

How can electronic structure provide understanding on Carbon-Carbon coupling reaction

Kaito Takahashi

IAMS, Academia Sinica Taiwan

email:kt@gate.sinica.edu.tw

Efficient utilization of CO₂ has been an important topic, and electrocatalytic reduction of CO₂ to C₂₊ products such as C₂H₄, C₂H₅OH, or C₃H₇OH is an ideal solution. However, real applications have been hindered by the slow kinetics due to the very high barrier of the Carbon-Carbon coupling (CC coupling) reaction. Here, we talk a look at the important electronic states of the adsorbates in the CC coupling reaction using theoretical calculations.

For the ethanol production of NiMn doped into N-vacancy graphitic-Carbon Nitride (NiMn@V-g-C₃N₄), we found that the *CO+*CHO reaction has a low barrier of 0.78 eV. Analysis of the charge distribution showed that bare NiMn@V-g-C₃N₄ has a 2+ charge on the NiMn diatom, while the V-g-C₃N₄ substrate had a 2- charge. Upon the adsorption of CO on top of Ni and CHO on top of Mn, we found that the NiMn kept its 2+ charge, but the V-g-C₃N₄ substrate had 1- charge, signifying electron transfer to the adsorbates CO+CHO from the V-g-C₃N₄ substrate. Evaluation of the gas phase reaction of CO+CHO and CO+CHO⁻ showed that the heat of reaction for the latter anionic reaction is 1 eV greater than the former neutral reaction. Thereby showing that the extra electron to the adsorbate promotes the CC coupling reaction in this case. Previous studies have mentioned the importance of the extra electron for the CC coupling in *CO+*CO, but this is the first instance where the importance of the extra electron has been mentioned in other CC coupling reactions.