Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

I.

Table 1 Comparison of O_2 and Ni properties with experiments in isolated and adsorbed states.

	Ni	EXP.	O_2	EXP.
Lattice parameter	3.52 Å	3.52 Å [1]		
Surface relaxation (111)	0.010Å	0.007±0.003Å [2]		
Spin moment /atom (bulk)	0.60 μ_B	0.60-0.62 μ_B [1,3]		
Bond-length			1.23 Å	1.21[4]
Spin-moment (gas-phase)			1.96 μ_B	
		O atom on Ni(111)		
O-Ni bond length		1.86-1.89Å	1.85 ± 0.05 Å [5]	
O atom vertical distance from Ni		1.20 Å	1.21 ± 0.09Å [5]	

References
[1] F Starrost, H Kim, S C Watson, E Kaxiras and E A Carter, *Phys. Rev. B* , 2001, 64, 235105.
[2] T Okazawa, F Takeuchi and Y. Kido *Phys. Rev. B,* 2005, 72, 075408.
[3] M Donath *Sur. Sci. Rep.* 1994, 20, 251.
[4] CRC Handbook of Chemistry and Physics, 86th ed., CRC Press, Boca Raton, FL, 2005.
[5] M Pedio, L Becker, B Hillert, S D Addato and J Haase Phys. Rev. B , 1990, 41, 7462.

II.

Further discussions for Equation (1) in the manuscript:

The $F_I(r - r_I)$ is a function with a norm (or value) 1 inside the sphere Ω_I and smoothly goes to zero at the boundary so that when it is multiplied to the magnetization density, $m(r)$ in equation (1), we get the $M_I = \int_{\Omega_I} m(r) d^3r$ inside the Ω_I and 0 at the boundary as expected.

The appropriate form of F_I is $\frac{\sin(x)}{x}$ because the limit of this function as x → 0 $is\ 1$ and 0 at x= π and from 0 to π, it decreases smoothly (monotonically). The $x = \pi(|r - r_I|)/R_I$, where R_I is the radius of the sphere, Ω_I, can describe such condition for F_I. If $r\ tends\ to\ r_I$ (inside sphere), x → 0, $F_I(r - r_I) = 1$ and $M_I = \int_{\Omega_I} m(r) d^3r$. If $|r - r_I| = R_I$ (boundary), x= π , $F_I(r - r_I) = 0$, so $M_I = 0$.