Supercomputers and Synchrotrons: A New Era of Scientific Discovery

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Outline

This presentation describes a replacement of ^{27}Al (3Q) MAS NMR spectroscopy by X-ray diffraction and anomalous X-ray diffraction methods. The talk reveals that solving difficult structural problems regarding the Al siting and Me(II) cationic sites in zeolites with a complex structure (e.g., ZSM-5) require high quality periodic DFT calculations with extensive conformational sampling (Molecular Dynamics) of the local structure of the Me(II) cationic sites.

AI

- "AI" is the abbreviation of the chemical element aluminum, not Artificial Intelligence .

Zeolites

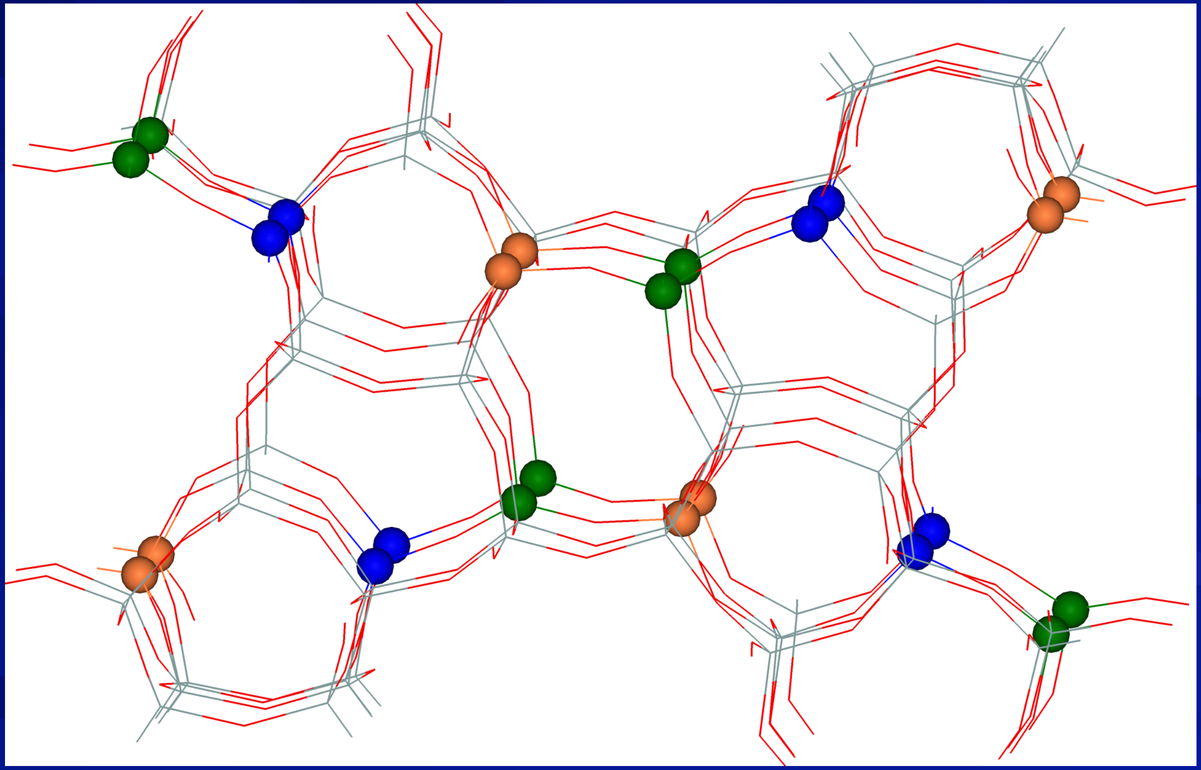
- Zeolites are crystalline microporous aluminosilicates widely used as molecular sieves and catalysts in industrial chemical processes.
- Zeolites feature cavities and channels.
- Zeolites occur naturally (as minerals formed from volcanic or sedimentary processes) as well as are synthesized artificially for industrial use.

Silicon-rich zeolites

- Silicon-rich zeolites (Si/Al > 8; ZSM-5, the beta zeolite, mordenite, ferrierite, …) are important industrial catalysts.
- Protonic forms - catalysts for hydrocarbon transformations in petrochemistry, syntheses of fine chemicals, utilisation of renewables, …
- Transition metal exchanged forms – have exceptional redox catalytic properties: deNOx, selective oxidation of hydrocarbons by N_2O, N_2O decomposition, …

Distinguishable framework T sites

- Silicon-rich zeolites have several (orthorhombic ZSM-5 has 12) crystallographically distinguishable framework T sites occupied mainly by Si and partly by Al due to the low concentration of the framework Al atoms (e.g., orange T1, green T5, and blue T6).

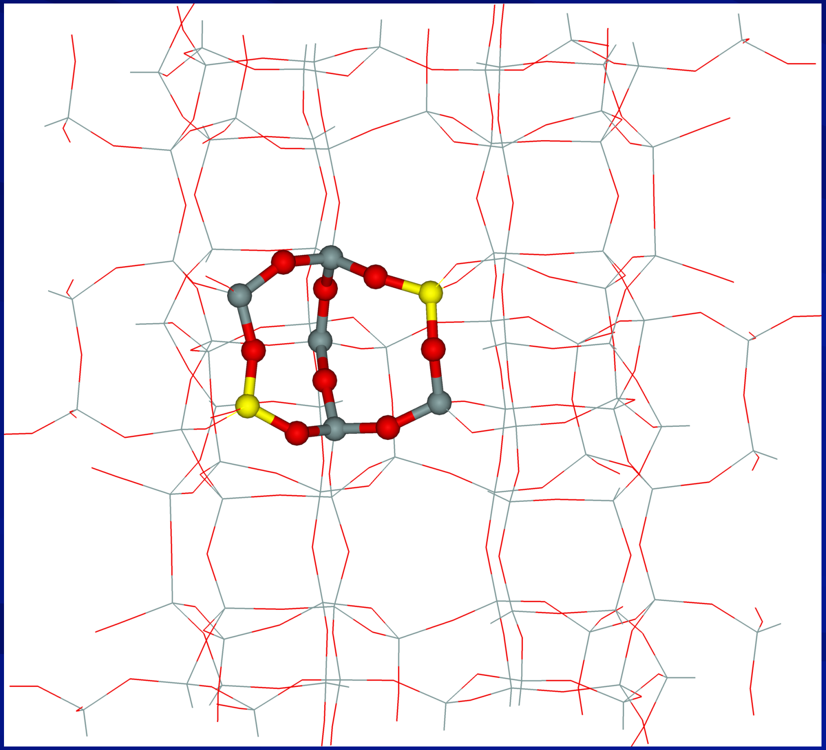


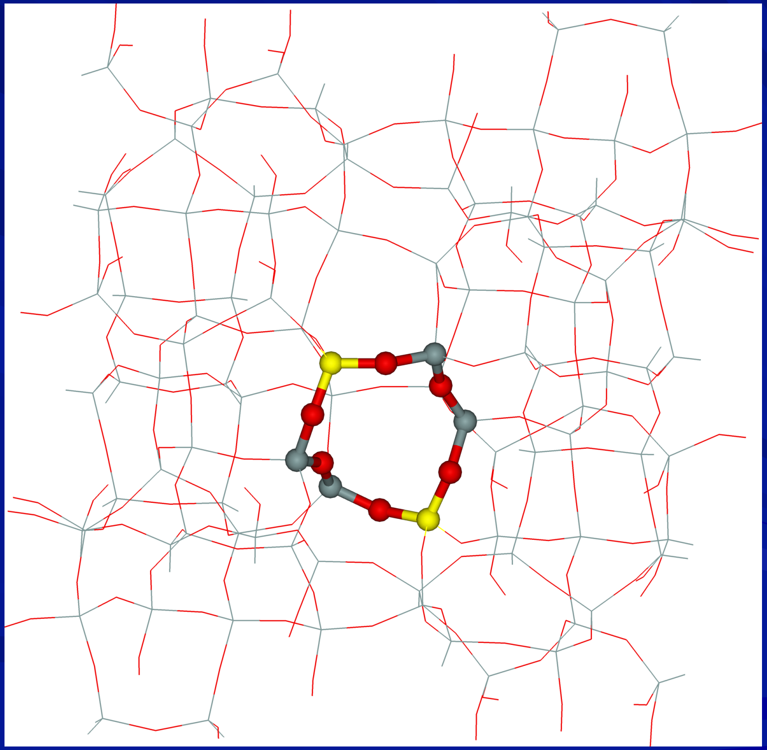
Distinguishable framework T sites

- The catalytically active species, i.e. (protons, metal cations, …), compensate the negative charge of AlO_4^-.
- The crystallographic positions of Al in frameworks govern the locations of the active sites which affect the catalytic activity and selectivity.
- Partial determination of the Al siting in ZSM-5 by ^{27}Al (3Q) MAS NMR spectroscopy and DFT calculations by Dedecek and Sklenak almost two decades ago.
  - Angew. Chem. Int. Ed. 2007, 46, 7286 –7289
  - PCCP, 2009, 11, 1237–1247

Cationic sites for bare Me(II) cations

- The catalytically active species, i.e. (Me(II)), compensate the negative charge of two AlO_4^- tetrahedra
- Dedecek proposed the Alpha (left) and Beta (right) Me(II) sites in 2000 (Microporous and Mesoporous Materials 35–36 (2000) 483–494) based on spectroscopic experiments. No XRD results till 2025.





Revisiting the Al siting and cationic sites for bare Me(II) cations in the ZSM-5 zeolite

- Employing X-ray diffraction instead of ^{27}Al (3Q) MAS NMR spectroscopy.
- Do we still need DFT calculations? (Yes!)

X-ray diffraction

- X-ray diffraction (XRD) is one of the most important characterization techniques for zeolites, as it provides information about their crystal structure, phase purity, crystallinity, and framework type.
- XRD used to determine the Co(II) sites in ZSM-5.

Al siting in ZSM-5 – AXRD used

- Anomalous X-ray diffraction (AXRD) is a powerful crystallographic technique used to obtain additional structural information from X-ray diffraction experiments by exploiting wavelength-dependent variations in atomic scattering factors near an aluminum’s X-ray absorption edge.
- By tuning the X-ray wavelength near this absorption edge, the scattering from Al atoms can be enhanced or reduced — creating “anomalous” differences in reflection intensities.

The Swiss Light Source

- SLS is a synchrotron located at the Paul Scherrer Institute (PSI) in Switzerland for producing electromagnetic radiation of high brightness.
- PHOENIX (PHOtons for the Exploration of Nature by Imaging and XAFS) is a beamline for X- ray absorption and microspectroscopy at soft and tender X-rays.

AXRD results regarding the Al siting in ZSM-5

- Anomalous X-ray diffraction results concerning the Al siting of the Alpha and Beta sites incompatible with the results of Dedecek from 2000.
- The Beta site had been assumed to be incorrect before AXRD experiments were performed based on unpublished results of neutron diffraction experiments in early 2010s.
- The Alpha site change is quite surprising.

How to interpret AXRD results?

- Carry out XRD experiments of Co(II) exchanged ZSM-5 and determine the local structure of Co(II) accommodated in the Alpha and Beta sites.
- Perform periodic DFT calculations including extensive conformational sampling (Molecular Dynamics) of the local structure of all the possible Alpha and Beta cationic sites.

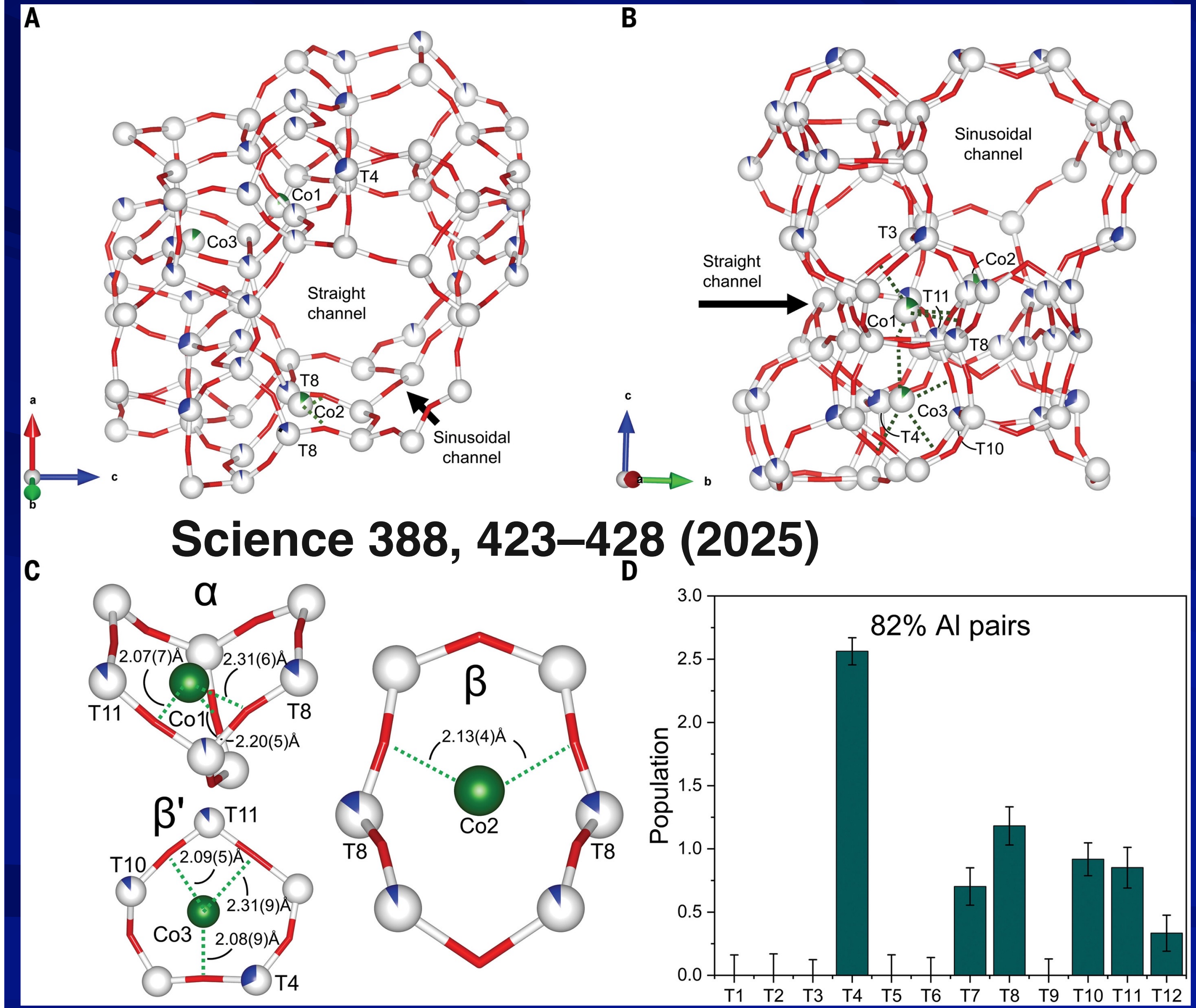
How to interpret AXRD results?

- Comparison of the experimental and theoretical results allows the determination of the ring and the Al siting of the two Al atoms forming the Alpha and Beta cationic sites.

Methods & Programs

- Molecular Dynamics (MD) and structure optimization (OPT):
  - Periodic-DFT (VASP program; Prof. Hafner of U Vienna)
    - Spin polarized Periodic-DFT calculations
    - PBE functional
    - Projector Augmented Wave method (PAW)
    - cutoff 600 eV for OPT
    - cutoff 400 eV for MD
    - Born Oppenheimer MD
    - NVT ensemble in MD

Comparison of the experimental and theoretical results



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The periodic DFT calculated structures were needed to interpret the experimental results to suggest the three cationic sites.

New Alpha site (very surprising because it differs from the 2000 suggested Alpha site and since the site is formed by Al-O-Si-O-Al sequence).

New Beta site (expected based on the unpublished neutron diffraction results).

Five-membered ring new site (Beta’) (very surprising since the site is formed by Al-O-Si-O-Al sequence).

(Near) Future work

- AXRD determination of the local structure of the Co(II) cations in the cationic sites and comparison with the periodic DFT calculated structures (near future).
- Independent verification (in the future):
  - Differently prepared ZSM-5 samples with high concentrations of the Alpha and Beta cationic sites.
  - Different diffraction method (Electron diffraction).

Conclusions

- Solving difficult structural problems concerning the Al siting and Me(II) cationic sites in zeolites with a complex structure (e.g., ZSM-5) require high quality periodic DFT calculations with extensive conformational sampling (Molecular Dynamics) of the local structure of the Me(II) cationic sites to interpret (A)XRD results.
- Cationic sites suggested based only on spectroscopic results (due to the absence of XRD data) are uncertain.

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