Detection of low levels of Brønsted acidity in Na^+Y and Na^+X zeolites

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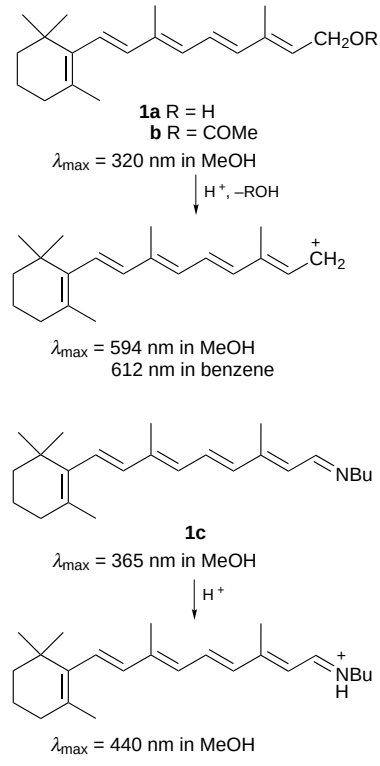
By using retinyl acetate, retinol and retinyl Schiff base as probes, zeolites NaY and NaX are demonstrated to possess a small number of Brønsted acidic sites; the color test employed here is potentially simple and may be universally applied.

Zeolites are finding increasing favor as supramolecular hosts for investigation of the photochemical and photophysical behavior of organic guests.[1] In this context, one would like to employ a reaction cavity that is 'passive'.[2] A set of zeolites that is commonly used as a reaction medium is M^+X and M^+Y.[3] The molecular formula as written for these X and Y zeolites, $M^+_x(AlO_2)_x(SiO_2)_y$, does not give any indication that they may possess reactive Brønsted acid sites.[4] However, it is becoming increasingly clear that the characteristics, especially Brønsted acidity, of commonly used monovalent cation exchanged zeolites can vary significantly from source to source. Even the presence of very small numbers of acidic sites may act in a catalytic manner and complicate the desired chemistry.[5] The characterization of the very small concentrations of Brønsted acid sites present in different samples of X and Y zeolites was, therefore, critical in order to rationalise the observed chemistry. Results of our investigation of Na^+X and Na^+Y zeolites are presented here.

One of our laboratories has recently developed new solid state double resonance NMR methods to probe the acidic sites present in zeolites.[6] Prompted by the success with H^+Y and $Ca^{2+}Y$ zeolites, we proceeded to investigate Na^+Y zeolites with solid state NMR. The basic probe molecules trimethylphosphine (TMP), dimethylamine and methylamine were used to test both Brønsted and Lewis acidity in these materials. Both room and low temperature studies were performed. Zeolite samples (obtained from Aldrich and Zeolyst International) were activated both in an oven at 500 °C in air or at *ca*. 300 °C under a vacuum, in order to mimic activation conditions used for the alkene reactions.[5] ^{1}H MAS NMR spectra of activated Na^+Y showed a resonance at δ 3.6 (both at −80 and −120 °C) possibly due to Brønsted acid sites.[7] The area underneath the peak was extremely small in comparison to the intensity of the residual water and the resonance due to the silanols. Hence it was very difficult to quantify the numbers of Brønsted acid sites per unit cell. A very weak signal was observed at $\delta -2$ in the ^{31}P MAS NMR spectrum (collected at −100 °C) of Na^+Y (from Aldrich) loaded with 26 molecules per unit cell of trimethylphosphine. This resonance was approximately 1/50 that of the main resonance at δ −60 from weakly bound/physisorbed TMP. Resonances from $TMPH^+$, formed by the protonation by the Brønsted acidic sites typically appear in the range δ 0 to −5.[6] Although the resonance at $\delta -2$ seen in the case of Na^+Y, cannot be definitely attributed to $TMPH^+$, it is clear that the number of acidic sites within Na^+Y is very small. From the intensity of this resonance, we estimate that there can be no more than *ca*. 0.5. Brønsted acid sites per unit cell in this sample. No resonances from $TMPH^+$ were observed in samples from Zeolyst (CBV-100) and Engelhardt (EZ-150). To check the presence of weakly acidic sites, stronger bases such as dimethylamine and methylamine were used as probes for Na^+Y. No Brønsted acid sites were detected in the ^{1}H MAS NMR with these probes. Based on these studies we conclude that the number of Brønsted acid sites in Na^+Y (CBV-100 and EZ-150) are small and beyond the detection limits of NMR when using these probe molecules (*i.e.* < *ca*. 0.5 acid sites per unit cell).

In spite of the above discouraging observations, we remained convinced that both Na^+Y and Na^+X contain acidic sites based on their influence on various alkenic substrates.[5] We, therefore, employed a different technique to detect the acidic sites within the zeolites. This involved detecting differences in electronic absorption characteristics between protonated and unprotonated forms of a probe molecule. Three probe molecules (**1a**, **1b** and **1c**) with different basicities were used (Scheme 1).

Both retinol (**1a**) and retinyl acetate (**1b**) in an acidic medium generate a blue color due to the formation of a short lived retinyl carbocation [Scheme 1, eqn. (1)].[8] We have adopted this color change to monitor the Brønsted acidity within zeolites. Four samples of Na^+Y (Aldrich, CBV-100, EZ-150 and LZY-52 from Union Carbide) and Na^+X (Aldrich) were tested for Brønsted acidity. The test consisted of monitoring the absorption changes upon addition of a small amount (50–200 mg) of an activated zeolite to a standard micromolar hexane solution (5 ml) of retinol or retinyl acetate. When activated Na^+Y was added to a standard solution of retinol or retinyl acetate, the zeolite immediately adopted a dark blue color. The color



(1)

(2)

Scheme 1

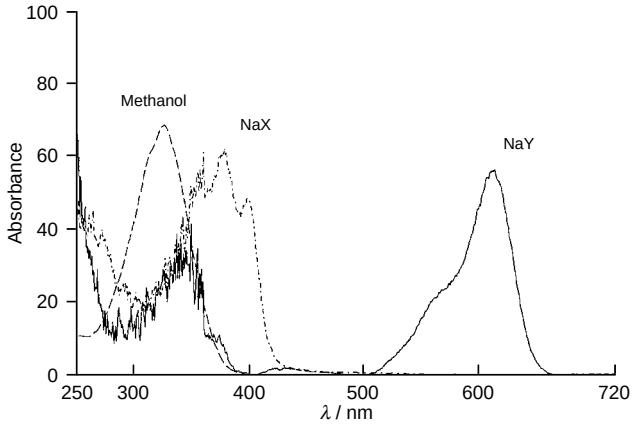


Fig. 1 The spectral change upon inclusion of retinyl acetate within NaY and NaX zeolites. A comparative spectrum in methanol solution is included. Absorption due to retinyl cation is observed in NaY. In NaX the absorption due to retinyl acetate is red shifted but no absorption due to retinyl cation is seen.

persisted for nearly an hour and the diffuse reflectance spectra of these samples are displayed in Fig. 1. The observed λ_{max} within zeolites is in the same range reported in solution.[8] The above observations can be interpreted to mean that Na^+Y contains Brønsted acidic sites that are strong enough to protonate **1a** and **1b**. Na^+X did not show a positive blue test with either **1a** or **1b**, indicating that Na^+X does not contain any protons that are sufficiently acidic to protonate **1a** and **1b**.

Another probe we employed to test the acidity is the more basic retinyl Schiff base **1c** [Scheme 1, eqn. (2)]. In methanol solution, the protonated Schiff base shows an absorption with a λ_{max} at 440 nm. Addition of the above four activated Na^+Y and Na^+X zeolites to a standard micromolar hexane solution of retinyl Schiff base resulted in a color change of the zeolite from white to light yellow orange. The orange colored species absorbs in the same region as the protonated retinyl Schiff base in CH_2Cl_2 solution (Fig. 2). The emission spectra recorded at 77 K are consistent with those reported for the protonated Schiff base.[9] As expected, addition of a large amount of *n*-butylamine displaced the Schiff base from the zeolite. Furthermore, while retinol and retinyl acetate did not indicate the presence of acidic sites within Na^+X, the more basic retinyl Schiff base showed that Na^+X zeolite is also acidic in nature. The difference is likely

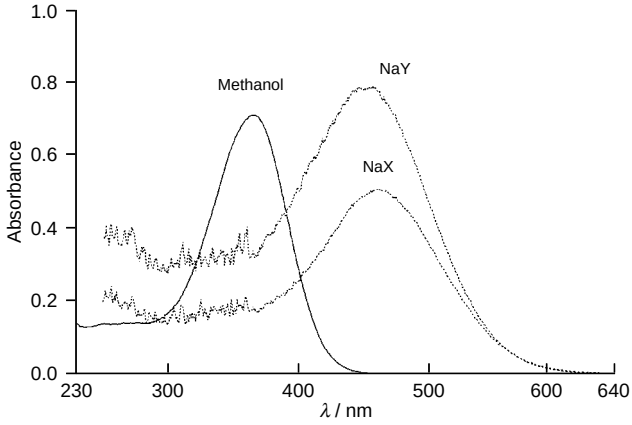


Fig. 2 The spectral change upon inclusion of retinyl Schiff base within NaY and NaX zeolites. A comparative spectrum of unprotonated Schiff base in methanol solution is included. Absorption due to protonated Schiff base is observed in NaY and NaX.

to result from the difference in strength of acidity of the sites present in these two structures.[10]

Diethylamine, a stronger base than **1a**, **1b** and **1c**, was added before the indicator, to react with the Brønsted acid sites, allowing us to estimate the number of acidic sites present in Na^+Y. Titration of the Brønsted acid sites was conducted with diethylamine as the base and **1a** and **1c** as the indicators.† Addition of 1 molecule of diethylamine per 12 supercages of Na^+Y completely quenched the protonation of the probe molecules **1a** and **1c**. This represents a maximum limit of acidic sites within NaY since the estimation assumes that all molecules of diethylamine are protonated under the experimental conditions.

Although extremely low levels of Brønsted acidity were detected, these levels were sufficient to alter the reaction pathways for a number of alkenic systems. We are in the process of characterizing the acidity distribution within different samples of Na^+Y and Na^+X with indicators of different basity. Our initial results suggest that these probes may serve to not only quantify the number of sites but to distinguish between sites of different acidity. Finally, because the method relies on the color changes of highly absorbent dye molecules, it extremely sensitive to low concentrations of acid sites.

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Footnotes and References

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† A known amount (1–10 μl) of diethylamine was added to the dried NaY (200 mg) in hexane and the mixture was stirred for 1 h; then 1 ml of a standard solution of **1a**, **1b** or **1c** was added to this slurry and stirred. The slurry was filtered and the diffuse reflectance spectrum of the solid was recorded. The intensity of the absorption due to the retinyl cation was dependent on the amount of the added diethylamine.

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