

# Assessing the effect of catalyst structure on the competitive CO<sub>2</sub> hydrogenation pathways to CO and Methanol on Copper

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#### Significance and Relevance

This work deciphers the effect of the catalyst structure on the different reaction pathways controlling the product selectivity towards methanol and carbon monoxide in copper (Cu)-based CO<sub>2</sub> hydrogenation. Our analysis, using atomistic modeling of detailed reaction mechanisms on different catalyst crystal facets, resolves the experimentally observed, often contradictory reports regarding the structure-dependent activity, the effect of water in accelerating the reaction rates and whether the different product pathways share common intermediates, paving the way for rational catalyst design.

Preferred and 2<sup>nd</sup> choice:CO<sub>2</sub> utilization and recycling, Fundamental advances in understanding catalysis Preferred presentation: Oral / Short Oral

### **Introduction and Motivations**

Methanol (MeOH) synthesis through CO<sub>2</sub> hydrogenation is regarded as a key technology to recycle waste CO<sub>2</sub> into valuable base chemicals closing the carbon loop<sup>1</sup>. However, there is still significant discrepancy in the research community on the exact kinetic mechanism behind the selectivity towards methanol/ CO, hindering the development of efficient catalysts for the process<sup>1</sup>. Kinetic studies have suggested that the MeOH formation and reverse water-gas shift reaction (rWGS) take place through parallel pathways with no common intermediates<sup>2</sup>. However, isotope tracing experiments have shown that in the presence of water or at low temperatures, methanol is primarily produced from CO, suggesting a sequential reaction mechanism<sup>3</sup>. Recent structure sensitivity studies have further speculated that the product pathways may vary drastically between Cu(111), Cu(100) compared to Cu(211), Cu(110) surfaces<sup>4</sup>. Ultra-high vacuum studies have shown that the catalytic activity can also differ by orders of magnitude between Cu facets such as Cu(111) and Cu(110), making it challenging to experimentally assess the catalyst structure effects<sup>5</sup>. This work uses first-principles based atomistic modeling to the shed light on different and often contradictory experimental observations regarding the methanol/ CO selectivity on Cu at operationally relevant temperature and pressure conditions. **Materials and Methods** 

Density Functional Theory (DFT) calculations are carried out on multiple Cu planar facets using Quantum ESPRESSO suite with GGA-PBE pseudopotentials, a plane wave basis set, Grimme D3 dispersion, represented by five-layer slabs of p(3x2) periodic unit cells with vacuum spacing of 12 Å. In total, *19 adsorbate species and 32 elementary reactions are assessed*, to address the complexity of CO and MeOH formation. Climbing-Image Nudged-elastic band calculations are used to detect the transition states. Vibrational analysis is used to determine the ZPE corrections, temperature dependent heat capacities and entropy contributions for determining the Gibbs free energies. **Results and Discussion** 

Fig. 1 shows the comparison between the minimum energy path for the rWGS reaction on Cu(111) and Cu(110) facets. For both the surfaces, CO production through direct CO<sub>2</sub> dissociation is energetically more favorable over the CO2 hydrogenation-based carboxyl route. However, our analysis shows that an alternate water-assisted CO<sub>2</sub> hydrogenation route exists with significantly lower activation barrier making the carboxyl pathway most energetically feasible. While such a pathway may not be observed under UHV experiments, pressurized experimental conditions may result in lowering the overall CO formation energy barrier through this route along an integral reactor. Also, Fig. 1 shows that the Cu(110) facet is energetically much more favorable towards CO formation compared to



Cu(111), due to preferential surface stabilization of the CO<sup>\*</sup> and OH<sup>\*</sup> adsorbates, explaining the experimental observation of the three orders of magnitude higher CO formation rates on Cu(110) compared to Cu(111), seen in UHV studies of Yoshihara et al.<sup>3,5</sup>



Figure 1. Free energy surface for rWGS pathways on (a) Cu(110) and (b) Cu(111), at T=528K,p=30bar with respect to the reference state: CO<sub>2(g)</sub>+H<sub>2(g)</sub>+H2O<sub>(g)</sub>

The potential energy surface for the different reaction pathways towards MeOH formation are shown in Fig,2. On both the surfaces formate (HCOO\*)-based pathway is the energetically most favorable, agreeing with experimental observation of high formate species coverage<sup>3,4</sup>. However, one interesting difference can be observed in terms of the most energy demanding steps towards MeOH formation on the different surfaces. Fig. 2(a) suggests that on Cu(110), with increasing pressures towards industrial scales (>75-90 bar), as the formate pathway opens up ( $\Delta G$  becomes <0, for the shaded section), other routes remain energetically unfeasible. This stems from the lower activation barriers of water formation steps on Cu(110) and suggests a dominant HCOO\*-based pathway towards MeOH formation on this surface, explaining the recent particle size effect observed by Barberis et al.<sup>4</sup>



Figure 2. Free energy surface for MeOH pathways on (a) Cu(110) and (b) Cu(111), at T=528K,p=30bar with respect to the reference state: CO<sub>2(g)</sub>+3H<sub>2(g)</sub>

On the Cu(111) surface, on the other hand, the activation barriers towards MeOH formation are higher and appear downstream along the reaction coordinate (Fig. 2(b)). As a consequence, when the formate pathway opens up, the carboxyl (COOH\*)-based pathway also becomes energetically accessible for MeOH formation. A significant consequence of this result is that on Cu(111), CO and MeOH may no longer be formed through separate parallel paths but through a common carboxyl intermediate, making it challenging for selectivity tuning by catalyst structuring for large-sized Cu nanoparticles, where Cu(111) surface dominates. Our work thus provides key fundamental insights on the coupling between different catalytic cycles on different Cu facets, paving the way for the rationalization of experimental observations of the competitive  $CO_2$  hydrogenation on Cu.

## References

- 1. R. Schlogl, Angew. Chem. Int. Ed., 2022, 61, e202007397
- 2. T.C. Lin, A. Bhan, J. Cat., 2024, 429, 115214.
- 3. Y. Yang et al., J. Cat., **2013**, 298, 10-17.
- 4. L. Barberis et al., Nanoscale, **2022**, 14, 13551.
- 5. J. Yoshihara & C.T. Campbell, J. Cat, **1996**, 367, 661–666.

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