Supplementary information

Appendix A

Calculation of the free energies of adsorption from chromatographic retention times.

Snyder[32] has shown that chromatographic retention times can be used to determine free energies of adsorption. The method is to calculate a distribution coefficient $K_i^{'}$, which is the ratio of the concentration of solute in a monolayer of solvent on the adsorbate to the concentration of solute in the bulk solution. Then the thermodynamic relationship $\Delta G = -RT\ln K_i^{'}$ is used to calculate the free energy of adsorption.

Data

For 1 ml column contents, voidage 70%,

Volume of solution = 0.7 mL; volume of solid = 0.3 mL

Solid density = 2.85 g mL^{-1}; mass = 0.855 g

Solid area = 150 m^2 g^{-1}

Density of liquid ammonia at 120°C/130 bara = 0.435 g mL^{-1}

Surface coverage of ammonia[17] = 11.76 μmol m^{-2},

so volume of monolayer = 11.76 x 10^{-6} x 17.03/0.435 = 4.6 x 10^{-4} mL m^{-2}

Volume of monolayer of ammonia on alumina in 1 mL of column is

4.6 x 10^{-4} x 150 x 0.855 = 5.9 x 10^{-2} mL

Volume of solution = 0.7 - 5.9 x 10^{-2} = 0.641 mL

$K_i^{'} = k_i^{'} \frac{V_{solution}}{V_{monolayer}}$ so $K_{MB}^{'}$ = 1.29 and $K_{BZ}^{'}$ = 19.6

At 120°C, ΔG_{MB} = -RTln1.29 = 0.83 kJ mol^{-1}; ΔG_{BZ} = -RTln19.6 = 9.7 kJ mol^{-1}

Appendix B

Reaction profile data at 120°C

Concentrations are molar, corrected for expansion to 120°C.

Run 1		***Run 2***		***Run 3***	
τ (min)	C_{MB}	*τ (min)*	C_{MB}	*τ (min)*	C_{MB}
0.000	0.02570	0.000	0.0515	0.000	0.103
0.322	0.02040	0.298	0.0411	0.301	0.089
0.429	0.01870	0.396	0.0384	0.401	0.084
0.643	0.01610	0.595	0.0336	0.602	0.077
0.919	0.01330	0.850	0.0286	0.860	0.068
1.290	0.01060	1.190	0.0237	1.200	0.057
		4.240	0.0062		
		8.480	0.0003		
	C_{NH3}		C_{NH3}		C_{NH3}
	25		24.9		24.75
Run 4		***Run 5***		***Run 6***	
τ (min)	C_{MB}	*τ (min)*	C_{MB}	*τ (min)*	C_{MB}
0.000	0.208	0.000	0.261	0.000	0.313
0.287	0.185	0.200	0.233	0.285	0.284
0.383	0.171	0.299	0.225	0.381	0.271
0.574	0.158	0.399	0.212	0.571	0.250
0.820	0.144	0.598	0.190	0.815	0.226
1.150	0.128	0.855	0.170	1.140	0.195
	C_{NH3}		C_{NH3}		C_{NH3}
	24.4		24.2		24
Run 7		***Run 8***		***Run 9***	
τ (min)	C_{MB}	*τ (min)*	C_{MB}	*τ (min)*	C_{MB}
0.000	0.500	0.000	0.525	0.000	1.074
0.388	0.438	0.396	0.473	0.432	1.004
0.581	0.418	0.595	0.445	0.652	0.967
0.830	0.392	0.576	0.441	0.926	0.902
1.160	0.357	0.850	0.412	1.260	0.891
		1.190	0.368	1.300	0.827
		2.130	0.275	1.880	0.816
		4.240	0.200	2.680	0.730
		8.480	0.110	3.760	0.601
		17.100	0.068		
	C_{NH3}		C_{NH3}		C_{NH3}
	23.4		23.3		21.4
Run 10	C_{BZ0}	***Run 11***	C_{BZ0}	***Run 12***	C_{BZ0}
	0.0103		0.0258		0.0515
τ (min)	C_{MB}	*τ (min)*	C_{MB}	*τ (min)*	C_{MB}
0.000	0.0515	0.000	0.0515	0.000	0.0515
0.202	0.0450	0.292	0.0416	0.320	0.0436
0.302	0.0426	0.390	0.0393	0.427	0.0422
0.404	0.0398	0.584	0.0349	0.640	0.0396
0.606	0.0358	0.835	0.0293	0.914	0.0363
0.864	0.0307	1.169	0.0236	1.281	0.0323
1.211	0.0236				
	C_{NH3}		C_{NH3}		C_{NH3}
	24.9		24.8		24.75
Run 13	C_{BZ0}				
	0.2577				
t (min)	C_{MB}				
0.000	0.0534				
0.416	0.0500				
0.555	0.0489				
0.831	0.0467				
1.188	0.0439				
1.664	0.0399				
	C_{NH3}				
	24				