Supplementary Material for PCCP

Supplementary Information

Experimental and theoretical determination of adsorption heats of CO_2 over alkali metal exchanged ferrierites with different Si/Al ratio

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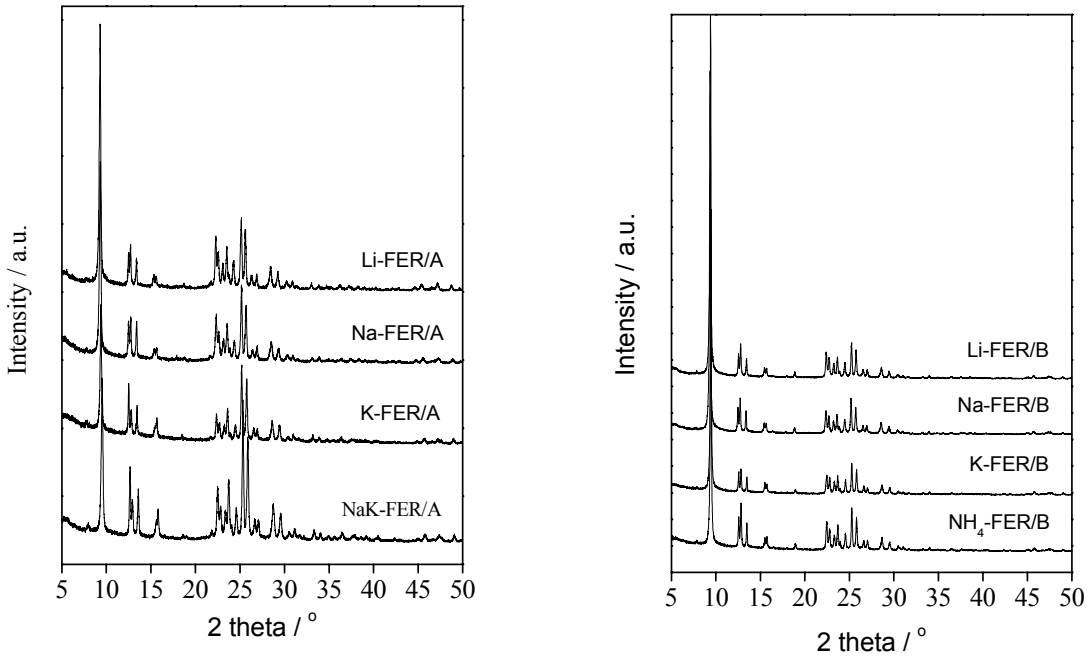

Fig. S1. X-ray diffraction patterns of parent ferrierites and their alkali forms obtained after the complete ion exchange.

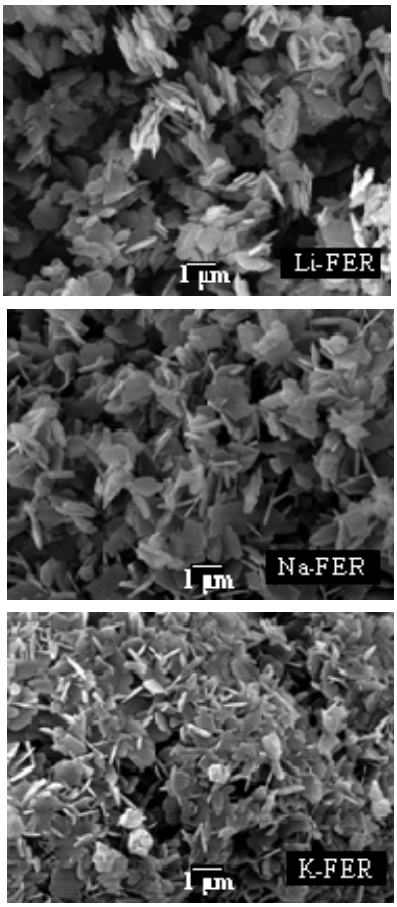

Fig. S2. Scanning electron micrographs of Li-, Na- and K-FER/A.

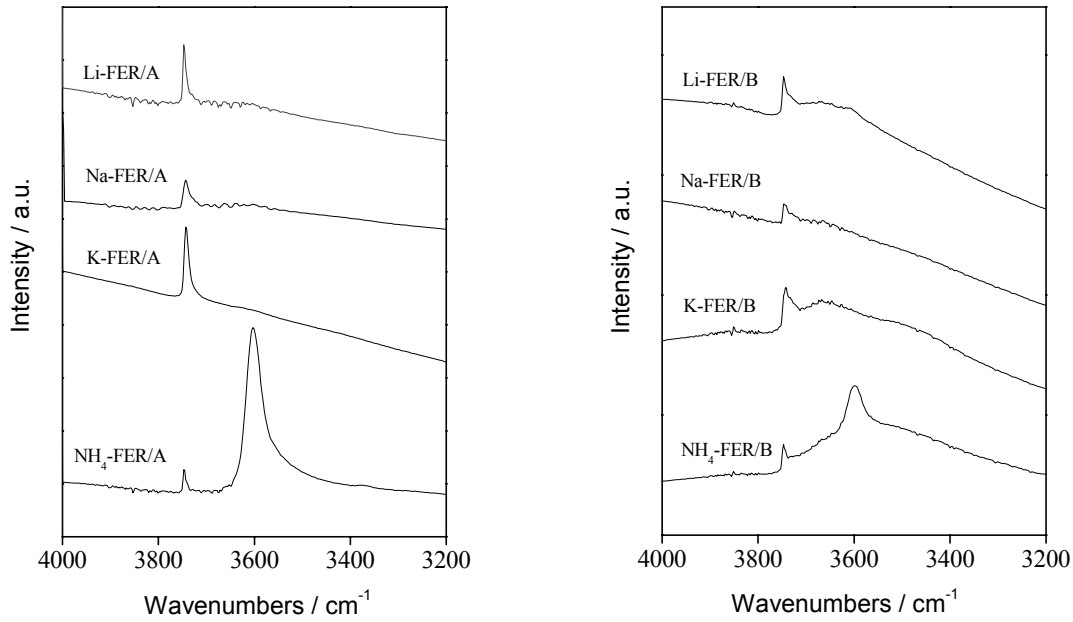

Fig. S3. FTIR spectra of the protonic forms of FER/A and FER/B and their respective alkali metal exchanged forms.

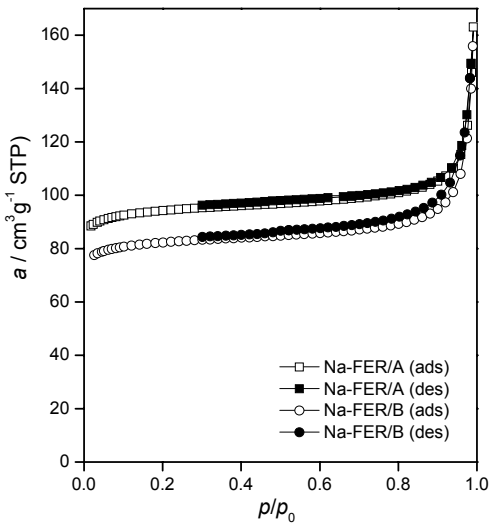

Fig. S4. Adsorption isotherms of nitrogen on Na-FER/A and Na-FER/B at 77 K. (Adsorption isotherm for the sample Na-FER/A is offset vertically by 10 cm^3g^{-1} STP.)

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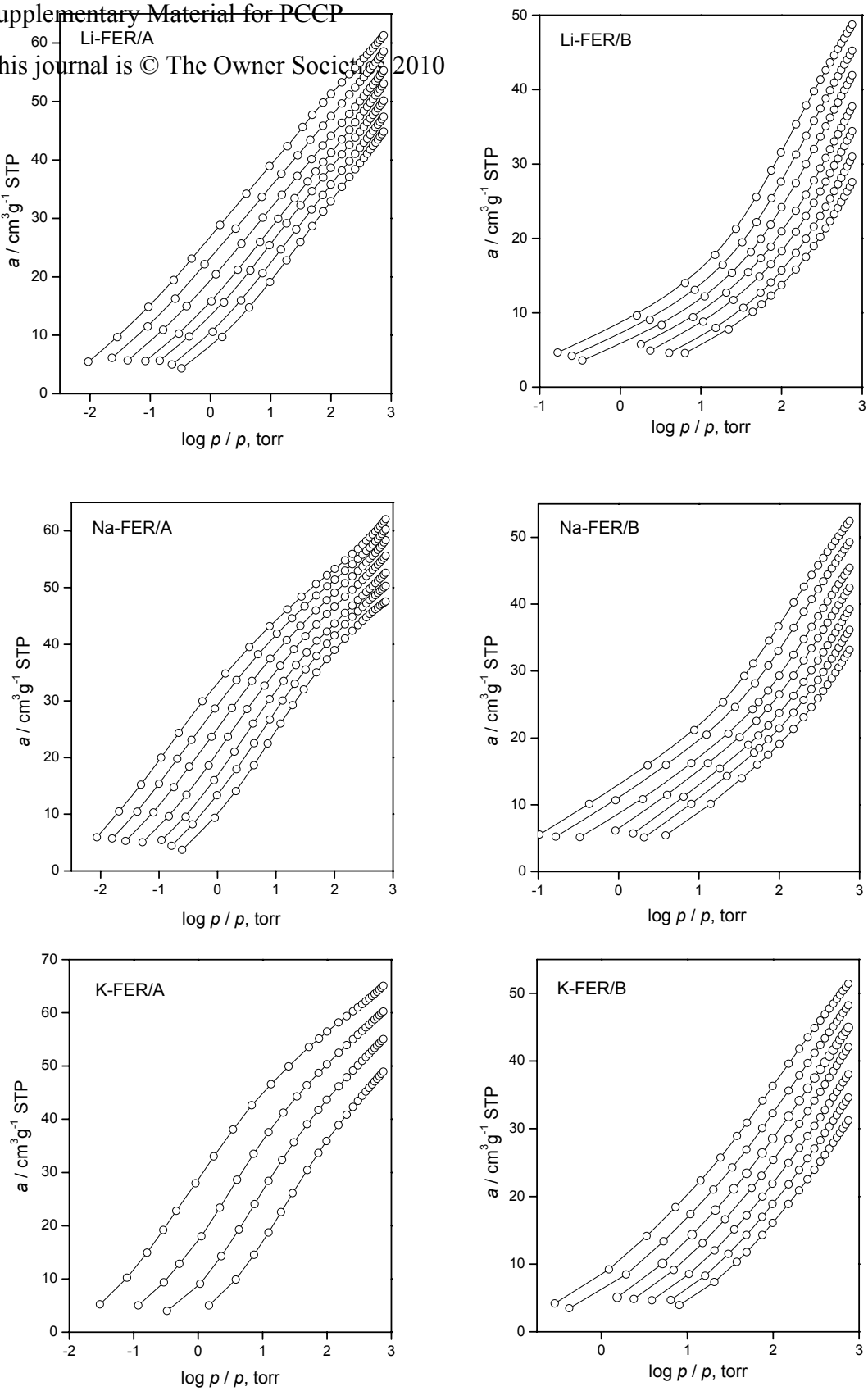

Fig. S5. Adsorption isotherms of carbon dioxide for Li-, Na- and K-FER at 273, 283, 293, 303, 313, 323 and 333 K (in the direction from left to right) in semilogarithmic coordinates. (CO_2 isotherms on the sample K-FER/A were measured at four temperatures only.)

Table S1. Calculated characteristics of CO_2 adsorption complexes on Na-FER.

Na^+ siting[a]	D(Na^+—O)[b]	CO_2/uc	$\Delta\omega_3$[c]	$\Delta E_{\text{int}}^{DFT}$ [d]	ΔZPVE[d]	$\Delta E^{DFT/CC}$ [d]	$-\Delta H_{ads}^{0}$ [d]
Single cation sites							
P6/T1	2.33	1	19	-23	1	-20	42
I2/T2	2.34	1	16	-29	2	-18	45
M7/T3	2.36	1	12	-29	2	-20	47
I2/T4	2.34	1	19	-28	2	-18	44
P8/T4	2.31	1		-26	1	-19	44
M5/T4	2.37	1	17	-28	2	-20	46
Dual cation sites							
P6/T1..P6T1 (7.6)	2.33 / 3.06	1		-25	1	-22	46
I2/T2..I2/T2 (7.3)	2.47 / 2.50	1	30	-40	2	-17	55
M7/T3..P8/T2 (7.4)	2.58 / 3.01	1	10	-32	2	-28	58
I2/T4..M5/T4 (6.2)	2.34 / 2.48	1		-35	2	-23	56
M5/T4..I2/T2 (6.8)	2.37 / 2.50	1	26	-37	2	-22	57
Geminal CO_2 complexes							
P6/T1	2.44, 2.51	2		-16	3	-20	33
I2/T2	2.37, 2.38	2	17, 12	-24	3	-18	39
M7/T3	2.40, 2.42	2	15, 5	-21	1	-20	40
I2/T4	2.37, 2.37	2		-25	2	-18	41
M5/T4	2.33, 3.95	2		-11	3	-29	37

[a] Distance between two M^+ cations forming a dual cation site are given in parentheses (in Å).
[b] Distance between M^+ and oxygen atoms of CO_2; distances for both CO_2 oxygen atoms to the closest M^+ are given in the case of dual cation sites.
[c] CO_2 asymmetric frequency shift with respect to gas phase CO_2 (2365 cm^{-1} at periodic PBE level), in cm^{-1}.

[d] In kJ/mol.