Chain growth mechanism on bimetallic surfaces for higher alcohol synthesis from syngas

Wang, Jingbo; Zhang, Xiurong; Sun, Qiang; Chan, Siew Hwa; Su, Haibin

2014

Wang, J., Zhang, X., Sun, Q., Chan, S., & Su, H. (2015). Chain growth mechanism on bimetallic surfaces for higher alcohol synthesis from syngas. *Catalysis communications*, 61(10), 57–61.

<https://hdl.handle.net/10356/107128>

<https://doi.org/10.1016/j.catcom.2014.12.010>

© 2014 Elsevier B.V. This is the author created version of a work that has been peer reviewed and accepted for publication by *Catalysis Communications*, Elsevier B.V. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1016/j.catcom.2014.12.010>].

Downloaded on 26 Apr 2023 20:54:36 SGT

Chain Growth Mechanism on Bimetallic Surfaces for Higher Alcohol Synthesis from Syngas

Jingbo Wang,^{1,2} Xiurong Zhang,³ Qiang Sun,^{1,4*} Siewhwa Chan,^{1,5*} Haibin Su^{1,2*}

¹. Singapore-Peking University Research Centre, Campus for Research Excellence & Technological Enterprise (CREATE), Singapore 138602, Singapore

². School of Materials Science and Engineering, Nanyang Technological University, Singapore, 639798, Singapore

³. School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

⁴. College of Engineering, Peking University, Beijing 100871, China

⁵. School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, 639798, Singapore

ABSTRACT

Density function theory calculations are performed to investigate the chain growth mechanism on bimetallic surfaces during the syngas conversion. The weighted *d*-band center correlates well with the adsorption energy of two reactants on bimetallic surface. The boundary between Cu and Co domains facilitates the association reaction of chain growth. Particularly, the reduction of barrier for CO insertion step accelerates the formation of acyl intermediate and thus provides paths to higher alcohol synthesis. The present work demonstrates the synergistic effect in the bimetallic surface from the microscopic view.

Keywords: Bimetallic surface; Chain growth; Higher alcohol synthesis; Catalytic design

1. Introduction

The catalytic conversion of syngas (mixture of CO and H₂) to higher alcohols is important with the increasing energy demand. Among the catalysts for higher alcohol synthesis (HAS) [1-8], Cu-modified Fischer-Tropsch (FT) catalyst, Cu-Fe, Cu-Co and Cu-Ni etc., is considered as one of the most promising catalyst due to its high selectivity and low cost [2,5]. HAS needs the collaborative function between Cu and FT elements, as suggested by the dual-site model in Cu-Co experiments where Co ensemble generates hydrocarbon precursors and Cu ensemble chemisorbs CO species [6]. In the vicinity of two phases facilitates the reaction between alkyl groups and carbonyls, finally leading to higher alcohols [1,4,6]. Hence the identification of active site, the boundary between Co and Cu phases, is important to HAS from theoretical aspect.

Generally the alcohol formation mechanism involves the formations of long chain alkyl and acyl intermediate [1,5]. Intensive efforts have been made to the formation of long chain alkyl in FT catalysts [9-13]. There are mainly two mechanisms to account for the chain growth. The first is the carbide mechanism in which chain growth is achieved by polymerization of C₁ monomer (C, CH, CH₂ and CH₃)

*Corresponding author:

Tel.: +86 10 62752043. sunqiang@pku.edu.cn (Qiang Sun).

Tel.: +65 67904862. MSHCHAN@ntu.edu.sg (Siewhwa Chan).

Tel.: +65 67904346. HBSu@ntu.edu.sg (Haibin Su).

on the surface [9]. Theoretical studies of the carbide mechanism suggest that Co(0001) surface catalyzes effectively the $RC + CH$ ($R = H$ or alkyl) coupling whereas $RC + C$ might be a major channel for chain growth on Ru surface [9,10]. The second, as an alternative to carbide mechanism, CO insertion mechanism is proposed in which the chain growth occurs by inserting CO into alkyl intermediates as supported by the recent transient kinetic experiment on Co catalyst [12,13]. A propagation cycle starting with CO insertion into CH_2 and subsequent intermediates is proposed on Co catalyst [11]. The coupling of CO with alkyl is connected with HAS, the formed acyl species is hereafter hydrogenated to higher alcohols [5,14-16]. Recent study illustrates the fundamental difficulty in using pure transition metal to produce higher alcohol [15]. Nanoscale Cu_6Co_7 cluster boosts the selectivity towards higher alcohol. The microkinetic study shows reactions involving CH_3 and CH_3CO control the selectivity [16]. Accelerating the rate of CO insertion reactions on bimetallic catalyst is a possible solution to solve the difficulty encountered by HAS.

In the present work, we aim to study the chain growth mechanism on several bimetallic surfaces using density function theory (DFT) calculation. We select $CH_3 + CO$ as the target reaction owing to its highest barrier among CO insertion reactions on Co(0001) [11]. Our study suggest that the boundary between Cu and Co phases exhibits a higher activity for chain growth and hence gains insight into the active site to HAS. The understanding of bimetallic interaction on catalytic activity is useful for the design of new catalytic materials.

2. Computational methods

Fig. 1 depicts several metal surfaces in which the adsorption can be tuned by the composition and microstructure [17,18]. Co(0001) and Co(111) are described by 3×3 supercell with 4 layers of atoms. Cu(111) is modeled with 3 layers of atoms. In Cu(111)/Co surface, the Co sublayer is initially placed at the idealized position corresponding to the substrate. The segregated metal prefers to stay at the second layer as explained by the theoretical study [19]. The optimized lattice constants for Cu (fcc), Co (fcc) and Co (hcp) are 3.635 Å, 3.522 Å and 2.490 Å [11]. The microstructures of bimetallic catalyst are constructed in the bottom panel of Fig. 1 with 3×6 supercell, which are supported by the quantitative structure of Co deposited on Cu(111) as reported by Prieto et al. based on the fitting of the results from STM and LEED [20]. The quantitative structure contains the Co bilayer islands with fcc stacking and Cu capped domains. Co deposited phase is stable while progressively annealing up to 900 K [21].

DFT calculations are performed with the Vienna *Ab initio* Simulation Package (VASP) [22]. PBE functional [23] is used to treat the exchange-correlation effects with cutoff energy 400 eV. Core electrons are described with PAW approach [24]. A vacuum spacing of 10 Å is used to avoid interaction between slabs. For the structures in the top panel of Fig. 1, a $5 \times 5 \times 1$ Monkhorst-Pack grid [25] is used to sample the Brillouin zone with a generalized Gaussian smearing technique [26]. For the structures in the bottom panel of Fig. 1, a $6 \times 3 \times 1$ k -point mesh is used. The spin polarization is included when the surface contains Co or Ni. The top two layers are relaxed whereas the remaining layers are fixed to the corresponding bulk lattice parameter. The reaction barriers are computed using the climbing image nudged elastic band (CI-NEB) method [27]. The vibrational frequencies are calculated with finite differences method, all the transition states are confirmed by the existence of a single imaginary vibrational mode.

Fig. 1. The structures of metal surfaces. Colors: Cu (dark pink), Co (blue), Ni (cyan).

The d -band center of individual atom ϵ_d^M ($M = \text{Co}, \text{Ni}, \text{Cu}$) is calculated by the first moment of the projected d -band density of states relative to Fermi level [28,29]. Considering different interactions of Co, Ni and Cu with adsorbate, weighted d -band center [30] is calculated with following equation:

$$\epsilon_{\text{wd}} = \frac{\sum_M V_M^2 \cdot \epsilon_d^M \cdot N^M}{\sum_M V_M^2 \cdot N^M}$$

where V_M^2 is coupling matrix element for surface atom ($V_{\text{Cu}}^2=1$, $V_{\text{Ni}}^2=1.16$, $V_{\text{Co}}^2=1.34$) [31]. N^M is the number of bonds between metal atom and adsorbate.

3. Results and discussion

3.1. Chemisorption of Initial State (IS) and Transition State (TS)

We begin by studying the association reaction of CH_3 with CO to CH_3CO on metal surfaces. The corresponding reaction paths are shown in Fig. 2. At IS, CO and CH_3 prefer the hollow site and bind to surface through C atom. At TS, CH_3 binds at an off-top site interacting mainly with single metal atom on all surfaces; CO tilts at the bridge or hollow site sharing one metal atom with CH_3 . The tilt of CO at TS introduces the interaction of O atom with surface which is absence at IS. Table 1 summarizes the reaction information, including adsorption energy E_b of IS, activation barrier E_a and geometric parameters at IS and TS. In this table C-C represents the distance between CO and CH_3 . M- CH_3 gives the average distance between C and the metal atoms interacting with it. The M-CO (M-O) distance is calculated as the average between C (O) atom in CO and metal atoms interacting with it. The adsorption of reactant is most favorable on Cu/Ni-III with a binding energy of -3.68 eV. The E_b on Co(111) is -3.55 eV slightly lower than that on Cu/Ni-III. In contrast to these surfaces, the adsorption on Cu(111) is significantly weaker with a binding energy of -2.28 eV. The IS and TS parameters are almost identical on Co(0001) and Co(111), hence the barrier difference is small from one to the other. Intermediate strength of adsorption occurs on the boundary of Cu and Co, as shown on Cu/Co-II and Cu/Co-III, with binding energy of -3.4

eV. The metal-C distance appear to correlate with the adsorption energy, the same trend is shown by the adsorption of ethylene on Pd overlayer surfaces [18]. For instance, M-CO is longer on Cu(111) where the reactants are weakly bound at the IS. The distance is shorter about 0.10 Å on Cu/Ni-III which exhibits the strongest interaction with reactant. As to chemisorption of TSs, the longer C-C, M-CO and M-CH₃ distances on Cu(111)/Co and Cu(111) imply that surface with weak adsorption ability can not stabilize the TS very well. The M-O distance is reduced from IS to TS, between 0.17 and 0.57 Å depending on surfaces, reflecting the enhancement of interaction between O atom and surface.

The adsorption behavior on surfaces can be understood with the weighted d -band center ϵ_{wd} , as tabulated in Table 1, which means the surface reactivity can be changed by changing the electronic structure of surfaces [28,29]. The d -band centers in Co(0001) and Cu(111) are -1.16 and -2.21 eV which are comparable with the literature values of -1.17 and -2.67 eV [31]. For Cu(111)/Co surface, the sublayer atoms shift the d -band center up illustrating the strain effect and ligand effect [17,29,31]. Fig. 3 shows that there is a strong correlation between E_b and ϵ_{wd} . For example, the ϵ_{wd} of Cu/Ni-III is closest to the Fermi level and the E_b of reactant on it is strongest. The good correlation of E_b on the ϵ_{wd} in the boundaries as shown in the bottom panel of Fig. 1 demonstrates the transferability of d -band model where multiple reactants forming bonds with more than one type of metal atom.

Fig. 2. Top view and side view (insets) of the ISs and TSs for $\text{CH}_3 + \text{CO} \leftrightarrow \text{CH}_3\text{CO}$ on different surfaces. Two consecutive graphs represent a reaction path on a surface, the former is the structure of IS and the latter shows the

geometry of TS. (a,b) Cu/Ni-III; (c,d) Co(111); (e,f) Cu(111); (g,h) Co(0001); (i,j) Cu/Co-II; (k,l) Cu/Co-III; (m,n) Cu(111)/Co. Colors: Cu (dark pink), Co (blue), Ni (cyan), C (brown), O (red), H (white).

Table 1. Reaction information for $\text{CH}_3 + \text{CO}$ on surfaces. Energy in eV and distance in Å.

Surface	ε_{wd}	E_b	E_a	Geometric parameters at IS				Geometric parameters at TS			
				C-C	M-CO	M-CH ₃	M-O	C-C	M-CO	M-CH ₃	M-O
Cu/Ni-III	-1.16	-3.68	1.44	3.27	1.95	2.18	2.89	1.90	1.86	2.16	2.32
Co(111)	-1.22	-3.55	1.37	3.31	1.99	2.17	2.95	1.87	1.76	2.23	2.54
Co(0001)	-1.16	-3.54	1.34	3.28	1.98	2.17	2.94	1.87	1.76	2.22	2.58
Cu/Co-II	-1.36	-3.40	1.02	3.81	1.98	2.20	2.93	1.88	1.76	2.21	2.64
Cu/Co-III	-1.37	-3.35	0.96	3.03	1.99	2.22	2.93	1.87	1.76	2.21	2.59
Cu(111)/Co	-2.10	-2.53	1.29	4.46	2.05	2.23	3.00	1.95	1.98	2.25	2.83
Cu(111)	-2.21	-2.28	1.17	4.50	2.05	2.24	2.99	1.96	1.96	2.27	2.77

Fig. 3. Chemisorption energy versus the weighted d -band center.

3.2. The optimal catalytic surface

From Table 1, one can see E_a is 1.44 eV on Cu/Ni-III which is remarkably reduced to 0.96 eV on Cu/Co-III. Fig. 4 clearly shows that with the change of binding energy from Cu/Ni-III to Cu/Co-III, the weaker the binding of reactant to surface results in lower barrier and hence higher reactivity. However, overdo to reduce the adsorption energy, as shown from surface Cu/Co-III to Cu(111), lead to increase on the barrier. Finally there is an optimal catalytic surface for this association reaction. **The trend can be understood by the following explanations.** The association reaction for CH_3 and CO involves the breaking of metal-C bonds and the formation of C-C bond. When CH_3 and CO bind strong on surface, such as on Cu/Ni-III, the metal-C bonds are difficult to break to form the new C-C bond, so the activation barrier is high. On the other hand, surface with weak adsorption capability, such as Cu(111), can not stabilize the reactive TS as shown by the longer distances at TS (see Table 1), which results in the high barrier as well. There is another reason to account for non-linearity of the trend. Different interactions between O atom and surface at IS and TS imply that their adsorption energies can not be scaled with unified variables. Single variable, chemisorption energy of carbon, is enough to scale the adsorption energy of reactants CH_3 and CO. But it can not scale the adsorption energy of TS very well without mixing the oxygen chemisorption energy [32,33]. Consequently an intrinsic non-linearity exists for this reaction as shown in

Fig. 4. The surface with intermediate adsorption strength, the boundary between Cu and Co domains, appears to favor the association reaction. **The optimal surface with right adsorption does exist for specific type of reaction such as CO insertion reaction.** However different reactions have different requirements on the right adsorption. In the next section, we study the chain growth mechanism on Cu/Co-III surface.

Fig. 4. Activation barriers versus the binding energies on metal surfaces.

3.3. CO insertion into CH_x ($x=1-3$) species

The calculated CO insertion barriers are listed in Table 2 together with the results on Co(0001) surface [11]. The corresponding reaction paths are presented in Fig. S2. Table 2 show that CO insertion reactions on Cu/Co-III have lower barriers than the corresponding reactions on Co(0001). The barrier for $CH_3 + CO$ coupling is 0.96 eV much less than the barrier 1.34 eV on Co(0001). CO insertion into CH_2 has lowest barrier 0.77 eV. It is the most effective growth pathway to acyl intermediate which is consistent with the results on Co(0001) [11]. Considering the fast hydrogenation of CH_2 to CH_3 , 0.63 eV on Co(0001) [34], reaction $CH_3 + CO$ is important pathway for chain growth although it unlikely occurs on Co(0001) due to the high barrier [11,14]. Owing to the reduction of barriers, CO insertion mechanism play more important role on Cu-Co catalyst, provide paths to the formation of acyl intermediate which is the precursor to form alcohol by sequential hydrogenation [15,16].

Table 2. E_a for CO insertion into CH_x . Energy in eV.

Reactions	Co(0001)	Cu/Co-III
$CH_3 + CO \leftrightarrow CH_3CO$	1.34	0.96
$CH_2 + CO \leftrightarrow CH_2CO$	0.83 ^a	0.77
$CH + CO \leftrightarrow CHCO$	1.11 ^a	0.99

^a Ref. 11.

3.4. The $C_1 + C_1$ coupling reactions

In this section, the TSs of coupling reactions between C_1 species are located on Cu/Co-III. Fig. S3 illustrates the structures. Coupling barriers are listed in Table 3 together with previous results on Co(0001) [9]. The barriers on Cu/Co-III are lower than those on Co(0001) for all coupling reactions except $CH_2 + CH$. For example, the barrier for $CH_2 + C$ coupling is 0.44 eV much less than the barrier 0.74 eV

on Co(0001). Reaction $\text{CH}_2 + \text{CH}$ has larger barrier on Cu/Co-III that means it prefers stronger adsorption on Co(0001) to increase the reactivity. The reduction of barriers for most of reactions demonstrates Cu/Co-III meets the general requirement for chain growth reactions that is the intermediate adsorption of reactants, but obviously it can not suitable to all association reactions. The coupling of $\text{CH}_2 + \text{C}$ has the lowest barrier on Cu/Co-III and should be a major channel for chain growth. In addition, $\text{CH}_2 + \text{CH}_2$ and $\text{CH} + \text{C}$ contribute to the chain growth significantly which are the major growth paths on Co(0001) and Ru(0001) respectively [9,10].

Table 3. E_a for $\text{C}_1 + \text{C}_1$ coupling reactions. Energy in eV.

Reactions	Co(0001) ^a	Cu/Co-III
$\text{C} + \text{C} \leftrightarrow \text{CC}$	1.22	0.92
$\text{CH} + \text{C} \leftrightarrow \text{CHC}$	0.91	0.70
$\text{CH}_2 + \text{C} \leftrightarrow \text{CH}_2\text{C}$	0.74	0.44
$\text{CH}_3 + \text{C} \leftrightarrow \text{CH}_3\text{C}$	0.94	0.78
$\text{CH} + \text{CH} \leftrightarrow \text{CHCH}$	0.86	0.80
$\text{CH}_2 + \text{CH} \leftrightarrow \text{CH}_2\text{CH}$	0.76	0.92
$\text{CH}_3 + \text{CH} \leftrightarrow \text{CH}_3\text{CH}$	1.05	0.83
$\text{CH}_2 + \text{CH}_2 \leftrightarrow \text{CH}_2\text{CH}_2$	0.70	0.61
$\text{CH}_3 + \text{CH}_2 \leftrightarrow \text{CH}_3\text{CH}_2$	1.11	0.74

^a Ref. 9.

Simply from the kinetic data, $\text{C}_1 + \text{C}_1$ coupling reactions are faster than the CO insertion reactions. However microkinetic simulation is necessary in order to gain the full understanding on HAS as the work done by Medford and Prieto [15,16]. Besides the reaction barrier, surface coverage is an important factor to determine the reaction rate. CO insertion reaction can be accelerated by the abundant coverage of CO particularly on Cu domain [35]. Finally CO insertion mechanism play important role in chain growth process on Cu-Co catalyst and then provide paths to produce higher alcohol.

4. Conclusion

The chain growth mechanisms on bimetallic surfaces have been investigated to provide understanding on the collaborative catalytic effect between Cu and Co domains. Cu/Co-III is the better surface for association reaction owing to its intermediate strength of adsorption which can balance the demand to break the metal-adsorbate bond in IS and the requirement to stabilize the reactive TS. The d -band model is applicable to determine the strength of adsorption of multiple reactants on bimetallic surface. The reduction of CO insertion barriers on boundary surface provides paths to produce higher alcohol. The insight into the bimetallic structure on catalytic activity can guide the design of new catalysts for HAS.

Acknowledgment

This research programme/project is funded by the National Research Foundation (NRF), Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme.

References

- [1] X. D. Xu, E. B. M. Doesburg, J. J. F. Scholten, *Catal. Today*. 2 (1987) 125-170.
- [2] K. Xiao, X. Z. Qi, Z. H. Bao, X. X. Wang, L. S. K. G. Zhong, Fang, M. G. Lin, Y. H. Sun, *Catal. Sci. Technol.* 3 (2013) 1591-1602.
- [3] J. J. Wang, P. A. Chernavskii, A. Y. Khodakov, Y. Wang, *J. Catal.* 286 (2012) 51-61.
- [4] N. D. Subramanian, G. Balaji, C. S. S. R. Kumar, J. J. Spivey, *Catal. Today*. 147 (2009) 100-106.
- [5] K. G. Fang, D. B. Li, M. G. Lin, M. L. Xiang, W. Wei, Y. H. Sun, *Catal. Today*. 147 (2009) 133-138.
- [6] R. M. Bailliard-Letournel, A. J. Gomez Cobo, C. Mirodatos, M. Primet, J. A. Dalmon, *Catal. Lett.* 2 (1989) 149-156.
- [7] J. E. Baker, R. Burch, S. E. Golunski, *Appl. Catal.* 53 (1989) 279-297.
- [8] X. H. Mo, Y. T. Tsai, J. Gao, D. S. Mao, J. G. Goodwin Jr, *J. Catal.* 285 (2012) 208-215.
- [9] J. Cheng, X. Q. Gong, P. Hu, C. M. Lok, P. Ellis, S. French, *J. Catal.* 254 (2008) 285-295.
- [10] Z. P. Liu, P. Hu, *J. Am. Chem. Soc.* 124 (2012) 11568-11569.
- [11] M. K. Zhuo, K. F. Tan, A. Borgna, M. Saeys, *J. Phys. Chem. C* 113 (2009) 8357-8365.
- [12] H. Pichler, H. Schulz, *Chem. Ing. Techn.* 42 (1970) 1162-1174.
- [13] J. Schweicher, A. Bundhoo, N. Kruse, *J. Am. Chem. Soc.* 134 (2012) 16135-16138.
- [14] J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly, C. M. Lok, *J. Phys. Chem. C* 112 (2008) 6082-6086.
- [15] A. J. Medford, A. C. Lausche, F. Abild-Pedersen, B. Temel, N. C. Schjodt, J. K. Nørskov, F. Studt, *Top. Catal.* 57 (2014) 135-142.
- [16] G. Prieto, S. Beijer, M. L. Smith, M. He, Y. Au, Z. Wang, D. A. Bruce, K. P. de Jong, J. J. Spivey, P. E. de Jongh, *Angew. Chem. Int. Ed. B* 53 (2014) 6397-6401.
- [17] J. R. Kitchin, J. K. Nørskov, M. A. Barteau, J. G. Chen, *J. Chem. Phys.* 120 (2004) 10240-10246.
- [18] V. Pallassana, M. Neurock, *J. Catal.* 191 (2000) 301-317.
- [19] A. Christensen, A. V. Ruban, P. Stoltze, K. W. Jacobsen, H. L. Skriver, J. K. Nørskov, F. Besenbacher, *Phys. Rev. B* 56 (1997) 5822-5834.
- [20] J. de la Figuera, J. E. Prieto, G. Kostka, S. Muller, C. Ocal, R. Miranda, K. Heinz, *Surf. Sci.* 349 (1996) L139-L145.
- [21] M. T. Kief, W. F. Egelhoff, *Phys. Rev. B* 47 (1993) 10785-10814.
- [22] G. Kresse, J. Hafner, *Phys. Rev. B* 48 (1993) 13115-13118.
- [23] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865-3868.
- [24] P. E. Blöchl, *Phys. Rev. B* 50 (1994) 17953-17979.
- [25] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* 13 (1976) 5188-5192.
- [26] M. Methfessel, A. T. Paxton, *Phys. Rev. B* 40 (1989) 3616-3621.
- [27] G. Henkelman, B. P. Uberuaga, H. Jonsson, *J. Chem. Phys.* 113 (2000) 9901-9904.
- [28] B. Hammer, J. K. Nørskov, *Surf. Sci.* 343 (1995) 211-220.
- [29] M. Mavrikakis, B. Hammer, J. K. Nørskov, *Phys. Rev. Lett.* 81 (1998) 2819-2822.
- [30] V. Pallassana, M. Neurock, L. B. Hansen, J. K. Nørskov, *J. Chem. Phys.* 112 (2000) 5435-5439.
- [31] A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver, J. K. Nørskov, *J. Mol. Catal. A: Chem.* 115 (1997) 421-429.

- [32] F. Studt, F. Abild-Pedersen, Q. Wu, A. D. Jensen, B. Temel, J. Grunwaldt, J. K. Nørskov, *J. Catal.* 293 (2012) 51-60.
- [33] S. Wang, V. Petzold, V. Tripkovic, J. Kleis, J. G. Howalt, E. Skulason, E. M. Fernandez, B. Hvolbæk, G. Jones, A. Toftelund, H. Falsig, M. Bjorketun, F. Studt, F. Abild-Pedersen, J. Rossmeisl, J. K. Nørskov, T. Bligaard, *Phys. Chem. Chem. Phys.* 13 (2011) 20760-20765.
- [34] X. Q. Gong, R. Raval, P. Hu, *J. Chem. Phys.* 122 (2005) 024711.
- [35] G. A. Beitel, C. P. M. de Groot, H. Oosterbeek, J. H. Wilson, *J. Phys. Chem. B* 101 (1997) 4035-4043.