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Temperature-Programmed Desorption of Ammonia and *n*-Butylamine on Mordenites

To evaluate the catalytic activity of a zeolite it is important to characterize the nature (Brønsted or Lewis), number, and strength distribution of the acid sites. Such characterization can be done by using various methods such as titration, calorimetry, and infrared spectroscopy. Temperature-programmed desorption (TPD) of a base preadsorbed on a solid catalyst is considered to be a potential method to determine the amount and distribution of acid sites. The most commonly used base in TPD studies is ammonia and it has been used for the characterization of zeolite acidity (*1–7*). Thermal desorption of ammonia shows at least two desorption peaks, the peak(s) in the higher temperature range being considered to be due to the presence of strong acid sites which, for instance, are catalytically active for methanol conversion into hydrocarbons (*8*). *n*-Butylamine (pK_b = 3.23), which is a relatively strong base, is widely used in the titration method, and it will react with weaker acid sites than ammonia (pK_b = 4.75). The use of *n*-butylamine in TPD is reported only on alumina (*9*) and silica–alumina (*10, 11*). TPD spectra of *n*-butylamine show two desorption peaks, the higher temperature peak being due to the decomposition of the base adsorbed on the strong sites. The present note describes the qualitative thermal desorption of ammonia and *n*-butylamine from a hydrogen mordenite and two dealuminated hydrogen mordenites.

The hydrogen mordenite was obtained from Norton Company and the dealuminated mordenites (SiO_2/Al_2O_3 ratios 18 and 26) used were prepared by treating hydrogen mordenite with concentrated HCl at its boiling temperature. The zeolite samples were dried at 423 K in air and then compressed and made into granules of 44–100 mesh size. The catalysts were then activated at 773 K *in vacuo* for 2 h and cooled down to room temperature. About 2.0 g of previously activated catalyst was packed in a glass column in a temperature-programmed GC oven. The catalyst was washed in flowing oxygen (25 cm^3/min) at 773 K for 1 h, then cooled down to the desired adsorption temperature at 373 K when the oxygen flow was replaced by helium and continued for 30 min, after which the catalyst surface was saturated by adsorbing ammonia (purity 99.9%) or *n*-butylamine (previously distilled and dried). Excess reagent was removed in a flow of helium (25 cm^3/min) at the same temperature for 30 min. The base was then desorbed up to the maximum oven temperature of 773 K at a heating rate of 10 K/min. A mass spectrometer was used to analyze the desorbed product.

The mass chromatograms of the desorption of ammonia from the mordenites used are similar and show a broad peak maximum at about 473 K (see Fig. 1). These results show that most of the chemisorbed ammonia was desorbed in the temperature range 373–573 K and only a trace amount of the base was detected above this temperature, indicating the catalysts possess only a small amount of strong acid sites. However, the possibility of another peak at higher temperature (e.g., above 773 K) cannot be ruled out because the desorption was limited to 773 K in the present study. An infrared study (*12*) of ammonia adsorbed on these samples shows a strong band at ca. 1450 cm^{-1} indicating that the mordenites possess a significant number of Brønsted

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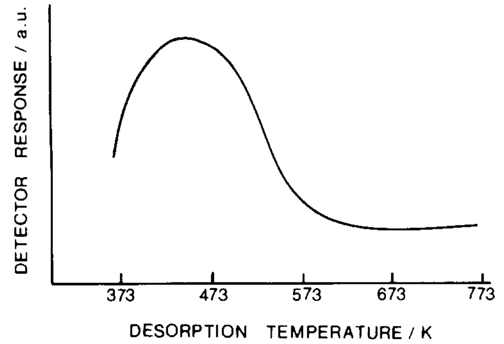


FIG. 1. TPD spectrum of NH_3 preadsorbed on dealuminated hydrogen mordenite (SiO_2/Al_2O_3 ratio 26).

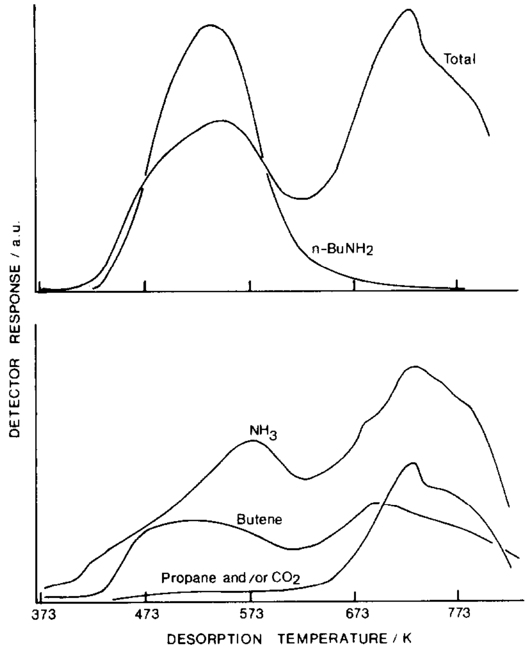
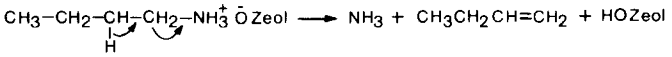


FIG. 2. TPD spectra of *n*-butylamine preadsorbed on hydrogen mordenite.

acid sites. Infrared spectra of adsorbed ammonia at different evacuation temperatures indicate that the NH_4^+ band at ca. 1450 cm^{-1} almost completely disappears at 573 K. The results of TPD and infrared studies are in agreement in the sense that ammonia was desorbed almost completely at about 573 K. Previous authors (*1, 2, 5, 7*) found that ammonia was strongly held on acid sites of mordenites and ZSM-5 zeolites giving desorption peaks at 410–460 and 680 or 790 K, but Y-zeolites and HZSM-11 showed only one peak at around 430 K.

TPD spectra of *n*-butylamine are shown in Fig. 2. The dealumination of zeolite changes the strength distribution of its acidity and it is therefore expected that the TPD peaks should occur at different temperatures for the mordenites. However, this was not observed; for all mordenites used, the TPD spectra of *n*-butylamine show two broad peaks with maxima at about 550 and 730 K. The mass spectrometric analysis of the peak at 550 K shows the presence of ammonia, butene, *n*-butylamine, and trace amounts of propane and/or CO_2. It is evident that at least a small amount of adsorbed *n*-butylamine was decomposed on thermal desorption at these lower temperatures. In support of this, a previous infrared study (*12*) showed that the *n*-butylammonium ion on mordenite was decomposed with the formation of surface butoxy groups. However, TPD studies of *n*-butylamine on alumina (*8*) or silica–alumina (*9, 10*) showed no decomposition in the lower temperature range.

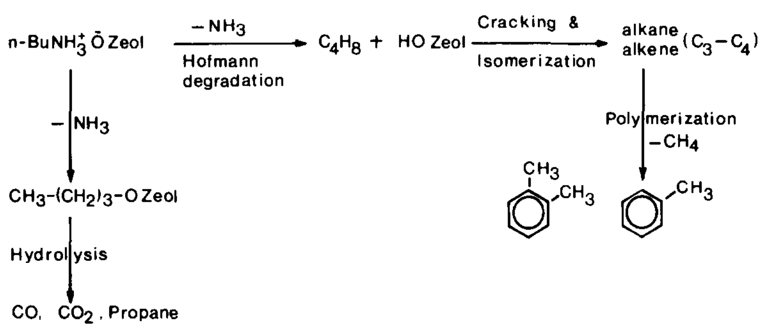
In their infrared spectroscopic study Jacobs and Uytterhoeven (*13*) reported that *n*-butylamine was the desorption product of *n*-butylammonium-Y zeolite below 623 K but above this temperature high amounts of ammonia and butene were detected. The authors suggested the Hofmann degradation of the butylammonium ion:



$$CH_3{-}CH_2{-}\underset{H}{CH}{-}CH_2{-}NH_3^+\ \bar{O}Zeol \longrightarrow NH_3 + CH_3CH_2CH{=}CH_2 + HOZeol$$

The same reaction mechanism has been proposed for the decomposition of adsorbed alkylamines on surfaces like alumina (*8*) and silica–alumina (*10*). From an infrared study of the decomposition of n-$BuNH_3$-Y and dimethylammonium-Y, Jacobs and Uytterhoeven (*13*) reported the presence of alkoxy groups, which could be eliminated by hydrolysis, in which case the presence of an alkane, CO and CO_2 would be expected (*14*). In the present study, mass spectrometric analysis was not able to detect CO because the computer programs automatically deleted mass 28.

Because only a small amount of hydrocarbon was detected in the desorbed components at lower temperatures, the Hofmann degradation of the butylammonium ion was considered to be negligible in this temperature range. The higher temperature TPD peak is due to the presence of ammonia, butene, propane and/or CO_2, toluene and xylene, and a trace amount of n-butylamine. Similar analyses of the second peak of n-butylamine desorption from alumina (*8*) and silica–alumina (*9, 10*) have been reported and they show the presence of butene and propene. The preadsorbed n-butylamine on the zeolites was decomposed into a mixture of hydrocarbons, both aliphatics and aromatics. The deomposition of n-butylammonium ion was favored at higher temperature and it occurred through a Hofmann degradation, followed by isomerization and polymerization:



In conclusion, the present results show that n-butylamine is not a suitable base for thermal desorption studies because the origin of the peak(s) is not always a simple desorption of the parent amine. The adsorbed amine is decomposed into different hydrocarbons and this must be taken into account particularly in quantitative determination. In contrast, TPD studies of ammonia on a solid catalyst can be suitably used in characterization of the amount and distribution of acid sites.

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