Electronic supplementary information

Potassium adsorption behavior on hcp cobalt as model systems for the Fischer-Tropsch synthesis: A density functional theory study

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1. Calculation methods of zero-point energy (E_{ZPE}) and entropy for K adsorption

The zero-point energy (E_{ZPE}) of K adsorbed on the cobalt surface and entropy [2-4] were calculated by the equations below:

$$E_{ZPE} = \sum_{i=1}^{3N} \frac{hv_i}{2},$$

$$S_{K/Co} = \sum_{i=1}^{3N} \left[-R\ln(1-e^{-hv_i/\mathrm{k_B T}}) + \frac{N_A hv_i}{T} \frac{e^{-hv_i/k_B T}}{\left(1-e^{-hv_i/k_B T}\right)} \right],$$

$$S_{gas} = A*\ln(\mathrm{t}) + \mathrm{B}*\mathrm{t} + \mathrm{C}*\mathrm{t}^2/2 + D*t^3/3 - E/(2*\mathrm{t}^2) + \mathrm{G},$$

,where R is the universal gas constant, k_B is Boltzmann's constant, N_A is Avogadro's number, h is Planck's constant, v_i is the frequency of the normal mode, N is the number of atoms, and T is temperature (K), t is T/1000. The parameters of A, B, C, D, E, and G are 20.66122, 0.391869, -0.417344, 0.145582, 0.003764, 185.2650, respectively.

2. Fig. S1

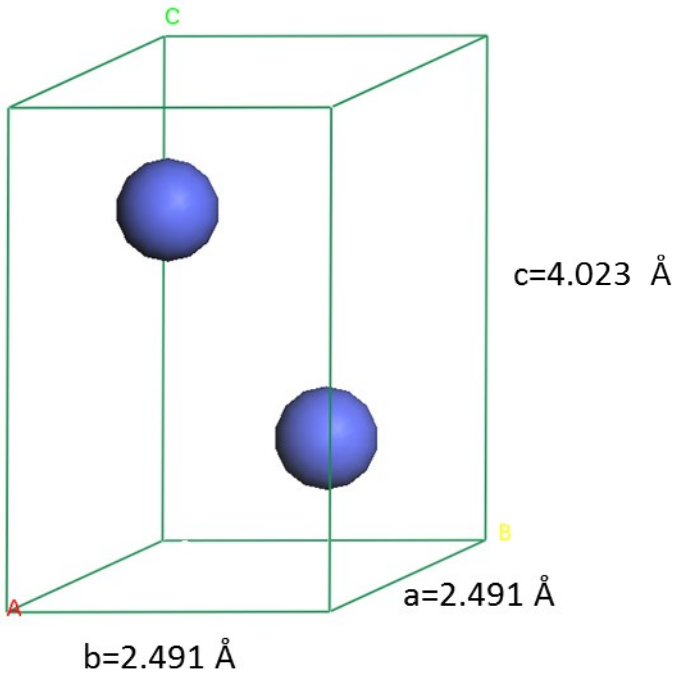

Fig. S1 The calculated equilibrium lattice of the bulk hcp Co

3. Fig.S2

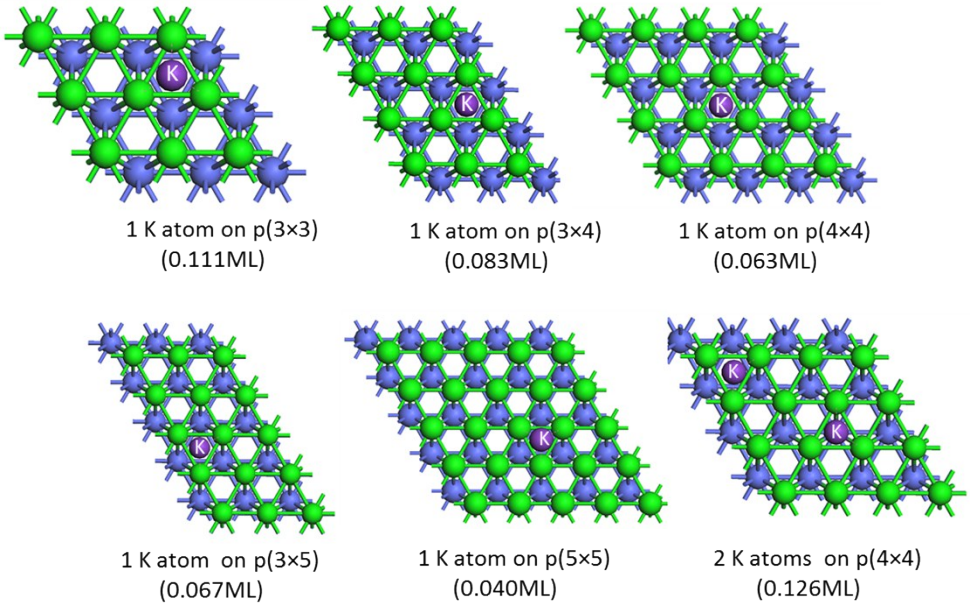

Fig. S2 The adsorption configurations of K at different coverages on (0001) facet. The Co atoms in the first layer of the slab are colored green, and in other layers are colored blue.

4. Fig. S3

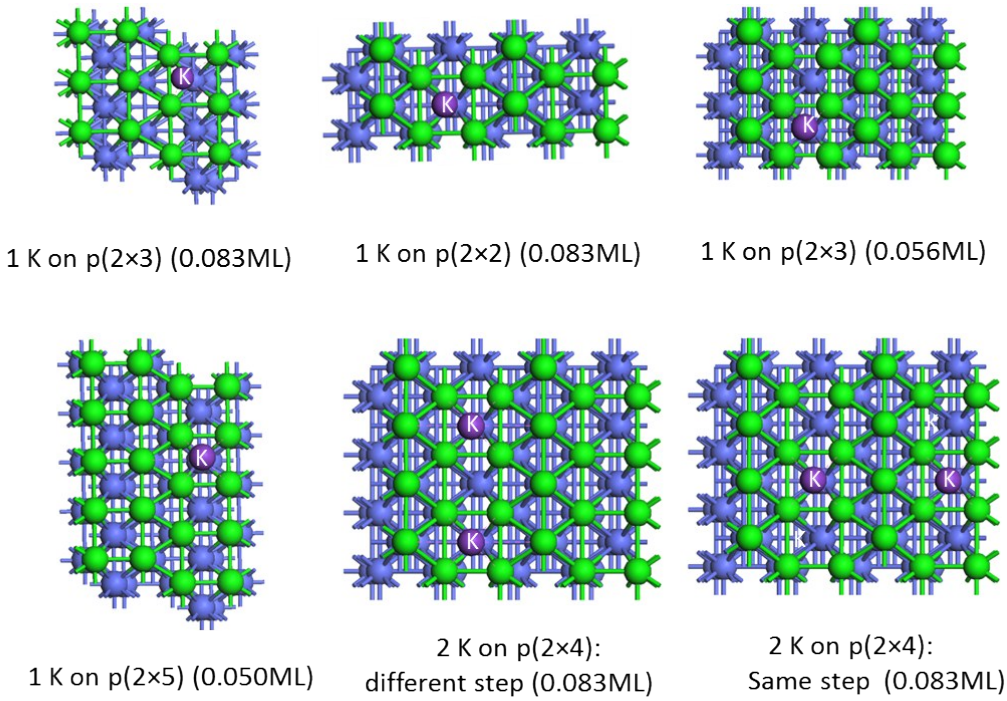

Fig. S3 The adsorption configurations of K at different coverages on (a) Co(10-11) and (b) Co (10-12). The Co atoms in the first layer of the slab are colored green, and in other layers are colored blue.

5. Table S1

Table S1. Wulff construction results calculated based on the facets exposed in Ref. 1.

Facet	Surface unit cell	Surface energy (eV/Å^2)		Surface area proportion (%)	
		This work	Ref.[1]	This work [a]	Ref.[1]
{0001}	p(1×1)	134	131	17	18
{10-10}	p(1×1)	143	140	27	28
{10-11}	p(1×2)	152	149	35	35
{10-12}	p(1×2)	159	156	13	12
{11-20}	p(1×1)	157	155	6	6
{11-21}	p(1×1)	166	163	1.6	1

Note:, [a] calculated based on the surface energies in this work and facets exposed in Ref. 1.

6. Reference

1 J.-X. Liu, H.-Y. Su, D.-P. Sun, B.-Y. Zhang and W.-X. Li, *J. Am. Chem. Soc.*, 2013, **135**, 16284-16287.

2 G. Wen, Q. Wang, R. Zhang, D. Li and B. Wang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27272-27283.

3 R.D. Cortright, J.A. Dumesic, *Adv. Catal.*, 2001, **46**, 161-264.

4 Y.-A. Zhu, D. Chen, X.-G. Zhou, W.-K. Yuan, *Catal. Today*, 2009, **148**, 4260-267.

5 M.W. Jr. Chase, *NIST-JANAF Themochemical Tables*, *Fourth Edition*, 1998, 1-1951.