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INFRARED STUDY OF HCN POLYMER ON ALUMINA

By

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Abstract

Infrared spectra were recorded of HCN adsorbed on alumina. In general, the results indicate that HCN adsorbed and polymerized rapidly at room temperature to form a mixture of molecular and polymeric HCN. At least three HCN polymers formed. Pumping and heating to 200–300°C caused the desorption of the more volatile materials, much like the removal of HCN polymer from porous glass, and some conversion to less volatile materials. Degradation of the HCN polymers to coke-like material occurred above 300°C along with minor reactions with the adsorbent to produce surface OH groups.

Introduction

In recent year there have been several infrared studies dealing with the adsorption of HCN on solids. KORTÜM and DELFS used reflection techniques and found HCN to polymerize on Al_2O_3 , MgO, CeO_2 , but not on SiO_2 .¹⁾ Dissociative chemisorption of HCN on silica-supported Rh, Pd, and Ag was mentioned by DUNKEN and HOBERT,²⁾ and a variety of bands and spectral shifts induced by HCN adsorption on evaporated alkali halides were described by KOZIROVSKI and FOLMAN.³⁾ The latter also reported HCN to adsorb and polymerize on porous glass.⁴⁾ More recently the adsorption and polymerization of HCN was studied using highly degassed porous glass and pure, boria and alumina-impregnated silicas, and it was concluded that aluminum ions present as impurity on the porous glass surface acted as adsorption sites and as centers for the polymerization.⁵⁾ This result and the lack of detail concerning the reactions prompted the present study of the HCN polymer formed on pure alumina.

Experimental

Most of the procedures employed have been described elsewhere.⁶⁾ Alon-C alumina was used as adsorbent.⁷⁾ Samples in the form of 10 mm-diameter

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M. J. D. LOW and P. RAMAMURTHY

discs weighing approx. 40 mg were prepared by pressing the powder at 20 tons/inch². Spectra were recorded with Perkin-Elmer Model 521 or 621 spectrophotometers. The ordinates of Figs. 1 and 2 are displaced to avoid overlapping of spectra.

The experiments consisted of exposing a sample of the adsorbent to HCN at room temperature, usually for one hour so that some polymer was built up, and then recording a series of spectra of the sample at various stages of degassing. The windows of the sample cell were heated at 100° during degassing in order to prevent the condensation of substances desorbed from the sample. In order to determine if the degree of dehydration of the alumina affected the polymer, tests were carried out with fresh samples degassed at 200, 500, 600,

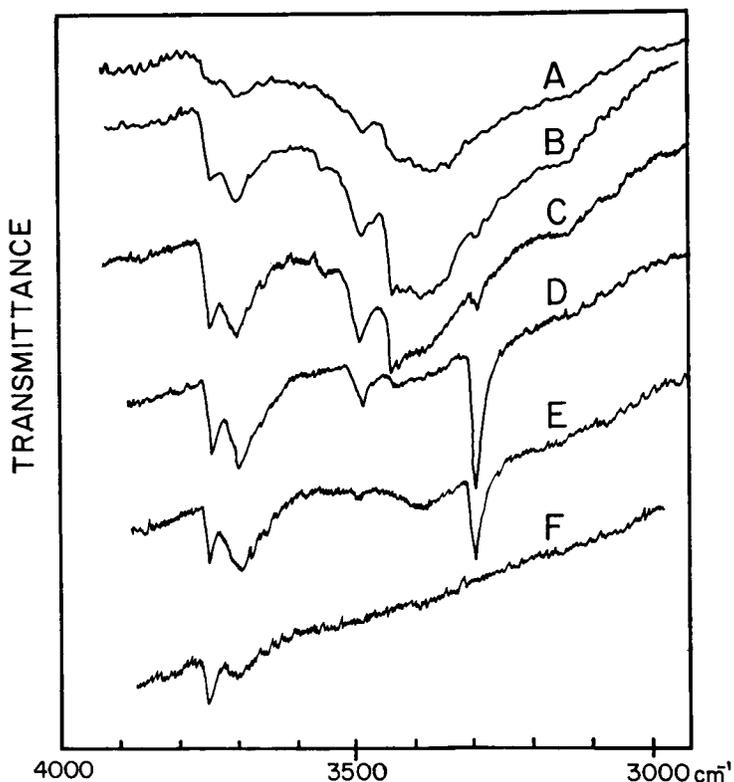


Fig. 1. HCN on Alumina

The alumina sample was degassed, treated with oxygen, then degassed at 750° for 20 hrs. After being exposed to 12 torr HCN at room temperature for 1 hr. the sample was degassed sequentially at the following temperatures and times in hrs. A: 30°, 14; 100°, 2; 200°, 2; 250°, 1; 300°, 1. B: 400°, 1. C: 450°, 1. D: 500°, 1; E: 550°, 6; 600°, 2. F: 650°, 6; 700°, 4.

Infrared Study of HCN Polymer on Alumina

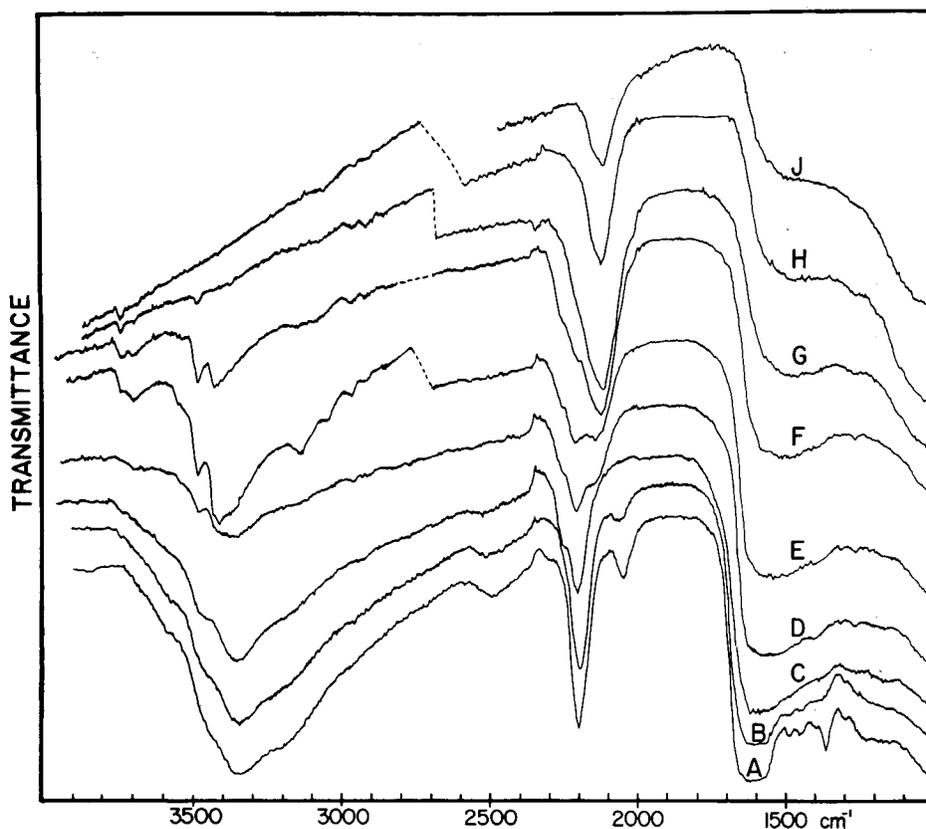


Fig. 2. HCN on Alumina

The alumina sample was degassed for 2 hrs., heated in 60 torr O₂ and degassed after 12 hrs., all at 650°. After an exposure to 100 torr HCN for 2 hrs. at room temperature, the sample was sequentially degassed at the following temperatures and times in hrs. A: 30°, 12; B: 50°, 2 plus 100°, 1; C: 150°, 1 plus 200°, 1; D: 250°, 1 plus 300°, 1; E: 350°, 1 plus 400°, 1; F: 400°, 2; G: 500°, 2 plus 550°, 3-5; H: 600°, 2 plus 650°, 2; J: 700°, 3-5 (no bands in 4,000-2,500 cm⁻¹ region). Ordinates are displaced to avoid overlapping. The 4,000-2,300 cm⁻¹ region for E to H are shown at 5×, whole other regions and A to D are at 1× ordinate scale expansion.

650, or 750°C. Initial HCN pressures ranged from 2 to 100 Torr.

Results and Discussion

The results of all experiments were similar. The adsorbent became discolored immediately upon being exposed to HCN and was orange-red within minutes. After some polymer had formed at room temperature, spectra show-

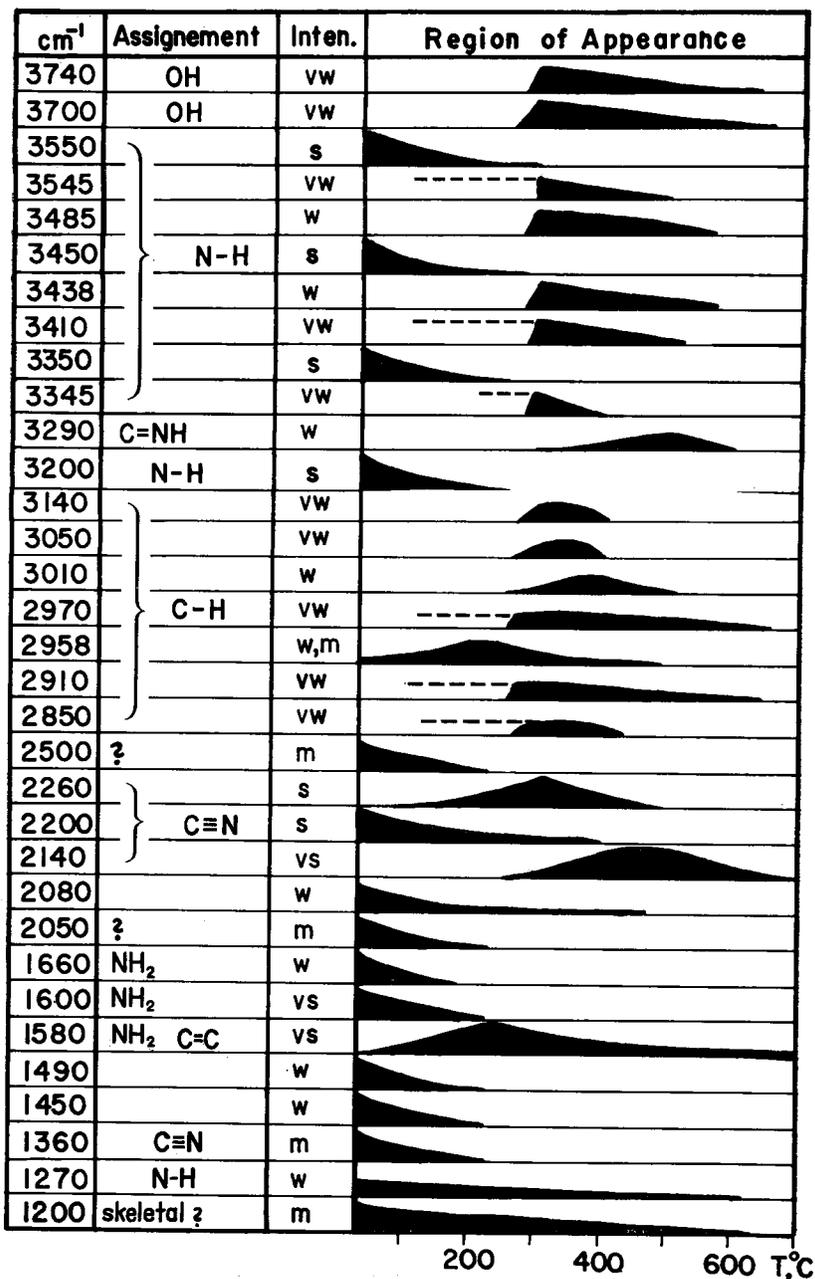


Fig. 3. Summary of Results

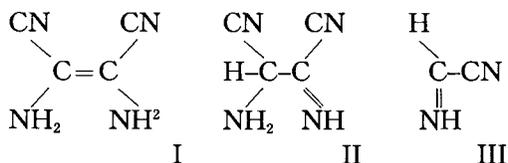
--- Band assignments were made on the basis of group frequencies. Intensities: vw, very weak; w, weak; m, medium; s, strong. The temperatures at which bands were detected and changes in intensities are crudely indicated by the small graphs; dashed lines indicated uncertainty.

Infrared Study of HCN Polymer on Alumina

ing structure like that of spectrum A of Fig. 1 were obtained. A rather broad absorption centering near $3,550\text{ cm}^{-1}$ formed from $3,700$ to $2,500\text{ cm}^{-1}$; these were ill-defined shoulders near $3,570$, $3,470$, and $3,200\text{ cm}^{-1}$, and intense bands at $2,600$ and $1,600\text{ cm}^{-1}$. The intensities of these absorptions and of other, minor bands increased with increasing initial HCN pressure and the degree of dehydration of the solid. However, some of the minor bands became less distinct with increasing amounts of polymer.

A variety of changes occurred when sample were degassed at progressively higher temperatures. Typical effects are shown in Figs. 1 and 2 by some of the spectra of degassing sequences. Samples changed progressively in color from orange-red to red-brown, yellowish-brown, yellow, to light yellow with increasing temperature. The pellet sometimes turned black at the highest temperatures with samples of high polymer content. The various bands observed are listed in Fig. 3, which also summarizes the changes observed. Each small graph crudely shows the change in intensity with degassing temperature. The various spectra, particularly those obtained at low polymer concentrations, indicated that the $1,600\text{ cm}^{-1}$ band was due to two strongly overlapping bands at $1,600$ and $1,580\text{ cm}^{-1}$ plus a shoulder near $1,660\text{ cm}^{-1}$. The shoulder and $1,600\text{ cm}^{-1}$ band declined on pumping, so that the band center moved from $1,600$ to $1,580\text{ cm}^{-1}$ near 250° . The complexity of the effects as well as the uncertainty concerning the regions of appearance of minor, weak bands do not permit a completely detailed analysis to be made. However, reactions occurring in three overlapping temperature regions appear to be important.

With increasing temperatures up to 250 – 300° , the $3,700$ – $2,500\text{ cm}^{-1}$ absorption declined progressively but the shoulders remained largely indistinct. The intense $2,200\text{ cm}^{-1}$ band declined, shifted to $2,220\text{ cm}^{-1}$, and vanished between 300° and 400° . Also, the $1,660\text{ cm}^{-1}$ shoulder declined and the intense $1,600\text{ cm}^{-1}$ band shifted to $1,580\text{ cm}^{-1}$. These changes, and decreases in minor bands shown in Fig. 3, suggest that appreciable amounts of tetramer had formed. The crystalline tetramer of HCN has been shown⁸⁾ to be diaminomaleonitrile,^{9–15)} I, rather than aminoiminosuccinonitrile,¹⁶⁾ II. Band assignments¹⁵⁾ were: at $3,450$, $3,370$, $3,314$, $3,260$, $3,219$, and $3,184\text{ cm}^{-1}$ to the N–H stretching vibration of $-\text{NH}_2$; $2,172$, $2,222\text{ cm}^{-1}$ to $-\text{CN}$; $1,648$, $1,611\text{ cm}^{-1}$ to $-\text{NH}_2$ bending; $1,624\text{ cm}^{-1}$ to $\text{C}=\text{C}$; $1,370\text{ cm}^{-1}$ to $-\text{CN}$; and $1,249\text{ cm}^{-1}$ to $-\text{NH}_2$.



The absorption in the present spectra at 3,450, 3,350, and 3,200 cm^{-1} can be taken as the N-H bands of I, broadened by hydrogen-bonding; the 2,220 cm^{-1} band as -CN; absorption in the 1,700-1,500 cm^{-1} region to -NH₂ and C=C vibrations; 1,360 cm^{-1} to -CN, and 1,270 cm^{-1} to NH₂. However, weak bands observed in the N-H and C-H regions at low temperatures would imply the existence of substances other than I, which has no C-H bands. Dimers¹⁷⁾ III or trimers may exist, although a weak absorption at 3,290 cm^{-1} attributable to C=NH was observed only at higher temperatures.

An absorption near 2,260 cm^{-1} became more prominent with increasing temperature and then declined above 300°; in some cases, a definite band rather than a shoulder was formed. The absorption in the 1,500-1,200 cm^{-1} region increased slightly (approx. to 250-300°) and then decreased. Also, bands were detected in the C-H region, although their weak intensities causes uncertainty about the region of their appearance. However, there seems to be a relation between the 2,260 cm^{-1} band and some of the weak C-H bands such as the 3,140 cm^{-1} band. It is known that with conjugated systems the -CN absorption occurs at lower frequencies than in unconjugated systems.¹⁸⁾ Taking the 2,260 cm^{-1} absorption as a -CN band, the changes in the latter and the existence of some C-H bands suggest that II and/or similar unconjugated structures were formed.

In the range 200-300° a shoulder was detected which grew into an intense band at 2,140 cm^{-1} , declined above 500° but was detected at 700°. Minor bands at 2,970, 2,910, 1,580, and 1,270 cm^{-1} , and a broad absorption near 1,200 cm^{-1} , were observed until approx. 600-650°. The intense 1,580 cm^{-1} band was observed at 700° and, as bands in the N-H region were weak, seems more likely to be a C=C rather than an NH₂ vibration. Assigning the 2,140 cm^{-1} band to -CN, 2,970 and 2,910 cm^{-1} bands to C-H, and a substantial fraction of the 1,580 cm^{-1} band to C=C, the result suggest that a relatively nonvolatile, stable material was formed. Containing C=C, -CN, some C-H, but little or no N-H structures, the material may be similar in nature to the well-known catalytic coke.

When a freshly degassed sample was exposed to HCN, the bands at 3,740 and 3,700 cm^{-1} of residual surface OH groups disappeared because of hydrogen bonding to sorbed HCN and polymer.^{4,5)} The OH bands reappeared with approximately the same intensity after degassing near 250°, suggesting that the species responsible for the hydrogen bonding had been largely removed from the surface (or converted to surface species not capable of hydrogen bonding). However, the OH bands, particularly the 3,700 cm^{-1} band, then increased with increasing temperature and subsequently declined. The changes were small but

Infrared Study of HCN Polymer on Alumina

definite, and appeared to be paralleled by changes of minor bands in the OH region. This may have come about from a reaction of NH_3 , formed through the thermal decomposition of $(\text{HCN})_n$, with the adsorbent to yield OH and $-\text{NH}_2$ groups in analogy to the reaction of gaseous NH_3 with alumina,¹⁹⁾ or from the direct abstraction of hydrogen from the polymer.

In general, the results indicate that HCN adsorbed and polymerized rapidly at room temperature to form a mixture of adsorbed HCN and I and other substances similar to II and III. Pumping and heating to 200–300° caused the desorption of the more volatile materials, much like the removal of HCN polymer from porous glass⁵⁾ at 250°, and some conversion to a less volatile material similar in structure to II. Degradation of residual I and of II and similar structures to coke-like material occurred above 300° along with minor reactions with the adsorbent to produce surface OH groups.

Acknowledgment

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M. J. D. LOW and P. RAMAMURTHY

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