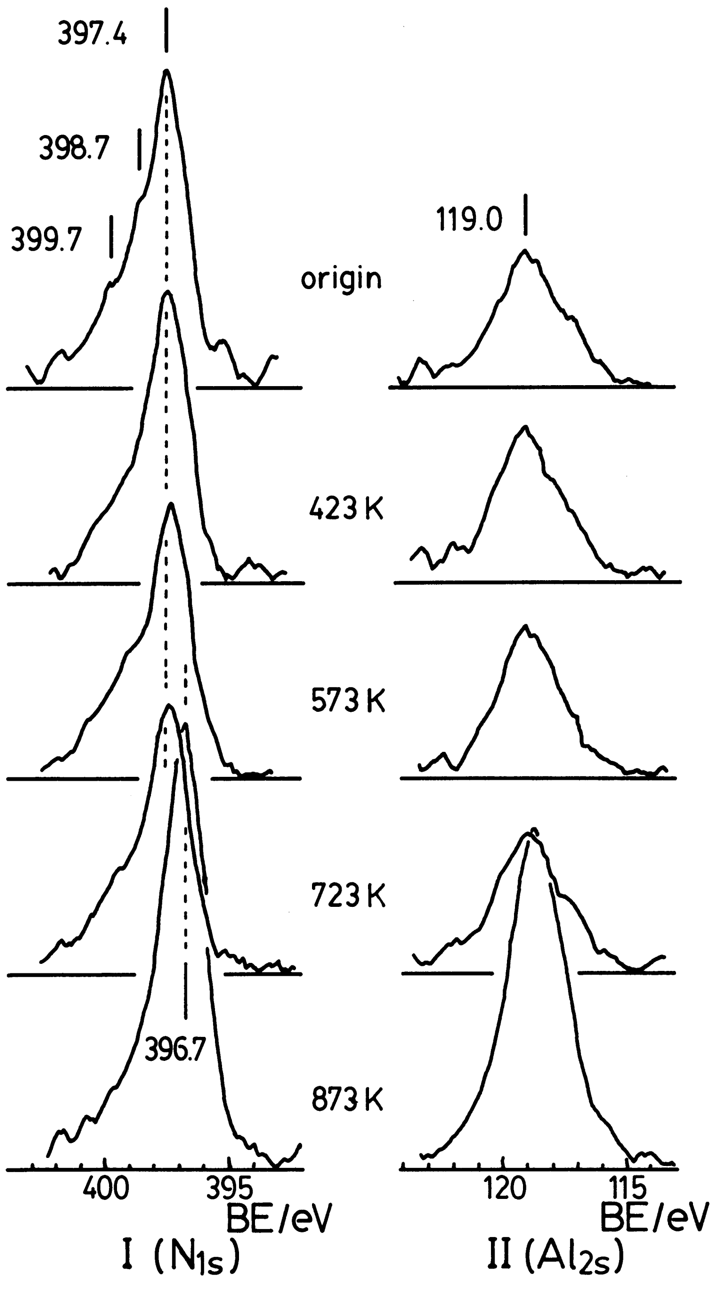

Fig. 2. Change of XPS spectra (N 1s) of adsorbed nitrogen on Raney-Ru during TPR. Dinitrogen was adsorbed at 623 K, and the sample was cooled to 298 K. TPR started from 298 K (origin) to the indicated temperature under the stream of hydrogen, and a part of the quenched sample was moved to XPS chamber. Spectra were recorded at 298 K.

Binding energy values of surface nitrogen atoms (N 1s) have been reported to be ca. 397 eV on Ru(001),[12)] 397.4 eV on Ru(1,1,10),[13)] 397.6 eV on W(110),[14)] 397.4 eV on Fe(110),[16)] 397.4 eV on Ni(100),[14)] and so on. Thus the peak at 397.4 eV on Raney-Ru in this study (Figs. 1 and 2) was assigned to atomic nitrogen, which corresponded to (active intermediate) and/or nitrogen in the previous paper.[10)]

XPS spectrum of AlN supplied by Soekawa Chemicals showed the binding energy of N 1s to be 396.7 eV. Thus the peak at 873K in TPR was assigned to AlN. Adsorbed nitrogen is considered to migrate into the surface or the bulk of Al. . It is interesting that the nitrogen migration occurs only with the presence of hydrogen. Al 2s peak was also measured during TPR and found to increase at 873 K as is shown in Fig. 2. Surface concentration of Al is increased at this temperature. This is perhaps the reason why N 1s intensity is increased at this temperature in Fig. 2.

A shoulder peak at 398.7 eV in Fig. 1 or 2 was assigned to NH_x

(x=1 or 2) by referring the data on W(110),14) Ru(1,1,10),13) or an industrial ammonia catalyst.1) In order to assign another shoulder at 399.6 eV, NH_3 was adsorbed on slightly oxidized Raney-Ru surface for XPS measurement, because moleculary adsorbed ammonia is stabilized by chemisorbed oxygen.14, 15) A peak was observed at 399.6 eV with a shoulder at around 397.4 eV, while the peak was decreased to a half in scale during XPS measurement for 2 h due to the desorption. When NH_3 was introduced on "reduced" Raney-Ru, it was almost completely decomposed and a similar spectrum to Fig. 1 or 2 was observed. The observed small shoulder at 399.7 eV was thus considered to be due to adsorbed NH_3. But, we cannot deney this peak to be due to NH_2.17) The existence of NH_x or NH_3 during TPD (Fig. 1) in the absence of hydrogen suggests the incompleteness of pre-desorption of hydrogen at 623 K. It is difficult to determine whether those NH_x species exist under the reaction condition or those are formed from adsorbed hydrogen during the cooling process for XPS measurements.

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