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An Auger Electron Spectroscopic Study of the Reaction of Ammonia with Fe(110)

Decomposition of ammonia on a Fe(110) surface was studied by Weiss *et al.* (*1*) by means of UPS, LEED, AES, $\Delta\phi$, and TPD measurements. These authors concluded that partial decomposition of the adsorbate starts around 310 K, leading to the formation of a single surface intermediate at 340 K. This intermediate was postulated to be a surface =NH species. A recent EELS study (*2*), on the other hand, suggested that ammonia decomposes on Fe(110) surfaces directly to its constituent atoms at 315 K. Kinetic studies of the decomposition and formation of ammonia on a large number of metal and supported metal catalysts have also been carried out by different researchers. The rate equations derived can be explained (*3*) by postulating a decomposition route via intermediate formation of $-NH_2$ and =NH species. Auger line shapes arising from core–valence–valence ($1sVV$) transitions reflect the chemical environment of the atom containing the initial core hole. Characteristic line shapes are observed for different chemisorbed species, thus providing a powerful fingerprinting technique. In view of the success of Auger line-shape analysis in identifying CH_x species formed by the decomposition of C_2H_4 and C_2H_2 on Fe(110) (*4*) and on Ni(110) (*5*), a similar study was undertaken to follow the reaction of ammonia with Fe(110).

The present investigation was carried out in a UHV chamber with a base pressure of 2×10^{-11} torr. Auger transitions were excited by an electron beam (0.4 μA, 3 keV) diffused over an area ~3 mm in diameter. The Auger spectra were recorded digitally in the differential, dN_E, mode by means of a hemispherical electron energy analyser giving a spectral energy resolution of 2 eV. Digital integration of a dN_E spectrum gave the corresponding N_E spectrum. Spec-pure ammonia was used as the adsorbate. During exposure of the crystal to ammonia all filaments in the spectrometer chamber were switched off and the pressure was monitored by ion gauge readings measured at a remote gauge positioned just above the diffusion pump. The crystal was cleaned by Ar-ion bombardment and annealed at 500 K. For each temperature and coverage of adsorption, Auger spectra were recorded over different intervals of time ranging from 12 to 100 s to determine the electron dose needed to cause noticeable beam damage of the adsorbate. The spectra presented here were recorded within the safe limit. Surface species formed at crystal temperatures below 400 K were found to be highly beam sensitive. For physisorbed ammonia on Fe(110) at 100 K an exposure to electron beams for 75 s corresponding to a total dose of ~5 C m^{-2} caused noticeable beam damage. The spectra presented here were recorded in 50 s. For temperatures above 400 K, however, exposures to the electron beam of up to 15 min did not cause any noticeable change in the spectra.

Previous studies (*1, 2*) showed that ammonia adsorbs molecularly on Fe(110) at 120 K. The EELS study (*2*) also distinguished three types of molecularly adsorbed ammonia corresponding to three modes of bonding to the surface. The nitrogen Auger ($N1sVV$) spectrum of molecular adsorbed ammonia on Fe(110) at 100 K is shown in Fig. 1a. The line shape of the spectrum did not change as a function of

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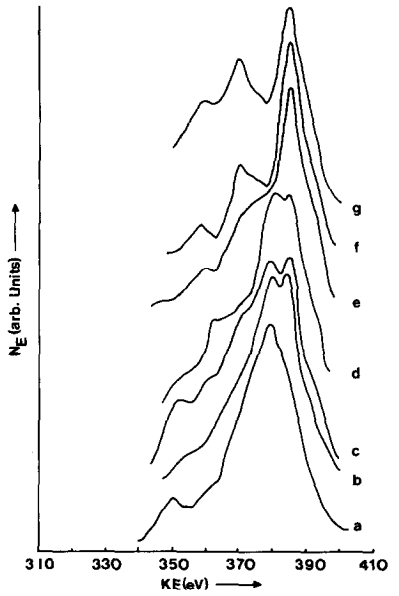

FIG. 1. Nitrogen Auger spectra of a clean Fe(110) surface saturated with ammonia at 100 K and subsequently heated to different temperatures. Saturated surface at (a) 100 K; (b) 180 K; (c) 300 K; (d) 310 K; (e) 350 K; (f) 400 K; and (g) 800 K.

exposure to ammonia, showing that it was insensitive to the changes in the mode of bonding of the adsorbate suggested by EELS studies.

Thermal decomposition of molecularly adsorbed ammonia on a clean Fe(110) surface was followed by saturation of the clean surface with ammonia at 100 K and subsequent heating of the crystal to specific temperatures and recording of Auger spectra at those temperatures. The results are summarised in Figs. 1b–1g. Heating the crystal to temperatures below 180 K had no effect on the Auger line shape of the molecular adsorbate, indicating that ammonia remained undissociated on the surface at these temperatures. The line shape of the spectrum abruptly changed at 180 K, indicating decomposition of the adsorbate (Fig. 1b). This new line shape, which we refer to as spectrum A, remained essentially unchanged in the temperature range 180–310 K. In addition to other minor features, spectrum A is seen to have a doublet of peaks at 379 and 384.5 eV. Heating the crystal to temperatures above 310 K gradually changed the line shape of spectrum A into a three-peaked spectrum B at 400 K (Fig. 1f). The Auger line shape of the adsorbate remained essentially unchanged in the temperature range 400–800 K. It is seen that spectrum B has three peaks with increasing intensities at 359.5, 371, and 385.6 eV.

The line shape of the Auger spectrum of ammonia adsorbed on a clean Fe(110) surface at 400 K did not change with coverage up to saturation and was identical to that of spectrum B. This suggests the presence of a single adsorbed species at 400 K which has a distinctive Auger spectrum B. Nitric oxide is known (*6*) to dissociate completely to its constituent atoms on a Fe(110) surface at 300 K. The line shape of the Auger spectrum of chemisorbed nitrogen atoms obtained by thermal decomposition of nitric oxide on the clean surface and recorded in the present investigation is identical to that of spectrum B. This indicates that ammonia dissociated completely to its constituent atoms at 400 K, in agreement with the conclusions derived by Weiss *et al.* (*1*).

Nitrogen Auger spectra of a clean Fe(110) surface following varying exposures to ammonia, up to saturation, at 180 and 300 K were recorded. The line shapes of all the spectra were found to be identical to that of spectrum A. This clearly shows that, in disagreement with the conclusions derived from the two previous studies (*1, 2*), decomposition of ammonia on a clean Fe(110) surface produced a single NH_x surface species in the temperature range 180–310 K. On the basis of present data, however, it is not possible to determine the stoichiometry of the NH_x species.

In conclusion, the decomposition of ammonia on a Fe(110) surface derived from the present Auger study is seen to proceed via intermediate formation of surface NH_x species.

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