

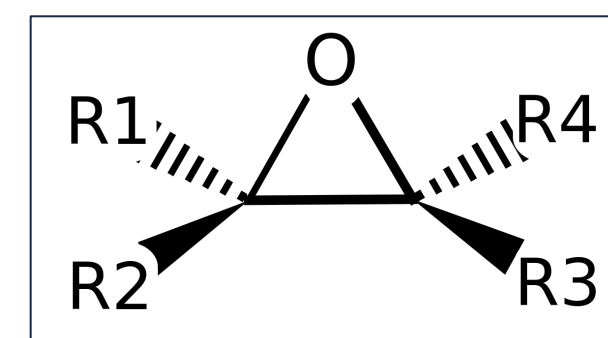
Effects of Hydrophobicity of Group IV and V Framework-Substituted Zeolite Catalysts on Rates and Selectivities for Olefin Epoxidation

Alayna Johnson, Daniel Bregante, David Flaherty

Department of Chemical and Biomolecular Engineering, College of Liberal Arts and Sciences, University of Illinois at Urbana-Champaign

Rationale

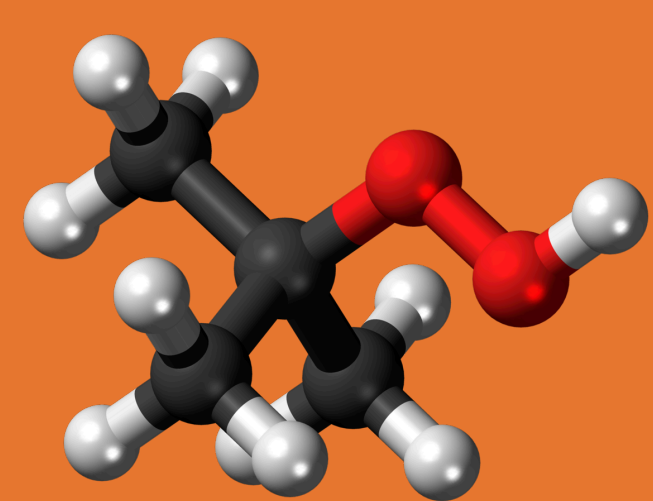
- Epoxides are important for the production of plastics, fragrances, and pharmaceuticals.¹
- Current methods for epoxide synthesis use harmful oxidants:



Skeletal structure of an epoxide

Organic oxidizers

- ✓ Enantioselective
- ✗ Produce toxic co-products that must undergo energy-intensive separation steps²



tert-Butyl hydroperoxide, a common organic oxidizer

Chlorine

- ✓ Effective on a large scale
- ✗ Produces harmful co-products (e.g. propylene chlorohydrin and 1,2-dichloropropane)³



Oxygen gas

- ✓ Potential for perfect atom economy
- ✗ 10% over-oxidizes to form carbon dioxide⁴
- ✗ Ineffective for large olefins



- Hydrogen peroxide (H₂O₂), which produces only water, could replace less-green oxidants, but a catalyst is required.
- Hydrophobicity is known to influence the effectiveness of such catalysts.

Materials and Methods

Catalyst synthesis and characterization

Starting material: *BEA zeolite Si:Al ~12.5

Starting material: *BEA zeolite Si:Al ~150

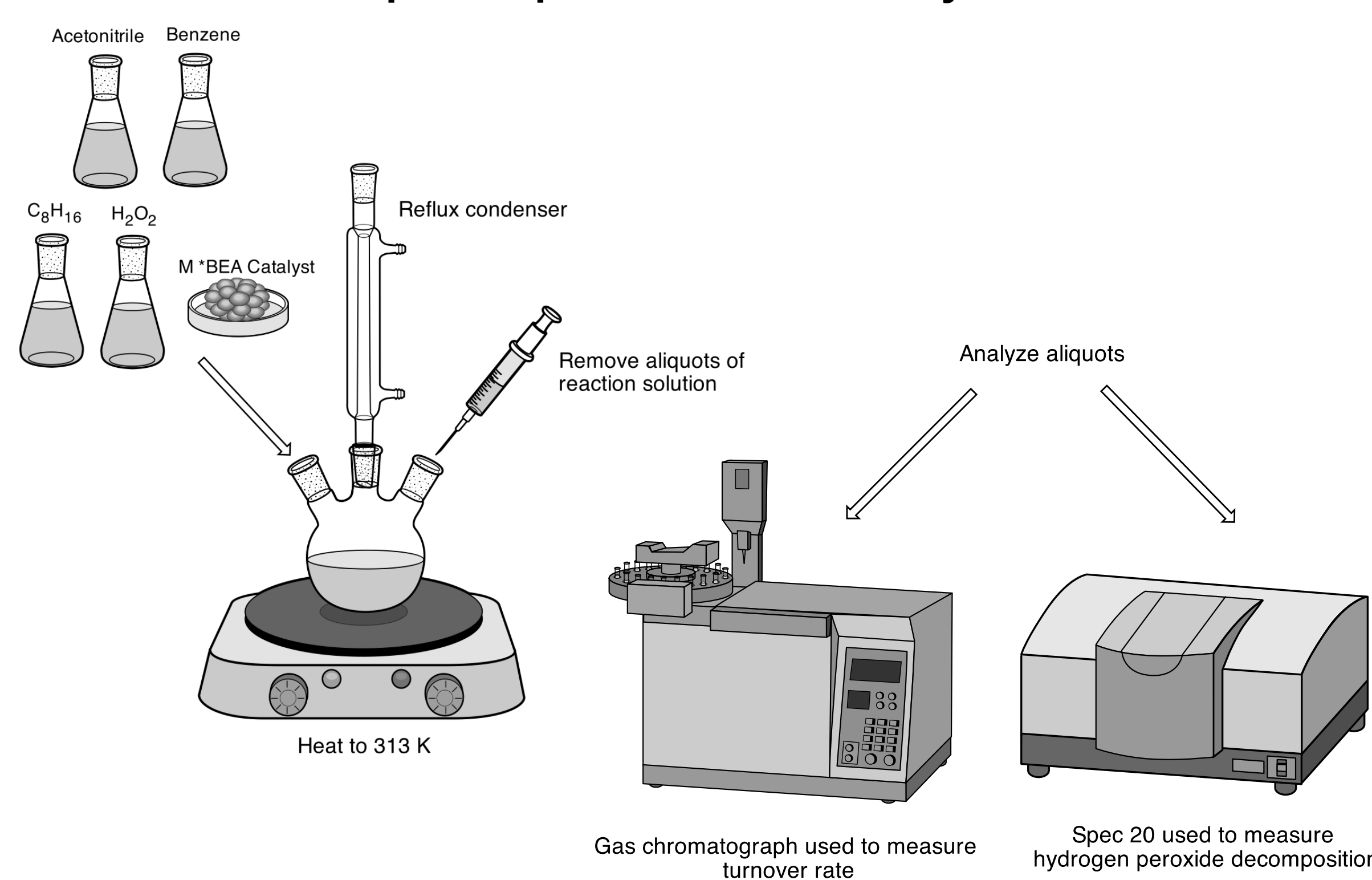
Dealumination, metal incorporation, and heat treatment⁵

Hydrophilic *BEA catalyst

Hydrophobic *BEA catalyst

Characterization: EDXRF, p-XRD, DRUV, and FTIR

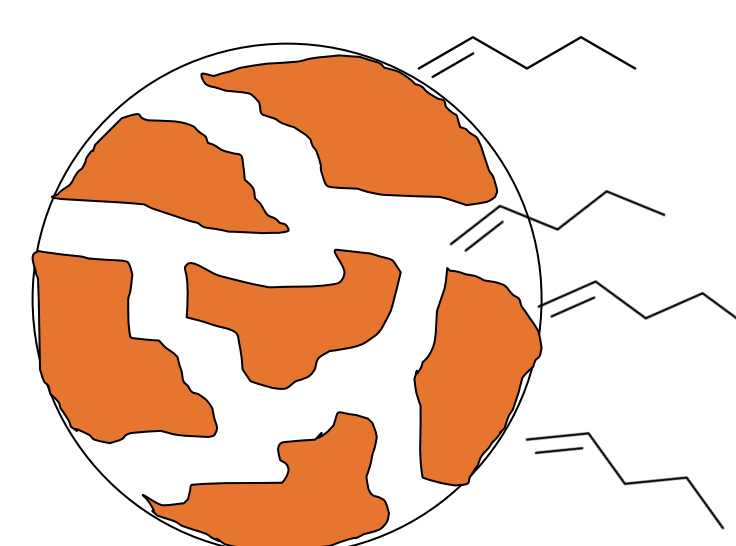
Epoxide production and analysis



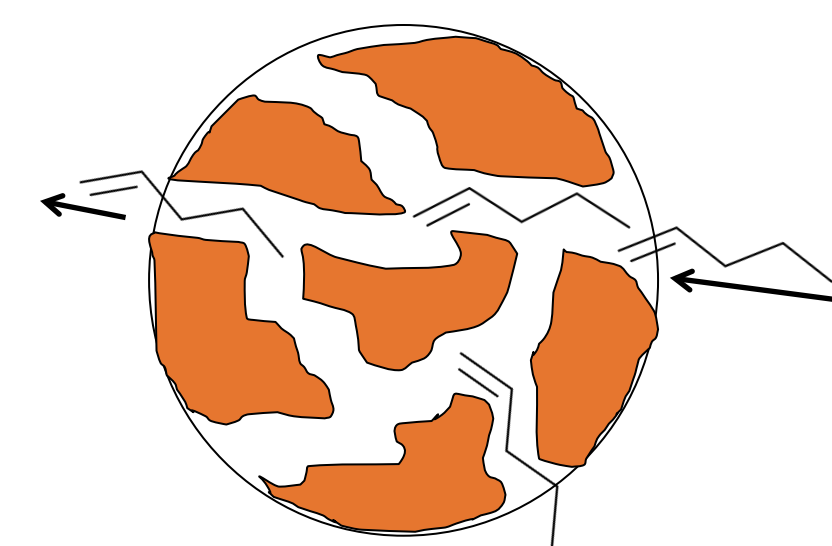
Aims and Theoretical Background

1. Determine what weight percent of catalyst should be used as to avoid mass-transfer limitations.

- If olefins diffuse too slowly or react too quickly, a concentration gradient occurs. This prevents meaningful comparison of reaction rates.
- For systems that are not mass-transfer limited, turnover rate is independent of catalyst loading.

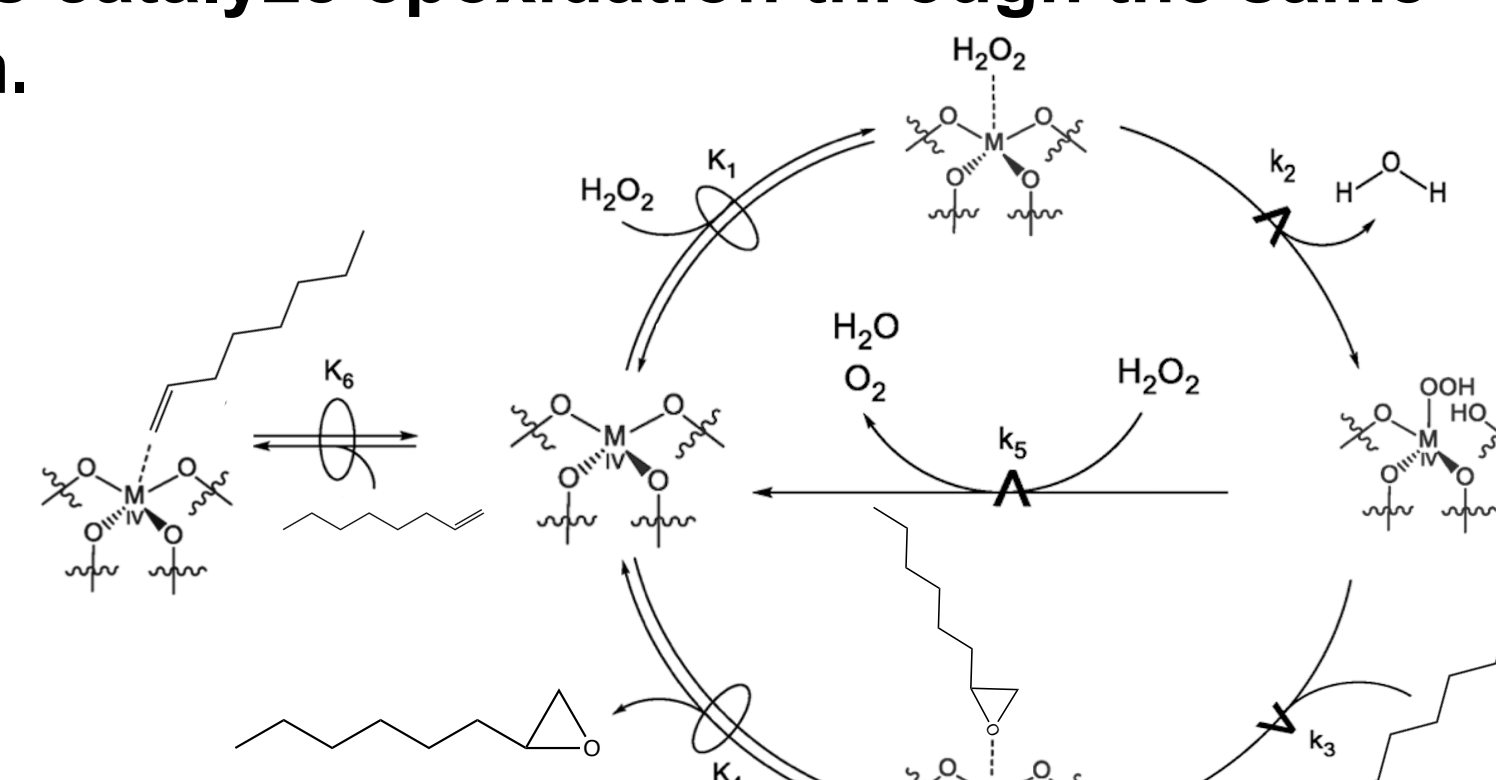


- System with mass transfer-limitations
- Olefin molecules are interacting with only the outside of the catalyst.
- Molecules are not diffusing into the catalyst fast enough, creating a concentration gradient.



- System without mass transfer-limitations
- Olefin molecules are interacting with both the inside and outside of the catalyst.
- Molecules are quickly diffusing into the catalyst so olefin concentration is the same throughout the catalyst.

2. Confirm the mechanism for olefin epoxidation and ensure that all materials catalyze epoxidation through the same mechanism.



Mechanism for octene epoxidation⁶

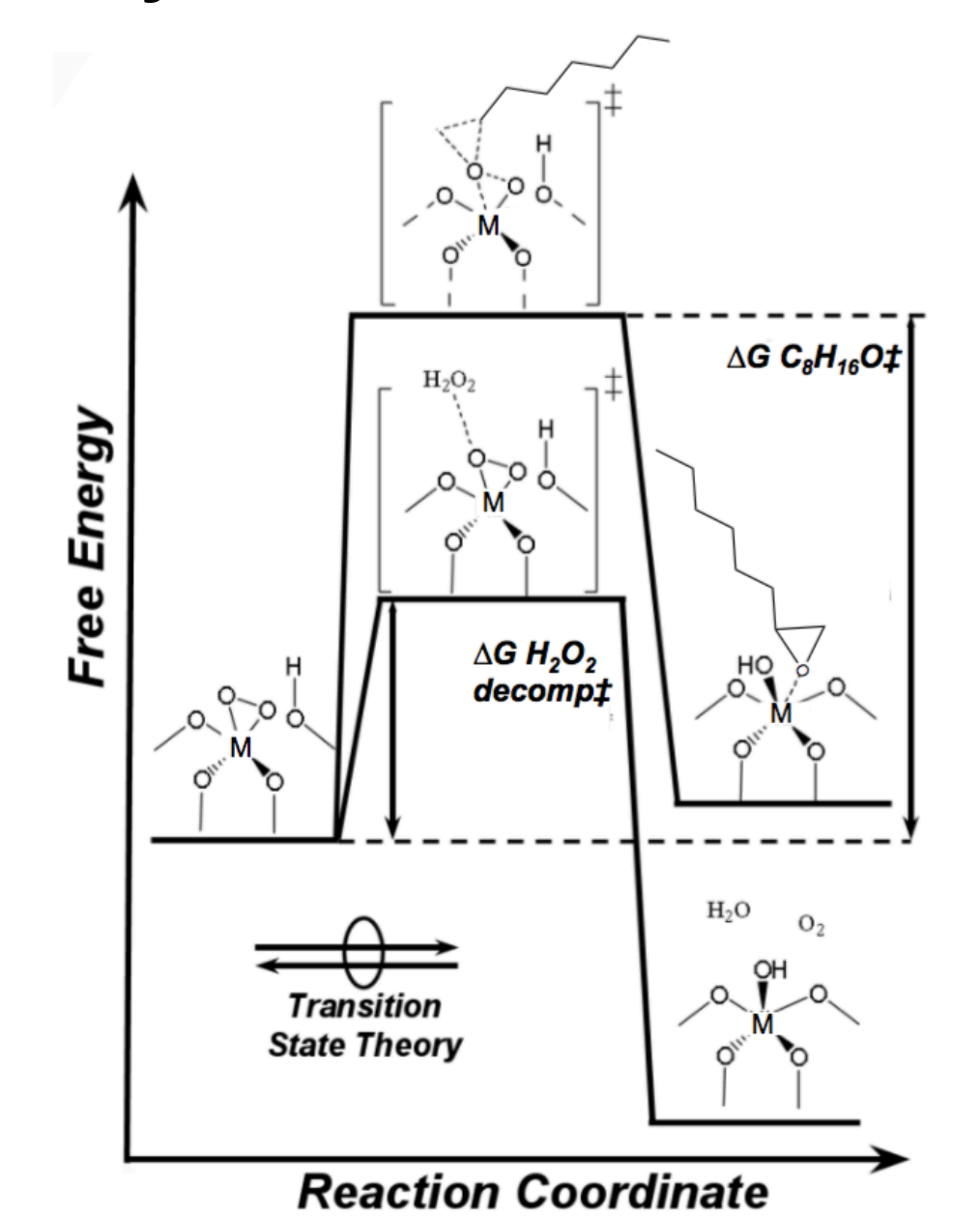
- The general rate expression for octene epoxidation is

$$\frac{r}{[L]} = \frac{k_3 k_4 K_2 [C_8H_{16}] \cdot [H_2O_2]}{(k_4 [C_8H_{16}] + k_6 [H_2O_2]) (1 + K_1 [C_8H_{16}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{k_4 [C_8H_{16}] + k_6 [H_2O_2]} + K_5 [C_8H_{16}O])}$$

- When M-(O₂) is the most abundant surface intermediate (MASI), the expression simplifies to $\frac{r}{[L]} = k_4 [C_8H_{16}]^{-1} [H_2O_2]^0$
- Under conditions where this rate expression is true, the MASI is known so activation barriers are comparable.

3. Investigate how catalyst hydrophobicity affects rates and selectivities for olefin epoxidation.

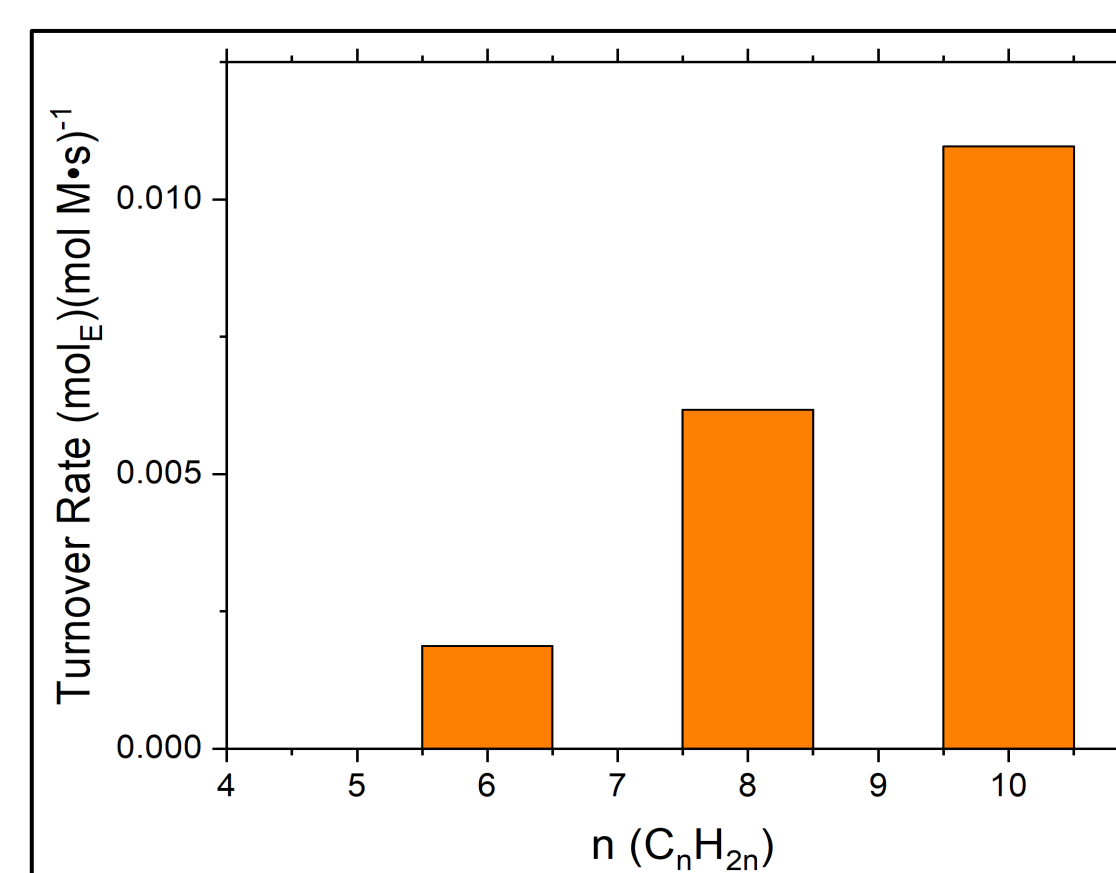
- Turnover rates are directly related to K[‡], the equilibrium constant for the formation of the transition state.
- The slope and y-intercept of a K[‡] v. inverse temperature plot are related to the enthalpy and entropy of a reaction respectively according to the Eyring equation: $\ln(K^\ddagger) = \Delta S^\ddagger/R - \Delta H^\ddagger/RT$



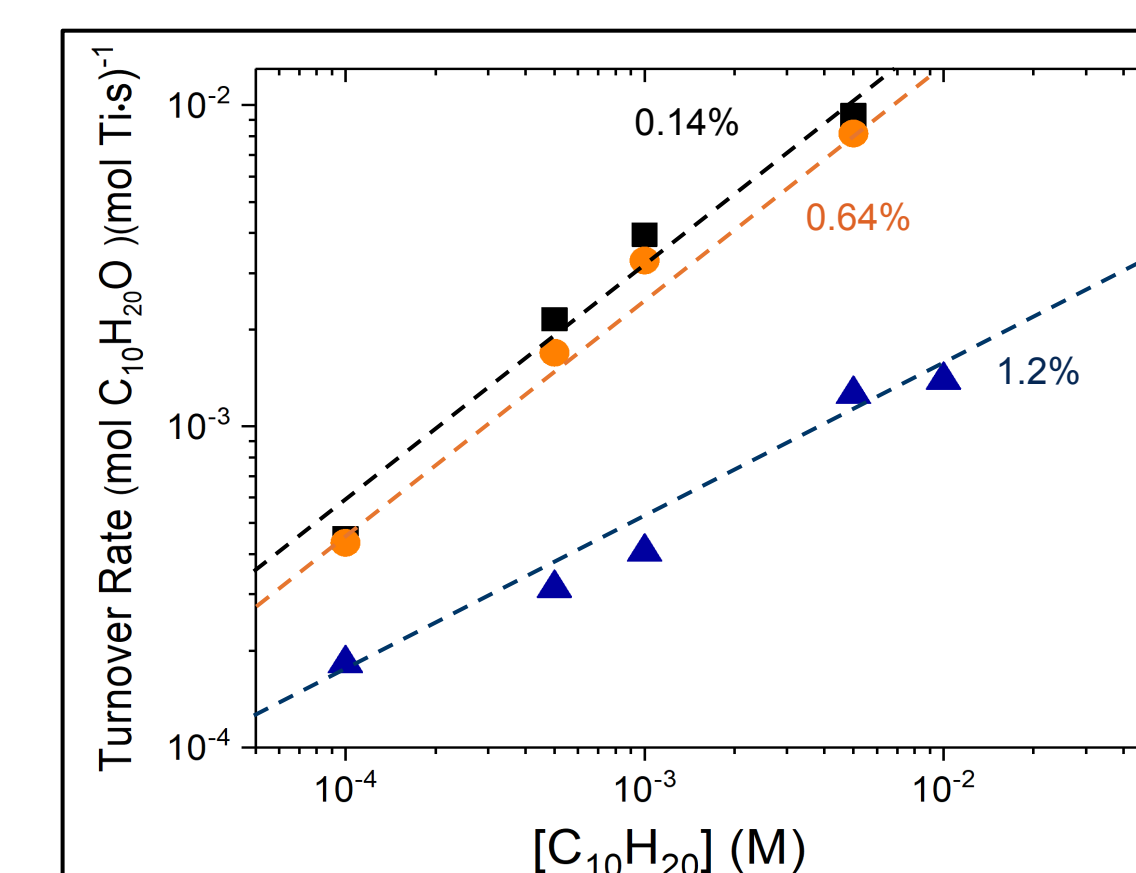
Thermochemical cycle for octene epoxidation⁷

Results

1. Determination of mass-transfer limitations



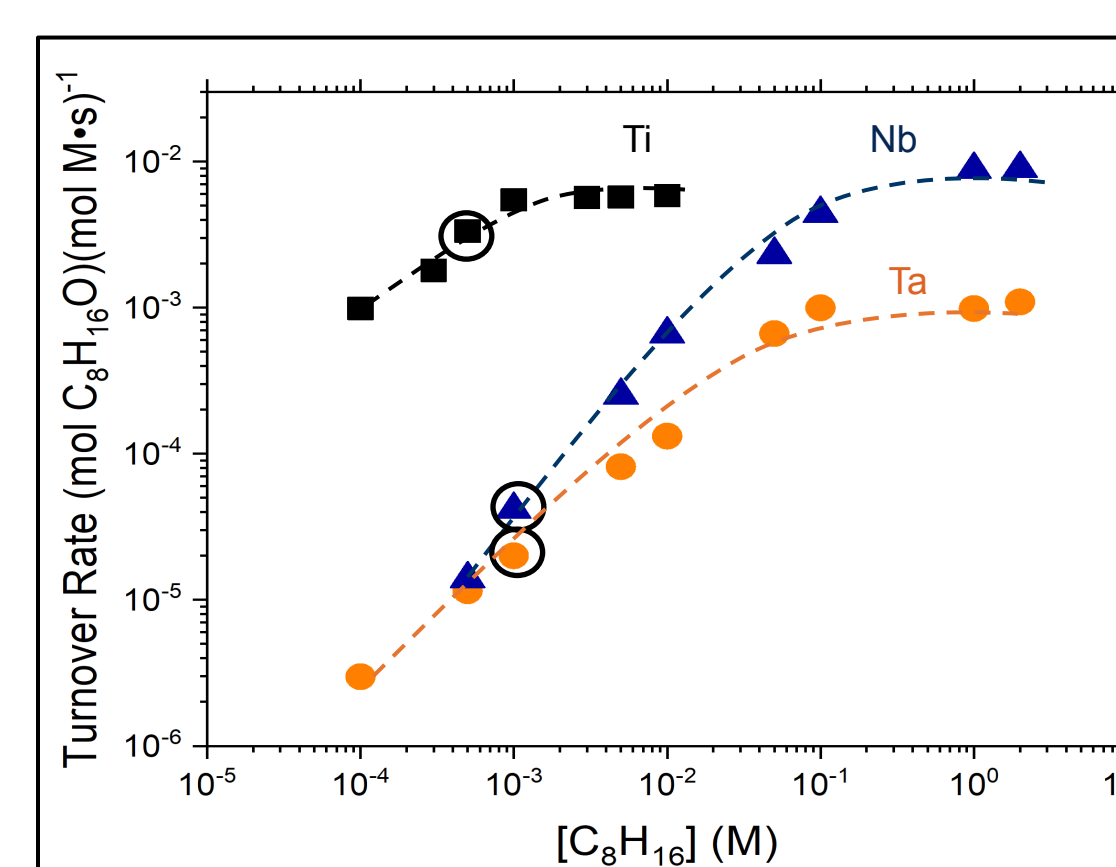
Turnover rate as a function of olefin chain length.



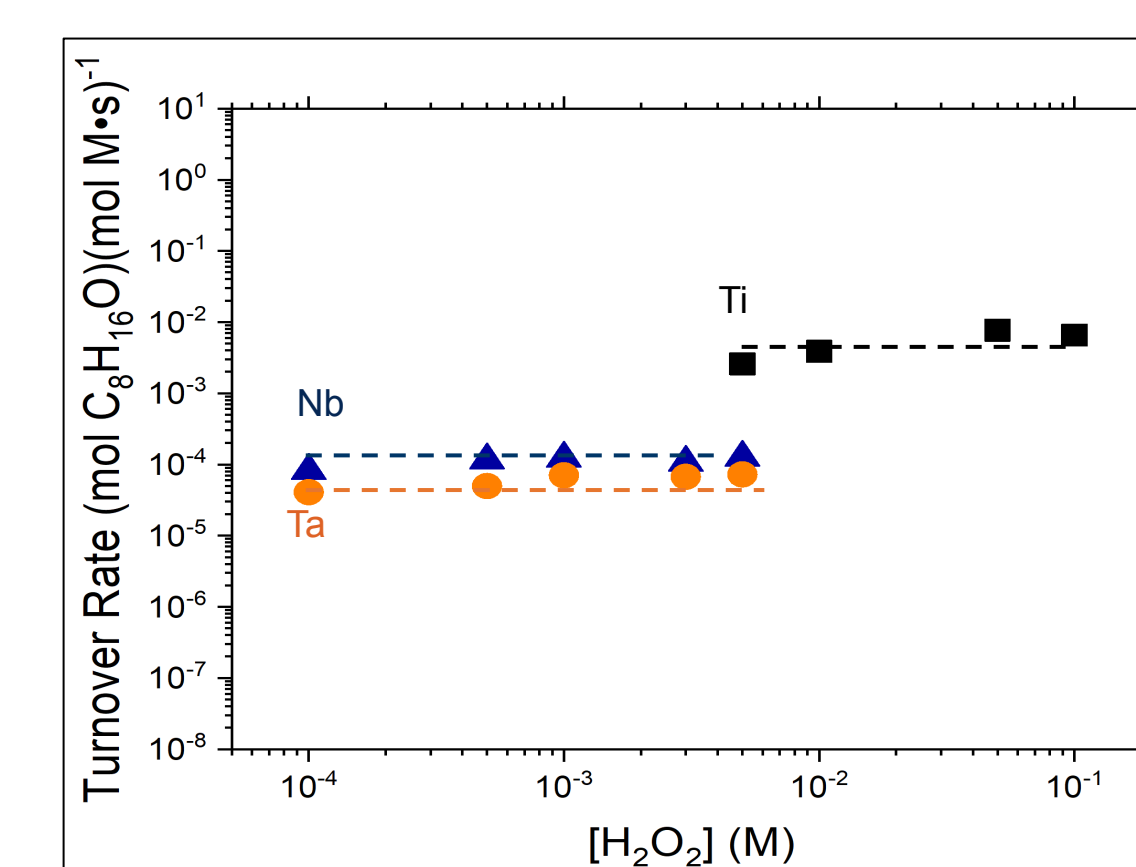
Turnover rate as a function of olefin concentration for various weight percents of Ti *BEA catalyst.

- Large olefins are most likely to be mass-transfer limited.
- Turnover rate does not depend on weight loading in the range of 0.14% to 0.64%—not mass-transfer limited.
- Turnover rates are ~10x smaller for weight loadings of 1.2% and larger—mass-transfer limited.

2. Determination of epoxidation mechanisms



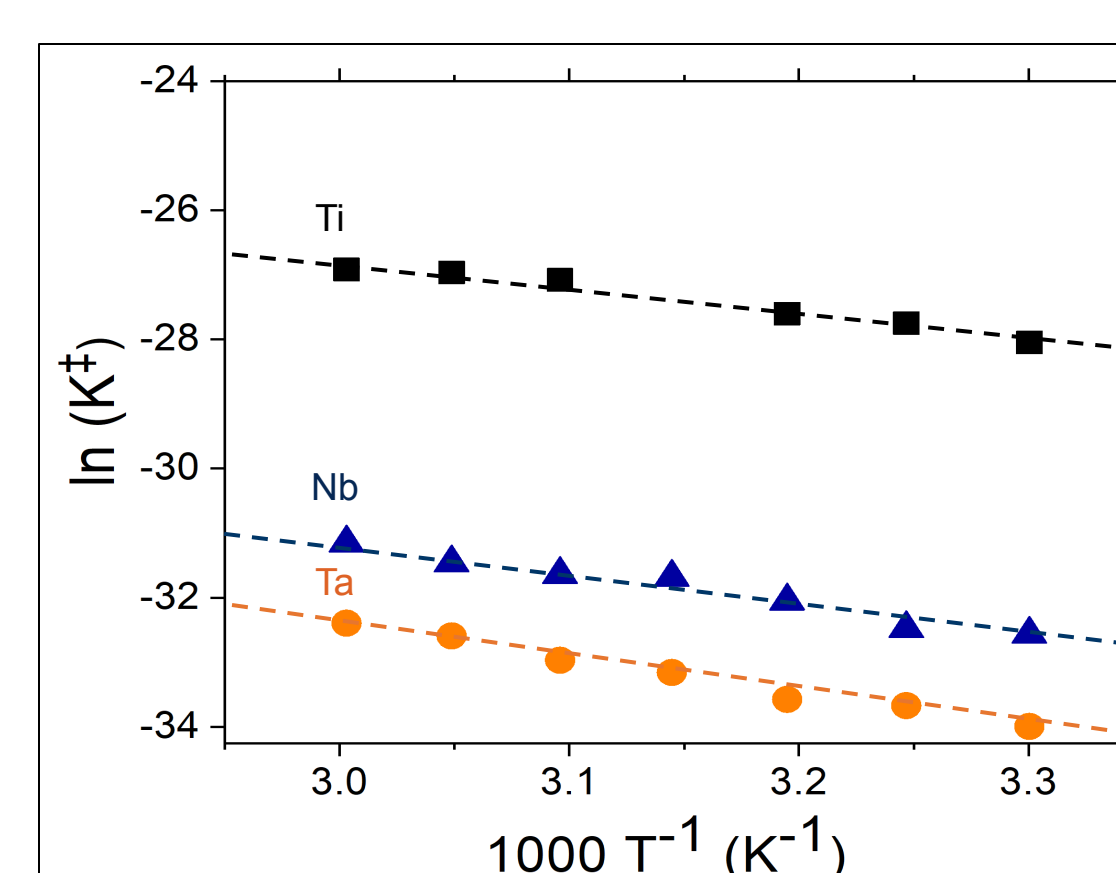
Turnover rate as a function of octene concentration for Ti *BEA, Nb *BEA, and Ta *BEA catalysts. Circled data represent the octene concentrations used for the hydrogen peroxide-dependent experiments (right).



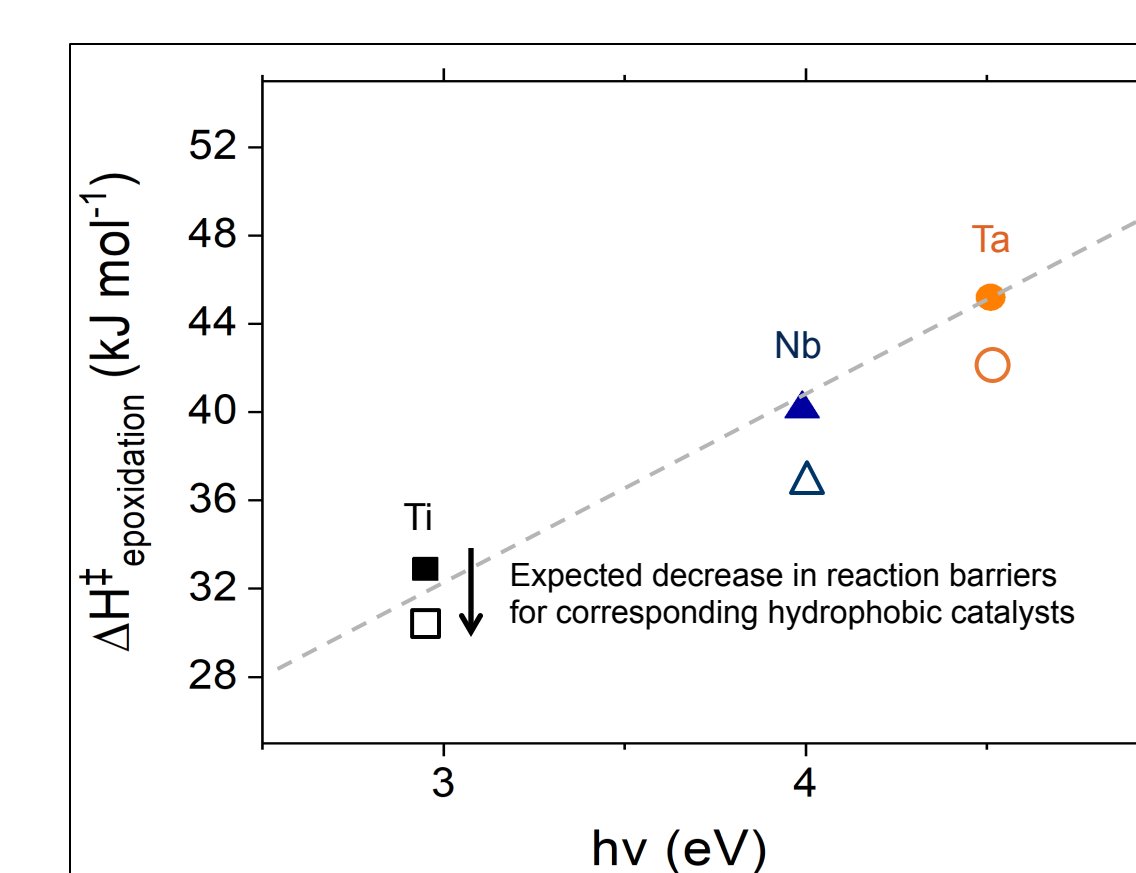
Turnover rate as a function of H₂O₂ concentration for Ti *BEA, Nb *BEA, and Ta *BEA catalyst.

- Conditions have been found such that turnover rate is first-order dependent on octene concentration and zero-order dependent on H₂O₂ concentration.
- Under these conditions, the MASI is known.

3. Determination of reaction barriers



Natural log of K[‡] as a function of inverse temperature for Ti *BEA, Nb *BEA, and Ta *BEA catalysts.



Activation barriers as a function of metal identity (expressed as hv) for Ti *BEA, Nb *BEA, and Ta *BEA catalyst

- Ti is the most active for olefin epoxidation
- Since octene is hydrophobic and H₂O₂ is hydrophilic, activation barriers should decrease for more hydrophobic catalysts.

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