Surface Catalysis

Today we learned about the different mechanisms by which surfaces can catalyze reactions. You will now explore how surface modifications affect adsorption energy and reaction rates using given parameters and propose methods to evaluate your hypotheses.

1. First, draw a schematic energy profile of an uncatalyzed and a catalyzed reaction and explain why the catalyzed reaction is faster using also the Arrhenius equation (below), where E_a is the activation energy and A is a pre-exponential factor.

You are tasked with improving the efficiency of a Fe-based catalyst for ammonia synthesis. Consider two modifications:

- Creating a nanostructured Fe surface to increase active sites
- Alloying Fe with Ru

2. Using the Lennard-Jones potential equation for adsorption energy:
   Where:
   - Depth of the potential well (ϵ) = 0.5 eV
   - Distance where potential is zero (σ) = 3.0 Å
   - Distance between adsorbate and surface (r) = 2.5 Å

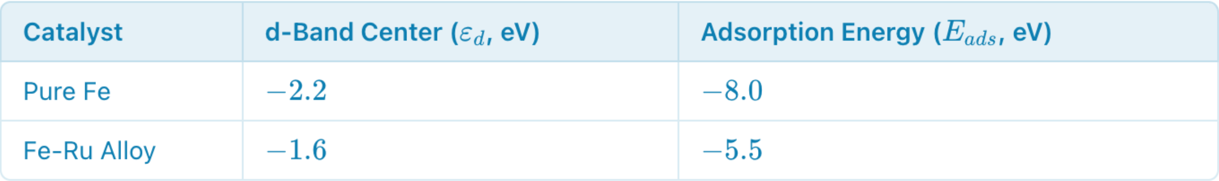
$$E_{ads} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

   Calculate the adsorption energy before and after nanostructuring if the distance between the adsorbate and the surface changes to 2.3 Å due to increased surface interactions? Further, can you please explain why nanostructuring would decrease this distance?

3. From the adsorption energy calculated in the previous problem, we can relate this to the activation energy of the catalytic process. What is the relationship and how can we make this correlation?

4. In what contexts does this approximation of E_{ads} and E_a fail?

5. Alloying Fe with Ru shifts the d-band center of the catalyst surface closer to the Fermi level. This change weakens the bond between the adsorbate and the catalyst. Consider the following data for the d-band center (ε_d) and adsorption energy (E_{ads}):



Catalyst	d-Band Center (ε_d, eV)	Adsorption Energy (E_{ads}, eV)
Pure Fe	-2.2	-8.0
Fe-Ru Alloy	-1.6	-5.5

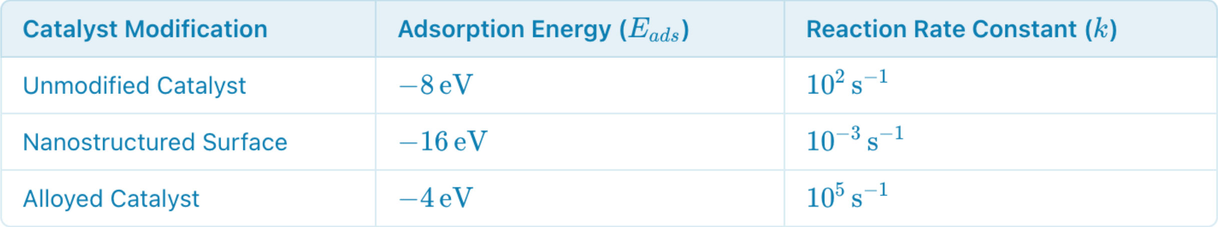
a) Explain why shifting the d-band center closer to the Fermi level weakens adsorption energy.

b) Calculate the fractional change in adsorption energy after alloying Fe with Ru.

c) Discuss how alloying affects the trade-off between adsorption strength and reaction turnover frequency (TOF).

d) Given that alloying often introduces heterogeneity in the surface composition, propose an experimental technique (that you've seen in this class) to study whether the alloyed catalyst surface has uniform activity.

6. Consider a catalytic reaction where the adsorption energy (E_{ads}) is a critical factor in determining the reaction rate. Using the following table, which shows the adsorption energy and reaction rate constants (k) for different catalyst modifications, analyze the trends and answer the questions below.



Catalyst Modification	Adsorption Energy (E_{ads})	Reaction Rate Constant (k)
Unmodified Catalyst	$-8\,\mathrm{eV}$	$10^{2}\,\mathrm{s}^{-1}$
Nanostructured Surface	$-16\,\mathrm{eV}$	$10^{-3}\,\mathrm{s}^{-1}$
Alloyed Catalyst	$-4\,\mathrm{eV}$	$10^{5}\,\mathrm{s}^{-1}$

a) **Identify the Trend:** What is the relationship between E_{ads} and k in the table? Does increasing the adsorption energy always lead to higher reaction rates? Why or why not?

b) **Hypothesize the Cause:** Based on your observations, hypothesize why excessively strong adsorption energy might hinder reaction rates.

c) **Propose an Optimal Catalyst:** Suggest an adsorption energy range (E_{ads}) that would balance reactant interaction and desorption to maximize k. Justify your suggestion.

d) **Explain with Real-World Relevance:** Relate your conclusion to an industrial catalytic process, such as ammonia synthesis, where both adsorption and desorption are critical.

Key Takeaways from this Exercise:

- Catalysis is a surface phenomenon where changes in surface properties directly affect adsorption and reaction rates. We emphasize the importance of finding a balance between molecular interactions, energy landscapes, and reaction dynamics.

- Methods like alloying (changing electronic properties) and nanostructuring (increasing surface interactions) are ways to fine-tune catalysts for specific applications.

- Catalyst optimization requires careful consideration of trade-offs (adsorption energy, surface area, reaction kinetics) to achieve optimal performance.

- Understanding the adsorption-desorption balance and its relation to the turnover frequency (TOF).