Unveil the Mechanism of Catalytic Conversion of CO and CO_2 to Methanol

Albert Dearden, Malihe Shaban, and Chen Huang
Department of Scientific Computing, Florida State University

Introduction

Methanol is a main building block for synthesizing many other chemicals, and is also considered as an alternative to oxygen for fuel cells which have a widespread use in automotive and other mobile applications. Catalytic conversion of CO and CO_2 to methanol is a major route to synthesize methanol in industry. The synthesis gas mixtures ($CO/CO_2/H_2$), which are produced by mixing fossil fuel with oxygen or water steam at high temperature, are catalyzed to methanol by $Cu/ZnO/Al_2O_3$ at $230\sim280C^{\circ}$. Despite several decades of research on the methanol synthesis technology, there are still several open questions. One unresolved puzzle is what the main reaction pathway is. CO hydrogenation (CO + $2H_2$ → CH_3OH) was assumed to be the main reaction pathway, however isotope labeling experiments suggested that CO_2 hydrogenation (CO_2+3H_2 → CH_3OH+H_2O) is the main reaction pathway. This puzzle becomes even more difficult to resolve, by realizing that copper is an excellent catalyst to convert CO to CO_2 and vice versa, via the water-gas-shift reaction ($CO+H_2O \leftrightarrow CO_2+H_2$).

Motivation

Nearly all previous theoretical studies of methanol synthesis were based on the widely-used density functional theory (DFT) (e.g. Ref.[1]). To understand this complicated catalytic process, the major task is to obtain accurate binding energies and reaction barriers for each intermediate reaction step in methanol synthesis, however DFT is known to give inaccurate binding energies and incorrect binding sites for CO on copper surface,[2] which strongly hinders the predictive power of DFT. Furthermore, DFT simulations based on conventional exchange-correlation functionals cannot describe van der Waals interaction between adsorbates and metal surfaces, which is another error source for binding energies of adsorbates. To unveil the true mechanism of methanol synthesis, we herein go beyond DFT and in the meanwhile keep the computational cost affordable by performing multi-scale quantum mechanics calculations. Very accurate energy diagrams are obtained, which gives us great insight into methanol synthesis.

Models and Computational Methods

Surface defects are found to be the active sites to catalyze methanol synthesis.[1] We model surface defects by employing the stepped copper face-centered-cubic (fcc) (211) surface. In Fig.1, we show several main intermediate steps during the catalytic conversion of CO_2 to methanol. CO_2 is initially adsorbed on the stepped copper surface. The hydrogenation of CO_2 starts by attaching hydrogen atoms to CO_2 to form radicals $HCOO^*$ and H_2COOH^*. H_2COOH^* then decomposes to H_2CO^* and OH^*. More hydrogen atoms later join the hydrogenation process. OH^* combines with one extra hydrogen atom to form one water molecule (H_2O). H_2CO^* combines with another hydrogen atom to form the methanol molecule, which is the desired product.
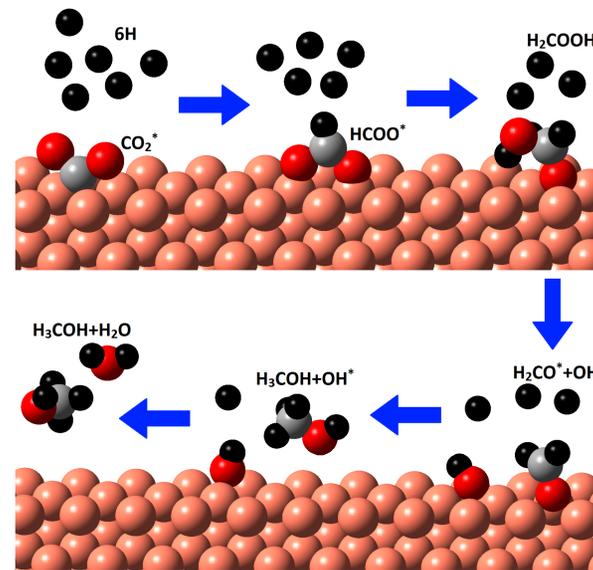

Figure 1: Main steps to converting CO_2 to methanol, catalyzed by stepped copper surface. Black balls: hydrogen. Red balls: oxygen. Grey balls: carbon. Brown balls: copper. The notation * indicates that the molecule is adsorbed on the surface.

We employ the *O*ur own *N*-layered *I*ntegrated molecular *O*rbital and molecular *M*echanics (ONIOM) method[3] to obtain highly accurate binding energies of these intermediate states. ONIOM is a multi-scale quantum mechanics simulation method. It treats the region of interest (ROI) (in our case, the chemical bonding between adsorbates and copper surfaces) using very accurate quantum mechanics method, and treats the rest of the system with computationally cheap, physically correct method. The ONIOM energy of the total system is obtained from three independent calculations

$$E^{ONIOM} = E_{tot}^{DFT} + (E_{ROI}^{MP2} - E_{ROI}^{DFT}).$$

We perform DFT calculations on the entire system (copper surface plus adsorbed molecule), with the energy denoted as E_{tot}^{DFT}. Generalized gradient approximation exchange-correlation functional is employed in all DFT simulations. The adsorbate together with a small copper cluster underneath is then marked as the region of interest (ROI). The energy of ROI is calculated using both the second order Møller−Plesset perturbation theory (MP2) (denoted as E_{ROI}^{MP2}) and DFT (denoted as E_{ROI}^{DFT}). MP2 is believed to accurately describe the surface chemistry here, which only involves non-spin-polarized systems.

Results

Energy diagrams from both DFT and ONIOM calculations are shown in Fig.2. With ONIOM, we have completely overcome the inaccuracy of DFT in treating oxygen-rich molecules, such as CO_2, and molecules of very few electrons, such as H_2. The ONIOM energy diagrams are obtained without applying any ad hoc corrections [1] to the energies of gas phase CO_2 and H_2. Both DFT and ONIOM results show that the rate-limiting step is the (H_2CO^* + OH^*) step. We note that ONIOM gives a barrier that is about 0.3 eV lower than DFT. On the other hand, for the CO hydrogenation (not shown), we found that ONIOM and DFT give very similar barriers for the rate-limiting step HCO^*+OH^*. These findings suggest that CO_2 hydrogenation is very likely to be the dominating reaction pathway in methanol synthesis. In catalyst design, deeply trapped states need to be avoided. In Fig.2, ONIOM gives much lower binding energy for the intermediate step $HCOO^*+H^*$, indicating a possible trapped state.
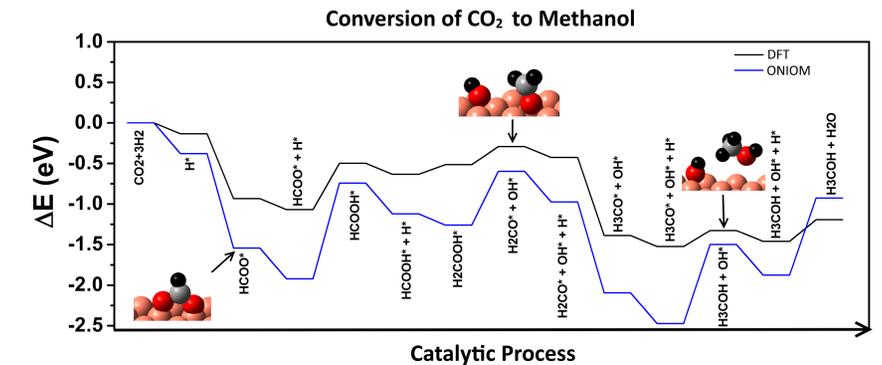

Figure 2: Energy diagrams of the catalytic conversion of CO_2 to methanol (H_3COH). Results from both DFT and ONIOM are shown.

Summary

We have identified that CO_2 hydrogenation is the main reaction pathway in methanol synthesis. Our work shows that it is possible to understand or even predict surface catalysis with unprecedented accuracy by employing multi-scale quantum mechanics method. Future work based on our density-functional embedding theory[2] which is more accurate than ONIOM is in progress.

References

[1] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, BL. Kniep, M. Tovar, RW. Fischer, JK. Nrskov, and R. Schlögl. *Science*, 336:893, 2012.

[2] C. Huang, M. Pavone, and E. A. Carter. *The Journal of Chemical Physics*, 134:154110, 2011.

[3] S. Dapprich, I. Komáromi, K. S. Byun, K. Morokuma, and M. J. Frisch. *Journal of Molecular Structure (Theochem)*, 462:1, 1999.

Acknowledgements