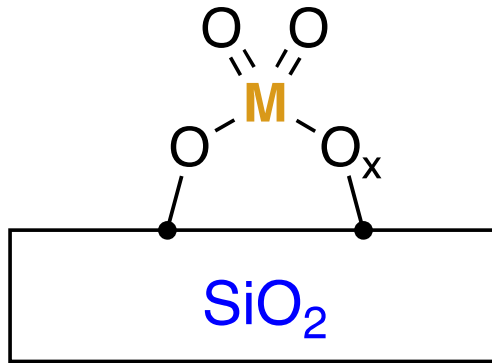




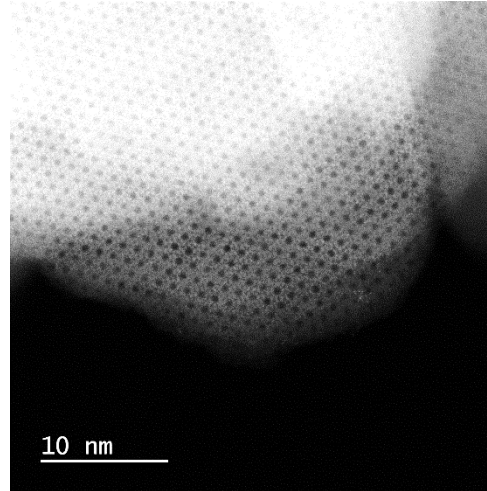
# Elucidating the structure of surface sites using sensitivity enhanced NMR methods

# Heterogeneous Catalysts

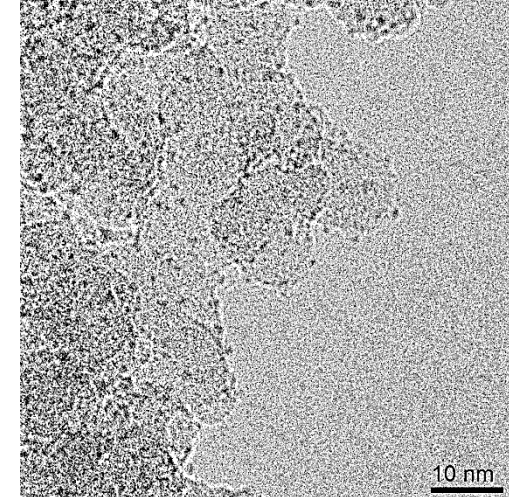
Supported  
metal oxides



Zeolites



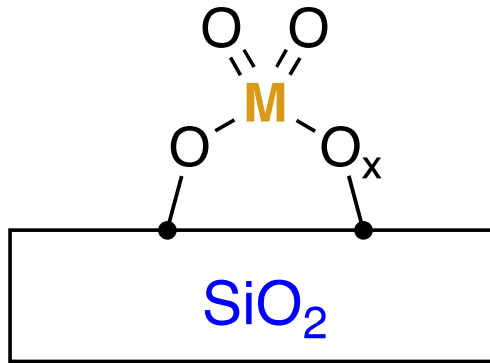
Supported  
metal nanoparticles



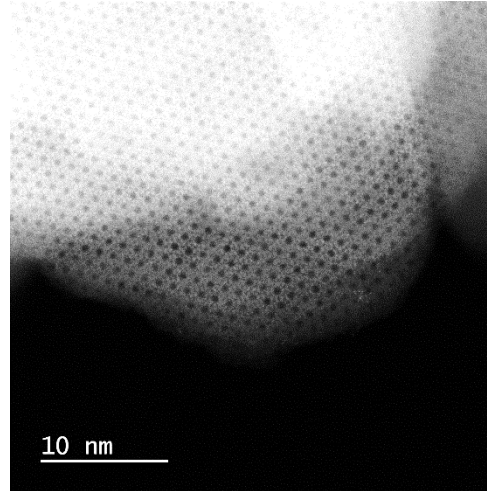
- Involved in numerous industrial catalytic processes
  - Metathesis
  - Dehydrogenation
  - Polymerization
  - Epoxidation
  - Hydrogenation
  - .....

# Heterogeneous Catalysts

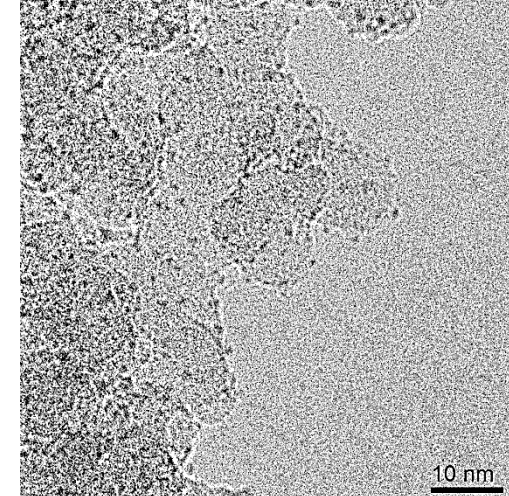
Supported  
metal oxides



Zeolites



Supported  
metal nanoparticles

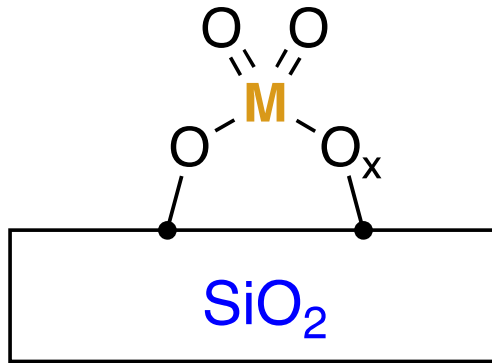


Main goal:  
Can we further improve these industrial catalytic processes?

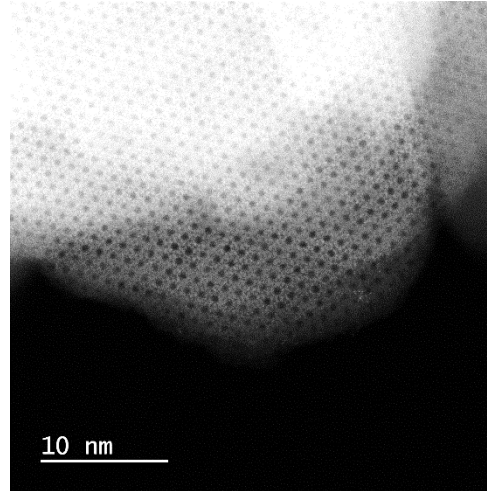


# Heterogeneous Catalysts

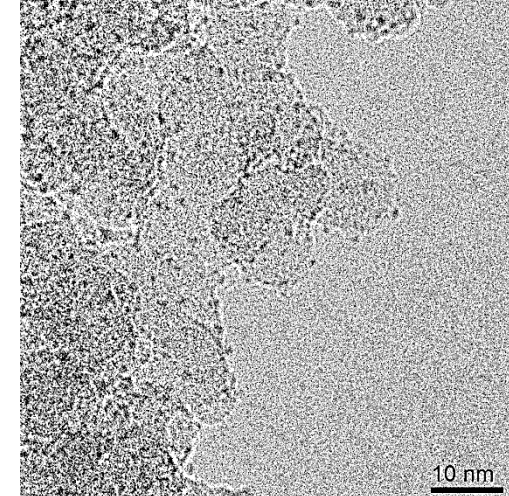
Supported  
metal oxides



Zeolites



Supported  
metal nanoparticles



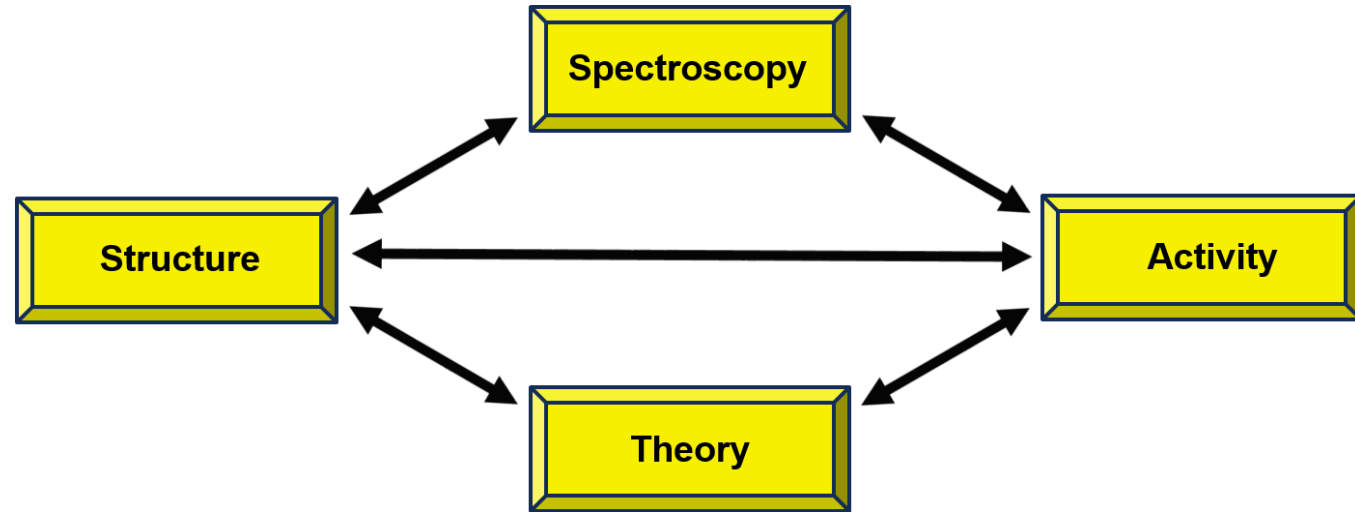
Main goal:

**Can we further improve these industrial catalytic processes?**

- What is the structure of the active sites?
- What are the roles of: supports, interfaces, additives, promoters, size and composition?
- How do these properties affect: Structure, Activity, Selectivity and Stability?

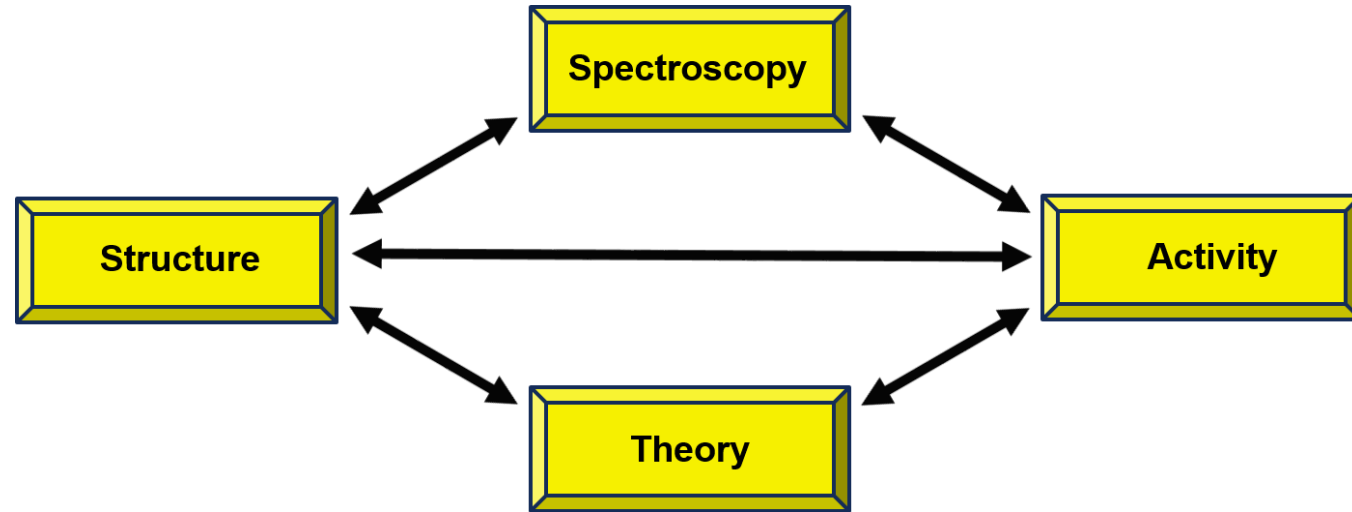
# Major aspects within the group

- Controlling the grafting of tailored molecular precursor (SOMC)
- Detailed characterization of surface species (spectroscopy and computational chem.)
- Catalyst evaluation and further development



## Major aspects within the group

- Controlling the grafting of tailored molecular precursor (SOMC)
- Detailed characterization of surface species (spectroscopy and computational chem.)
- Catalyst evaluation and further development

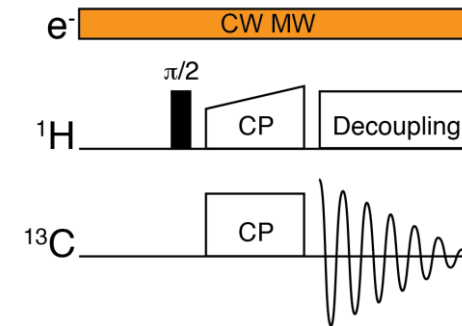
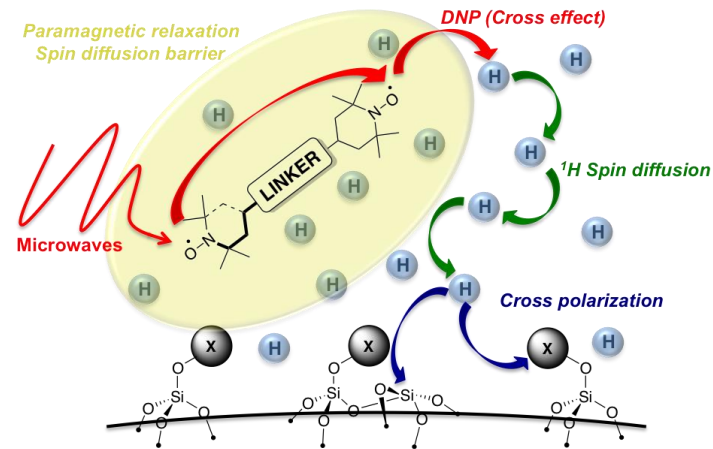


Today's challenges and directions:

**Bridging the gap between industrial and well-defined heterogeneous catalysts**  
**Bridging the gap between single-sites and nanoparticle-based catalysts**  
**Detailed and efficient structural characterization of surface species by NMR**

# Dynamic Nuclear Polarization

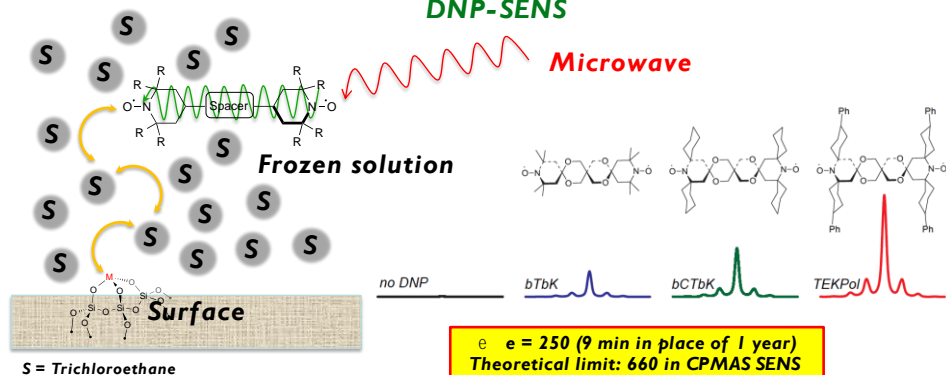
- Sample preparation – solid sample is impregnated with biradical solution, *i.e.* polarizing agent.



- Potential to enhance the signals by a factor of 660

# Dynamic Nuclear Polarization

## Surface-Enhanced NMR Spectroscopy by Dynamic Nuclear Polarization DNP-SENS



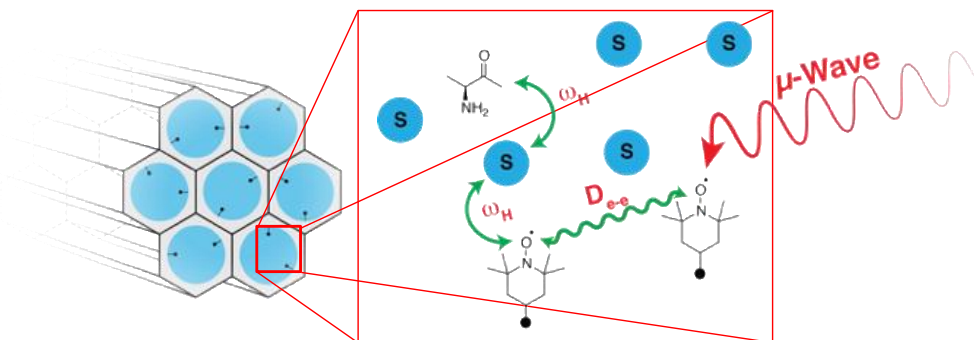
Lesage et al. JACS 2010, 132, 15459.

Rossini et al. ACR 2013, 46, 1942.

Zagdoon et al. JACS 2012, 134, 2284.

Liao et al. Curr. Op. Coll. Interf. Sci. 2018, 33, 63.

## Solid Polarization Matrixes

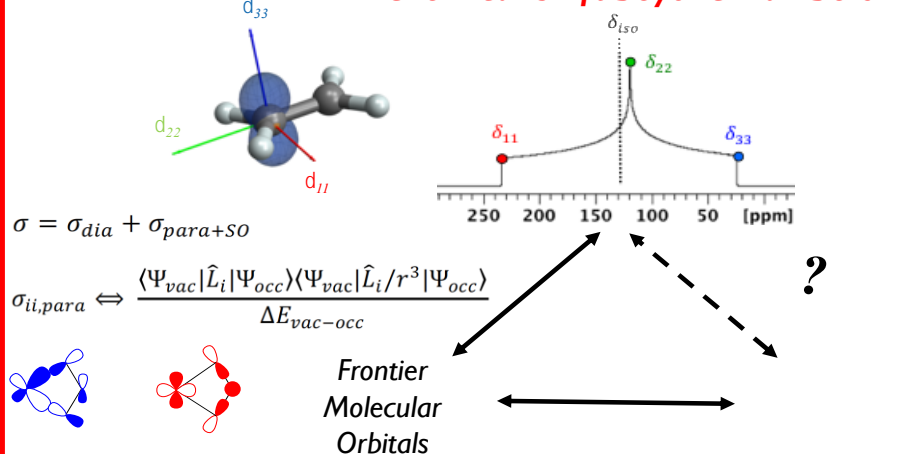


Gajan et al. JACS, 2013, 135, 15459.

Cavailles et al. ACIE 2018, 57, 7453.

Gajan et al. PNAS 2014, 111, 14693.

## NMR Chemical Shift beyond Numbers



Copéret et al. JACS 2017, 139, 10588.

Gordon et al. PNAS 2018, 115, E5867.

Gordon et al. ACS Cent. Sci. 2017, 3, 759.

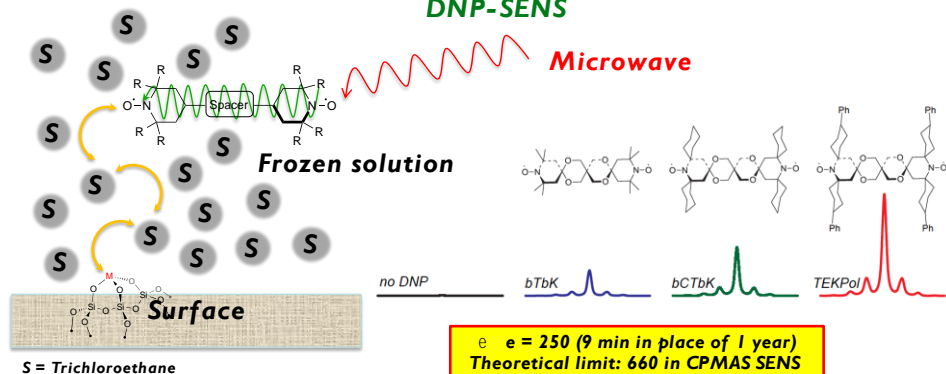
Gordon et al. Acc. Chem. Res. 2019, 52, 2278.

- DNP has been crucial to characterize low abundant surface species



# Dynamic Nuclear Polarization

## Surface-Enhanced NMR Spectroscopy by Dynamic Nuclear Polarization DNP-SENS



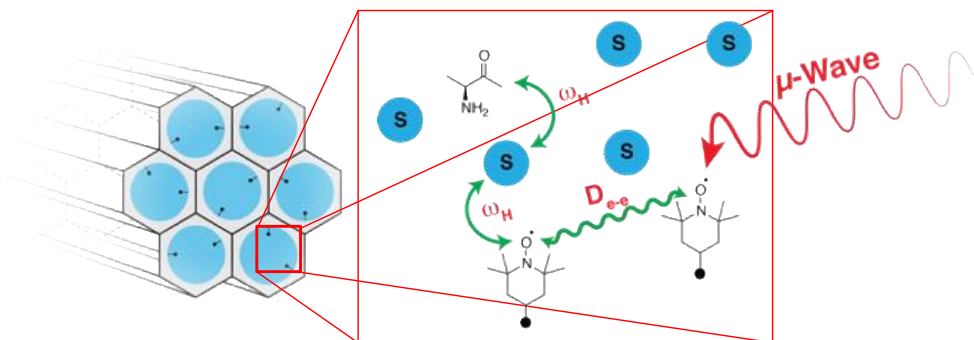
Lesage et al. JACS 2010, 132, 15459.

Rossini et al. ACR 2013, 46, 1942.

Zagdoon et al. JACS 2012, 134, 2284.

Liao et al. Curr. Op. Coll. Interf. Sci. 2018, 33, 63.

## Solid Polarization Matrixes

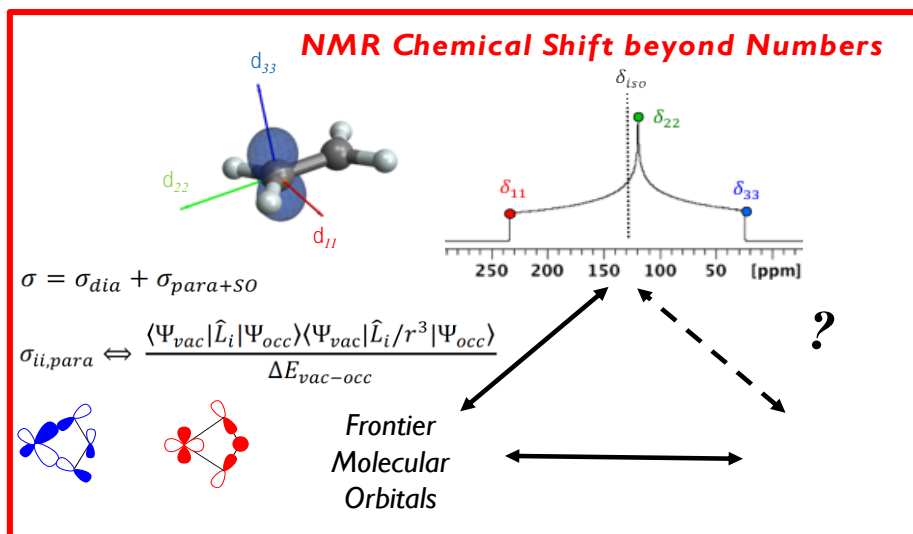


Gajan et al. JACS, 2013, 135, 15459.

Cavailles et al. ACIE 2018, 57, 7453.

Gajan et al. PNAS 2014, 111, 14693.

## NMR Chemical Shift beyond Numbers



Copéret et al. JACS 2017, 139, 10588.

Gordon et al. PNAS 2018, 115, E5867.

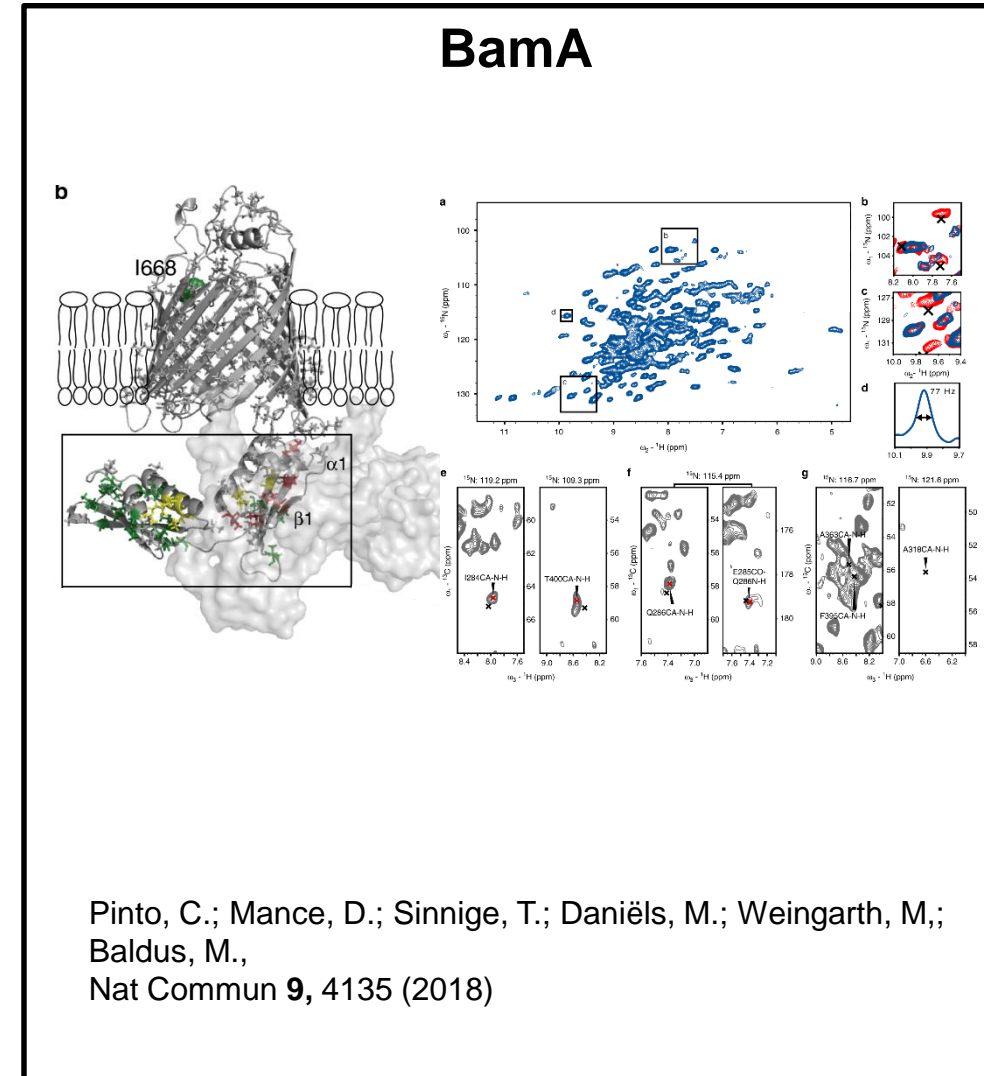
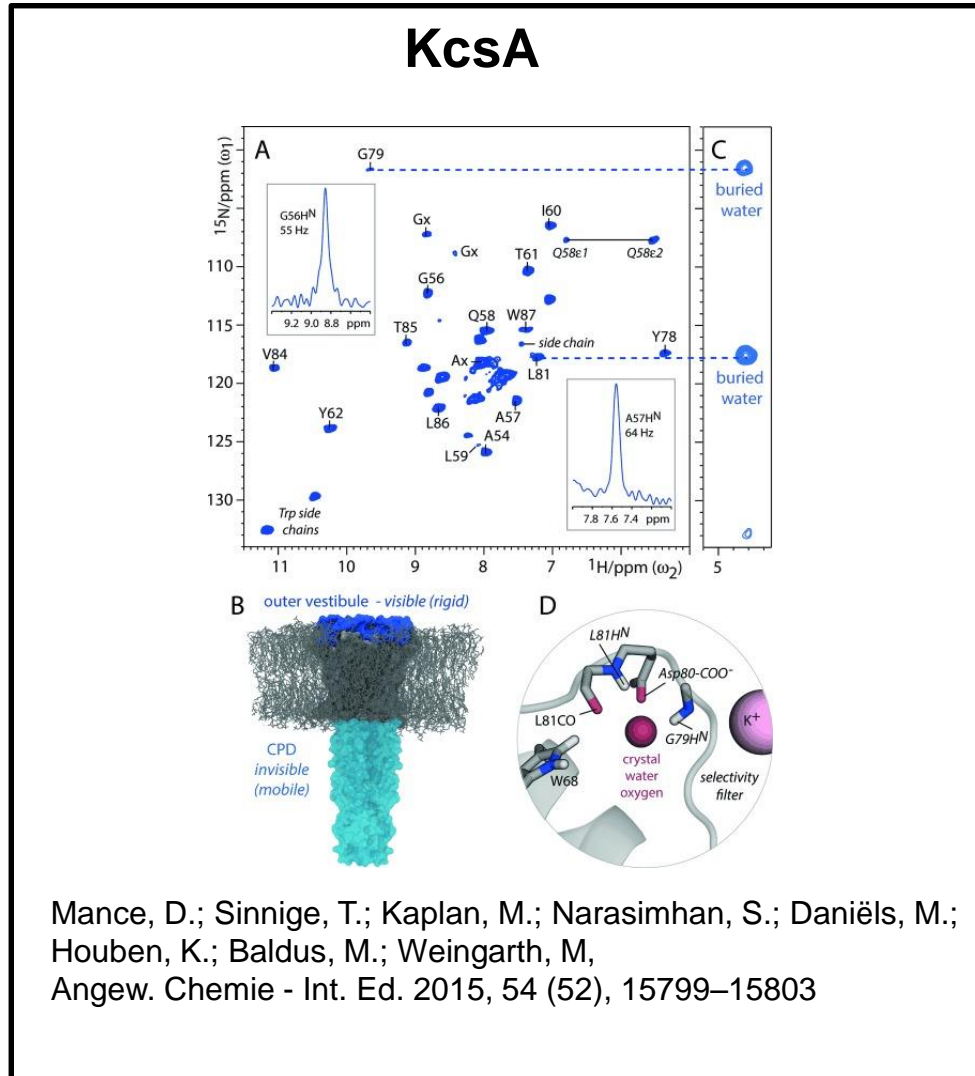
Gordon et al. ACS Cent. Sci. 2017, 3, 759.

Gordon et al. Acc. Chem. Res. 2019, 52, 2278.

- DNP has been crucial to characterize low abundant surface species

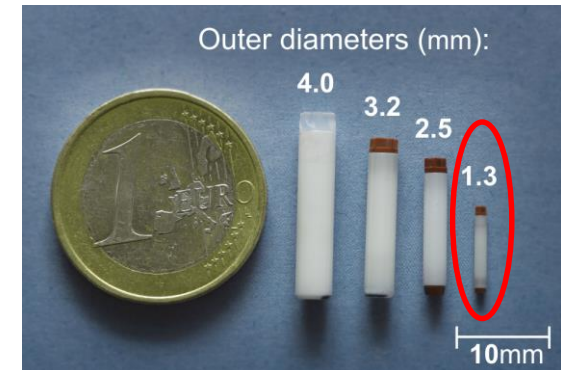
- Performance tends to be unpredictable
- Radical or solvent might interact with the catalyst

# $^1\text{H}$ Detection in combination with fast MAS



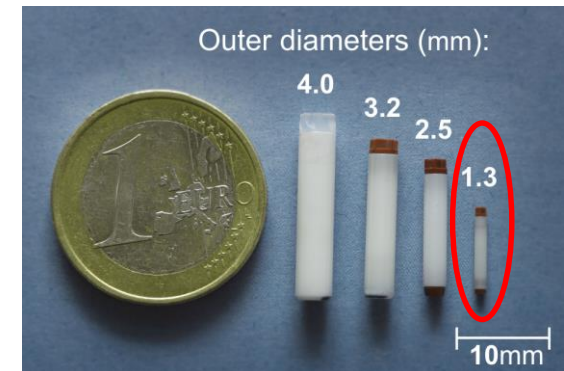
# $^1\text{H}$ Detection in combination with fast MAS

- Use of  $^1\text{H}$  detected experiments to overcome sensitivity issues
- Small quantity of sample required
- No modification of sample required



# $^1\text{H}$ Detection in combination with fast MAS

- Use of  $^1\text{H}$  detected experiments to overcome sensitivity issues
- Small quantity of sample required
- No modification of sample required

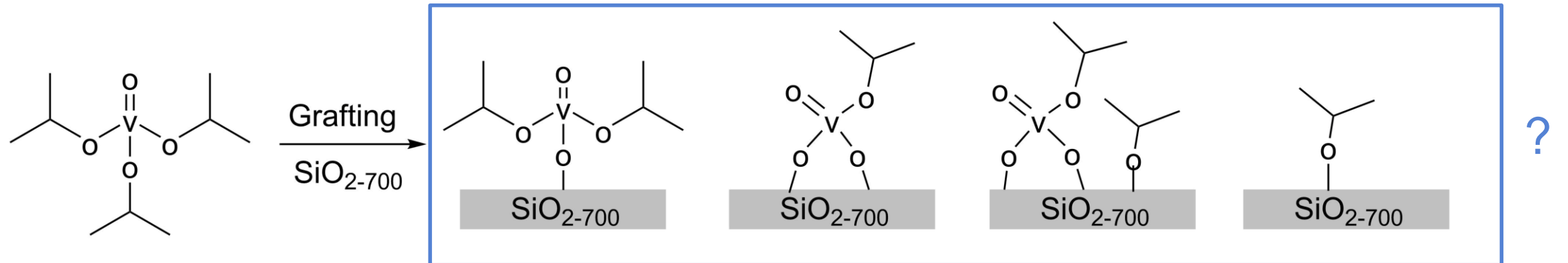


- Demonstrate performance on a unlabelled system (Vanadium Oxide Catalyst)



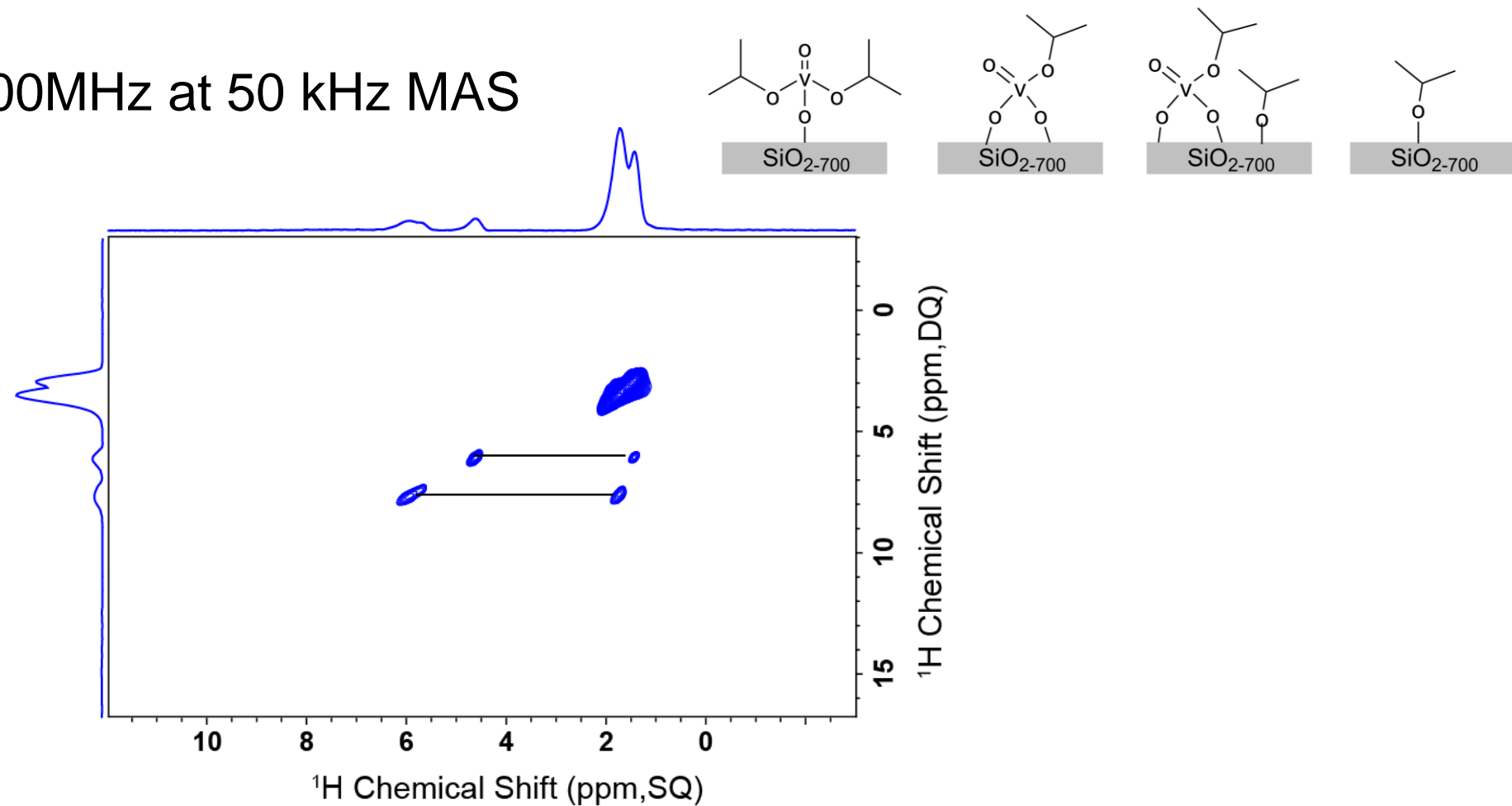
# $^1\text{H}$ Detection in combination with fast MAS

- Preparation of Vanadium Oxide Catalyst through SOMC approach



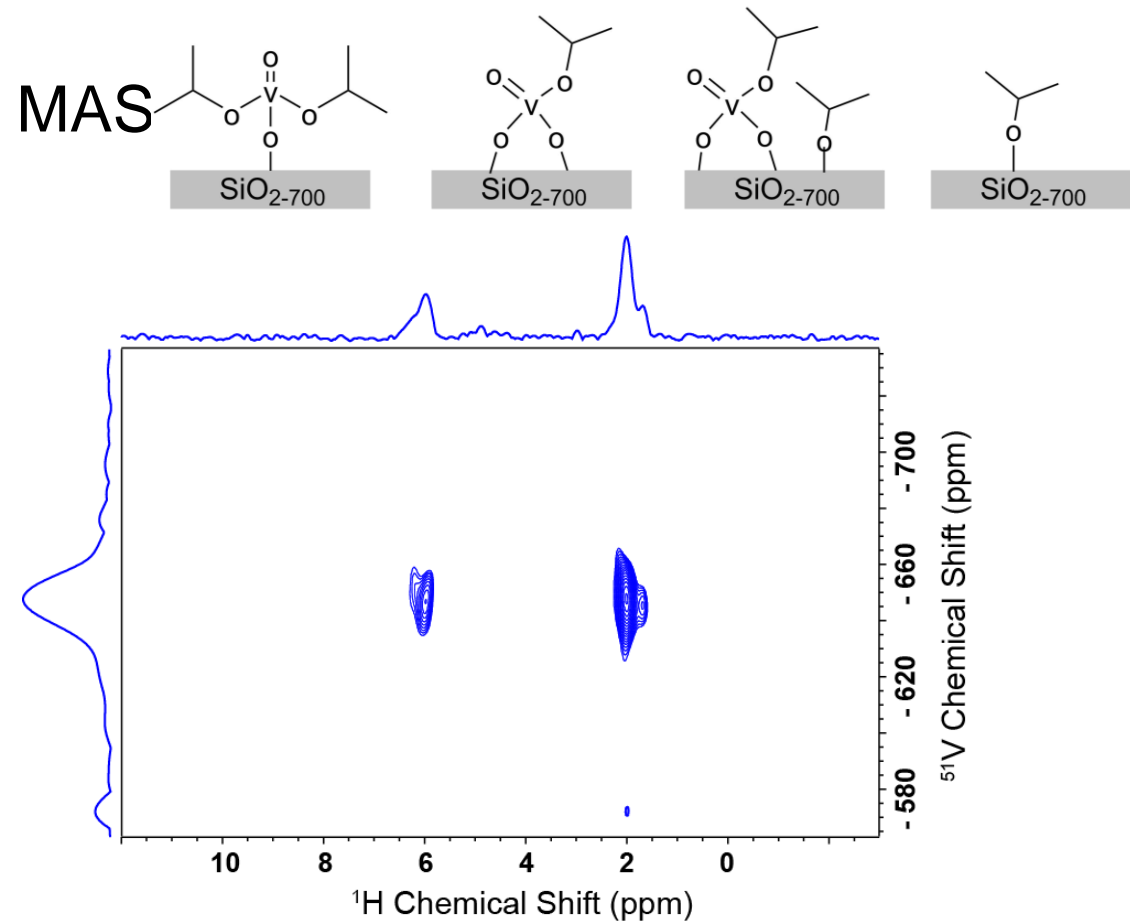
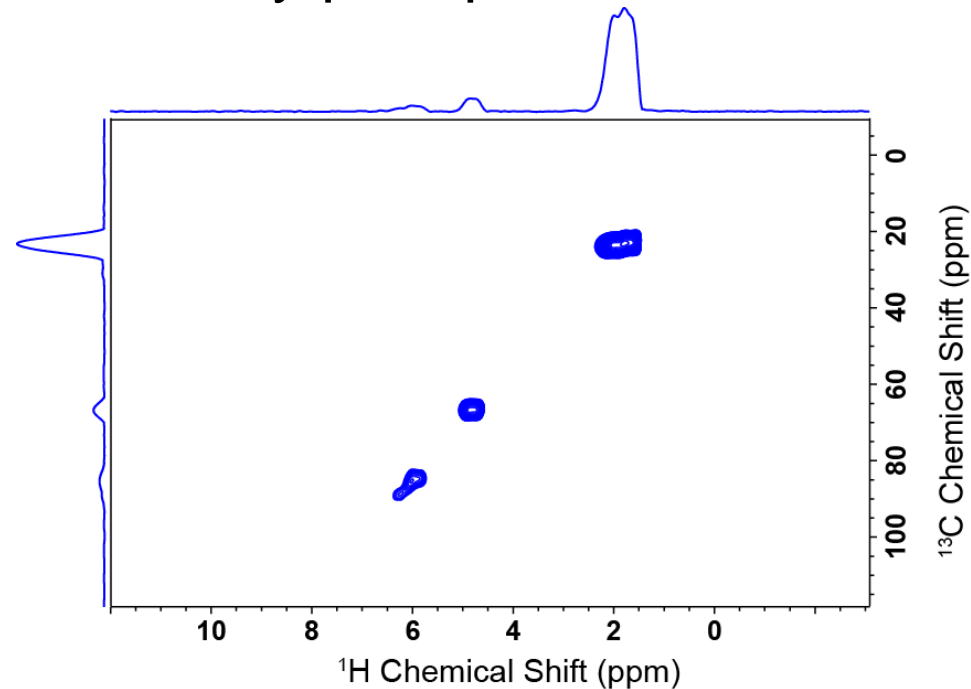
# $^1\text{H}$ Detection in combination with fast MAS

- $^1\text{H}$ - $^1\text{H}$  DQ-SQ, 700MHz at 50 kHz MAS



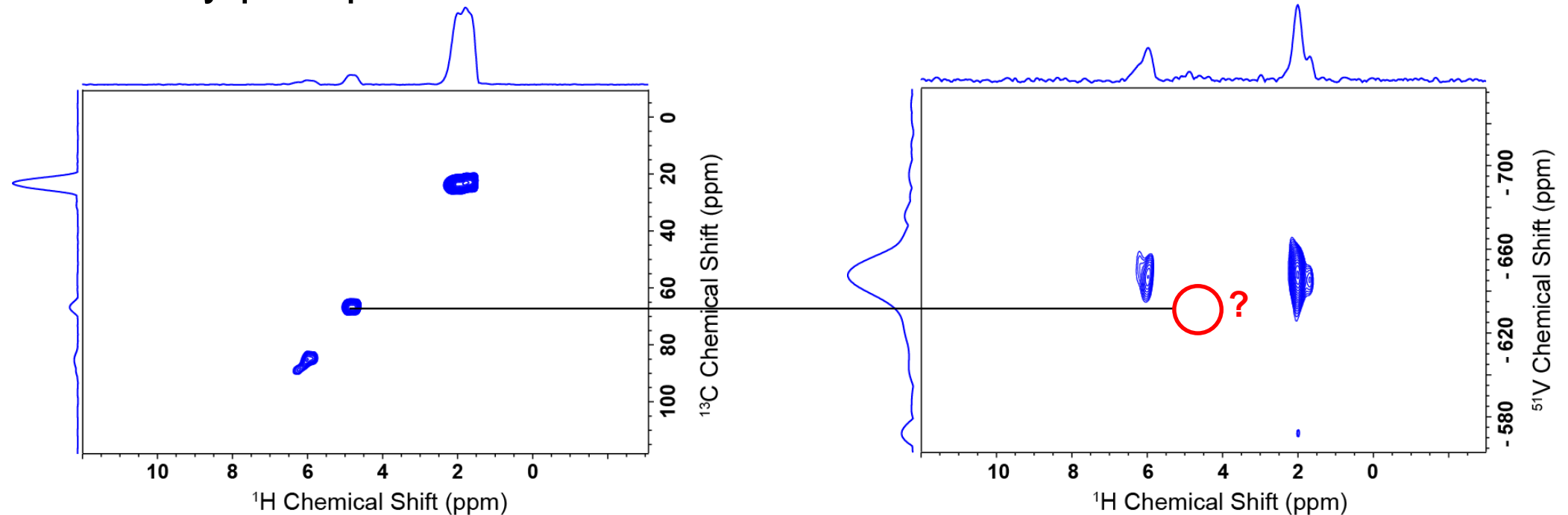
# $^1\text{H}$ Detection in combination with fast MAS

- $^1\text{H}$ -Detected D-HMQC, 700MHz at 50 kHz MAS
- Approx. 1 day per spectra



# $^1\text{H}$ Detection in combination with fast MAS

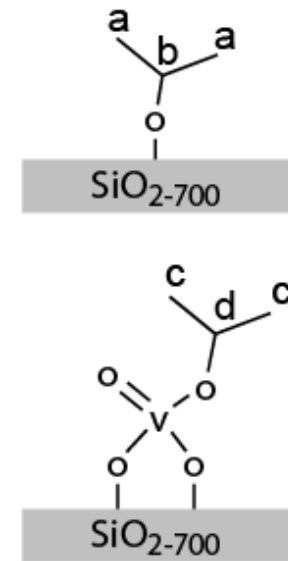
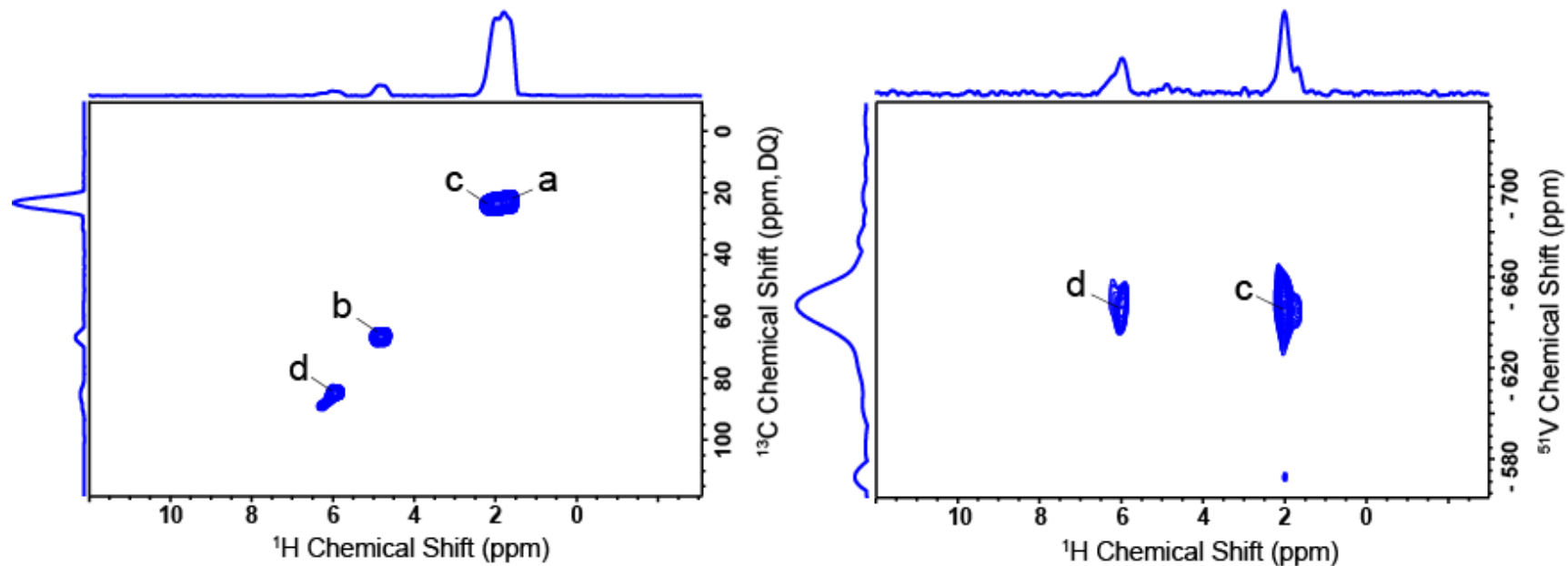
- $^1\text{H}$ -Detected D-HMQC, 700MHz at 50 kHz MAS
- Approx. 1 day per spectra





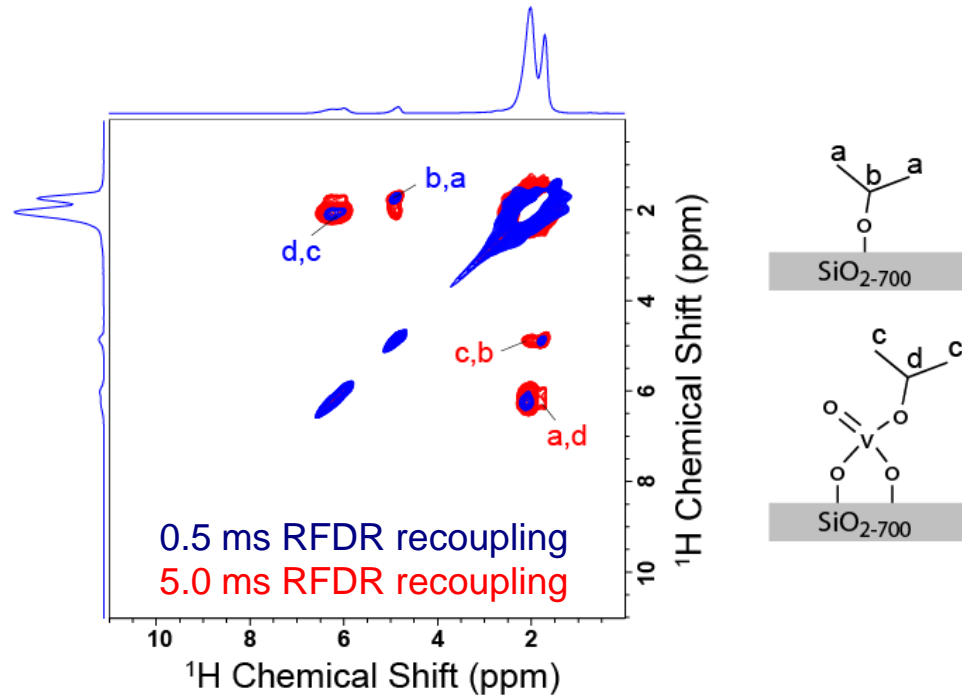
# $^1\text{H}$ Detection in combination with fast MAS

- $^1\text{H}$ -Detected D-HMQC, 700MHz at 50 kHz MAS
- Approx. 1 day per spectra



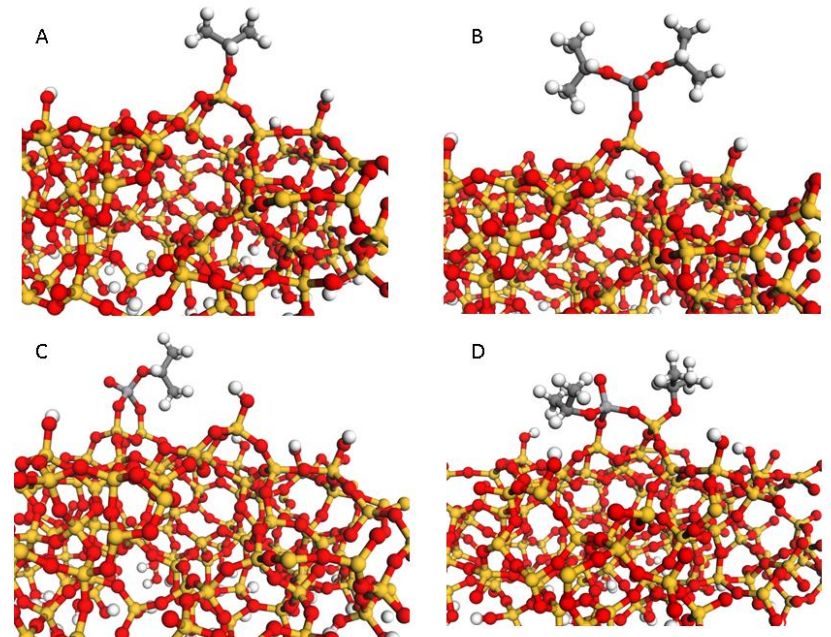
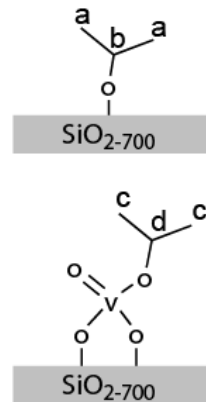
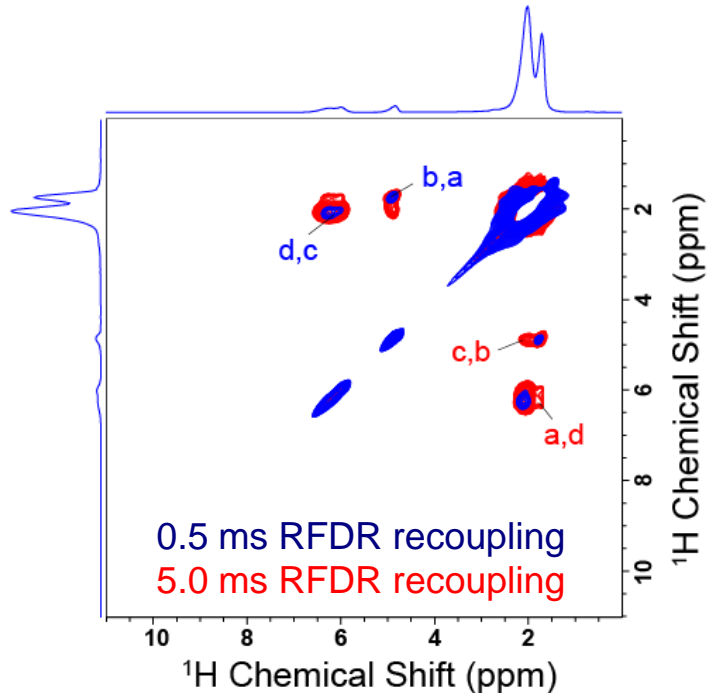
# $^1\text{H}$ Detection in combination with fast MAS

- $^1\text{H}$ - $^1\text{H}$  RFDR, 700MHz at 50 kHz MAS



# $^1\text{H}$ Detection in combination with fast MAS

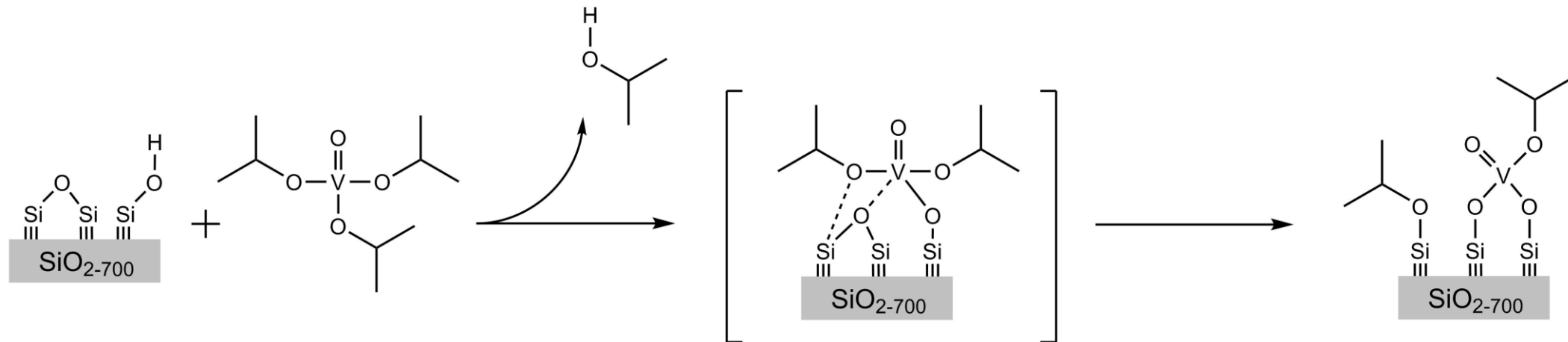
- $^1\text{H}$ - $^1\text{H}$  RFDR, 700MHz at 50 kHz MAS



- Validating assignments by Computational Chemistry/NMR calculations

# $^1\text{H}$ Detection in combination with fast MAS

- Proposed grafting mechanism





# Summary

- Sensitivity enhanced methods are an effective method for characterization of Catalysts
- NMR provides us a unique tool in correlating NMR parameters with catalytic performance
- The small quantities required make isotope enrichment more practical

# Summary

- Sensitivity enhanced methods are an effective method for characterization of Catalysts
- NMR provides us a unique tool in correlating NMR parameters with catalytic performance
- The small quantities required make isotope enrichment more practical

## Outlook:

- Development of more dedicated experiments
- Focus on characterizing Catalysts pre- and post- reaction in order to understand reaction-mechanism's, deactivation mechanism, etc.

# Acknowledgement



Copéret Group, 2019