UNIVERSITY of HOUSTON
OFFICE OF THE PROVOST
Graduate School

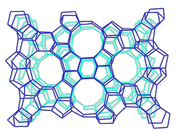
Tailoring the Morphology and the Spatial Acid Site Distribution of ZSM-5 Catalysts

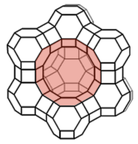
UNIVERSITY of HOUSTON
CULLEN COLLEGE of ENGINEERING

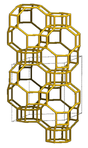
Wei Qin, Matthew D. Patton, and Jeffrey D. Rimer
Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204

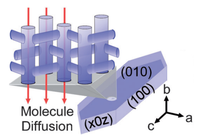
Introduction

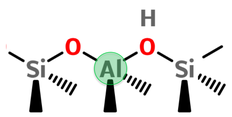
- Zeolite catalyst: refinery, petrochemical processes, emission control, biomass conversion, etc.
- The main properties of zeolites are related to their topology, morphology, and chemical composition.


ZSM-5 (MFI)

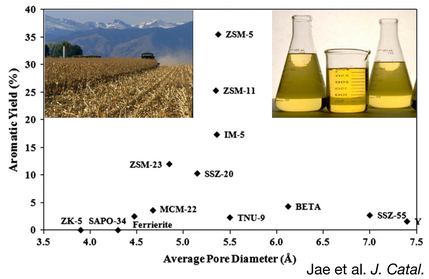

USY (FAU)


SSZ-13 (CHA)





- Zeolite catalysts for biomass conversion



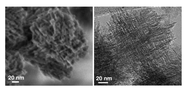
Jae et al. *J. Catal.* 2011

- Challenges: catalyst stability in condensed phase, aromatic selectivity, etc.

Tuning Zeolite Morphology

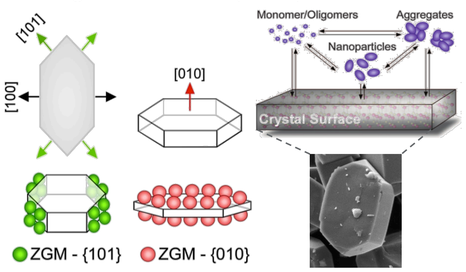
- Adjustments of synthesis parameters
- Sacrificial templating strategies
- Structure-directing agents (SDAs)

Pérez-Ramírez et al. *Chem. Soc. Rev.* 2008



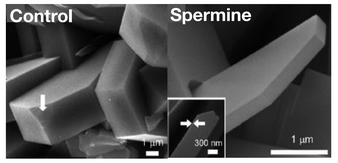
Zhang et al. *Science* 2012

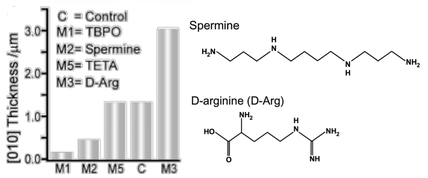
- Zeolite growth modifiers (ZGMs)



Lupulescu, Qin and Rimer, *Langmuir* 2016

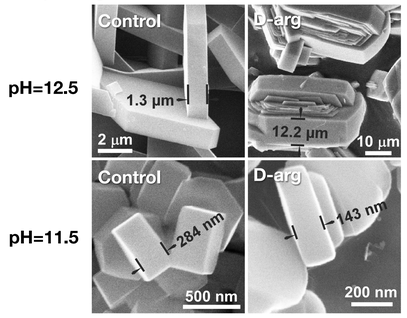
Effect of Zeolite Growth Modifiers

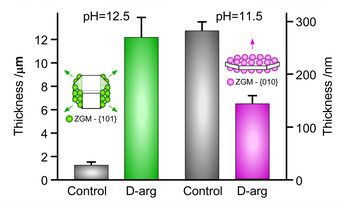




Lupulescu and Rimer, *Angew. Chem. Int. Ed* 2012

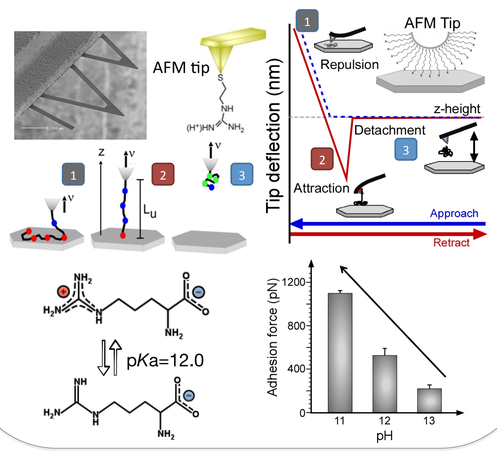
- ZGM binding specificity can be altered by adjusting the solution pH





Modifier-Crystal Interactions

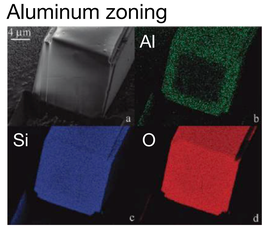
- Chemical force microscopy



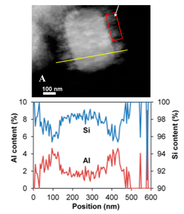
Tuning Zeolite Composition

- The physicochemical properties (hydrophobicity and acidity) and the catalytic behavior of zeolites are related to the spatial distribution of *Aluminum*.

Aluminum zoning

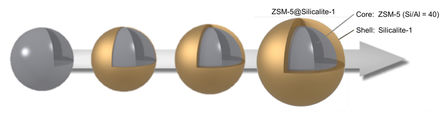


Danilina et al. *J. Phys. Chem. C* 2010



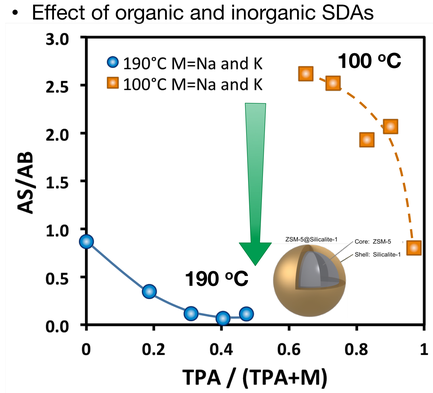
Ding et al. *JACS* 2015

- Surface passivation methods: dealumination, silylating treatment, multi-step core-shell synthesis.

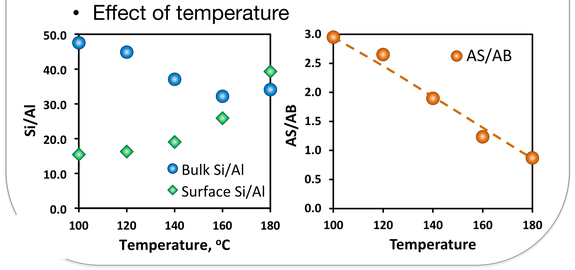


Ghorbanpour et al. *ACS Nano* 2015

- Elemental analysis techniques:
  - Energy-dispersive X-ray spectroscopy (~10 μm) detects aluminum in the bulk, AB.
  - X-ray photoelectron spectroscopy (~5 nm) detects aluminum near the surface, AS
  - Descriptor :
    - AS/AB > 1 , Al zoning
    - AS/AB = 1 , Homogeneous
    - AS/AB < 1 , Si zoning
- Effect of synthesis parameters on Al distribution
  - Effect of organic and inorganic SDAs

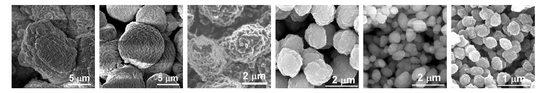


  - Effect of temperature



Catalytic Performance

- Mildly Si-zoned samples with different sizes

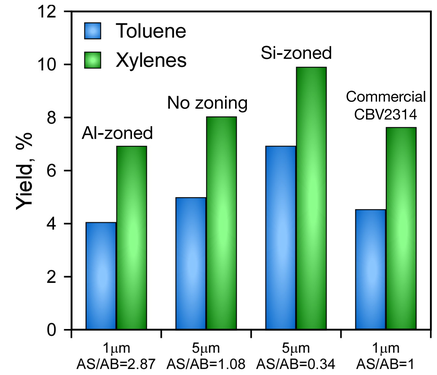


14 μm AS/AB=0.35 | 10 μm AS/AB=0.41 | 3.6 μm AS/AB=0.28 | 1.6 μm AS/AB=0.51 | 0.8 μm AS/AB=0.57 | 0.4 μm AS/AB=0.74

- Strongly Si-zoned samples with different sizes

12 μm AS/AB=0.11 | 10 μm AS/AB=0.09 | 9 μm AS/AB=0.07 | 6 μm AS/AB=0.08 | 3 μm AS/AB=0.00

- Catalytic activity tests were performed by our collaborators at Shell Technology Center Houston
- Feed (mimicking bio-oil composition): a mixture of water, isopropanol, 1,3-propanediol, acetone, acetic acid, and tetrahydrofuran (THF)
- Reactor type: pulse micro reactor
- Fresh activity for selected samples:



- Future work: assessing the hydrothermal stability and the lifetime of ZSM-5 catalysts
- Summary:
  - ZGMs are effective and inexpensive for tailoring zeolite morphologies
  - Al distribution can be controlled by adjusting synthesis parameters
  - This study could provide a general platform for zeolite design for a wide range of applications

References & Acknowledgments

(1) Jae, J., Tompsett, G.A. Foster, A.J. et al. *J. Catal.* 2011
(2) Pérez-Ramírez, J. et al. *Chem. Soc. Rev.* 2008
(3) Zhang, X., Liu, D., Xu, D., Asahina, S. et al. *Science* 2012
(4) Lupulescu, A.I., Rimer, J.D. *Angew. Chem., Int. Ed.* 2012
(5) Lupulescu, A.I., Qin, W; Rimer, J.D., *Langmuir* 2016
(6) Danilina, N., Krumeich, F. et al. *J. Phys. Chem. C* 2010
(7) Ding, K., Corma, A. et al. *J. Am. Chem. Soc.* 2015
(8) Ghorbanpour, A., Gumidyala, A. et al. *ACS. Nano.* 2015

Shell
NSF
THE Welch FOUNDATION