Improving Ammonia Production Using Zeolites

Supporting Information

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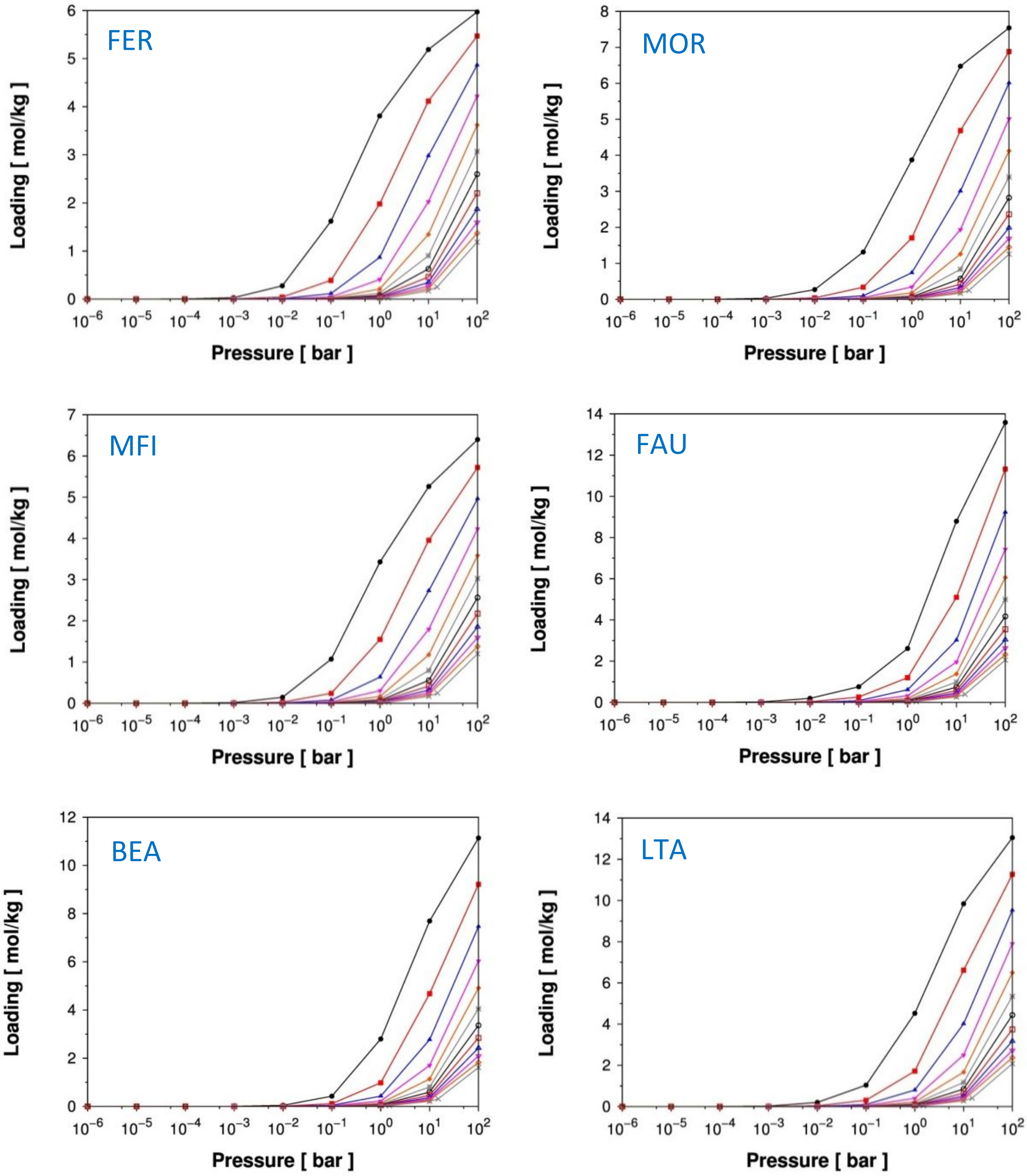

Figure S1: Adsorption isotherms of hydrogen at 80 K (black full circles), 100 K (red full squares), 120 K (blue full up-triangles), 140 K (pink full down-triangles), 160 K (orange full diamonds), 180 K (grey asterisks), 200 K (black empty circles), 220 K (red empty squares), 240 K (blue empty up-triangles), 260 K (pink empty down-triangles), 280 K (orange empty diamonds), and 300 K (grey crosses).

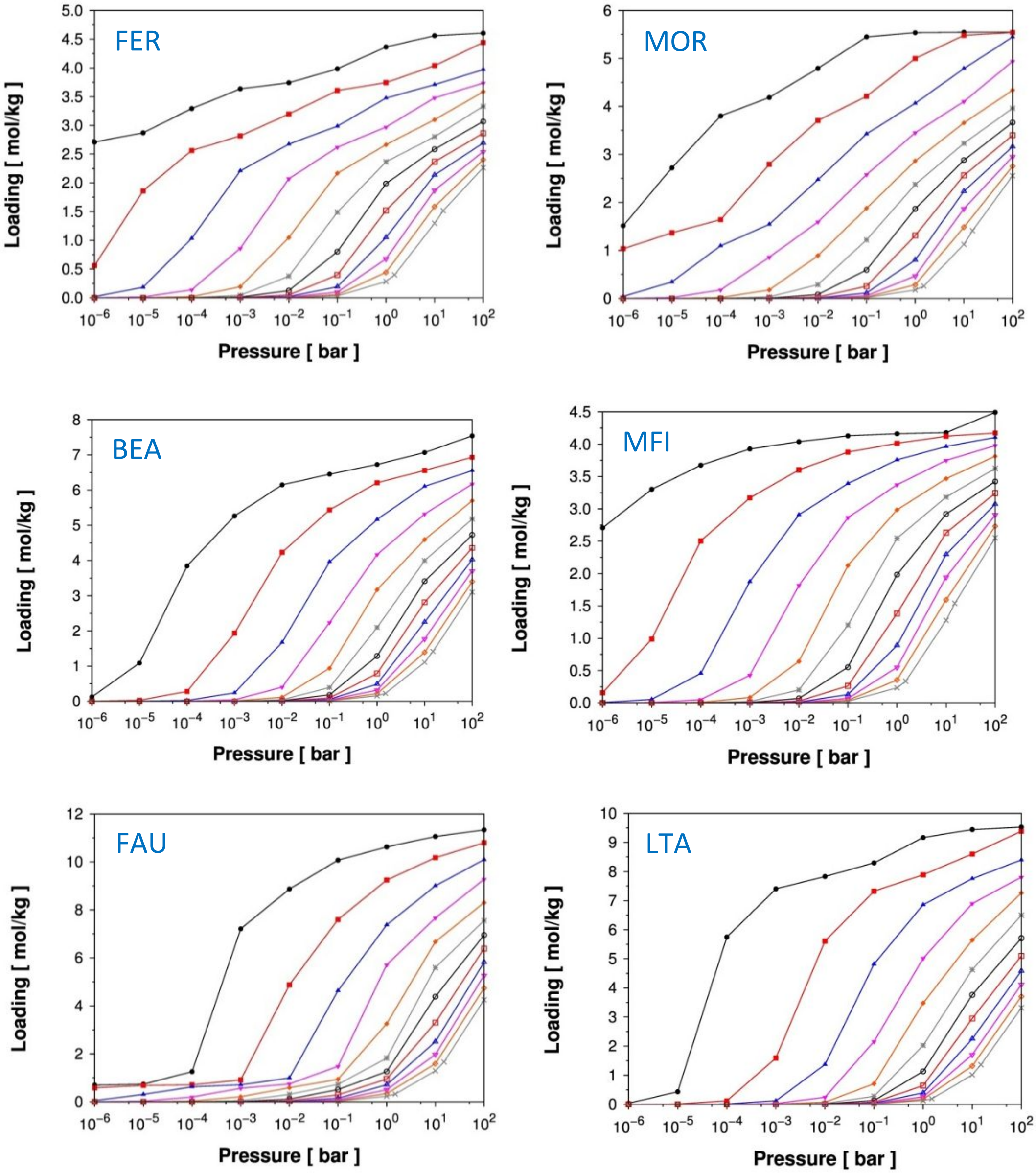

Figure S2: Adsorption isotherms of nitrogen at 80 K (black full circles), 100 K (red full squares), 120 K (blue full up-triangles), 140 K (pink full down-triangles), 160 K (orange full diamonds), 180 K (grey asterisks), 200 K (black empty circles), 220 K (red empty squares), 240 K (blue empty up-triangles), 260 K (pink empty down-triangles), 280 K (orange empty diamonds), and 300 K (grey crosses).

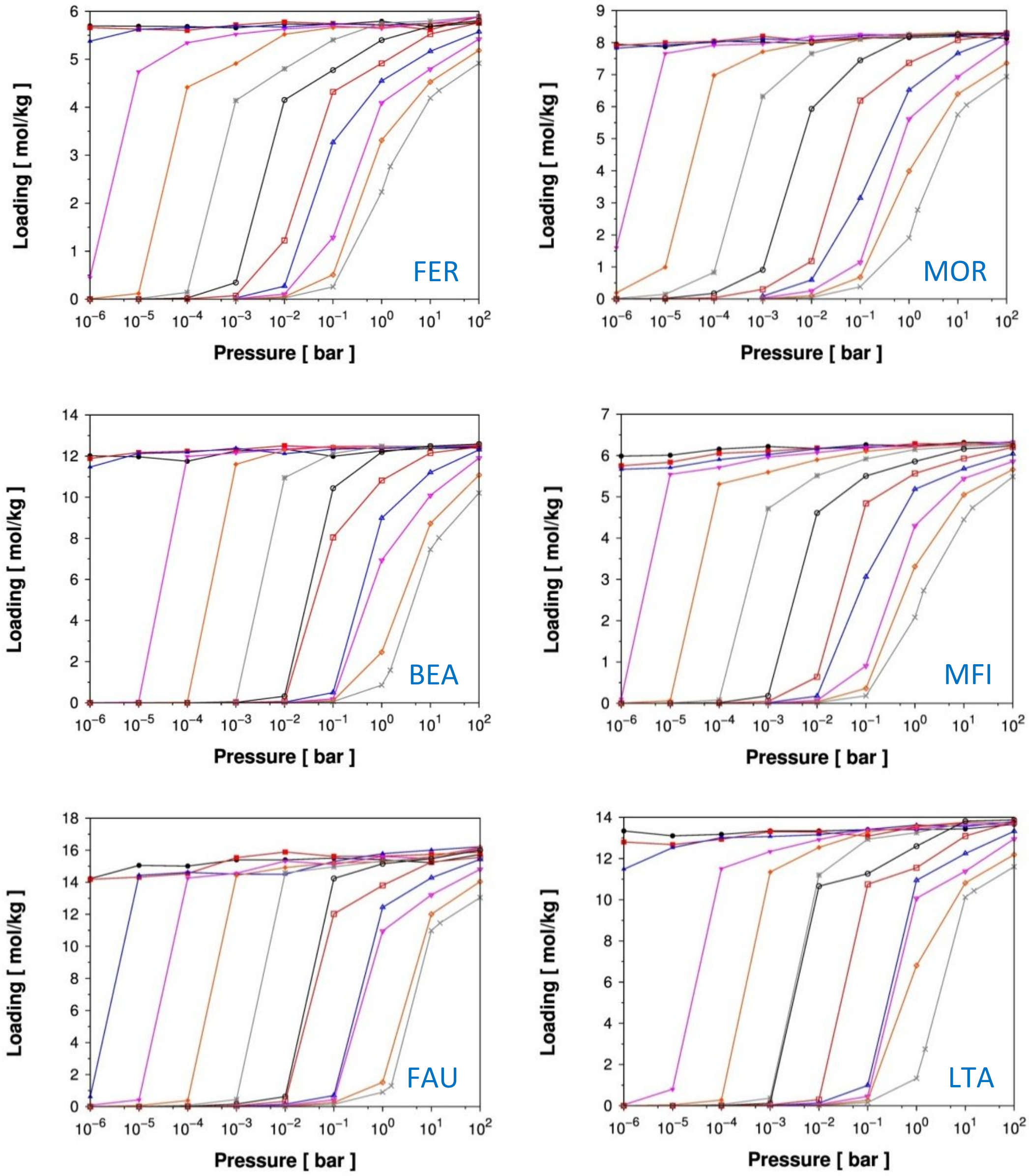

Figure S3: Adsorption isotherms of ammonia at 80 K (black full circles), 100 K (red full squares), 120 K (blue full up-triangles), 140 K (pink full down-triangles), 160 K (orange full diamonds), 180 K (grey asterisks), 200 K (black empty circles), 220 K (red empty squares), 240 K (blue empty up-triangles), 260 K (pink empty down-triangles), 280 K (orange empty diamonds), and 300 K (grey crosses).

Table S1: Ideal-gas partition functions of nitrogen, hydrogen and ammonia[1,2].

	N_2	H_2	NH_3
T (K)	q/Λ^3 (Å^{-3})	q/Λ^3 (Å^{-3})	q/Λ^3 (Å^{-3})
573	$2.60 \cdot 10^{90}$	$6.46 \cdot 10^{40}$	$1.50 \cdot 10^{110}$
673	$6.89 \cdot 10^{77}$	$1.28 \cdot 10^{35}$	$5.42 \cdot 10^{94}$
773	$3.44 \cdot 10^{68}$	$8.28 \cdot 10^{30}$	$2.12 \cdot 10^{83}$
873	$2.42 \cdot 10^{61}$	$5.08 \cdot 10^{27}$	$3.65 \cdot 10^{74}$

Table S2: Cell parameters for FER[3], MOR[4], BEA[5], MFI[6], FAU[7] and LTA-ITQ-29[8].

	a (Å)	b (Å)	c (Å)	α	β	γ
FER	18.7202	14.0702	7.41971	90	90	90
MOR	18.11	20.53	7.528	90	90	90
BEA	12.661	12.661	26.406	90	90	90
MFI	20.022	19.899	13.383	90	90	90
FAU	24.2576	24.2576	24.2576	90	90	90
LTA (ITQ-29)	11.8671	11.8671	11.8671	90	90	90

Table S3: Molar fractions of the components of the mixture obtained by RxMC in the bulk for several working conditions.

P/bar	Mole fraction – NH_3				Mole fraction – N_2				Mole fraction – H_2			
	573K	673K	773K	873K	573K	673K	773K	873K	573K	673K	773K	873K
100	0.56	0.27	0.12	0.05	0.11	0.18	0.22	N2	0.33	0.55	0.66	0.71
200	0.69	0.41	0.20	0.09	0.08	0.15	0.2	0.24	0.23	0.44	0.6	0.68
300	0.78	0.49	0.26	0.14	0.06	0.13	0.19	0.225	0.16	0.37	0.55	0.64
400	0.82	0.57	0.32	0.17	0.05	0.11	0.17	0.22	0.13	0.32	0.5	0.62
500	0.86	0.62	0.37	0.20	0.04	0.1	0.16	0.21	0.1	0.28	0.47	0.60
600	0.88	0.66	0.42	0.24	0.03	0.09	0.15	0.2	0.09	0.25	0.43	0.57
700	0.90	0.69	0.45	0.27	0.03	0.08	0.14	0.19	0.07	0.23	0.4	0.55
800	0.91	0.73	0.50	0.30	0.02	0.07	0.13	0.18	0.07	0.2	0.37	0.52
900	0.93	0.77	0.53	0.33	0.02	0.06	0.12	0.18	0.05	0.17	0.35	0.50
1000	0.94	0.79	0.56	0.35	0.02	0.05	0.11	0.17	0.04	0.16	0.33	0.49

Table S4: Effect of confinement on ammonia production: increment and percentage of enhancement.

573K										
Pressure (bar)	100	200	300	400	500	600	700	800	900	1000
Zeolite	INCREMENT									
FER	0.373	0.277	0.218	0.177	0.156	0.118	0.093	0.082	0.074	0.056
MOR	0.363	0.273	0.216	0.176	0.155	0.118	0.093	0.082	0.074	0.056
MFI	0.361	0.273	0.216	0.176	0.155	0.117	0.092	0.082	0.073	0.056
BEA	0.307	0.246	0.203	0.167	0.149	0.113	0.089	0.079	0.071	0.054
LTA	0.329	0.259	0.211	0.174	0.154	0.117	0.092	0.082	0.074	0.056
FAU	0.302	0.244	0.204	0.169	0.151	0.115	0.091	0.081	0.073	0.056
	% ENHANCEMENT									
FER	41%	29%	23%	18%	16%	12%	9%	8%	7%	6%
MOR	41%	29%	22%	18%	16%	12%	9%	8%	7%	6%
MFI	41%	29%	22%	18%	16%	12%	9%	8%	7%	6%
BEA	37%	27%	21%	17%	15%	11%	9%	8%	7%	5%
LTA	38%	28%	22%	18%	16%	12%	9%	8%	7%	6%
FAU	36%	27%	21%	17%	15%	12%	9%	8%	7%	6%
673K										
Pressure (bar)	100	200	300	400	500	600	700	800	900	1000
Zeolite	INCREMENT									
FER	0.393	0.395	0.358	0.326	0.288	0.261	0.223	0.201	0.181	0.161
MOR	0.357	0.370	0.341	0.314	0.280	0.255	0.218	0.192	0.178	0.159
MFI	0.354	0.371	0.343	0.317	0.282	0.257	0.220	0.199	0.180	0.160
BEA	0.259	0.293	0.282	0.269	0.244	0.226	0.194	0.178	0.163	0.146
LTA	0.297	0.324	0.307	0.290	0.263	0.242	0.208	0.190	0.174	0.155
FAU	0.254	0.285	0.276	0.266	0.245	0.228	0.197	0.182	0.167	0.150
	% ENHANCEMENT									
FER	61%	51%	43%	37%	32%	29%	24%	22%	19%	17%
MOR	58%	49%	42%	36%	32%	28%	24%	21%	19%	17%
MFI	58%	49%	42%	37%	32%	28%	24%	21%	19%	17%
BEA	50%	43%	37%	33%	29%	26%	22%	20%	18%	16%
LTA	54%	46%	39%	35%	30%	27%	23%	21%	18%	16%
FAU	50%	43%	37%	33%	29%	26%	22%	20%	18%	16%

Table S4: Continue

773K										
Pressure (bar)	100	200	300	400	500	600	700	800	900	1000
Zeolite	INCREMENT									
FER	0.235	0.302	0.319	0.338	0.322	0.316	0.303	0.288	0.270	0.251
MOR	0.198	0.263	0.282	0.306	0.294	0.292	0.281	0.271	0.255	0.238
MFI	0.202	0.268	0.288	0.312	0.301	0.299	0.289	0.276	0.261	0.244
BEA	0.135	0.188	0.205	0.233	0.226	0.231	0.227	0.221	0.210	0.197
LTA	0.160	0.218	0.236	0.263	0.256	0.258	0.254	0.245	0.233	0.219
FAU	0.129	0.179	0.197	0.225	0.219	0.226	0.224	0.220	0.210	0.199
	% ENHANCEMENT									
FER	69%	62%	56%	52%	47%	43%	40%	36%	33%	30%
MOR	65%	59%	52%	49%	44%	41%	38%	35%	32%	29%
MFI	65%	59%	53%	50%	45%	42%	38%	35%	32%	30%
BEA	56%	50%	45%	42%	38%	35%	33%	30%	28%	25%
LTA	60%	54%	48%	45%	41%	38%	35%	33%	30%	27%
FAU	54%	49%	44%	42%	37%	35%	33%	30%	28%	26%
873K										
Pressure (bar)	100	200	300	400	500	600	700	800	900	1000
Zeolite	INCREMENT									
FER	0.089	0.169	0.211	0.228	0.240	0.260	0.262	0.264	0.268	0.254
MOR	0.068	0.137	0.175	0.192	0.230	0.224	0.226	0.230	0.237	0.225
MFI	0.073	0.144	0.184	0.201	0.214	0.234	0.238	0.241	0.248	0.235
BEA	0.045	0.097	0.127	0.138	0.147	0.164	0.165	0.170	0.179	0.168
LTA	0.054	0.113	0.146	0.161	0.172	0.190	0.193	0.198	0.206	0.194
FAU	0.041	0.090	0.118	0.131	0.140	0.158	0.160	0.165	0.174	0.165
	% ENHANCEMENT									
FER	62%	65%	62%	59%	55%	53%	49%	46%	45%	41%
MOR	56%	60%	58%	54%	54%	49%	46%	43%	42%	38%
MFI	57%	62%	59%	56%	52%	50%	47%	44%	43%	39%
BEA	45%	52%	50%	46%	43%	41%	38%	36%	35%	31%
LTA	50%	56%	54%	50%	47%	45%	42%	39%	38%	35%
FAU	43%	50%	48%	45%	42%	40%	37%	35%	34%	31%

References

(1) Poursaeidesfahani, A.; Hens, R.; Rahbari, A.; Ramdin, M.; Dubbeldam, D.; Vlugt, T. J. H. Efficient Application of Continuous Fractional Component Monte Carlo in the Reaction Ensemble. *J. Chem. Theory Comput.* **2017**, 1–49.

(2) Poursaeidesfahani, A.; Hens, R.; Rahbari, A.; Ramdin, M.; Dubbeldam, D.; Vlugt, T. J. H. Supporting Information for : Efficient Application of Continuous Fractional Component Monte Carlo in the Reaction Ensemble Partition Function of Serial Rx / CFC. *J. Chem. Theory Comput.* **2017**, 1–37.

(3) Morris, R. E.; Weigel, S. J.; Henson, N. J.; Bull, L. M.; Janicke, M. T.; Chmelka, B. F.; Cheetham, A. K. A Synchrotron X-Ray Diffraction , Neutron Diffraction , 29Si MAS — NMR , and Computational Study of the Siliceous Form of Zeolite Ferrierite. *J. Am. Chem. Soc.* **1994**, *116*, 11849–11855.

(4) Gramlich, V. *Untersuchung Und Verfeinerung Pseudosymmetrischer Strukturen*; Zurich, 1971.

(5) Newsam, J. M. Structures of Dehydrated Potassium Zeolite L at 298 and 78 K and at 78 K Containing Sorbed Perdeuteriobenzene. *J. Phys. Chem.* **1989**, *93*, 7689–7694.

(6) van Koningsveld, H. On the Location and Disorder of the Tetrapropylammonium (TPA) Ion in Zeolite ZSM-5 with Improved Framework Accuracy. *Acta Cryst.* **1987**, *B43*, 127–132.

(7) Hriljac, J. A.; Eddy, M. M.; Cheetman, A. K. Powder Neutron Diffraction and Si

MAS NMR Studies of Siliceous Zeolite-Y. *J. Solid State Chem.* **1993**, *106*, 66–72.

(8) Corma, A.; Rey, F.; Rius, J.; Sabater, M. J.; Valencia, S. Supramolecular Self-Assembled Molecules as Organic Directing Agent for Synthesis of Zeolites. *Nature* **2004**, *431*, 287–290.