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INFRARED STUDY OF CHEMISORBED AMMONIA ON AN EVAPORATED IRON FILM

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The infrared absorption at 500 cm^{-1} was observed during the course of ammonia decomposition on an evaporated iron film. It was assigned to an iron-nitrogen stretching vibration of surface nitrogen species which may be described as $Fe\text{-}NH_x$. The assignment was confirmed by the exchange reaction with ^{15}N labeled ammonia.

The IR spectroscopic studies of ammonia adsorbed on supported iron catalysts have been reported by several authors.[1,2] No IR spectra in the lower wavenumber region, however, have been investigated so far owing to the difficulties due to the strong absorption by the supports, although the information concerning the metal-nitrogen bond may be obtained in this region. In this communication the adsorbed species on an evaporated iron film observed by IR spectroscopy in the lower wavenumber region during the course of decomposition of ammonia will be reported.

Iron was evaporated onto both sides of a silicon plate under a 10^{-6} Torr vacuum from a resistively heated tungsten boat containing iron wire (Koch-Light Lab. Ltd. 99.999%). No impurities were detected except for carbon and oxygen by ESCA. The sample was reduced in 100 Torr of hydrogen at 400°C for 24 hr in an IR cell connected with a closed circulating system with a liquid nitrogen cold trap. Ammonia was purified by distillation in vacuo at -78°C and ^{15}N labeled ammonia (Hikari Kogyo, 96 atom%) was used without further purification.

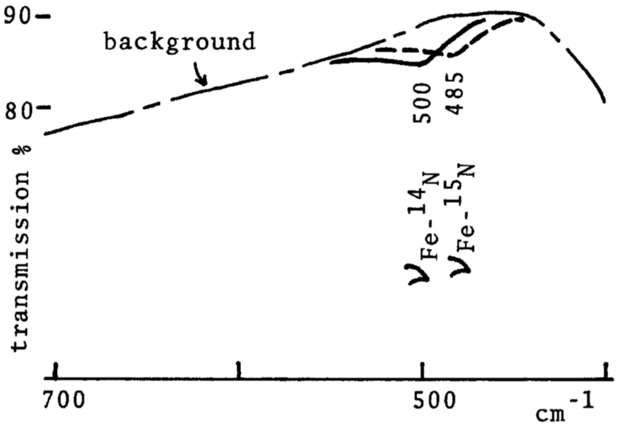

FIGURE. Infrared spectra of chemisorbed species on the iron film after NH_3 decomposition at 400°C.
solid line: $^{14}NH_3$ decomposition
broken line: $^{15}NH_3$ decomposition

The figure shows the IR spectra of chemisorbed or decomposed ammonia ($^{14}NH_3$ and $^{15}NH_3$) which were obtained by exposing the iron sample to 30 Torr of ammonia and cooled to room temperature in vacuo. The absorption bands at 500 cm^{-1} for ^{14}N species and 485 cm^{-1} for ^{15}N were observed. It was confirmed that the adsorbed nitrogen species could be exchanged with ambient labeled ammonia above 300°C. The intensities of the absorption bands remained nearly constant for a while when the nitrogen species thus chemisorbed was treated in 70 Torr of hydrogen at 300°C, but subsequently started to decrease rather rapidly. Since several layers of iron nitride are formed under the experimental condition of ammonia decomposition,[3)] such behavior of surface nitrogen species is interpreted as follows: the absorption bands of the chemisorbed nitrogen species may be attributed to the iron-nitrogen bond in the top-layer of the surface, which stayed almost unchanged in the initial stage of the hydrogenation as far as the nitrogen is supplied from the surface nitride layers underneath, which is followed by the decrease in the intensities of the bands when the nitride layers are exhausted. When the chemisorbed nitrogen species were hydrogenated by deuterium, the ammonia produced contained mostly protium and the intensities of the absorption bands were increased by introducing hydrogen to the adsorbed species at 200°C, indicating that the surface species may be described as Fe-NH_x (x= 1 or 2). Although the absorption bands due to a N-H stretching or deformation vibration of NH_x species were not observed in this system by the IR technique because of the small extinction coefficients of such modes, on a magnesia supported catalyst, however, the absorption bands assigned to N-H deformation vibrations were observed reproducibly by the FTIR multiscanning technique. The results of the supported catalyst will be published elsewhere.

To examine the effects of contamination by oxygen, a small amount of oxygen was admitted to the evaporated iron film at 400°C. The film exhibited better transparency on admitting oxygen, such a behavior was not observed when it was treated with ammonia. The IR spectrum of the oxidized iron film showed strong absorption bands at 520 and 435 cm^{-1}. The absorption bands at 500 cm^{-1} and 485 cm^{-1} are, accordingly, not attributed to iron oxides.

Molybdenum nitride which was prepared by the reaction of a molybdenum evaporated film and ammonia at 400°C[4,5)] showed no absorption bands in this region. As iron nitride is less stable than molybdenum nitride, it can not be expected to give absorption bands in this region, and the absorption band at 500 cm^{-1} is not assigned to iron-nitrogen stretching vibration of iron nitride. The peak position at 500 cm^{-1} is too high to be assigned to the iron-nitrogen stretching vibration of coordinated ammonia, which gives an absorption band at about 310 cm^{-1} in $Fe(NH_3)_6X_2$ complexes.[6)]

The absorption bands at 500 cm^{-1} (^{14}N) and 485 cm^{-1} (^{15}N), consequently, are assigned to the iron-nitrogen stretching vibration of surface NH_x (x=1 or 2) species. It is the first evidence that demonstrated a bonding of nitrogen on an iron surface by means of IR spectroscopy.

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