Supporting Information of

Dual Lewis Site Creation For Activation of Methanol on Fe_3O_4(111) Thin Films

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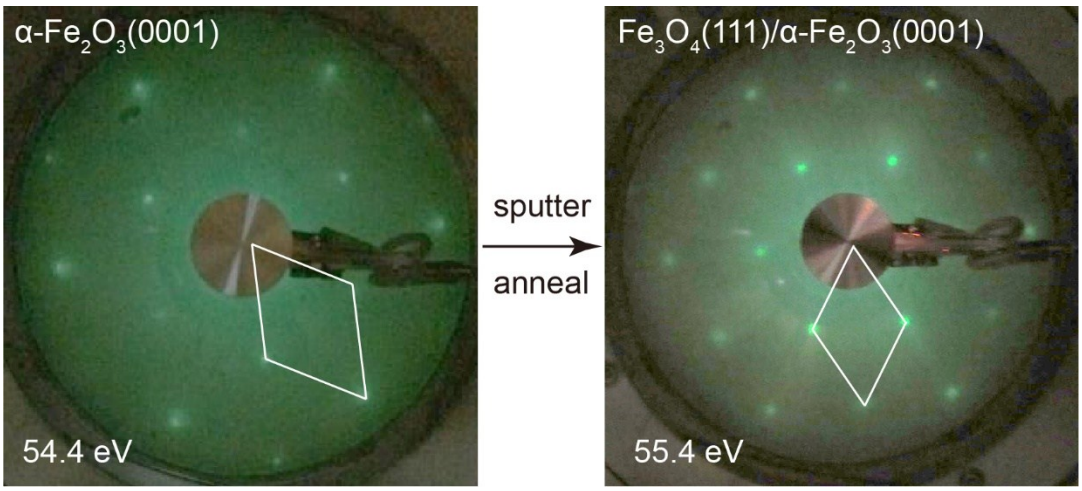

Figure S1. Preparation of Fe_3O_4(111) by applying Ar^+ sputter-annealing cycles on an α-Fe_2O_3(0001) single crystal in ultrahigh vacuum. LEED patterns clearly show a structural change. The beam energy is indicated in each panel. Left panel shows a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern of α-Fe_2O_3(0001); right panel shows a (2 × 2) LEED pattern of Fe_3O_4(111)

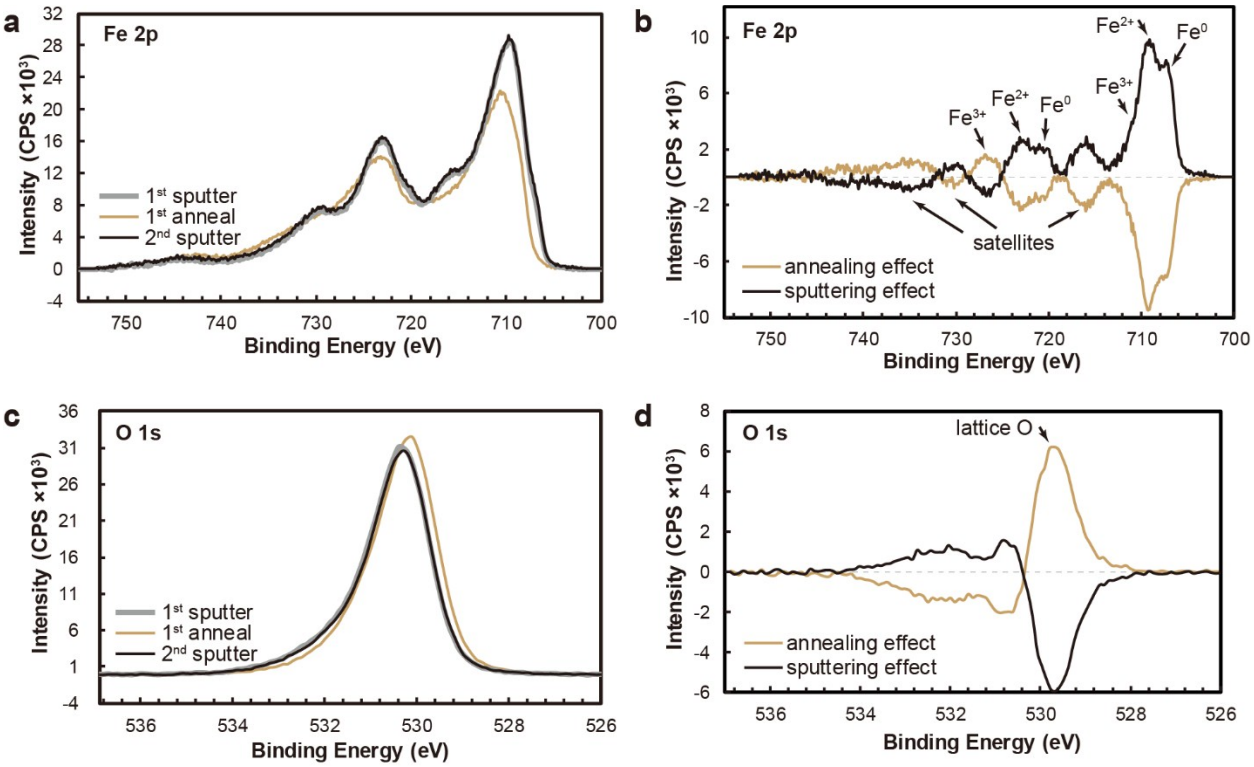

Figure S2. Reduction of $Fe_3O_4(111)/\alpha\text{-}Fe_2O_3(0001)$ during sputtering (15 min) and self-re-oxidation during annealing (20 min) cycles in UHV. Change of oxygen and iron in top layers during consecutive sputter-annealing cycles is shown by calibrated and normalized XPS data of (a) Fe 2p and (c) O 1s of $Fe_3O_4(111)$ films. A more obvious change of (b) Fe 2p and (d) O 1s was obtained by subtracting previous procedure in the sputter-annealing cycles.

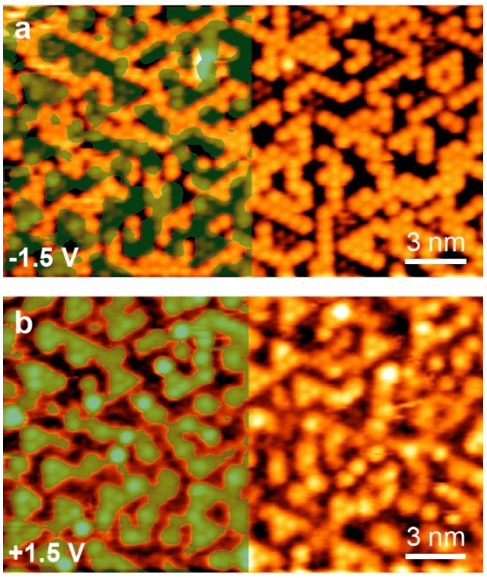

Figure S3. Electronic effect of oxygen adatoms and uncovered Fe_{tet1} atoms evidenced by STM contrast change at (a) -1.5 V and (b) +1.5 V gap voltages. The green mask shows the same area in (a) and (b). Scanning current: 0.025 nA.

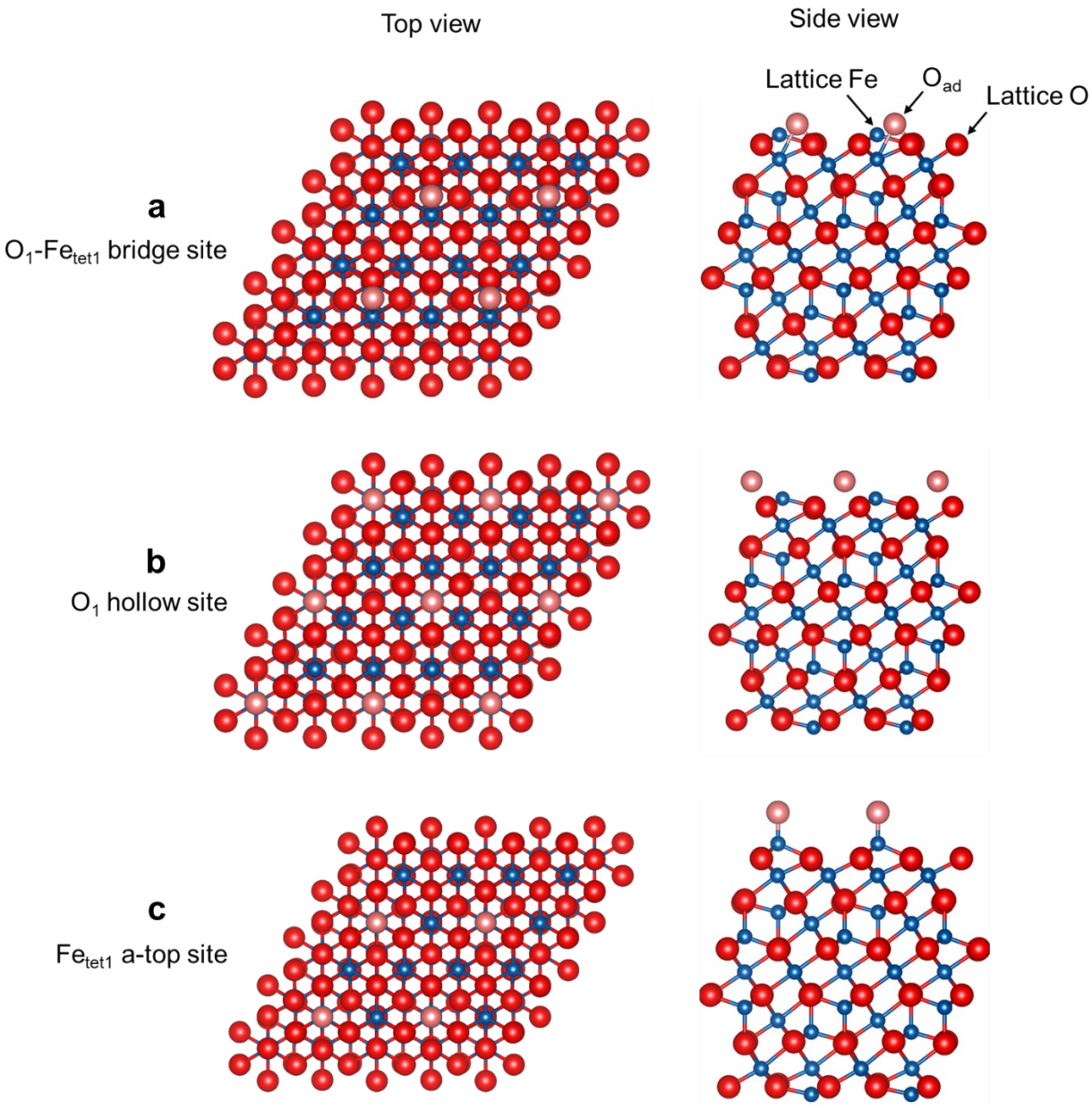

Figure S4. DFT calculated O_{ad} adsorption on (a) O_1-Fe_{tet1} bridge site, (b) O_1 hollow site, and (c) Fe_{tet1} a-top site, on Fe_{tet1} terminated $Fe_3O_4(111)$. Their relative energies per O are calculated as 1.48 eV, 3.06 eV, and 0.00 eV, respectively.

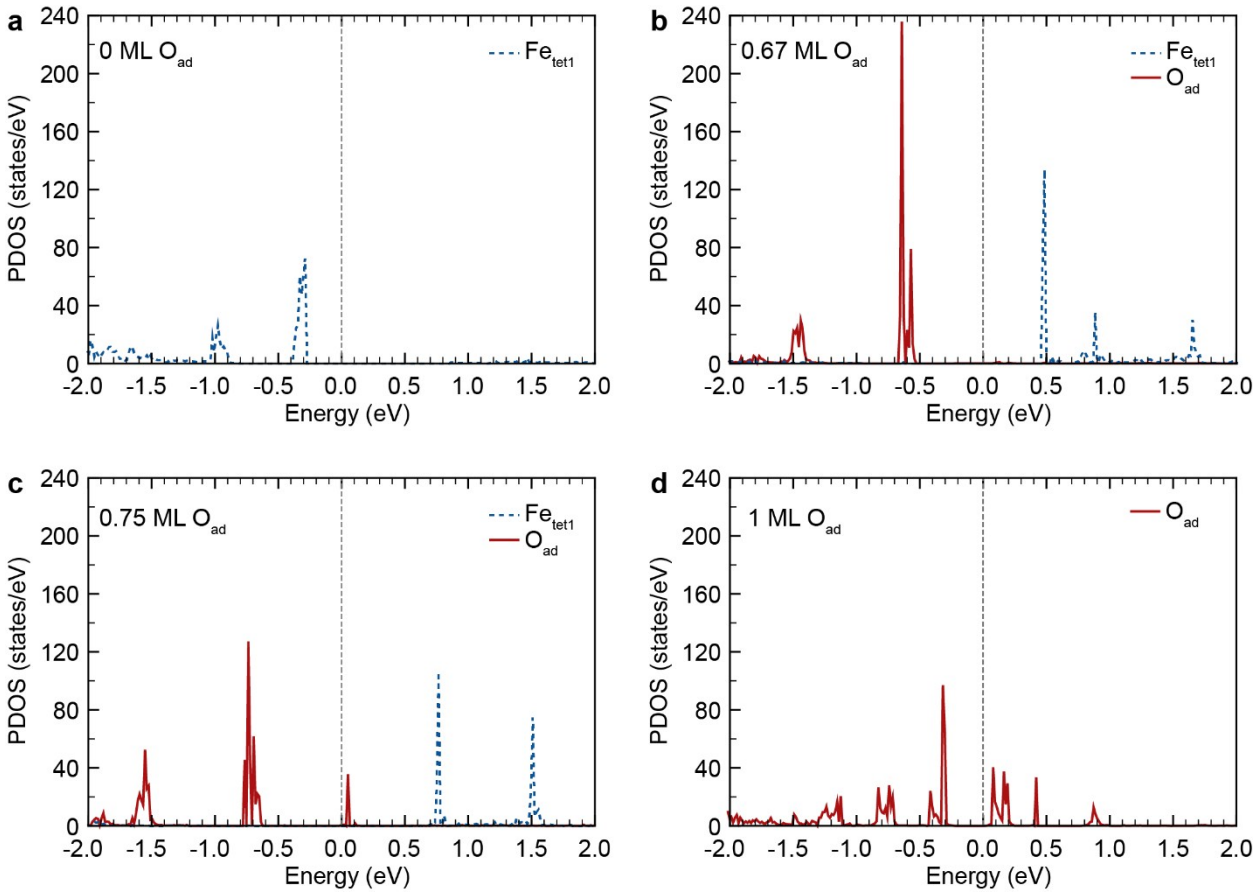

Figure S5. Site-projected density of states (PDOS) of oxygen adatoms (O_{ad}) and uncovered Fe_{tet1} atoms on the top layer of DFT model when O_{ad} coverage is (a) 0 ML, (b) 0.67 ML), (c) 0.75 ML, and (d) 1 ML. Only results in (c) were calculated using a 2×2 supercell, the rest in a $\sqrt{3} \times \sqrt{3}$ unit cell.

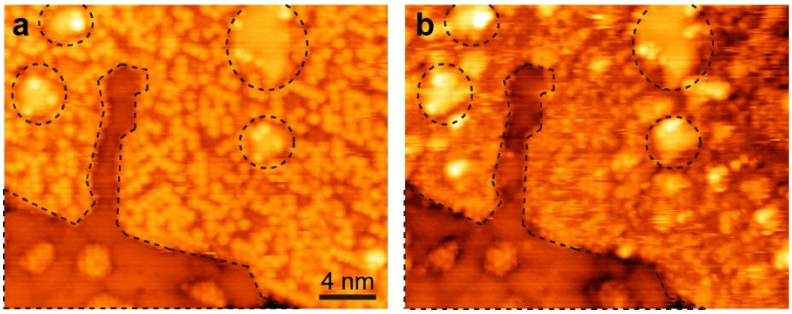

Figure S6. Inertness of dense packed area towards methoxy adsorption. (a) and (b) are STM images of the same area before and after methanol exposure. Flat and smooth areas are highlighted in black dash boxes.

DFT data

The relaxed structure with 0.67ML of O adatoms in the VASP POSCAR format is shown below.

Fe3O4
1.00000000000000
10.3368467145000000 0.0000000000000000 0.0000000000000000
5.1684233572500000 8.9519718497799996 0.0000000000000000
0.0000000000000000 0.0000000000000000 29.2370185852000013
Fe O
51 76
Selective dynamics
Direct
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