ELECTROCATALYTIC CONVERSION OF METHANE TO METHANOL

ABSTRACT

As methane is the primary component of natural gas, it is abundant and widely available. However, transporting methane, especially from remote locations, is challenging and often uneconomical. Converting methane to methanol, a liquid makes it easier and more cost-effective to transport and store. In this research, we will be focusing on the conversion of methane to methanol involving selective oxidation. Methanol is a versatile chemical with wide range of applications such as alternative fuel, chemical feedstock, reduction of flaring and microbial cultivation.

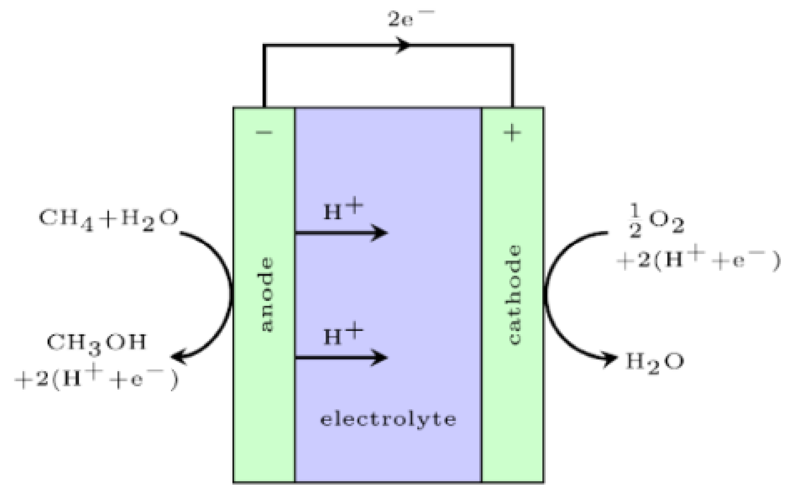

Figure 1: Electrocatalytic cell diagram

Proposed reaction mechanism

Water Splitting

$$* + 2H_2O \rightarrow *OH + H_2O + (H^+ + e^-)$$
$$\rightarrow *O + H_2O + 2(H^+ + e^-)$$
$$\rightarrow *OOH + 3(H^+ + e^-)$$
$$\rightarrow * + O_2 + 4(H^+ + e^-)$$

Methane Oxidation

$$*O + CH_4(g) \rightarrow *O\cdots CH_4$$
$$\rightarrow *(OH\cdots CH_3)$$
$$\rightarrow *CH_3OH$$
$$\rightarrow * + CH_3OH(g)$$

Limitations of the catalysts

- Activate CH4 and form CH3OH
- Avoid O2 evolution
- Avoid CH3OH oxidization to CO2

$$E_{act}^{estimated} = (E_{CH_3(g)} - E_{CH_4(g)}) + (E_{*OH} - E_{*O})$$

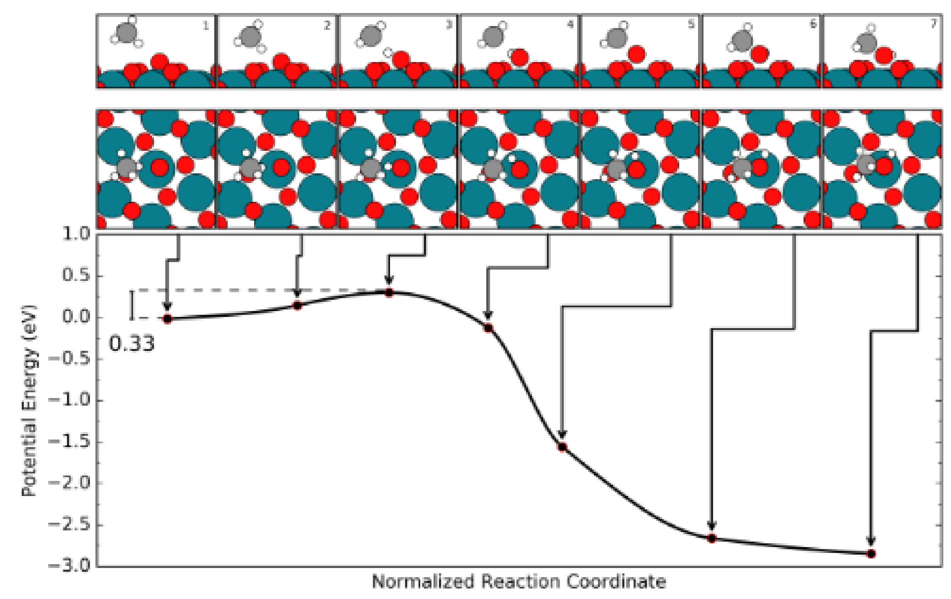

Figure 2: Methane oxidation reaction pathway calculated using CI-NEB method on RhO2

OER free energy diagrams

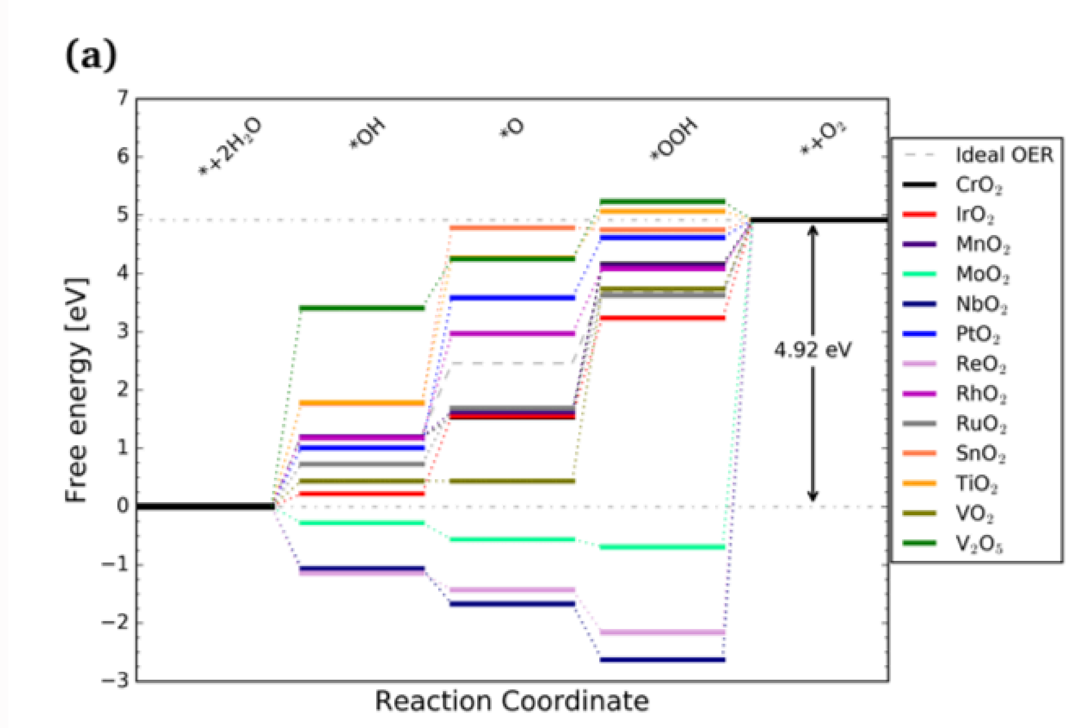

Figure 3: OER free energy diagram for Metal oxides

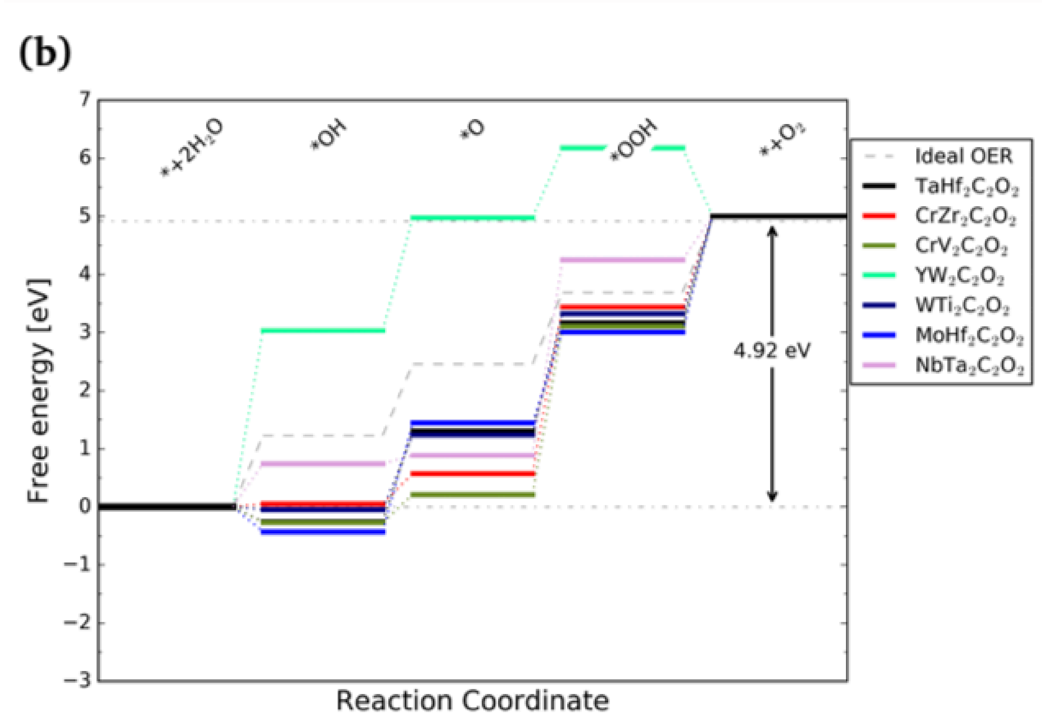

Figure 4: OER free energy diagram for MXenes

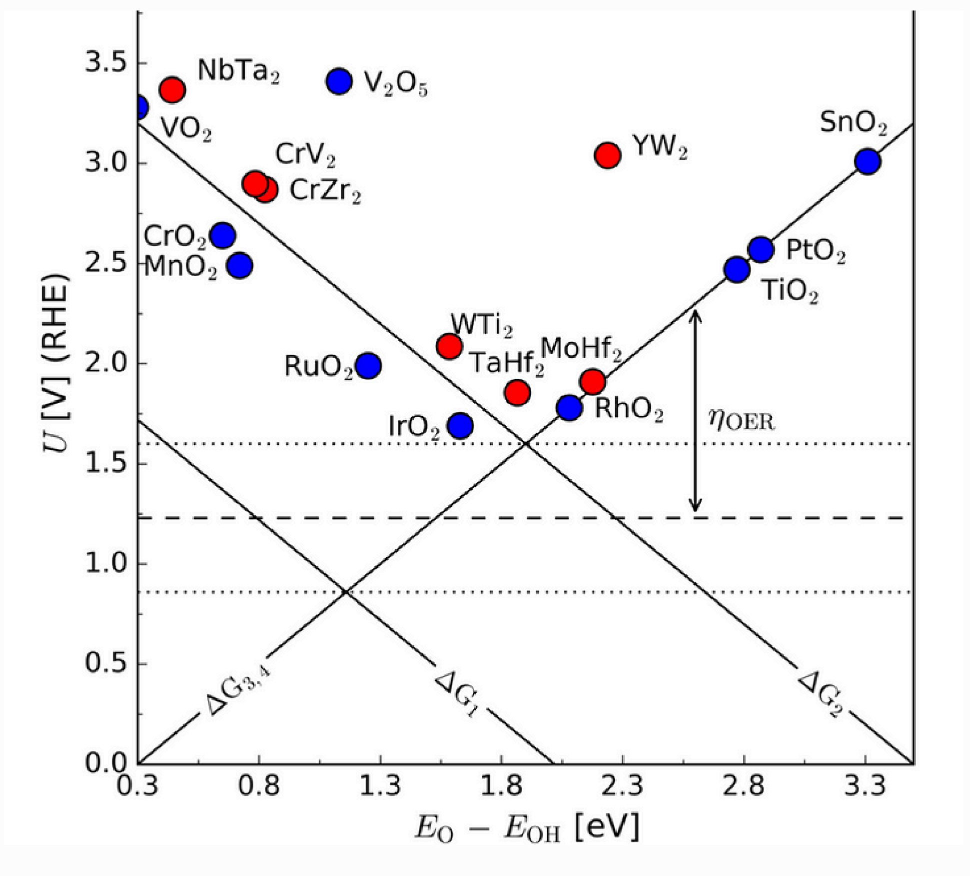

Figure 5: Limiting potential for Metal Oxides (blue) and MXenes (red)

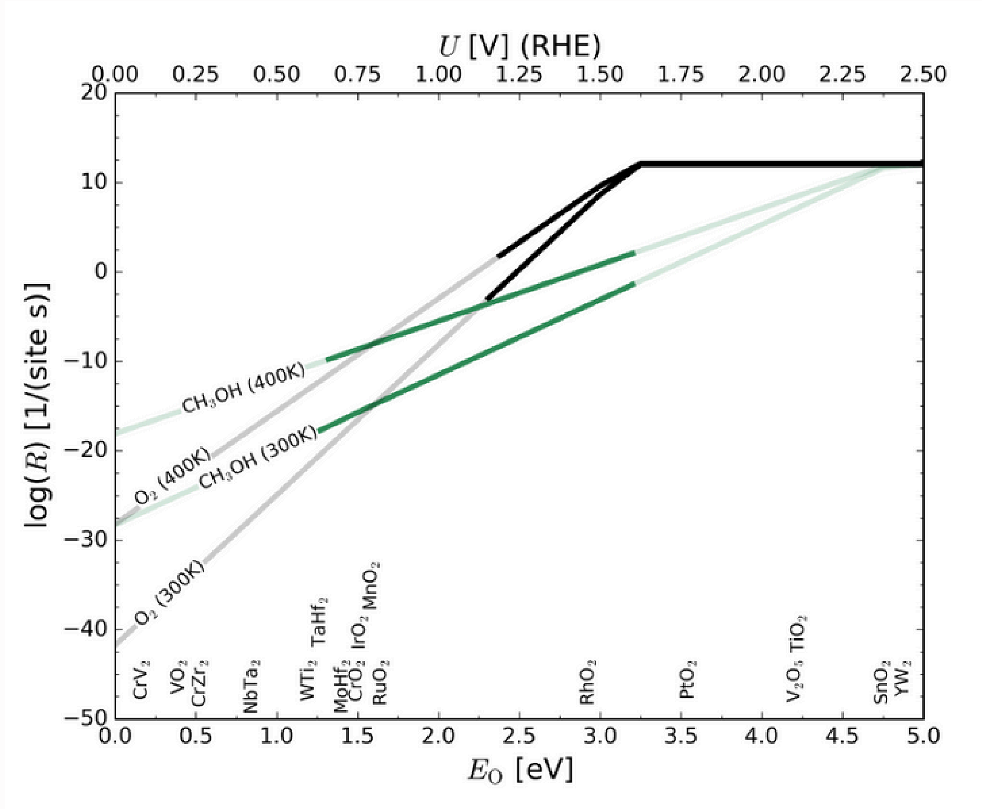

Figure 6: Rate for methanol production and oxygen evolution

$$E_{act}^{calculated} = E_{*(OH\cdots CH_3)} - E_{*O\cdots CH_4}$$

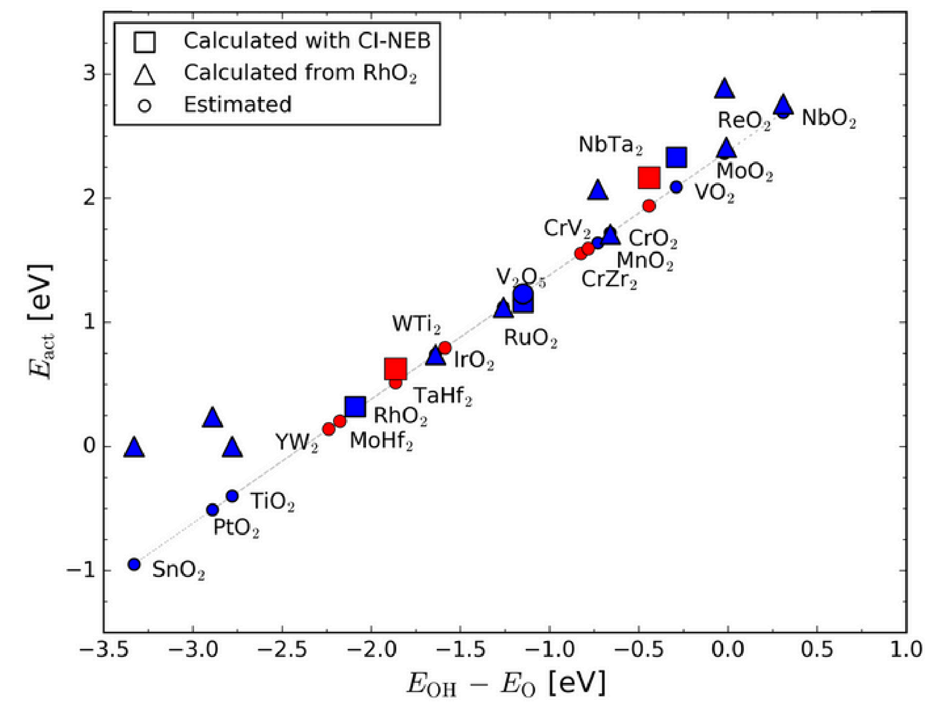

Figure 10: Activation energy of methane Metal Oxides (blue) and MXenes (red)

The activation energy for Methanol and Oxygen evolution:

$$E_{act}^{CH_3OH} = -\frac{1}{2}G_O + 2.4$$

$$E_{act}^{O_2}(U) = -\frac{1}{2}G_O + 3.2 - eU$$

Rate constant:

$$K_1 = \frac{k_1^+}{k_1^-} \quad k_2^+ = \frac{k_BT}{h}\exp\frac{E_{act}^{CH_3OH}}{k_BT} \quad k_3^+(U) = \frac{k_BT}{h}\exp\frac{E_{act}^{O_2}(U)}{k_BT}$$

Structure characterization of P-Tri-RhO2 and Rh-NA/RhO2

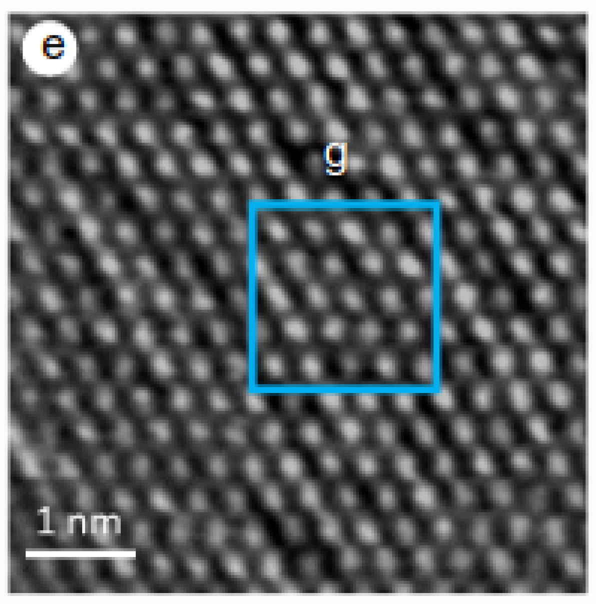

Figure 7: STEM showing the atomic arrangement of Rh

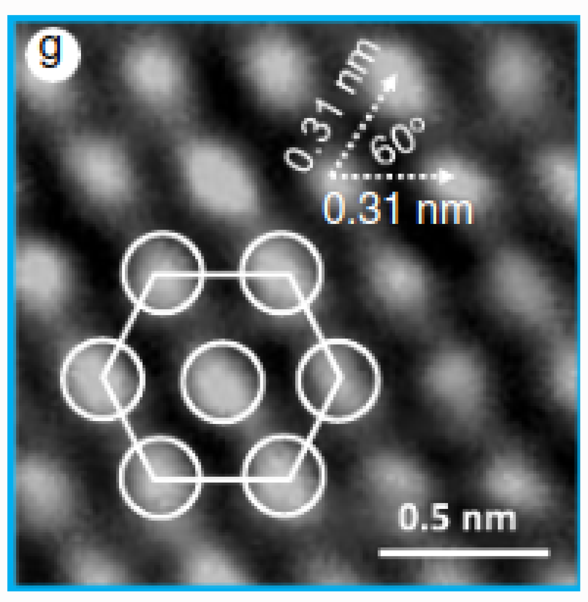

Figure 8: Zoomed in STEM image

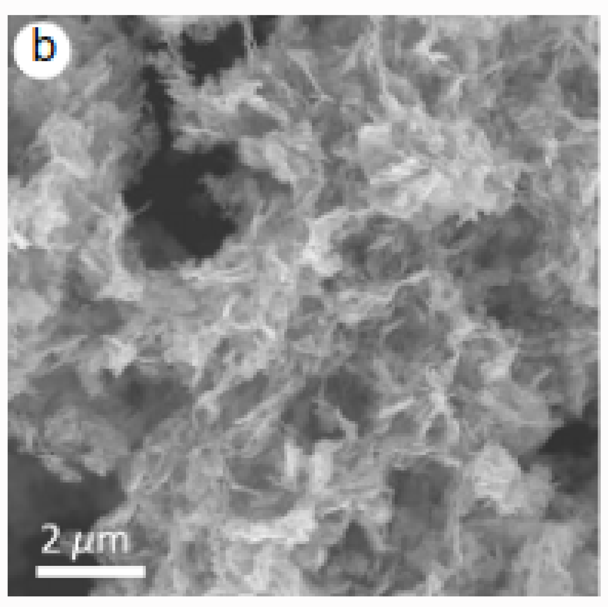

Figure 9: SEM, showing 2d nanosheets morphology

References

1. L Arnarson, PS Schmidt, M Pandey, A Bagger, KS Thygesen, I EL Stephens, J Rossmeisl, "Fundamental limitation of electrocatalytic methane conversion to methanol". Physical Chemistry Chemical Physics, 2018, 20 (16), 11152-11159.

2. Fan, Zhenglong & Liao, Fan & Yujin, Ji & Liu, Yang & Huang, Hui & Wang, Dan & Yin, Kui & Yang, Haiwei & Ma, Mengjie & Zhu, Wenxiang & Wang, Meng & Kang, Z.H. & Li, Youyong & Shao, Mingwang & Hu, Zhiwei & Shao, Qi. (2022). Coupling of nanocrystal hexagonal array and two-dimensional metastable substrate boosts H2-production. Nature Communications. 13. 10.1038/s41467-022-33512-5.

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