Development of porous Silica-Alumina glasses with enhanced hydrothermal stability for biomass conversion

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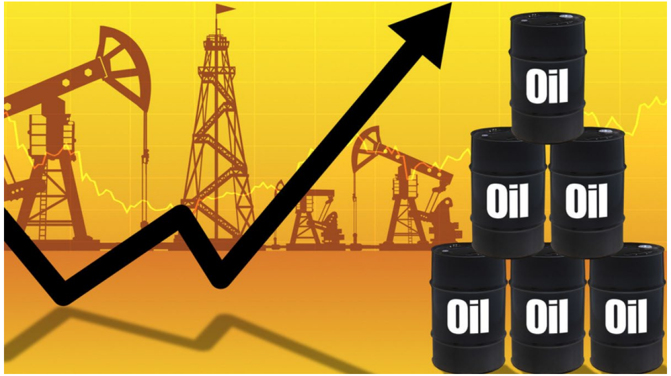
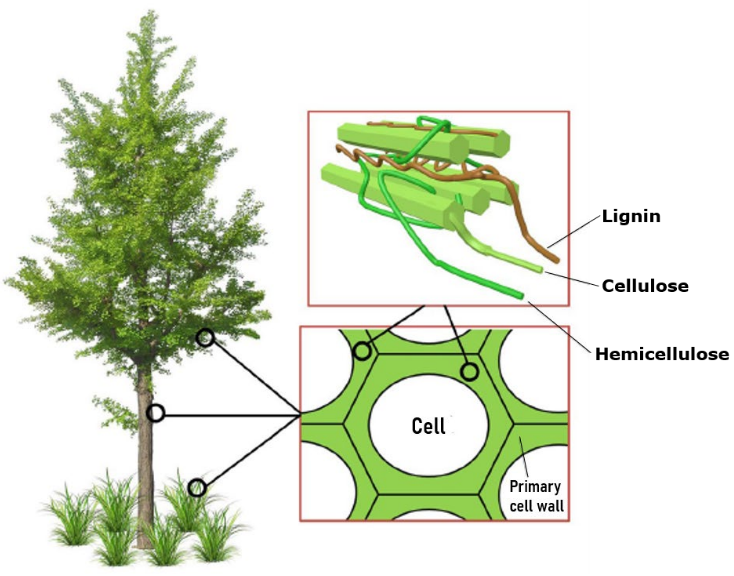
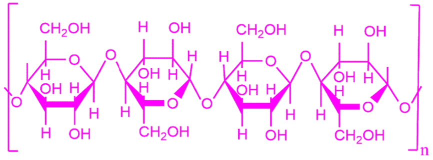
Ilmenau, 07.09.2023



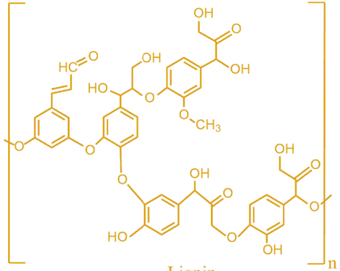
- Non-renewable feedstock
- Rising prices
- Greenhouse gases emissions

P. Gallezot *Chem. Soc. Rev.* 41 (2012) 1538 - 1558.

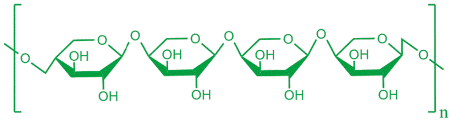




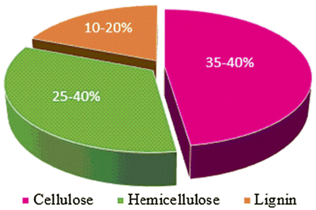
Cellulose



Lignin



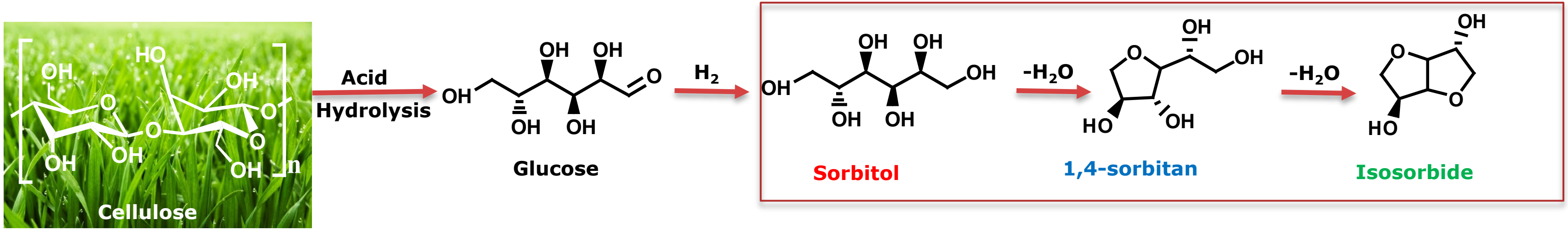
Hemicellulose



- ➢ Sustainable carbon sources
- ➢ Low (zero) carbon emissions, AE = ~100%

Huber *et al*. Chemical Reviews 106 (2006) 4044 - 4098.

AE = atom economy



Uses of 1,4-sorbitan:

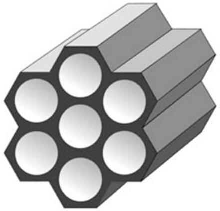
Uses of isosorbide:

- Industrial yield: 58 %
- Catalyst: H_2SO_4

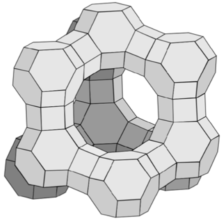
Brandi *et al*. ACS Sustainable Chem. Eng. 9 (2021) 927 - 935.
Yabushita *et al*. Bulletin of the Chem. Soc. Japan 88 (2015) 996 – 1002.

- Solid acid catalysts preffered
- Polar solvents (H_2O) at >200°C
- Lack of hydrothermal stability
- Restricted diffusion (zeolites)

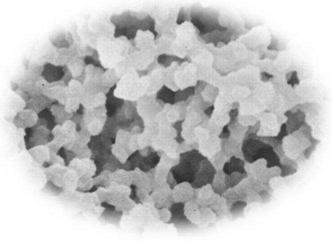
Al-MCM-41

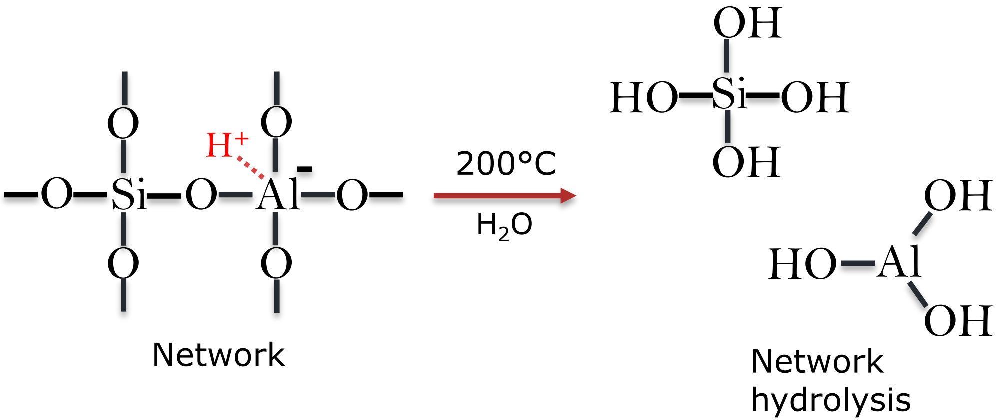


Zeolites



ASA

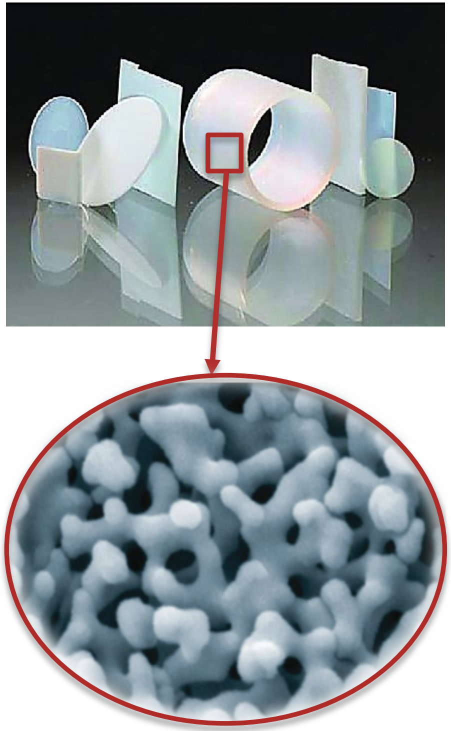




Hahn *et al.* ChemSusChem 6 (2013) 2304 - 2315.
Brandi *et al.* ACS Sustainable Chem. Eng. 9 (2021) 927 - 935.
Van der Bij *et al.* Chem. Soc. Rev. 44 (2015) 7406 – 7428.

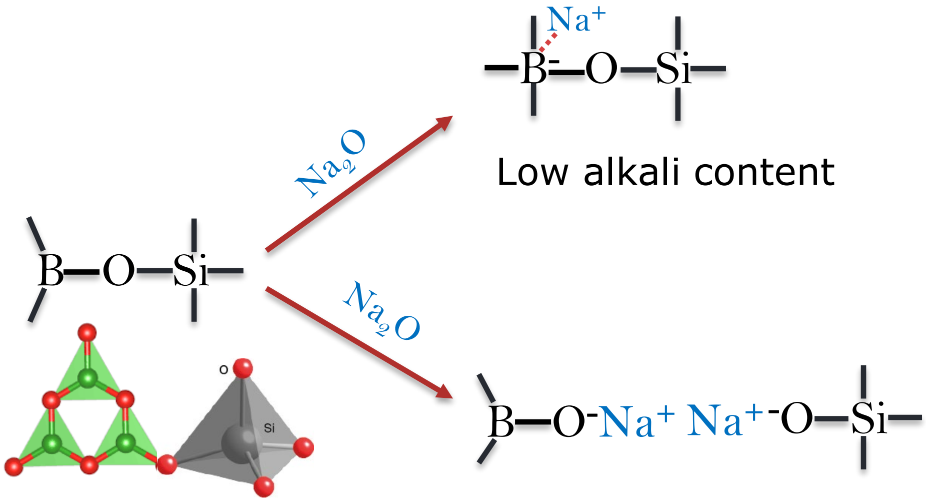
Legend: ASA = Amorphous silica-alumina

- Chemical stability: 6 M HCL at 90°C
- Adjustable shape: beads, rods etc
- Tunable textural properties:
  - ✓ Pore width: 0.6 – 1000 nm
  - ✓ Pore volume: 0.1 – 2 $cm^3\ g^{-1}$
  - ✓ Surface area: 20 – 500 $m^2\ g^{-1}$



Enke *et al*. J. Mater. Sci. 36 (2001) 2349 – 2357.
Janowski *et al*. Handbook of Porous Solids, Wiley-VCH Verlag GmbH (2002) 1432 – 1542.

Glass structure:

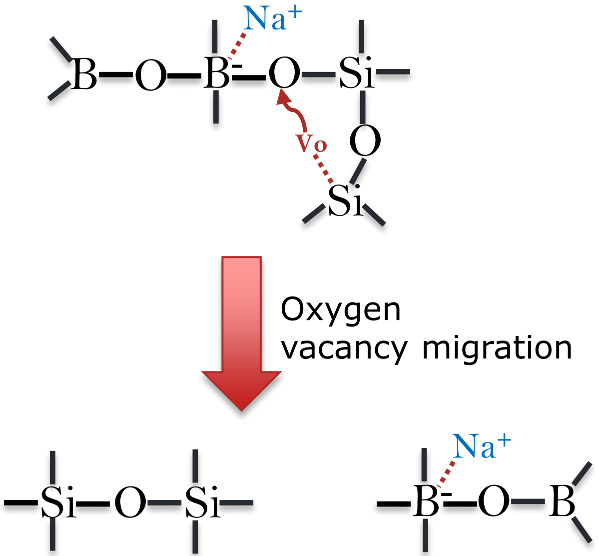


Low alkali content

High alkali content

Borosilicate glass

Phase separation:

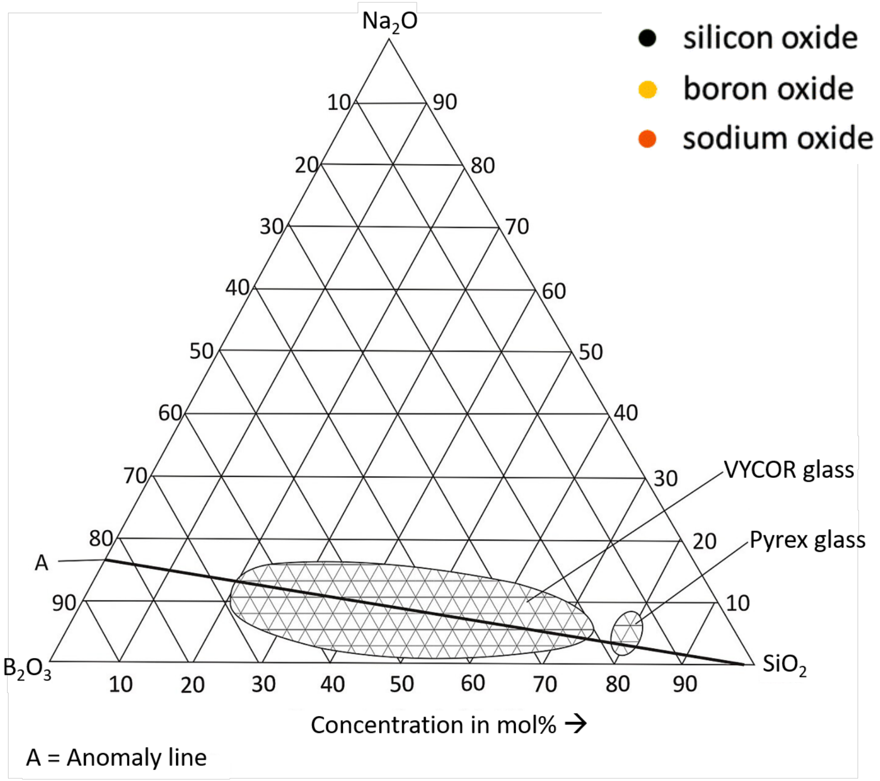


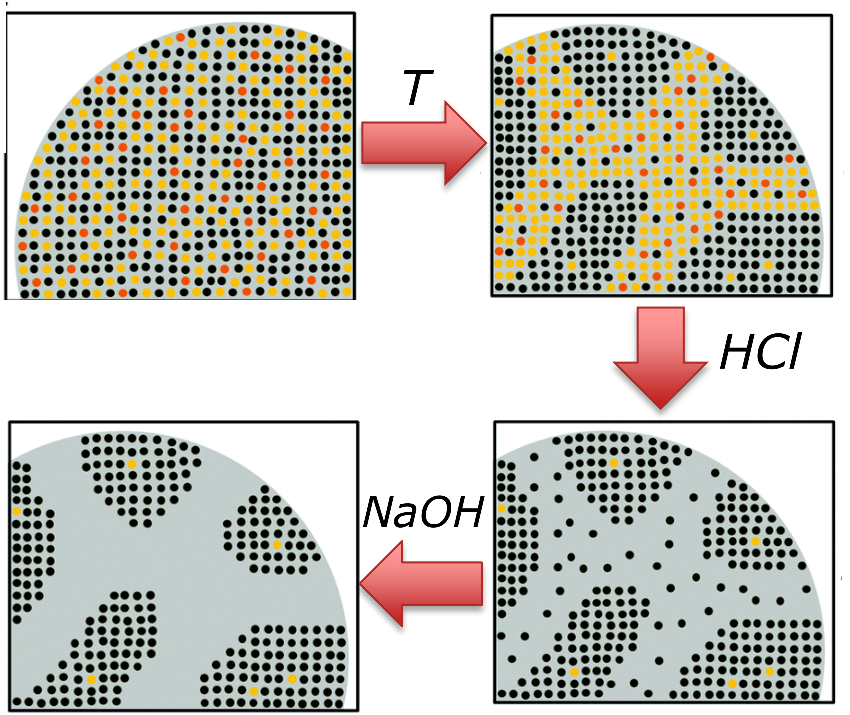
Silica-rich phase

Sodium-rich borate phase

W. Vogel, Glass Chemistry, Springer Berlin Heidelberg, 1994.
Yazawa *et al.* J. Phys. Chem. B 104 (2000) 2109 – 2116.

Legend: ● = Oxygen ● = Boron ● = Silica

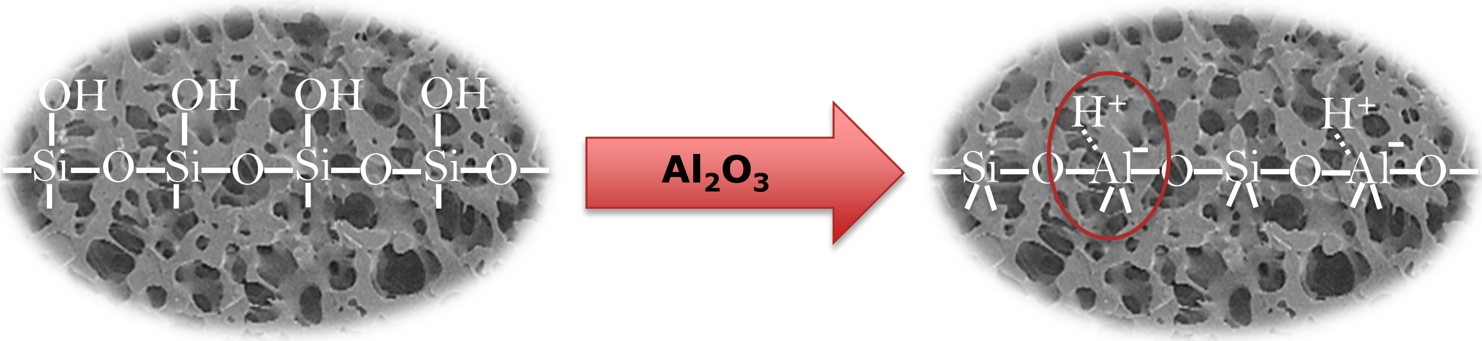




Janowski *et al*. Handbook of Porous Solids, Wiley-VCH Verlag GmbH (2002) 1432 – 1542.
Inayat *et al*. Chemical Society reviews 42 (2013) 3753 – 3764.

Porous glass surface:

Chemically modified porous glass:

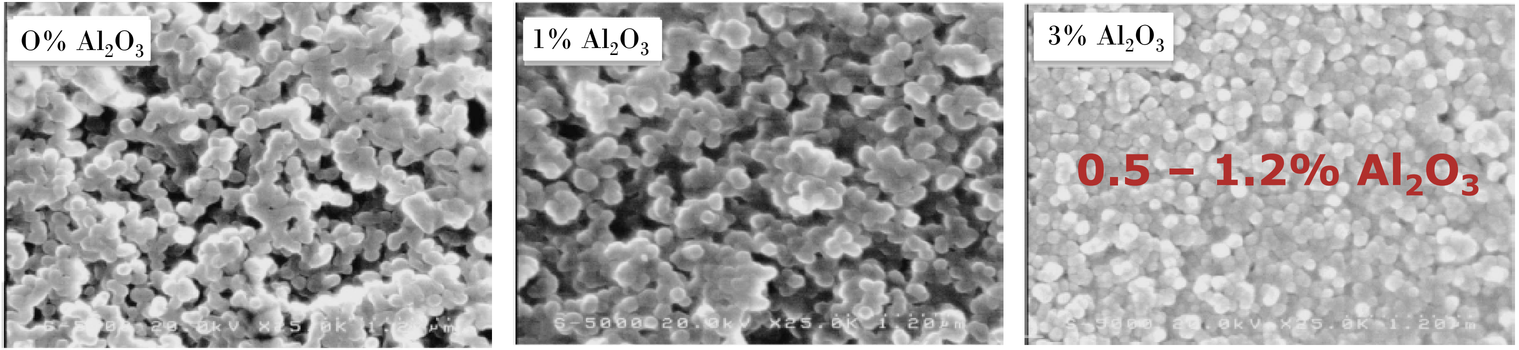


- ➢ Weak acidic silanol groups

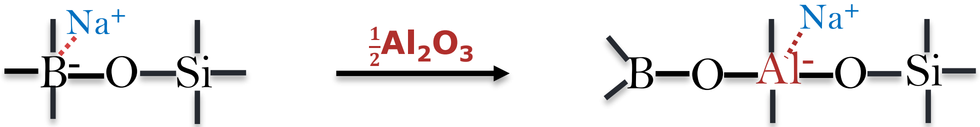
- ➢ Al in tetrahedral coordination
- ➢ Medium to strong acid sites

Du *et al*. J. Mater. Sci. 35 (2000) 4865 – 4871.
Enke *et al*. J. Mater. Sci. 36 (2001) 2349 – 2357.

Al_2O_3 containing Na_2O-B_2O_3-SiO_2 glass:



- ➢ Reduced microphase development



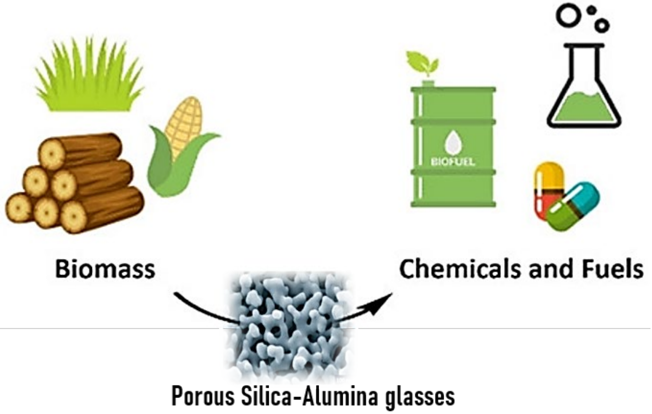
Du *et al*. J. Mater. Sci. 35 (2000) 4865 – 4871.
Kwinda *et al*. J. Non Cryst. Solids 531 (2020) 119849.

Aim and objectives

1. Post synthetic surface modification

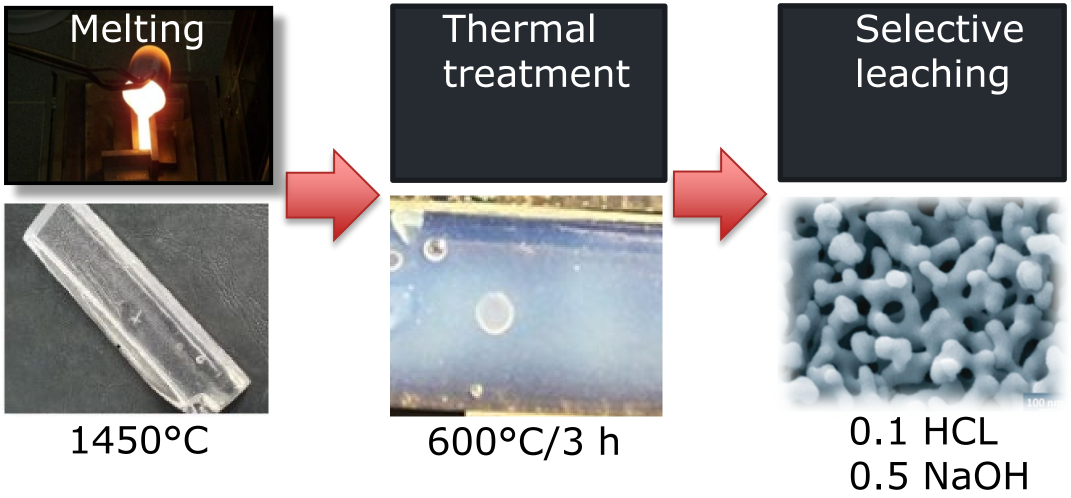
2. Hydrothermal stability evaluation

3. Catalytic applications



1. Post synthetic surface modification

1. VYCOR Process: $4Li_2O$-$29B_2O_3$-$61SiO_2$-$6Al_2O_3$ (wt%):

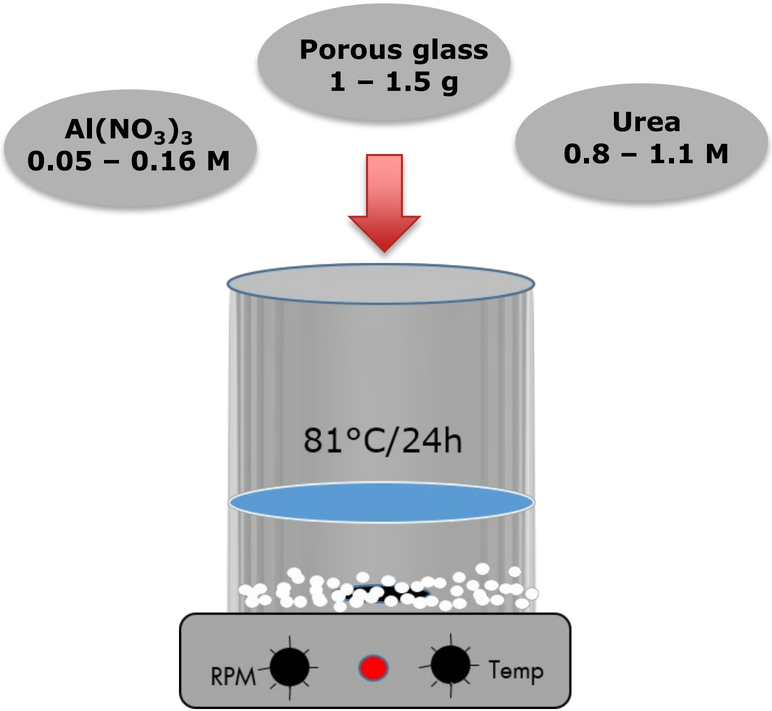


Characterization:

- ICP-OES
- DSC
- ^{29}Si, ^{27}Al, ^{11}B-MAS-NMR
- Nitrogen sorption
- Mercury intrusion
- SEM

Kwinda *et al.* Mater. Chem. and Phys. 289 (2022) 126504.
Kwinda *et al.* J. Non-Cryst. Solids 531 (2020) 119849.

2. Post synthetic surface modification:



- Calcination: 600 – 700°C/8 h

Characterization:

- ICP-OES
- Nitrogen sorption
- Mercury intrusion
- ^{27}Al-MAS-NMR
- SEM
- NH_3-TPD

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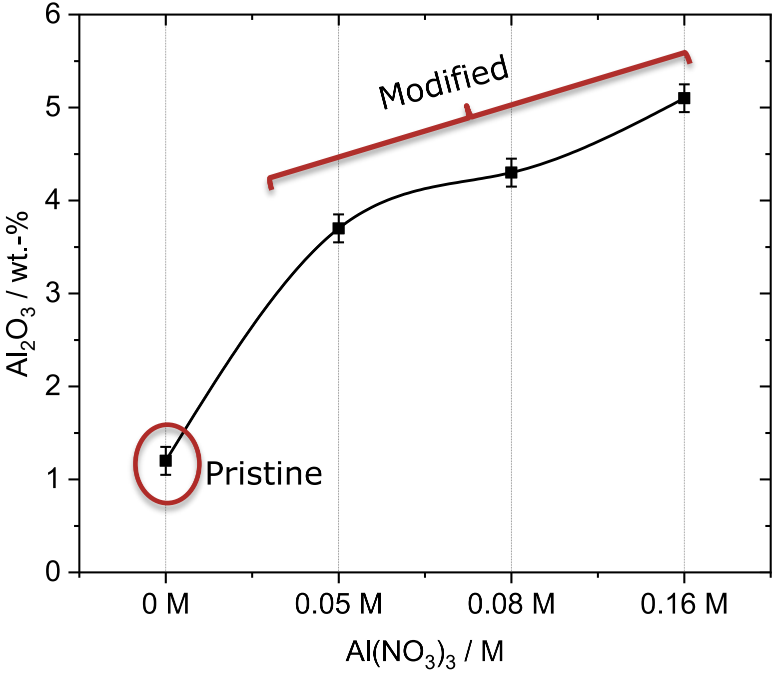
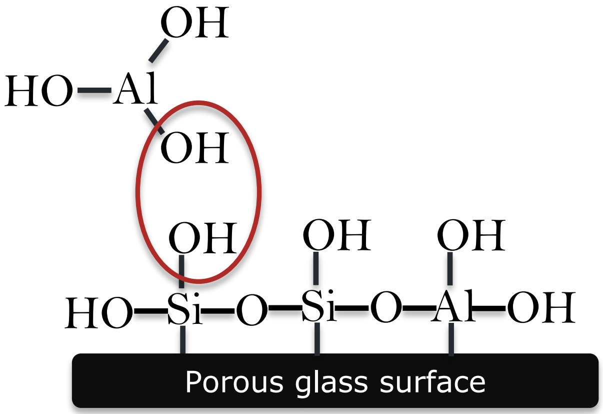
ICP-OES:



$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + CO_{2(g)} + \mathbf{2OH^-}$



- Condensation reaction
- Multilayers alumina

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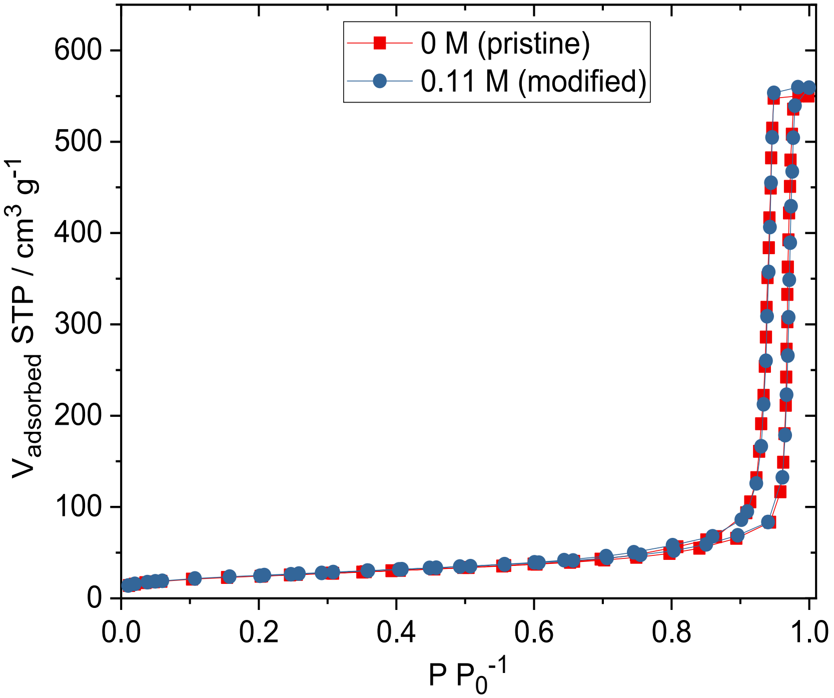
Nitrogen sorption:



- Ultrathin alumina layer (<< 1 nm)
- Preserved textural properties
- D_p = 36 nm, BET_{SA} = 75 – 85 $m^2 g^{-1}$

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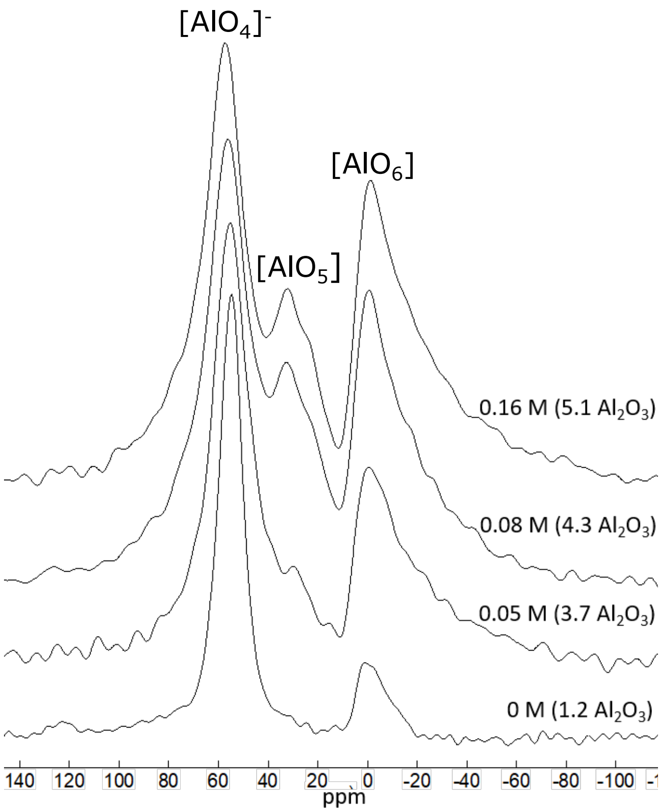
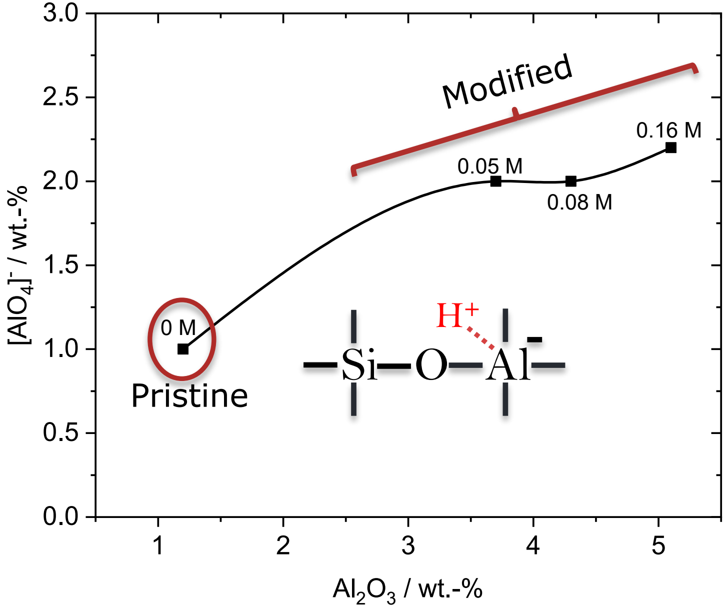
^{27}Al-NMR MAS:



^{27}Al-NMR MAS and ICP-OES:



- Diffusion of Al in the network

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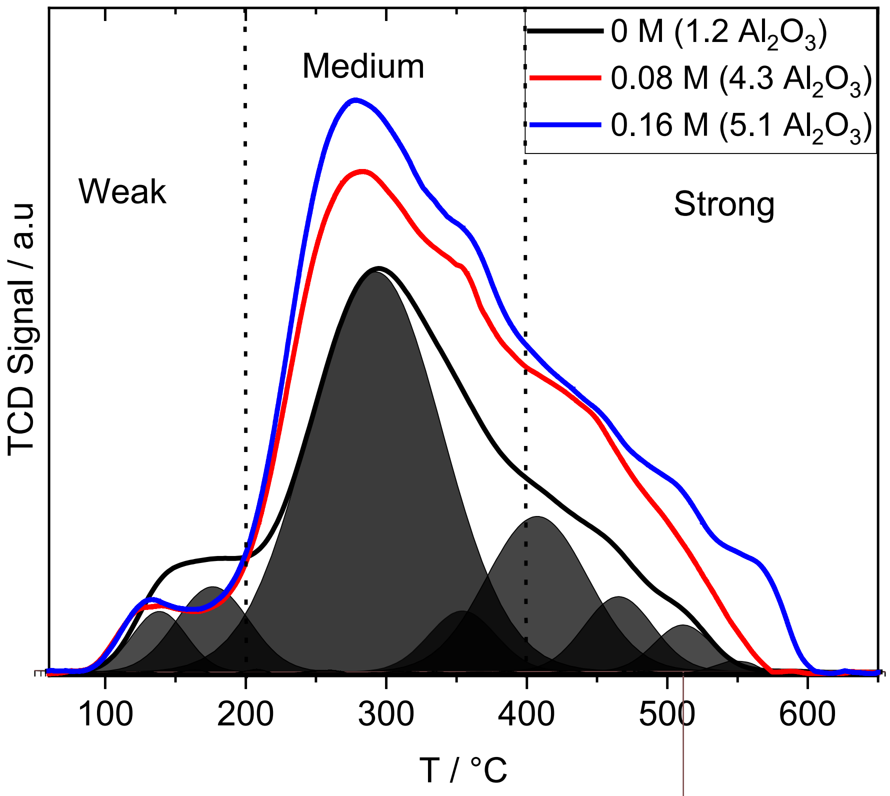
NH_3-TPD:



- Medium acid strength: 200 - 400 °C
- $[AlO_4]^-$ in the glass network
- Acid sites density: 100 - 170 µmol g^{-1}

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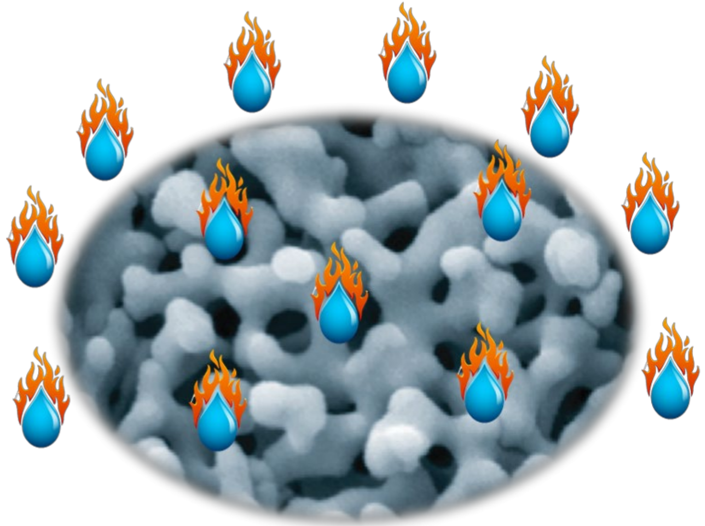
2. Hydrothermal stability evaluation



- 0.30 g modified PG
- 10 ml H_2O

- T = 200°C
- t = 24 h

Characterization:

- ICP-OES
- Nitrogen sorption
- Mercury intrusion
- SEM
- ^{27}Al-MAS-NMR
- NH_3-TPD

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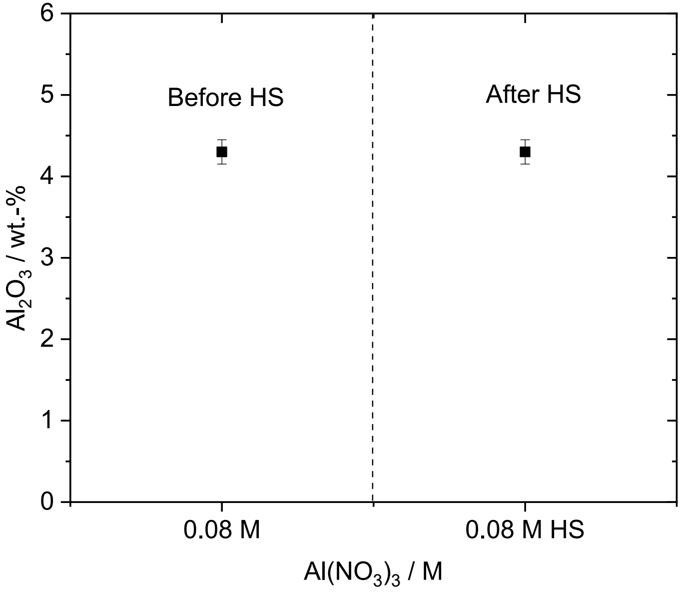
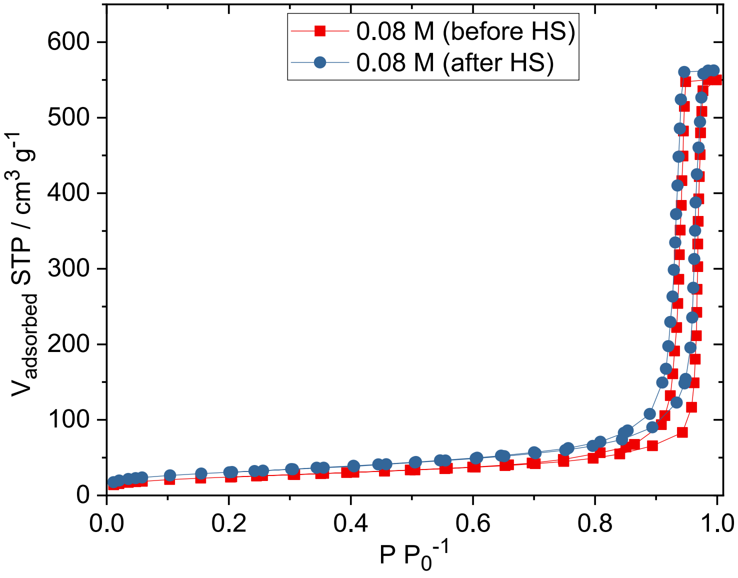
Legend: PG – Porous glass

ICP-OES:



➢ Preserved Al_2O_3 composition

Nitrogen sorption:



➢ Preserved pore structure

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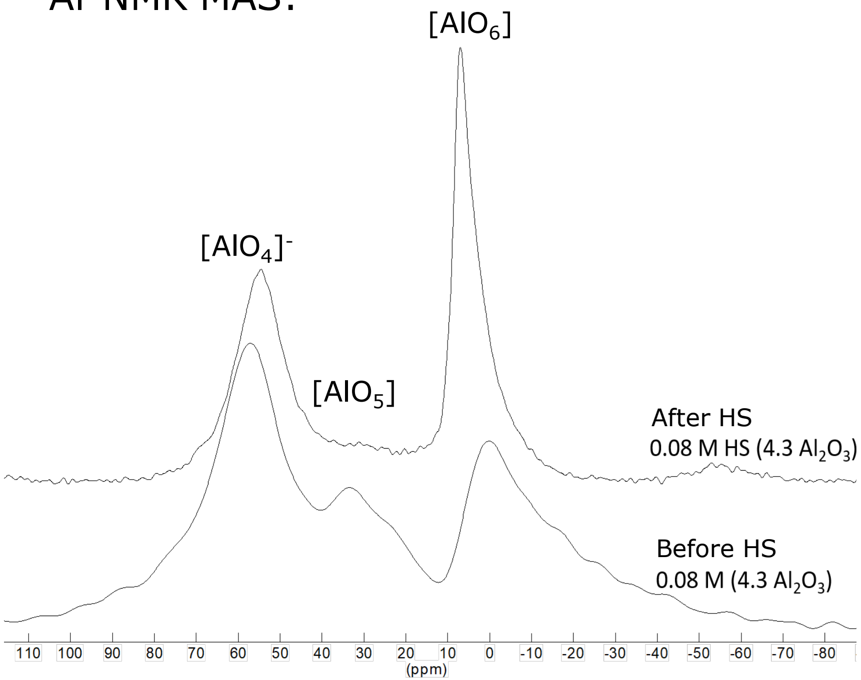
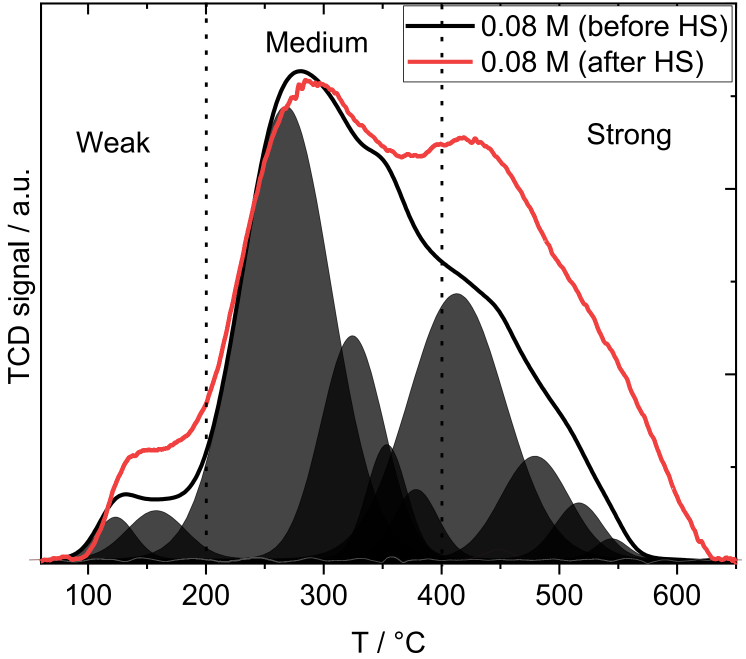
Legend: HS – Hydrothermal stability

^{27}Al-NMR MAS:



- Transformation of $[AlO_5]$ to $[AlO_6]$
- Preserved $[AlO_4]^-$ species (2 - 2.3 wt%)

NH_3-TPD:



- Increase acid sites density
- Strong acid sites activated

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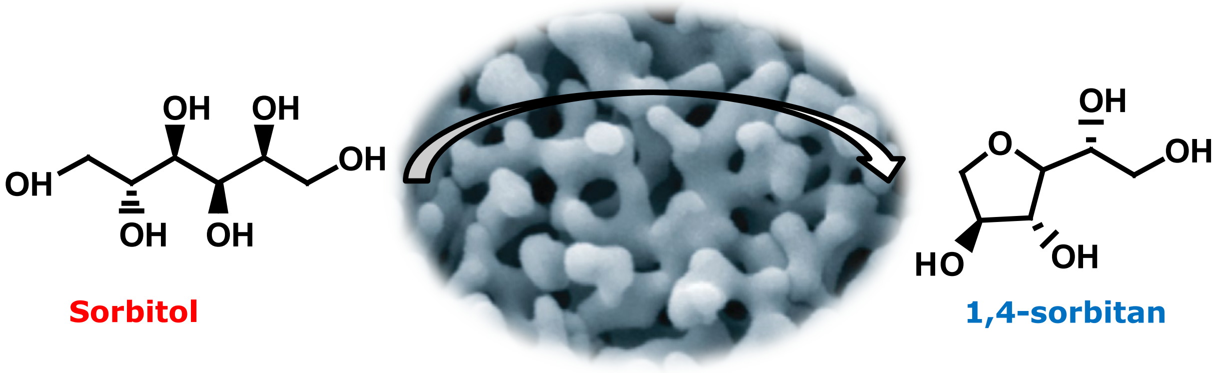
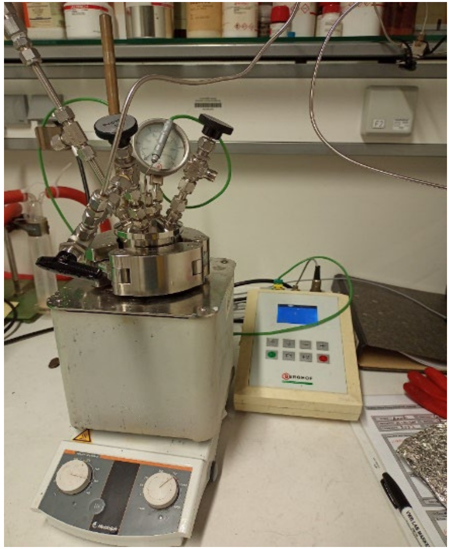
Legend: HS – Hydrothermal stability

3. Catalytic applications



Batch Reactor:



Berghof BR-100
Teflon: V = 170 ml
H = 165 mm
W = 42 mm

Conditions:

- Sorbitol = 0.05 M/60 ml
- T = 208°C
- t = 25 to 50 h
- Catalysts =2.0 g

Characterization:

- HPLC
- Nitrogen sorption
- Elemental analysis
- XRD

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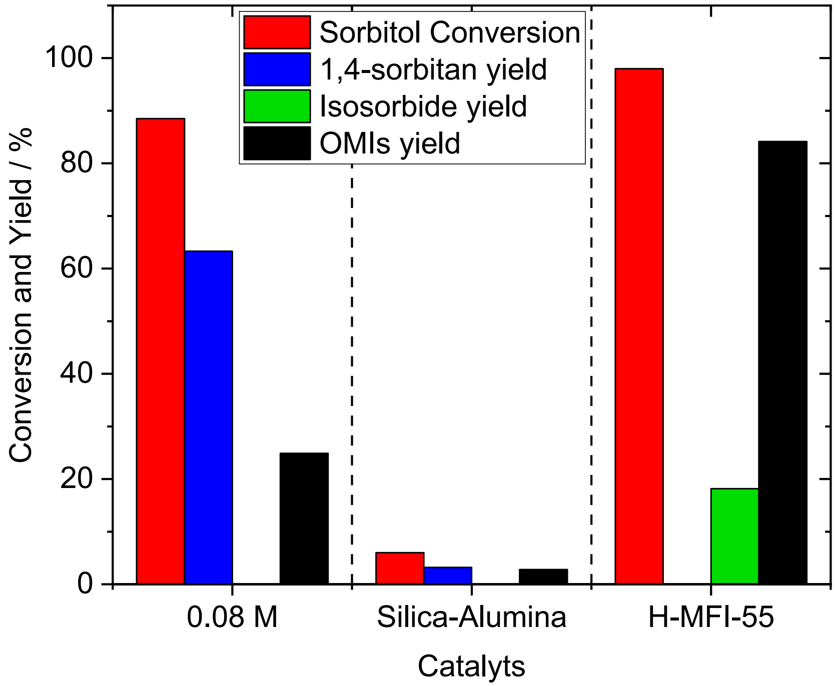
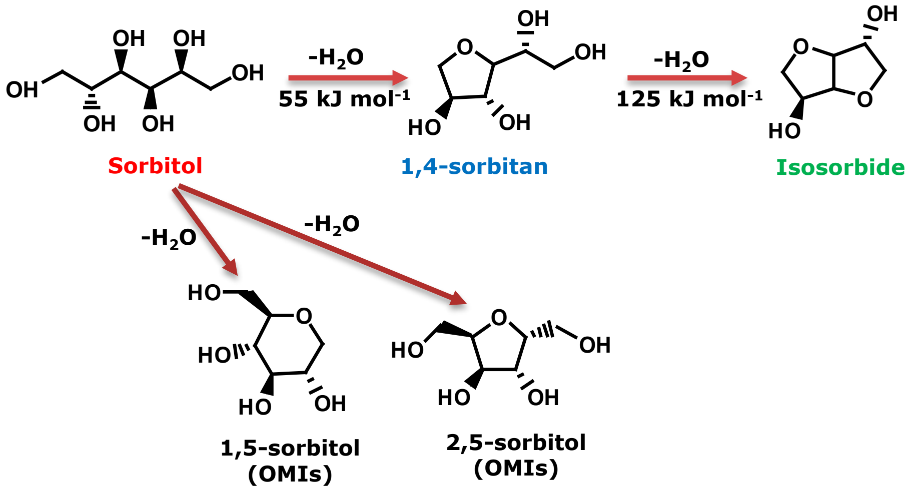
Catalytic activity:





- High selectivity to 1,4-sorbitan
- Medium strength acid sites

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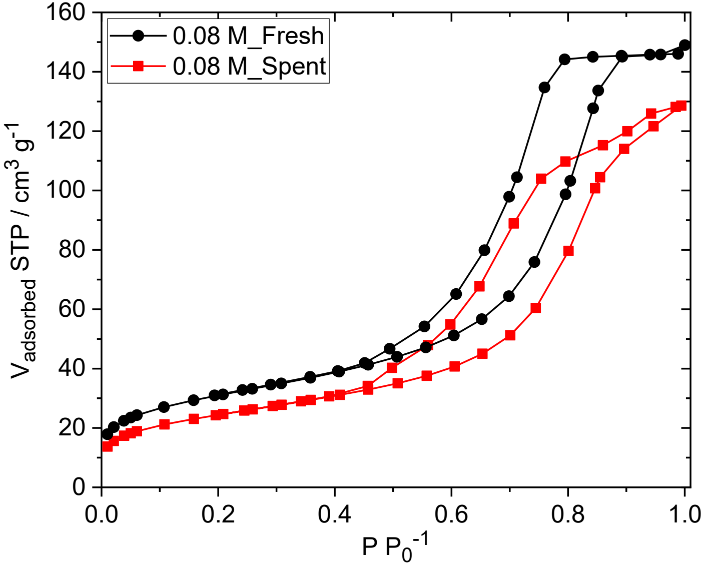
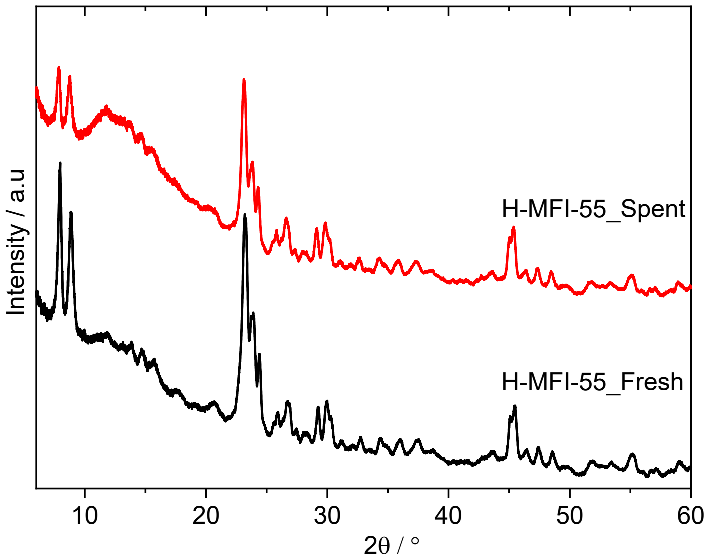
Legend: OMIs – Other monodehydrated isomers

Modified porous glass catalyst:



- Preserved pore structure
- Minor carbon deposits

Industrial catalyst:



- Low crystallinity (H-MFI-55)
- High coking degree

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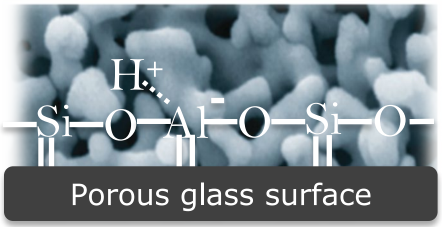
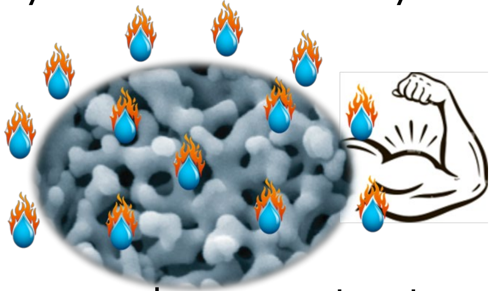
Conclusions

Surface modification:



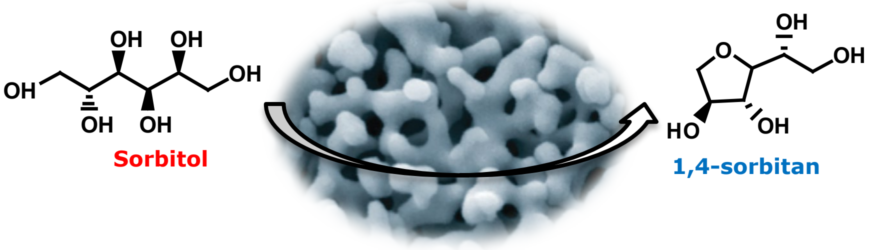
➢ Increased acid sites density

Hydrothermal stability:



➢ Preserved porous structure

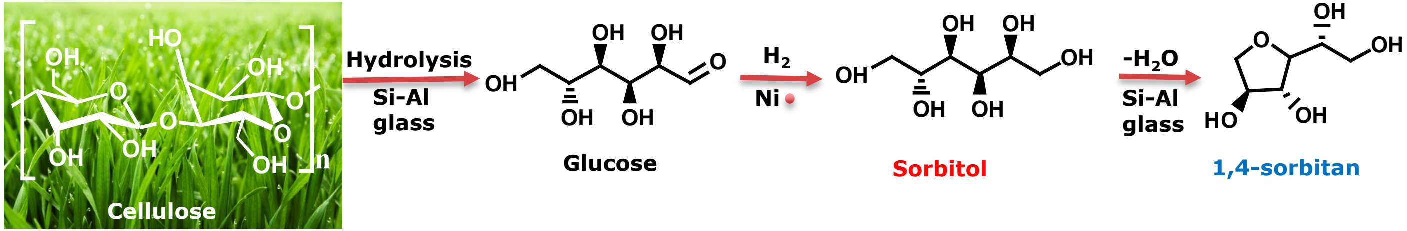
Catalytic application:



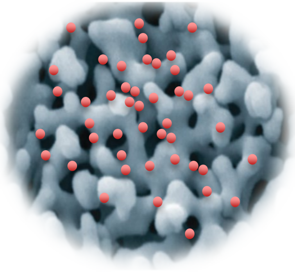
➢ Selective to 1,4-sorbitan

Outlook

One-pot synthesis of 1,4-sorbitan:



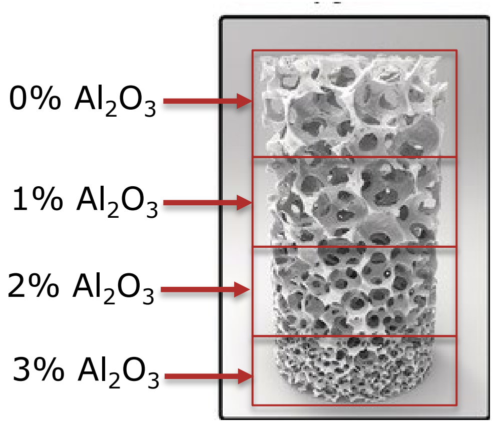
Ni supported porous silica-alumina glasses



Bifunctional catalyst:
- Acid sites
- Hydrogenation

Legend: ● – Nickel nanoparticles
Si-Al glass – porous Silica-Alumina glass

Control of pore width using Al_2O_3 in NBS:



- Pore Width gradients monoliths
- Sintering (Conventional/SLS)
- Multi-step enzyme support
- Other biomass conversion

Legend: SLS – Selective laser sintering
NBS – Sodium borosilicate glass

Aknowledgements

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M.Sc. Hieronymus Hölzig

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Sustainable · Porous · Materials

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