

A new method for the quantitative determination of zeolitic Brønsted acidity

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A new method for the quantitative determination of zeolitic Brønsted acidity is proposed utilizing the specific low-temperature reaction of NH₄⁺ ions fixed to Brønsted sites with NO–O₂ thus preventing the loss of acid sites normally encountered for the conventional temperature-programmed mode of NH₃ thermodesorption.

Acidity is one of the most prominent features established for microporous zeolite materials, besides the geometric diversities of crystal structures, pore sizes and pore arrangements. The term acidity mostly discriminates between sites of Brønsted character (protonic sites) and Lewis character (coordinatively unsaturated surface atoms or ions). For acidity characterization, among others, the temperature-programmed desorption of ammonia (TPDA) is routinely used today.^{1,2} Interaction of Brønsted-acid sites with NH₃ converts the latter into NH₄⁺ ions fixed to the zeolite framework, and the energy (equivalent to the temperature of desorption) required to release gaseous NH₃ is correspondingly high. Peak positions on the temperature axis during TPDA are indicative of the acid strength of sites whereas the peak areas contain information on the concentration of sites.

Mostly, the contributions of weak and strong acid sites overlap in the desorption profiles. Moreover, certain zeolite structures are thermally labile losing a part of the framework aluminium and thus acid sites. Thus it is reported³ that calcination of zeolite mordenite at 770 K resulted in a degree of dealumination of about 70%. The thermal conversion of zeolite Y (Si/Al atomic ratio = 2.4) from its NH₄⁺ form into the H⁺ form is accompanied by a loss of ca. 44% of its framework aluminium.⁴

This obvious drawback can be avoided by utilization of the method proposed in the following. The method is based on the isothermal catalytic low-temperature conversion (CLTC) of zeolite-fixed NH₄⁺ ions to N₂ by reaction with NO–O₂ at 373–393 K. Simultaneously, the NH₄⁺ form of zeolite structures is transformed into the H⁺ form. Three representative examples will be given (see Table 1) documenting the reliability of the new method.

Table 1 Brønsted acidity of zeolite structures as determined by conventional TPD of ammonia in comparison with the catalytic low-temperature conversion of zeolitic NH₄⁺ ions by NO–O₂

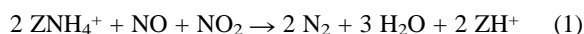
Zeolite	Theoretical composition (Na form)	V _p ^a /cm ³ g ⁻¹	Brønsted acidity/ mmol g ⁻¹		
			TPD of NH ₄ ⁺	TPD ^b of NH ₃	CLTC ^c of NH ₄ ⁺
ZSM-5	Na ₆ [Al ₆ Si ₉₀ O ₁₉₂] (Si/Al = 15.0)	0.16	0.85	0.65	0.90
Mordenite	Na ₈ [Al ₈ Si ₄₀ O ₉₆] (Si/Al = 5.0)	0.18	2.51	1.40	2.40
Y	Na ₅₈ [Al ₅₈ Si ₁₃₄ O ₃₈₄] (Si/Al = 2.3)	0.32	3.75	1.65	3.82

^a Micropore volume from nitrogen adsorption isotherms. ^b Adsorption of NH₃ after thermal decomposition of the NH₄⁺ form and subsequent temperature-programmed desorption (TPD). ^c Catalytic low-temperature conversion of NH₄⁺ by NO–O₂.

Zeolites ZSM-5, Y and mordenite whose ideal compositions and resulting Si/Al atomic framework ratios are given in Table 1, were obtained commercially in their ammonium form. The actual Si/Al framework ratios were determined to be 20.3 (ZSM-5), 2.6 (zeolite Y), and 5.6 (zeolite mordenite).

The CLTC of the NH₄⁺ ions were performed in an integral flow reactor with a feed containing 0.5 vol.% NO, 10 vol.% O₂ and helium as diluent. The gas analysis was accomplished by on-line gas chromatography.

After admission of the NO–O₂–He mixture to the NH₄⁺ form of the zeolite the NO is completely converted to N₂ with consumption of NH₄⁺ ions. The reaction does not proceed in the absence of O₂. Obviously, NO has to be oxidized to NO₂, at least partially, to enable the subsequent reduction step [eqn. (1)],



where Z symbolizes the zeolite, ZNH₄⁺ indicates the ammonium form of the zeolite and ZH⁺ its protonic form. The formation of NO₂–NO adducts, formally equivalent to N₂O₃, has been reported to occur on ZSM-5 either non-promoted or promoted following exposure to NO and O₂ at 295 K by Adelman *et al.*⁵

Fig. 1 shows the result of characteristic experiments, where the NH₄⁺ forms of three different zeolites representative of wide-pore (Y, MOR) and medium-pore (MFI) structures have been charged with an NO–O₂ gas mixture at 383 and 373 K, respectively. Prior to reaction the samples were flushed at 425

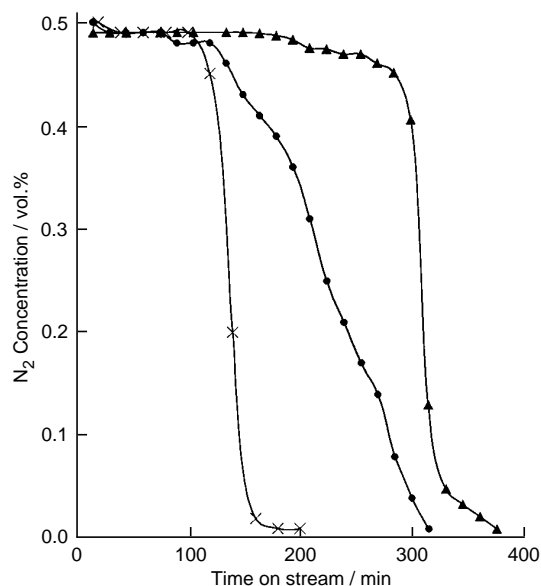


Fig. 1 Quantitative determination of zeolitic Brønsted acidity by catalytic low-temperature conversion (CLTC) of NH₄⁺ ions by NO–O₂ at low temperatures. Formation of N₂ vs. time on stream for (x) zeolite ZSM-5 (Si/Al ratio = 20.3), (●) zeolite mordenite (Si/Al ratio = 5.6) and (▲) zeolite Y (Si/Al ratio = 2.6). Reaction conditions: sample volume = 3.6 cm³, feed = 0.5 vol.% NO, 10 vol.% O₂, carrier gas helium, flow rate = 1 cm³ s⁻¹, reaction temperature = 373 K (ZSM-5) or 383 K (zeolite Y, mordenite).

K for 2 h with helium inside the reactor to remove physisorbed water.

All three investigated zeolite structures start with complete conversion of NO to N₂ during the first 120 min on stream. According to the concentration of NH₄⁺ ions (equivalent to the concentration of Brønsted-acid sites) the N₂ formation ceases. Note that the reaction temperature in the cases of zeolite Y and zeolite mordenite was slightly higher, 383 K, in order to accelerate the process. Because only one N atom comes from the NO, and the other one from NH₄⁺ surface ions, the volume concentration of N₂ is equal to that of NO, viz. 0.5 vol.%. The overall molar amount of N₂ formed was determined by numeric integration of the concentration–time curve and corresponds to the concentration of Brønsted-acid sites. The distinctly modified curve shape observed for the mordenite is tentatively attributed to the pore architecture where pores run only parallel to each other without crossings. Further experiments showed that the access of NO–NO₂ to the small side channels (2.6 × 3.7 Å) of the mordenite structure is hindered so that the CLTC of NH₄⁺ ions is further slowed down.

Values given in Table 1 underline that the concentration of Brønsted-acid sites calculated from a thermal decomposition of

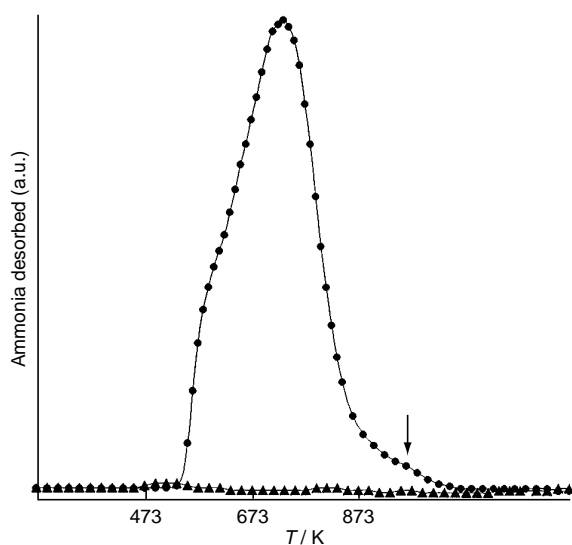


Fig. 2 Temperature-programmed decomposition of NH₄⁺ ions fixed to zeolite ZSM-5 before the CLTC (●) and after completion of the reaction (▲) according to curve (×) in Fig. 1. Sample mass = 0.2 g, heating rate = 10 K min⁻¹, carrier gas helium, flow rate = 0.5 cm³ s⁻¹. The arrow indicates the end of the temperature increase. Decomposition is completed isothermally at 923 K.

the NH₄⁺ form favourably coincides with that derived from the new method. A second run of temperature-programmed desorption following a reloading of the zeolite with gaseous NH₃ confirms that during the thermal decomposition of initial NH₄⁺ ions a dealumination had taken place, most severe for zeolite Y and zeolite mordenite.

The consumption of NH₄⁺ ions according to eqn. (1) is confirmed for zeolite ZSM-5 by the results shown in Fig. 2. Following an exhaustive treatment of the sample with NO–O₂ at 373 K the sample was checked for the presence of residual NH₄⁺ ions. As can be seen, no ammonia release is observed during temperature-programmed heating, i.e. no residual NH₄⁺ ions remain.

The NH₄⁺ form of the unused ZSM-5 is thermally decomposed with maximum release of ammonia at around 720 K. The Brønsted acidity calculated on the basis of this desorption profile amounts to 0.85 mmol g⁻¹ and is included in Table 1.

This result demonstrates that in turn the treatment by NO–O₂ might be utilized for the mild transformation of the zeolitic NH₄⁺ form into the H⁺ form which customarily requires temperatures higher than 770 K when performed thermally. The dealumination that accompanies this thermal treatment is demonstrated by the data given in the penultimate column of Table 1. Initial concentrations of Brønsted-acid sites cannot be reproducibly determined.

A further advantageous application of the described method is seen in the abatement of NO_x from exhaust gases by an alternating process including a period of regeneration where the zeolite is reloaded with the required NH₄⁺ ions.^{6,7}

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