

Role of the Zn atomic arrangements in Enhancing the Activity and Stability of the Kinked Cu(211) site in CH<sub>3</sub>OH Production by CO<sub>2</sub> Hydrogenation and Dissociation: First-principles Microkinetic Modeling Study

조덕연<sup>1</sup>, 함형철<sup>2</sup>, 이관영<sup>1,3,†</sup>

<sup>1</sup>고려대학교; <sup>2</sup>인하대학교; <sup>3</sup>KU-KIST 그린스쿨

(kylee@korea.ac.kr<sup>†</sup>)

We unravel the beneficial role of the Zn ensemble (in particular, an a single Zn atom) in the sixfold-coordinated kinked (Cu-vacant) site of the stepped Cu(211) for enhancing the reactivity and durability of catalyst in the CH<sub>3</sub>OH production from CO<sub>2</sub> and H<sub>2</sub>. Our results exhibit that the Zn atoms at the 7 fold-coordinated site of the Cu(211) tend to be isolated and acts as the modifier to suppress the loss of Cu atoms from the Cu(211). Second, we find that the catalysis of CH<sub>3</sub>OH synthesis strongly depends on the type of defects at the Cu(211). In particular, the single Zn atom-substituted stepped site in the Cu(211) is found to have the superior catalytic activity (TOF=3.07×10<sup>-5</sup> s<sup>-1</sup> @ P=75bar and T=523K) toward the CH<sub>3</sub>OH formation compared to the traditionally-known active Cu(211) (TOF=2.73×10<sup>-7</sup> s<sup>-1</sup>). The increased catalysis in the Zn-associated site is related to the significant enhancement of the surface affinity toward the adsorbate having the oxygen moiety leading higher activity toward adsorbate reduction.