

Structure-Property-Performance Catalyst Matrix:

Tuning Catalyst Design Pathways: A Holy Grail for Rational Design of Industrial Functional Materials



IICHE (NRC) and FAI, New Delhi

Recent Developments in Catalysis in Process Industry

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IITD ChemE
Department of Chemical Engineering

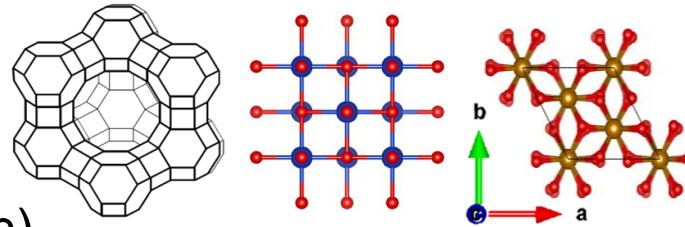
Overall Perspective: Catalyst System

Heterogeneous Catalytic System

□ Catalysts

- Lewis Acid Sites (Metal)
- Bronsted Acid Sites (Proton)

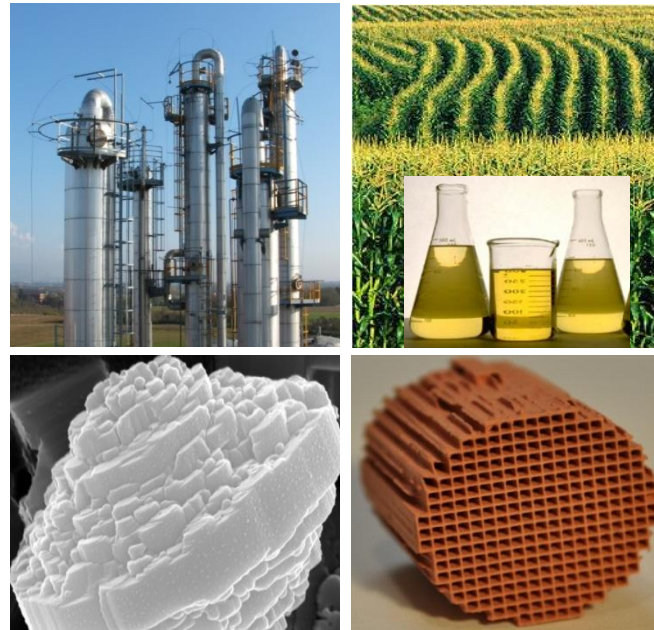
□ Support



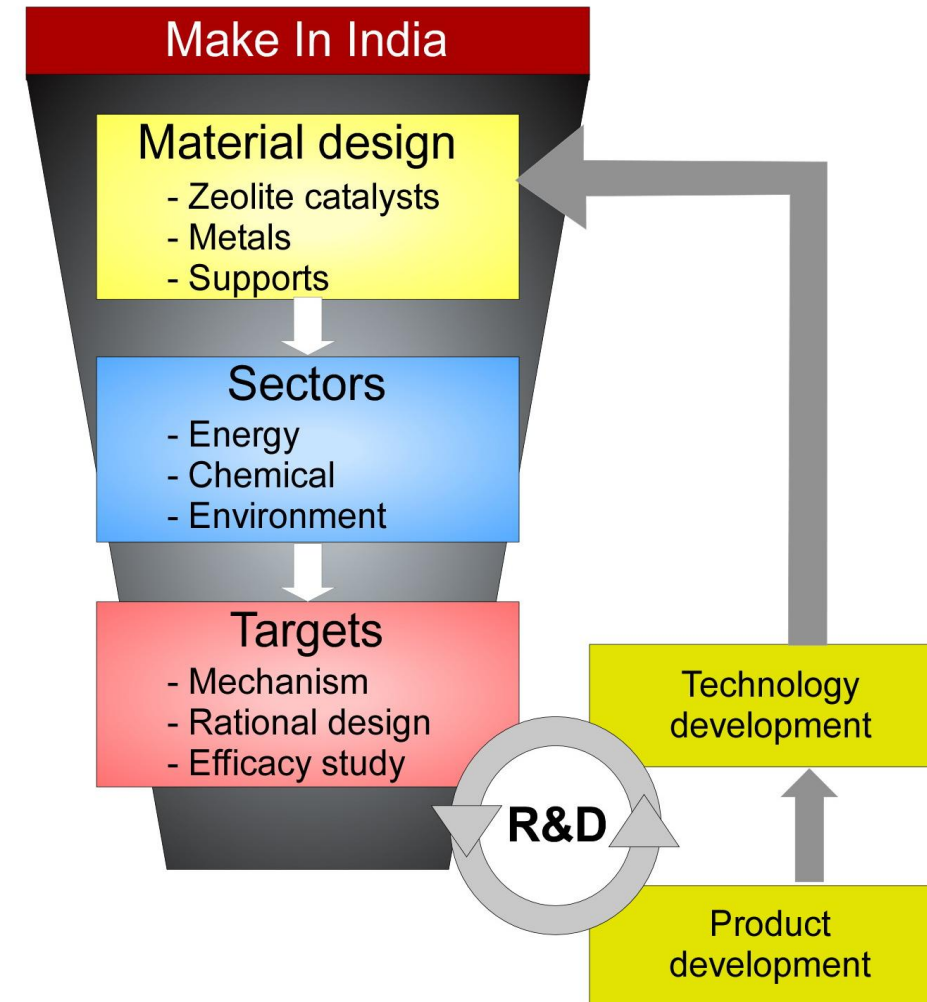
Bifunctional Material

Classic & Novel Application

- Petroleum refining
- Chemicals
- Biomass conversion
- Energy
 - MTH, MTO, MTD, H₂
- Emissions (NO_x, CCUS)



Catalyst Optimization Loop



Sustainable Structure-Property-Performance Catalyst Matrix

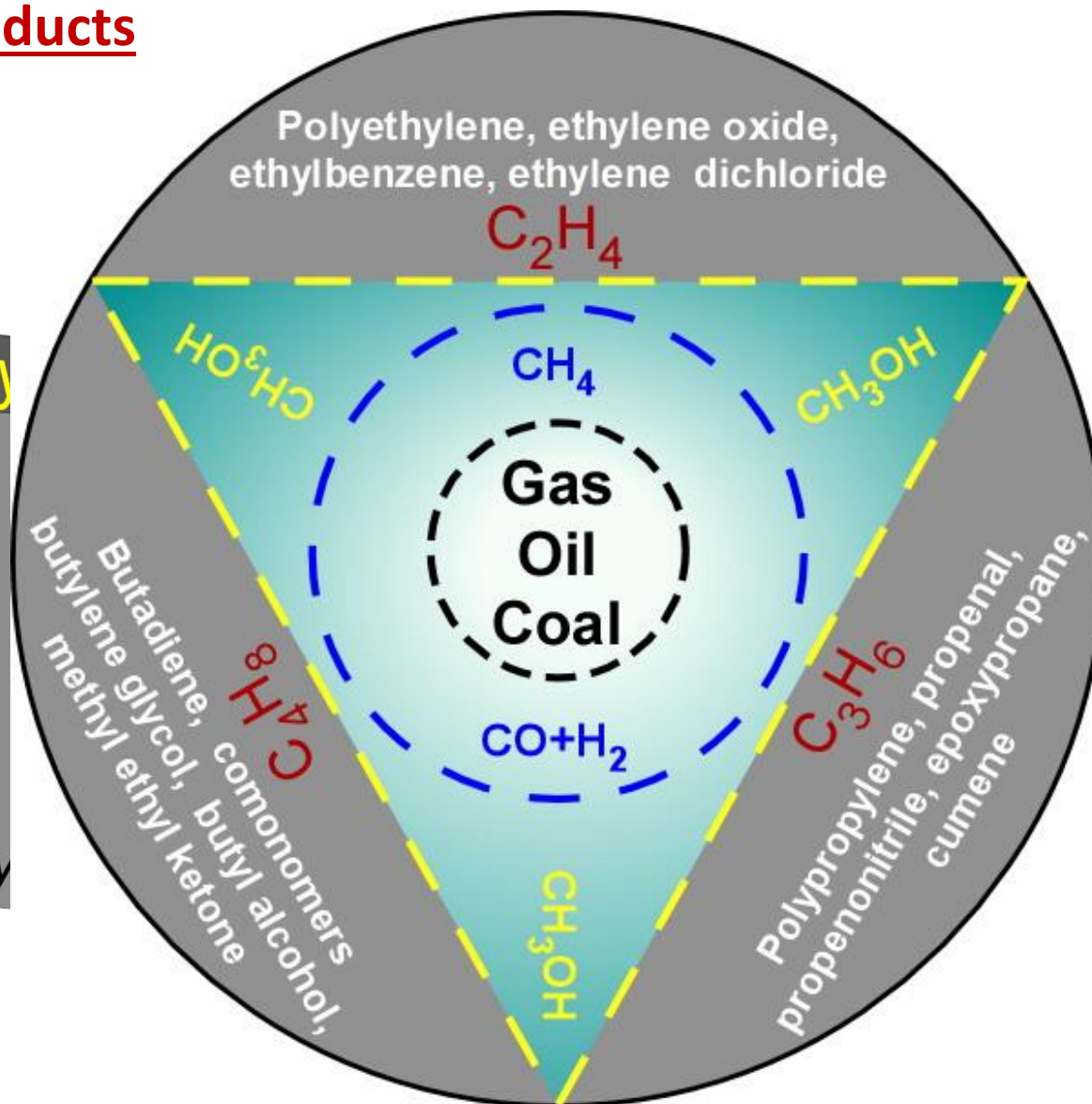


Case Study: Fossils to Products

□ Holy Grail

Structure-Property

- Pore Size
- Cage /Cavity Size
- Defects
- Crystal Size
- Acid sites
- Mesoporosity
- Hydrothermal stability

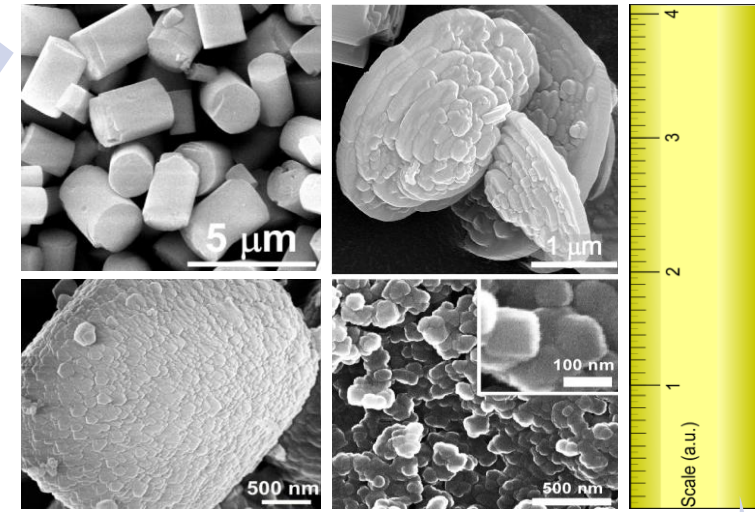
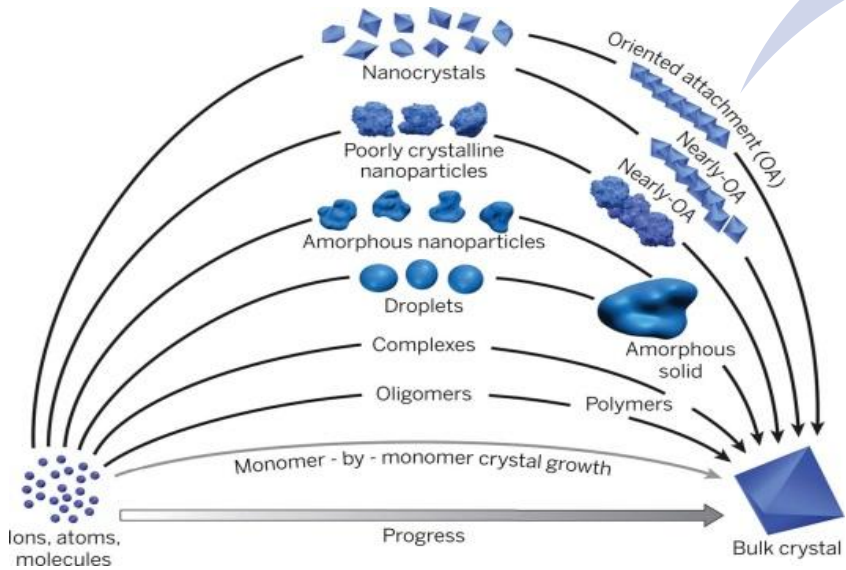


Performance

- Yield (conversion)
- Activity
- Stability (lifetime)

Knowledge Gap and Potential

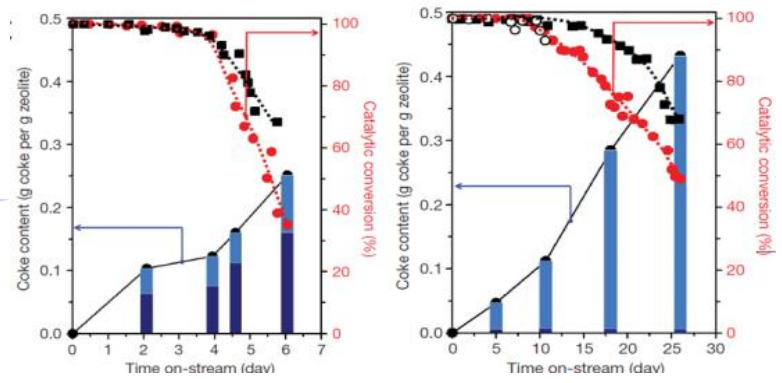
Complex Growth Mechanism (Fate determining step)



Novel Material (Properties)

- Particle Size
- Porosity
- Defects
- Acidity

Product Translation (Efficiency)



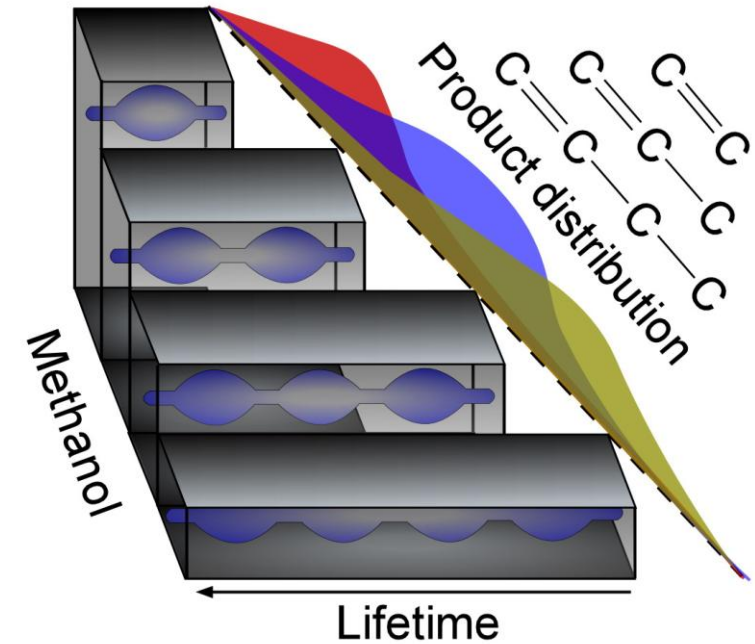
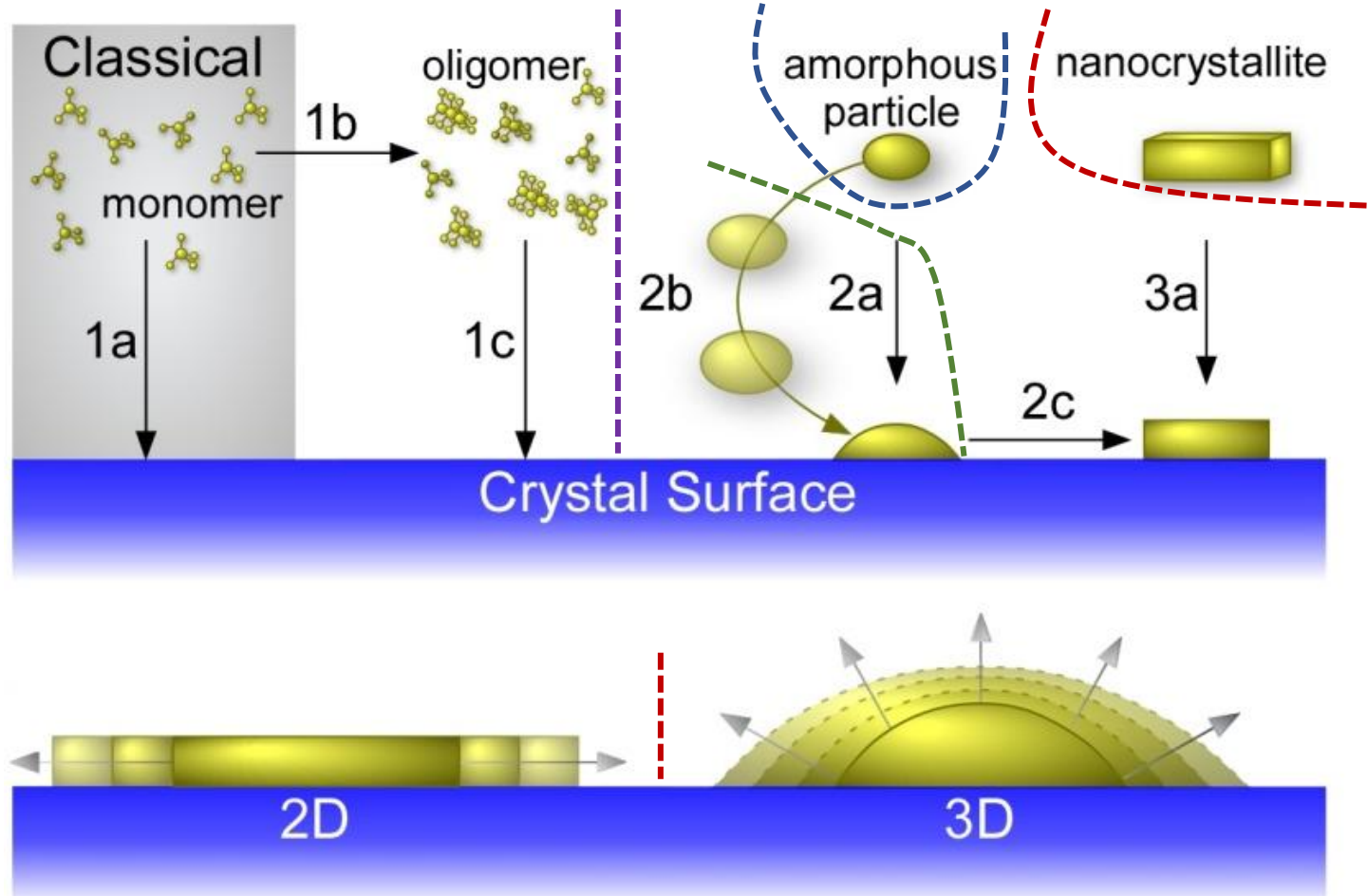
- Concerted Mechanism
- Nature of particles
- Control Strategy
- Effect of Additives

- Life-time
- Selectivity
- Stability

De Yoreo, ...Rimer, et al., *Science*, 2015
Choi et al., *Nature* 2009

Methodological Work Domain

Soft-walling of Growth Regime



Hypothetical Premise:

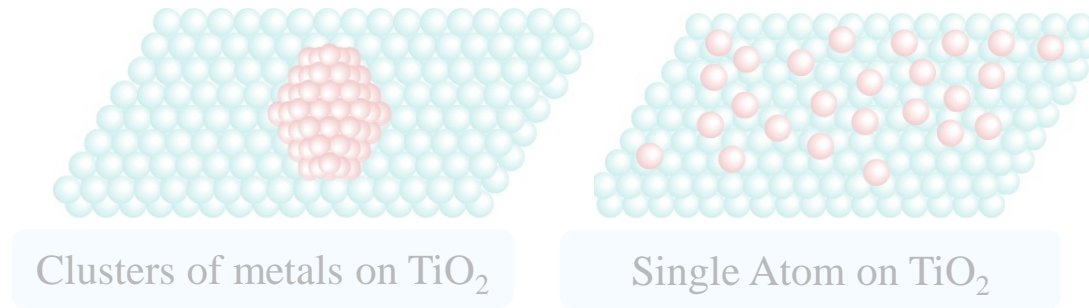
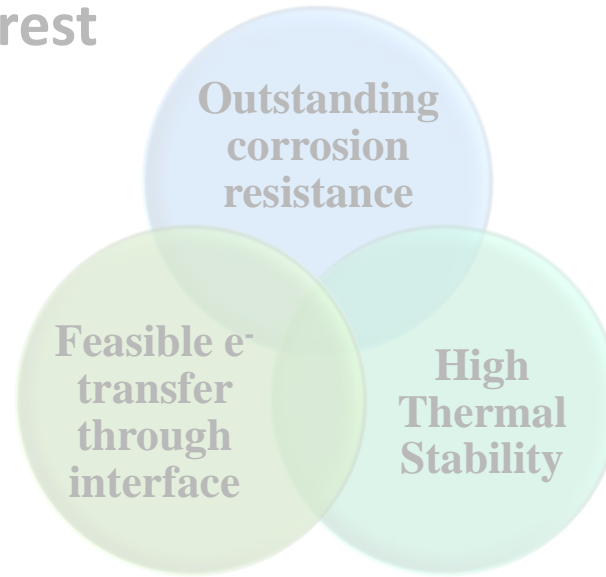
- Additive acting as precursor stabilizer
- Additive Binding to growth sites
- Barrier to nano-particle addition
- Polymer encapsulation

Case Study 1: Tuning & Control Titania

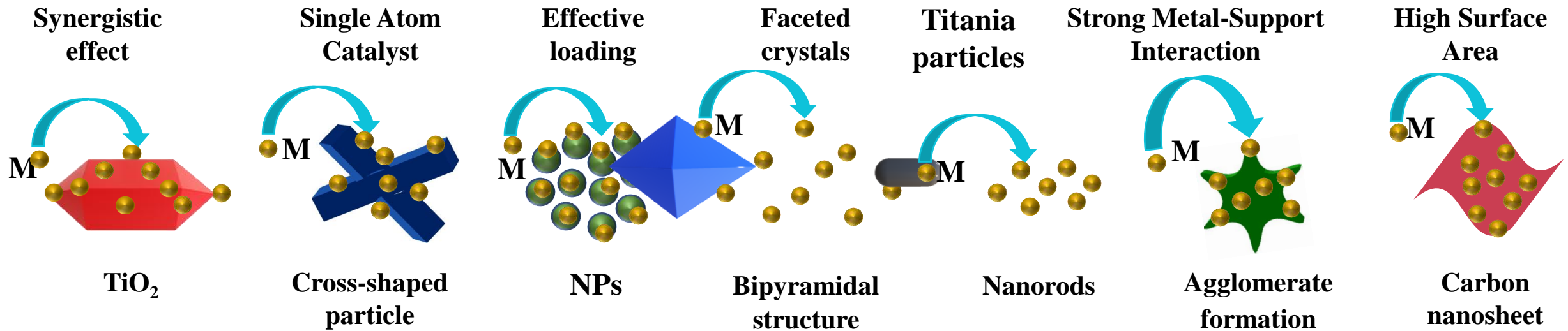
Anatase Phase: Material of interest

Applications

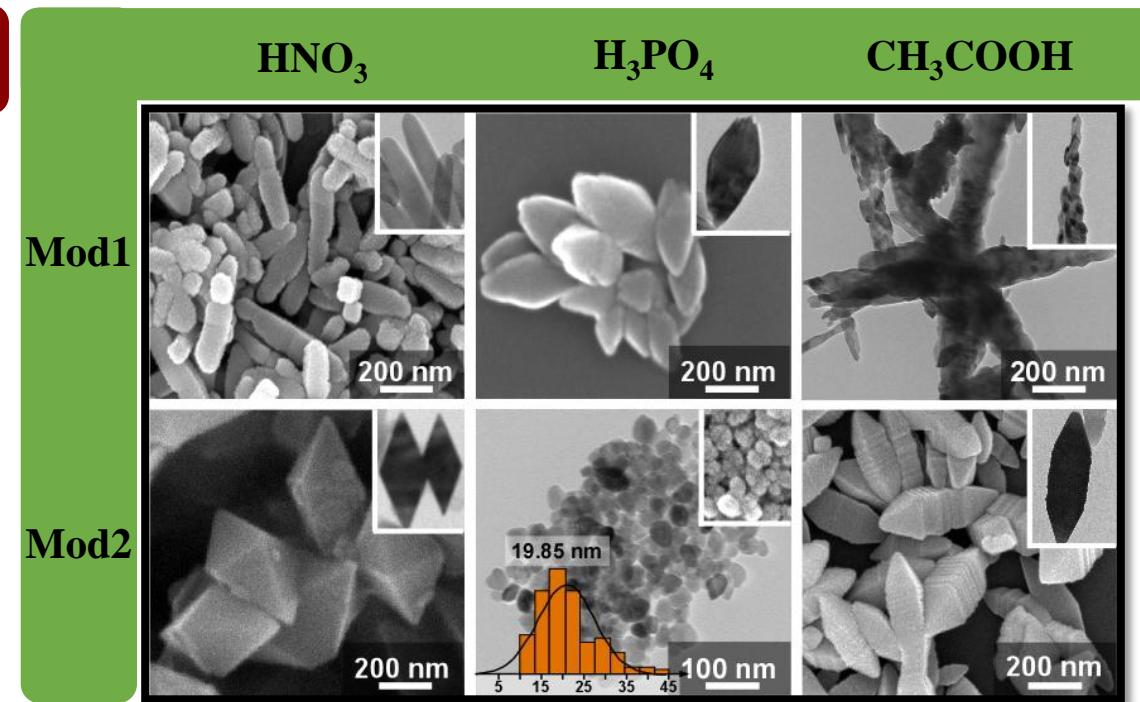
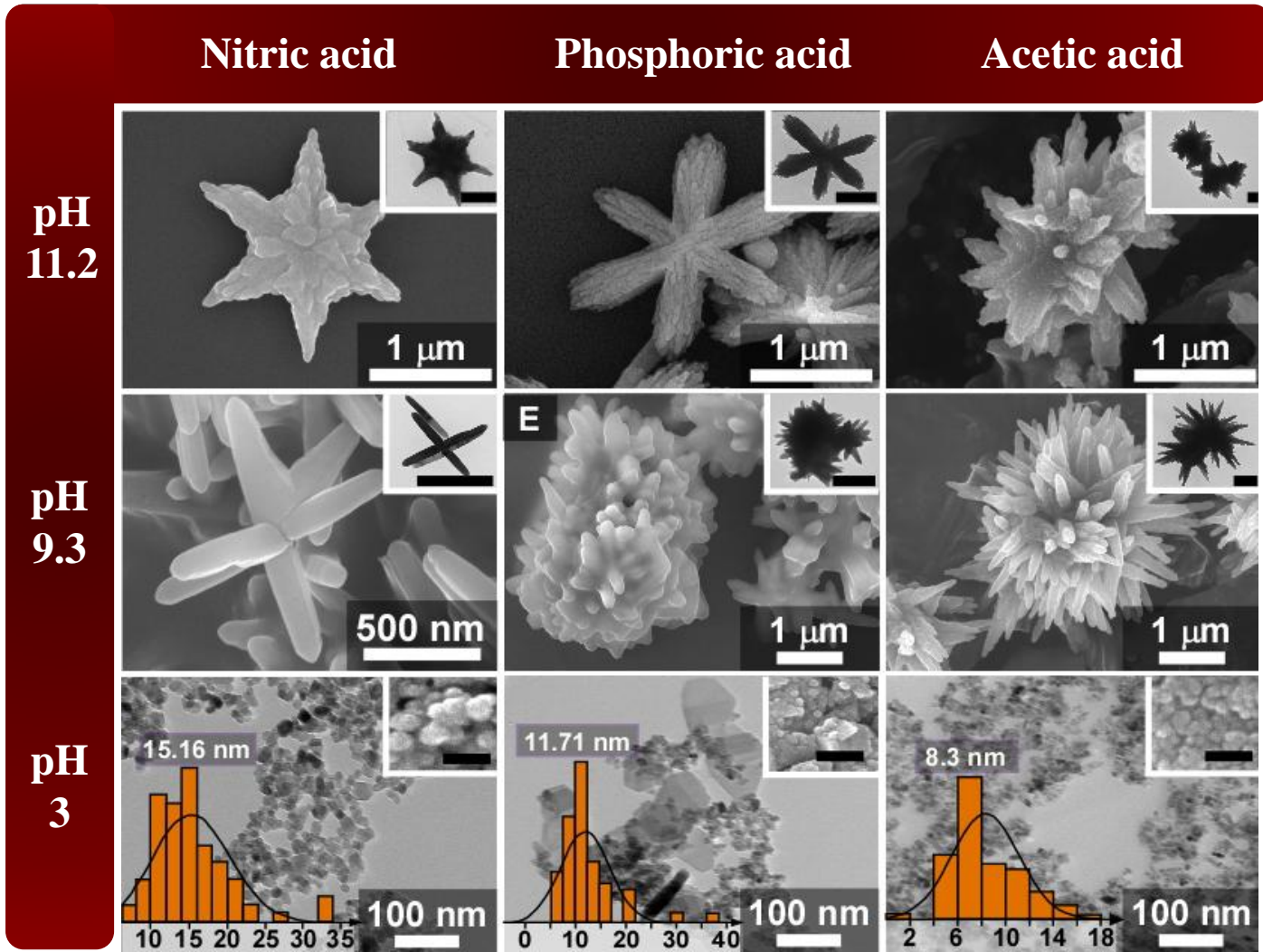
- Oxidation of aromatics
- CO₂ reduction reaction
- Hydrogenation of alkenes
- C-C Coupling



Bech et al., Nature Communications, 2020
 Chen et al., Angewandte Chemie, 2020
 Zhang et al., JACS, 2017



Tapestry of Anatase Crystals

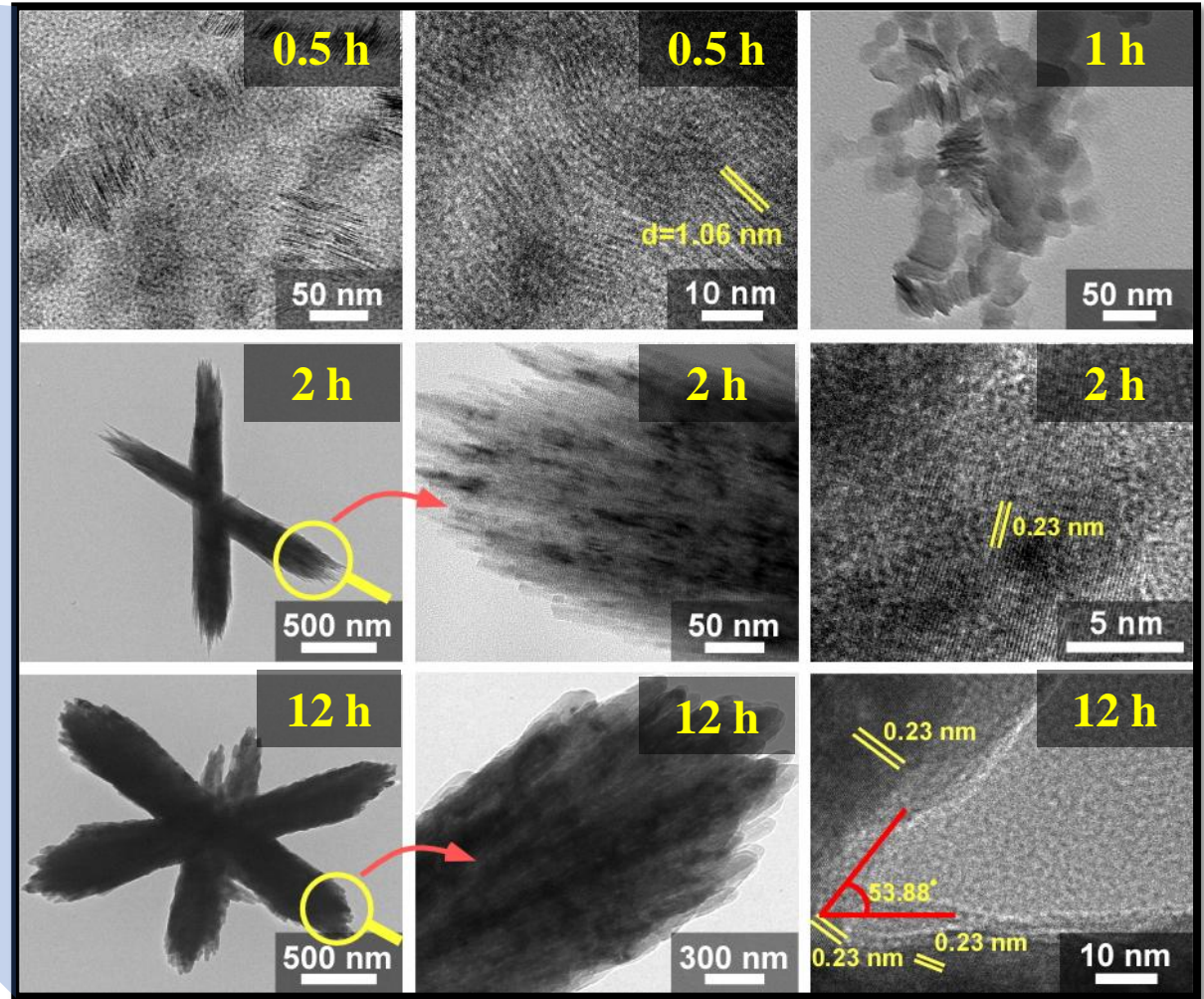
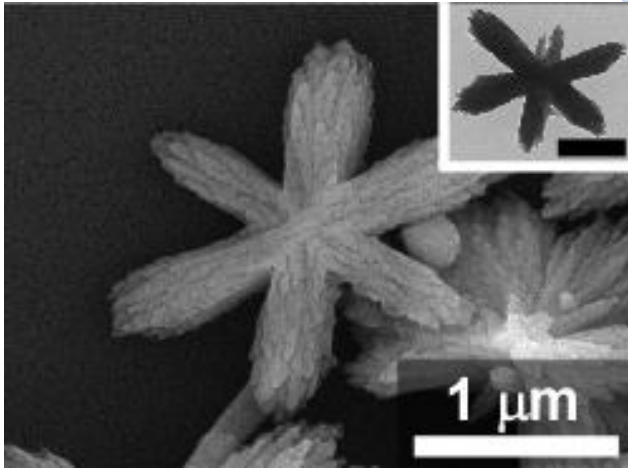


Observations

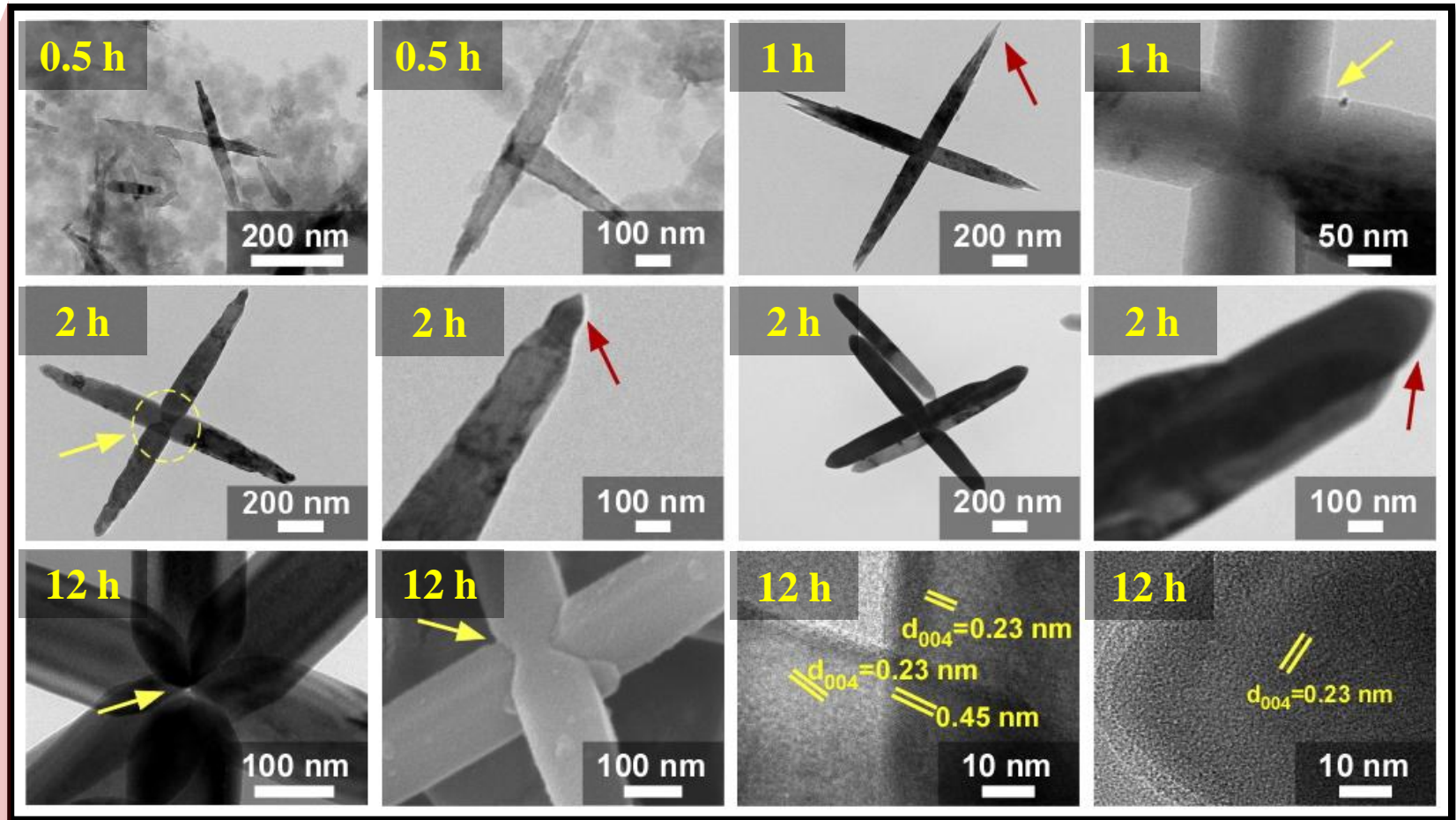
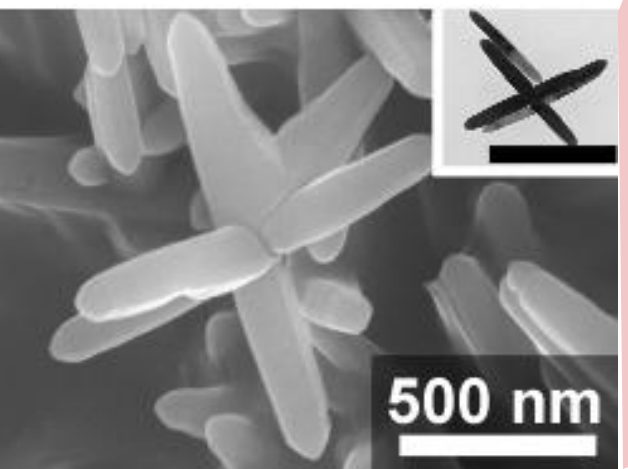
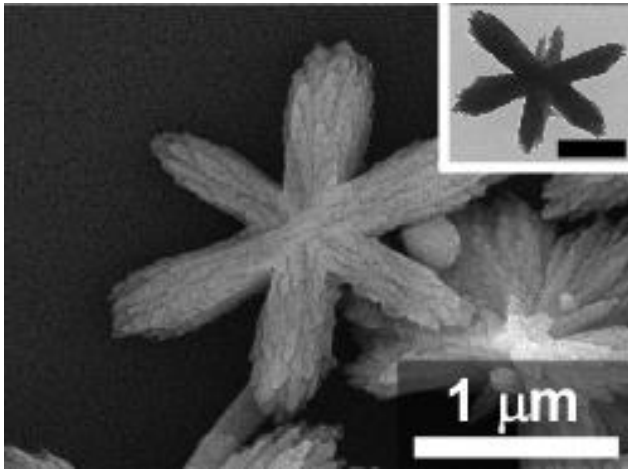
- Tuning size over 3 orders of magnitude
- Random to faceted structure
- 1D-2D-3D structure

Note: Pd/TiO₂ catalyst study in progress to study morphology effect showing promising results in collaboration with Prof Ali Haider

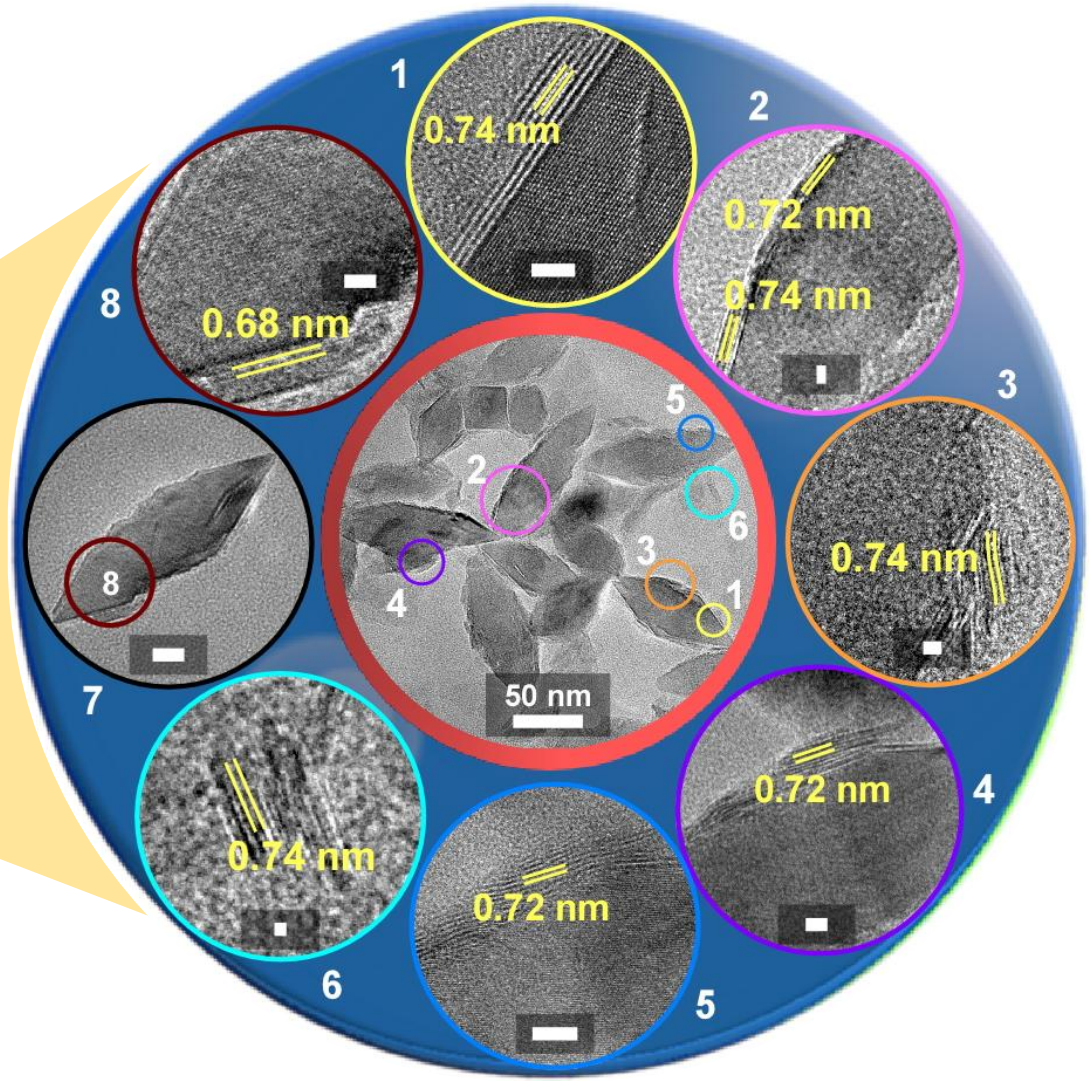
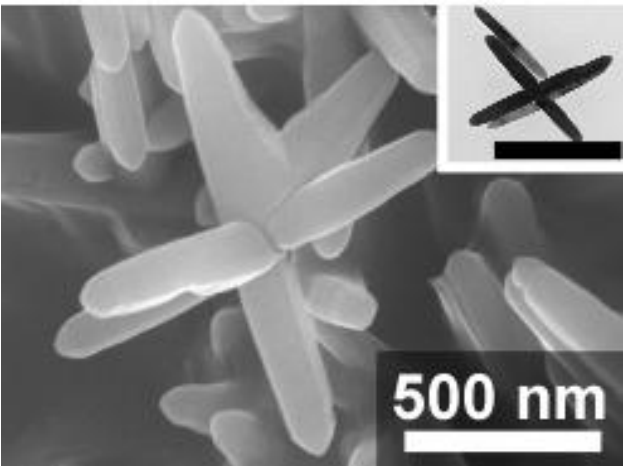
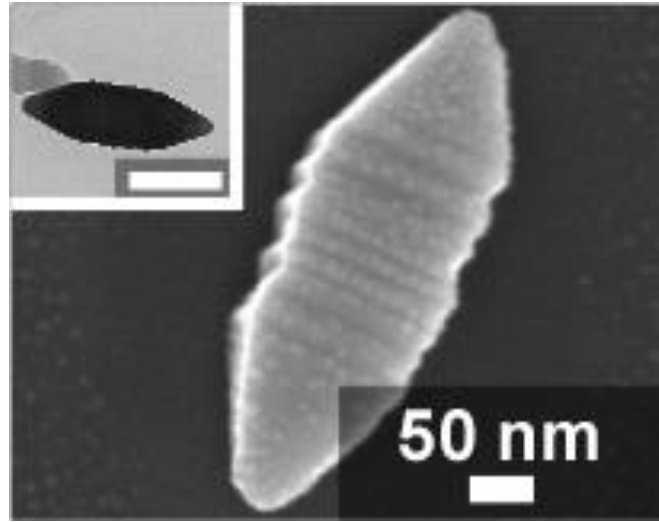
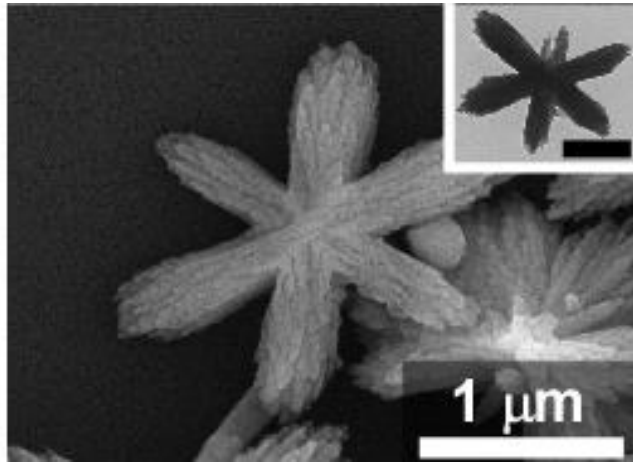
Pathways of Particle Formation



Pathways of Particle Formation

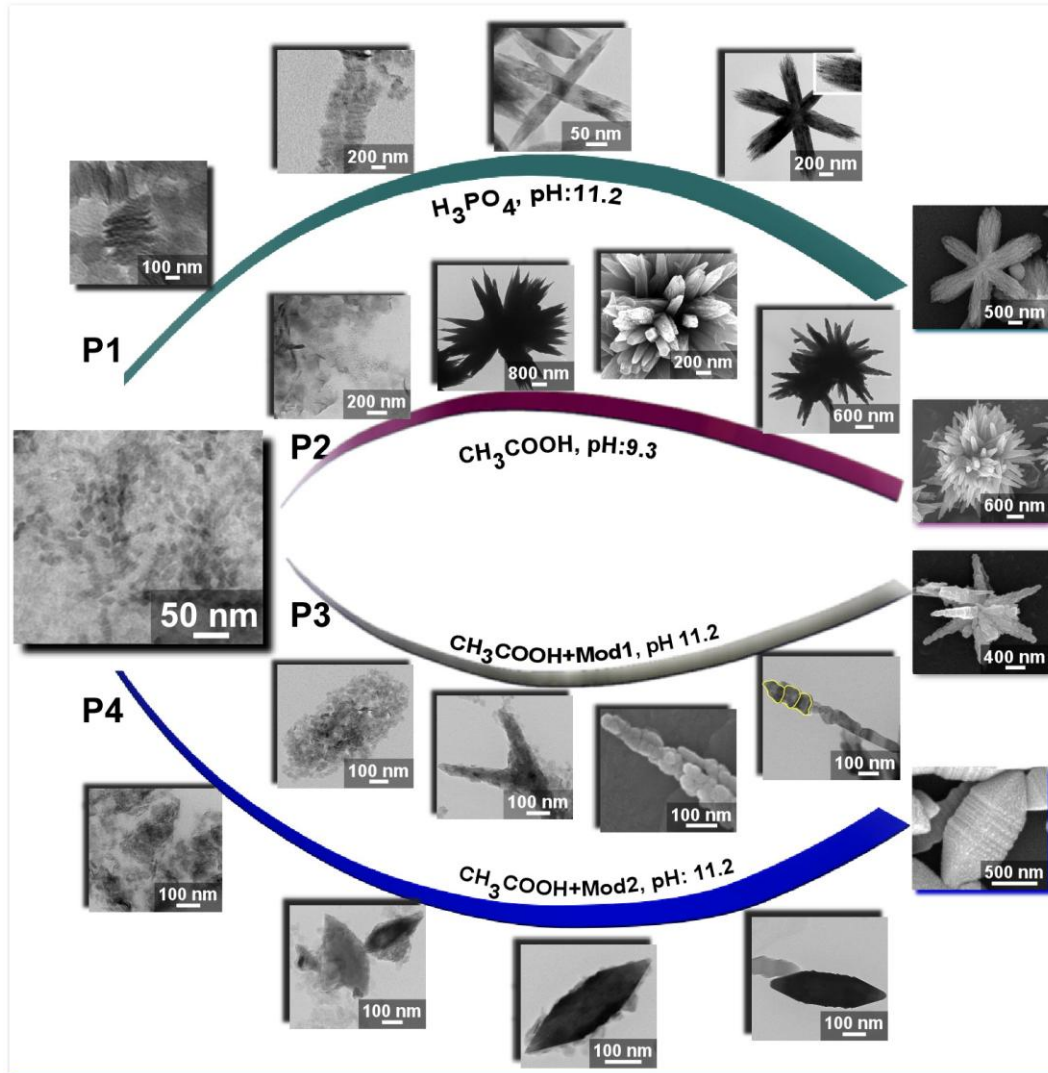


Pathways of Particle Formation



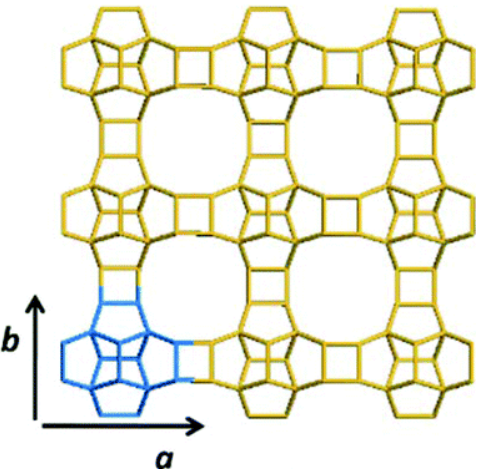
Time-Elapsed Study to Develop Blueprints

Complex Pathways of Anatase Crystallization



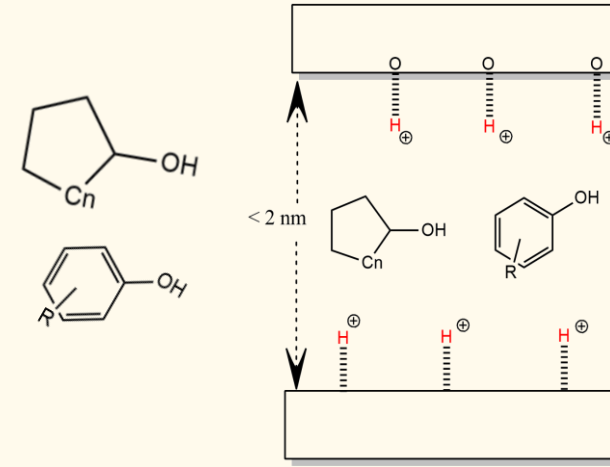
- Complex pathways for support synthesis
- Rational design calls for these detailed study
- Using knowledge of crystallization, we are making novel support
- Reaction studies under progress.

Case Study 2: Optimizing Acid Sites



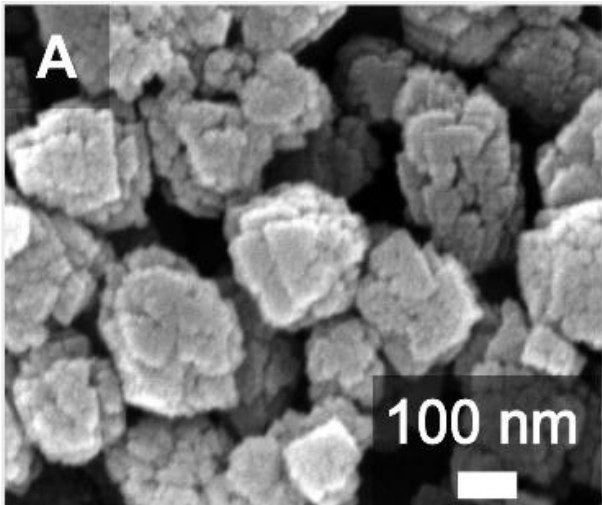
- ❑ 3-Dimensional large pore (0.6nm)
- ❑ 12-MR pore channel
- ❑ **Alkylation** reaction
- ❑ Tuning Bronsted Acid sites

Biomass Derivatives

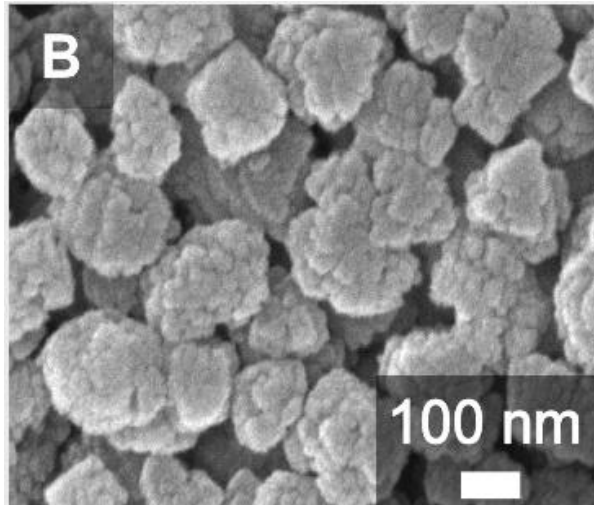


Sustainable Jet Fuel

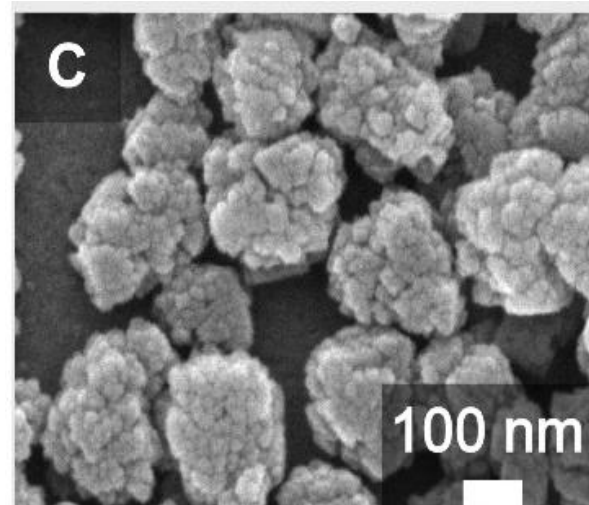
Modulating the Aluminum Content



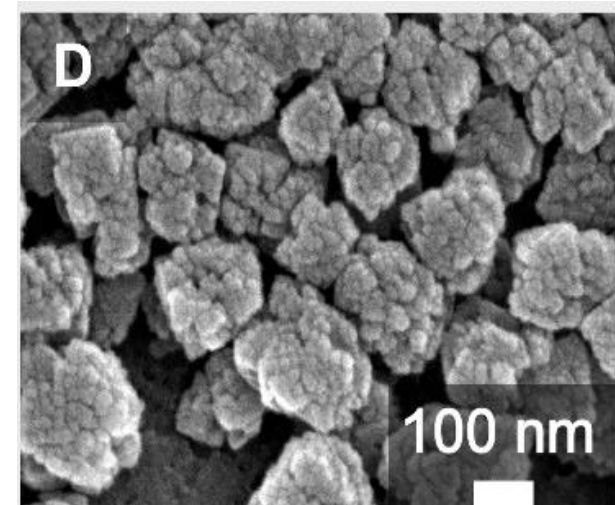
Control



Modifier 1



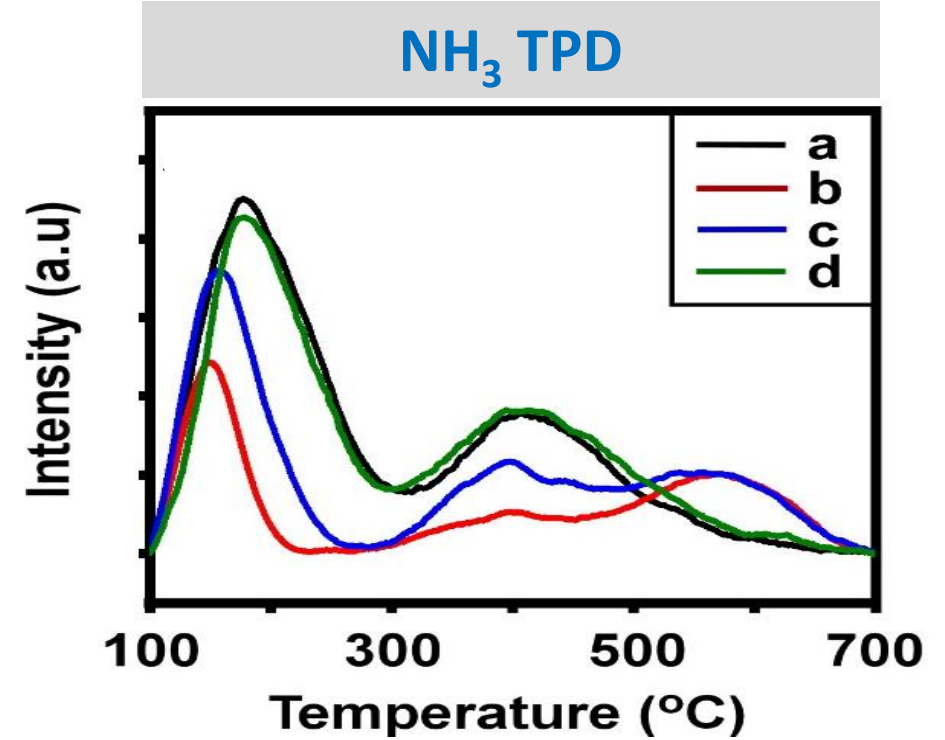
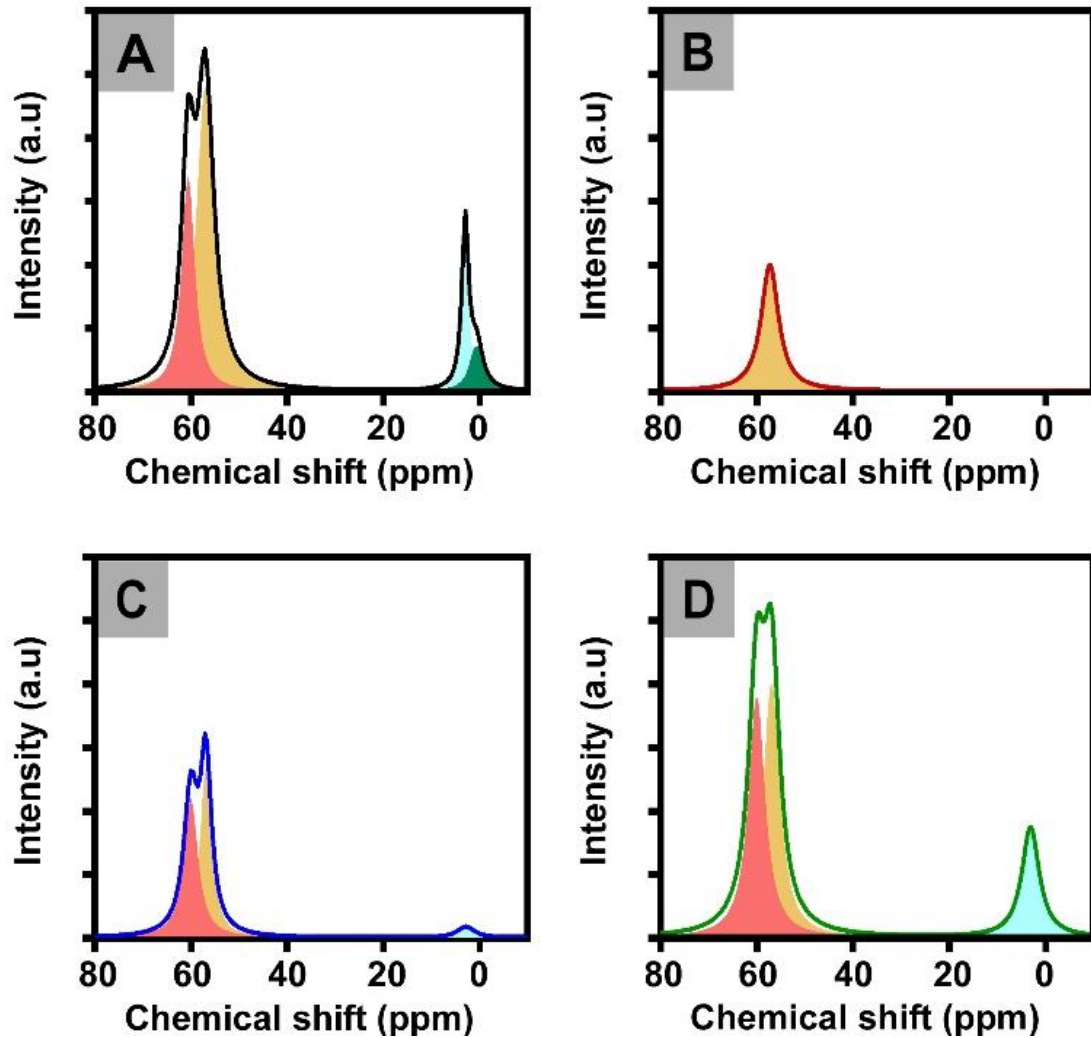
Modifier 2



Modifier 3

Characteristic Acidic Sites

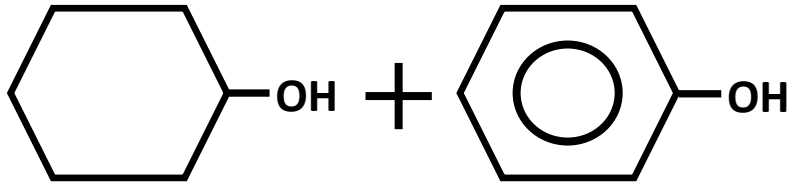
Removal and Rearrangement of Aluminum Sites



- ❑ Generation of super strong acid sites
- ❑ Selective removal of Aluminum
- ❑ Quantity and quality control on acidic sites

Enhanced Performance

Alkylation Reaction



Cyclohexanol

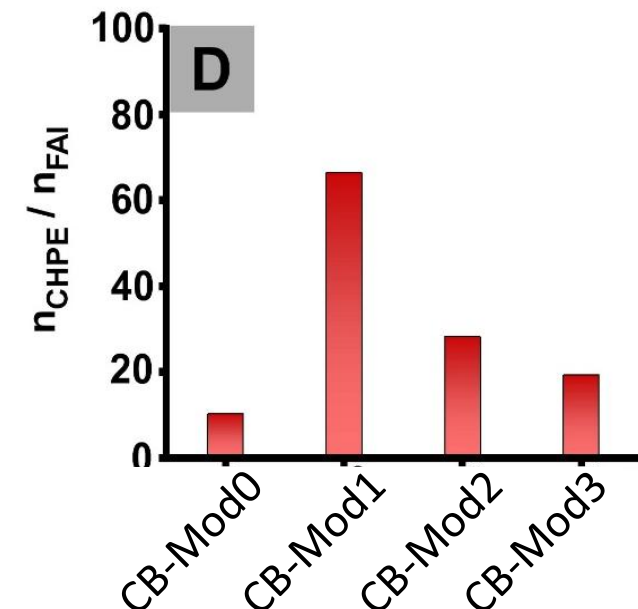
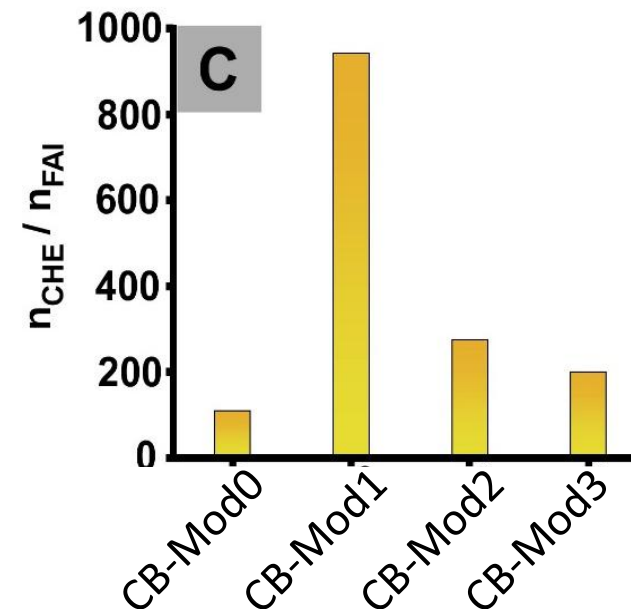
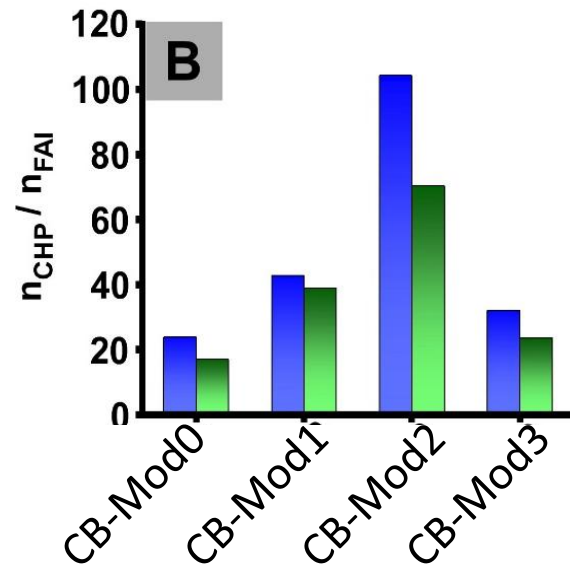
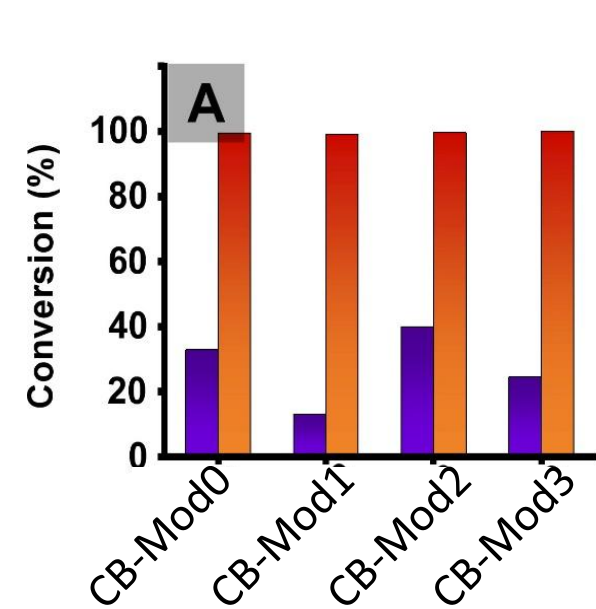
Phenol

C-C coupling

Cyclohexylphenols (CHP)
(2-CHP & 4-CHP)

C-O coupling

Cyclohexylphenyls ether
(CHPE)



Note: Optimal design of novel catalytic material

*Cyclohexene (CHE)

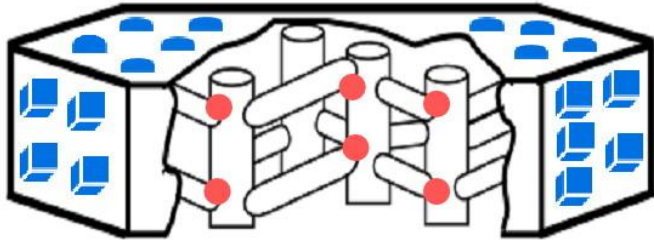
Case Study 3: Bifunctional Catalyst

Bifunctional Catalyst

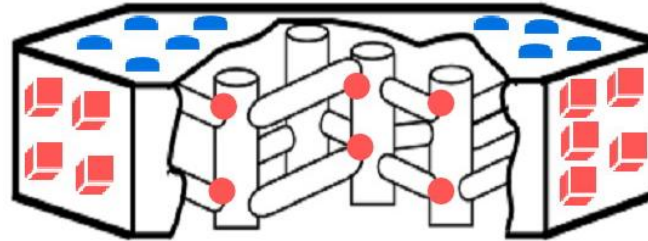
- Bronsted Acid site
 - Lewis Acid sites
 - Reaction examples: Hydroisomerization, Hydrocracking
- } Metal nanoparticles interspersed between acidic zeolite

- Metal Site Protection
- Miniaturization
- Enhanced performance

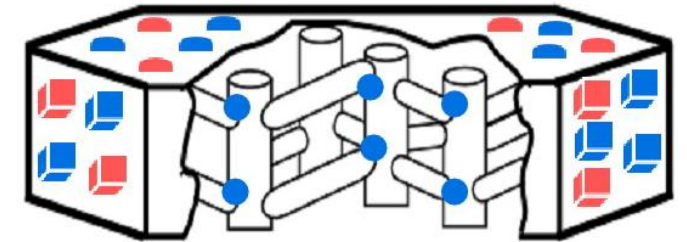
Facet Recognition



Facet Selectivity

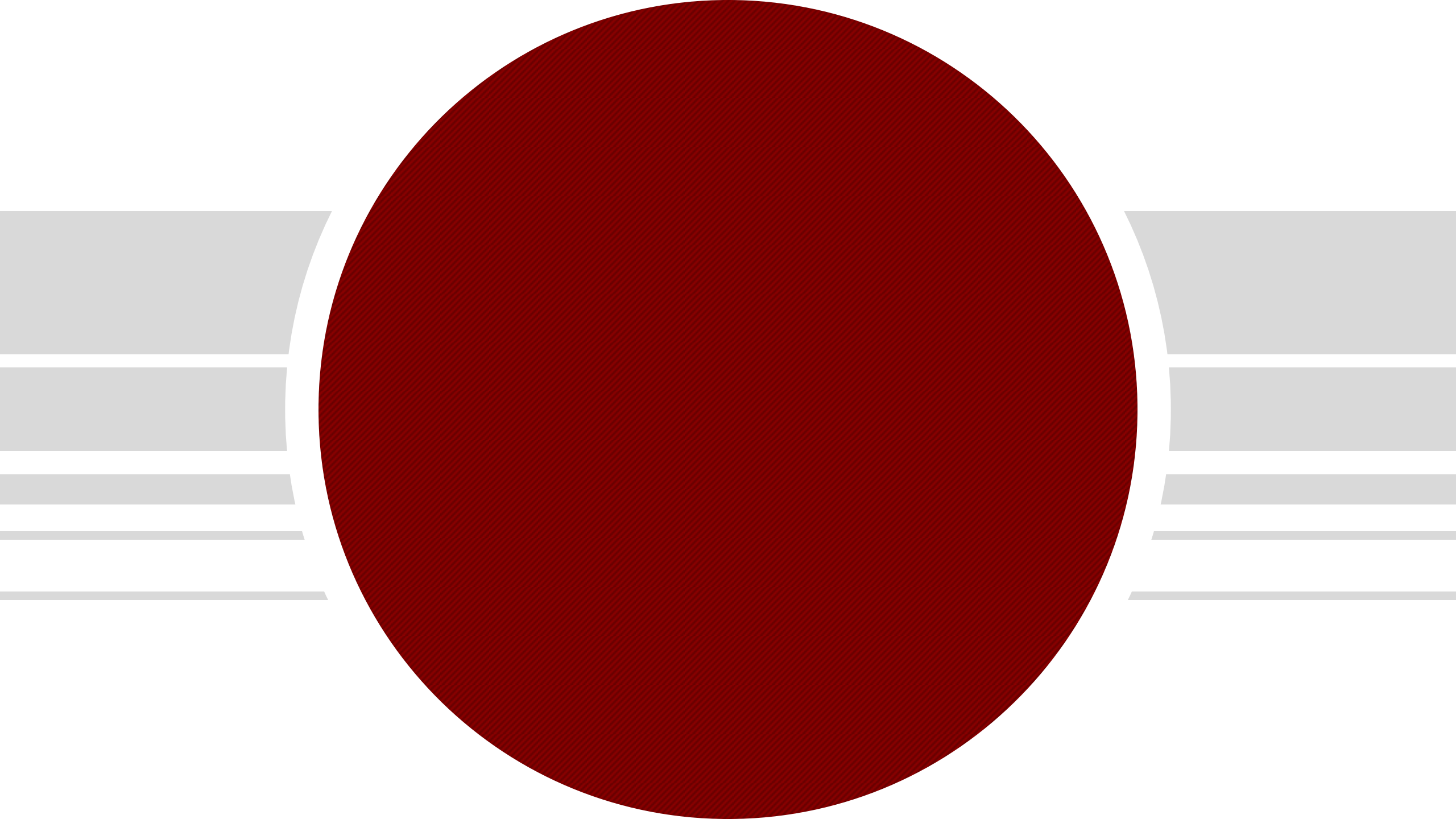


Active Site Synergy



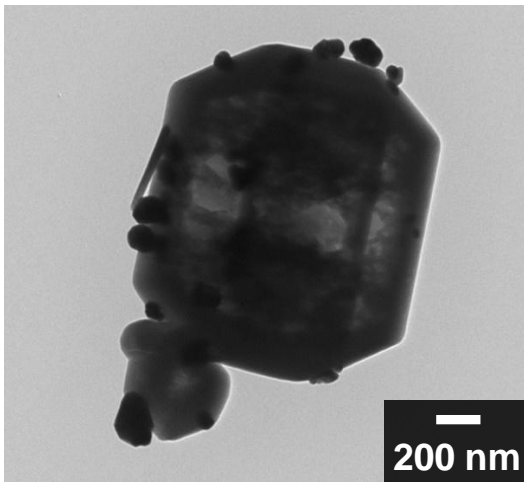
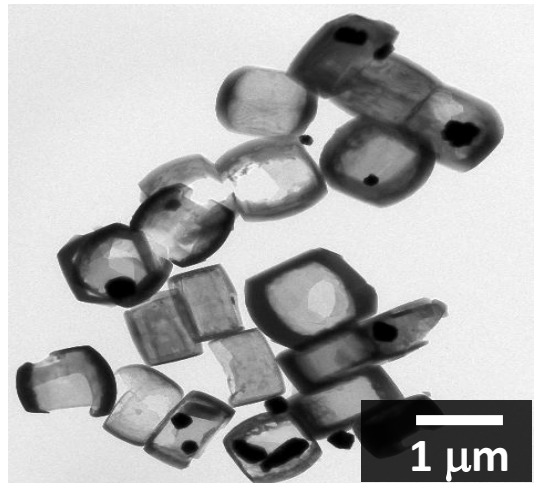
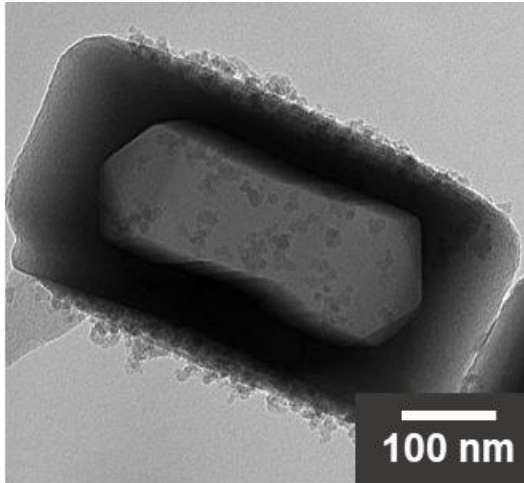
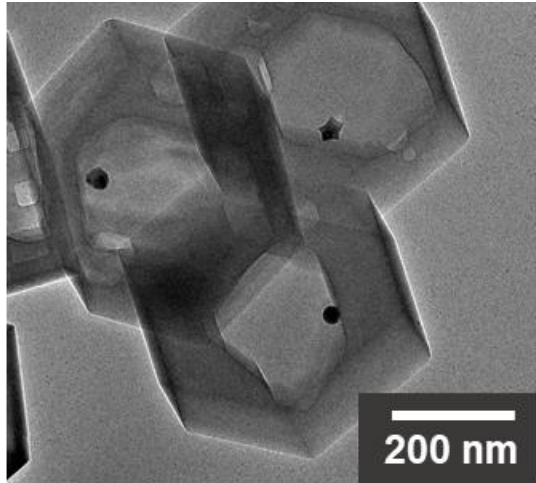
- Location of metal sites
- Size of metal sites
- Distribution of metal sites

MFI (Silicalite-1, ZSM-5), Pd, Ag

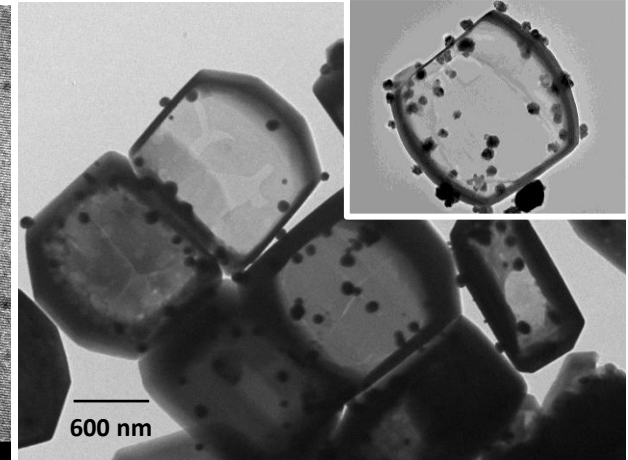
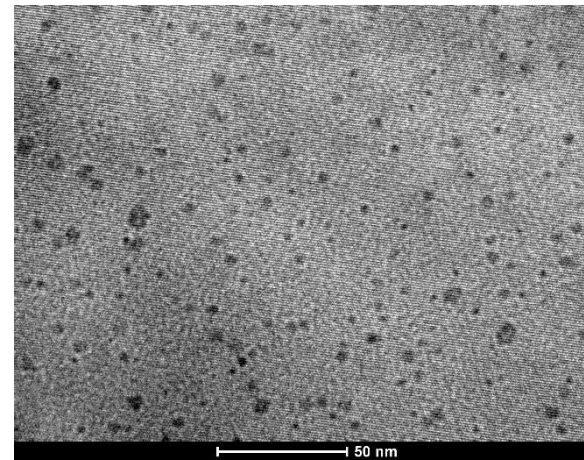
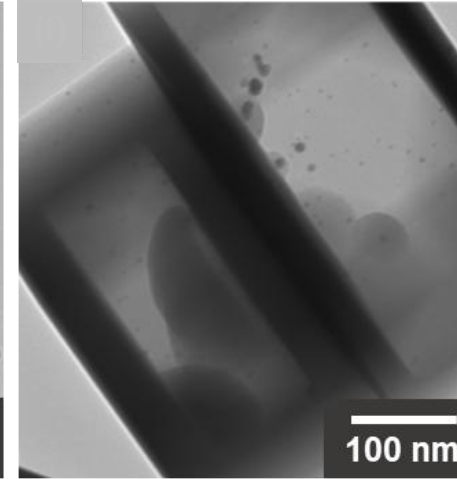
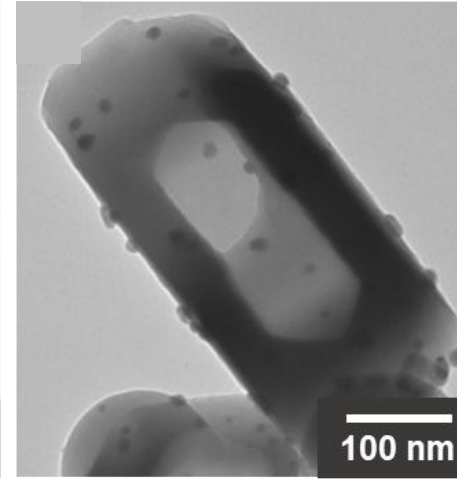
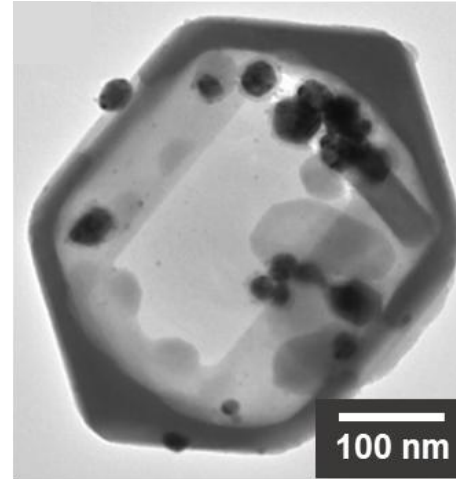


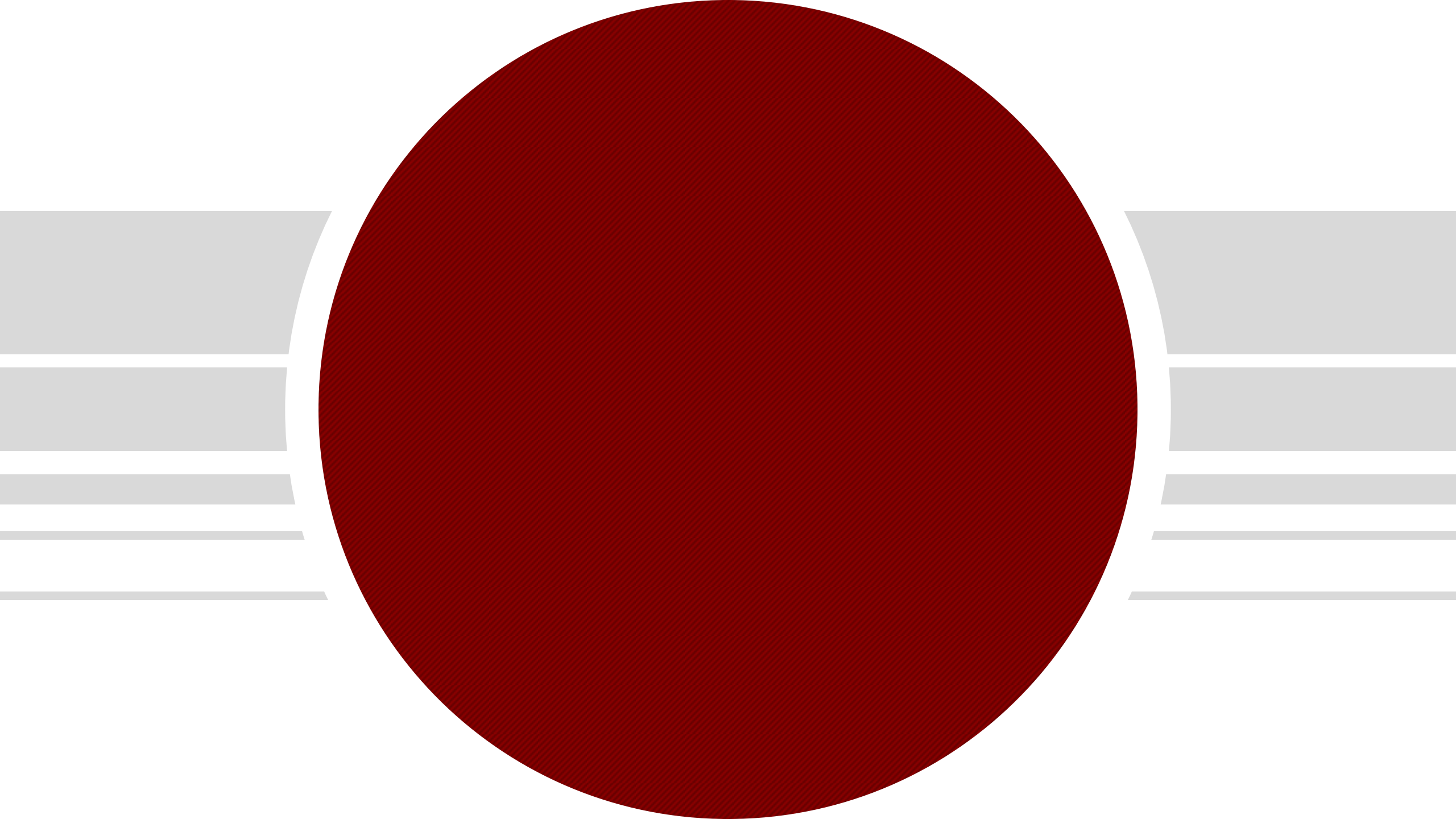
Effect of Metals on Zeolite

Metal Loading on Zeolite (Pd)

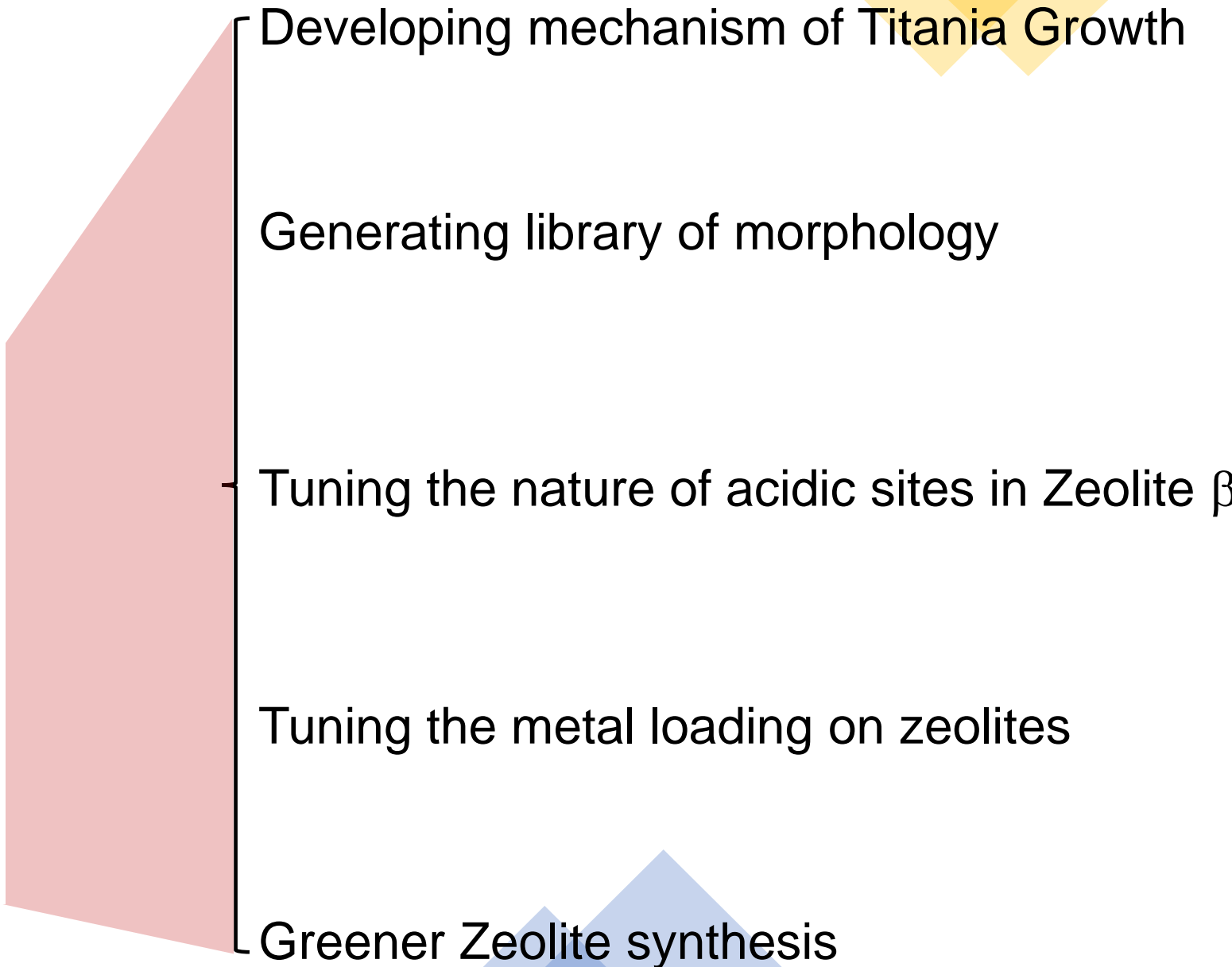
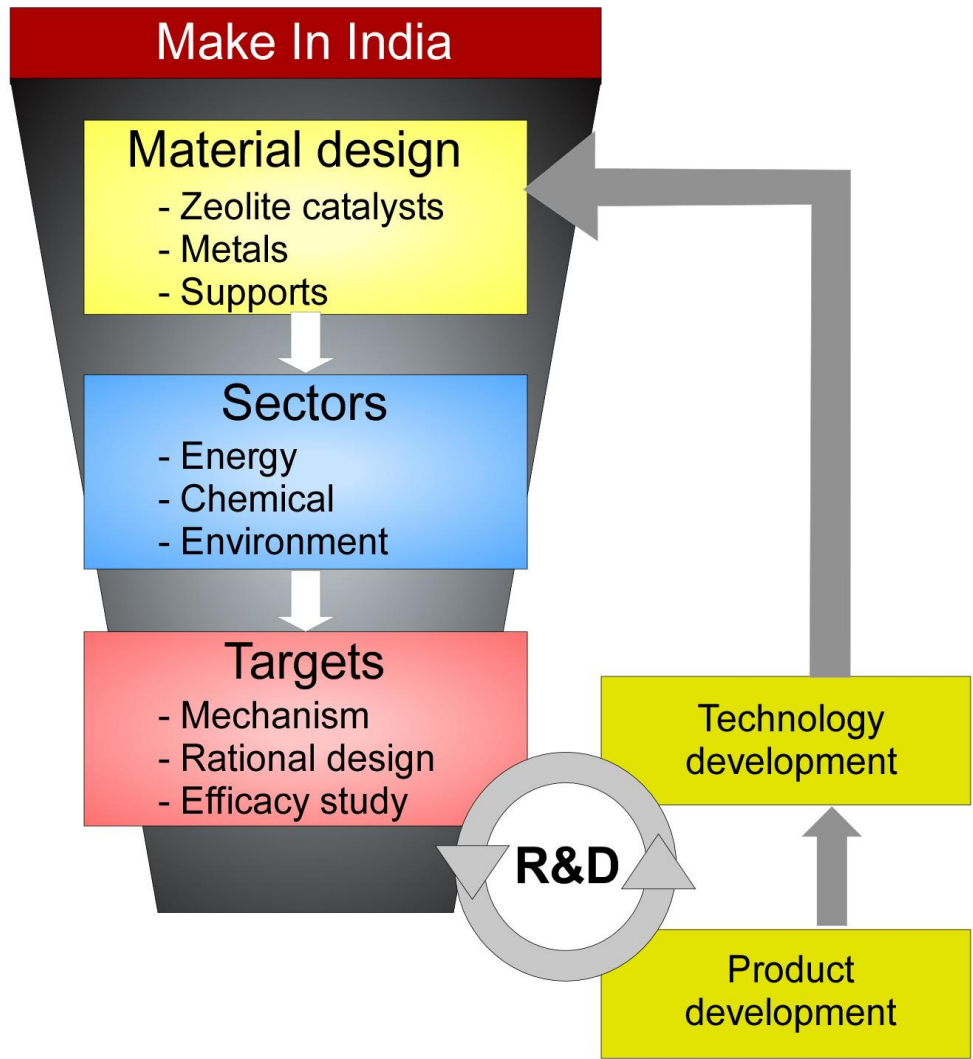


Metal Loading on Zeolite (Ag)





Summary



Acknowledgments

MCatLo Park (IIT Delhi)

- Anusha Jain
- Pranit
- Debkrishna
- Humam
- Aditya
- Urvashi Sharma (Postdoc)

Collaborators (IIT Delhi)

- Prof. K K Pant
- Prof. Ali Haider



Funding Sources



SERB-SRG Grant



FIRP IIT Delhi



Start-up Seed Grant



Central Research Facility IIT Delhi

The background of the slide is a grayscale scanning electron micrograph (SEM) of a porous, layered catalyst structure. The structure consists of numerous overlapping, wavy layers that create a highly textured, porous surface. The layers are roughly parallel to each other, with some smaller, more irregular layers interspersed. The overall appearance is that of a complex, three-dimensional porous material, likely used in catalysis.

Thank you

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