A comparative first principle study on trivalent ions incorporated SSZ-13 zeolites

Eelectronic Supporting Information

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Table S1 Relative energies (kJ.mol^{-1}) for B-, Al-, Ga- and Fe-incorporated in SSZ-13-type zeolite calculated with DFT-D2 (*ΔE* (DFT-D2)), DFT (*ΔE* (DFT-D2)) and dispersion correction (*ΔE*(D2)), respectively. The relative energies of the other structures are given with respective to the most stable structure.

Sructure	***ΔE* (DFT-D2)**	***ΔE* (DFT)**	***ΔE* (D2)**	**Sructure**	***ΔE* (DFT-D2)**	***ΔE* (DFT)**	***ΔE* (D2)**
H-B-8MR	1	-1	1	H-Ga-8MR	**0**	**0**	**0**
H-B-6MR	**0**	**0**	**0**	H-Ga-6MR	7	5	1
H-B-4MR	33	35	-2	H-Ga-4MR	20	29	-9
Li-B-8MR	14	-2	16	Li-Ga-8MR	21	-3	23
Li-B-6MR	**0**	**0**	**0**	Li-Ga-6MR	**0**	**0**	**0**
Li-B-Cage	38	14	23	Li-Ga-Cage	50	30	19
Na-B-8MR	**0**	**0**	**0**	Na-Ga-8MR	**0**	**0**	**0**
Na-B-6MR	11	14	-4	Na-Ga-6MR	21	4	17
Na-B-Cage	25	41	-16	Na-Ga-Cage	39	41	-2
K-B-8MR	10	14	-4	K-Ga-8MR	**0**	**0**	**0**
K-B-6MR	**0**	**0**	**0**	K-Ga-6MR	8	14	-7
K-B-Cage	25	22	3	K-Ga-Cage	30	34	-4
H-Al-8MR	1	1	1	H-Fe-8MR	**0**	**0**	**0**
H-Al-6MR	**0**	**0**	**0**	H-Fe-6MR	2	1	1
H-Al-4MR	21	3	-9	H-Fe-4MR	14	22	-8
Li-Al-8MR	29	9	20	Li-Fe-8MR	22	-1	22
Li-Al-6MR	**0**	**0**	**0**	Li-Fe-6MR	**0**	**0**	**0**
Li-Al-Cage	50	59	-9	Li-Fe-Cage	49	44	6
Na-Al-8MR	25	10	15	Na-Fe-8MR	**0**	**0**	**0**
Na-Al-6MR	**0**	**0**	**0**	Na-Fe-6MR	24	9	15
Na-Al-Cage	41	43	-2	Na-Fe-Cage	38	41	-3
K-Al-8MR	**0**	**0**	**0**	K-Fe-8MR	**0**	**0**	**0**
K-Al-6MR	32	37	-4	K-Fe-6MR	33	26	8
K-Al-Cage	35	71	-36	K-Fe-Cage	38	71	34

Table S2 Atomic and ionic radii (in Å) for Si, B, Al, Ga, Fe, Li, Na, K, NH_4.

	Si	B	Al	Ga	Fe	Li	Na	K	NH_4
Atomic Radii [a] (Å)	1.11	0.82	1.18	1.26	1.17	1.34	1.54	1.96	-
Ionic Radii [a] (Å)	-	0.23	0.51	0.62	0.64	0.68	0.97	1.33	1.48

[a] The data from http://www.webelements.com/.

Table S3. Bond distances *M*-O(*M*=B, Al, Ga and Fe), *Y*-O(*Y*=H, NH_4, Li, Na, K) and cell volumes of B-, Al-, Ga- and Fe-incorporated SSZ-13-type zeolite.

Subtituted atoms		*M*–O(Å)	*Y*–O(Å)	Cell volume(Å^3)
B	**NH_4**	1.46,1.47,1.48,1.53	1.67[a]	2395.28
	H	1.38,1.38,1.39,2.43	0.98	2420.00
	Li	1.45,1.45,1.50,1.55	1.94	2402.86
	Na	1.45,1.46,1.51,1.51	2.25	2405.78
	K	1.46,1.46,1.50,1.51	2.71	2404.28
Al	**NH_4**	1.72,1.73,1.74,1.78	1.55 [a]	2439.01
	H	1.69,1.71,1.71,1.92	0.99	2451.37
	Li	1.70,1.72,1.74,1.80	1.92	2440.98
	Na	1.71,1.73,1.75,1.78	2.29	2448.35
	K	1.72,1.73,1.75,1.78	2.75	2437.46
Ga	**NH_4**	1.83,1.83,1.86,1.88	1.63 [a]	2436.76
	H	1.80,1.82,1.82,2.00	0.99	2446.95
	Li	1.80,1.82,1.85,1.91	1.92	2442.59
	Na	1.83,1.85,1.87,1.89	2.28	2446.99
	K	1.82,1.83,1.85,1.88	2.75	2446.07
Fe	**NH_4**	1.83,1.83,1.89,1.89	1.64 [a]	2433.51
	H	1.80,1.81,1.82,2.06	0.99	2451.35
	Li	1.81,1.83,1.86,1.93	1.89	2445.38
	Na	1.81,1.83,1.86,1.91	2.26	2449.25
	K	1.83,1.84,1.86,1.90	2.76	2434.80
Si [b]	**-**	1.62,1.62, 1.63,1.63	-	2436.79

[a] The distance from the nearest H of NH_4 to O.

[b] The pure silica SSZ-13 zeolites

Table S4. Substitution energies (E_{sub}, kJ.mol^{-1}) for the substitution of one Si atom with M (M = B, Al, Ga and Fe) and Y (Y = H, NH_4, Li, Na, K) in SSZ-13-type zeolite calculated with DFT-D2 (and DFT).

	B	**Al**	**Ga**	**Fe**
H	51(59)	–122(–111)	–54(–37)	124(146)
NH_4	–28 (11)	–253(–217)	–175(–132)	–39(–1)
Li	–156(–105)	–376(–327)	–301(–244)	–131(–80)
Na	–205(–166)	–440(–386)	–362–302)	–194(–139)
K	–209(–169)	–424(–384)	–347(–304)	–177(–133)

Table S5. Adsorption energies (E_{ads}, kJ.mol^{-1}) for the adsorption of NH_3 and pyridine in SSZ-13-type zeolite are calculated with DFT-D2 and DFT, respectively.

Structures	**E_{ads} (DFT-D2)**	**E_{ads}(DFT)**	**Structures**	**E_{ads} (DFT-D2)**	**E_{ads}(DFT)**
B-NH_3(B)	–100	–74	B-Py(B)	–163	–80
B-NH_3(L)	–96	–68	B-Py(L)	–138	–68
Al-NH_3(B)	–183	–151	Al-Py(B)	–228	–159
Al-NH_3(L)	–133	–113	Al-Py(L)	–154	–82
Ga-NH_3(B)	–167	–141	Ga-Py(B)	–215	–146
Ga-NH_3(L)	–148	–124	Ga-Py(L)	–154	–84
Fe-NH_3(B)	–165	–138	Fe-Py(B)	–207	–139
Fe-NH_3(L)	–142	–119	Fe-Py(L)	–156	–81

Table S6 Calculated Bader charges of trivalent atoms, alkali metals ions and the bridge oxygen that nearest to the monovalent atoms in the B-, Al-, Ga- and Fe-incorporated SSZ-13-type zeolite. (M = B, Al, Ga and Fe, Y = H, Li, Na and K)

strucures	q_M	q_Y	q_O
Al-H	2.43	1.00	–1.81
Al-Li	2.48	0.89	–1.63
Al-Na	2.48	0.86	–1.62
Al-K	2.48	0.92	–1.62
B-H	2.36	0.62	–1.40
B-Li	2.39	0.89	–1.61
B-Na	2.39	0.86	–1.58
B-K	2.39	0.92	–1.59
Ga-H	1.75	0.65	–1.36
Ga-Li	1.77	0.89	–1.47
Ga-Na	1.77	0.86	–1.46
Ga-K	1.76	0.92	–1.44
Fe-H	1.43	0.64	–1.33
Fe-Li	1.44	0.89	–1.41
Fe-Na	1.45	0.86	–1.39
Fe-K	1.45	0.92	–1.38

Table S7 Deprotonation energy (DPE, kJ.mol^{-1}) for the H-form Al, Ga, Fe and B incorporated SSZ-13 zeolites calculated with DFT-D2.

	B	**Al**	**Ga**	**Fe**
Vertical	429	368	374	365
Adiabatic	397	345	357	348

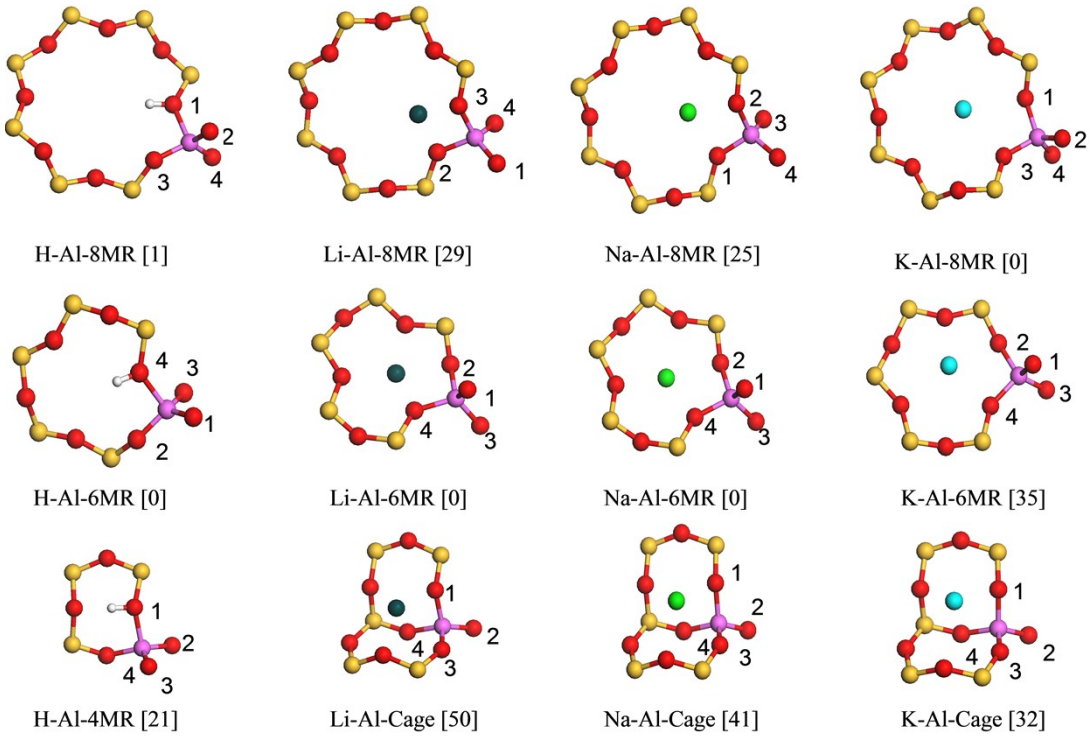

Fig. S1. The most local structures and relative energies (kJ.mol^{-1}) for Al substituted SSZ-13-type zeolite. H, Li, Na, K, O, Al and Si atoms are shown in white, dark slate green, green, blue, red, violet and yellow, respectively. The relative energy of the most stable structure is 0 kJ.mol^{-1} and the relative energies of the other structures are given with respective to the most stable structure. (Only related atoms were selectively shown for better viewing).

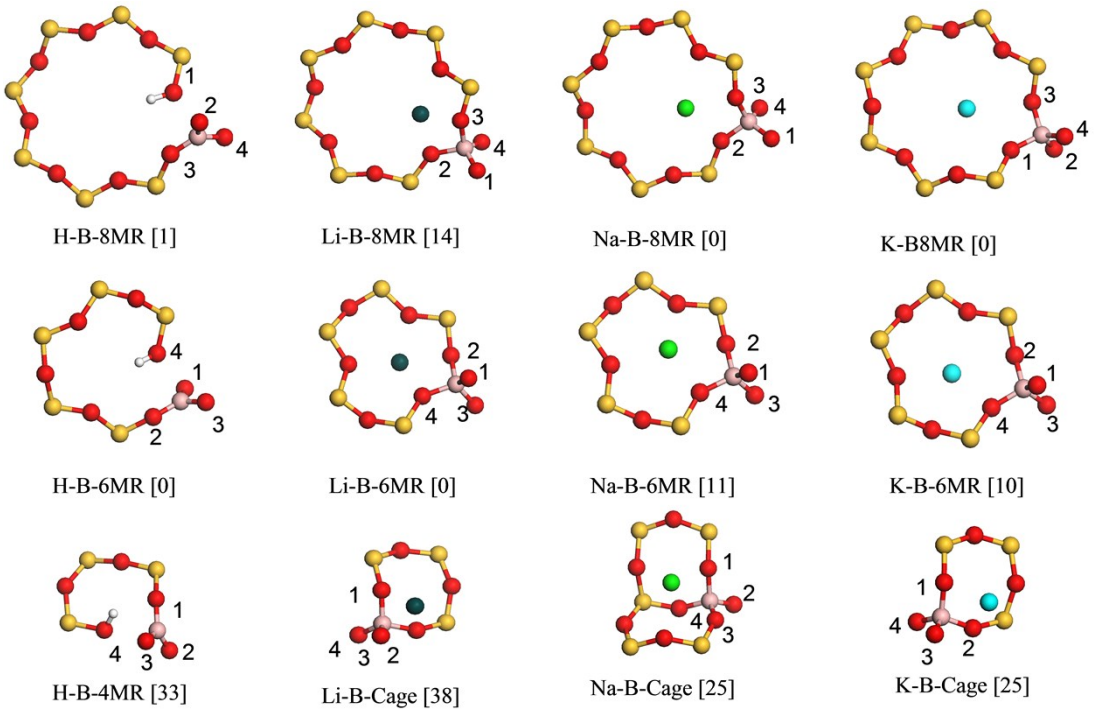

Fig. S2. Local structures and relative energies (kJ.mol^{-1}) for B substituted SSZ-13-type zeolite. H, Li, Na, K, O, B, and Si atoms are shown in white, dark slate green, green, blue, red, tan and yellow, respectively. The relative energy of the most stable structure is 0 kJ.mol^{-1} and the relative energies of the other structures are given with respective to the most stable structure. (Only related atoms were selectively shown for better viewing).

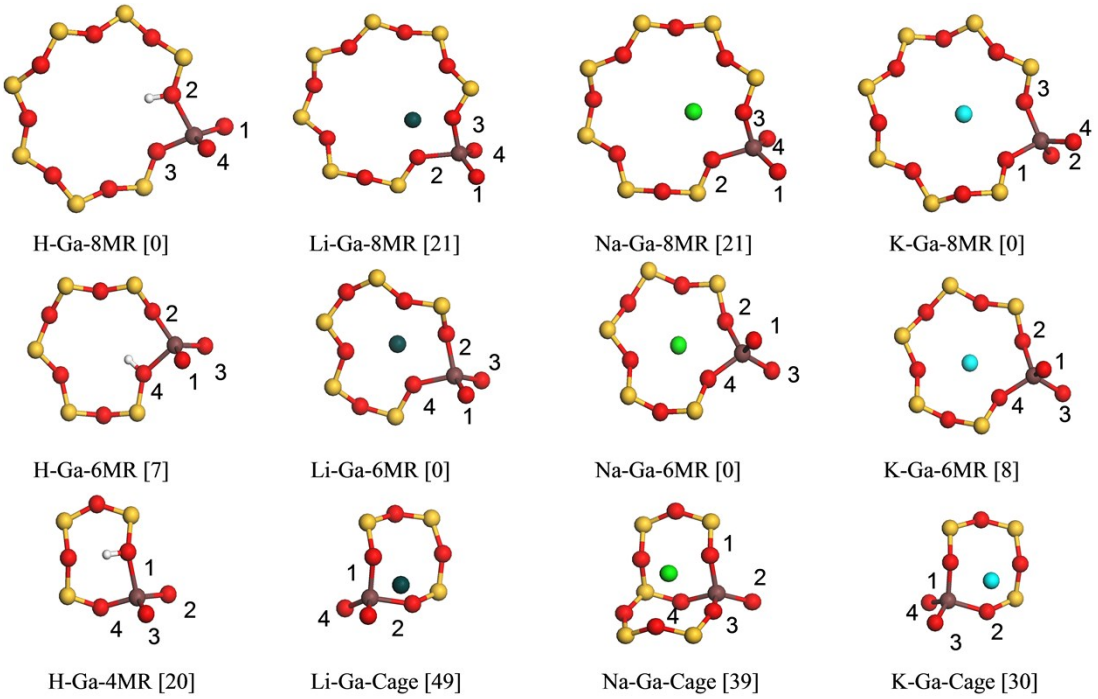

Fig. S3. Local structures and relative energies (kJ.mol^{-1}) for Ga substituted SSZ-13-type zeolite. H, Li, Na, K, O, Ga and Si atoms are shown in white, dark slate green, green, blue, red, brown and yellow, respectively. The relative energy of the most stable structure is 0 kJ.mol^{-1}, and the relative energies of the other structures are given with respective to the most stable structure. (Only related atoms were selectively shown for better viewing).

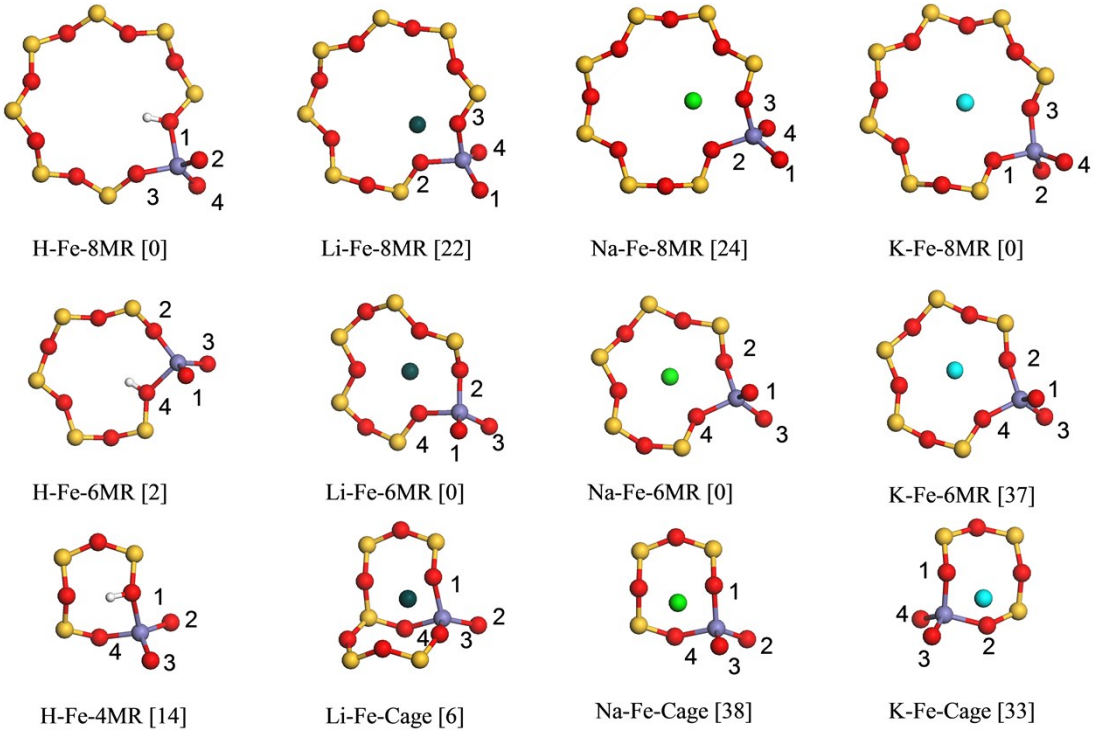

Fig. S4. Local structures and relative energies (kJ.mol^{-1}) for Fe substituted SSZ-13-type zeolite. H, Li, Na, K, O, Fe and Si atoms are shown in white, dark slate green, green, blue, red, gray and yellow, respectively. The relative energy of the most stable structure is 0 kJ.mol^{-1}, and the relative energies of the other structures are given with respective to the most stable structure. (Only related atoms were selectively shown for better viewing).