Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ADSORPTION EQUILIBRIUM OF NITROGEN DIOXIDE AND DINITROGEN TETROXIDE IN POROUS MATERIALS

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Supporting Information

Table S1 Structural and topological properties of the zeolites under study.

Zeolite	Pore Volume (cm3g)	Surface area (m^2/g)	Density (kgm3)	Channel System	Channel Diameter	Channel Diameter	Channel Diameter	Ring sizes
FER	0.066	235.07	1837.87	2D (1D)	4.69	3.4	-	10 8 6 5
TON	0.091	301.41	1968.716	1D	5.11	-	-	10 6 5
MOR	0.15	477.92	1711.056	1D	6.45	-	-	12 8 5 4
MFI	0.164	547.67	1796.342	3D	4.7	4.46	4.46	10 6 5 4
FAU	0.332	1020.88	1342.047	3D - Cages	7.35	7.35	7.35	12 6 4

Table S2 Mole fraction of NO_2 and N_2O_4 for the bulk phase reaction dimerization over a temperature range of 273-404 K and a pressure range of 0.1-5 atm. The table shows the results obtained in this work from RxMC simulations in the NPT ensemble and calculated data from Chao *et al.*[32] for direct comparison.

Pt [atm] = 0.1					**Pt [atm] = 0.5**				
	Mole Fraction		**Mole Fraction[32]**			**Mole Fraction**		**Mole Fraction[32]**	
T [K]	**NO_2**	**N_2O_4**	**NO_2**	**N_2O_4**	**T [K]**	**NO_2**	**N_2O_4**	**NO_2**	**N_2O_4**
273	0.362	0.638	0.342	0.658	273	0.183	0.817	0.172	0.828
298	0.704	0.296	0.672	0.328	298	0.435	0.565	0.405	0.595
318	0.888	0.112	0.879	0.121	318	0.674	0.326	0.659	0.341
360	0.988	0.012	0.987	0.013	360	0.946	0.054	0.942	0.058
375	0.994	0.006	0.994	0.006	375	0.973	0.027	0.971	0.029
404	0.998	0.002	0.998	0.002	404	0.992	0.008	0.992	0.008
Pt [atm] = 1					**Pt [atm] = 5**				
	Mole Fraction		**Mole Fraction[32]**			**Mole Fraction**		**Mole Fraction[32]**	
T [K]	**NO_2**	**N_2O_4**	**NO_2**	**N_2O_4**	**T [K]**	**NO_2**	**N_2O_4**	**NO_2**	**N_2O_4**
273	0.13	0.87	0.125	0.875	273	0.005	0.995	0.058	0.942
298	0.331	0.669	0.309	0.691	298	0.151	0.849	0.153	0.847
318	0.556	0.444	0.541	0.459	318	0.297	0.703	0.299	0.701
360	0.902	0.098	0.895	0.105	360	0.699	0.301	0.688	0.312
375	0.949	0.051	0.945	0.055	375	0.811	0.189	0.803	0.197
404	0.985	0.015	0.984	0.016	404	0.932	0.068	0.928	0.072

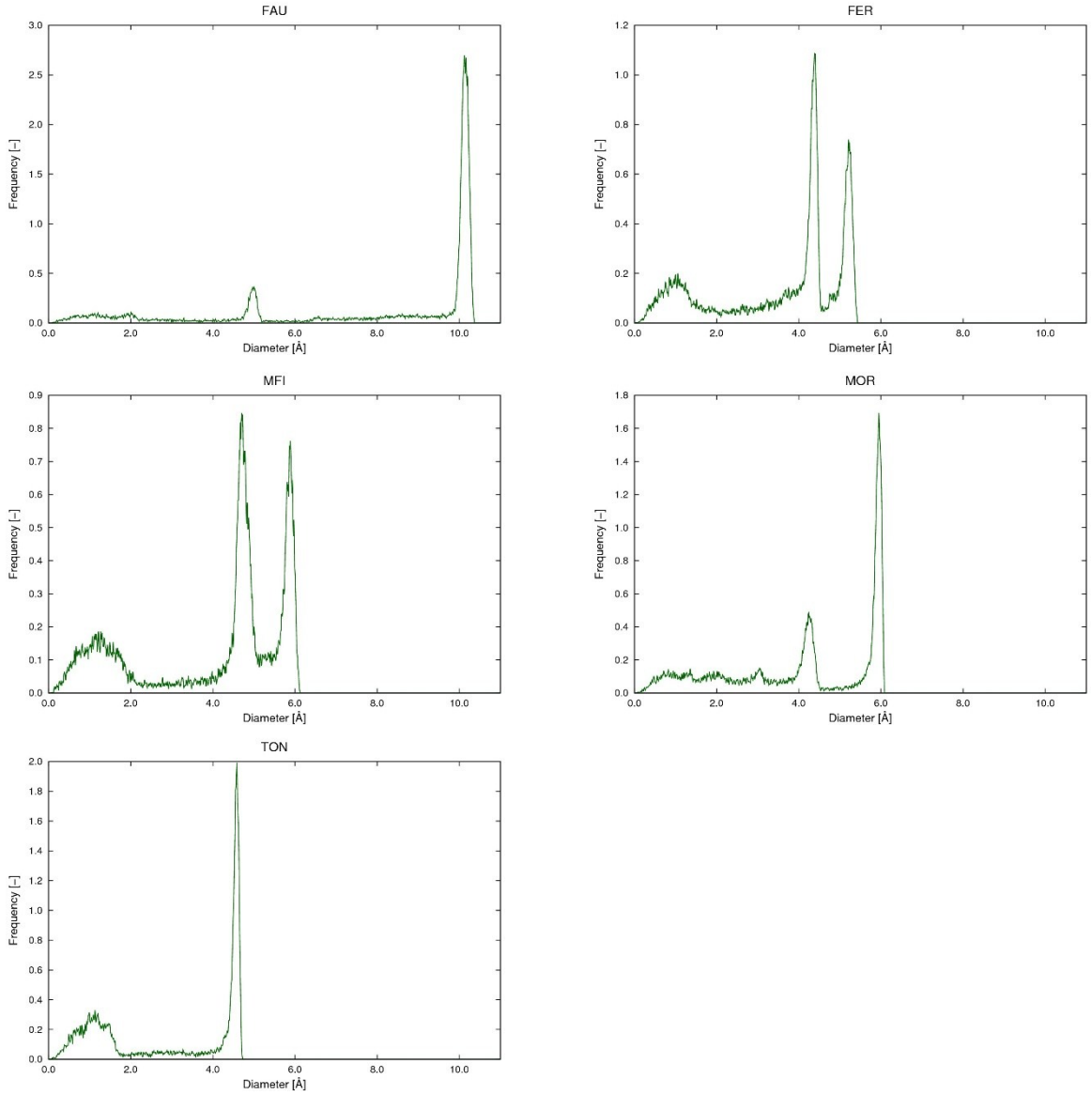

Fig. S1 Pore-size distributions of the zeolites under study (from top left to bottom right: FAU, FER, MFI, MOR, and TON).

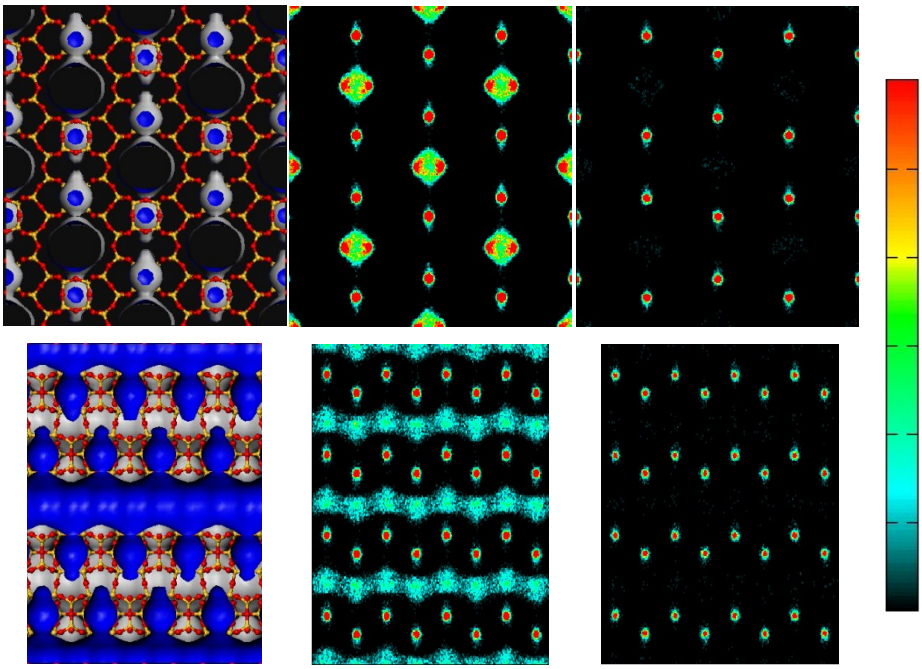

Fig. S2 Average occupation profiles for nitrogen dioxide in MOR zeolite at $5 \cdot 10^2$ kPa and room temperature, obtained from pure component (central column) and binary equimolar mixture NO_2-N_2O_4 (right column). The figures show the projection of the center of mass of the molecules over the *x*-*y* (top) and *z*-*y* (bottom) planes. The color graduation indicates the occupation density (from black to red). To guide the view a representation of the structure (left column) is added (oxygen atoms are depicted in red and silica atoms in yellow). A grid surface is also represented where the accessible part appears in blue while the non-accessible part is colored in gray.

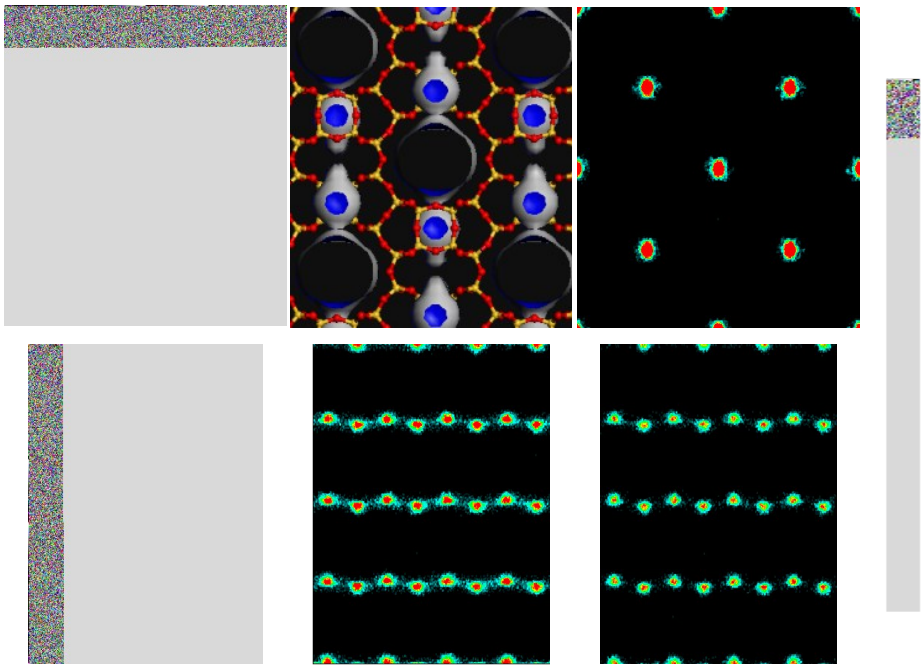

Fig. S3 Average occupation profiles for dinitrogen tetroxide in MOR zeolite obtained from pure component at room pressure (central column) and binary equimolar mixture NO_2-N_2O_4 at 10^3 kPa (right column) and room temperature in both cases. The figures show the projection of the center of mass of the molecules over the *x*-*y* (top) and *z*-*y* (bottom) planes. The color graduation indicates the occupation density (from black to red). To guide the view a representation of the structure (left column) is added (oxygen atoms are depicted in red and silica atoms in yellow). A grid surface is also represented where the accessible part appears in blue while the non-accessible part is colored in gray.

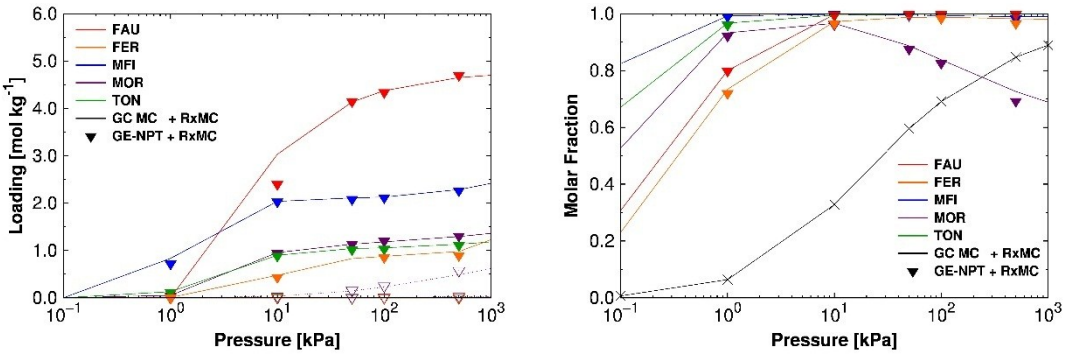

Fig. S4 Simulated binary mixture adsorption isotherms (left), and mole fractions (right) of NO_2 (empty symbols) and N_2O_4 (full symbols) at room temperature in FAU (red), FER (orange), MFI (blue down triangles), MOR (purple squares), and TON (green triangles). In both figures, results obtained using reactive Grand-Canonical Monte Carlo simulation are depicted as line and those obtained from constant pressure Gibbs ensemble reactive simulations as down pointed triangles. To clear the figure and guide the eye in (right), only the N_2O_4 mole fractions are plotted (the sum of both mole fractions is equal to 1) and the bulk mole fractions are also added in black. Reaction move is switched on here.