

Supplementary Material to:

C.O. Kowenje, D.C. Doetschman, J. Schulte, C.W. Kanyi, J. DeCoste, S.-W. Yang and B.R. Jones, *S. Afr. J. Chem.*, 2010, **63**, 6–10.

A: The ^{29}Si MAS NMR Results

In Fig. S1, the increased broadening of the NMR peaks for the 10 Cu/UC sample can be seen not to recover completely even after exposure to maximal ammonia. The broadening effect is especially evident in the δ -85 ppm peak at the low δ edge of the spectrum. Thus at 10 Cu/UC, some Cu-O_{zeo} interactions are not overcome by the presence of maximal ammonia.

In Fig. S2, the exposure of 24 Cu/UC to increasing amounts of ammonia is seen to decrease the broadening and improve the resolution of the peaks towards their appearances at pre-copper exchange levels. This effect is especially evident in the most intense δ -85 ppm peak at the low δ edge of the spectrum.

B: The IR Results

The zeolite-metal ion symmetric stretching mode at 896 cm^{-1} increases in intensity with an increase in the amount of Cu^{2+} applied per unit cell. The S4R T-O-T symmetric stretching

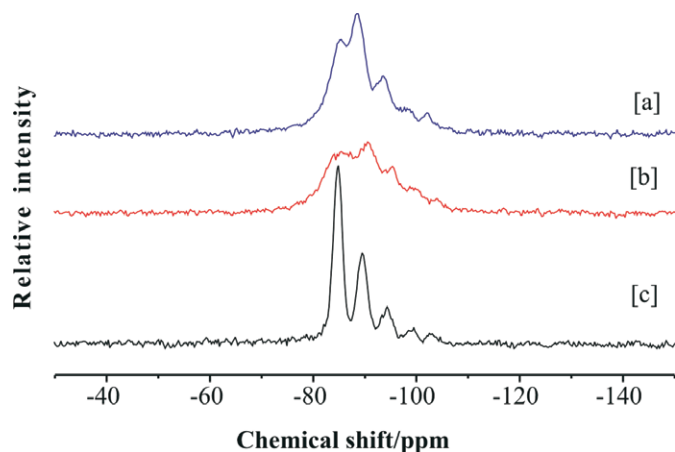


Figure S1 ^{29}Si MAS NMR for dehydrated (a) 10 Cu/UC + maximal NH_3 , (b) 10 Cu/UC and (c) NaX + maximal NH_3 .

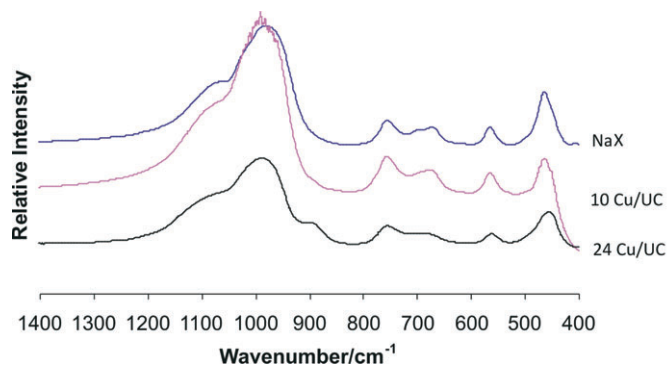


Figure S3 Infrared spectra in the 1400-400 cm^{-1} region for various Cu/UC. (The NaX, 10 and 24 Cu/UC are offset by ca. 1, 2 and 3 absorbance units, respectively.)

vibration mode at 756 cm^{-1} in dehydrated NaX did not shift, regardless of the amount of Cu^{2+} exchanged, while the D6R T-O-T symmetric stretching vibration at 566 cm^{-1} shifted to a constant position of 562 cm^{-1} for all the samples. Notably, the intensity of the 6R ring vibration mode at 407 cm^{-1} decreased as the amount of Cu^{2+} exchange increased.¹⁻³

In Fig. S4, several IR bands are shifted upon exposure of the CuX to ammonia, the S4R, the T-O-T symmetric stretching band at 756 cm^{-1} , the Si-O-Al symmetric stretching band at 685 cm^{-1} and the S4R symmetric bending band at 455 cm^{-1} (refs 1-3) moving to 979, 752, 695 and 460 cm^{-1} respectively. The D6R was minimally shifted from 561 to 563 cm^{-1} , a shift that is considered to be within the experimental error.

The deconvolution of the band at approximately 1270 cm^{-1} reveals the two species presented in Fig. 7 of the main text. From Fig. S5, as the concentration of the Cu/UC increases, the other species at ca. 1272 cm^{-1} becomes more dominant.

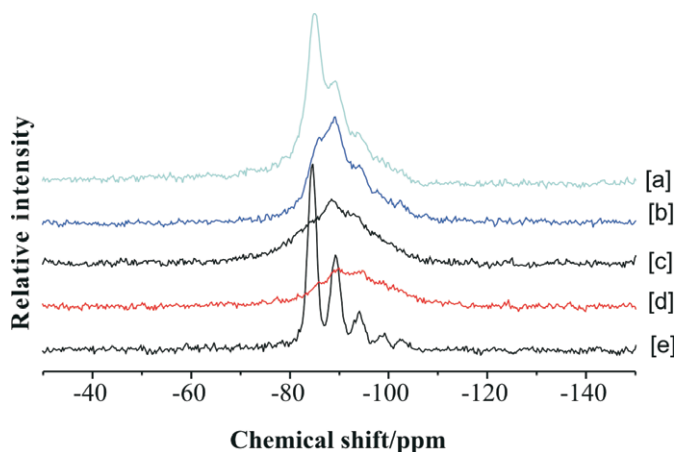


Figure S2 ^{29}Si MAS NMR for dehydrated (a) CuX + maximal NH_3 , (b) CuX + 3 NH_3 , (c) CuX + 1 NH_3 , (d) CuX and (e) NaX + maximal NH_3 .

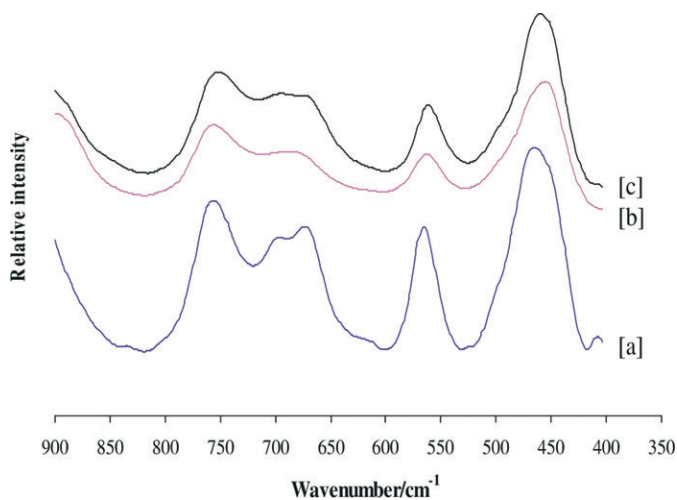


Figure S4 Effects of exposure to ammonia in the ring IR band regions of the zeolite: (a) for NaX, (b) for 24 Cu/UC and (c) for 24 Cu/UC + ammonia.

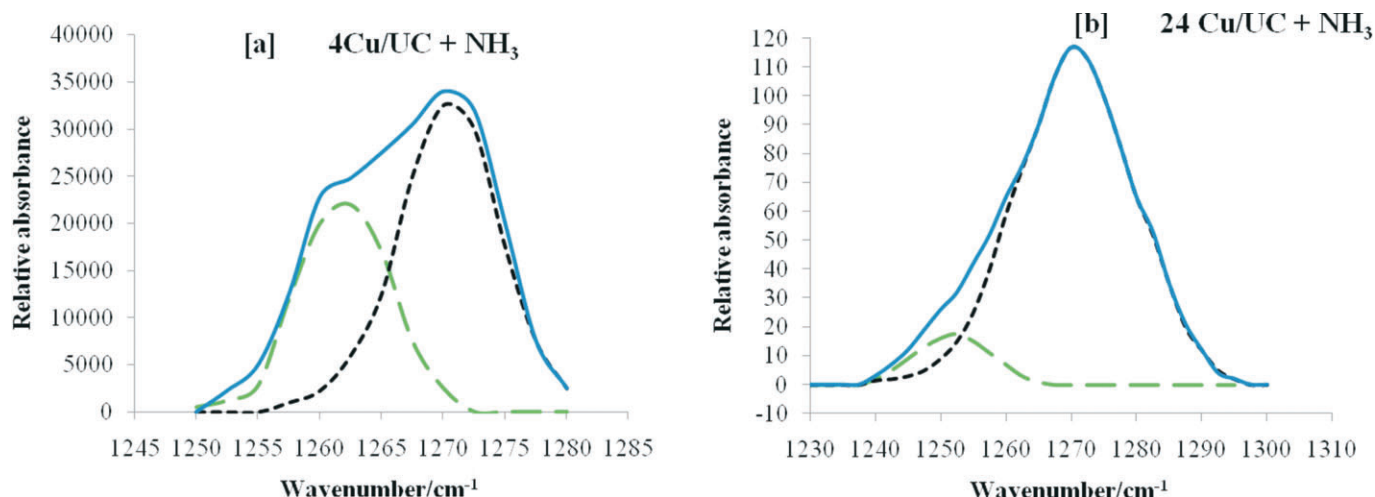


Figure S5 The deconvolved $ca. 1270\text{ cm}^{-1}$ band for various Cu/UC exposed to maximal ammonia. The fitted spectrum on the left occurs at $ca. 1263\text{ cm}^{-1}$ while that on the right occurs at $ca. 1272\text{ cm}^{-1}$. The graphs are for (a) 4 and (b) 24 Cu/UC samples. To bring them to scale, the absorbances of (a) and (b) were multiplied by 7×10^4 and 60, respectively.

C: The EPR Results

From Table S1, the changes brought about by the exposure to maximal ammonia were not significant for the case of 1 Cu/UC. However, some measurable changes were recorded for 10 Cu/UC.

References

- 1 C.S. Blackwell, *J. Phys. Chem.* 1979, **83**, 3257–3261.
- 2 J. Dwyer and R. V. Parish, *Inorg. Chim. Acta*, 1983, **75**, 229–234.
- 3 W. Mazgawa, *J. Mol. Structure*, 2001, **596**, 129–137.

Table S1 Spin Hamiltonians for 1 and 10 Cu/UC with and without ammonia. For 1 Cu/UC, $A_x = A_y \approx 0$, $A_z = A_{\parallel}$. The asterisks indicate values for which minimization could not be attained.

Sample	g value		Hyperfine splitting (A)/G		Line width (L)/G	
	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	L_{\parallel}	L_{\perp}
1Cu/UC; species (I)	2.363 (0.001)	2.051 (0.001)	127.0 (3.8)		55.0 (2.1)	45.5 (2.0)
1Cu/UC; species (II)	2.337 (0.002)	2.071 (0.006)	148.3 (4.8)		60.0 (3.0)	42.0 (2.5)
1 Cu/UC + ammonia	2.347 (0.011)	2.047 (0.002)	170.0 (15.0)		60.0 (10.0)	45.0 (4.1)
10 Cu/UC	2.320 (0.005)	2.066 (0.002)	140.0 (10.0)	93.0 (8.9)	55.5 (4.5)	47.0 (2.8)
10 Cu/UC + ammonia	2.35 (0.009)	2.080 (0.005)*	170.0 (8.4)*	99.7 (6.3)	60.2 (10.4)	49.8 (5.1)*