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Supplementary Information

A theoretical study on CO_2 at Li_4SiO_4 and Li_3NaSiO_4 surfaces

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In the following, the test results for the *k*-points grid size and Energy cutoff are reported. In all cases, the (0 0 1) surface for Li_4SO_4 is considered (see manuscript for details.)

Table S1. System energy, E_{sys}, for a (0 0 1) Li_4SO_4 surface, two-layers depth slab (2 × 2) supercell with 500 Ry energy cutoff as a function of the number of *k*-points.

k-points grid	E_{sys} / eV
2×5×5	-47899.25
3×2×2	-47899.18
3×3×3	-47899.23
3×4×4	-47899.27
3×5×5	-47899.29

Table S2. System energy, E_{sys}, for a (0 0 1) Li_4SO_4 surface, two-layers depth slab (2 × 2) supercell with 3×5×5 *k*-points grid, as a function of energy cutoff, E_{cutoff}.

E_{cutoff} / Ry	E_{sys} / eV
200	-47899.09
300	-47899.14
400	-47899.28
500	-47899.29

- **Properties of Li_4SiO_4 and Li_3NaSiO_4 bulk crystalline**

The experimental crystal structural parameters for this system are (*a,b,c*) = (11.546, 6.090, 16.645) Å, β = 99.5 [44,45] ; the values obtained in this work, Figure S2a, are slightly lower than experimental ones. Nevertheless, previous DFT studies[23,44] showed also minor deviations with experimental crystallographic data, these previous DFT studies showed slightly larger (*a,b,c*) parameters than experimental ones in comparison with values reported in this work which are slightly lower. This leads to deviations in the cell volume, e.g. the experimental cell volume (1153.9 $Å^3$)[45] compared with DFT values from Yan et al.[23] (1197.37 $Å^3$, 3.8 % larger) and the DFT values reported in this work (1105.8 $Å^3$, -4.2 % lower), which can be attributed to the use of different computational methods: PW91 for Yan et al.[23] and PBE in this work, and the consideration of Grimme's dispersive contribution in this work, which increases attractive forces, and thus decrease cell volume. Regarding the geometrical properties of SiO_4, Si-O bond distance (averaging 1.67 Å) is in fair agreement with previous DFT results (1.576 to 1.656 Å)[44] and with experimental data (1.58 to 1.69 Å)[45.] In the case of O-Si-O angle, the value obtained in this work (averaging 110.4 Å) also agrees with previous DFT studies (105.3 to 114.344)[44] and experimental values (103 to 106°).[45.] For the electronic distribution in the crystals, results in Figure S2b show the charge concentration around oxygen atoms and depletion on Si ones. The electronic properties are also analyzed through the calculated total Density of States (DOS) as reported in Figure S2c, which shows a band gap of 5.0 eV, which is lower than the previous DFT values, 5.24 eV [23] and 5.53 eV.[44] Although DFT estimations of band gap use to be lower than the real values, [23] the calculate value shows the non-conductive character of monoclinic Li_4SiO_4.

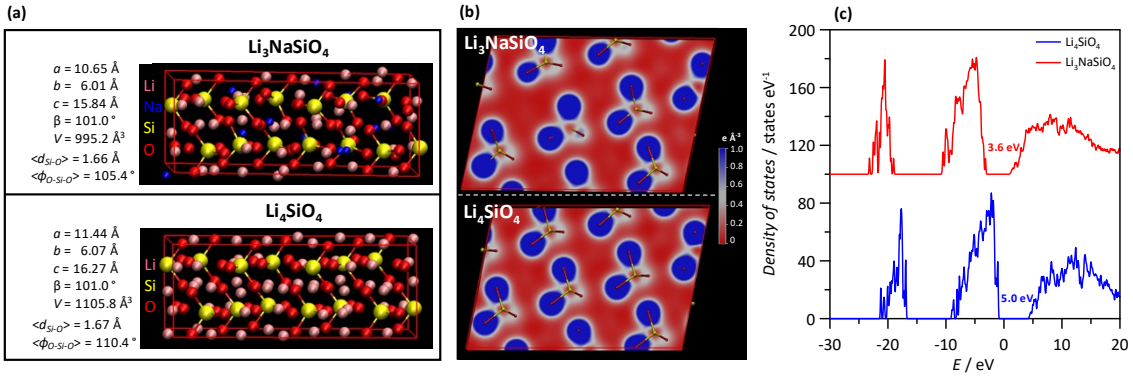
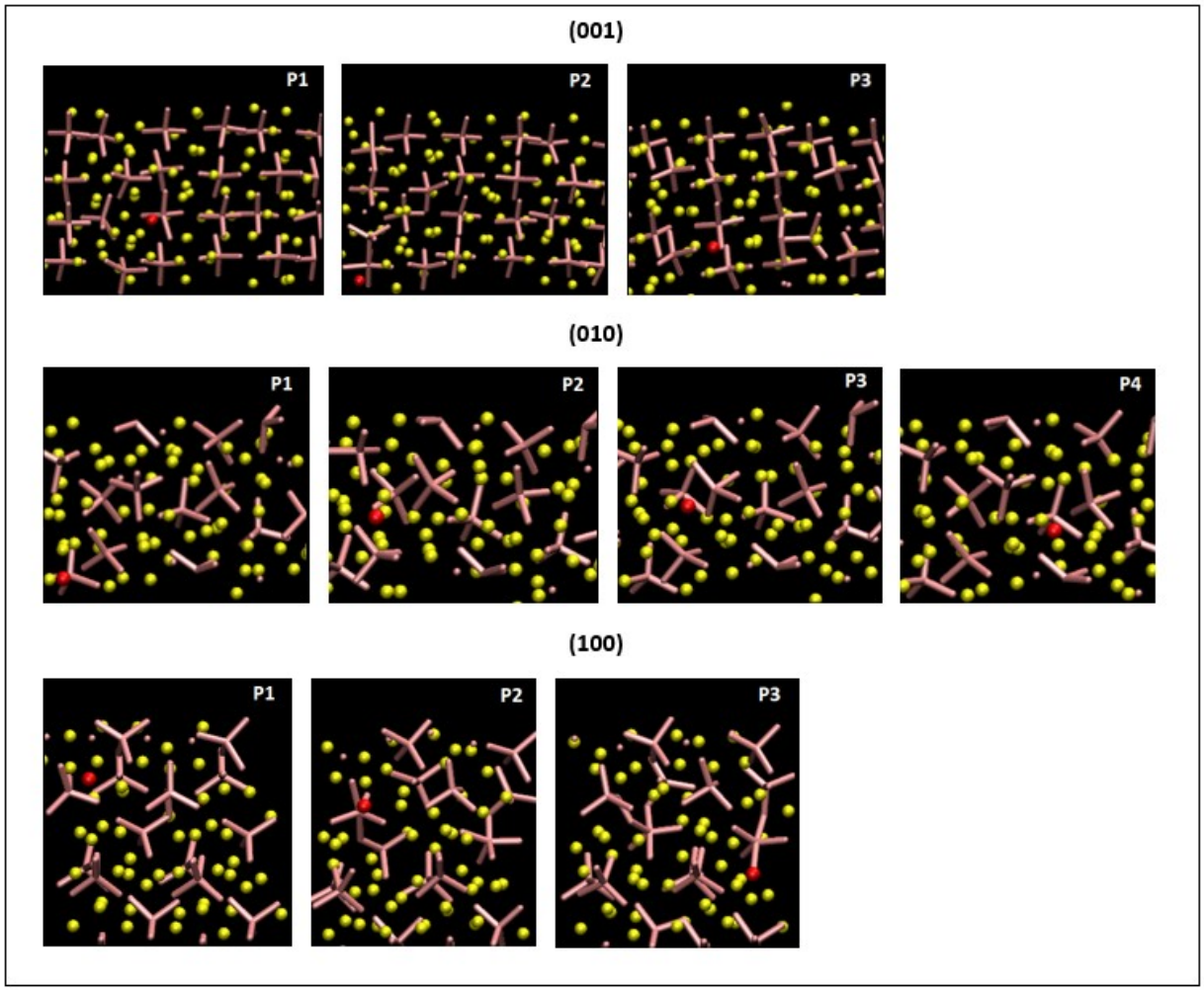


Figure S1 Results for Li_4SO_4 and Li_3NaSO_4 optimized monoclinic crystal superstructures. (a) optimized structures and cell parameters, $<d_{Si\text{-}O}>$ and $<\phi_{O\text{-}Si\text{-}O}>$ stand for the average bond and angle in SiO_4. (b) Electron density contour maps through SiO_4 (Li and Na atoms are omitted for the sake of visibility). (c) Density of States, with values inside the panel indicating direct band gaps.

(a) Li_4SiO_4 - CO_2



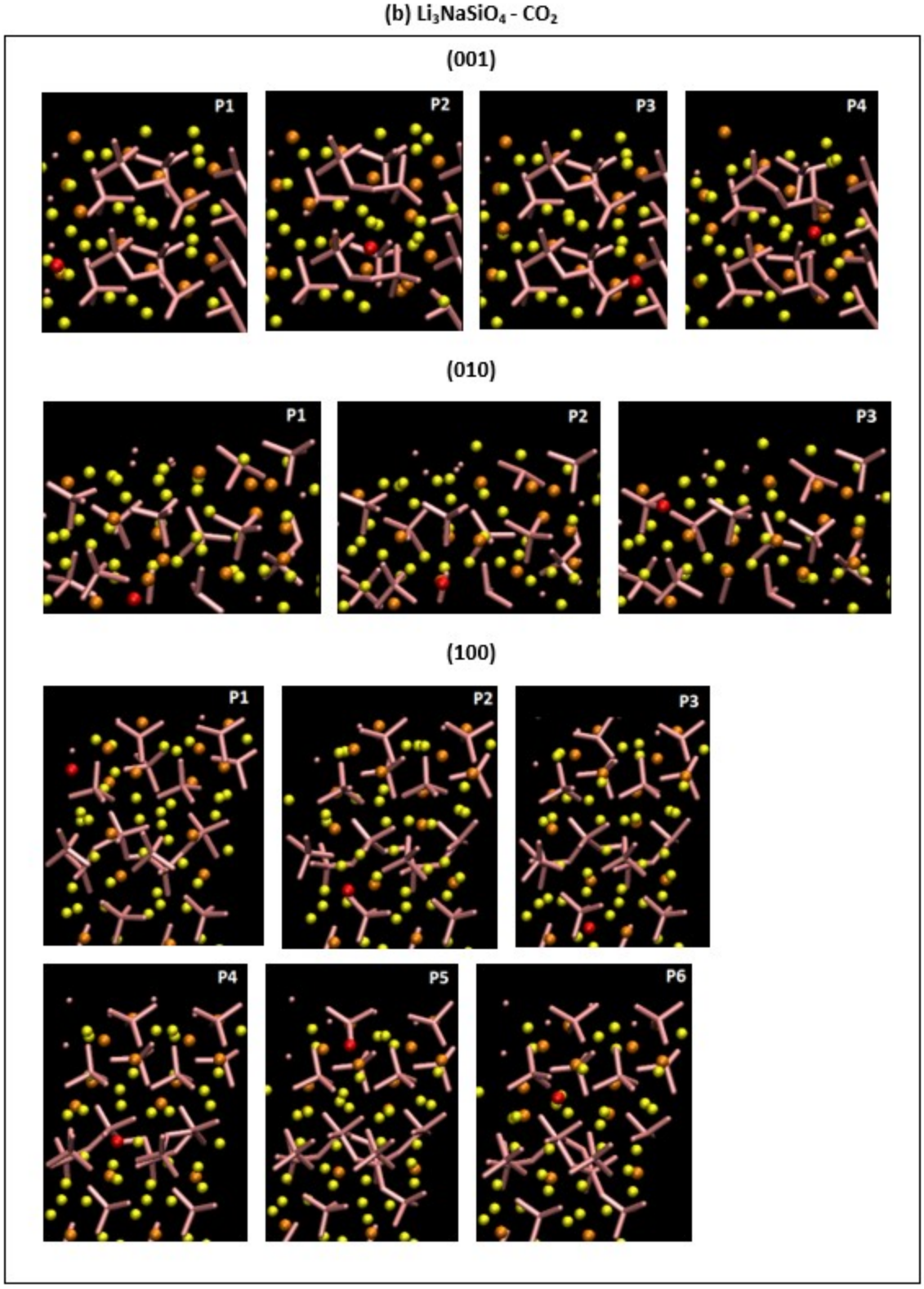


Figure S2. Definition of interaction sites on top of the studied (a) Li_4SiO_4 and (b) Li_3NaSiO_4 surfaces. (pink) SiO_4 anion, (yellow) Li cation, (orange) Na cation, (red) C atom in CO_2.