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# Zeolitter – Mekanismestudier som nøkkel til nye materialer

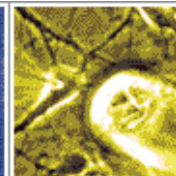
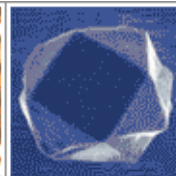
Morten Bjørgen

University of Oslo

NIS Centre of Excellence Turin



Nanostructured Interfaces and Surfaces  
Centre of Excellence



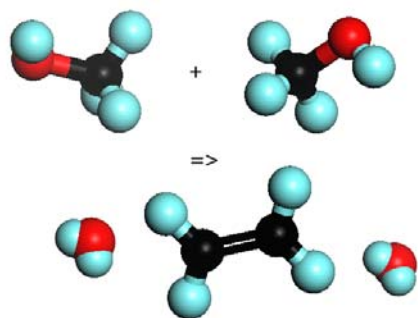
Università di Torino



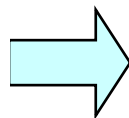
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# The catalysis group at UiO Research vision

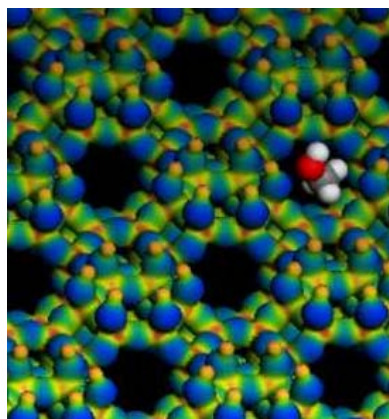
Reaction



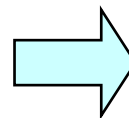
**MTO**



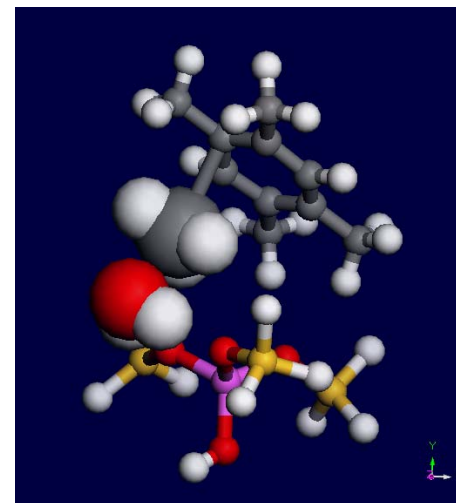
Catalyst



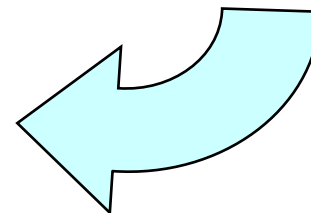
**Chabazite**  
(110 surface)



Reaction mechanism



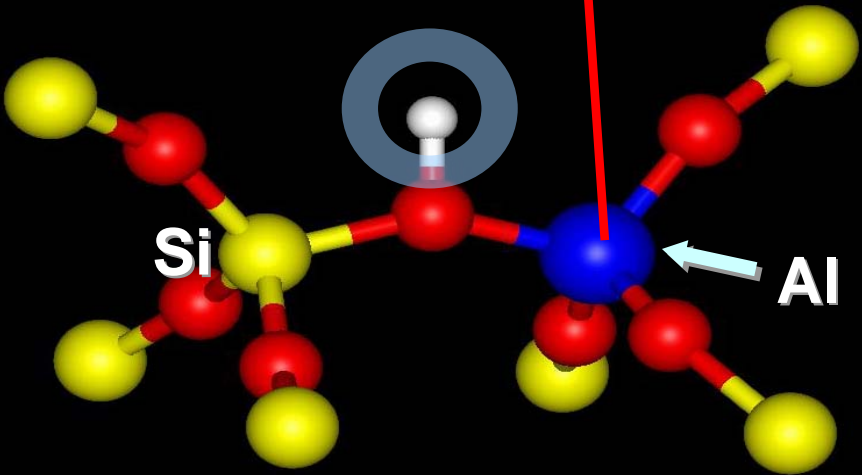
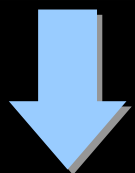
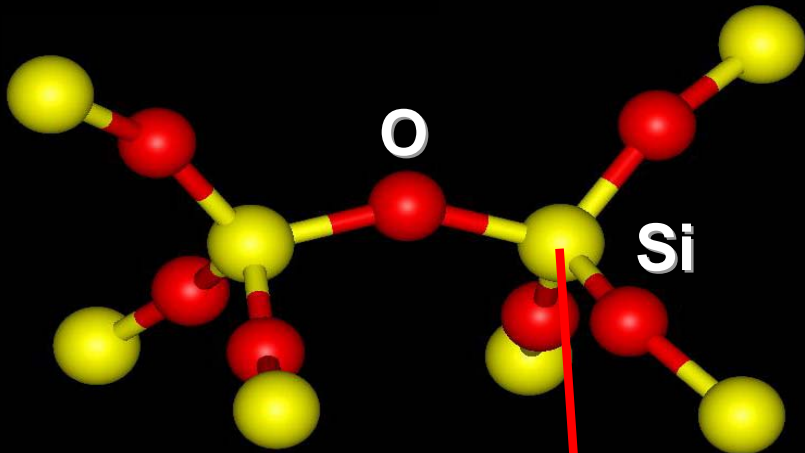
**New Catalyst**





# Zeolites

- Highly porous, high surface area, crystalline aluminosilicates
- Framework based on  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra
- Sharply defined channels/pores of molecular dimensions
- Stable over a wide temperature range
- Regenerable
- Fast deactivation
- Widely used as catalysts



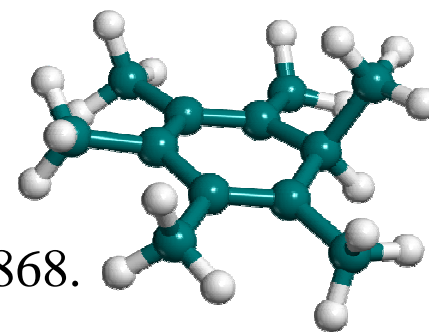
Framework charge  
balanced by mobile  
cations  
**Brønsted  
acidity**



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## In-situ FTIR studies of carbenium ions in zeolites have led to a new definition of zeolite acidity

- Until the early 90's, zeolites were believed to possess superacidity
- Carbocation stability is inherently linked to the acid strength of the zeolites
- Carbenium ions are likely reaction intermediates
- Recently, we provided the first evidence of proton transfer from a zeolite to a benzene ring (hexamethylbenzene)



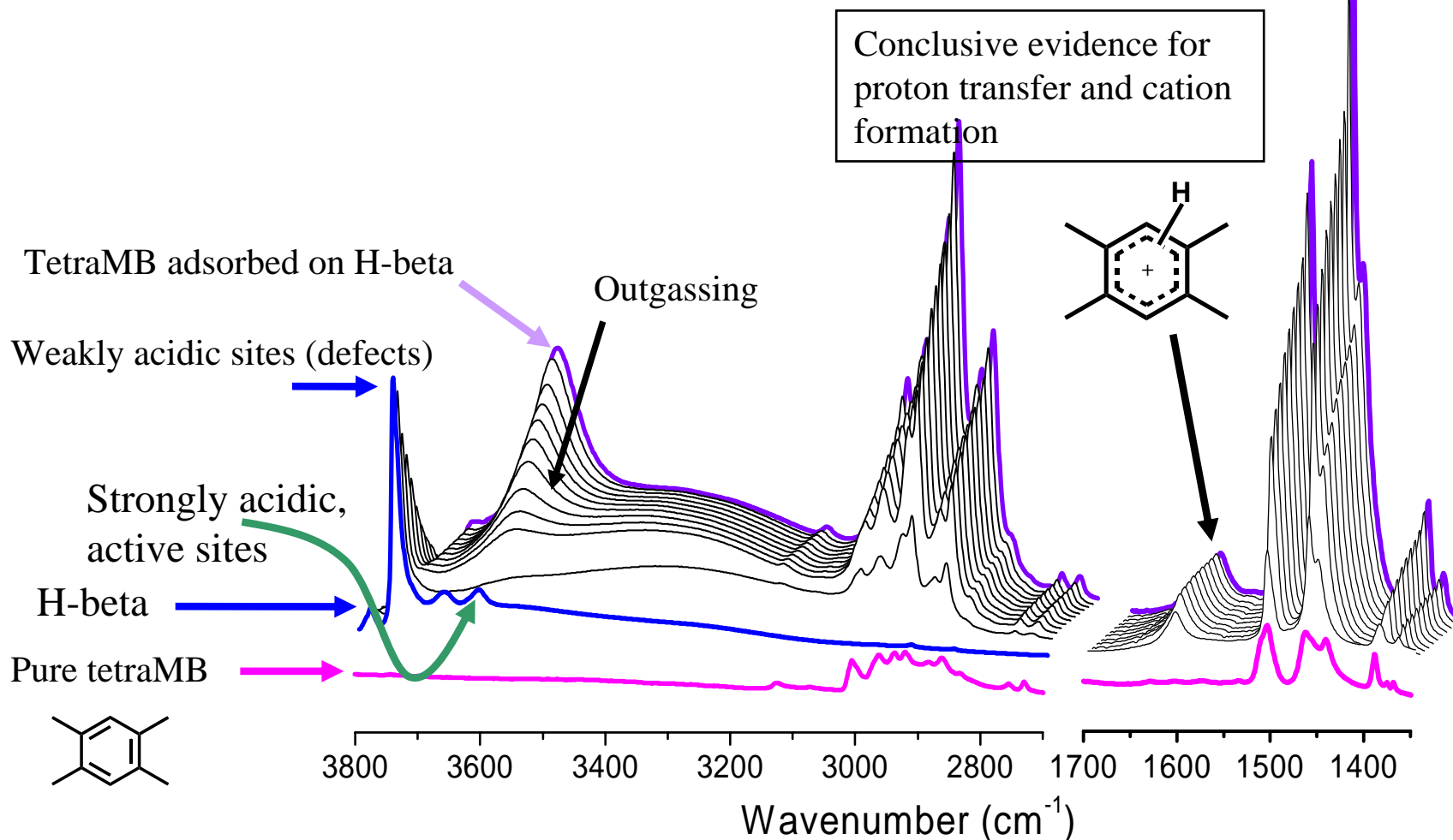
M. Bjørngen et al. *J. Am. Chem. Soc.* 2003, 125, 15863-15868.

M. Bjørngen et al. *ChemPhysChem*. In press 2004.



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## Spectroscopic evidence for the tetramethylbenzenium cation in zeolite H-beta

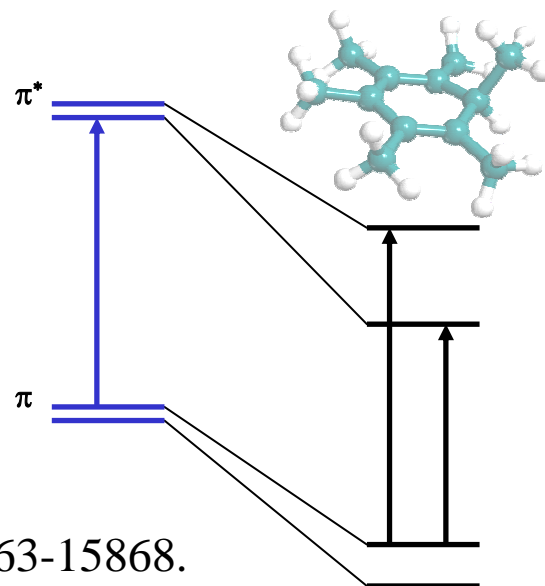
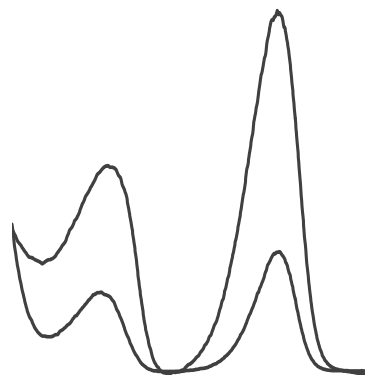




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--Complementary DRUV/VIS experiments gave support to the FTIR results

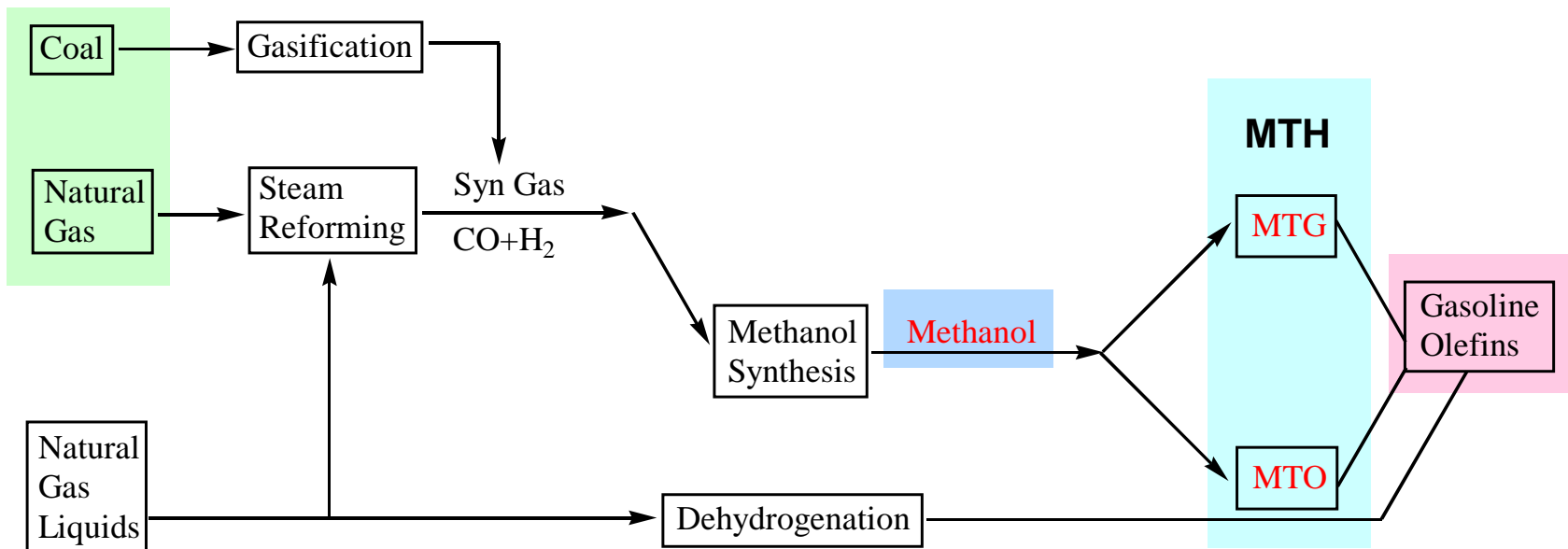
--From being classified as superacids, it now appears clear that zeolites have an acidic strength slightly lower than that of concentrated sulfuric acid





# Conversion of methanol to hydrocarbons/olefins

The methanol-to-hydrocarbons (MTH) technology represents a route for formation of olefins or gasoline from natural gas/coal

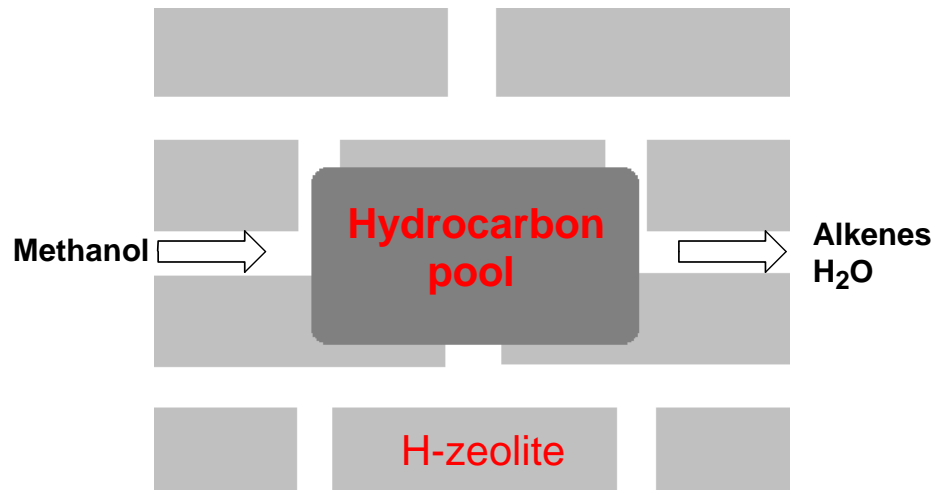






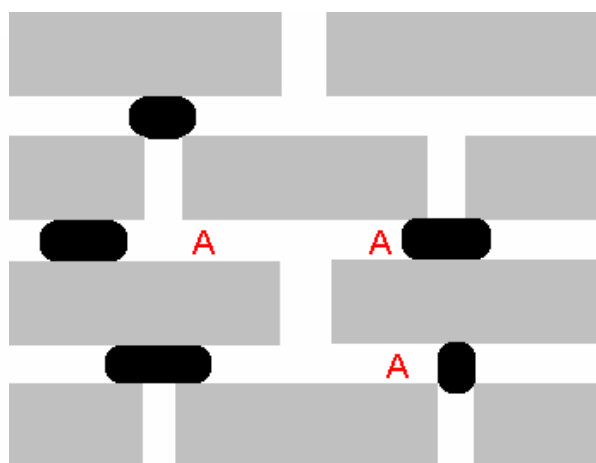
# MTH/MTO chemistry

- ✓ How can two or more  $C_1$ -entities react so that C-C bonds are formed?
- ✓ Which reactions lead to catalyst deactivation?
- ✓ The main catalytic cycle for olefin formation from methanol is based on a so-called hydrocarbon pool





## Hydrocarbons retained within the zeolite pores



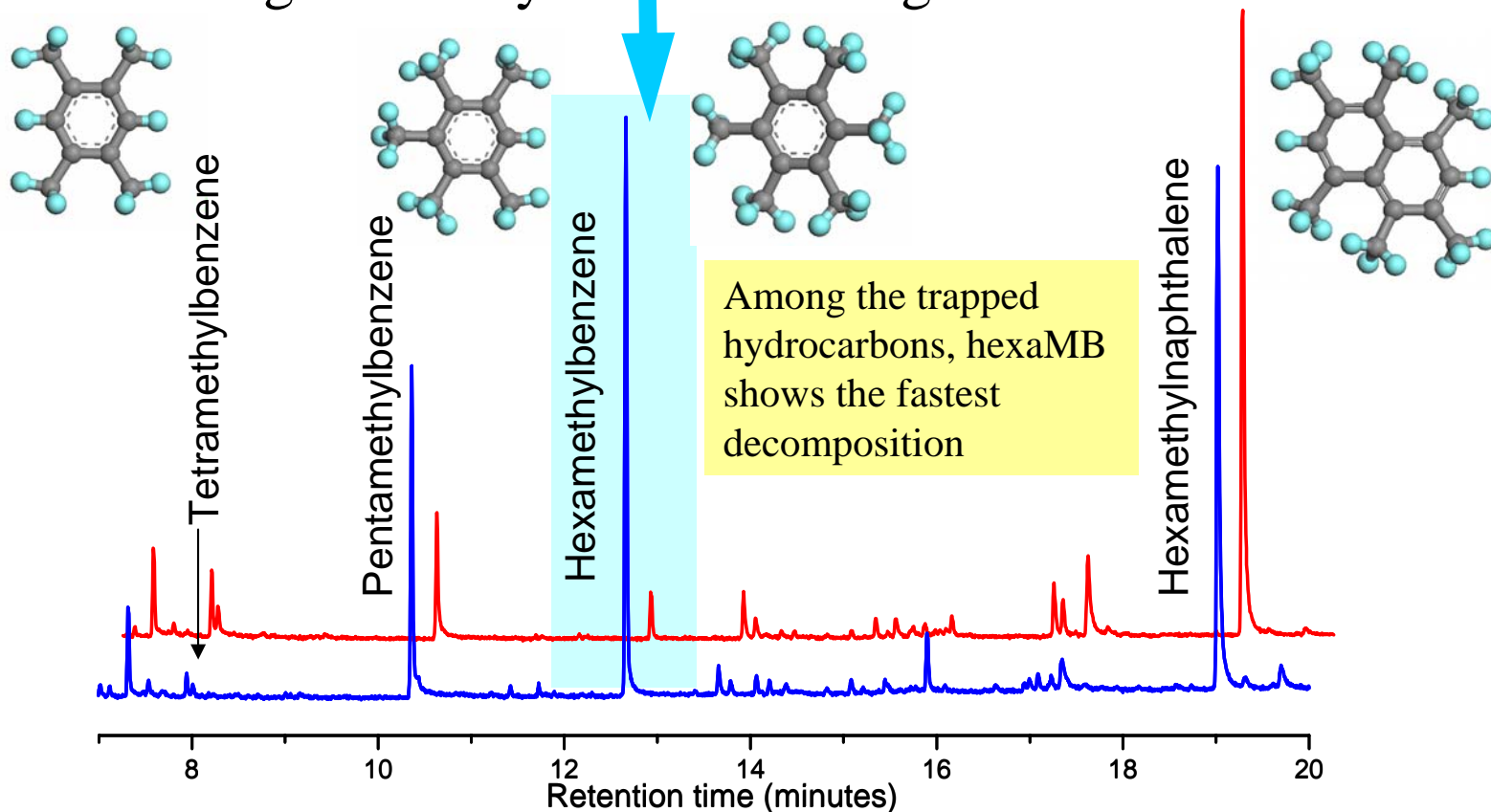
**Analysis** (GC-MS,  
HRMS, NMR)

- ✓ Analyzed *ex-situ* by:
  - ✓ Quenching the reaction (at a predetermined time)
  - ✓ Dissolving the zeolite (15% HF)
  - ✓ Extracting the organic material from the water phase
- ✓ Trapped organic species will be liberated and made available for analysis



# Hydrocarbons retained in the zeolite pores when methanol is reacted over the H-beta zeolite (GC-MS)

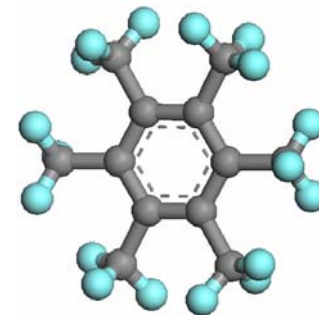
Stability of the retained hydrocarbons was probed by stopping the feed and flushing the catalyst with carrier gas for 1 minute





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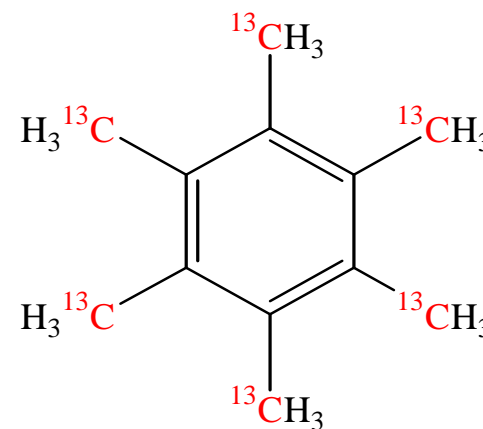
Hexamethylbenzene is not an inert spectator molecule



When fed alone over the beta zeolite, hexamethylbenzene gives the same products as methanol

How can these observations be rationalized?

*In-situ* synthesis of isotopically labeled hexamethylbenzene *inside the zeolite pores*

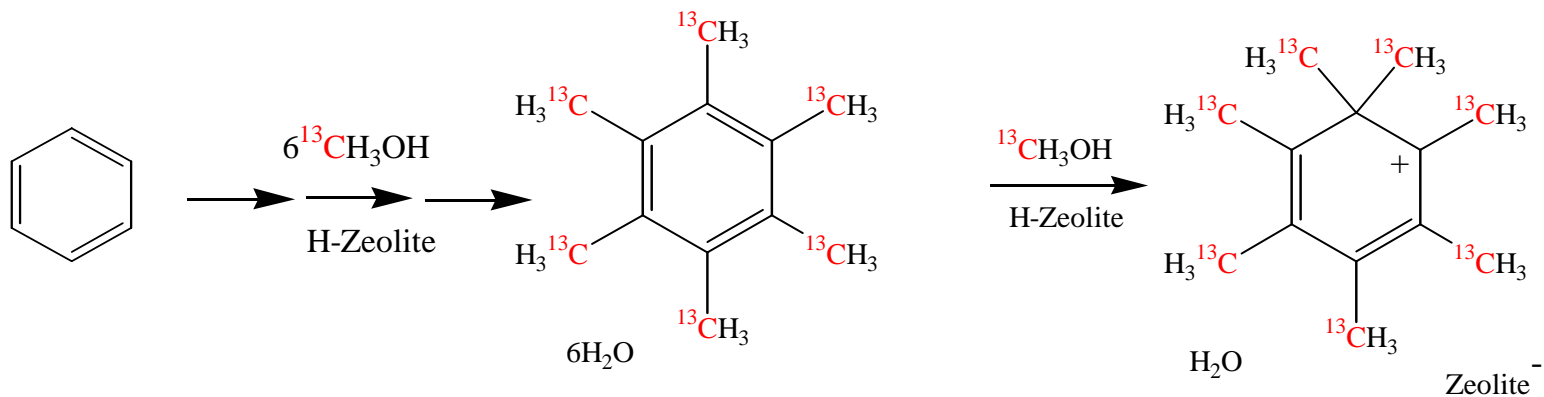


Bjørngen, M.; Olsbye, U.; Kolboe, S. *J. Catal.* 2003, 215, 30-44.

Bjørngen, M.; Olsbye, U.; Petersen, D.; Kolboe, S. *J. Catal.* 2004, 221, 1-10



# Co-reaction of $^{12}\text{C}$ -benzene and $^{13}\text{C}$ -methanol:



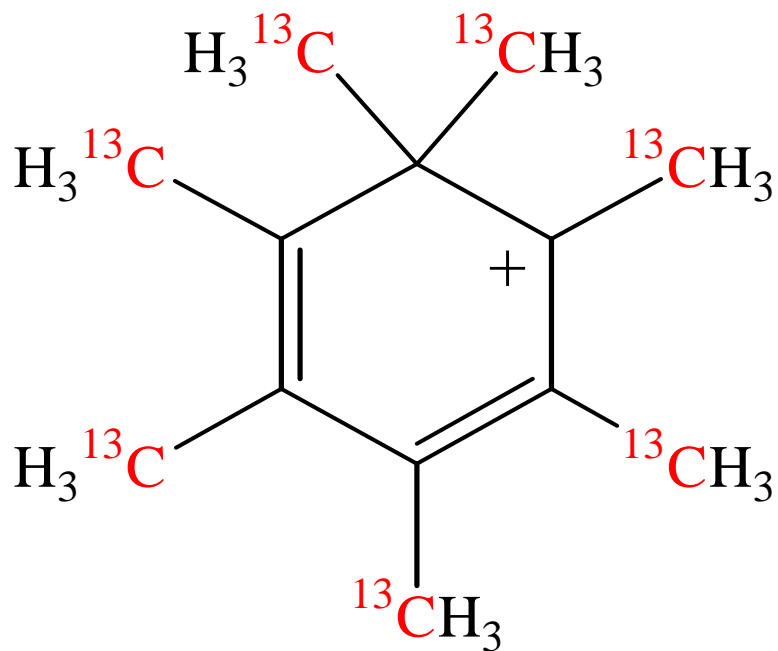
Hexamethylbenzene:  
Six labeled atoms

Heptamethylbenzenium:  
Seven labeled atoms



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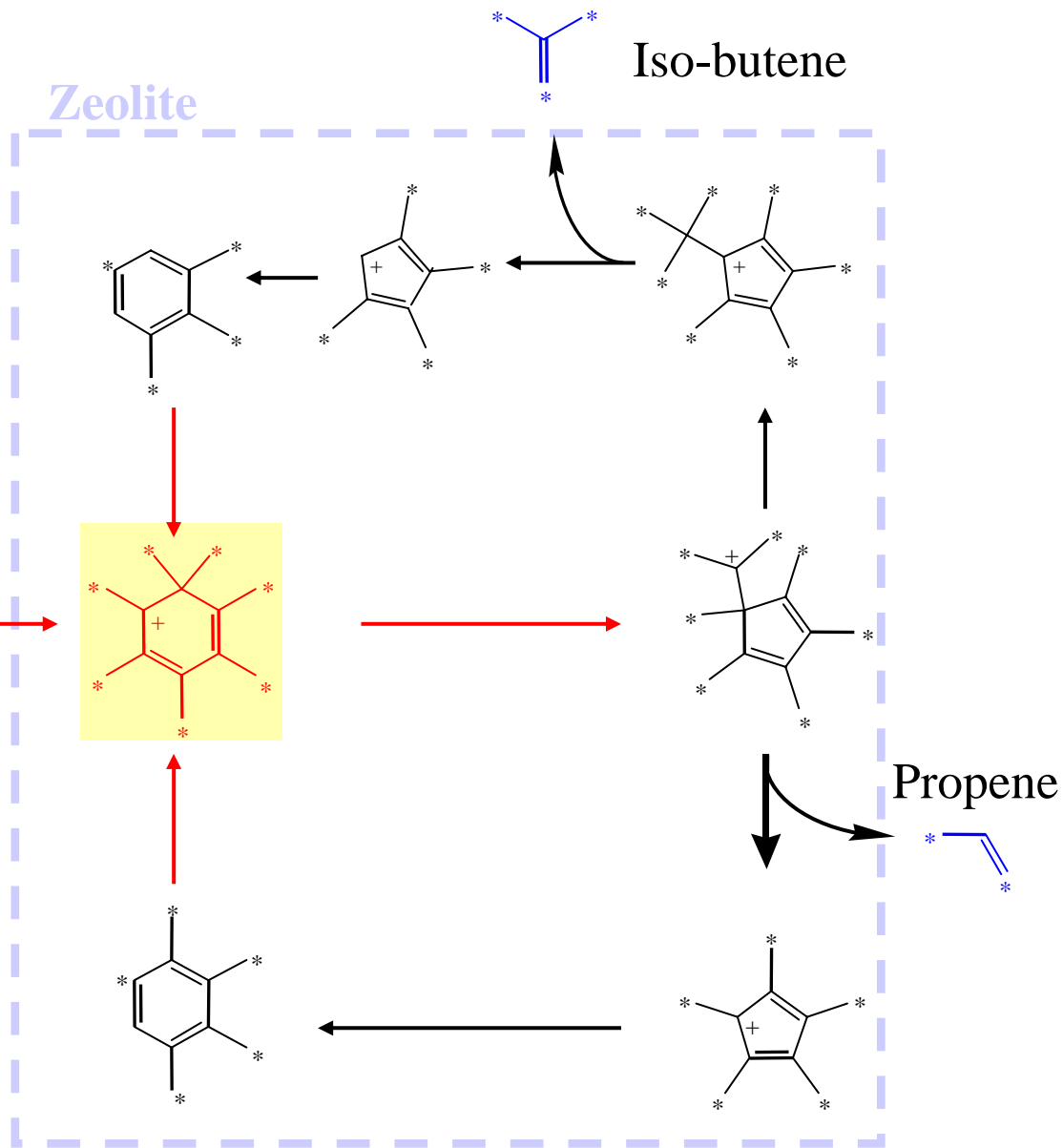
The heptamethylbenzenium cation was found to be the reaction intermediate (*i.e. the hydrocarbon pool*) of the MTH/MTO reaction





# The catalytic cycle of the MTO/MTH reaction

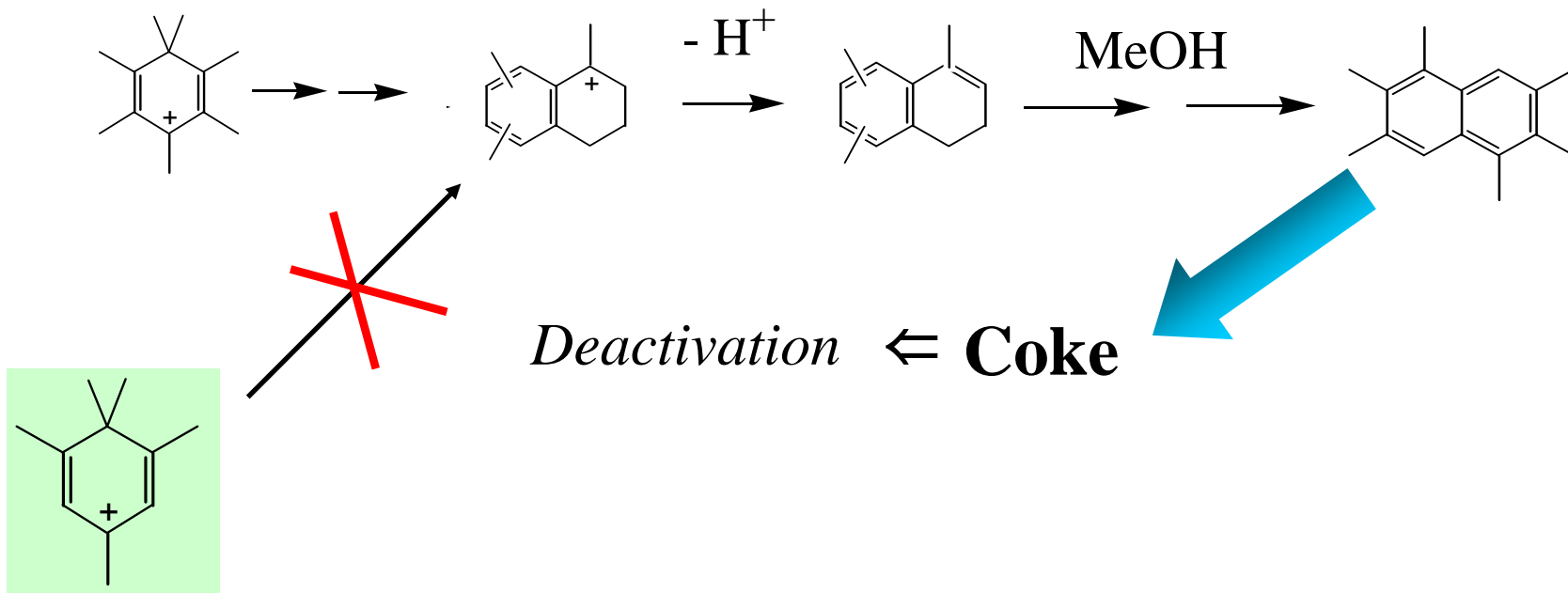
Methanol  
Reactant





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## The hydrocarbon pool may also lead to deactivation



A less steric demanding hydrocarbon pool is formed in zeolites with smaller channel dimensions (e.g. ZSM-5)



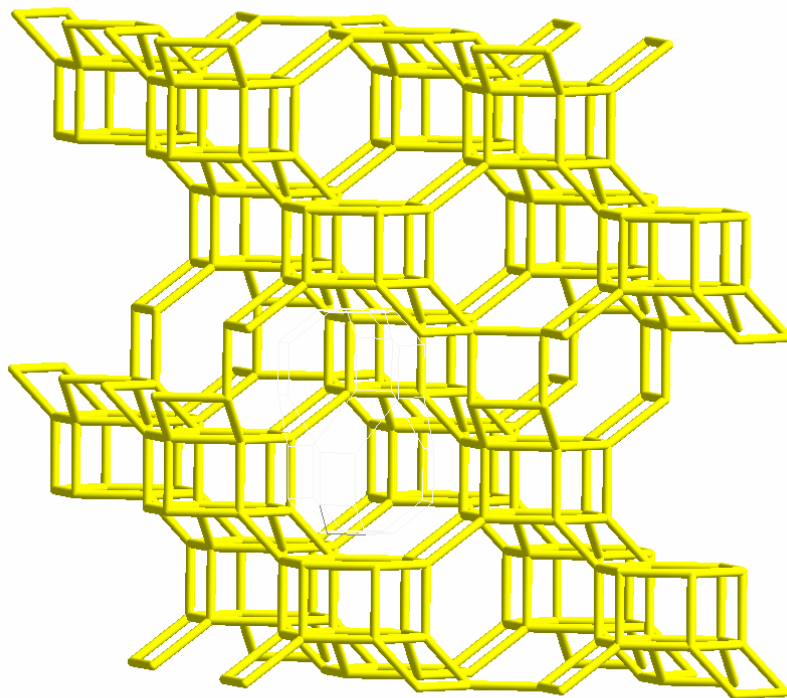


- We have obtained a detailed insight into the mechanism of the MTH/MTO reaction
- A deeper insight into the catalyst itself is also crucial for understanding product selectivities and catalyst deactivation

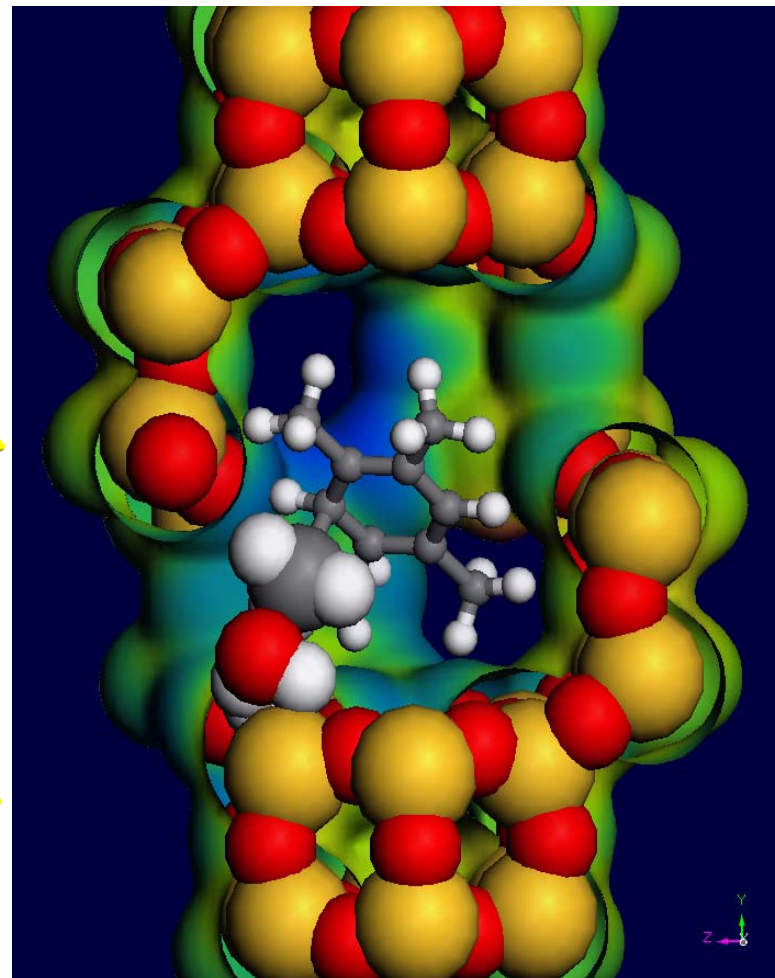


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# MTO catalysts based on the CHA topology

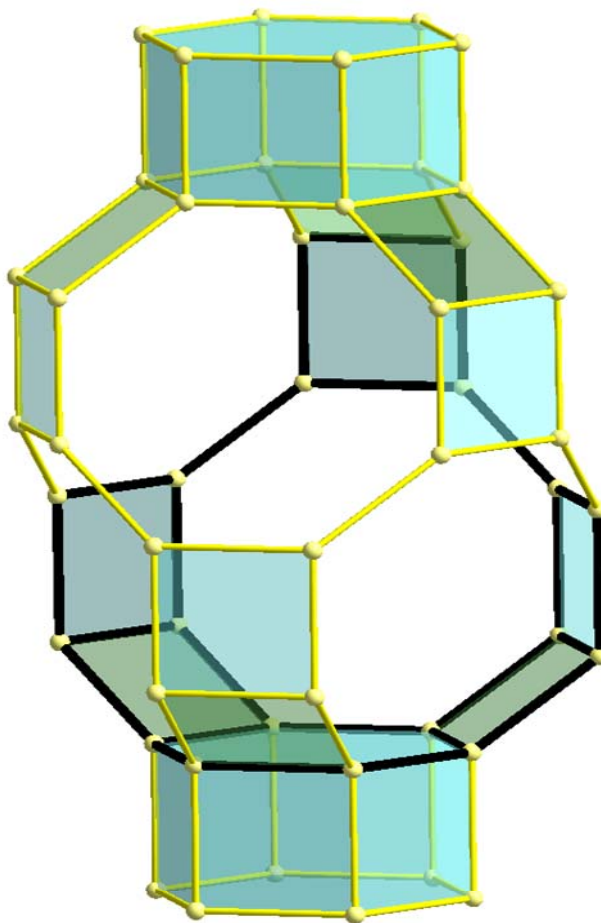


— a

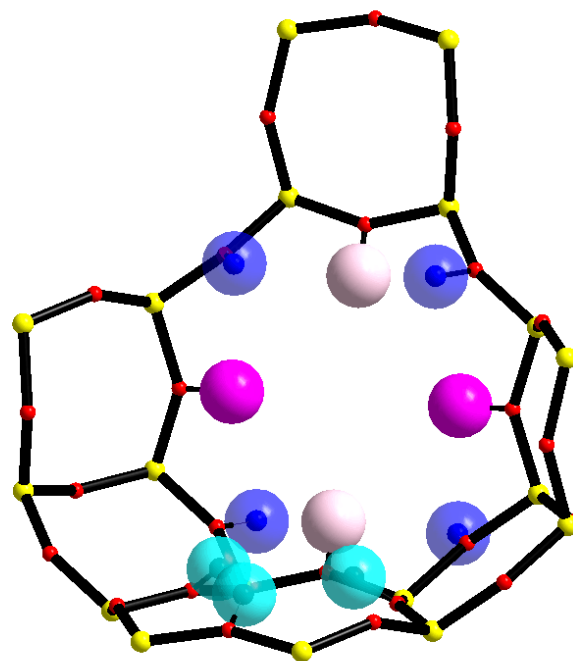




**1) The cage**



**2) Active sites, acidic protons in this example**



**Four different positions for  
the acidic sites**



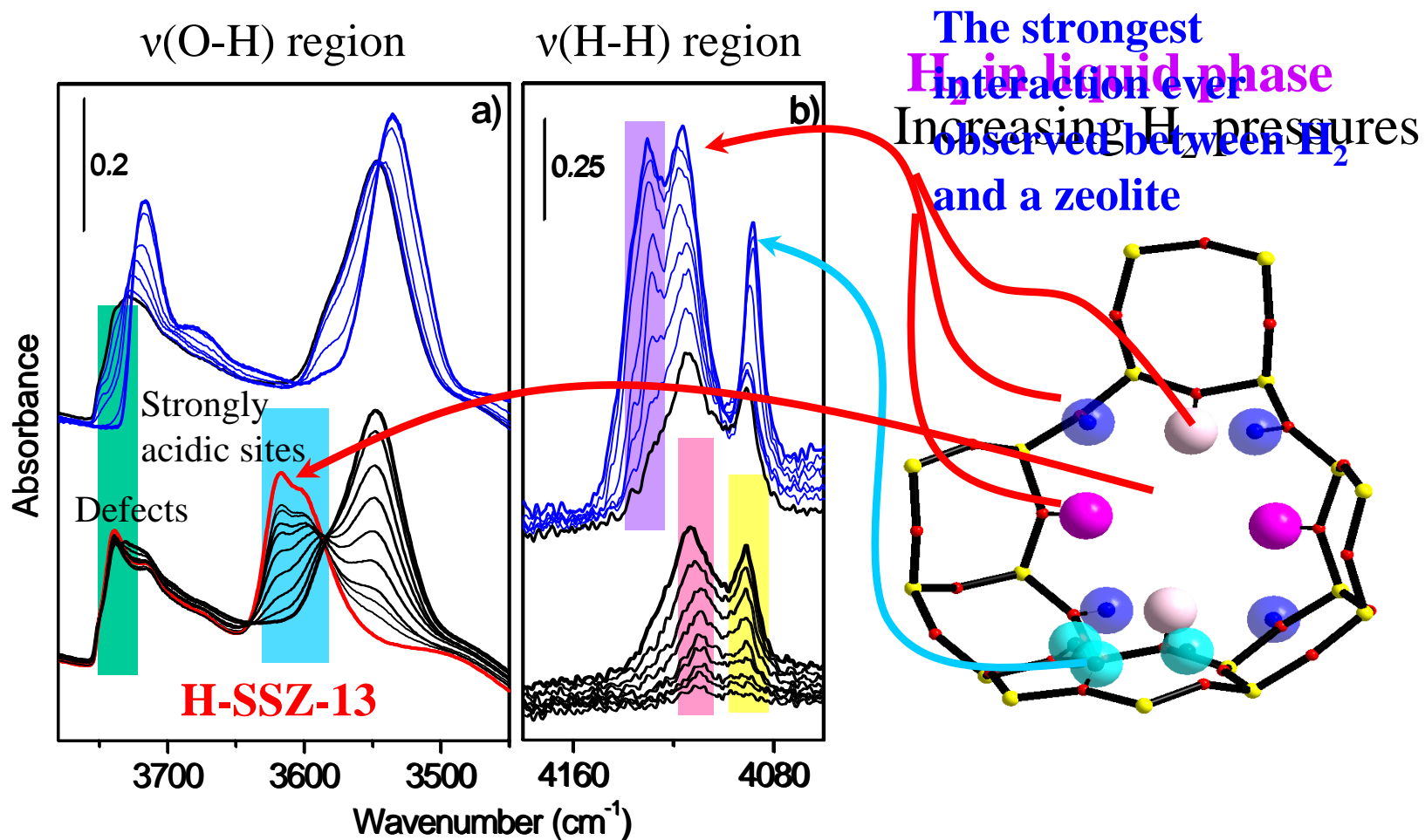
## H<sub>2</sub> for probing the local acidity in zeolites

- H<sub>2</sub> is a very sensitive probe molecule (single bond perturbation)
- The weak basic character requires low temperatures when studying interactions with zeolites



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# FTIR: H<sub>2</sub> on low Al chabazite (H-SSZ-13) at 20 K

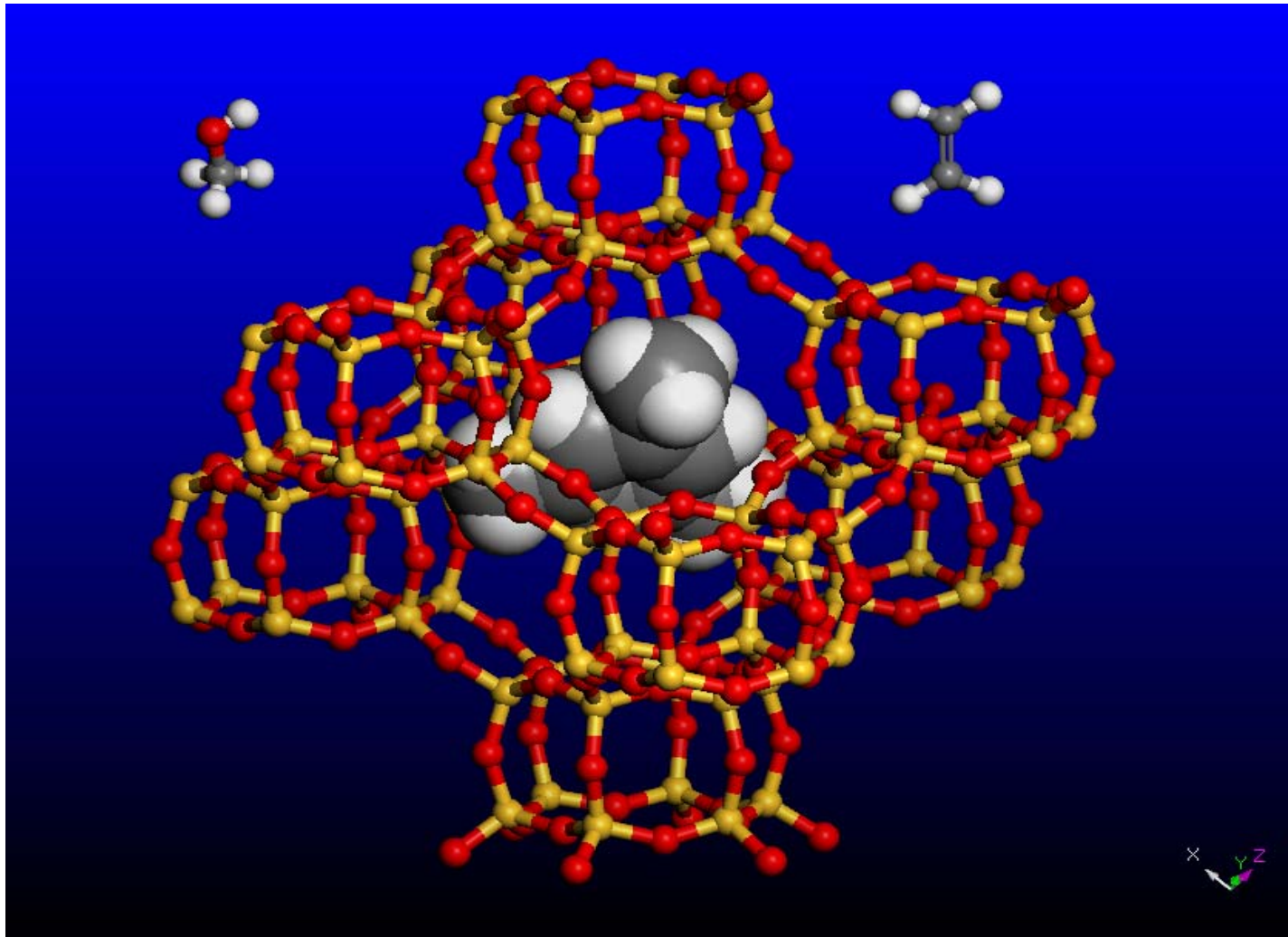


S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, A. Zecchina, M. Bjørgen, K. P. Lillerud, Submitted to *Science* (2004)



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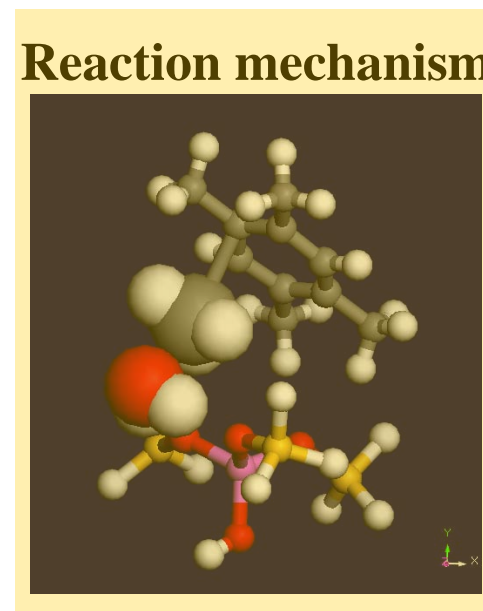
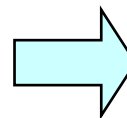
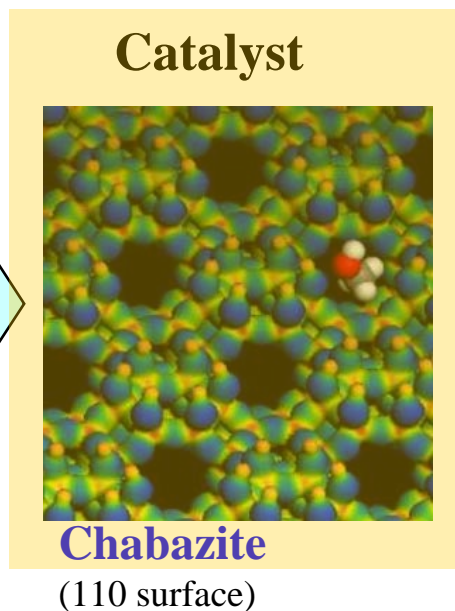
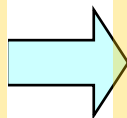
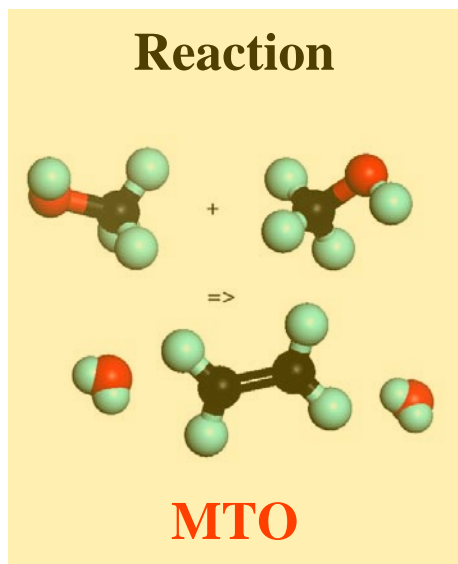
...and where does this knowledge lead us?



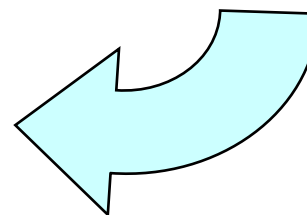


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# The catalysis group at UiO Research vision



**New Catalyst**





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Isotopic labelling studies indicate that the heptamethylbenzenium ion is the main intermediate for olefins AND coke formation over H-Beta zeolite.

\*

ZSM-5: Little deactivation.  
*gem*-pentamethylbenzenium ion probably main reaction intermediate.

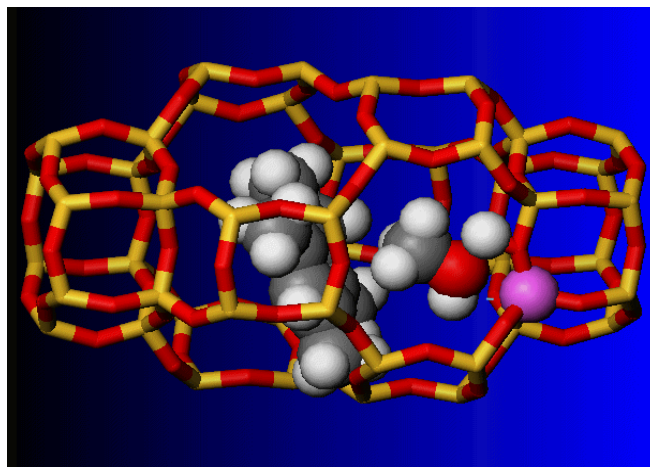
Would a smaller SAPO-34 cage lead to less coking, at similar olefin formation rates?  
And would the olefin selectivity change?



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## Could the acid strength be key to the MTH selectivity?

An obstacle is the difficulty of preparing the exact same pore structure and acid site density with different elements



A low-Al Si/Al chabazite was recently prepared and will be tested for the MTH reaction.



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UiO-12 AEN

UiO-20 DFT

OSO UiO-6

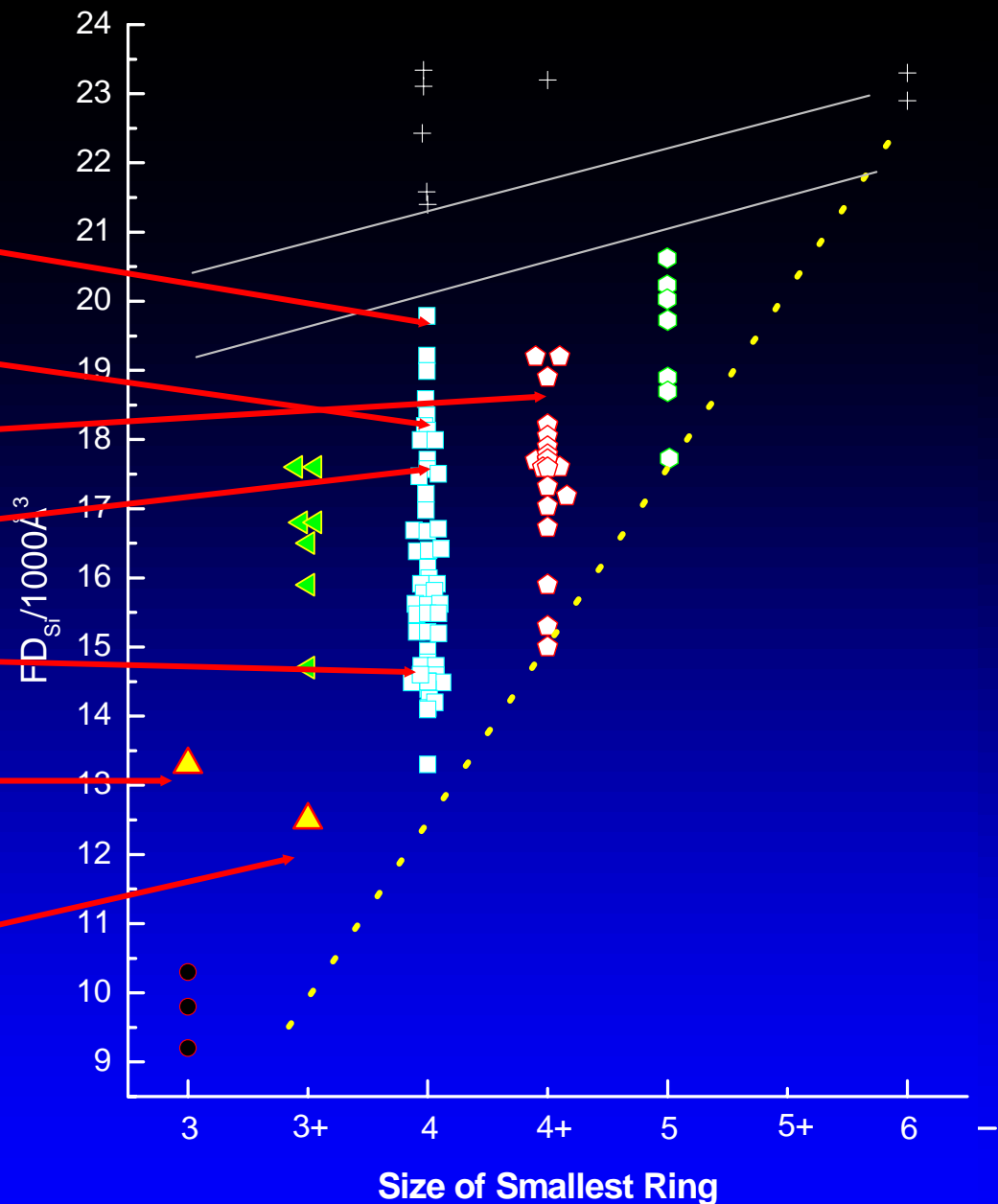
UiO-7 ZON

W.M. Meier

UiO-4 CHA

OSO OsloSantaBarbara-1

OBW OsloSantaBarbara-2

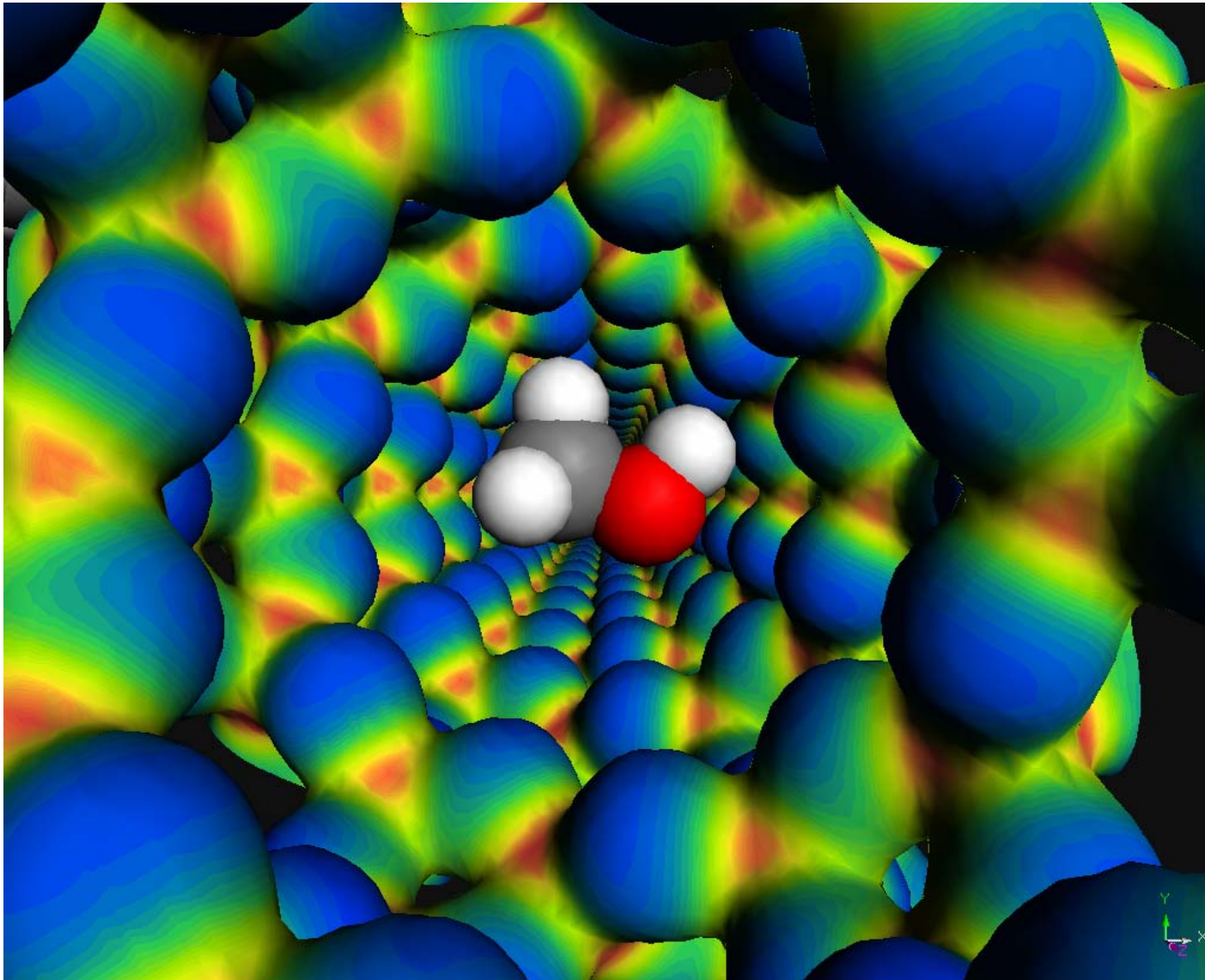




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OSO the only 3-ring only topology

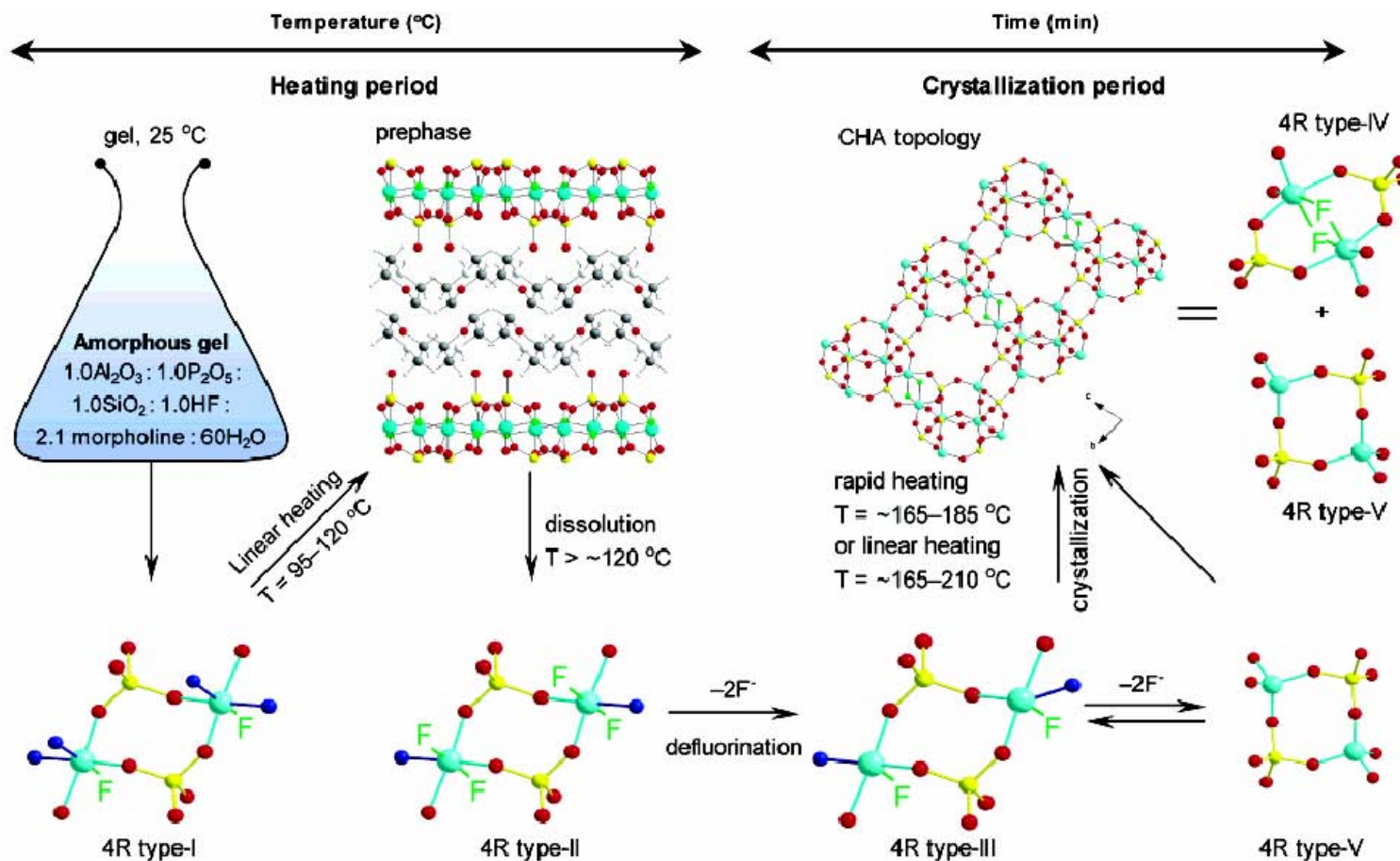
**0.3 nm**





# Crystallization of SAPO-34

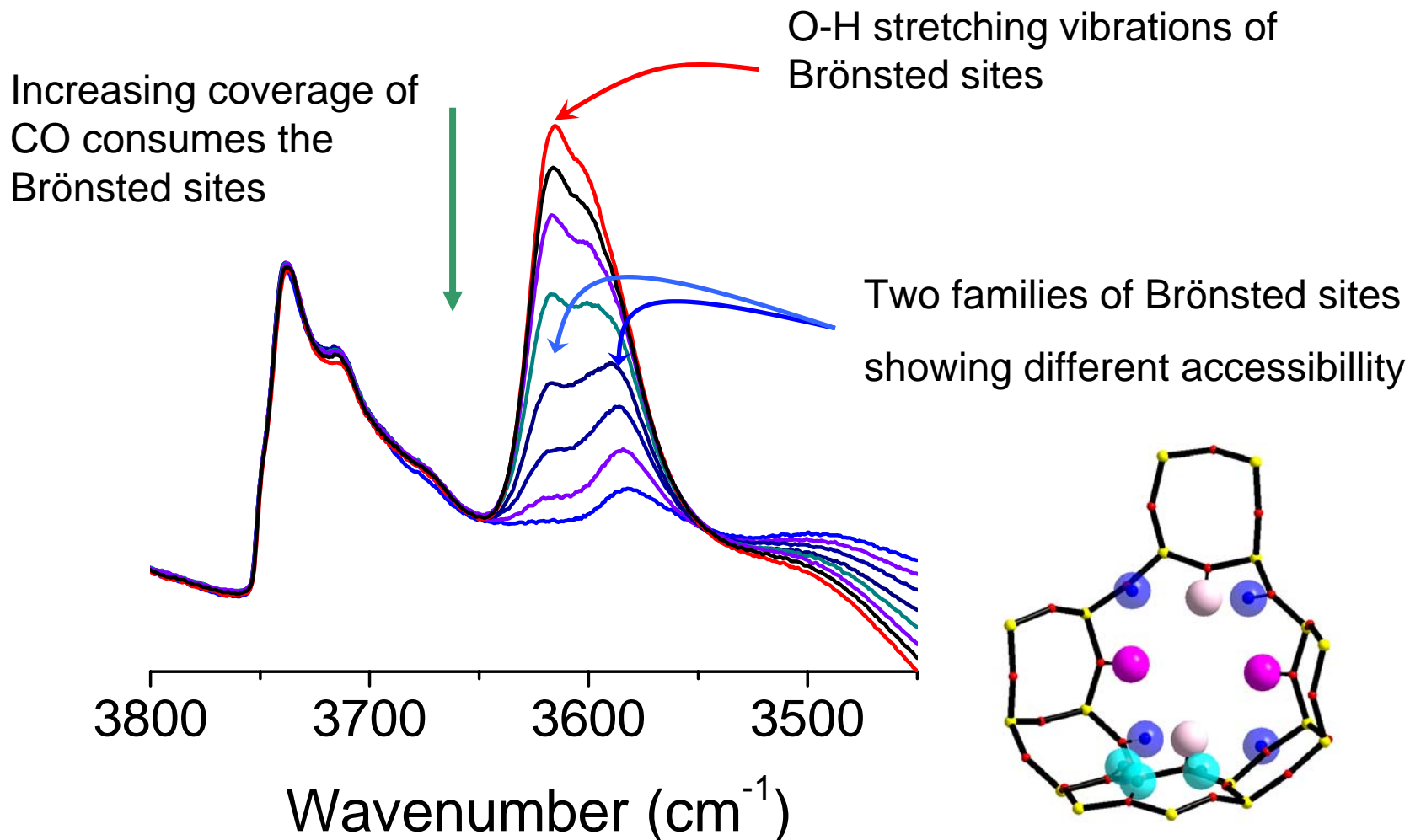
We are slowly moving towards understanding the crystallization





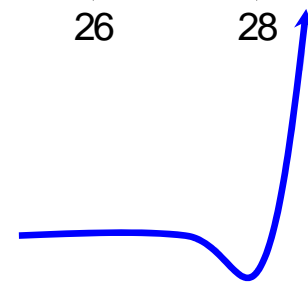
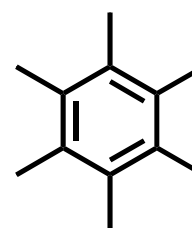
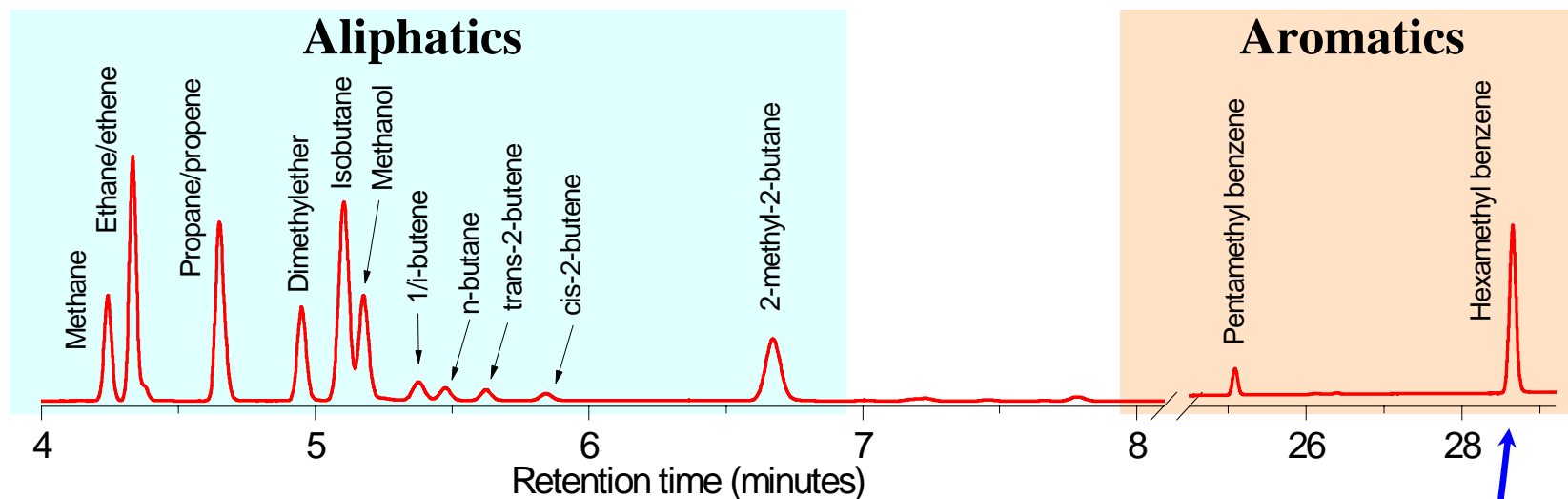
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## FTIR of interactions between CO and the Brønsted sites of H-SSZ-13





# Product distribution (400°C) when methanol is reacted over the H-beta zeolite (GC-FID)



Hexamethylbenzene is a dominant gas phase product



- ✓ Questions about the mechanism still remain unanswered:
  - ✓ Can two methanol molecules combine and form ethene?
  - ✓ How are the light olefins formed?
  
- ✓ More than 20 proposed mechanisms (Involving intermediates as radicals, carbenes, oxonium ions, carbocations)

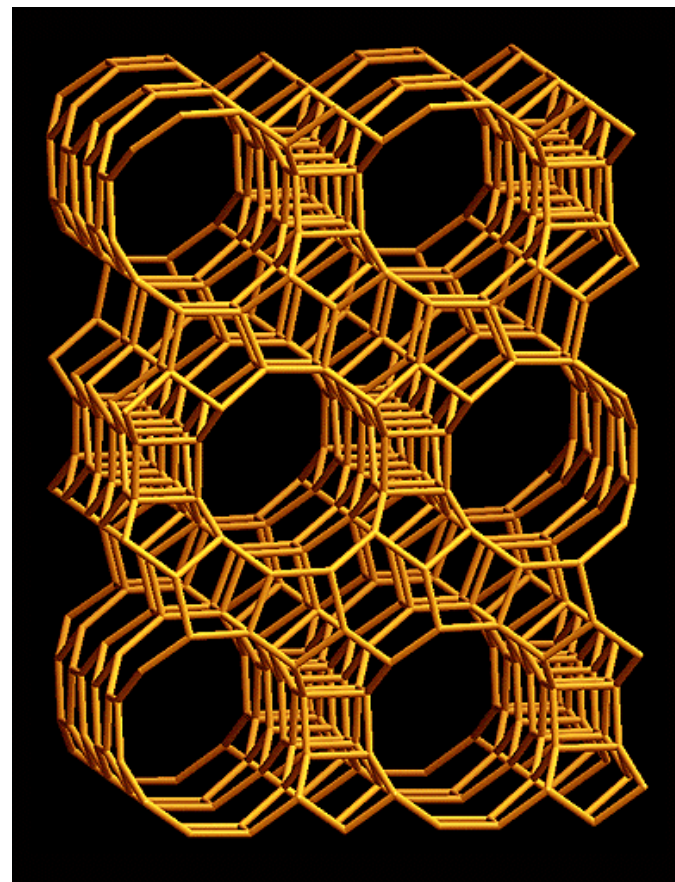




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## Conversion of methanol to hydrocarbons. Zeolite H-beta as a model system

- The beta zeolite is a wide pore zeolite (12-MR) allowing direct introduction of rather large molecules



Zeolite beta:  
7.7x6.6 Å

