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Catalysis Today 114 (2006) 205–210

CATALYSIS TODAY

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IR studies of the formation of ammonia dimers in zeolites TON

J. Datka [*], K. Góra-Marek

Faculty of Chemistry, Jagiellonian University, 30-060 Cracow, Ingardena 3, Poland

Abstract

Ammonia may be a very convenient probe molecule to study the acid properties of zeolites, the pores of which are so narrow that they are inaccessible to pyridine. Ammonia molecules interact with acidic hydroxyls forming ammonium ions, however upon the neutralization of acidic hydroxyls next introduced ammonia molecules can react with ammonium ions (which also act as Brønsted acid sites), forming dimers $NH_4^+ \cdot NH_3$. If ammonia is adsorbed at low temperatures (room temperature or less), ammonia can react with ammonium ions even before the neutralization of all acidic hydroxyls. Based on the results of our IR studies of formation and decomposition of dimers in zeolite TON optimal experimental conditions of IR quantitative studies of Brønsted acid concentration with ammonia were performed. The concentration of Brønsted sites determined by this method in zeolites TON of various Si/Al was practically the same as the values calculated from chemical analysis.

Keywords: Ammonia dimers; FTIR; Zeolites

1. Introduction

Even though zeolites can catalyse numerous reactions, the most important reactions both for large-scale industry and fine chemistry are catalysed by acid sites. The characterization of acid properties of zeolites is therefore essential for catalysis. Therefore the characterization of acid properties means the determination of concentration of both Brønsted and Lewis acid sites, characterization of their acid strength and heterogeneity. Since the first application of pyridine as a probe molecule by Parry [1], it was the most frequently used for both qualitative (distinguishing between Brønsted and Lewis sites) and quantitative (determination of sites concentration) studies (e.g. Refs. [2–4]). The advantage of using pyridine for quantitative IR studies is the constant value of extinction coefficient of 1545 cm^{-1} pyridinium ion band and the fact, that IR bands of complexes of adsorbed pyridine are relatively narrow which makes easy their intensities easy to meassure. On the other hand, the disadvantage of pyridine is its relatively large size, and the fact that it cannot penetrate zeolitic channels with a diameter smaller than ca. 0.5 nm. However, there are numerous zeolites, such as ferrierite, mordenite, clinoptilolite, TON and others of channels narrower than 0.5 nm which are inaccessible to pyridine.

Ammonia, since it was used by Mapes and Eischens [5] for the first time as a probe molecule for probing surface acidity in 1954 (this paper by Eischens was the first publication on the application of IR spectroscopy to the problems of catalysis!), was much less frequently applied to acidity studies than pyridine. The great advantage of ammonia is a very small molecule size and easy penetration of even very narrow zeolitic channels. On the other hand, the disadvantage of ammonia is the low value of extinction coefficient of 1620 cm^{-1} band of ammonia bonded to Lewis sites, which makes quantitative studies of Lewis acidity difficult. Another disadvantage of ammonia as the probe molecule in contrast to pyridine (for which the band of pyridinium ions increased linearly with the amount of pyridine adsorbed until all the acidic OH groups were neutralized and next—at higher pyridine loadings it was constant), in that the band of ammonium ions continues to increase at high ammonia loadings even upon the neutralization of all acid sites and changes its position and shape. Moreover, the position and the shape of the bands of ammonia reacting with Brønsted sites depend on adsorption temperature.

The nature of ammonia complexes in zeolites has been studied by Zecchina et al. [6]. These authors revealed that mostly bidendate and tridendate ammonium ions stabilized by zeolitic oxygens were formed in zeolites HZSM-5, Hbeta, HY and HSAPO-34. Only in mordenites were tetradendate ammonium

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[*] Corresponding author. Tel.: +48 12 633 6377; fax: +48 12 634 0515.
E-mail address: datka@chemia.uj.edu.pl (J. Datka).

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doi:10.1016/j.cattod.2006.01.009

ions formed inside narrow side pockets. At high ammonia loadings the solvation of ammonium ions and formation of dimmers $N_2H_7^+$ and oligomers $N_2H_7^+\cdot nNH_3$ was observed. Oligomers were formed at ammonia pressures: 20–40 T.

The present study was undertaken to get more information on the nature and properties of ammonia complexes formed at high loading and find optimal conditions to determine of Brønsted sites concentration by quantitative IR studies of ammonia adsorption. The zeolite TON (ZSM-22) was chosen for our study because of its uniform channel structure. It contains 10-ring parallel channels 0.46 nm × 0.57 nm)—all of the same diameter.

2. Experimental

Zeolites TON of Si/Al = 27, 55, 124 and 150 were synthesized in hydrothermal conditions at 430 Kin a rotating autoclave (56 cycles/min) for 70 h. The synthesis was carried out by using 1-ethylpyridinium bromide (EtPBr) as a template following the procedure reported in refs [7–9]. After synthesis the template was removed by careful calcination in dry air (80 cm^3/min). The final calcination temperature was 790 K. The calcined forms were converted into ammonium forms by an ion-exchange procedure with NH_4NO_3 (1 mol/dm^3) solution at 330 K for 24 h. The ion-exchange was carried out two times.

For IR studies zeolites TON were pressed into thin wafers (5–10 mg/cm^2) and activated in situ in an IR cell at 770 K for 1 h. The doses of ammonia (PRAXAIR, 99.96%) were sorbed at various temperature (250, 300 and 400 K).

The spectra were recorded by using a BRUKER EQUINOX 55 IR spectrometer equipped with MCM detector. The spectral resolution was 2 cm^{-1}.

3. Results and discussion

The spectra recorded upon the sorption of consecutive doses of ammonia in zeolite TON (Si/Al = 27) at 250, 300 and 400 K are presented in Figs. 1–3. The differences between the spectra recorded during consecutive sorption steps are presented as well. The sorption of the first doses of ammonia at high temperature 400 K (Fig. 1) results in the decrease of the IR band of Si–OH–Al groups (3602 cm^{-1}), which is accompanied by the appearance of ammonium ions bands: 1380, 1450, 3280 and 3380 cm^{-1} but at higher loadings (upon the neutralization of all Si–OH–Al groups) the NH_4^+ band shifts from 1450 to 1465 cm^{-1}. The analysis of difference spectra gives more information on the nature of complexes formed. At low ammonia loading the bands of ammonium ions (frequencies given above) are present but at higher loading these bands diminish and new bands: 1460, 1500, 3300 and 3400 cm^{-1} appear. These phenomena can be interpreted as the reaction of ammonia molecule with ammonium ions and formation of dimers $NH_4^+\cdot NH_3$ for which the new bands at 1460, 1500, 3300 and 3400 cm^{-1} are characteristic. The sorption of ammonia at

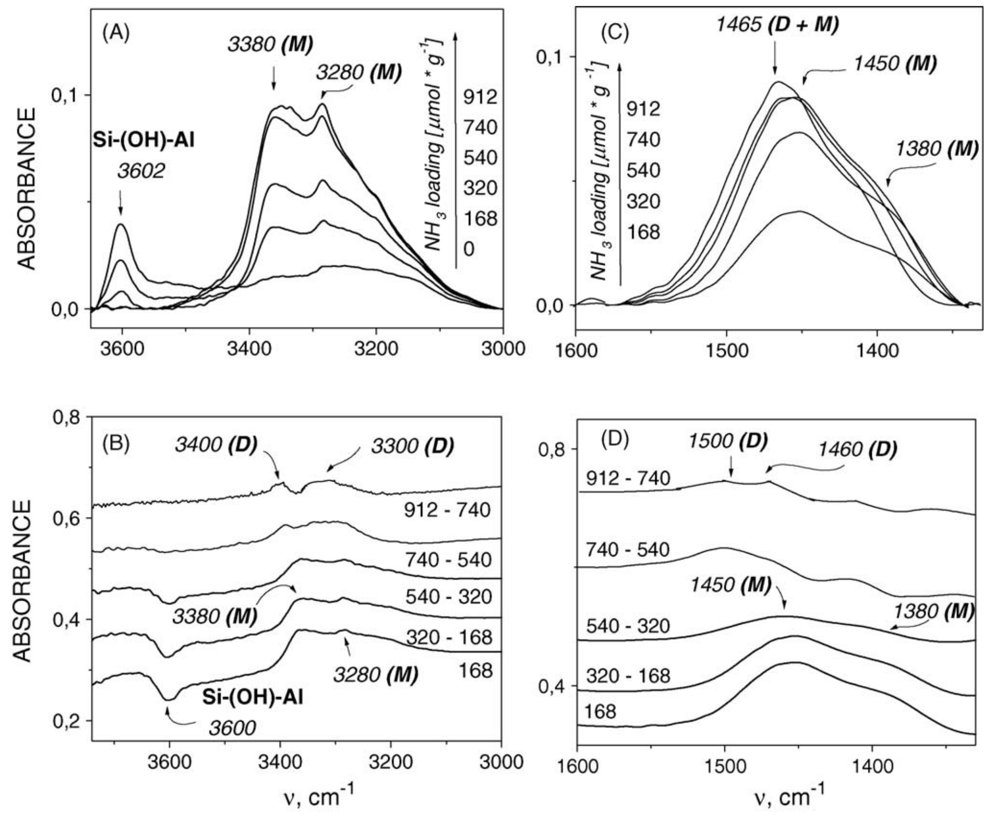

Fig. 1. (A and C) IR spectra recorded upon the sorption of increasing amounts of NH_3 (the amounts of ammonia are given) at 400 K in zeolite TON (Si/Al = 27); (B and D) the difference spectra (differences between the spectra of two consecutive portions of ammonia). The symbols M and D indicate the bands of monomeric ammonium ions and dimers, respectively.

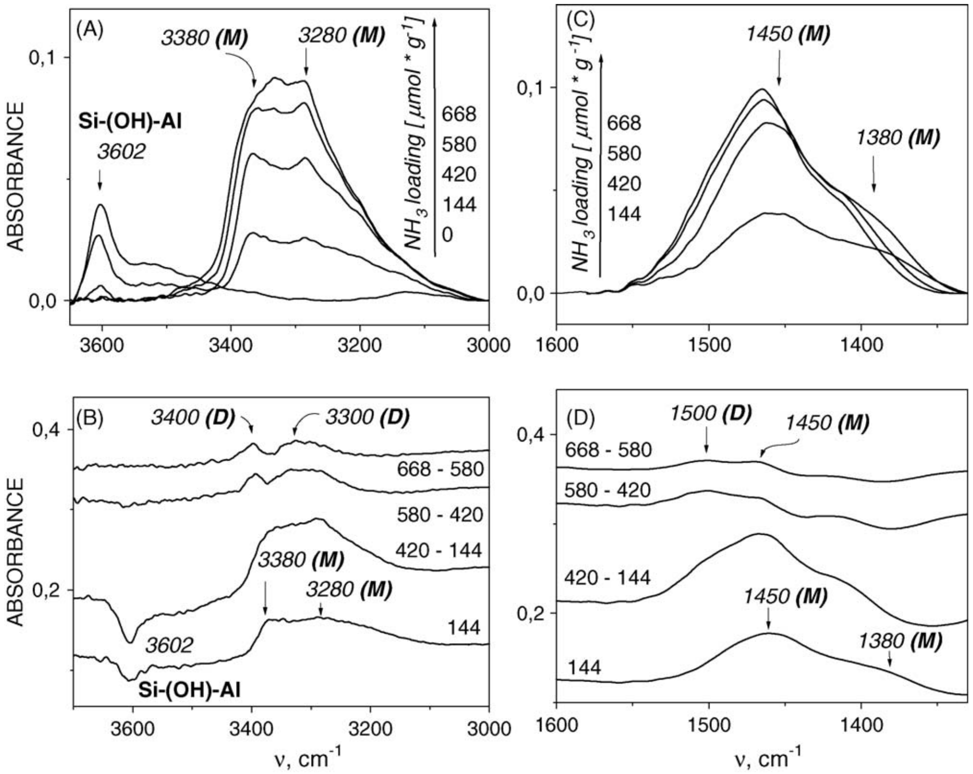

Fig. 2. (A and C) IR spectra recorded upon the sorption of increasing amounts of NH_3 (the amounts of ammonia are given) at 300 K in zeolite TON (Si/Al = 27); (B and D) the difference spectra (differences between the spectra of two consecutive portions of ammonia). The symbols M and D indicate the bands of monomeric ammonium ions and dimers, respectively.

room temperature (300 K)—Fig. 2 results at low loading in the formation of mainly ammonium ions and in their transformation into dimers at higher loading. The results obtained if ammonia is sorbed at low temperature (250 K) are presented in Fig. 3. Contrary to the sorption at 300 and 400 K, intense bands of dimers appear even with the sorption of first portions of ammonia at 250 K.

The obtained results can be interpreted as follows. Ammonia molecules react with acidic Si–OH–Al groups forming ammonium ions, which are mostly bidendate and tridendate. When all acidic hydroxyls are neutralized, the next sorbed ammonia molecules react with ammonium ions (which can also act as Brønsted acid sites), forming dimers $NH_4^+{\cdot}NH_3$. However, it is possible that some ammonia molecules can react with ammonium ions before all Si–OH–Al groups are neutralized. It may happen at low temperatures: 250 K but even at room temperature some dimers are formed before the complete neutralization of Si–OH–Al. It can take place at pore entrances where the concentration of ammonium ions may be higher. If acidic hydroxyls are still present, dimers dissociate, forming ammonium ions and ammonia molecule which can react with such hydroxyls, forming new ammonium ions. Since the dimer dissociation is an activated process, it is slow at low temperature (Table 1).

Slow transformation of dimers into monomers is seen in Fig. 4A and B showing the spectra of ammonia sorbed (the amount of ammonia was about half that of acidic hydroxyls) at room temperature recorded 5 min and 2 h after the sorption. The bands of dimers decrease and the bands of ammonium ions increase, which is accompanied by the decrease of the OH band indicating the dissociation of dimers, and the formation of new ammonium ions by the reaction of ammonia with Si–OH–Al. This is clearly seen in a difference spectrum (Fig. 4A and B, curves c). The same process (transformation of dimers into monomers) can be also observed in experiments in which ammonia was sorbed at 250 K and subsequently zeolite with ammonia was heated to 300 and 400 K (Fig. 4C and D). The sorption at 250 K produced mostly dimers, which were next transformed into ammonium ions at higher temperatures with the consumption of Si–OH–Al groups.

The decomposition of dimers was followed by evacuation at 420 K (Fig. 5). Ammonia was first sorbed at room temperature (both ammonium ions and dimers were formed) and the cell with zeolite was next evacuated at 420 K. The bands of dimers (1460, 1505 and 3400 cm^{-1}) decreased and the bands of ammonium ions (1380, 1440 and 3380 cm^{-1}) increased, but without the variation of Si–OH–Al band intensity. In this case, dimers were also transformed into monomers, but the molecules of ammonia formed by dimers decomposition left zeolite channels without the reaction with Si–OH–Al.

Generally, the decomposition of dimers produces ammonium ion and an ammonia molecule, which may desorb (at

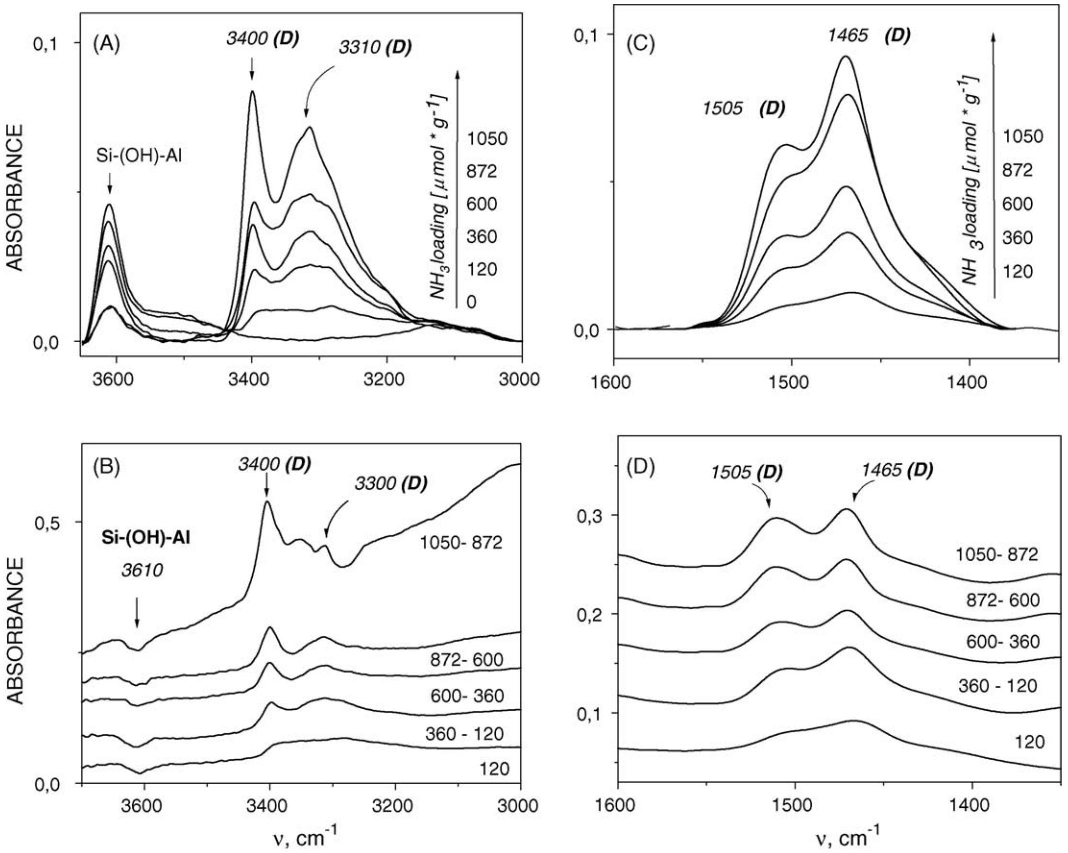

Fig. 3. (A and C) IR spectra recorded upon the sorption of increasing amounts of NH_3 (the amounts of ammonia are given) at 250 K in zeolite TON (Si/Al = 27); (B and D) the difference spectra (differences between the spectra of two consecutive portions of ammonia). The symbols M and D indicate the bands of monomeric ammonium ions and dimers, respectively.

evacuation conditions) or react with acidic hydroxyls (if they are still present) forming new ammonium ions.

These results provide information not only on the nature of ammonia complexes formed in zeolites, but also on the optimal experimental condition for quantitative IR studies of Brønsted acid sites concentration in zeolites. The quantitative IR experiment is composed of two main steps: the neutralization of all Brønsted sites by ammonia, i.e. replacing all Brønsted sites by ammonium ions, and the determination of the extinction coefficient of the ammonium ion band.

The first step (neutralization of Brønsted sites) is the sorption of ammonia excess (sufficient to neutralize all the acid sites) followed by the removal of physisorbed molecules and decomposition of dimers (if they are formed) by evacuation at a temperature which is high enough to decompose dimers but not high enough to decompose the monomeric ammonium ions. According to the results obtained in this study, the optimal temperature for ammonia sorption may be 400 K (practically only ammonium ions are formed) and optimal temperature for evacuation may be 400–420 K (dimmers—if present—decompose and are transformed into monomeric ammonium ions).

Table 1
The concentration of Brønsted acid sites calculated (equal to the amount of Al) and determined in quantitative IR studies of ammonia sorption

Si/Al	Concentration of Brønsted sites/u.c.	
	Calculated (amount of Al)	Determined with NH_3
27	0.86	0.59
55	0.43	0.40
124	0.19	0.19
150	0.16	0.15

The determination of the extinction coefficient of ammonium ions is the sorption of consecutive, measured ammonia doses which should react only with Si–OH–Al groups, forming exclusively ammonium ions (dimers must not be formed). According to the results obtained in this study, the optimal temperature for adsorption of doses of ammonia may be 400 K. A series of spectra should be recorded at various time intervals from the absorption, until the spectrum of ammonium ions does not change (indicating the transformation of dimmers—if formed—into ammonium ions).

The value of the extinction coefficient of 1375–1450 cm^{-1} ammonium ions band, determined according to procedure presented above for zeolite TON (Si/Al = 124 and 150), was 0.102 μmol/cm^2, and the concentrations of Brønsted sites determined with ammonia is presented in the Table. In zeolites TON of Si/Al 55, 124 and 150, the concentration of protonic sites determined by IR spectroscopy was practically the same as the concentration of Al (known from a chemical

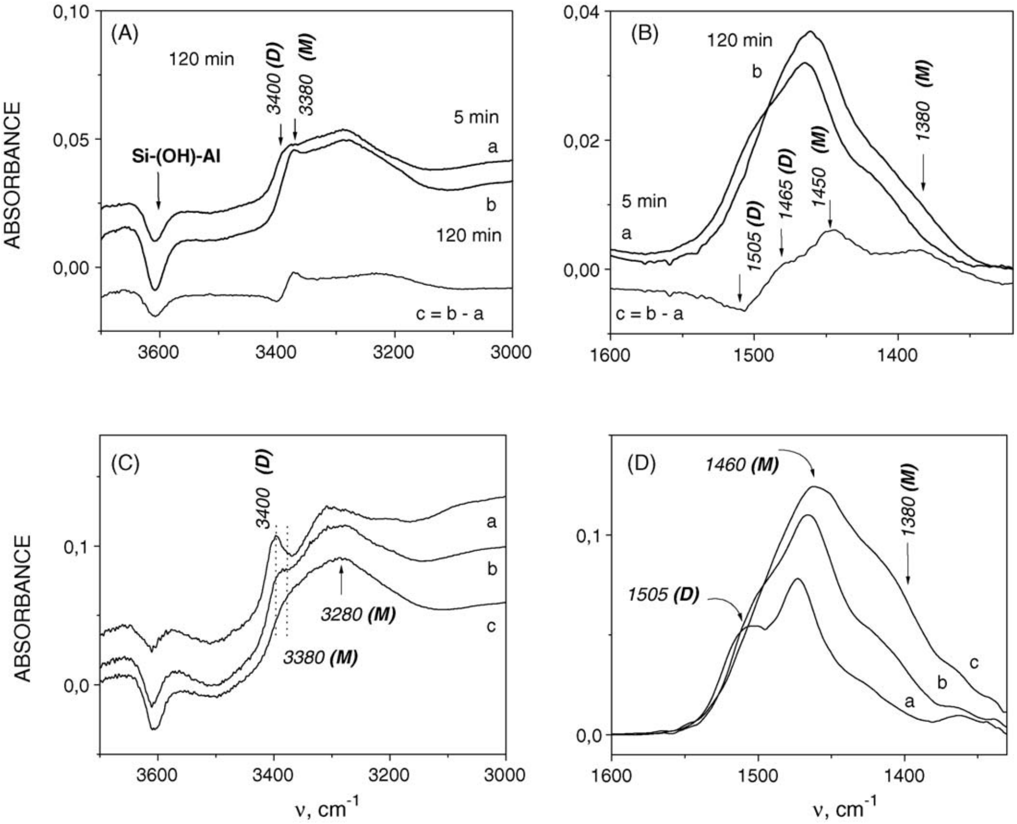

Fig. 4. (A and B) IR spectra recorded 5 min (a) and 2 h (b) upon the sorption of ammonia (about half of the acidic hydroxyls have been neutralized) at room temperature. (c) = (b) − (a) is a difference spectrum (spectrum (b) minus spectrum (a)). (C and D) IR spectra of ammonia (about half of the acidic hydroxyls have been neutralized) sorbed at 250 K (a) and after heating to 300 K (b) and to 400 K (c). The spectra of activated zeolite have been subtracted from the spectra of zeolite with ammonia. The symbols M and D indicate the bands of monomeric ammonium ions and of dimers, respectively.

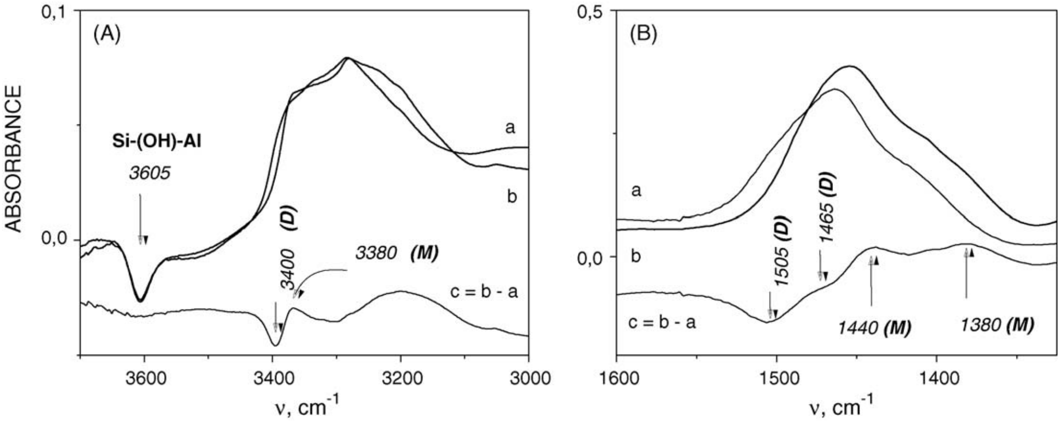

Fig. 5. IR spectra of ammonia (about half of the acidic hydroxyls have been neutralized) sorbed at room temperature (a) and after the evacuation at 400 K (b). (c) = (b) − (a) is a difference spectrum (spectrum (b) minus spectrum (a)) The spectra of activated zeolite have been subtracted from the spectra of zeolite with ammonia. The symbols M and D indicate the bands of monomeric ammonium ions and dimers, respectively.

analysis). This indicates that the procedure of quantitative IR studies of concentration of protonic sites with ammonia was correct. Ammonia can be used as good probe molecules for zeolites of narrow pores. In the case of zeolite TON of Si/Al = 27, the concentration of Brønsted sites determined by IR is lower than the amount of Al. In this zeolite however, some aluminium is in extraframework positions, which is evidenced in IR studies of CO sorption (spectra not shown here).

4. Conclusions

1. Ammonia molecules react with acidic hydroxyls forming ammonium ions. Upon the neutralization of acidic

hydroxyls, the next introduced ammonia molecules react with ammonium ions (which act as Brønsted sites) forming dimers $NH_4^+ \cdot NH_3$. However, at low temperature (300 K or less) some ammonia molecules can react with ammonium ions before the neutralization of all acidic hydroxyls. This may happen at pore entrances where the local concentration of ammonium ions may be the highest.

2. If non-neutralized acidic hydroxyls are still present, dimers decomposes, forming ammonium ions and a free ammonia molecule which can react with such hydroxyls, forming new ammonium ions. This process is slow at room temperature and faster at higher temperatures.
3. Based on the results obtained in this study, the optimal conditions for quantitative IR studies of concentration of Brønsted sites in zeolites could be proposed. Ammonia may be a very appropriate probe molecule to study the acidity of zeolites with narrow pores that are not accessible to pyridine.

Acknowledgments

This study was sponsored by Polish Ministry of Scientific Research and Informational Technology (grant No. 3 T09A 004 28). The samples of zeolites TON were kindly supplied by DSc. M. Derewiński.

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