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Adsorption and Decomposition of Ammonia on New Fe(1x1) Commensurate Overlayers on Ru(001) Surface with or without Co-adsorbed Oxygen

Chikashi EGAWA and Yasuhiro IWASAWA*

Department of Chemistry, Faculty of Science, The University of Tokyo,
7-3-1, Hongo, Bunkyo-ku, Tokyo 113

Adsorption and decomposition of ammonia on Fe(1x1) overlayers on Ru(001) surface with or without co-adsorbed oxygen were studied by means of AES, LEED and TDS. Adsorption of ammonia at 520 K on epitaxial Fe overlayers on Ru(001) surface gave a newly-ordered ($\sqrt{7}$x$\sqrt{7}$)R19° structure in the wide range of Fe coverages from 0.14 to above 1 ML. The desorption of N_2 from the ordered adsorbate-layers showed a sharp peak at 850 - 950 K, which is consistent with the decomposition of surface nitride, Fe_4N, observed for Fe single crystal planes. In contrast, c(4x2) ordered overlayer was observed upon the adsorption of oxygen on an annealed Fe/Ru(001) surface. The decomposition rate of ammonia at a steady state was enhanced by 3.5 times by co-adsorbed oxygen because nitrogen is effectively activated by surrounding oxygen atoms in c(4x2) mixed overlayers.

Both iron and ruthenium metals show good catalysis for ammonia synthesis and decomposition. The studies on adsorption of nitrogen molecules on various single crystal planes of Fe have revealed that the dissociative adsorption of nitrogen takes place preferentially on C_7 sites present on the (111) surface.[1] The Fe(111) surface has also been demonstrated to be most active for ammonia synthesis.[2] The interaction of ammonia with Ru and Fe surfaces using single crystal has also been investigated.[3,4] In contrast to these monometallic surfaces, we have recently employed a Fe/Ru(001) bimetallic system and observed an epitaxial growth of Fe overlayers on Ru(001) surface.[5] On the commensurate Fe (1x1) overlayer at 1 ML of coverage the bonding energy of CO was found to be strengthened due to the expanded Fe overlayer structure. On the contrary, the second Fe monolayer changed to another overlayer structure which is quite similar to bcc Fe(110) surface, exhibiting extra spots due to (6$\sqrt{3}$x6$\sqrt{3}$)R30° overlayer structure.[5] In the present paper, the bonding states of nitrogen, the local chemical interaction of co-adsorbed oxygen and nitrogen, and the effect of the oxygen on ammonia decomposition reaction on the Fe overlayer on Ru(001) surface are reported.

Experimental procedures were similar to those described previously.[6] AES and LEED measurements were carried out by a 4-grid type retarding field analyzer and Thermal desorption spectra of N_2 after NH_3 adsorption were taken by a QMS.

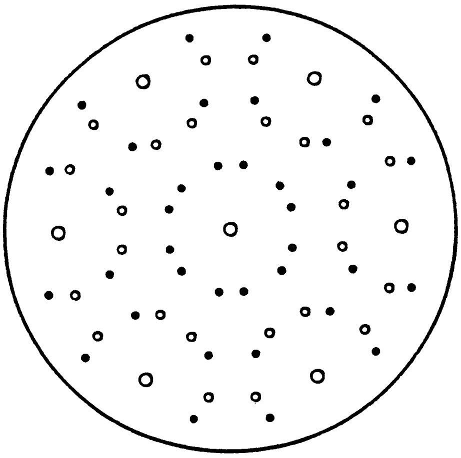

Fig. 1a. LEED pattern of (√7x√7)R19° structure obtained from NH_3 adsorption on Fe/Ru(001) surface.

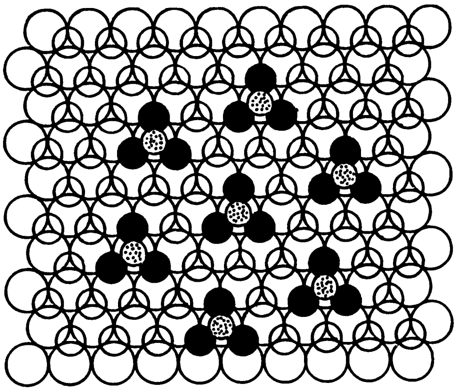

Fig. 1b. Surface structure model of (√7x√7)R19° structure.

○ :Ru atom; ○ ● :Fe atom; ⊛ :N atom

Adsorption of ammonia (10 L, 1 L= 1.33×10^{-4}Pa·s) on Fe-evaporated Ru(001) surface at 520 K produced new extra diffraction spots besides (1x1) spots due to the underlying lattice as shown in Fig. 1a. The LEED pattern is entirely different from that from diffused p(2x2) structure observed with a clean Ru(001) surface and is designated to (√7x√7)R19° surface structure, which has not been observed on bcc Fe crystal planes. The new overlayer structure was observed in the wide range of Fe coverages from 0.14 to above 1 ML. The LEED spot size due to (√7x√7)R19° structure was always as sharp as that for the substrate lattice. It suggests that the Fe overlayer structure is perfectly matched to the substrate Ru lattice structure during the growth of two-dimensional Fe islands.

Figure 2 shows a series of N_2 thermal desorption(TD) spectra obtained from ammonia adsorption at 520 K as a function of Fe coverage. For the Fe coverages below 0.5 ML the desorption peak at 850 K grew with an increase in Fe coverage. On increasing the coverage to more than 0.5 ML the peak at 850 K was replaced by a new desorption peak at 950 K. The drastic change in TD spectra around 0.5 ML of Fe coverage is entirely different from the monotonous peak shift toward the higher temperatures observed with the TD spectra of CO.5) The desorption peaks in each region are characterized by the narrow width and exhibit their peak maxima at essentially the same temperature. Therefore, the desorption of N_2 is most likely to be rate-limited by the decomposition of surface nitride like "Fe_4N" proposed in the adsorption of N_2 on Fe(111) and (110) surfaces,1) where the desorption of N_2 by the decomposition of surface nitride appeared in the temperature range 850-950 K, while bulk nitride contributed to only a continuous increase in background at the temperatures above 1000 K. The reason of the sudden shift in TD spectra is not clear at present, but it must be related with the properties of the Fe(1x1) commensurate structure on the Ru(001) surface. Strikingly, a nearest neighbour distance (2.68 Å) at (111) surface of fcc-Fe_4N bulk nitride is very close to that on the hcp Ru(001) plane (2.706 Å). Accordingly, the (√7x√7)R19°surface structure of the nitrogen overlayer may be displayed in Fig. 1b, where each nitrogen atom occupies on a three-fold hollow hcp site, binding to three nearest Fe atoms (filled circles) of the Fe(1x1) commensurate overlayer. On this adsorption structure the interaction of the nitrogen atom with Ru atom in the underneath substrate layer can also be operated.

On the annealed surface to 1030 K, on the other hand, the adsorption of oxygen molecules (3.6 L) at 520 K gave an ordered extra-diffraction spots as shown in Fig. 3a. It is referred to a c(4x2) ordered structure on hcp(001) surface as depicted in Fig. 3b where atomic oxygen is located on three-fold hollow sites similarly to a p(2x2)-O structure on a clean Ru(001) surface.7) The subsequent adsorption of ammonia on the oxygen-preadsorbed surface at 520 K did not change the extra-spots arisen from the c(4x2) structure. On the other hand, a very broad p(2x2) LEED pattern appeared upon the adsorption of oxygen on an epitaxial Fe overlayer, while the following exposure to ammonia produced the (√7x√7)R19° LEED pattern. It indicates that surface nitrides on the bare Fe domains uncovered by oxygen coexist with disordered overlayers of atomic oxygen.

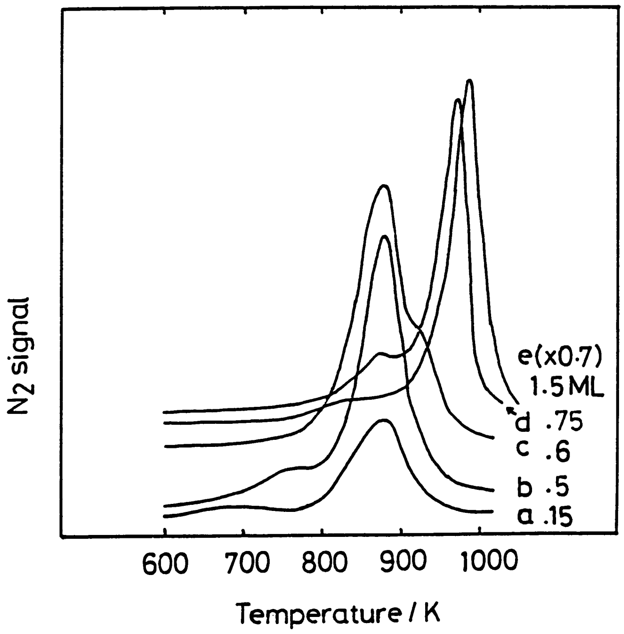

Fig. 2. N_2 TD spectra from NH_3 adsorption on Fe overlayers on Ru(001) surface.

β = 8.3 K/s, Fe coverage; (a) 0.15, (b) 0.5, (c) 0.6, (d) 0.75, (e) 1.5 ML

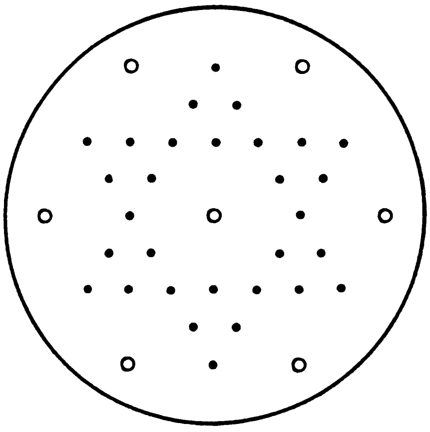

Fig. 3a. LEED pattern of c(4x2) structure obtained from O_2 adsorption on annealed Fe/Ru(001).

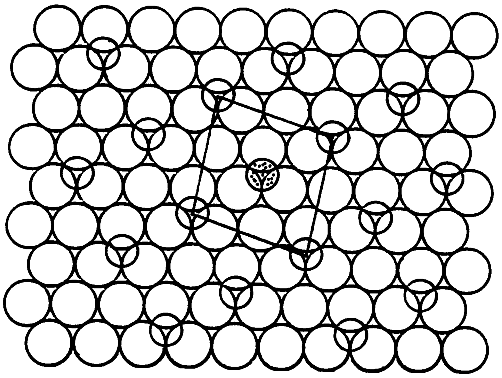

Fig. 3b. Surface structure model of c(4x2) structure.

○ :Fe atom; ○ :O atom; ⊛ :N atom

Next we investigated the local chemical interaction and the decomposition reaction of ammonia on the mixed overlayers. The effects of co-adsorbed oxygen on the desorption of N_2 at both epitaxial(b) and annealed(c) surfaces are shown in Fig. 4. For convenience of the comparison with a steady-state decomposition rate of ammonia, the adsorption of oxygen on epitaxial and annealed surfaces was followed by H_2 treatment (2.7×10^{-5} Pa at 900 K for 3 min) before NH_3 adsorption to remove excess oxygen and to get the surface equivalent to the steady-state reaction conditions. The temperature for maximum desorption was successively lowered in the order of (a) (annealed with no oxygen), (b), and (c) with the concomitant reduction in surface nitrogen coverage. The trend of lowering of desorption temperatures was closely related to the change in the decomposition rate of ammonia at a steady state on these surfaces. The relative decomposition rates at 735 - 780 K were observed to be (a):(b):(c)= 1: 2.5: 3.5. It is consistent with the result that the desorption of nitrogen is a rate-limiting step in the decomposition of ammonia.8) As shown in Fig. 4, the enhancement of nitrogen desorption by co-adsorbed oxygen was most effective on the surface (c) where the ordered c(4x2) structure was observed for the mixed overlayer of nitrogen and oxygen in contrast to the disordered overlayer structure on the surface (b). Accordingly, it is most likely that the nitrogen atom occupying central position of a c(4x2) unit-structure is effectively activated by surrounding co-adsorbed oxygen atoms as shown in Fig. 3b.

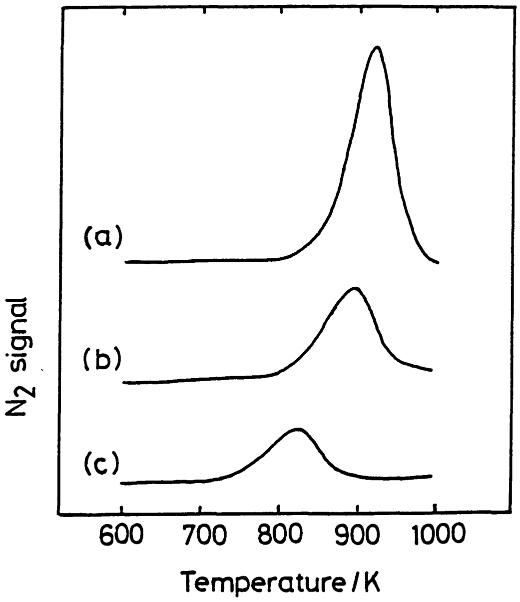

Fig. 4. N_2 TD spectra from NH_3 adsorption on modified Fe/Ru(001) surface with Fe coverage of 0.75 ML. β = 8.3 K/s, (a) after annealed to 1030 K, (b) O_2 adsorption (3.6 L) followed by H_2 reduction, (c) after annealed to 1030 K and subsequent O_2 adsorption (3.6 L) followed by H_2 reduction.

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