Toward Computational Design of Catalysts for CO_2 Selective Reduction via Reaction Phase Diagram Analysis

Mengru Han [a], Xiaoyan Fu [a], Ang Cao [a], Chenxi Guo [a], Wei Chu [a], and Jianping Xiao [a] *

[a] *State Key Laboratory of Catalysis , Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Da Lian , 116023, China*

* *xiao@dicp.ac.cn*

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Chemical conversion of carbon dioxide (CO_2) into value-added chemicals, for example, ethanol, has been recognized to be one of the most effective ways of carbon sources cycling. However, the selectivity controlling of CO_2 reduction is still a challenging problem due to the formation of a variety of products, such as methanol, methane, formic acid, and carbon monoxide, associating with complicated reaction mechanisms. Herein, a simple and effective theoretical analysis of "reaction phases diagram" to understand the selectivity of CO_2 reduction, based on the principle of reaction free energies with sequential priority is proposed. Using this principle, the fundamental understanding of the formation of different products in CO_2 reduction is rationalized. On the basis of reaction free energies' analysis, the selectivity trends of CO_2 reduction to methane, methanol, and ethanol from a number of experiments are discussed. At the end, the selectivity trends with a computer algorithm of searching full reaction pathways, explaining well the effects from catalyst sizes, substrate observed in experiments, are confirmed.