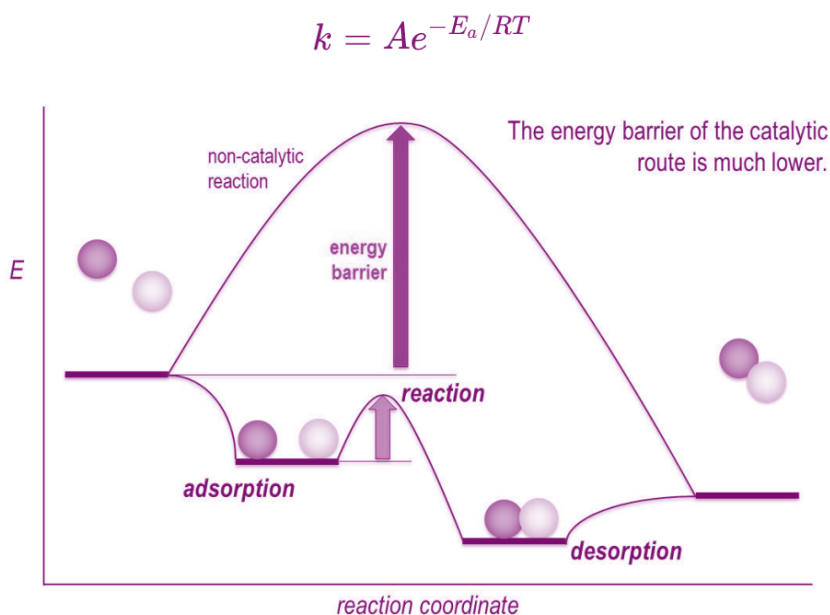


Surface Catalysis

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.



Activation barrier E_a of a catalyzed reaction is lower than for an uncatalyzed reaction. The Arrhenius equation describes the relationship between activation energy and reaction rate. Lower $E_a \rightarrow$ higher rate for given T .

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?

Adsorption energy before nanostructuring ($r = 2.5$ Å):

$$E_{ads} = 4(0.5) \left[\left(\frac{3.0}{2.5} \right)^{12} - \left(\frac{3.0}{2.5} \right)^6 \right]$$

$$E_{ads} = 11.86 \text{ eV}$$

Adsorption energy after nanostructuring ($r = 2.3$ Å):

$$E_{ads} = 4(0.5) \left[\left(\frac{3.0}{2.3} \right)^{12} - \left(\frac{3.0}{2.3} \right)^6 \right]$$

$$E_{ads} = 38.66 \text{ eV}$$

The nanostructured surface significantly increases adsorption energy, which enhances catalytic efficiency by strengthening surface interactions. Nanostructuring increases the surface roughness and creates unique geometric features (edges, steps, and corners). These features:

- Bring the adsorbate molecule closer to the surface atoms due to stronger local interactions (*e.g.*, enhanced van der Waals forces or chemical bonding).
- Provide a higher density of active sites that interact more efficiently with the adsorbate, effectively reducing r , the equilibrium distance.

By reducing r , nanostructuring amplifies the adsorption energy, making the catalyst more efficient.

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?

In catalytic processes:

- **Adsorption energy (E_{ads})** measures how strongly a reactant binds to the catalyst surface. Strong adsorption can lower the energy barrier for subsequent reaction steps.
- **Activation energy (E_a)** is the energy required for the reactant to transition from the adsorbed state to the reaction's intermediate or product state.

For simplicity, E_a can be **approximated** as proportional to $|E_{ads}|$ because the adsorption step is often the rate-limiting step (especially in reactions with weakly bound molecules). This assumes:

- The energy required to overcome the adsorbed state is closely linked to how strongly the reactant binds.
- The desorption or transition to the intermediate/product involves a similar amount of energy.

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

- **Weak Adsorption:** If adsorption is weak, the energy barrier for the reaction step could depend more on other factors, such as bond rearrangement or surface diffusion, and E_a might not equal $|E_{ads}|$. Only when adsorption dominates the reaction dynamics (e.g., reactant is immobilized on the surface), the energy barrier to proceed further correlates with adsorption strength.
 - **Multistep Reactions:** In complex mechanisms, E_a is determined by the highest energy barrier in the entire pathway, not just the adsorption step.
 - **Desorption-Limited Processes:** If desorption is the rate-limiting step (e.g., product release), E_a will depend on desorption energy rather than $|E_{ads}|$.
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.
- The d-band center (ϵ_d) reflects the energy level of the catalyst's d-electrons.
 - When ϵ_d is closer to the Fermi level, the overlap between the adsorbate's antibonding orbitals and the catalyst's d-orbitals decreases.
 - This weakens the chemical bond between the adsorbate and the surface, resulting in lower adsorption energy. Alloying Fe with Ru shifts ϵ_d from -2.2 eV to -1.6 eV, weakening the adsorption energy from -8.0 eV to -5.5 eV.
- b) Calculate the fractional change in adsorption energy after alloying Fe with Ru.

$$\Delta E_{ads, \text{fraction}} = \frac{|E_{ads, \text{initial}} - E_{ads, \text{final}}|}{|E_{ads, \text{initial}}|}$$

$$\Delta E_{ads, \text{fraction}} = \frac{|-8.0 + 5.5|}{8.0} = \frac{2.5}{8.0} = 0.3125$$

- c) Discuss how alloying affects the trade-off between adsorption strength and reaction turnover frequency (TOF).
- **Before Alloying ($E_{ads} = -8.0$ eV):** Strong adsorption ensures that reactants bind securely to the catalyst. However, this can lead to slower desorption of intermediates or products, reducing TOF.
 - **After Alloying ($E_{ads} = -5.5$ eV):** The weaker adsorption energy allows easier desorption, freeing active sites more quickly. This increases TOF and overall catalytic efficiency.
 - Alloying optimizes the balance between adsorption and desorption, enhancing catalytic performance.

- 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.

You could use STM to image the atomic-scale surface of the alloyed catalyst and map the local electronic density of states.

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 eV	10^2 s^{-1}
Nanostructured Surface	-16 eV	10^{-3} s^{-1}
Alloyed Catalyst	-4 eV	10^5 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?

The reaction rate (k) increases initially as adsorption energy becomes stronger (up to a certain point), but when adsorption energy becomes excessively strong ($E_{ads} = -16 \text{ eV}$), the reaction rate decreases significantly.

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

Strong adsorption ($E_{ads} = -16 \text{ eV}$) immobilizes the reactant on the catalyst surface, making it difficult for the reactant to desorb or proceed to the next reaction step, which leads to a "bottleneck" effect, where the surface is effectively blocked, and turnover frequency (TOF) is reduced. In contrast, moderate adsorption energy ($E_{ads} = -8 \text{ eV}$) allows the reactant to interact with the surface while still enabling efficient desorption.

- 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.

The optimal adsorption energy should strike a balance between:

- **Sufficient Reactant Interaction:** The adsorbate must stay on the surface long enough to participate in the catalytic reaction.
- **Efficient Product Desorption:** The products must leave the surface to free up active sites.

Based on the data:

- Excessively strong adsorption ($E_{ads} = -16 \text{ eV}$) hinders desorption.
- Weak adsorption ($E_{ads} = -4 \text{ eV}$) allows fast desorption but might reduce the surface coverage of reactants.

Suggested Range: An optimal adsorption energy is likely between -6 eV and -10 eV, where the balance between adsorption and desorption is most favorable.

- 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.

In ammonia synthesis, the adsorption of N_2 on iron-based catalysts is a critical step. If N_2 adsorption is too weak, insufficient N_2 molecules will bind to the surface, reducing the reaction rate. If N_2 adsorption is too strong, it will block active sites and hinder the formation of NH_3 due to poor desorption.

Catalyst optimization in this process involves alloying iron with promoters like potassium or ruthenium to adjust the adsorption energy and maximize catalytic efficiency.

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).