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Short communication

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

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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.

1. Introduction

The catalytic conversion of syngas (mixture of CO and H_2) 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, 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]. 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 a 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 C_1 monomer (C, CH, CH_2 and CH_3) 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 that 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 suggests that the boundary between Cu and Co phases exhibits a higher activity for chain growth and hence gains insight into the active site to

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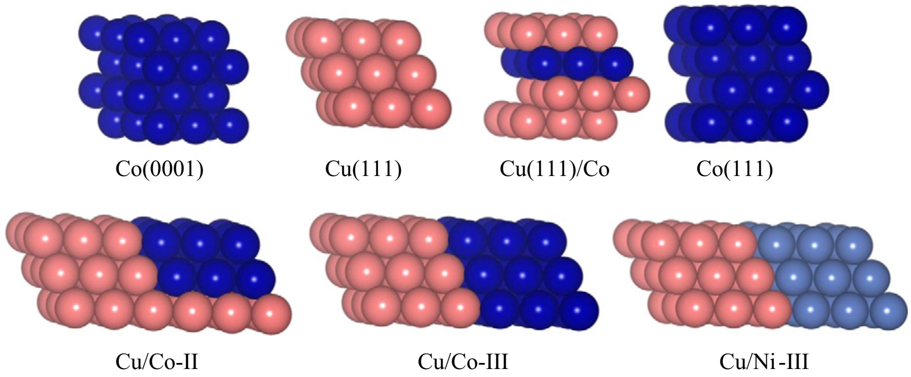

Fig. 1. The structures of metal surfaces. Colors: Cu (dark pink), Co (blue), and Ni (cyan).

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

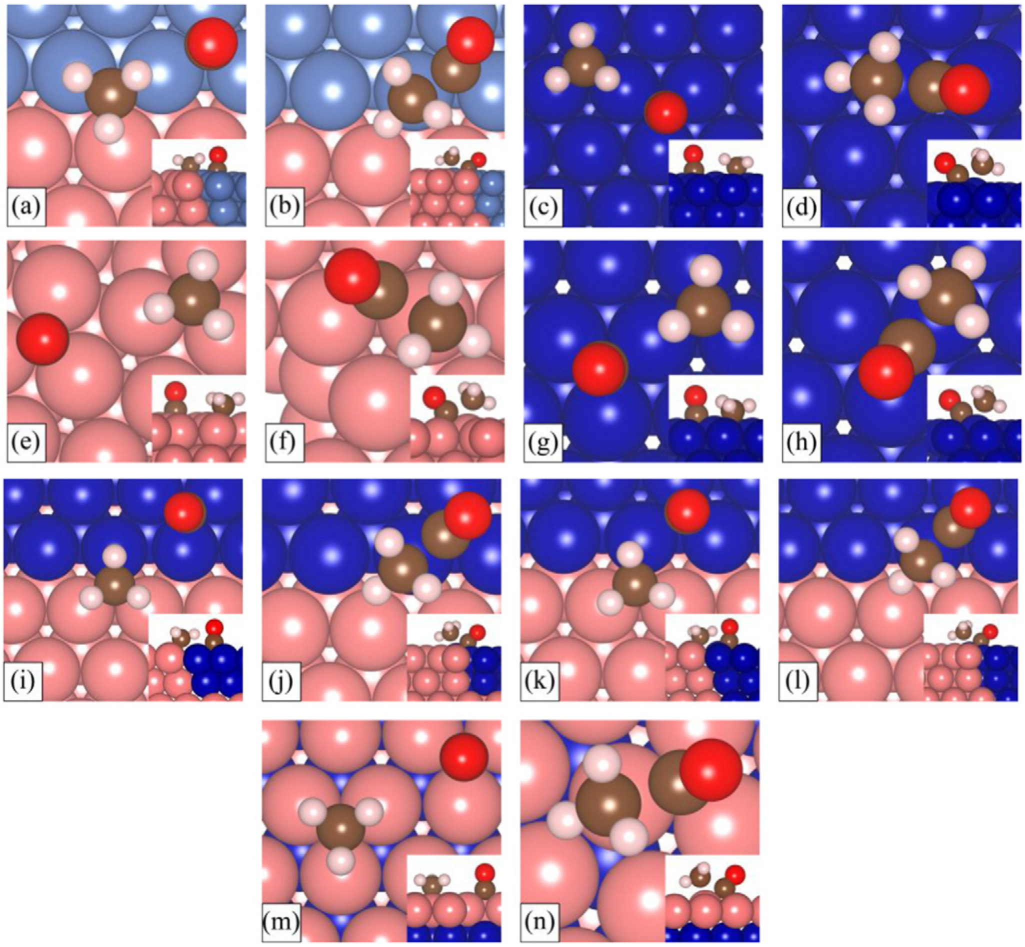

Fig. 2. Top view and side view (insets) of the ISs and TSs for $CH_3 + CO \leftrightarrow CH_3CO$ on different surfaces. Two consecutive graphs represent a reaction path on a surface, the former is the structure of IS and the latter shows the geometry of TS. (a,b) Cu/Ni-III; (c,d) Co(111); (e,f) Cu(111); (g,h) Co(0001); (i,j) Cu/Co-II; (k,l) Cu/Co-III; and (m,n) Cu(111)/Co. Colors: Cu (dark pink), Co (blue), Ni (cyan), C (brown), O (red), and H (white).