Analyzing Molecular-Level Methanol Adsorption Dynamics on Zeolite-Based Catalysts using Solid-State NMR

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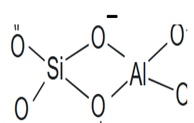
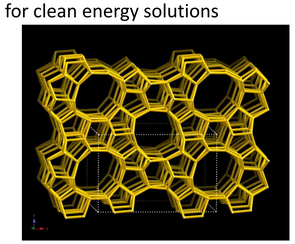
Motivation

- Molecular-level interactions are key to designing new catalytic processes
- Methanol conversion is a focus for sustainable feedstock utilization
- Classifying adsorption and reaction sites provides insights for efficient catalyst design
- Enhanced catalytic materials improve methanol conversion to fuel-grade hydrocarbons
- This supports upgrading renewable feedstocks for clean energy solutions

Active Site M^+ ← Na^+, NH_4^+ ,H^+



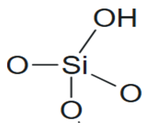
Q4(mAl)

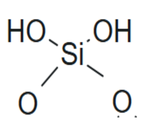


ZSM-5 ZEOLITE (MFI FRAMEWORK)
IZA Structure.org

Challenge

The primary challenge lies in the complexity and distribution of adsorption sites. Additionally, during biomass conversion, reactions between water, oxygenated molecules, and surface defects impacts the catalytic performance.



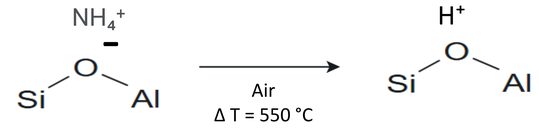


Research Question

How do the molecular adsorption properties of different sites in a zeolite catalyst collectively impact its overall reactivity in the methanol-to-hydrocarbon (MTH) conversion process?

Methodology

Catalyst Preparation: Commercial NH_4^+-ZSM-5 with different Si/Al ratios



Solid-State NMR: Performed solid state ^1H, ^{13}C, ^{29}Si, and ^{27}Al NMR analysis using multidimensional techniques to characterize acid and defect site distributions and methanol interactions

Results and Analysis

- **ZSM-5 Zeolites:** NH_4^+ form with varying Si/Al ratios: 23:1, 30:1, 50:1
- The XRD patterns confirms a well-ordered crystalline structure for the zeolite samples with different Si/Al ratios

SEM IMAGE(1µm)

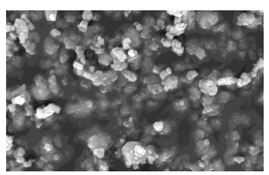
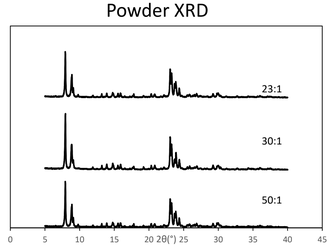


Image Courtesy of Nguyen,Self lab

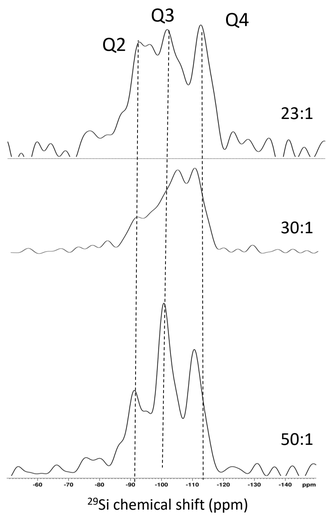
Powder XRD



- Sub-µm Crystallites
- No change in long range crystallinity with different Si/Al ratios for thermal treatment

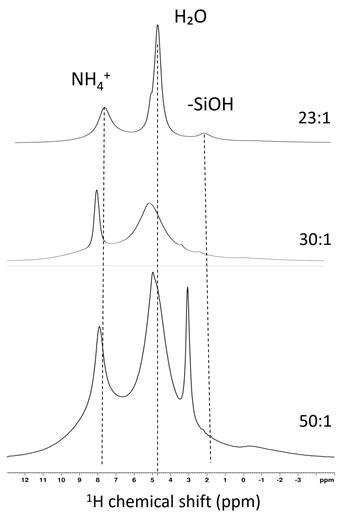
Types and distribution of framework and defect sites

Solid-state ^{29}Si MAS NMR
Conditions: 9.4 T, 298 K, 12.5 kHz MAS



^{29}Si chemical shift (ppm)

Solid-state ^1H MAS NMR

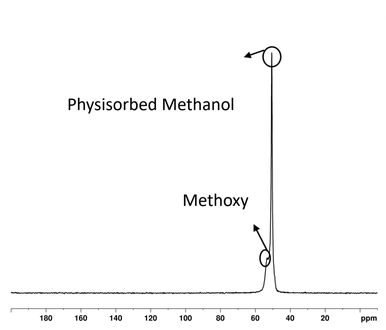


^1H chemical shift (ppm)

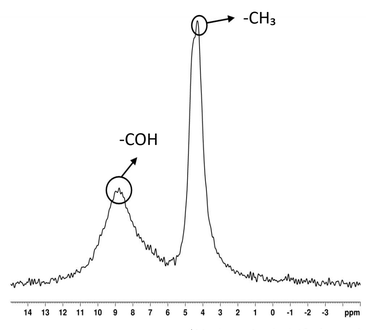
- Single-pulse ^{29}Si NMR enables quantitative comparison of defect types across samples.
- Proton NMR reveals ammonium, water, and -SiOH content variations in samples with differing Si/Al ratios.

Methanol Adsorption and Reaction

- Introduced ^{13}C labelled methanol onto calcined ZSM-5 zeolite with varying Si/Al ratios in a glove box
- Analyzed methanol adsorption using solid-state **^{13}C NMR** and **^1H NMR** techniques
- Investigated defect site interactions with methanol



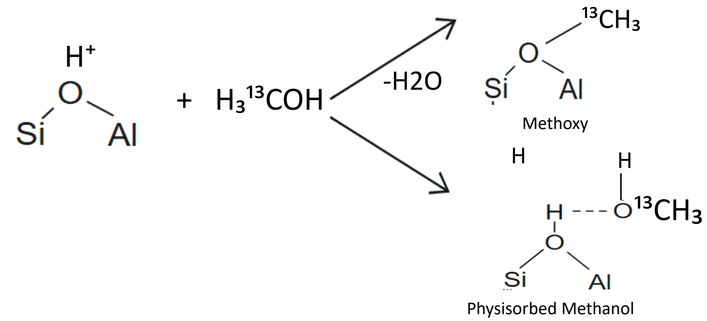
^{13}C Chemical shift (ppm)



^1H chemical shift (ppm)

- Physisorbed methanol and methoxy species formed by reaction with zeolite acid sites

Proposed MeOH Reactions and Interactions



Ongoing Work

•Investigate the relationship between catalytic properties and bulk phase behavior
•Solid-state 2D heteronuclear correlation analysis to determine atomic structure of different adsorption sites
•Use solution NMR to track methanol dehydration catalytic reaction kinetics and product selectivities
•Expand NMR characterization to alternate zeolite frameworks and catalytic reactions

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