Supplementary Information

Iron oxides with reverse spinel structure : impact of active sites on molecules adsorption

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The surface energy of all the structures is considering as follows formula:[1]

$$\gamma = \frac{1}{2A}[E^{slab} - n_{Fe}\mu_{Fe}^{slab} + n_O\mu_O^{slab}] \tag{S1}$$

where A is the surface area, slab represents the (111) surface or (001) surface, E^{slab} is the total energy of the relative relaxed surface structure, n is the number of atoms in the supercell, and μ is the chemical potential. The factor of 1/2 represents two identical surfaces in the slab models. The chemical potential μ_{Fe}^{slab} of Fe_3O_4 and γ-Fe_2O_3 are written as a sum of the chemical potential of each species within the crystal:[2]

$$\mu_{Fe_3O_4}^{slab} = 24\mu_{Fe}^{slab} + 32\mu_O^{slab} \tag{S2}$$

$$\mu_{\gamma-Fe_2O_3}^{slab} = 21.34\mu_{Fe}^{slab} + 32\mu_O^{slab} \tag{S3}$$

At 0 K and constant pressure, the chemical potential of the surface is in equilibrium with the chemical potential of bulk to give $\mu_{Fe_3O_4}^{slab} = \mu_{Fe_3O_4}^{bulk}$ and $\mu_{\gamma-Fe_2O_3}^{slab} = \mu_{\gamma-Fe_2O_3}^{bulk}$. Thus, the surface energy can be expressed as:

$$\gamma_{Fe_3O_4} = \frac{1}{2A}[E_{Fe_3O_4}^{slab} - n_{bulk}E_{Fe_3O_4}^{bulk} + n_O\mu_O^{slab}] \tag{S4}$$

$$\gamma_{\gamma-Fe_2O_3} = \frac{1}{2A}[E_{\gamma-Fe_2O_3}^{slab} - n_{bulk}E_{Fe_3O_4}^{bulk} + n_O\mu_O^{slab}] \tag{S5}$$

where n_O represent the number of excessive oxygen beyond Fe_3O_4 and γ-Fe_2O_3 units in the slab.

The chemical potential of oxygen in the slab must be less than the chemical potential of oxygen in its bulk phases or the composite slab will be unstable and form the more favorable bulk phase energetically. Therefore, the thermodynamic range of the O chemical potential is:[3]

$$\mu_O^{mol} + \frac{1}{2}\Delta H_f^0 \leq \mu_O^{slab} \leq \mu_O^{mol} \tag{S6}$$

$$\frac{1}{2}\Delta H_f^0 \le \mu_O \le 0 \tag{S7}$$

Here, ΔH_f^0 is the heat of formation contained in the bulk energy, which is composed of the energy of the metal phase Fe atom (E_{Fe}^{met}) and molecular O_2($E_{O_2}^{mol}$):

$$E_{Fe_3O_4}^{bulk} = 24E_{Fe}^{met} + 32\frac{1}{2}E_{O_2}^{mol} + \Delta H_f^0(Fe_3O_4) \tag{S8}$$

$$E_{\gamma-Fe_2O_3}^{bulk} = 24E_{Fe}^{met} + 32\frac{1}{2}E_{O_2}^{mol} + \Delta H_f^0(\gamma - Fe_2O_3) \tag{S9}$$

Δ_{tet}=0.7 eV

Δ_{oct}=1.6 eV

High spin   Low spin
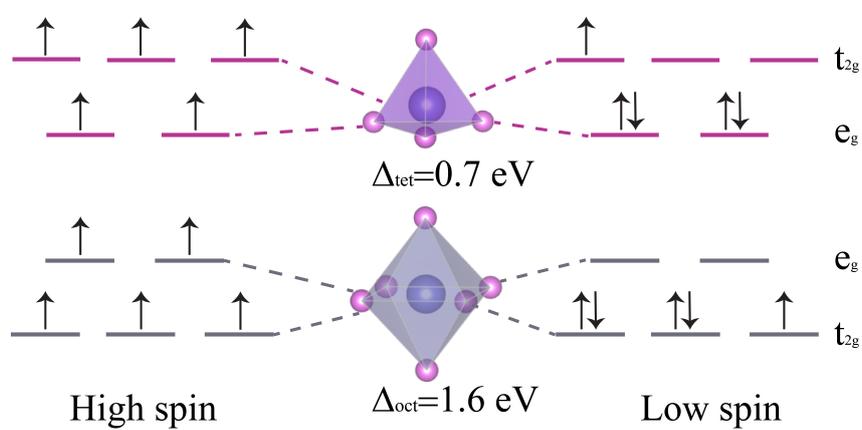
Fig. S1 Fe^{3+} electron configurations in tetrahedral and octahedral sites based on crystal-field theory.
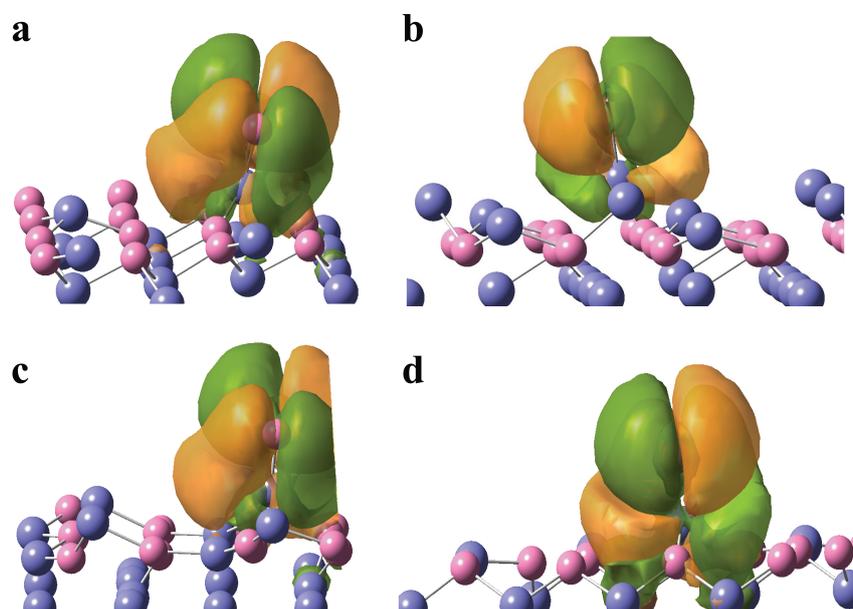
Fig. S2 NBOs for O-O π^* on (111) surface of (a)Fe_3O_4-tet (b)Fe_3O_4-oct (c) γ-Fe_2O_3-tet and (d) γ-Fe_2O_3-oct. For the sake of clarity, the symmetric parts of the bottom optimized slabs were not shown.

compound	NBO	occupancy	center(bond % contribution)	hybridization (function,%)
Fe_3O_4-tet	Fe-O_4 σ	1.880	Fe (26)	s 19, p 16, d 65
			O_4 (74)	s 5, p 95
	Fe-O_4 σ^*	0.239	Fe (74)	s 19, p 16, d 65
			O_4 (26)	s 5, p 95
	Fe-O_5 σ	1.886	Fe (27)	s 10, p 12, d 78
			O_5 (73)	s 8, p 92
	Fe-O_5 σ^*	0.358	Fe (74)	s 10, p 12, d 78
			O_5 (26)	s 8, p 92
Fe_3O_4-oct	Fe-O_4 σ	1.920	Fe (25)	s 23, p 16, d 61
			O_4 (75)	s 9, p 91
	Fe-O_4 σ^*	0.236	Fe (73)	s 23, p 16, d 61
			O_4 (27)	s 9, p 91
	Fe-O_5 σ	1.920	Fe (25)	s 23, p 16, d 61
			O_5 (75)	s 9, p 91
	Fe-O_5 σ^*	0.236	Fe (75)	s 23, p 16, d 61
			O_5 (25)	s 9, p 91
γ-Fe_2O_3-tet	Fe-O_4 σ	1.924	Fe (30)	s 10, p 9, d 81
			O_4 (70)	s 6, p 94
	Fe-O_4 σ^*	0.243	Fe (75)	s 10, p 9, d 81
			O_4 (25)	s 6, p 94
	Fe-O_5 σ	1.923	Fe (25)	s 10, p 9, d 81
			O_5 (75)	s 6, p 94
	Fe-O_5 σ^*	0.240	Fe (75)	s 10, p 9, d 81
			O_5 (25)	s 6, p 94
γ-Fe_2O_3-oct	Fe-O_4 σ	1.910	Fe (26)	s 21, p 15, d 64
			O_4 (74)	s 8, p 92
	Fe-O_4 σ^*	0.261	Fe (74)	s 21, p 15, d 64
			O_4 (26)	s 8, p 92
	Fe-O_5 σ	1.911	Fe (26)	s 21, p 15, d 64
			O_5 (74)	s 8, p 92
	Fe-O_5 σ^*	0.253	Fe (74)	s 21, p 15, d 64
			O_5 (26)	s 8, p 92

Table. S1   NBOs for O_2 adsorption on (111) surface of catalysts

References

[1] K. Zhao, L. Zhang, J. Wang, Q. Li, W. He and J. J. Yin, *Journal of the American Chemical Society*, 2013, **135**, 15750–15753.

[2] Q. Li and X. Hu, *Physical Review B*, 2006, **74**, 035414.

[3] G. Chen, Z. Hou and X. Gong, *Computational Materials Science*, 2008, **44**, 46–52.