Solid state NMR spectroscopy: basic principles and applications in heterogeneous catalysis

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Bulgarian Academy of Sciences**

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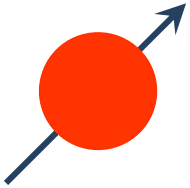
OUTLINE

- Solid state NMR – basic principles and methods
- SS NMR characterization of zeolites – Zeolite beta, Ag-Beta, Al-ZSM5 and Ga-ZSM5
- SS NMR characterization of polyoxometalate/MCM-41 hybrid catalyst

I. Nuclear interactions and the magic in NMR

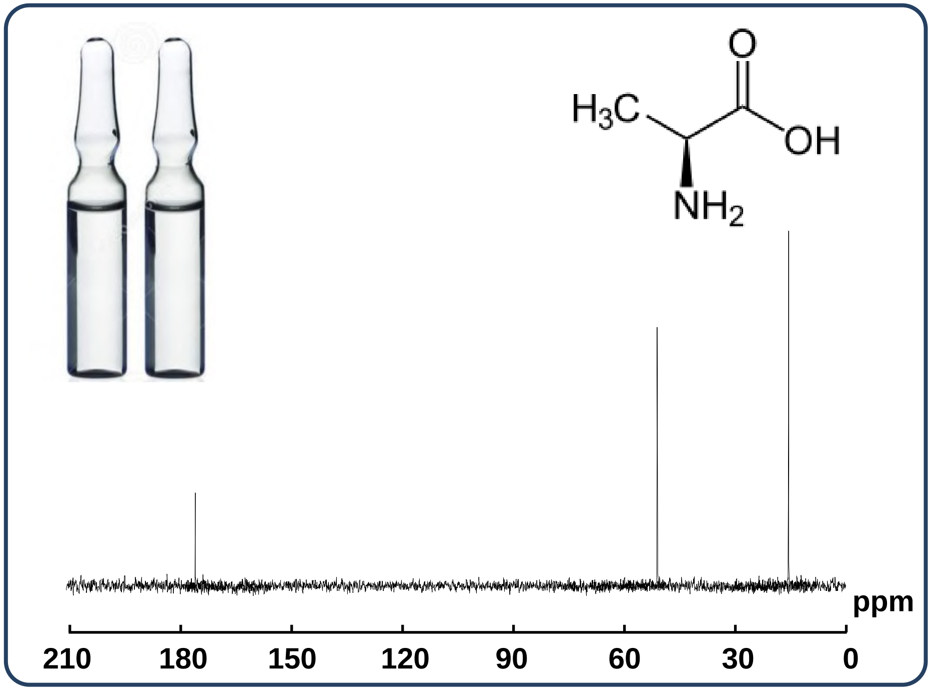


$I > 0$

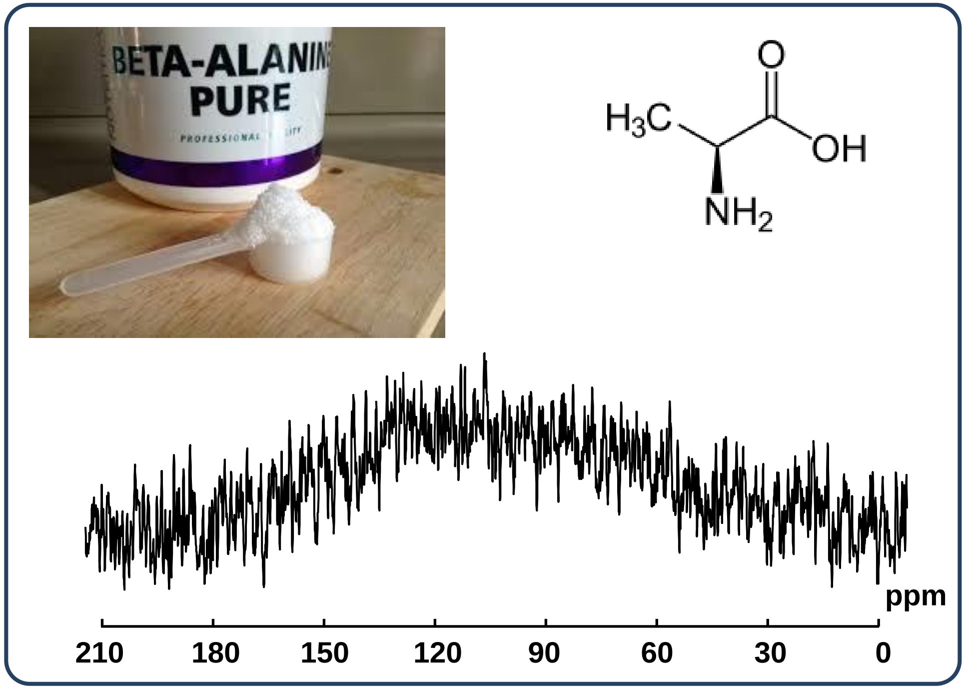
$\mu = \gamma I$

- **NMR measures the interactions of the nuclei with their environment**
- **NMR spectrum – information about structure, dynamics and interactions within the investigated samples at atomic (molecular) level**
- **Nuclear interactions depend on state of matter**

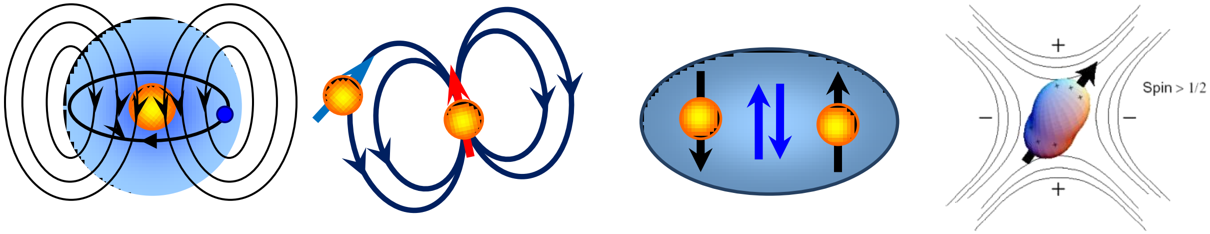
^{13}C NMR spectrum of alanine in solution



^{13}C NMR spectrum of powder alanine



I. Nuclear interactions and the magic in NMR



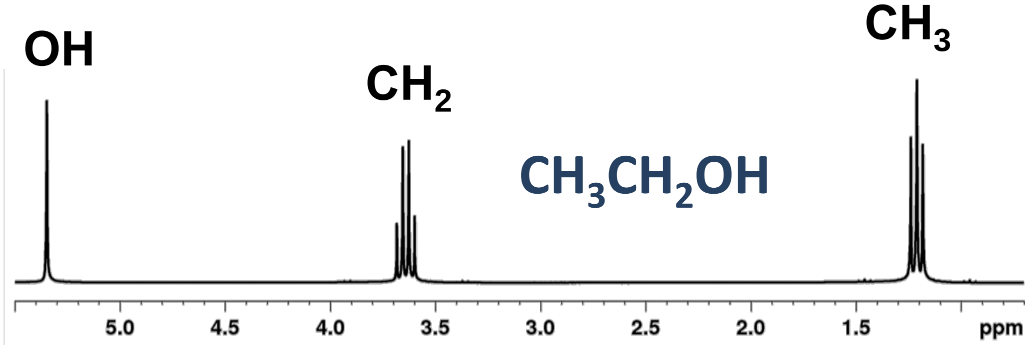
$$\hat{H}_{\mathrm{spin}} = \underbrace{\hat{H}_{stat} + \hat{H}_{RF}} + \underbrace{\hat{H}_{CS} + \hat{H}_{DD} + \hat{H}_{J} + \hat{H}_{Q}}$$

$\hat{H}_{ext}$ – with NMR spectrometer

- Static magnetic field B_0
- RF field B_1
- NMR phenomenon

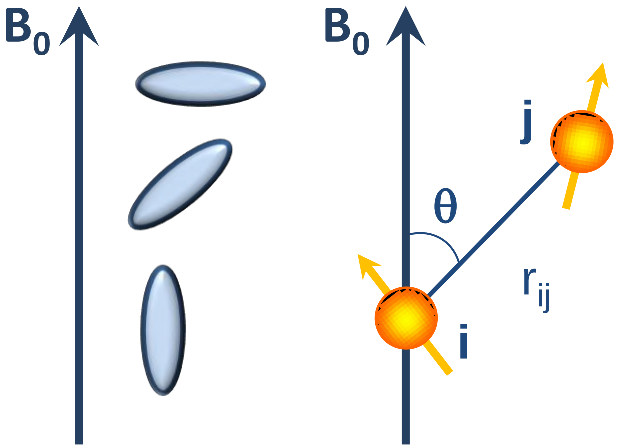
$\hat{H}_{int}$ – within the sample

- Depend on state of matter
- Sample structure and dynamics
- NMR spectrum



I. Why we need a Magic in NMR of solids?

Nuclear interactions are generally anisotropic (orientation dependent)



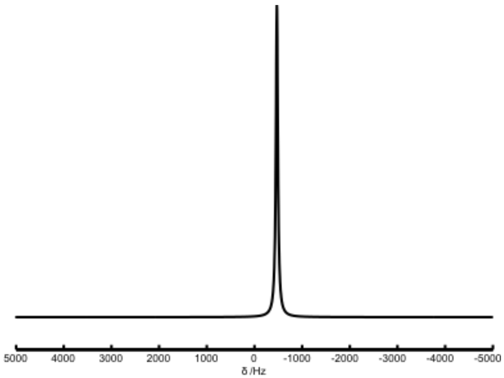
$$\hat{H}_{int} = \hat{H}_{iso} + \underbrace{\hat{H}_{CSA} + \hat{H}_{DD} + \hat{H}_{Q}}$$

$\propto (3\cos^2\theta - 1)$

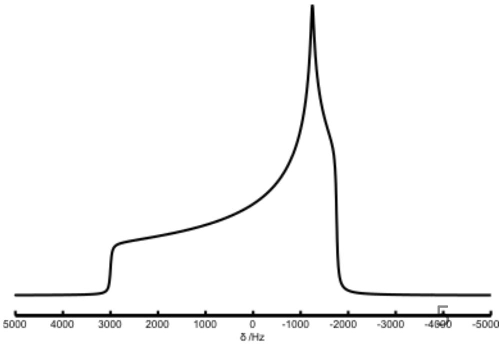
orientation independent

orientation dependent

In solution



In solid powder



- **Solution: fast molecular tumbling results in time averaging of the orientation dependent interactions**

- **Solids: restricted motion results in characteristic splitting and/or broadening of resonance lines**

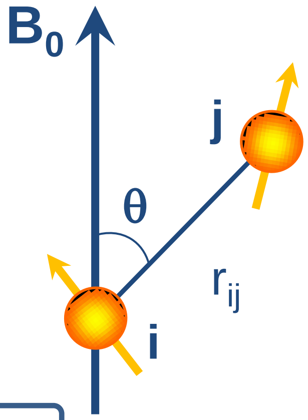
I. How the magic works in NMR: magic angle spinning NMR

Anisotropic interactions: strong NMR line broadening

$$\hat{H}_{\mathrm{int}} = \hat{H}_{iso} + \cancel{\hat{H}}_{DD} + \cancel{\hat{H}}_{CSA} + \cancel{\hat{H}}_{Q}$$

3.2 mm; 24 kHz ⇔ 240 m/s (864 km/h)

$$\left.\begin{array}{l}\hat{H}_{DD}\\[1em] \hat{H}_{CSA}\\[1em] \hat{H}_{Q1}\end{array}\right\} \propto (3\cos^2\theta - 1)$$

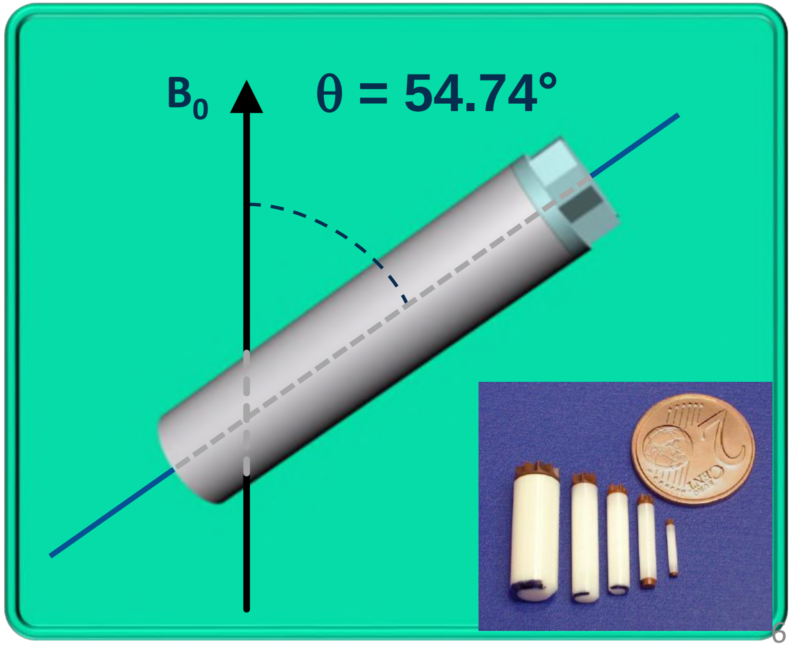


4 mm => 15 kHz
3.2 mm => 25 kHz
2.5 mm => 35 kHz
1.2 mm => 75 kHz
0.7 mm => 110 kHz

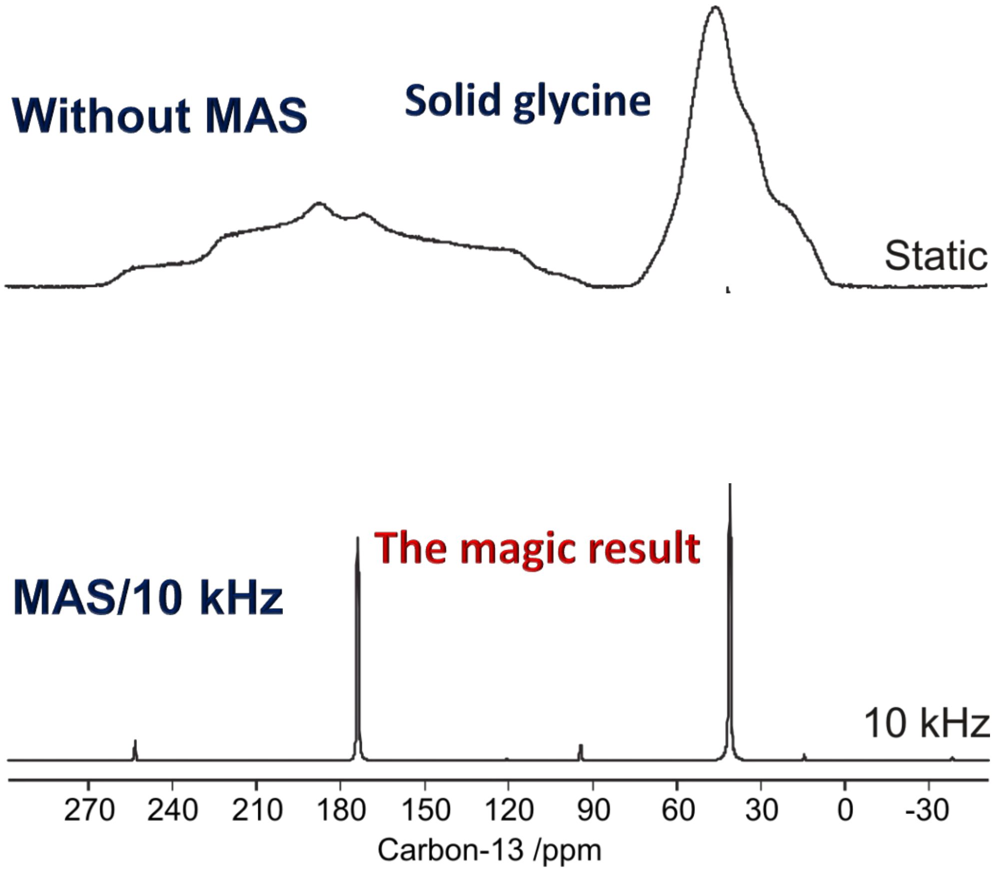
At θ_{ij} = 54.74°, $\cos^2\theta = 1/3$

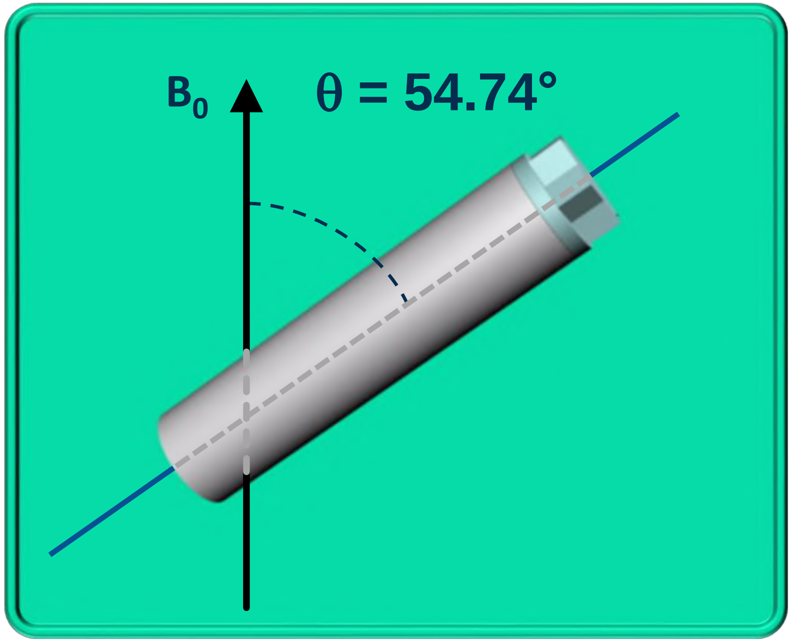
Magic angle spinning (MAS)

- **Reduces/eliminates signal broadening due to chemical shift anisotropy, dipolar and first order quadrupole interactions**
- **Better resolution**
- **Higher sensitivity**



I. The Magic Result





I. SS NMR Spectroscopy: methodological and experimental aspects

- Heteronuclear ^{29}Si, ^{27}Al, ^{119}Sn, ^{31}P, ^{23}Na, ^{13}C, ^{15}N, etc.
- Magic angle (54.7°) spinning: 15 – 25 kHz, fast and ultrafast MAS at 65 – 80 kHz.
- High-power decoupling: homo- and heteronuclear; to remove dipolar interactions with ^{1}H, enhancing spectral resolution
- Cross-polarization (CP): significant improvement in sensitivity
- ^{1}H spectra: ultrafast MAS at 65 – 80 kHz, special decoupling schemes (FSLG, PMLG, DUMBO)
- 2D $^{1}\mathrm{H} \rightarrow {}^{13}\mathrm{C}$ CP HETCOR experiments
- 2D ^{1}H-^{1}H experiments under fast MAS
- NMR crystallography – combination of ssNMR and first principle calculations

Cambridge Sequential Total Energy Package (CASTEP): predicts key NMR properties of molecules and solid state materials from first principles calculations without the need for any empirical parameter.

II. Solid State NMR Spectroscopy: Application in catalysis

Solid state NMR can answer the following questions:

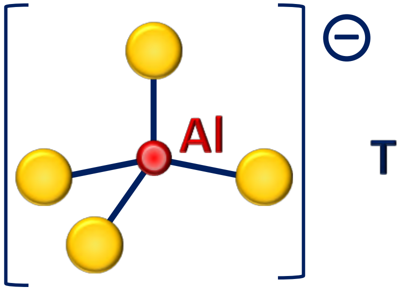
- What is the chemical structure of the catalytic system
- Is the material/active phase crystalline or amorphous
- Structural features of catalyst framework
- Characterization of surface sites: type of surface sites, framework and extra-framework species
- Local structure of particles during the synthesis of solid catalysts
- Investigation of reaction mechanism catalyzed by solid materials

Advantages:

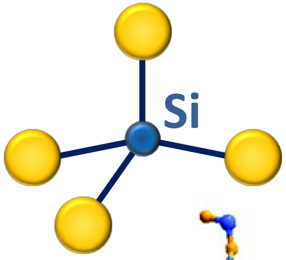
- Non-destructive and non-invasive technique
- Quantitative and selective
- Information about structure as well as dynamics at molecular and supramolecular level

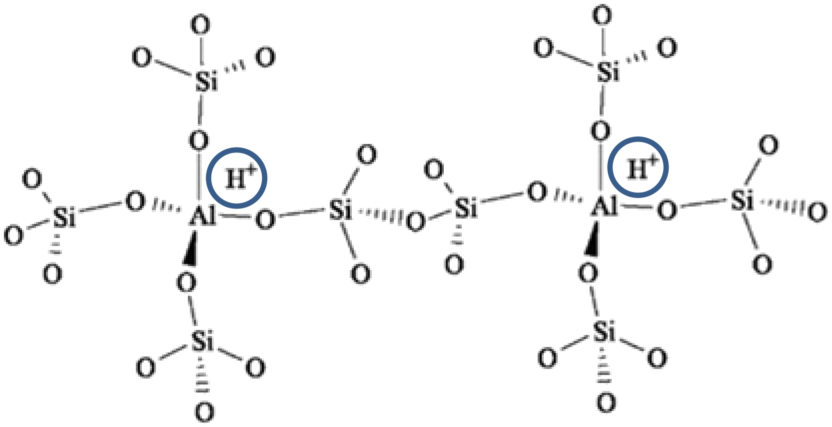
II. SS NMR – Characterization of zeolite based catalysts

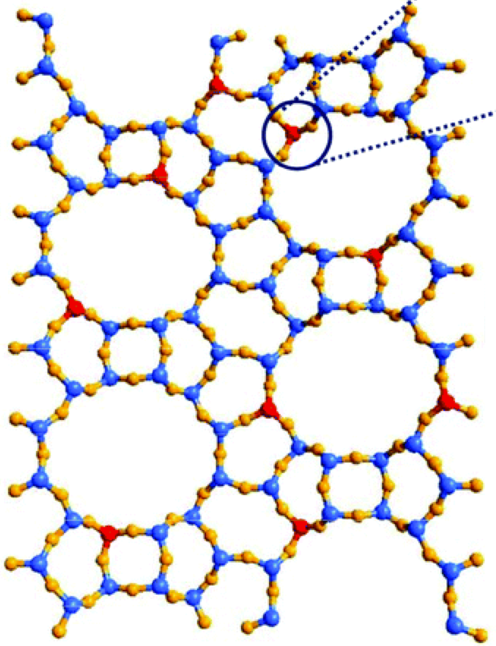
- The zeolite framework is composed of primary building units of tetrahedral AlO_4 and SiO_4 building blocks sharing oxygen ions
- Cations (H^+, Na^+, NH_4^+, Ag^+, transition metals) located inside the channels/pores, to balance the negative charges in the framework

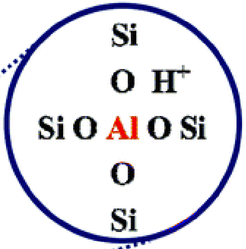


TO_4 units; T = Al or Si





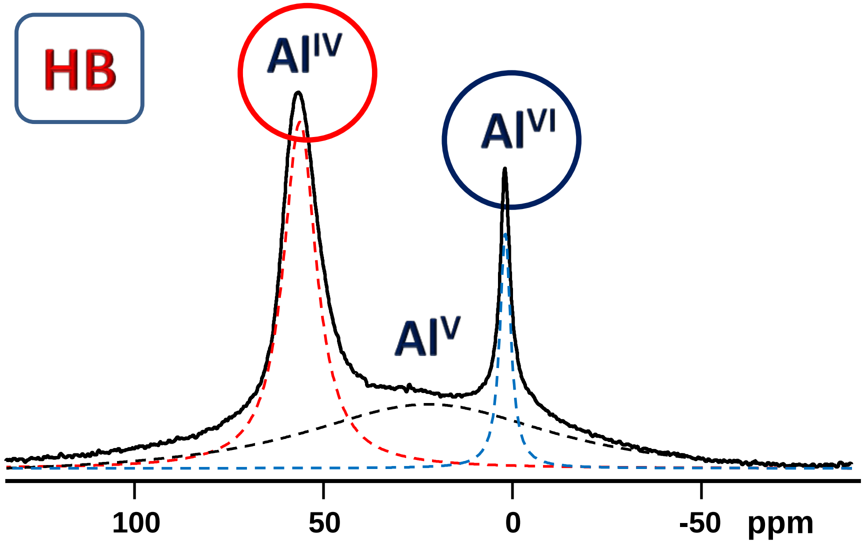


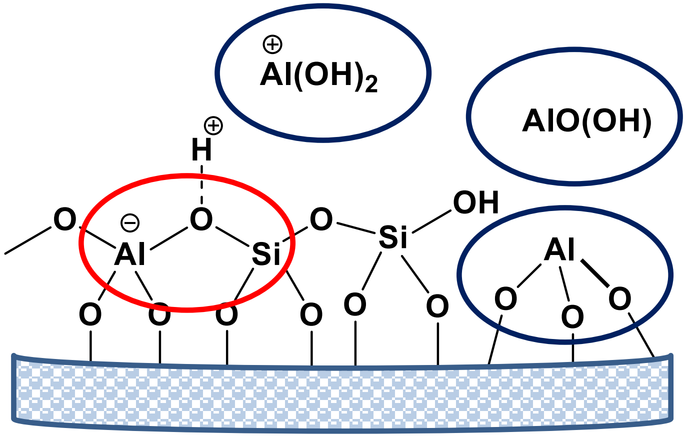


II. Characterization of zeolite structure: type of Al coordination

- Parent zeolite beta, **HB**
- Ag modified zeolite beta, **AgB**, obtained by solid state ion exchange

^{27}Al MAS NMR spectra





[FAL]:[EFAL] = 78:22

Al^{IV} – tetrahedral framework Al
Al^{VI} – octahedrally coordinated species
Al^{V} – pentacoordinated or disturbed tetrahedral sites

- Six-coordinated EFAl [$Al(OH)_3.3H_2O$]
- Defect framework octahedral sites of three-coordinated framework Al species with 3 adsorbed H_2O molecules

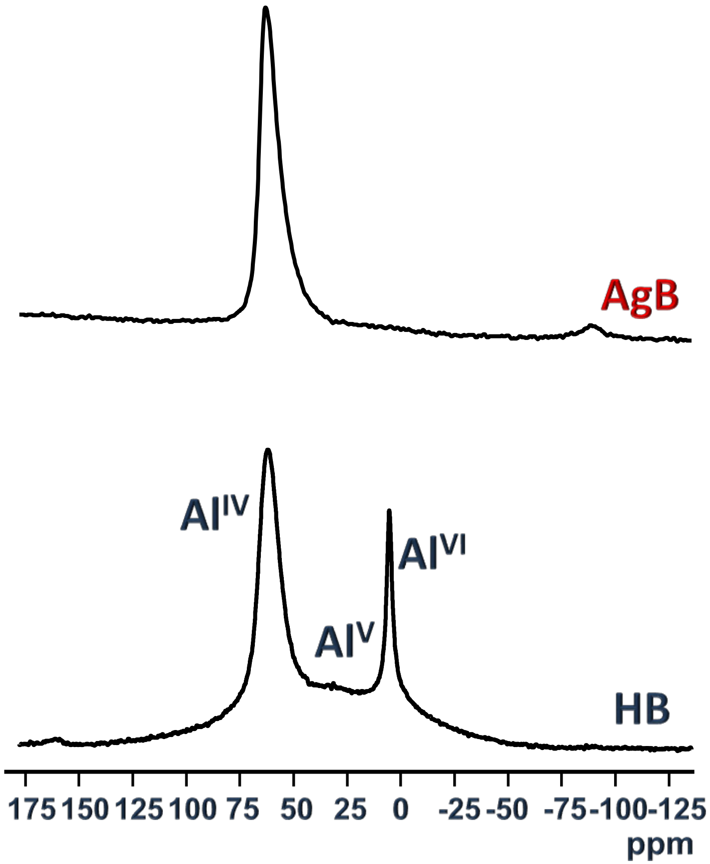
P. Shestakova, C. Martineau, V. Mavrodinova, M. Popova, RSC Adv., 2015, 5, 81957

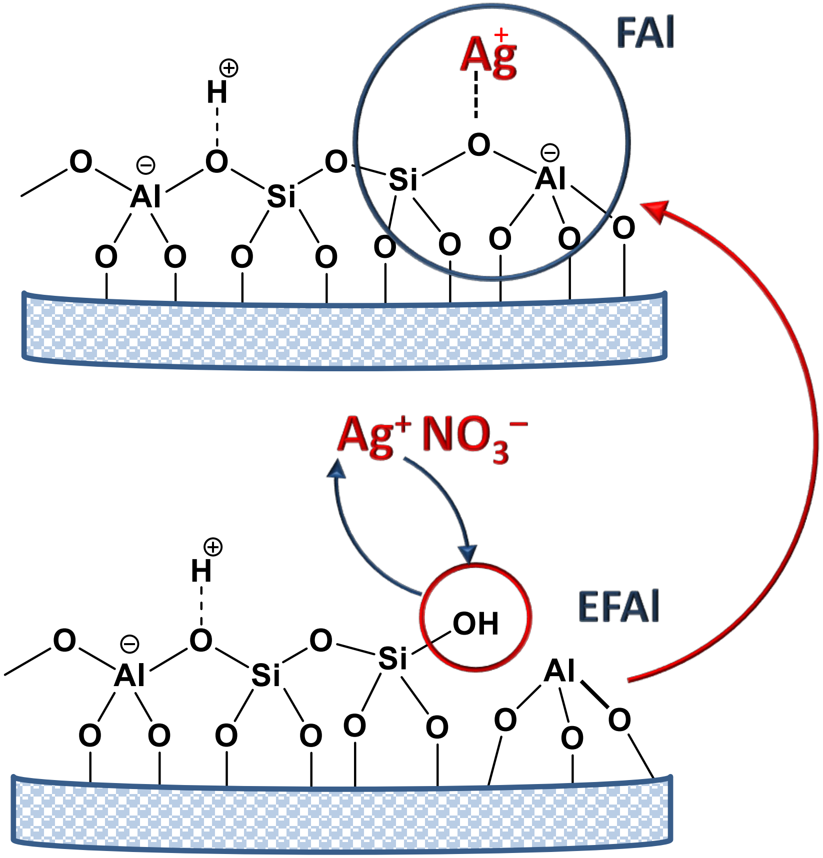
II. Changes in zeolite structure

^{27}Al MAS NMR spectra

Transformation of EFAl species to FAl:

Involvement of the silanol groups originating either from the opening of the SiOHAl bridges or from the silanol groups in the vicinity of the framework defect Al sites





II. Quantitative distribution of Si units and calculation of Si:Al ratio

Single pulse ^{29}Si MAS NMR spectra

Si
O
Al O Si O Al
O
Si

Q^2 => Si(2Al)

Si
O
Si O Si O Al
O
Si

Q^3 => Si(1Al)

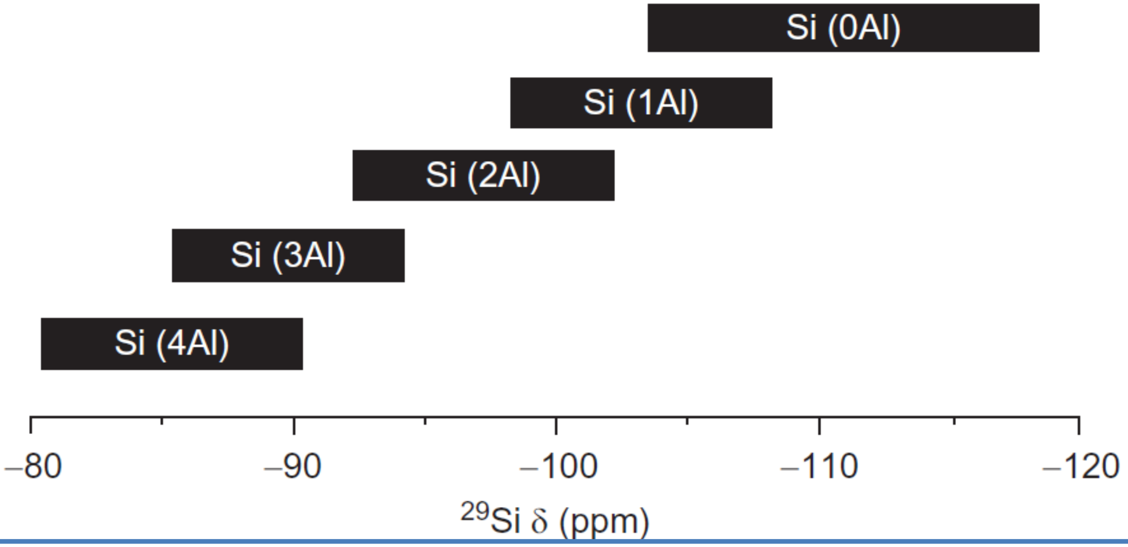
Si
O
Si O Si O H
O
Si

Q^3 => Si(1OH)

Si
O
Si O Si O Si
O
Si

Q^4 => Si(0Al)

$$Si/T = \frac{\sum_{n=0}^{4} I_{Si(nT)}}{\sum_{n}^{4} 0.25nI_{Si(nT)}}$$



T. Todorova, P. Shestakova, T. Petrova, M. Popova, H. Lazarova, Y. Kalvachev, *J. Mater.Sci*. (2020), accepted.

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Si
O
Al O **Si** O Al
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O
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O
Si

Q^3 => Si(1Al)

Si
O
Si O **Si** O H
O
Si

Q^3 => Si(1OH)

Si
O
Si O **Si** O Si
O
Si

Q^4 => Si(0Al)

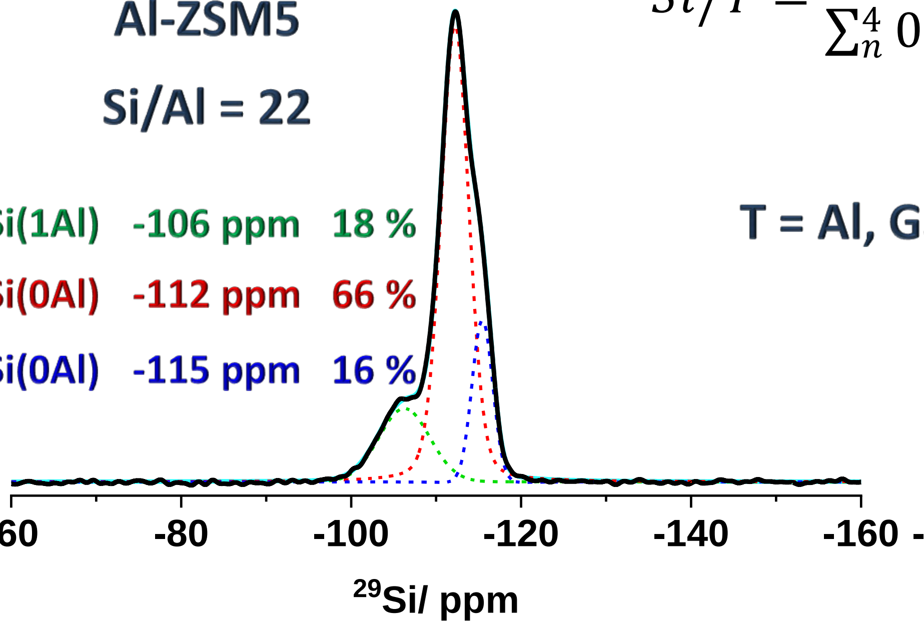
$$Si/T = \frac{\sum_{n=0}^{4} I_{Si(nT)}}{\sum_{n}^{4} 0.25nI_{Si(nT)}}$$

T = Al, Ga, P, B, etc.

Al-ZSM5

Si/Al = 22

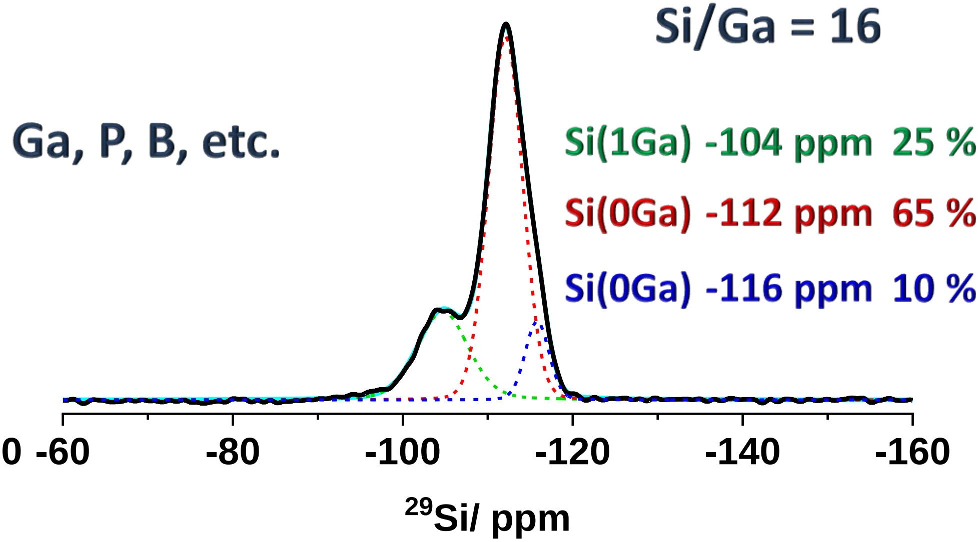
Si(1Al)	-106 ppm	18 %
Si(0Al)	-112 ppm	66 %
Si(0Al)	-115 ppm	16 %



Ga-ZSM5

Si/Ga = 16

Si(1Ga)	-104 ppm	25 %
Si(0Ga)	-112 ppm	65 %
Si(0Ga)	-116 ppm	10 %

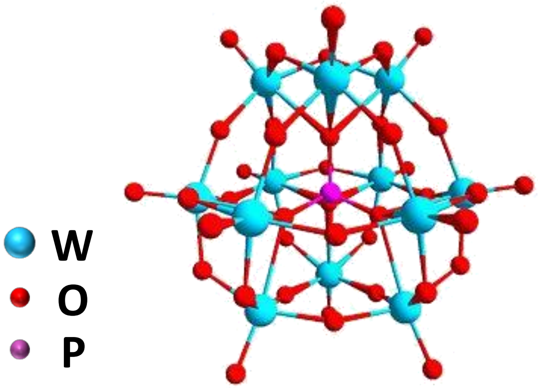


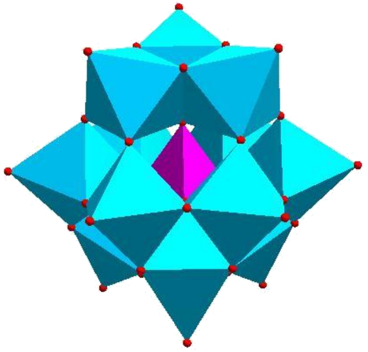
T. Todorova, P. Shestakova, T. Petrova, M. Popova, H. Lazarova, Y. Kalvachev, *J. Mater.Sci*. (2020), accepted.

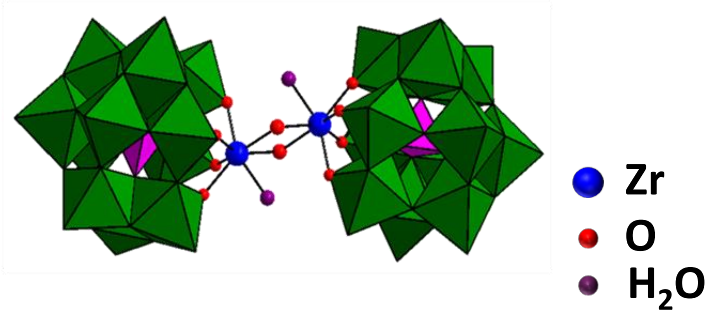
III. Polyoxometalate-modified mesoporous silicas as efficient catalysts for renewable levulinic acid esterification

Polyoxometalates (POMs): versatile class of metal-oxygen clusters

Lewis metal substituted POMs





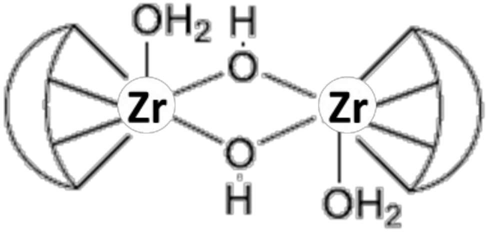


Keggin Heteropolyanion α-$[PW_{12}O_{40}]^{3-}$

Binuclear Zr^{IV} substituted Keggin POM (ZrK2:2)

- V(V), Mo(VI) or W(VI) and O
- High negative charge
- Dynamic solution behavior
- Coordination sites
- Brønsted acids

- Combining the Brønsted acidity of POM with the Lewis acidity of the metal center



Applications: catalysis, electrochemistry, biomedicine, materials science

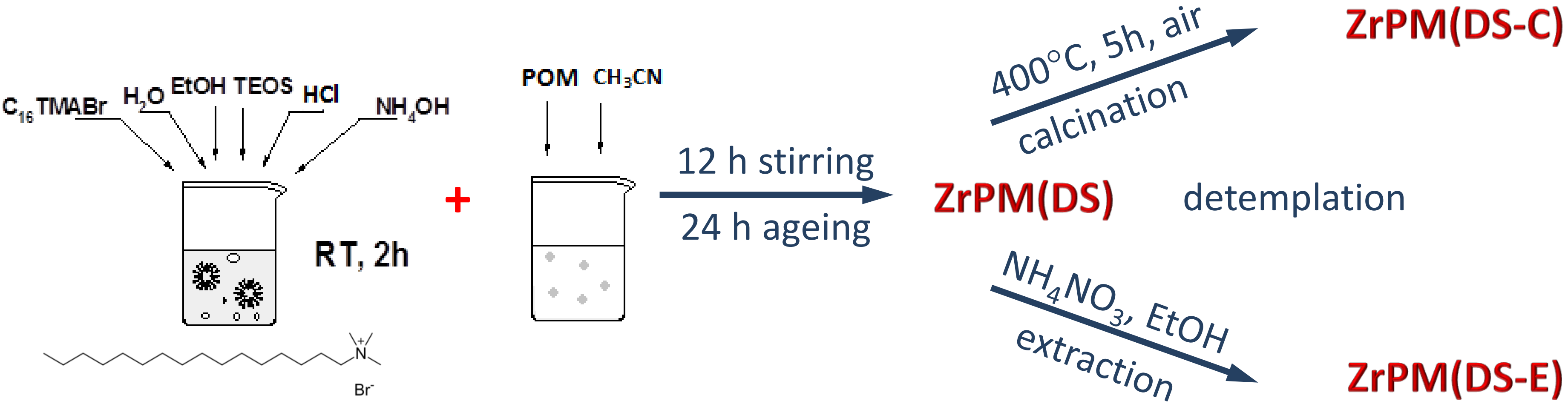
P. Shestakova, M. Popova, H. Lazarova, T. Parac-Vogt, T. K. N. Luong, I. Trendafilova, J. Mihály, Á. Szegedi, Appl.Catal. A-Gen, submitted.

III. Preparation of ZrK2:2/MCM-41 hybrid catalysts

Bulk POM catalysts: low surface area, agglomeration, low reusability

Supported POM catalyst: high surface area, dispersion, preservation of active sites

- **Direct synthesis**



12 h stirring $\xrightarrow{\quad}$ 24 h ageing

ZrPM(DS) detemplation

400°C, 5h, air $\rightarrow$ calcination: **ZrPM(DS-C)**

NH_4NO_3, EtOH $\rightarrow$ extraction: **ZrPM(DS-E)**

- **Incipient wetness impregnation**

MCM-41-NH2

Impregnation $\rightarrow$ POM, CH_3CN

ZrPM-NH_2(PS)

III. NMR characterization of ZrK2:2/MCM-41 hybrid catalysts

Insight into:

- POM stability during synthesis, template removal, impregnation and reaction
- Structural characteristics and transformations of the MCM-41 silica matrix
- Leaching of the active phase during reaction

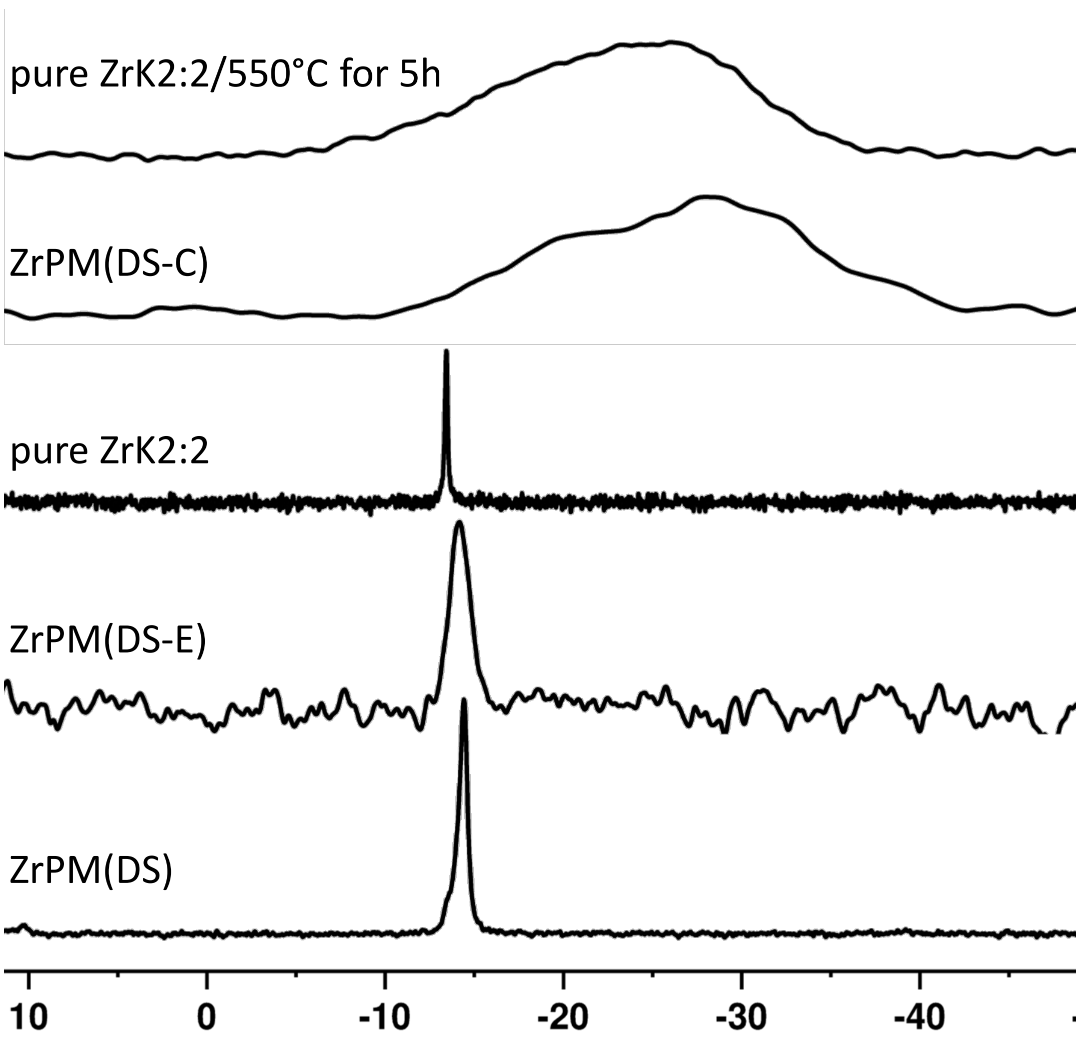
NMR techniques:

- Single pulse ^{31}P and ^{1}H→^{31}P CP MAS NMR spectra
- Single pulse ^{29}Si and ^{1}H→^{29}Si CP MAS NMR spectra
- ^{1}H, ^{13}C and ^{31}P liquid state NMR spectra of reaction mixture

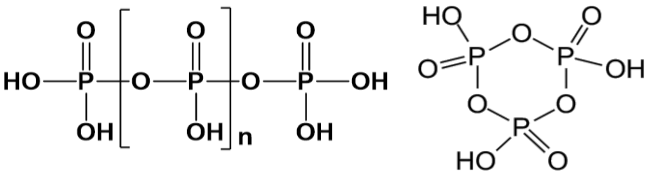
III. ZrK2:2/MCM-41 hybrid catalysts obtained by Direct Synthesis (DS)

Insight into ZrK2:2 stability during synthesis and template removal

- **Single pulse ^{31}P MAS NMR spectra**



Decomposition of ZrK2:2

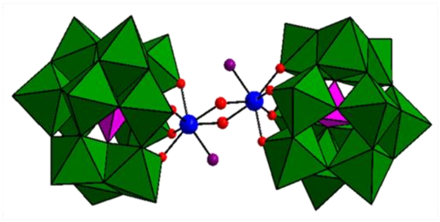


$(\equiv ZrO)PO(OH)_2$, $(\equiv ZrO)_2PO(OH)$,

$(\equiv ZrO)_3PO$ and $Zr(HPO_4)_2\cdot nH_2O$

ZrO_2/WO_x

Preservation of ZrK2:2 structure

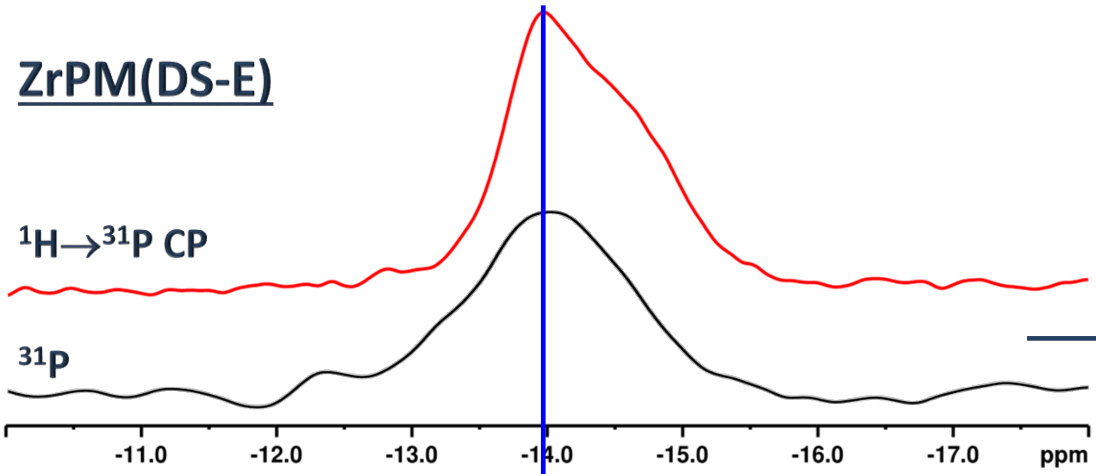


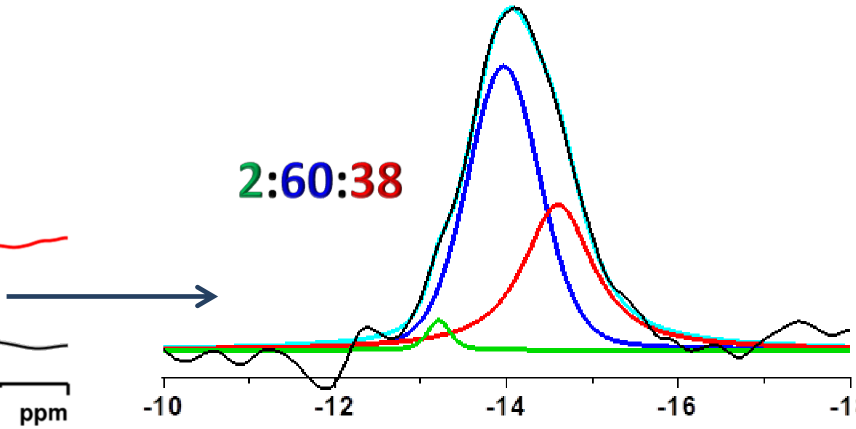
III. ZrK2:2/MCM-41 hybrid catalysts obtained by Direct Synthesis (DS)

Type of ZrK2:2 species in silica framework

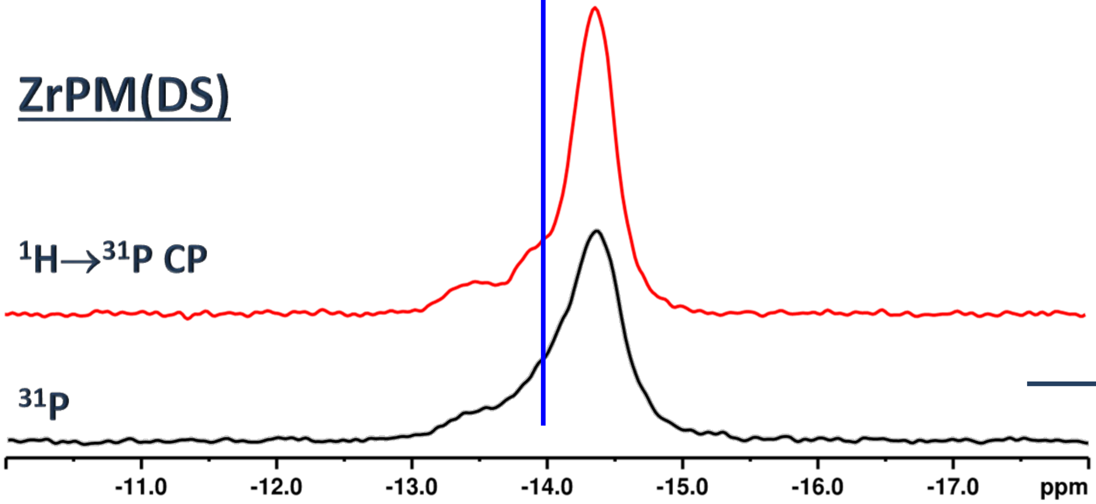
- Single pulse ^{31}P and $^{1}H \rightarrow ^{31}P$ CP MAS spectra

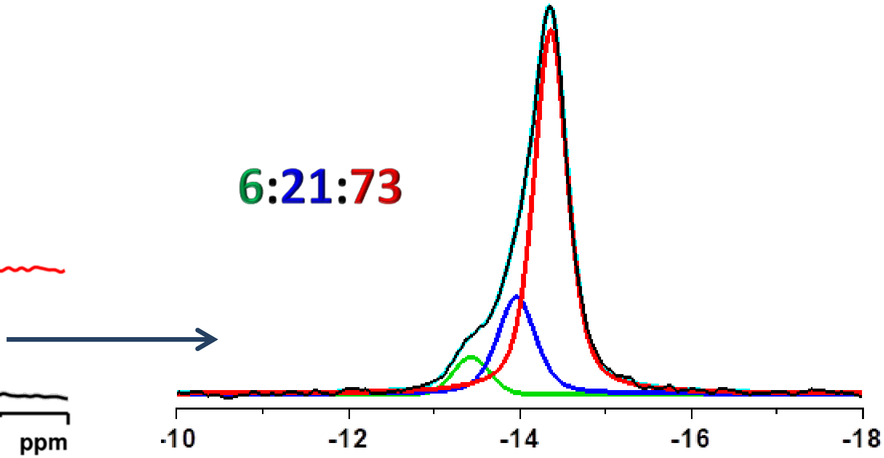
ZrPM(DS-E)





ZrPM(DS)





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Type of ZrK2:2 species in silica framework

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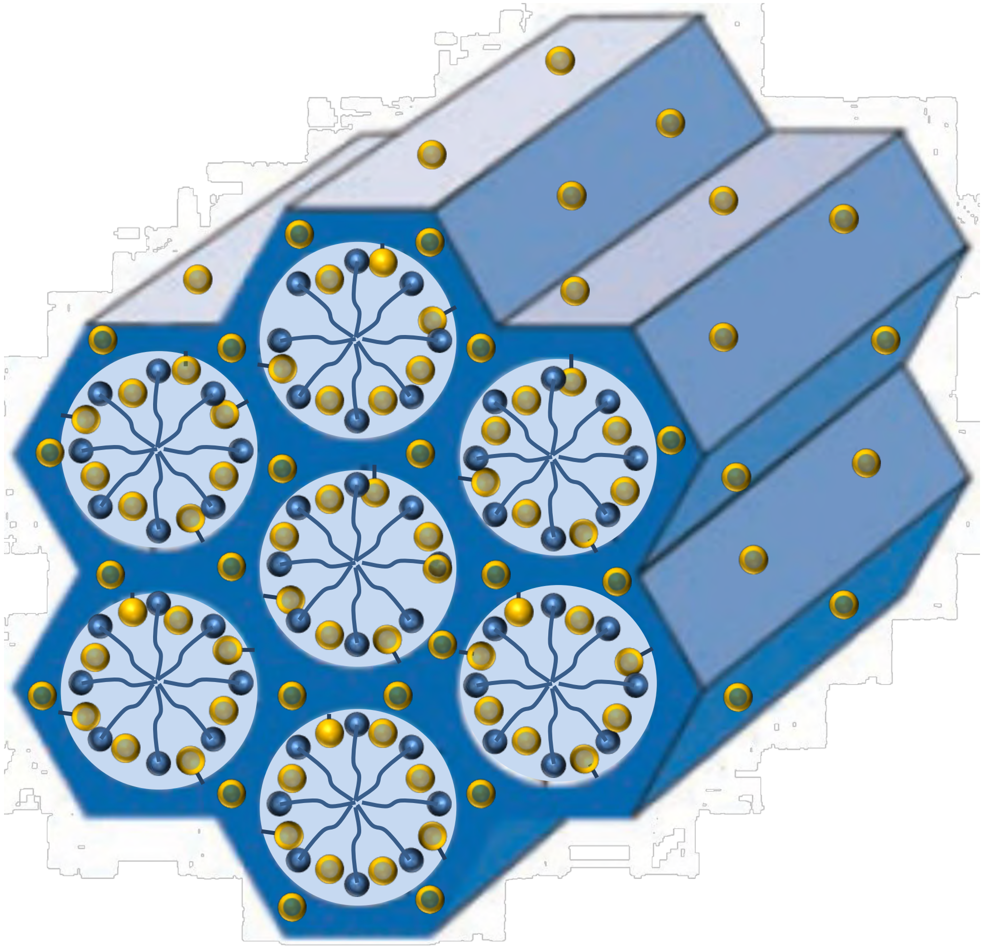

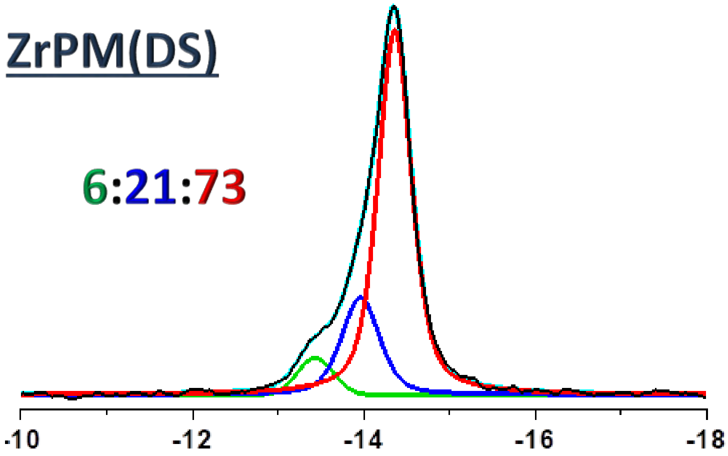

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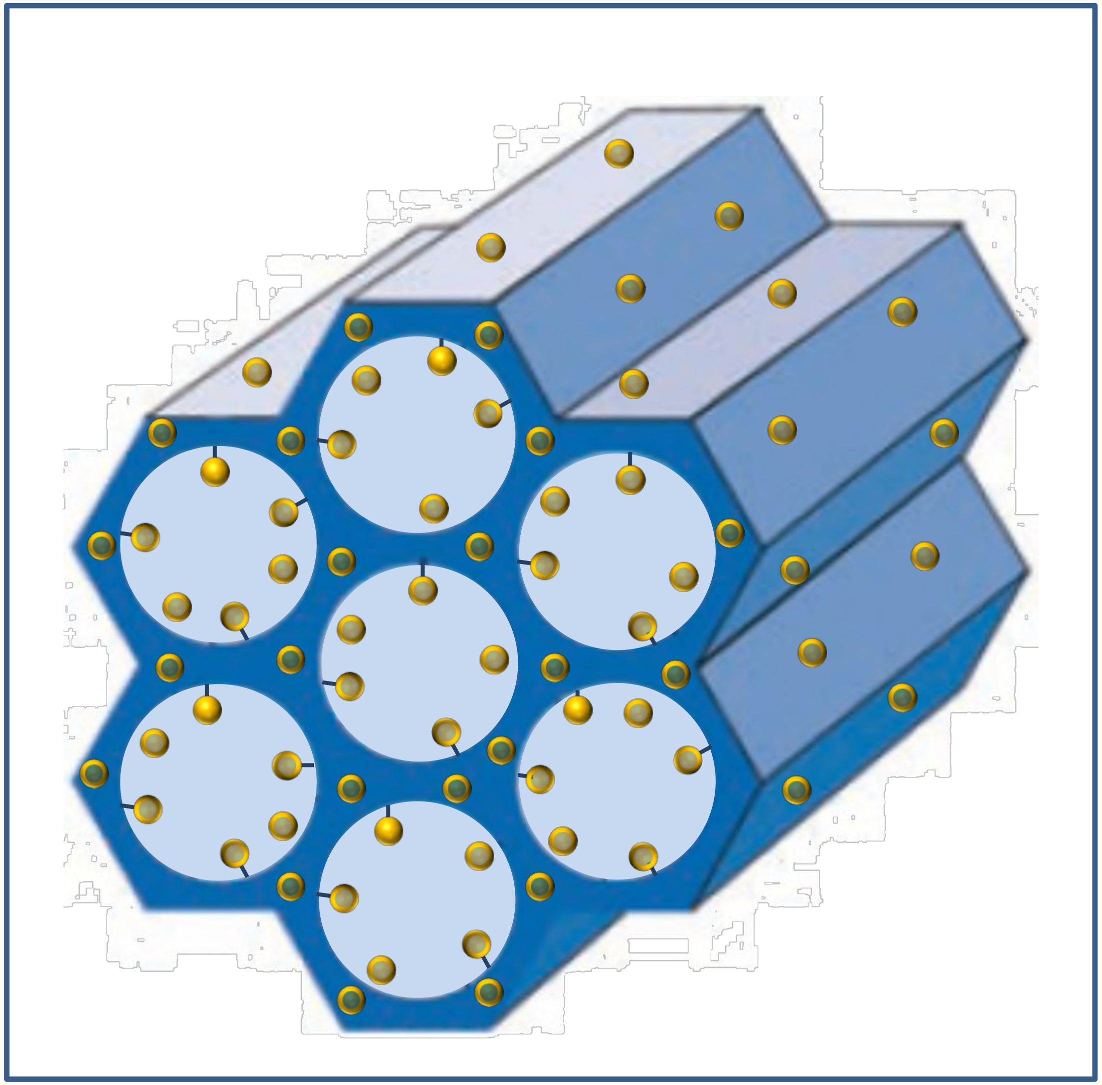
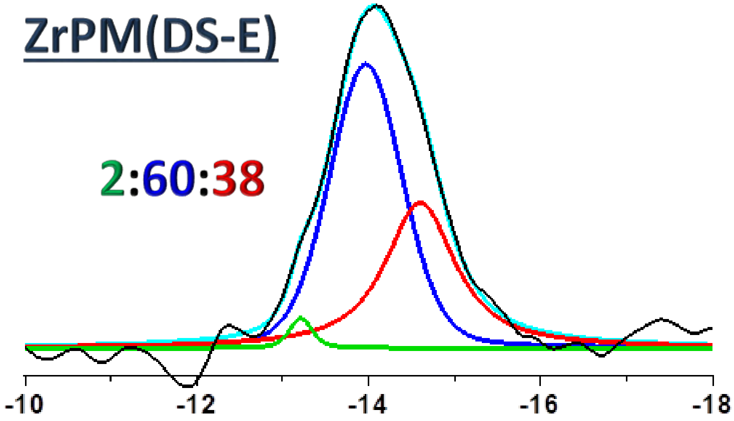
- **Single pulse ^{31}P and $^{1}H \rightarrow {}^{31}P$ CP MAS spectra**





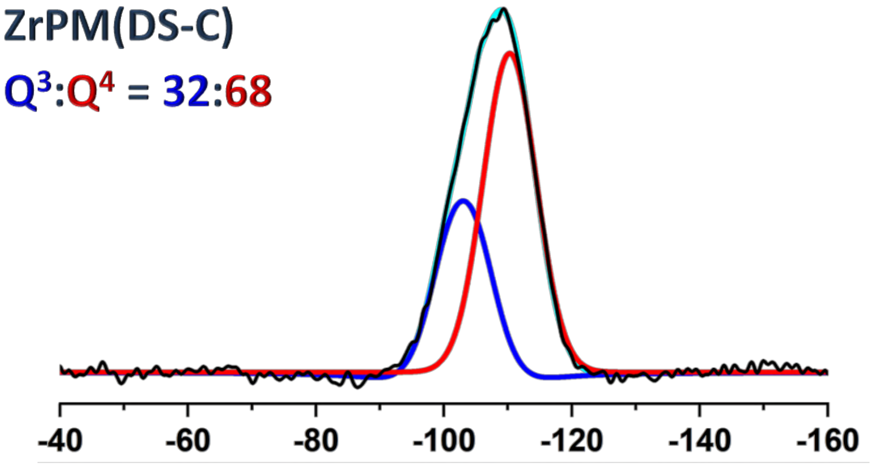
III. ZrK2:2/MCM-41 hybrid catalysts obtained by Direct Synthesis (DS)

Structural transformations of MCM-41 silica framework

- **Single pulse ^{29}Si MAS spectra**

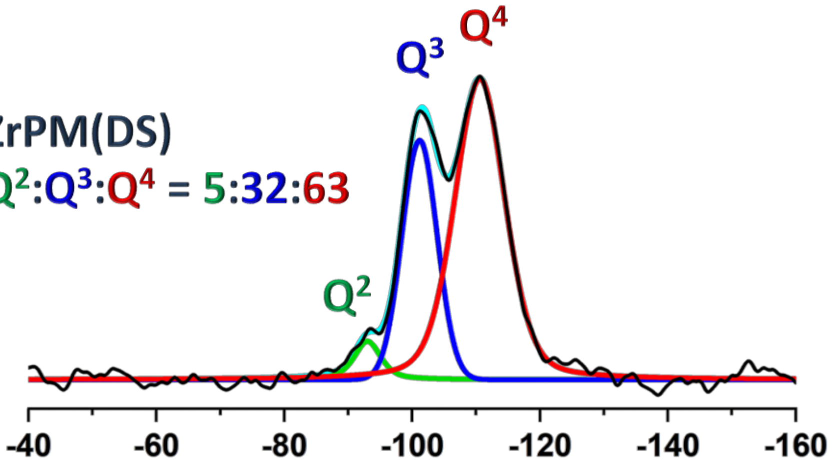
ZrPM(DS-C)

Q^3:Q^4 = 32:68



ZrPM(DS)

Q^2:Q^3:Q^4 = 5:32:63



Calcination

- Condensation of Si-OH
- Formation of highly crosslinked Q^4 units
- Consolidation of silica framework

$$2\ \equiv SiOH \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$$

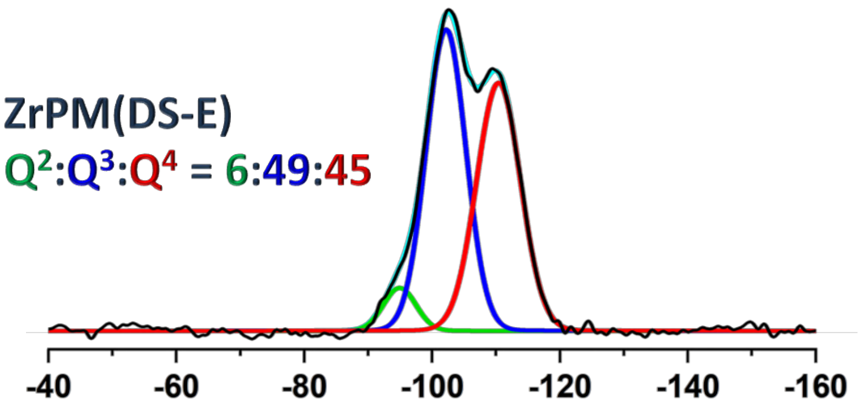
Extraction

- Dissociation of Si-O-Si bridges
- Formation of Si-OH groups
- Silica framework with lower degree of condensation

$$\equiv Si\text{-}O\text{-}Si\equiv + H_2O \rightarrow 2\ \equiv SiOH$$

ZrPM(DS-E)

Q^2:Q^3:Q^4 = 6:49:45

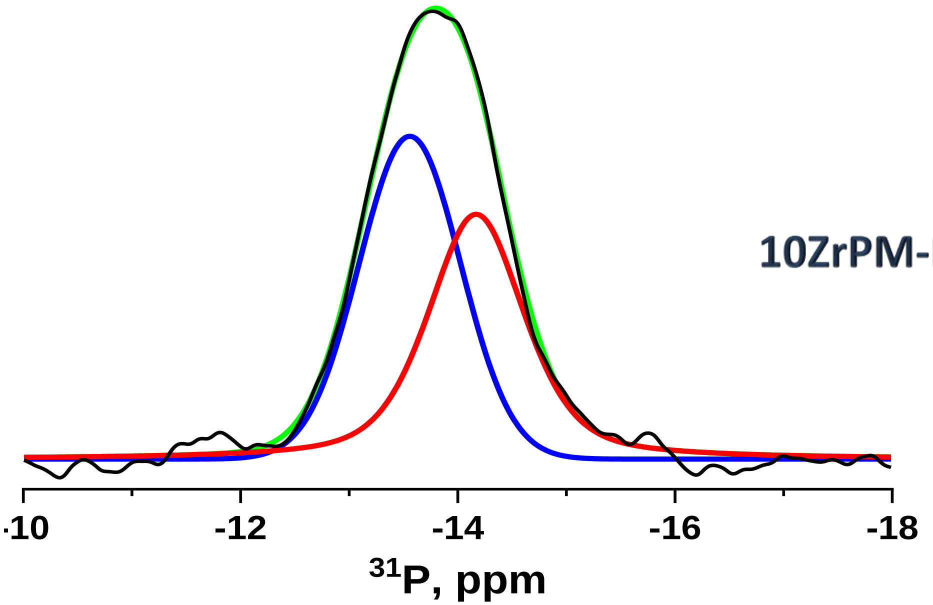


III. ZrK2:2/MCM-41 hybrid catalysts obtained by post synthesis method

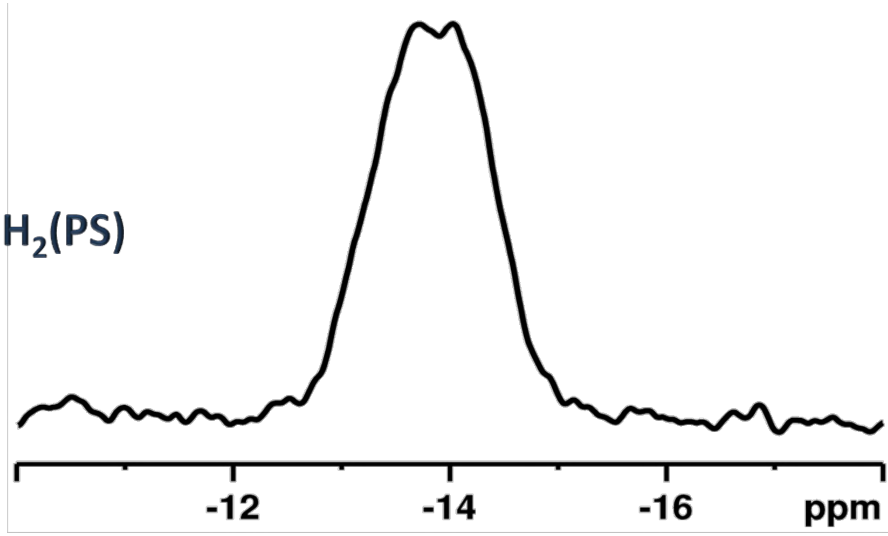
Type of ZrK2:2 species in silica framework

- Single pulse ^{31}P MAS spectrum
- $^{1}H \rightarrow ^{31}P$ CP MAS spectrum

- Preservation of ZrK2:2 structure after impregnation
- Two types of ZrK2:2 species



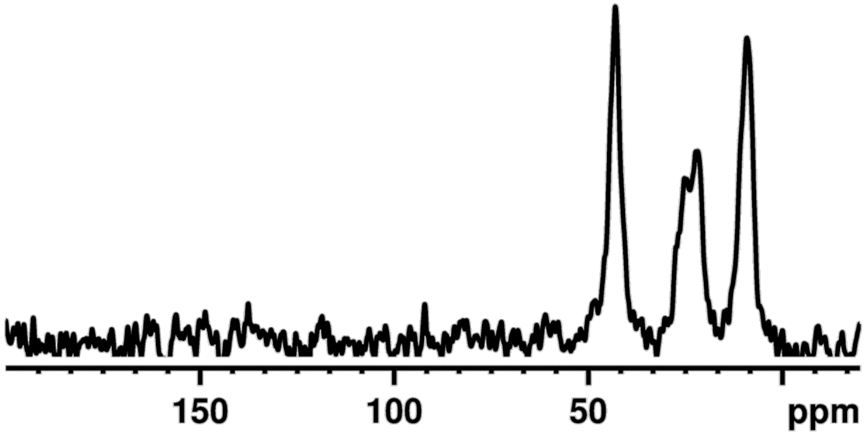
10ZrPM-NH_2(PS)



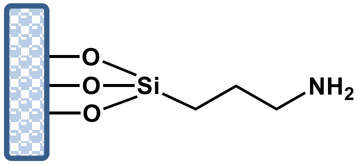
III. ZrK2:2/MCM-41 hybrid catalysts obtained by post synthesis method

ZrPM-NH$_2$(PS) Characterization of the silica framework

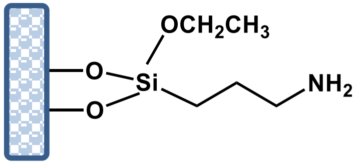
- $^1H \rightarrow ^{13}C$ CP MAS spectrum



T^3



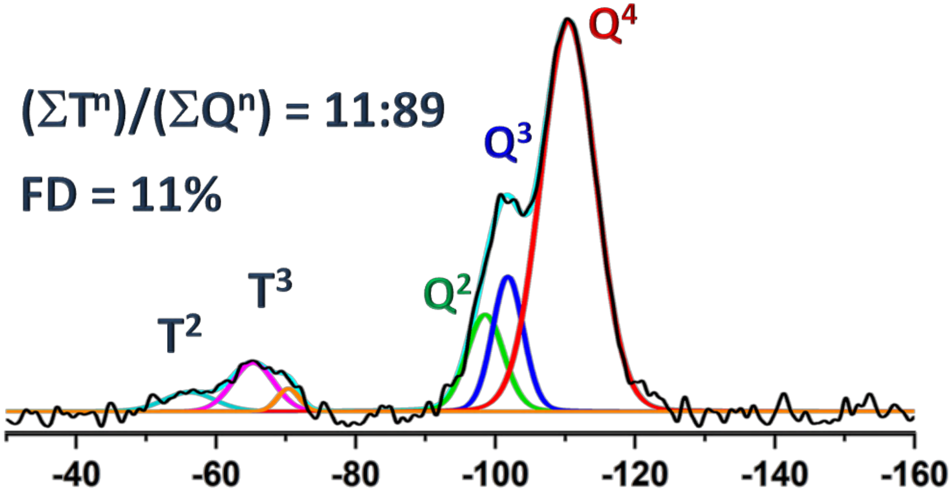
T^2



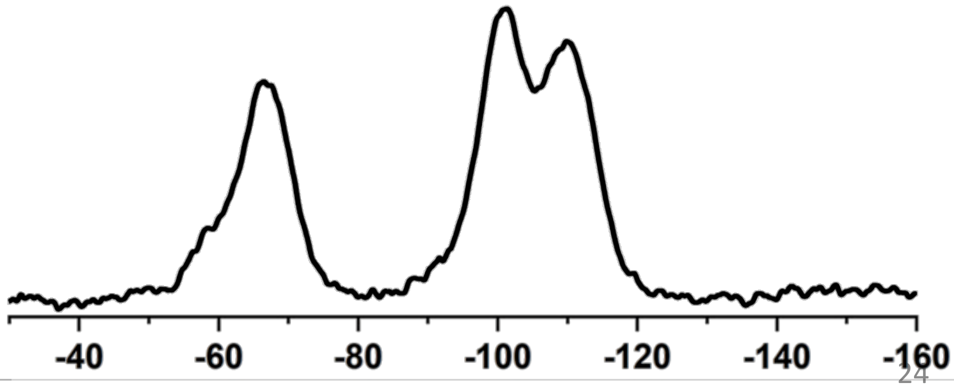
- Single pulse ^{29}Si CP MAS spectrum

$(\Sigma T^n)/(\Sigma Q^n) = 11:89$

FD = 11%

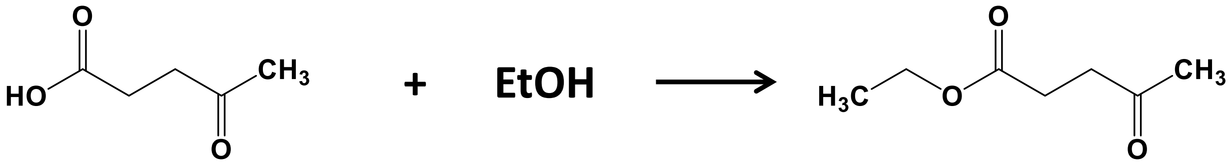


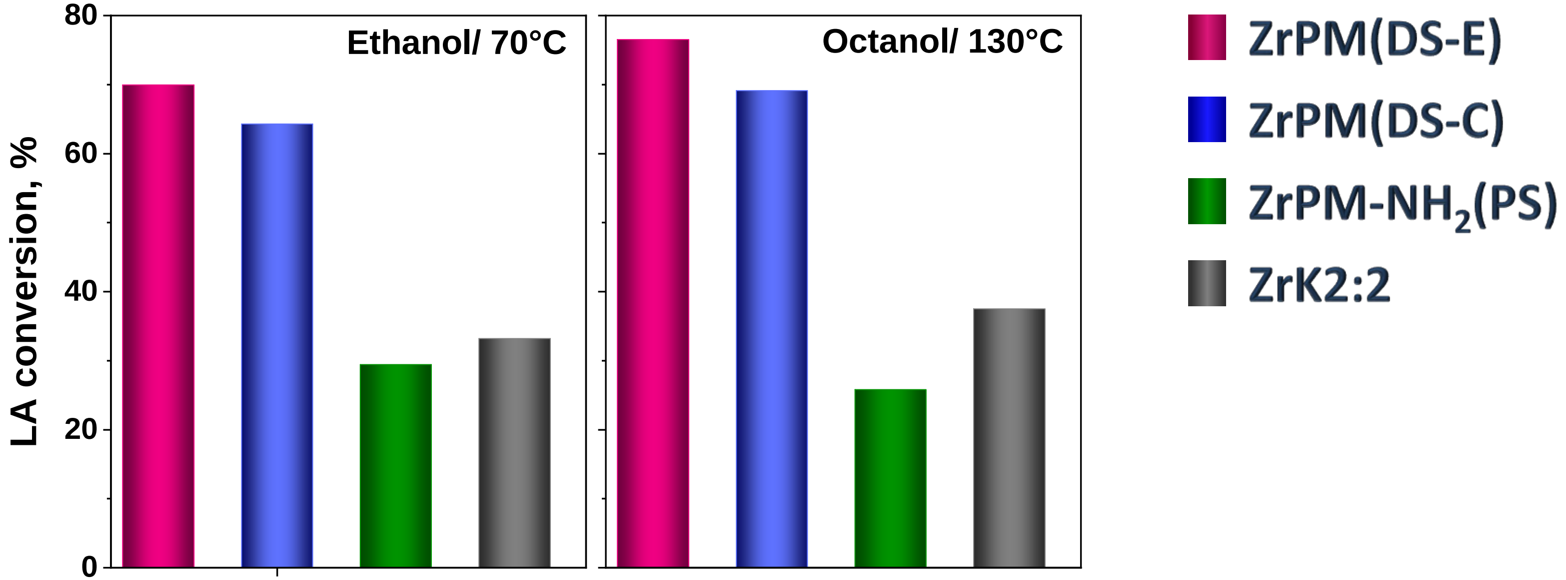
- $^1H \rightarrow ^{29}Si$ CP MAS spectrum



III. Esterification of levulinic acid with ethanol and octanol

Catalytic activity of the ZrK2:2/MCM-41 hybrid catalysts



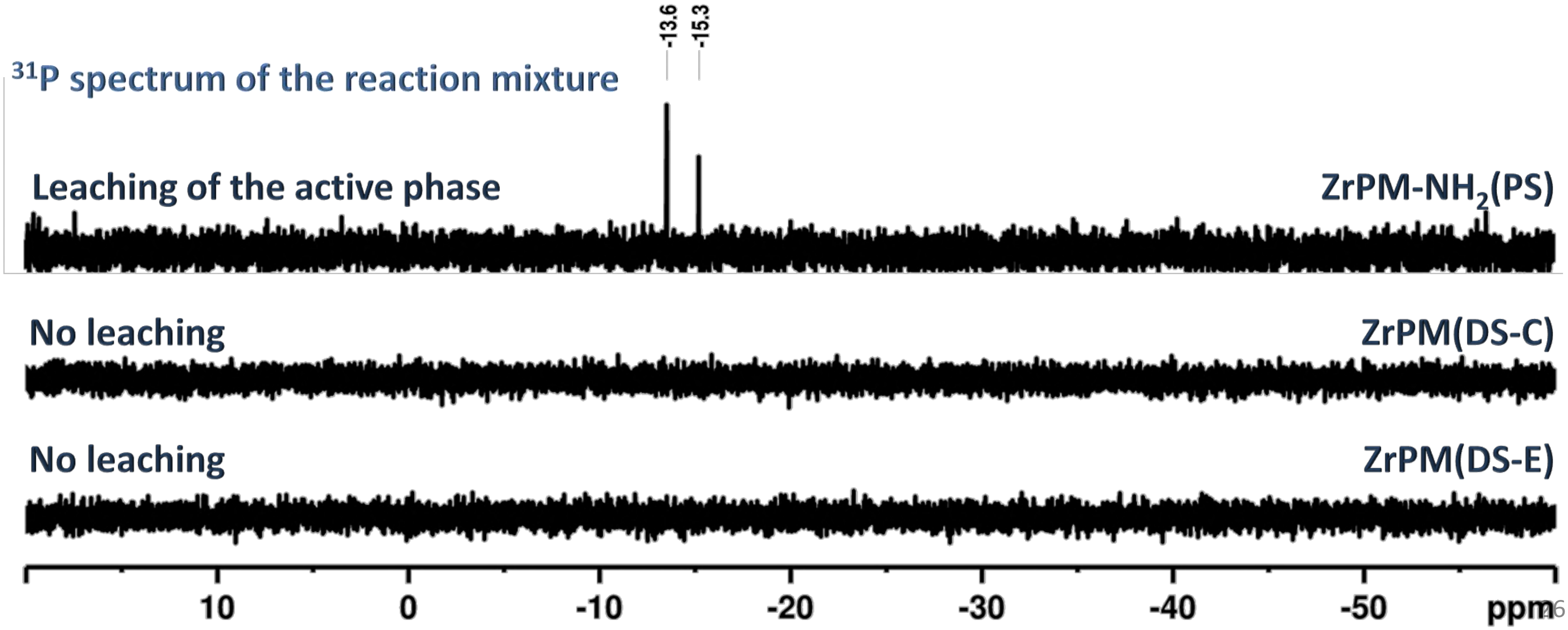


Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Acidity (mmol/g)
ZrPM(DS-E)	325	0.24	1.9	0.82
ZrPM(DS-C)	617	0.40	3.0	0.65
ZrPM-NH$_2$(PS)	318	0.28	2.9	0.46

III. Catalytic stability and reuse

Catalytic stability of the ZrK2:2/MCM-41 hybrid catalysts

Catalyst	LA/EtOH in first cycle, %	LA/EtOH in third cycle, %	LA/octanol first cycle, %	LA/octanol in third cycle %
ZrPM(DS-E)	69.2	64.5	76.7	74.9
ZrPM(DS-C)	64.5	58.9	69.3	62.3
ZrPM-NH$_2$(PS)	25.8	16.1	10.6	7.8



^{31}P spectrum of the reaction mixture

III. NMR study of ZrK2:2/MCM-41 hybrid catalysts

CONCLUSIONS

- MCM-41 silica matrix is a suitable host for deposition of POMs by both methods: direct synthesis and post-synthesis impregnation
- Extraction of the template proceeded with preservation of the intact POM structure, while calcination resulted in collapse of the Keggin structure
- Polyphosphoric acids and metal (W, Zr) oxide species formed during calcination remained immobilized on silica surface ensuring large number of active acid sites and excellent catalytic activity despite POM decomposition
- DS catalysts showed higher catalytic activity, stability against leaching and recyclability in esterification of levulinic acid with EtOH
- The newly developed materials could be applied as green, low cost and efficient heterogeneous catalysts with both Lewis and Brønsted acidity in esterification reactions for preparation of biofuels and biolubricants.

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