PENNSTATE

CHEMICAL ENGINEERING

# DFT Analysis of Elementary $N_2$ Electro-Reduction Kinetics on Transition Metal Surfaces

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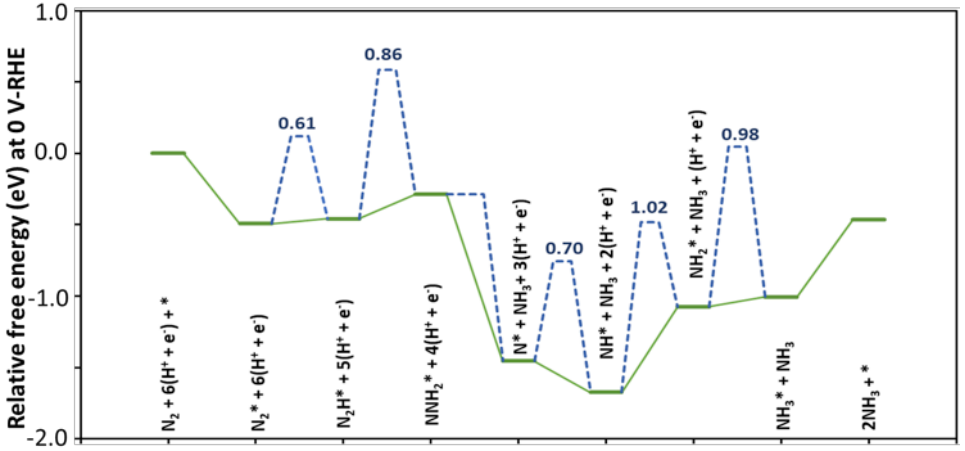
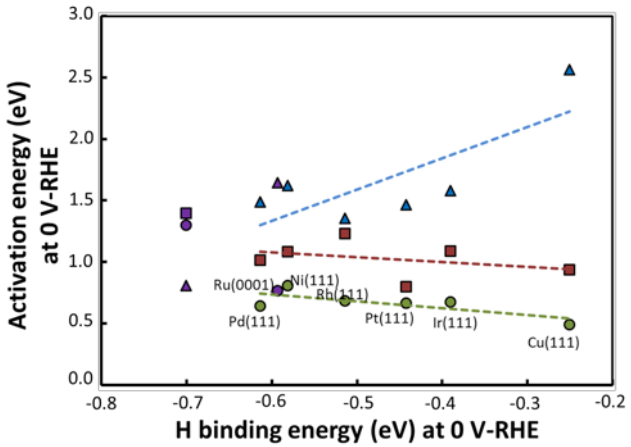
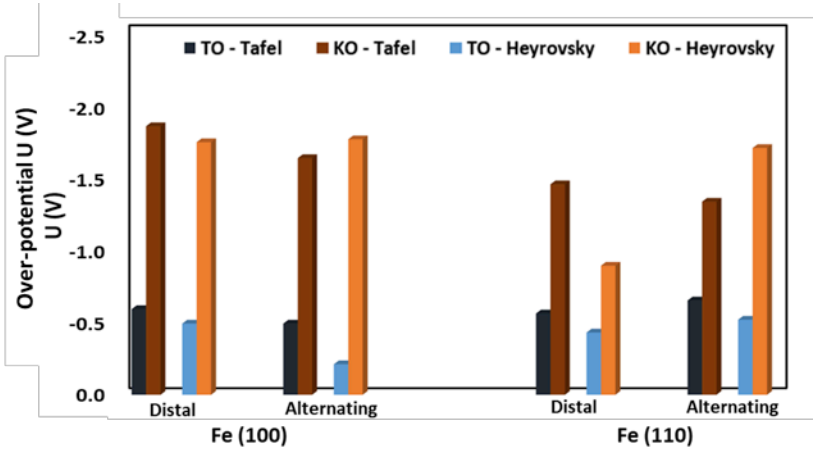
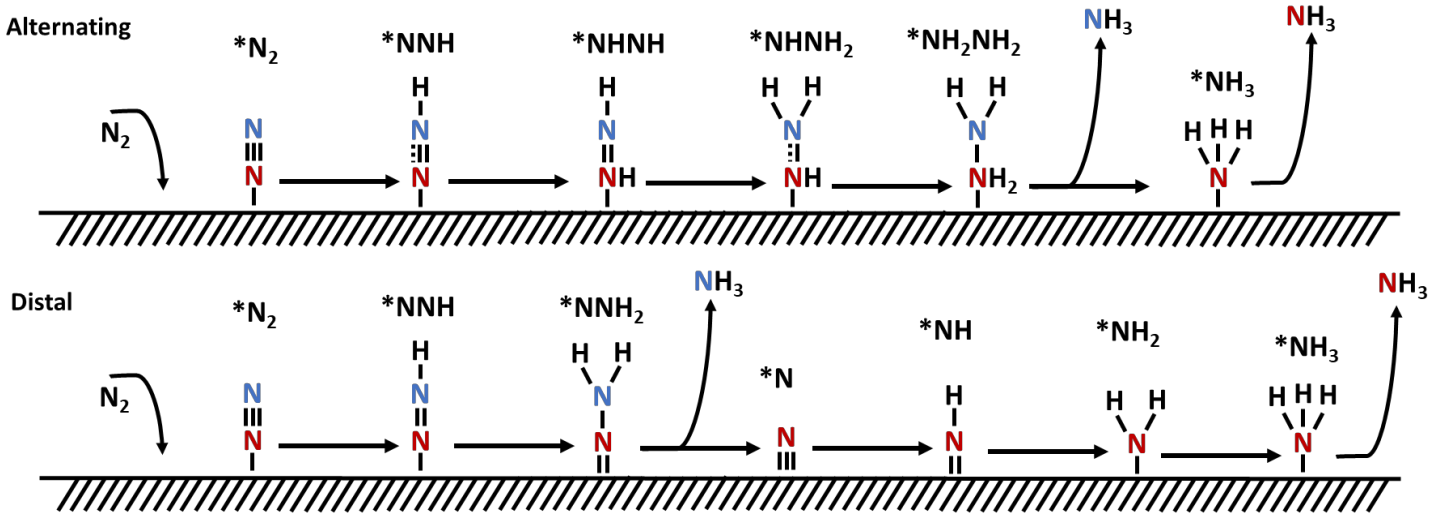
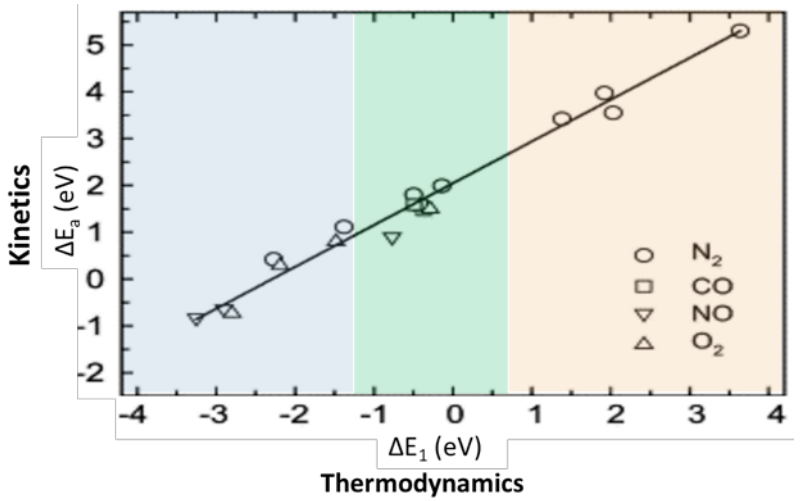


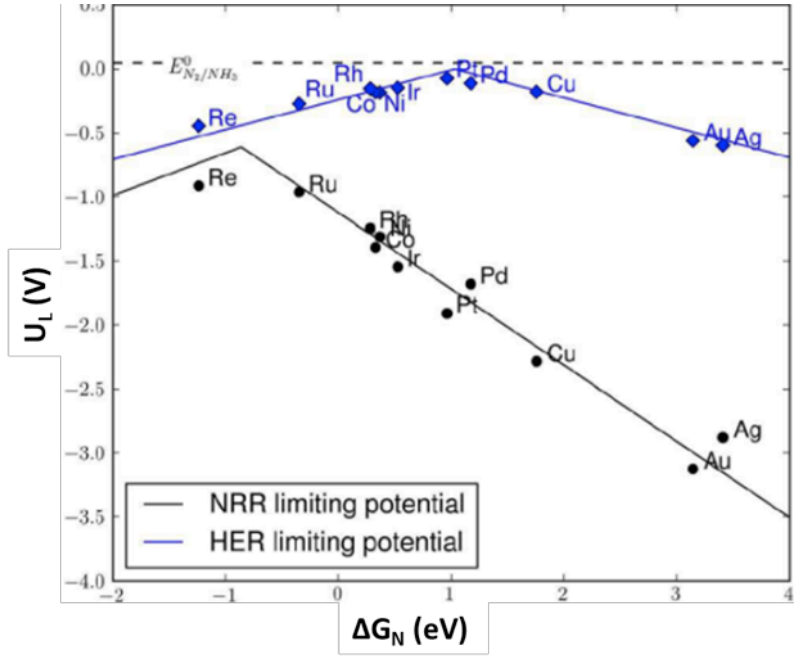



# Associative mechanism – an opportunity?



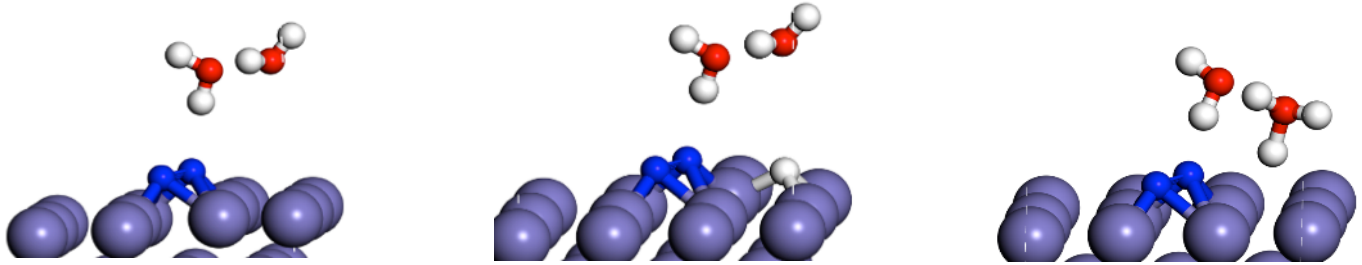

**Key assumptions made:**

- Uses only elementary thermodynamics; no barriers
- Assumes BEP for all elementary intermediates of associative mechanism

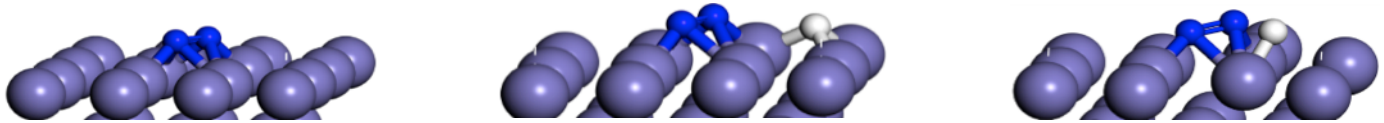

Montoya, J. H., et al. (2015). Chemsuschem **8**(13): 2180-2186.
Bligaard, T. et al. J. Catal. **224**(1): 206-217.

# Tafel and Heyrovsky-like schemes on Fe (100) and Fe (110)

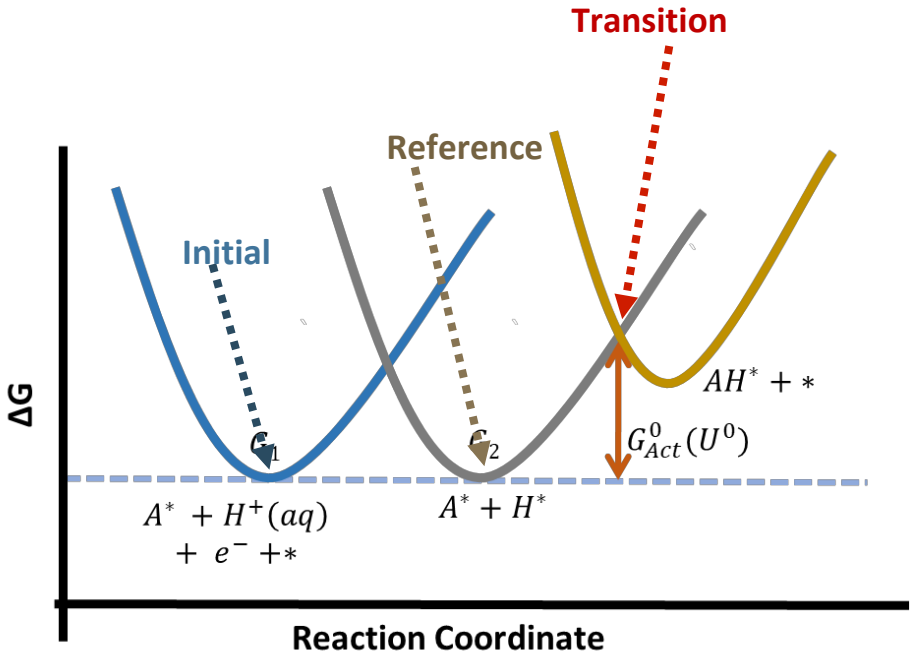
**Heyrovsky-like**



**Tafel-like**

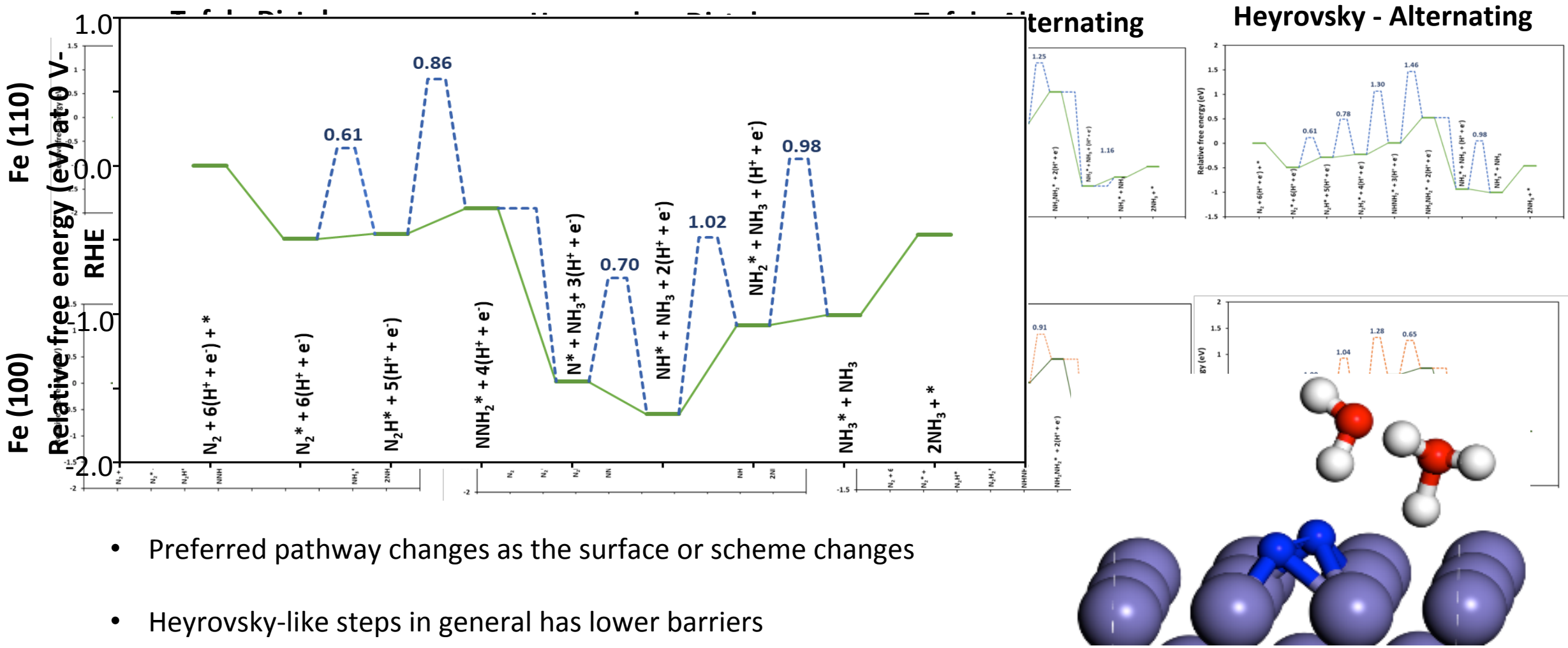


Initial "Reference" Transition




G. Rostamikia, et al., *Journal of Power Sources* **2011**, *196*, 9228-9237.

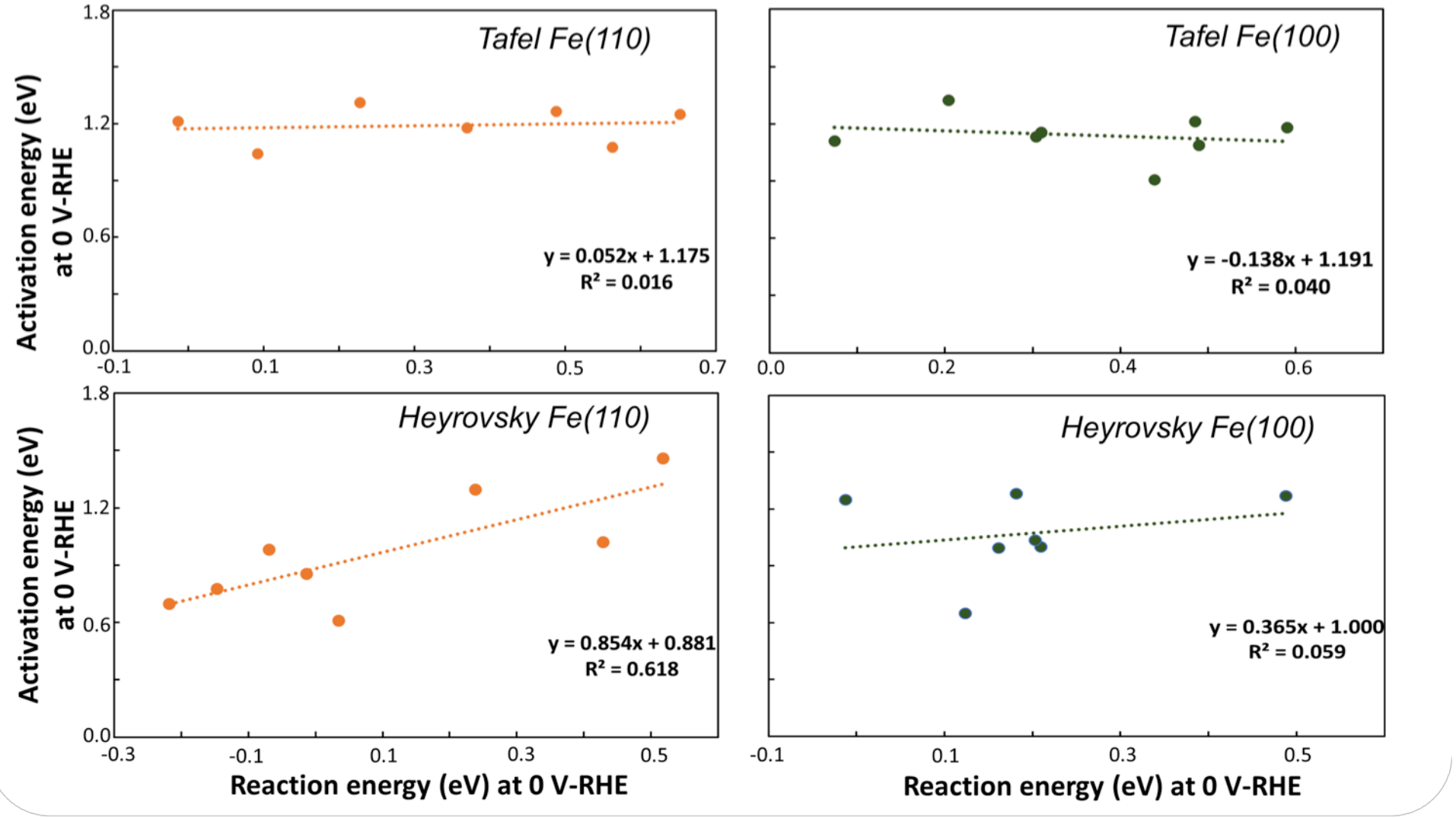
# Distal pathway under Heyrovsky-like steps on Fe (110) has lowest barriers



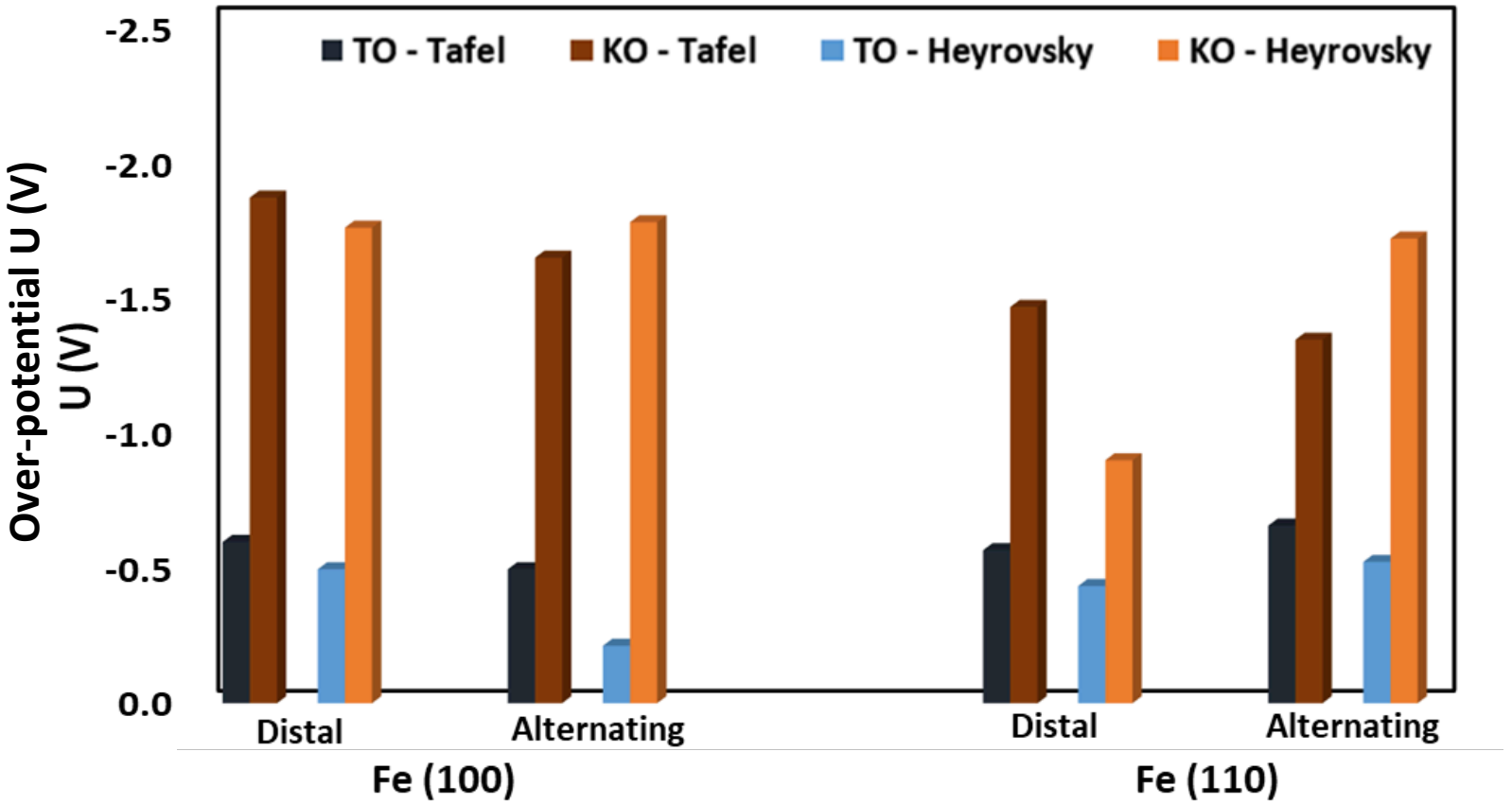

- Preferred pathway changes as the surface or scheme changes
- Heyrovsky-like steps in general has lower barriers

S. Maheshwari et al., Journal of Chemical Physics, (2018) (Accepted)

# BEP relationships fail to hold across N-H formation steps on Fe



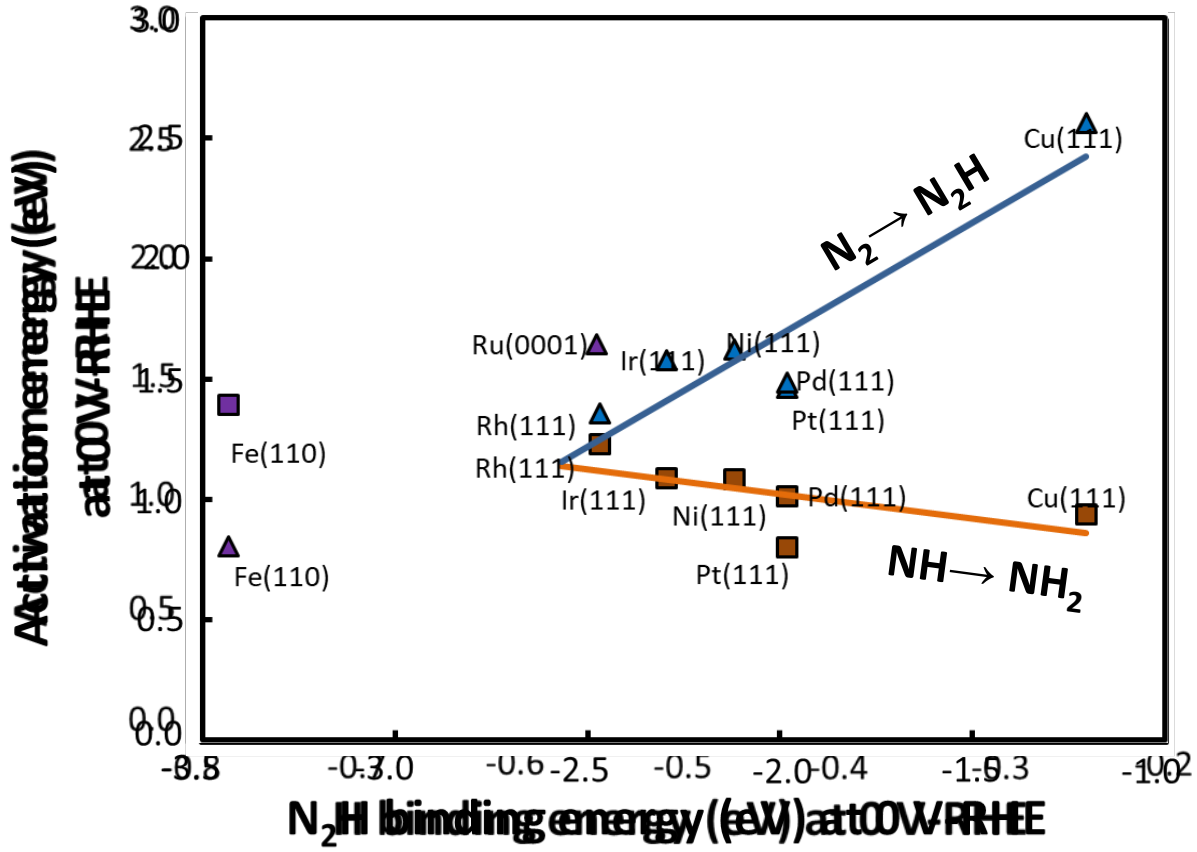
# Kinetic over-potential larger than thermodynamic over-potential




**KO –** Over-potential to make barrier for each step ≤ 0.4 eV at 0 V-RHE

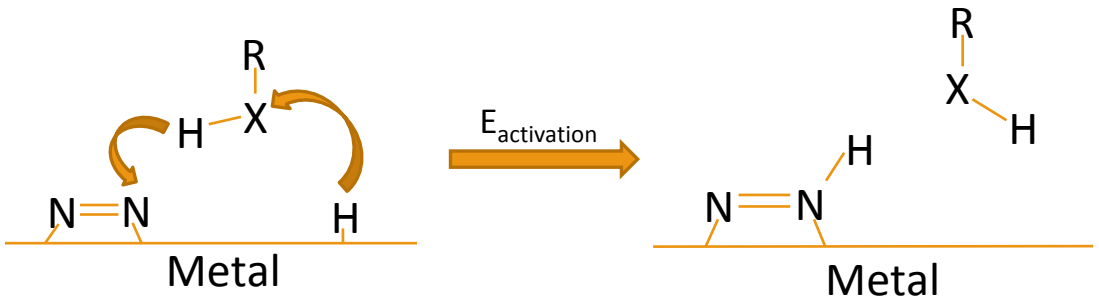
**TO** – Over-potential to make ΔG of each step ≤ 0 eV

# Kinetic Volcano and HER limits NRR on transition metals

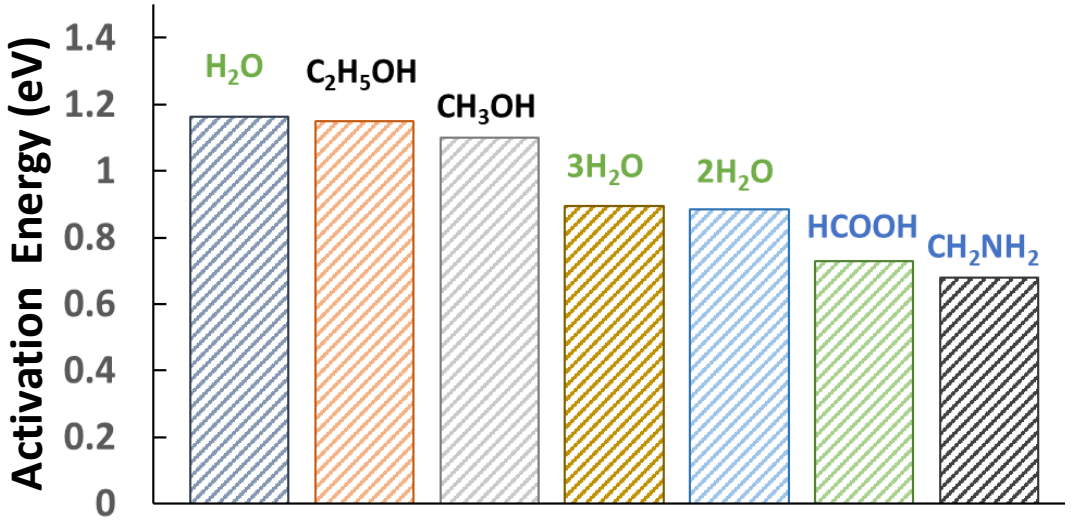



- BEP relationship across transition metals do not hold very well
- HER is highly selective across all transition metals

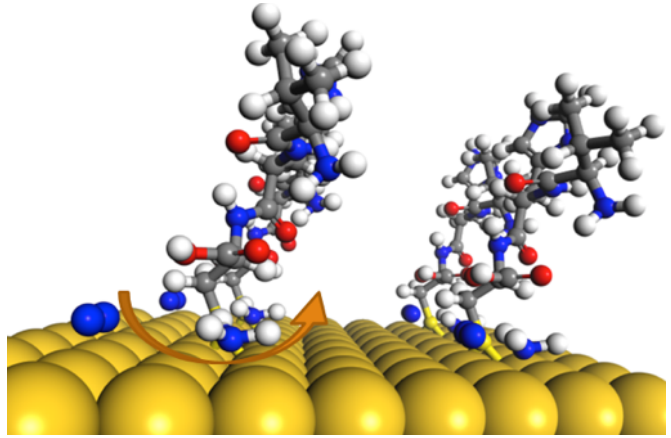
# Proton transfer agent can alter the activation barrier




RXH – Co-catalyst like $H_2O$, MeOH, HCOOH, $CH_3NH_2$ etc.




- Using explicit water molecules, essentially captured the solvation effects with 3 $H_2O$
- Amine and carboxylic acid have relatively smaller barrier



# Acknowledgement

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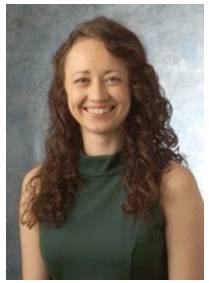

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# Thank You!