Dry-gel Synthesis of Microporous and Mesoporous Solid Catalysts

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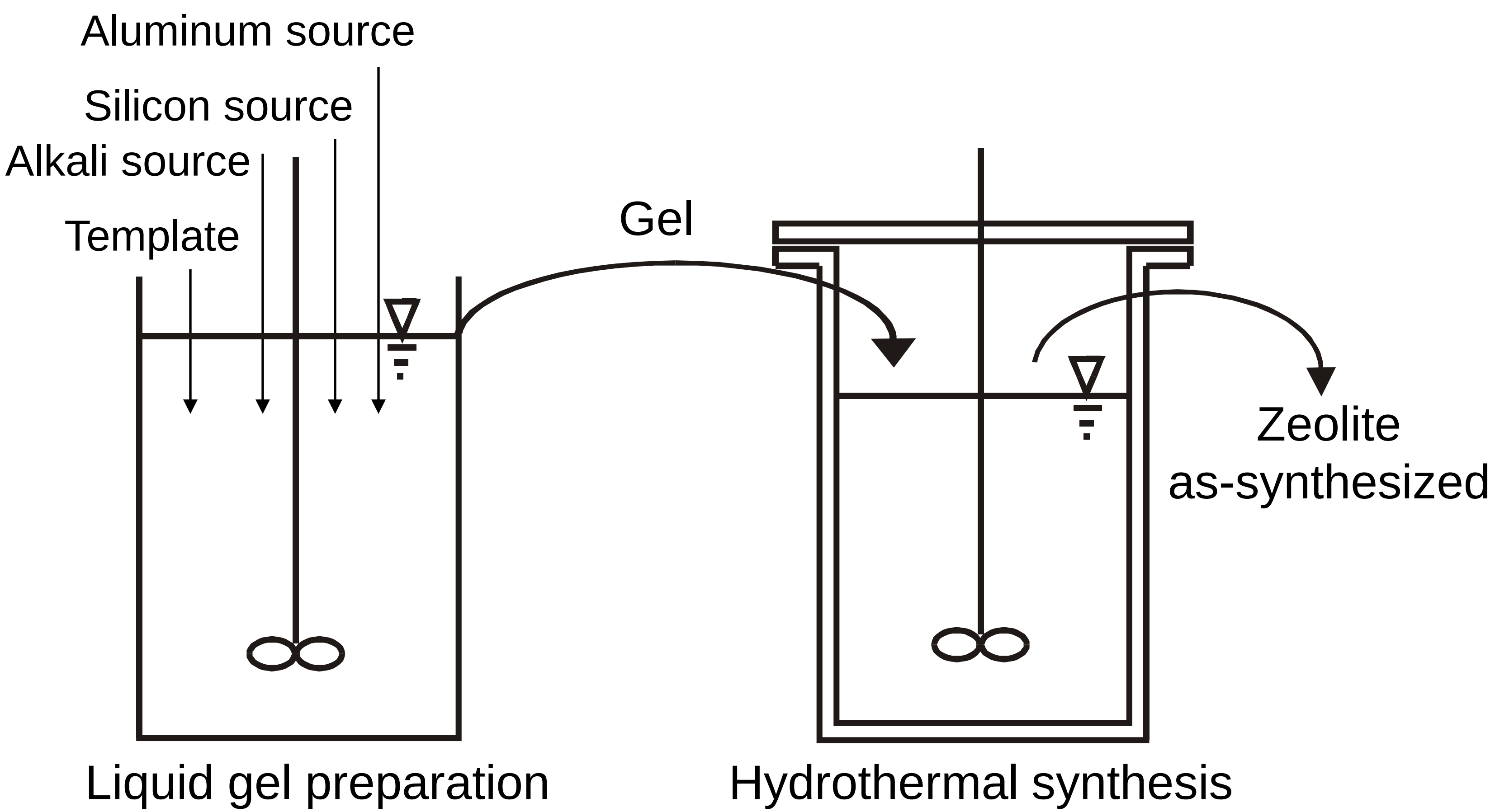
Principle of hydrothermal synthesis



The „vapour method" after Xu et al.

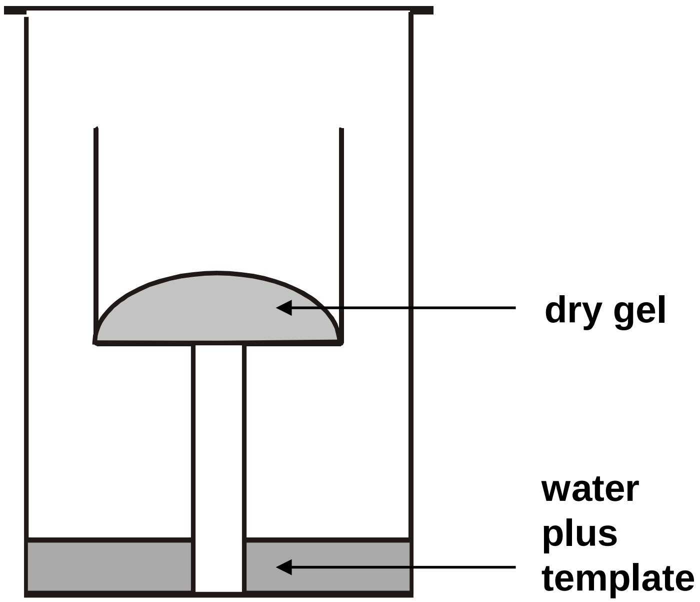
In 1990, Xu *et al.* described a novel method for the synthesis of ZSM-5 [1]:

- **a gel was prepared from aluminum sulphate, sodium silicate and sodium hydroxide; after drying the gel, it was placed on a porous plate in an autoclave**
- **at its bottom, the autoclave contained a solution of ethylenediamine and triethylamine in water**
- **there was no contact between the dry gel and the liquid phase**
- **after 5 to 7 days at 453 K, ZSM-5 (MFI) had formed**
- **the synthesis method was referred to as the "vapour method"**

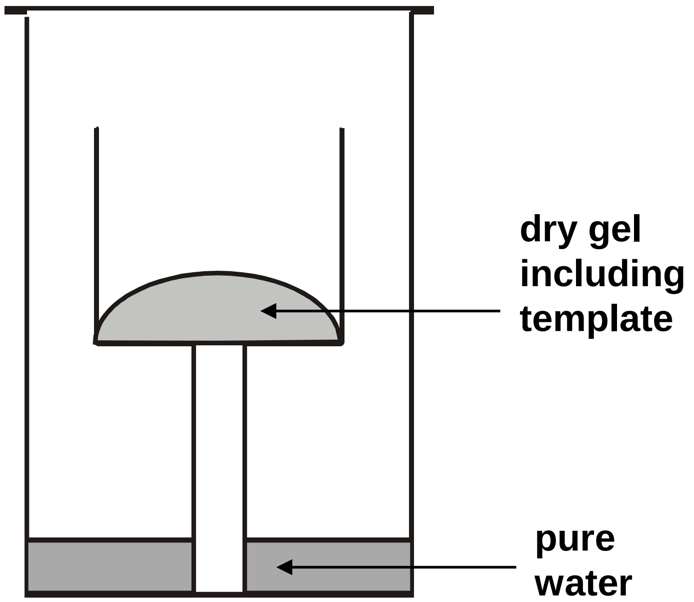
[1] W. Xu, J. Dong. J. Li, J. Li, F. Wu, Chem. Commun. (1990) 755.

Dry-gel conversion (DGC) methods

Vapor-phase transport (VPT)



Steam-assisted conversion (SAC)



M. Matsukata, M. Ogura, T. Osaki, P.R.H.P. Rao, M. Nomura, E. Kikuchi, Top. Catal. 9 (1999) 77.

Vapor-phase transport syntheses (VPT):

- ZSM-5 (MFI), W. Xu, J. Dong. J. Li, J. Li, F. Wu, Chem. Commun. (1990) 755.

- ZSM-22 (TON), S.G. Thoma, D.E. Trudell, F. Bonhomme, T.M. Nenoff, Microporous Mesoporous Mater. 50 (2001) 33.

- $AlPO_4$-5 (AFI), $AlPO_4$-11 (AEL), M. Bandyopadhyay, R. Bandyopadhyay, Y. Kubota, Y. Sugi, Chem. Lett. (2000) 1024.

- ZnAPO-34 (CHA), L. Zhang, G.R. Gavalas, Chem. Commun. (1999) 97.

Zeolites prepared via DGC

Steam-assisted conversion syntheses (SAC):

- Beta (BEA), P.R.H.P. Rao, M. Matsukata, Chem. Commun. (1996) 1441.
- Faujasite (FAU), M. Matsukata, M. Ogura, T. Osaki, P.R.H.P. Rao, M. Nomura, E. Kikuchi, Top. Catal. 9 (1999) 77.
- EMT (EMT), M. Matsukata, K. Kizu, M. Ogura, E. Kikuchi, Cryst. Growth Des. 1 (2001) 509-516.
- NU-1 (RUT), A. Bhaumik, T. Tatsumi, Microporous Mesoporous Mater. 34 (2000) 1.

Steam-assisted conversion syntheses (SAC):

- ZSM-5 (MFI), ZSM-12 (MTW), R. Bandyopadhyay, Y. Kubota, N. Sugimoto, Y. Fukushima, Y. Sugi, Microporous Mesoporous Mater. 32 (1999) 81.
- SAPO-5 (AFI), SAPO-11 (AEL), $AlPO_4$-5 (AFI), $AlPO_4$-11 (AEL), M. Bandyopadhyay, R. Bandyopadhyay, Y. Kubota, Y. Sugi, Chem. Lett. (2000) 1024.
- SAPO-34 (CHA), M. Bandyopadhyay, R. Bandyopadhyay, S. Tawada, Y. Kubota, Y. Sugi, Appl. Catal. A: General 225 (2002) 51.

Contents

- Selected zeolite syntheses: [Ga]Beta (BEA), [Al]Beta (BEA), [Ga]EU-1 (EUO), and [Al]EU-1 (EUO)
- Insight into the chemistry of dry-gel synthesis of zeolites
- Catalytic characterization of the synthesized zeolites
- Dry-gel synthesis of MCM-41/ZSM-5 hydride materials
- Conclusions

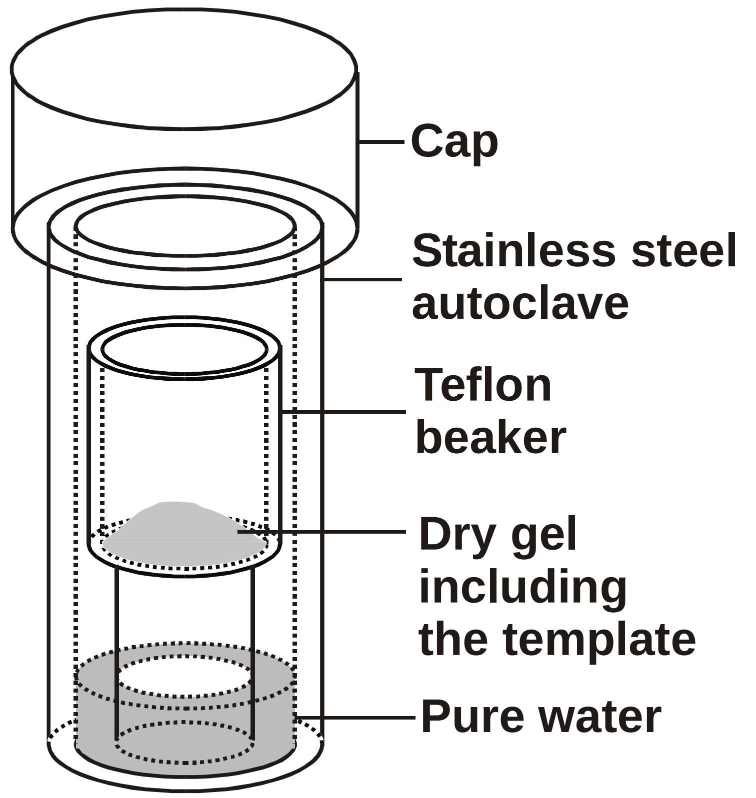
Selected Zeolite Syntheses:

[Ga]Beta (BEA), [Al]Beta (BEA),

[Ga]EU-1 (EUO), and [Al]EU-1 (EUO)

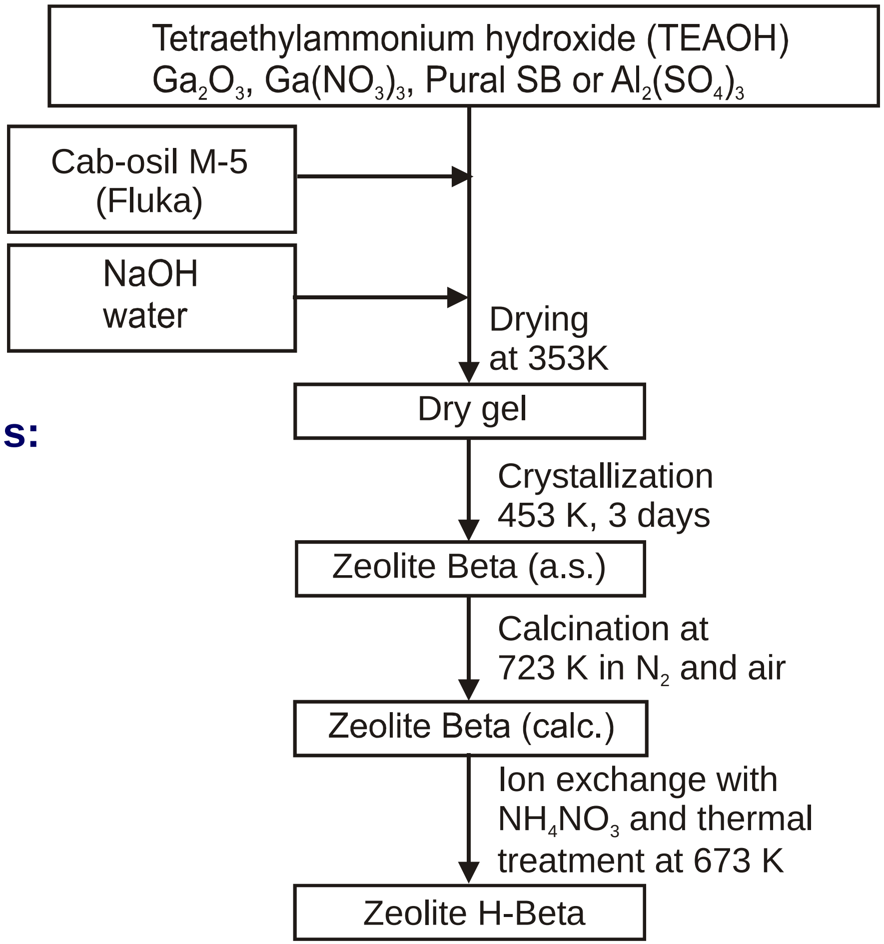
SAC procedure used in the present work

- preparation of the hydrogel
- ageing at room temperature
- drying at 353 K
- crystallization by dry-gel conversion under water vapor
- washing and drying of the product
- removal of the template by calcination at 723 K (Beta) or 813 K (EU-1)



SAC syntheses of zeolites [Ga]Beta and [Al]Beta

Procedure:

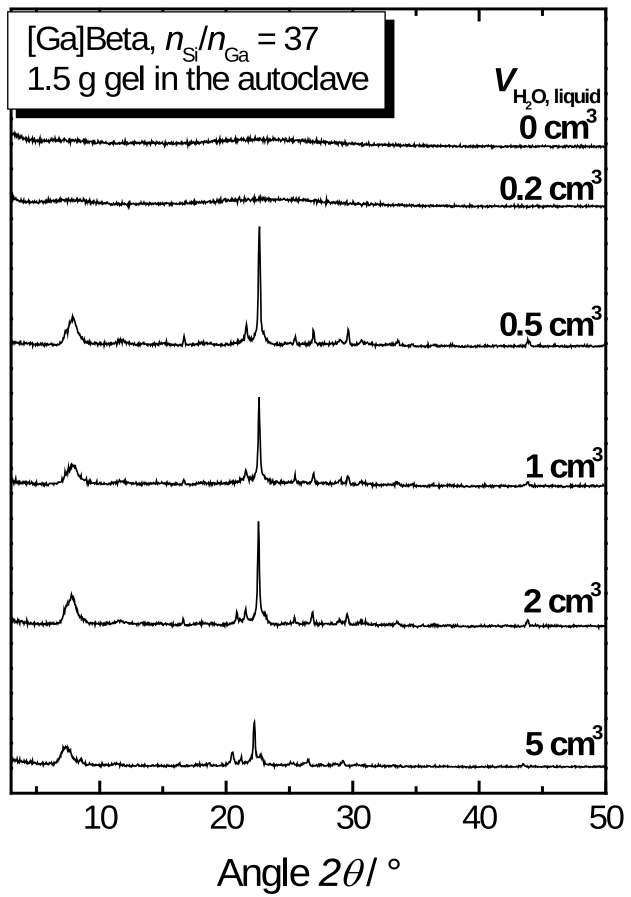


- **molar compositions of the dry gels:**
  17.0 –76.1 SiO_2 : Ga_2O_3 :
  0.5-2.2 Na_2O : 6.2-27.9 TEAOH
  25.2 –68.0 SiO_2 : Al_2O_3 :
  0.7-2.0 Na_2O : 9.3-25.2 TEAOH

- **autoclave volume: 110 cm^3**
  Teflon beaker: 14.5 cm^3

SAC syntheses of zeolite [Ga]Beta

influence of the amount of water in the autoclave:



- **the amount of water has a significant influence on the crystallization process**
- **at 453 K and V_{H2O} > 0.5 cm³, there is liquid water present in the autoclave**

→ **optimum: m_{H2O} / m_{gel} = 0.33**

Zeolites [Ga]Beta and [Al]Beta obtained by SAC syntheses

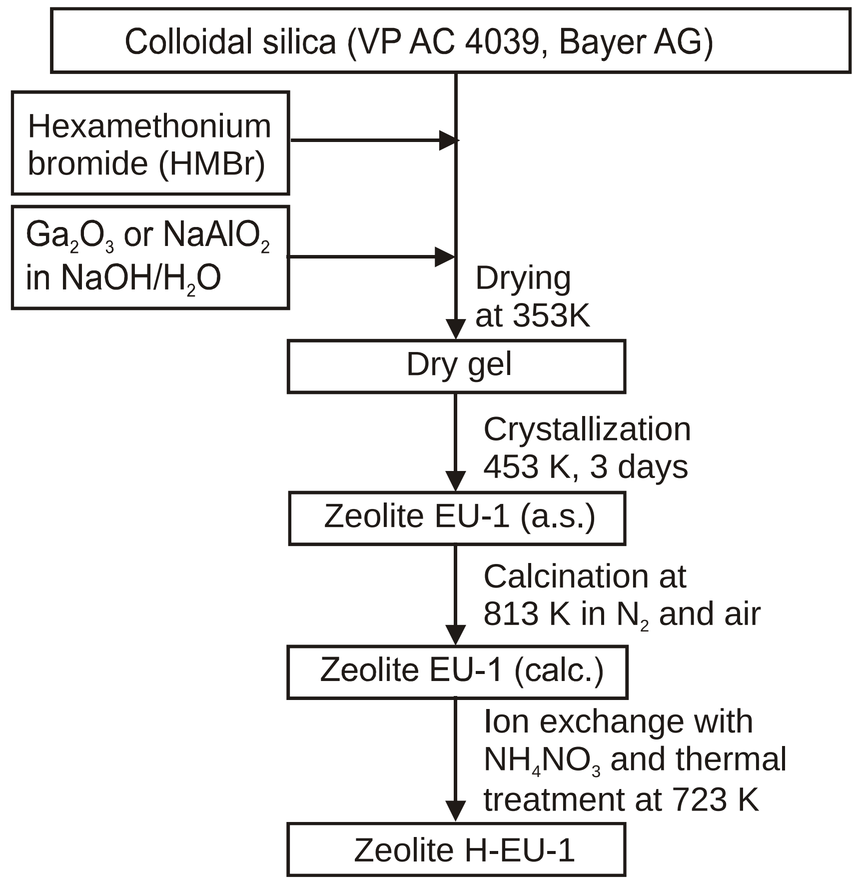
- **n_{Si}/n_{Ga}-ratios of [Ga]Beta zeolites prepared via hydrothermal syntheses: 13 [1] to 63 [2]**
- **n_{Si}/n_{Ga}-ratios of [Ga]Beta zeolites made by the dry-gel conversion method: 8, 14, 19, 34, 37, 72**
- **characteristic samples:**

No.	**Ga source**	$\left(\frac{n_{Si}}{n_T}\right)_{\text{chem.}}^{\text{dry gel}}$	$\left(\frac{n_{Si}}{n_T}\right)_{\text{chem.}}^{\text{zeolite calc.}}$	$\left(\frac{n_{Si}}{n_T}\right)_{\text{NMR}}^{\text{zeolite calc.}}$
1	$Ga(NO_3)_3$	37.6	37.8	37.8
2	Ga_2O_3	8.5	8.0	11.6
	Al source			
3	$Al_2(SO_4)_3$	34.0	35.7	35. 9
4	Pural SB	12.6	11.9	11.8

[1] M.L. Occelli, H.Eckert, A. Wölker, A. Auroux, Microporous Mesoporous Mater. 30 (1999) 219.
[2] K.J. Chao, S.P. Sheu, L.-H. Lin, M.J. Genet, M.H. Feng, Zeolites 18 (1997) 18.

SAC syntheses of zeolites [Ga]EU-1 and [Al]EU-1

Procedure:

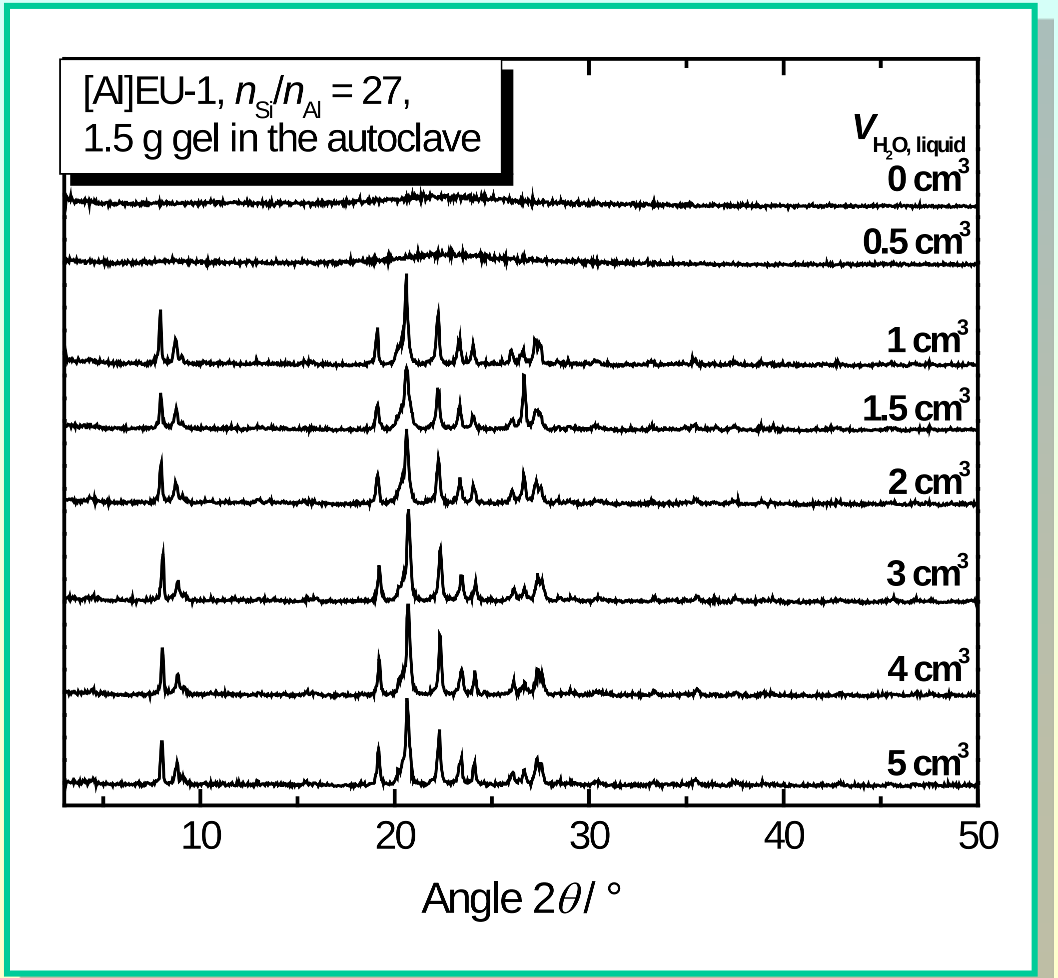


- **molar compositions of the dry gels:**
  20.0-100.0 SiO_2 : Ga_2O_3 :
  3.0-25.0 Na_2O : 3.1-15.4 HMBr
  30.0-600.0 SiO_2 : Al_2O_3 :
  8.0-150.0 Na_2O : 4.6-92.3 HMBr

- **autoclave volume: 110 cm^3**
  Teflon beaker: 14.5 cm^3

SAC syntheses of zeolites [Al]EU-1

influence of the amount of water in the autoclave:

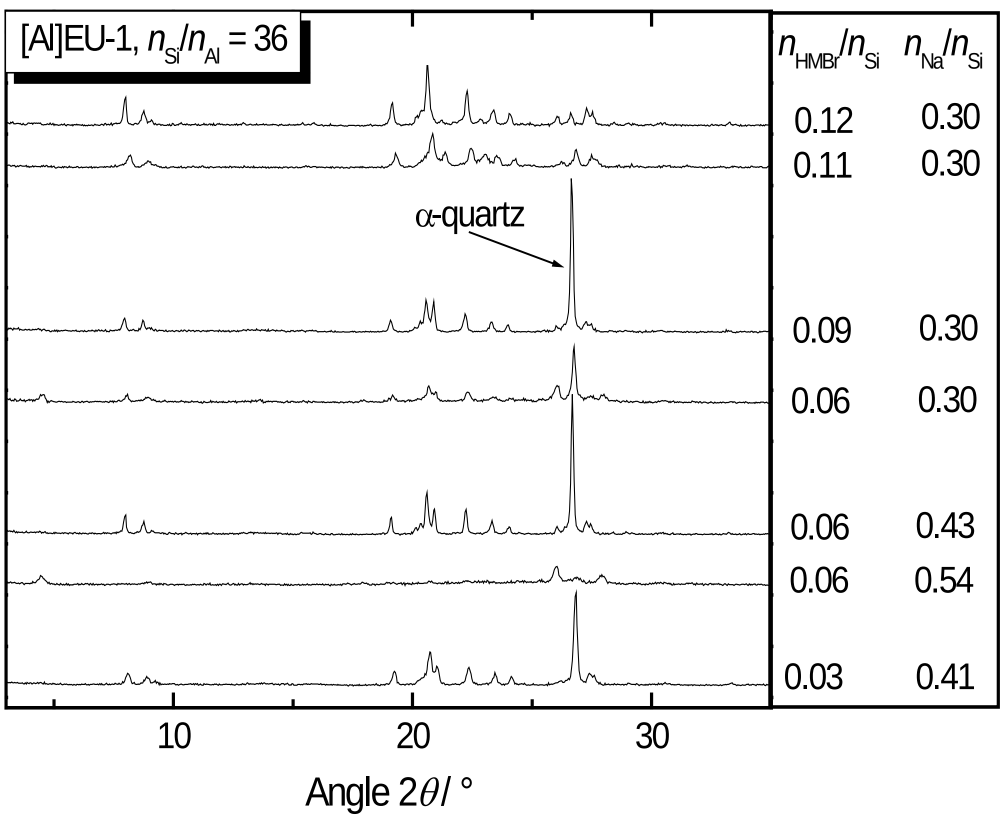


- **at 453 K and V_{H2O} > 0.5 cm³, there is liquid water present in the autoclave**
- **the amount of water has a significant influence on the crystallization process**
- **at least 1 cm³ of water is necessary to obtain highly crystalline EU-1 zeolites**

→ **range: m_{H2O} /m_{gel} > 0.67**

SAC syntheses of zeolites [Al]EU-1

influence of the amount of template in the dry gel:



- **minimum n_{HMBr}/n_{Si}-ratio of 0.11, at which pure [Al]EU-1 is obtained**
- **lower n_{HMBr}/n_{Si}-ratios give more α-quartz as impurity**
- **higher amounts of Na^+ do not suppress the formation of α-quartz**

Zeolites [Ga]EU-1 obtained by SAC syntheses

- n_{Si}/n_{Ga}-ratios of [Ga]EU-1 zeolites prepared via hydrothermal syntheses (HMBr as template): 27 to 50 [1]

$(n_{Si}/n_{Ga})^{\text{dry gel}}$	$(n_{Na}/n_{Si})^{\text{dry gel}}$	$(n_{Si}/n_{Ga})^{\text{zeolite}}$	Product
10	0.30	11.7	[Ga]EU-1
13	0.30	15.1	[Ga]EU-1
27	0.30	29.0	[Ga]EU-1
50	0.30	-	amorphous
	0.47	45.1	[Ga]EU-1
100	0.30	-	amorphous
	0.50	85.6	[Ga]EU-1
	0.75	-	amorphous

[1] G.N. Rao, V.P. Shiralkar, A.N. Kotsthane, P. Ratnasamy, in: M.L. Occelli, H.E. Robson (Eds.), Synthesis of Microporous Materials, Volume 1, Molecular Sieves, van Nostrand Reinhold, New York, 1992, p. 153-166.

Zeolites [Al]EU-1 obtained by SAC syntheses

- **n_{Si}/n_{Al}-ratios of [Al]EU-1 zeolites prepared via hydrothermal syntheses (HMBr as template): 16 to 60 [1]**

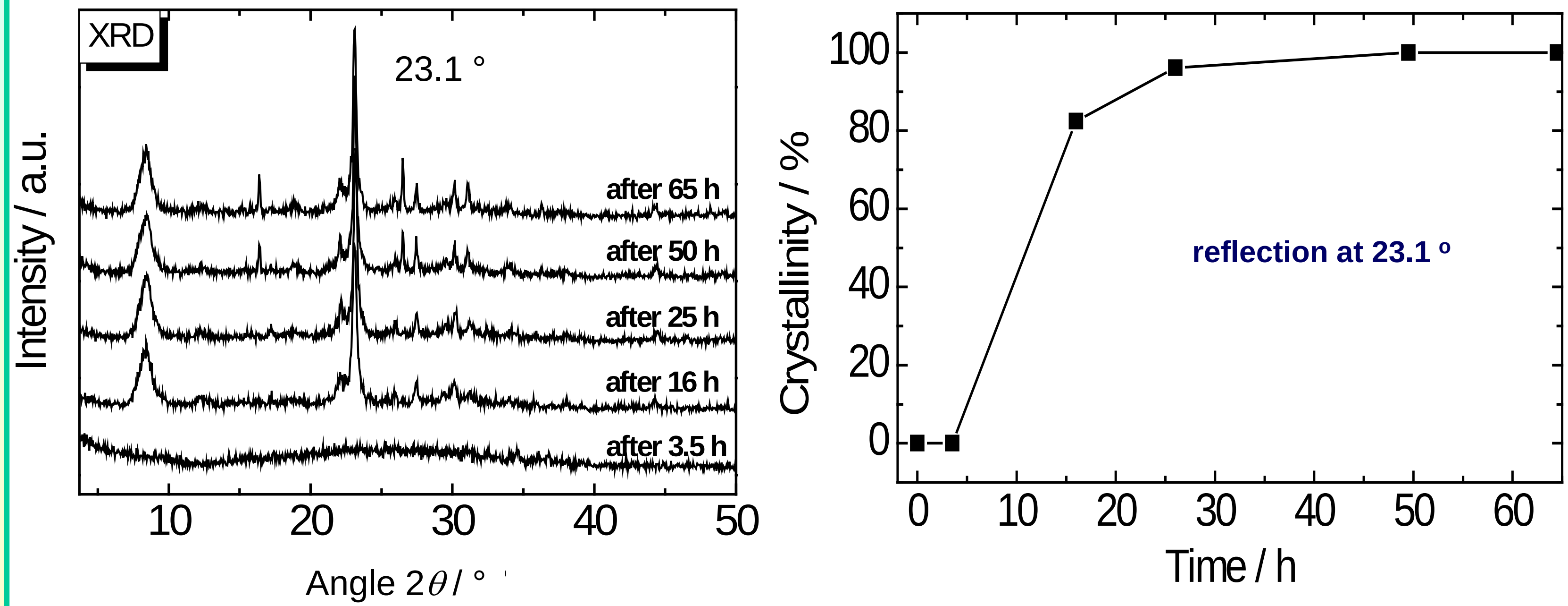
$(n_{Si}/n_{Al})^{\text{dry gel}}$	$(n_{Na}/n_{Si})^{\text{dry gel}}$	$(n_{Si}/n_{Al})^{\text{zeolite}}$	**Product**
15	0.37	-	amorphous
	0.53	17.6	[Al]EU-1
27	0.30	28	[Al]EU-1
36	0.30	37	[Al]EU-1
50	0.30	54	[Al]EU-1
60	0.30	-	amorphous
	0.36	55.9	[Al]EU-1
100	0.30	104.4	EU-1 + EU-2
	0.51	66.1	[Al]EU-1
300	0.50	141.8	[Al]EU-1

[1] G.N. Rao, P.N. Joshi, A.N. Kotasthane, P. Ratnasamy, Zeolites 9 (1989) 483.

Insight into the Chemistry of the Dry-gel Synthesis

Crystallinity of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.5)

- **powder X-ray diffractograms and crystallinity as a function of the dry-gel conversion time**

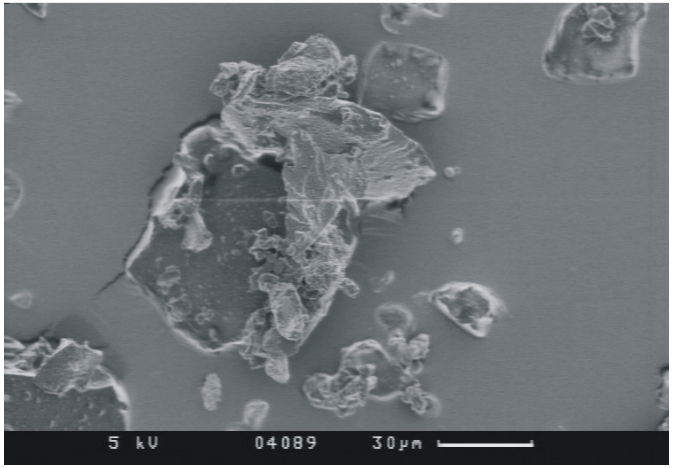


→ **formation of zeolite particles already within the first 16 h**

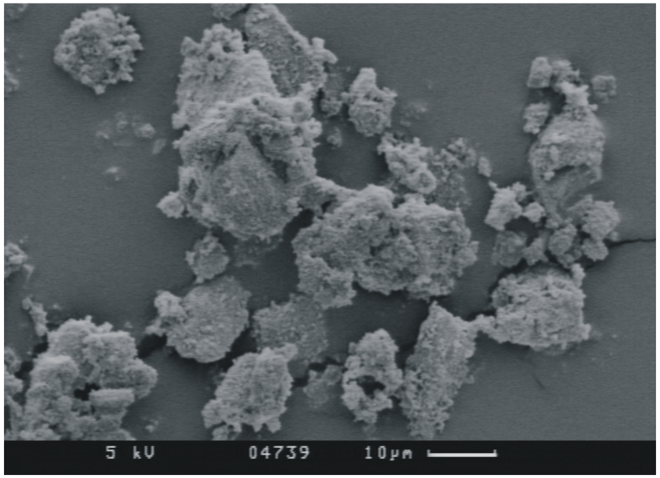
Synthesis of [Ga]Beta (n_{Si}/n_{Ga} = 8.5): Particle morphology

- **SEM performed at different crystallization times:**

dry-gel particles (ca. 30 µm) before DGC



zeolite particles (< 0.5 µm) obtained after 65 h

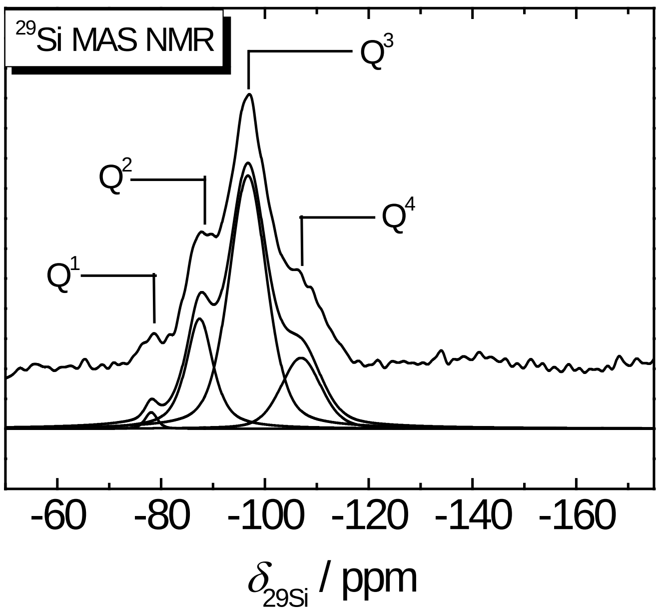


→ **dissolution and rearrangement of the solid material**

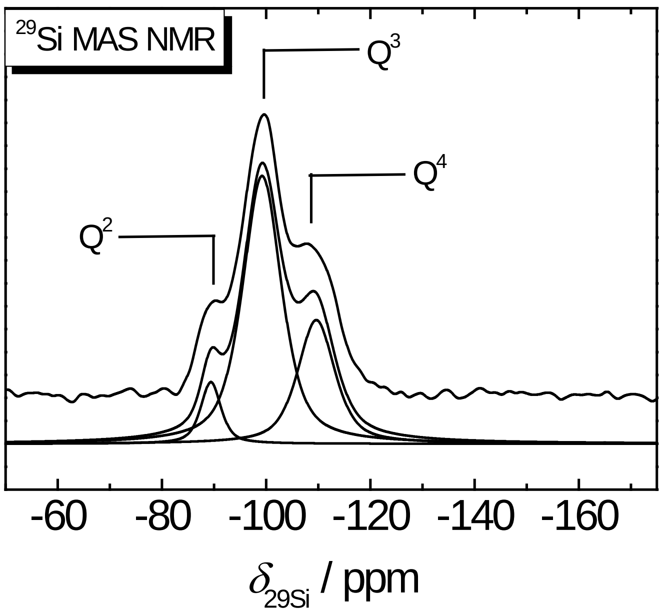
^{29}Si MAS NMR of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.5)

- **^{29}Si MAS NMR spectra recorded after different conversion times**

fresh dry-gel particles (0 h)

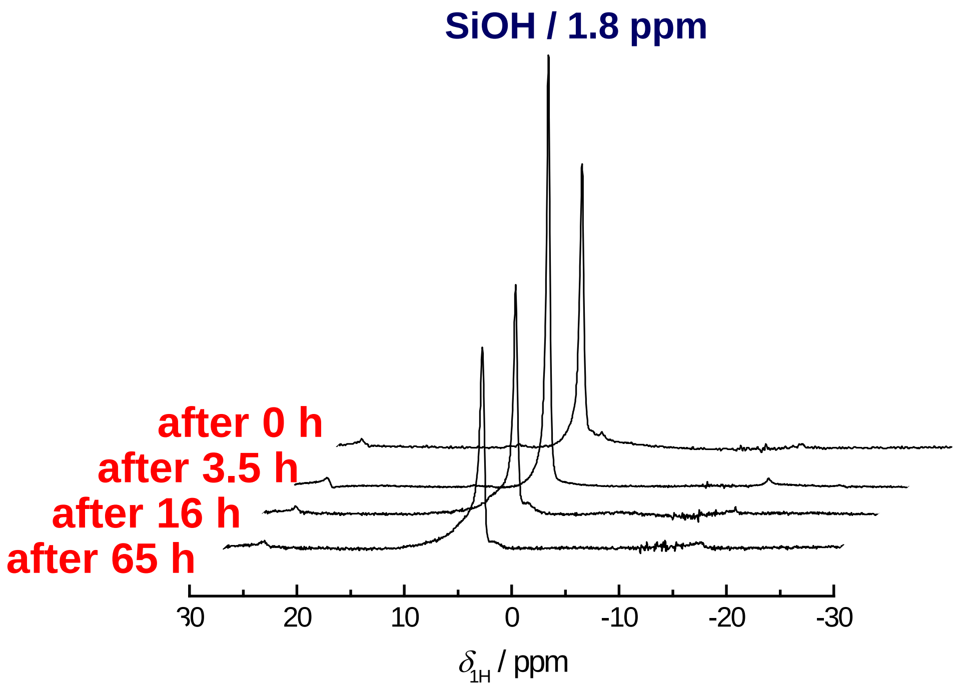


conversion time of 3.5 h



Quantitative ^{1}H MAS NMR of calcined [Ga]Beta

concentrations of SiOH groups:



sample	**c_{SiOH} / (mmol g^{-1})**
dry gel, after 0 h	0.8
after 3.5 h	2.5
after 16 h	1.4
after 65 h	1.6

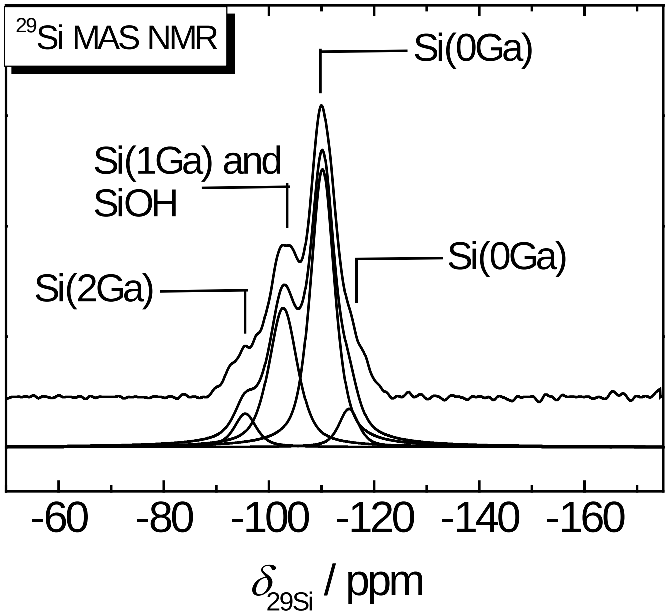
accuracy: ± 10 %

→ **strong increase of SiOH groups due to dissolution of dry-gel particles**

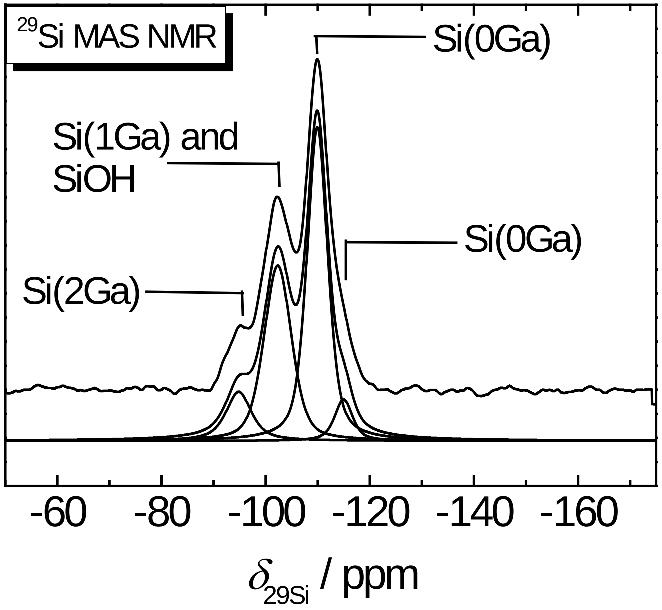
^{29}Si MAS NMR of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.5)

- ^{29}Si MAS NMR spectra recorded after different conversion times

conversion time of 16 h

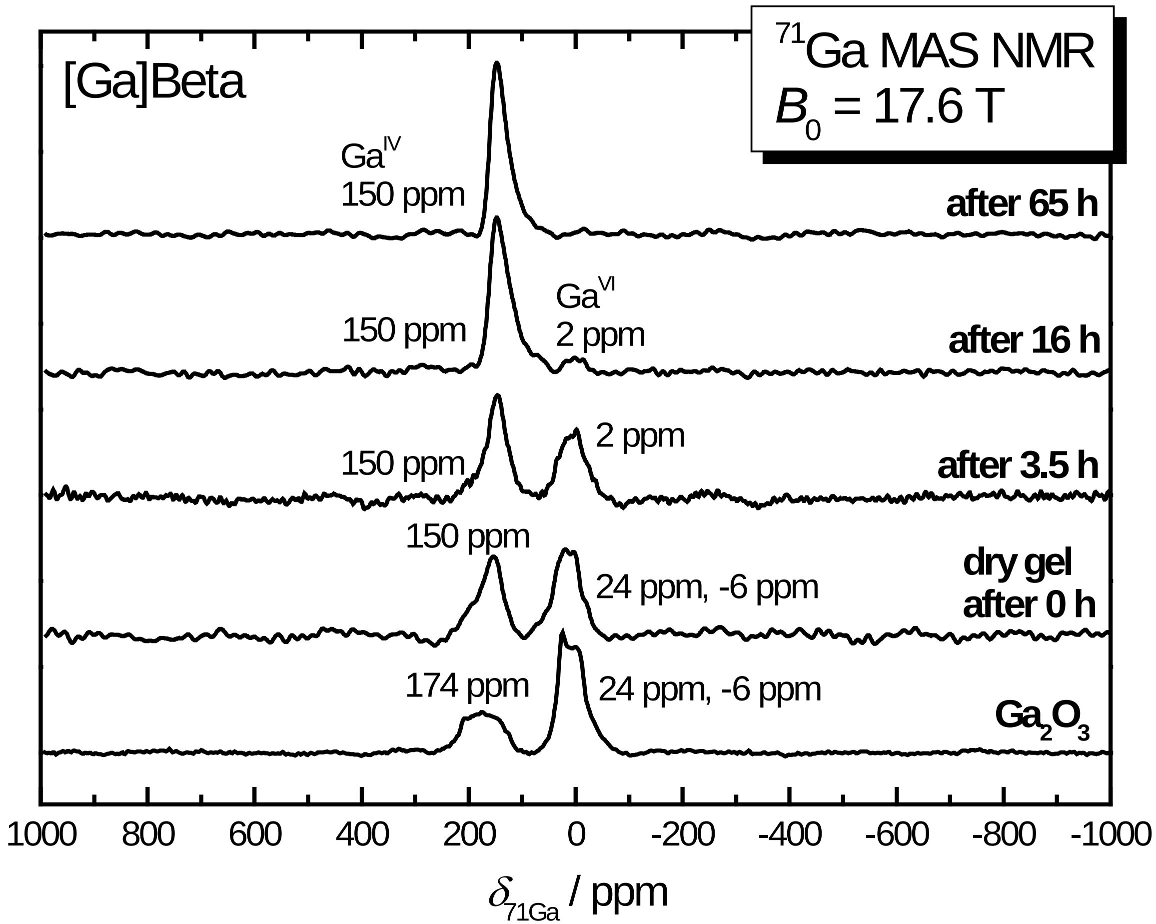


conversion time of 65 h



→ **incorporation of gallium into the zeolite framework**

^{71}Ga MAS NMR of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.5)



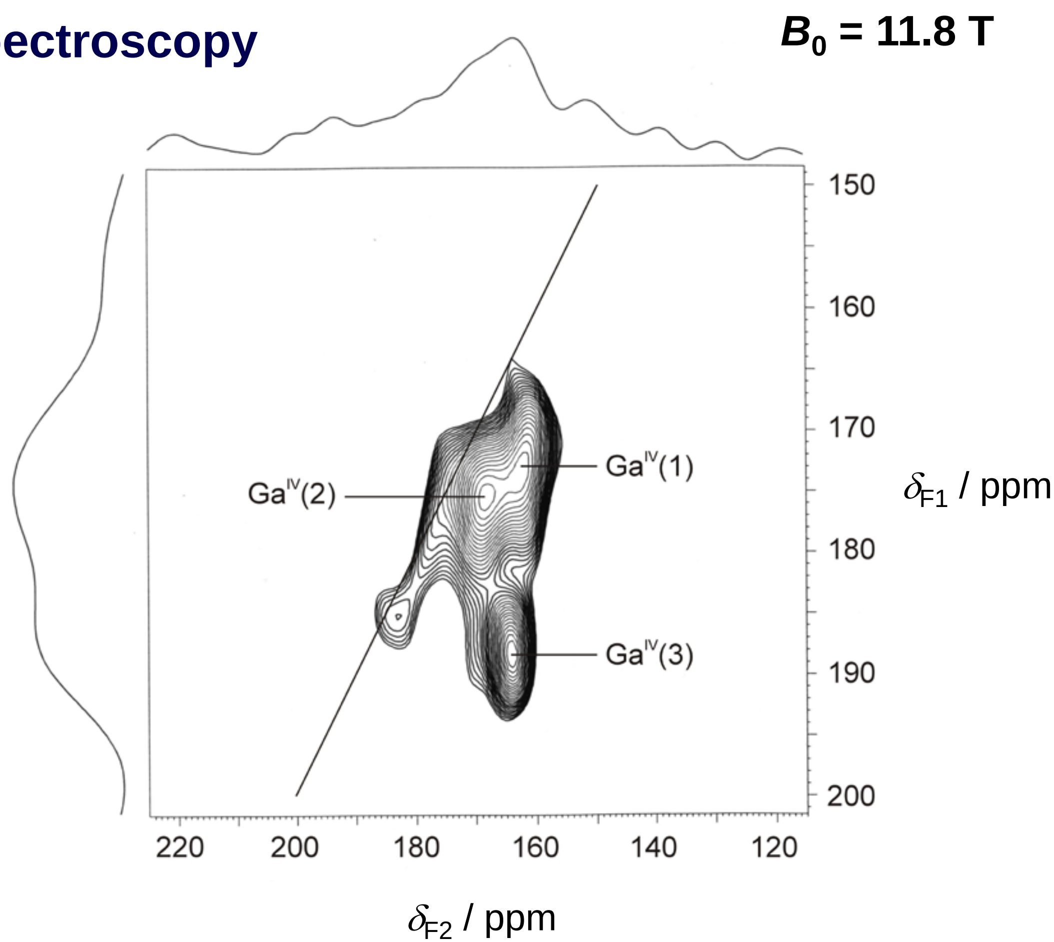
Ga^{IV}	Ga^{VI}
100	0
93	7
58	42
45	55
34	66

Two-dimensional ^{71}Ga MQMAS NMR spectroscopy of [Ga]Beta obtained after 65 h

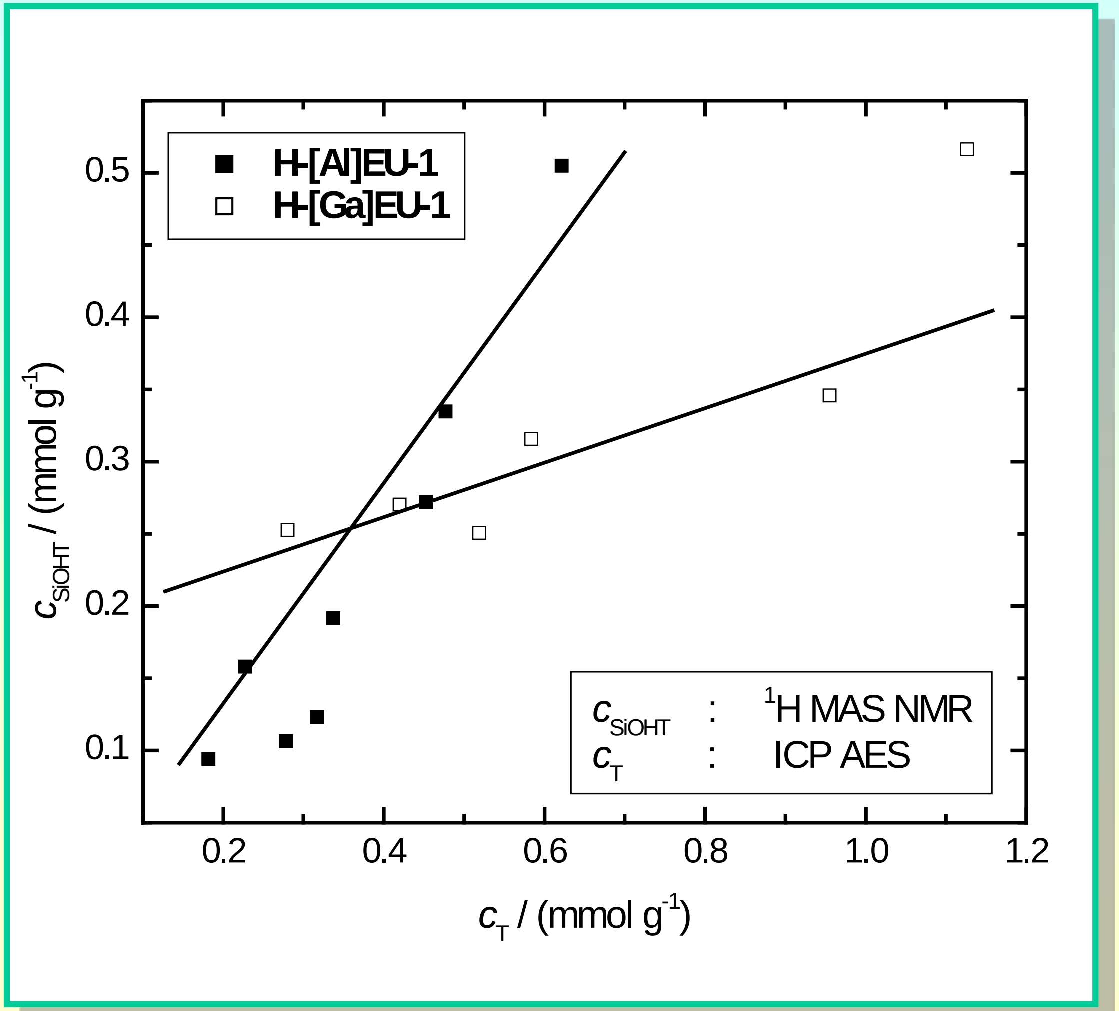
- **different types of Ga^{IV} as evidenced by ^{71}Ga MQMAS NMR spectroscopy**

Ga^{IV}(1, 2):
framework gallium species

Ga^{IV}(3):
extra-framework gallium species at defect sites or in an amorphous phase



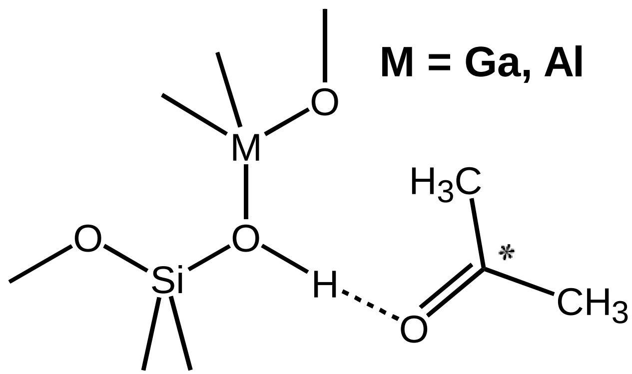
Formation of acid sites in [Al]EU-1 and [Ga]EU-1



- **concentration of SiOHT groups as a function of the concentration of T atoms (T: Al, Ga)**
- **formation of ca. 1 SiOHAl per 1 Al in [Al]EU-1.**
- **formation of ca. 1 SiOHGa per 2 to 3 Ga in [Ga]EU-1.**

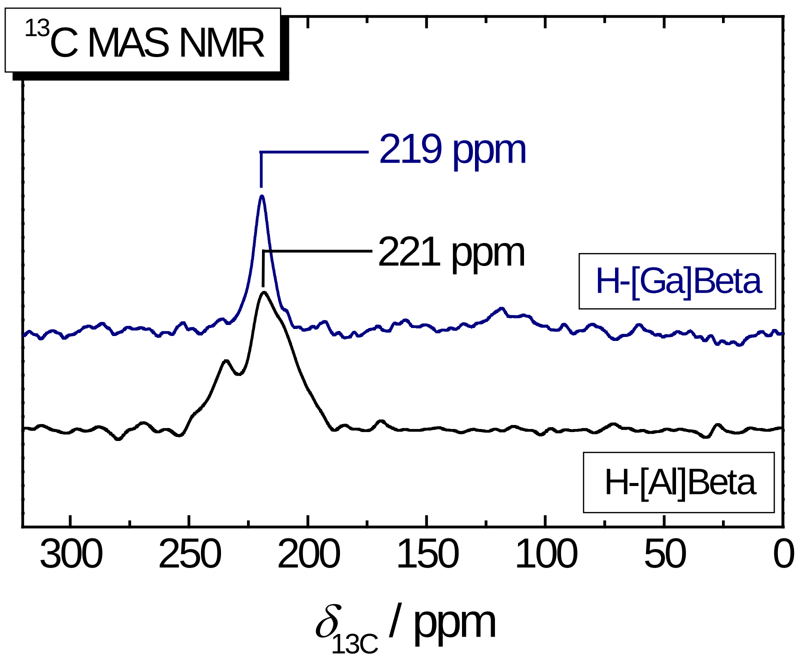
Acid strength of zeolites Beta and EU-1

- adsorption of ^{13}C-2-acetone as probe molecule



Zeolite	δ_{13C} / ppm
H-[Ga]EU-1	214
H-[Al]EU-1	215
H-[Ga]Beta	219
H-[Al]Beta	221
H-ZSM-5	223

- ^{13}C MAS NMR shift as a measure of the acid strength

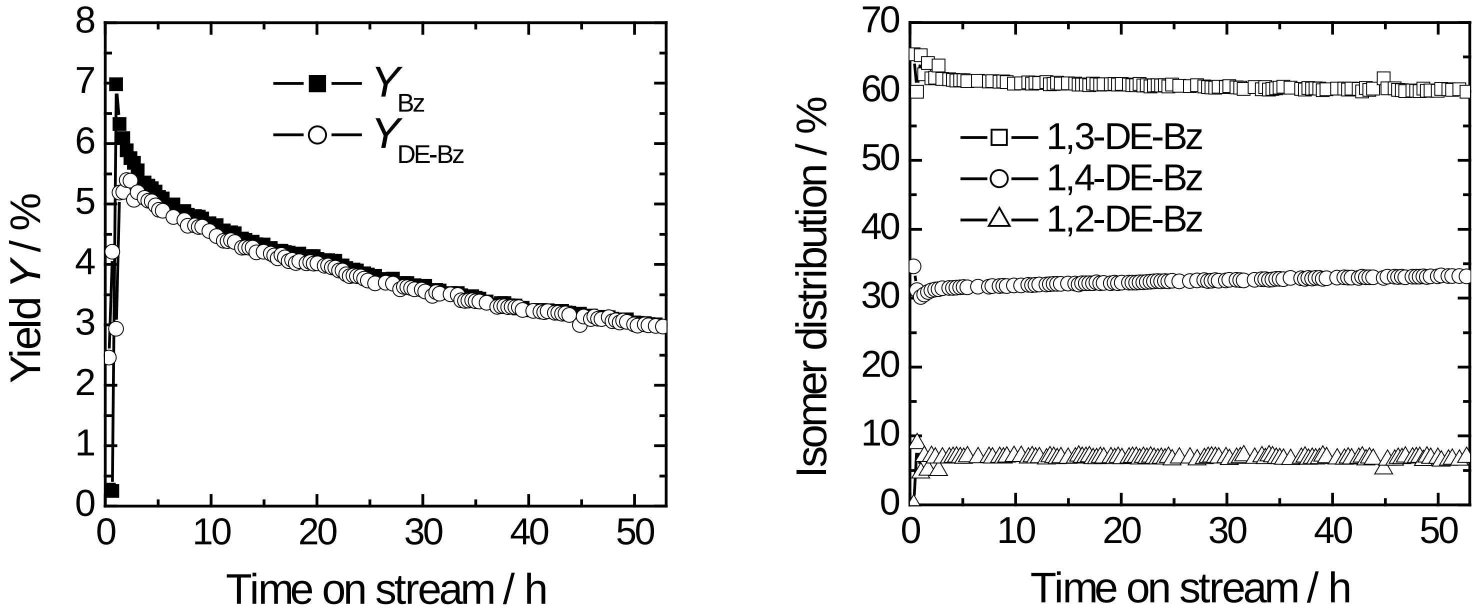


Catalytic Characterization of the Synthesized Materials

Catalysis on zeolite H-[Ga]Beta

- **disproportionation of ethylbenzene:**

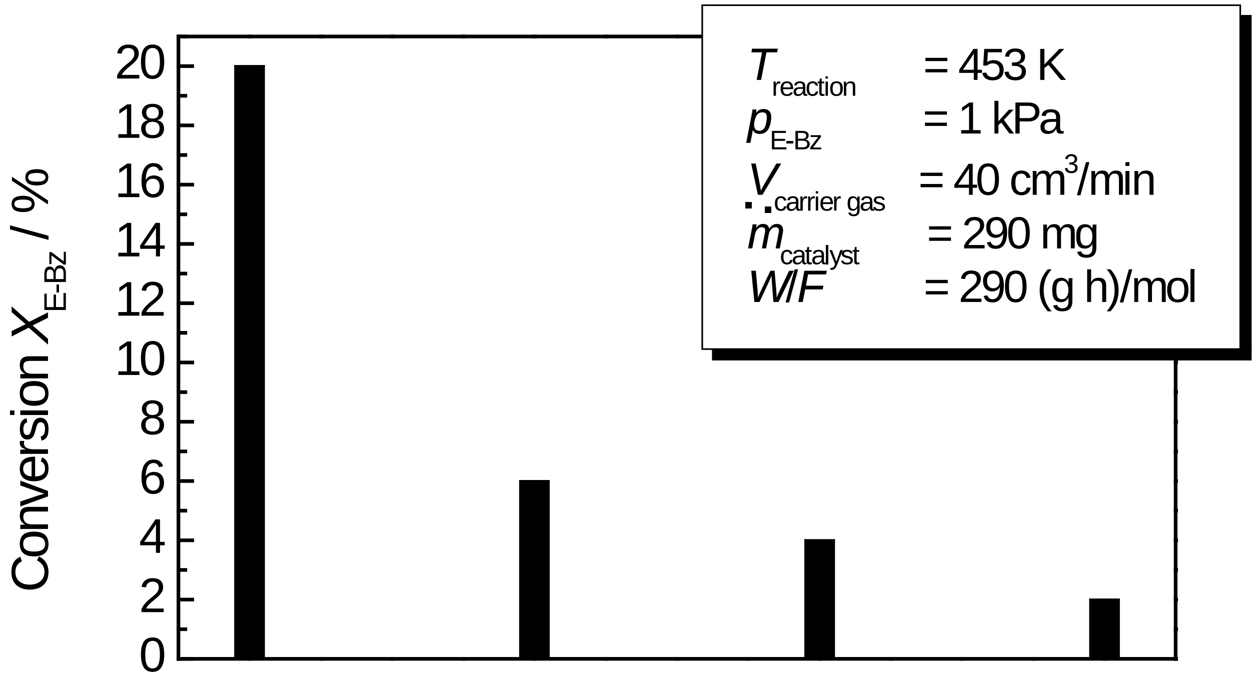
n_{Si}/n_{Ga}	= 8.2	$p_{E\text{-}Bz}$	= 1 kPa	$V_{carrier\ gas}$	= 40 cm^3/min
$T_{reaction}$	= 453 K	W/F	= 290 g h/mol	$m_{catalyst}$	= 290 mg



Catalysis on zeolites H-[Al]Beta and H-[Ga]Beta

- **disproportionation of ethylbenzene:**

comparison of different catalysts



	H-[Al]Beta	H-[Al]Beta	H-[Ga]Beta	H-[Ga]Beta
	n_{Si}/n_{Al} = 11.8	n_{Si}/n_{Al} = 36.6	n_{Si}/n_{Ga} = 12.4	n_{Si}/n_{Ga} = 39.2
c_{SiOHT}:	0.39 mmol/g	0.25 mmol/g	0.30 mmol/g	0.24 mmol/g

Dry-gel Synthesis of
MCM-41/ZSM-5 Hydride Materials

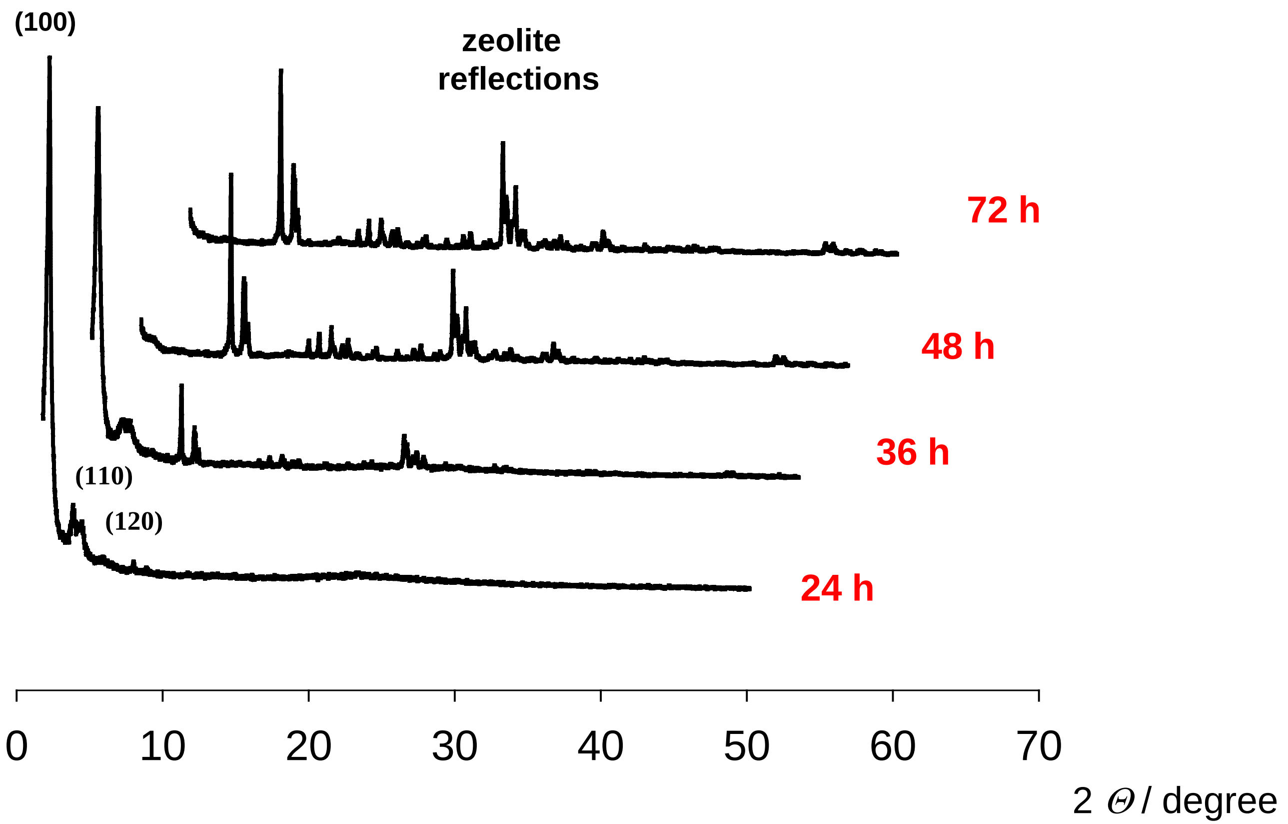
Preparation of MCM-41/ZSM-5 hybrides

Dry-gel synthesis procedure with a zeolite ZSM-5 hydrogel:

- **preparation of a hydrogel for the synthesis of ZSM-5 with tetrapropylammonium hydroxide (TPAOH) as template and ageing of this gel for 18 h at 323 K**
- **the ZSM-5 hydrogel was added to cetyltrimethylammonium bromide (CTAB), stirred for 2 h at room temperature, and dried for 20 h at 353 K**
- **3 g of the dry gel was placed in an autoclave (*V* = 110 ml) together with 4 g deionized water**
- **the dry-gel conversion was performed at 423 K for 24 to 72 h**
- **obtained samples are denoted MZH-*t* (MZH: MCM-41/ZSM-5 Hybride, *t*: duration of dry-gel conversion)**

X-ray patterns of MZH-t materials

X-ray diffractograms recorded as a function of the dry-gel conversion time:

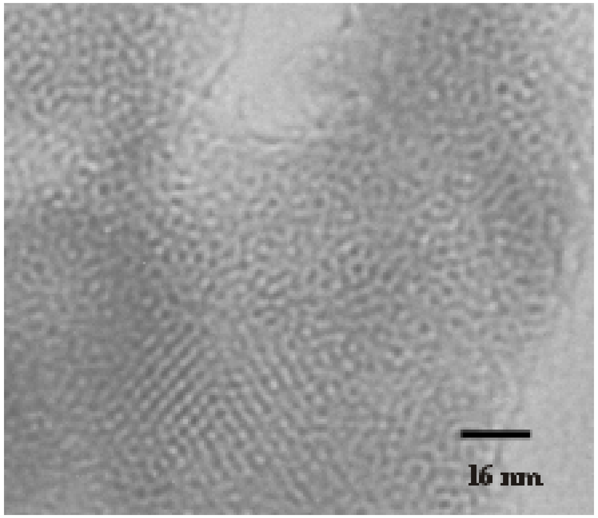


→ **increasing zeolite domains with increasing conversion time**

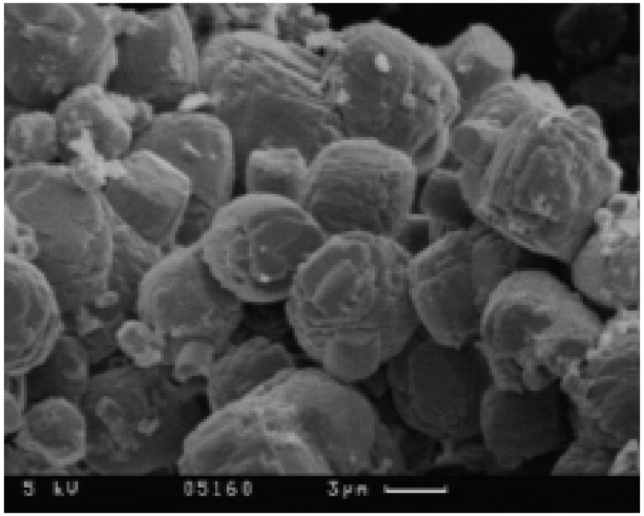
Particle morphology of MZH-t materials

- **TEM and SEM pictures recorded at different conversion times:**

dry-gel conversion time of 36 h



dry-gel conversion time of 72 h



→ **meso-structured material is totally converted to ZSM-5 crystals**

Pore structure of MZH-t materials

- **characterization of the pore system by nitrogen adsorption**

properties of MZH-*t* materials in comparison with a reference ZSM-5:

Sample	n_{Si}/n_{Al}	**BET surface area / $m^2 \cdot g^{-1}$**	$V_{mesopore}$ **/ $cm^3 \cdot g^{-1}$**	$V_{micropore}$ **/ $cm^3 \cdot g^{-1}$**
MZH-24h	59	1248	0.82	0.01
MZH-36h	67	1126	0.76	0.06
H-ZSM-5	22	300	0.06	0.15

→ **significant aluminum incorporation and micropore volume**

^{29}Si MAS NMR of MZH-t materials

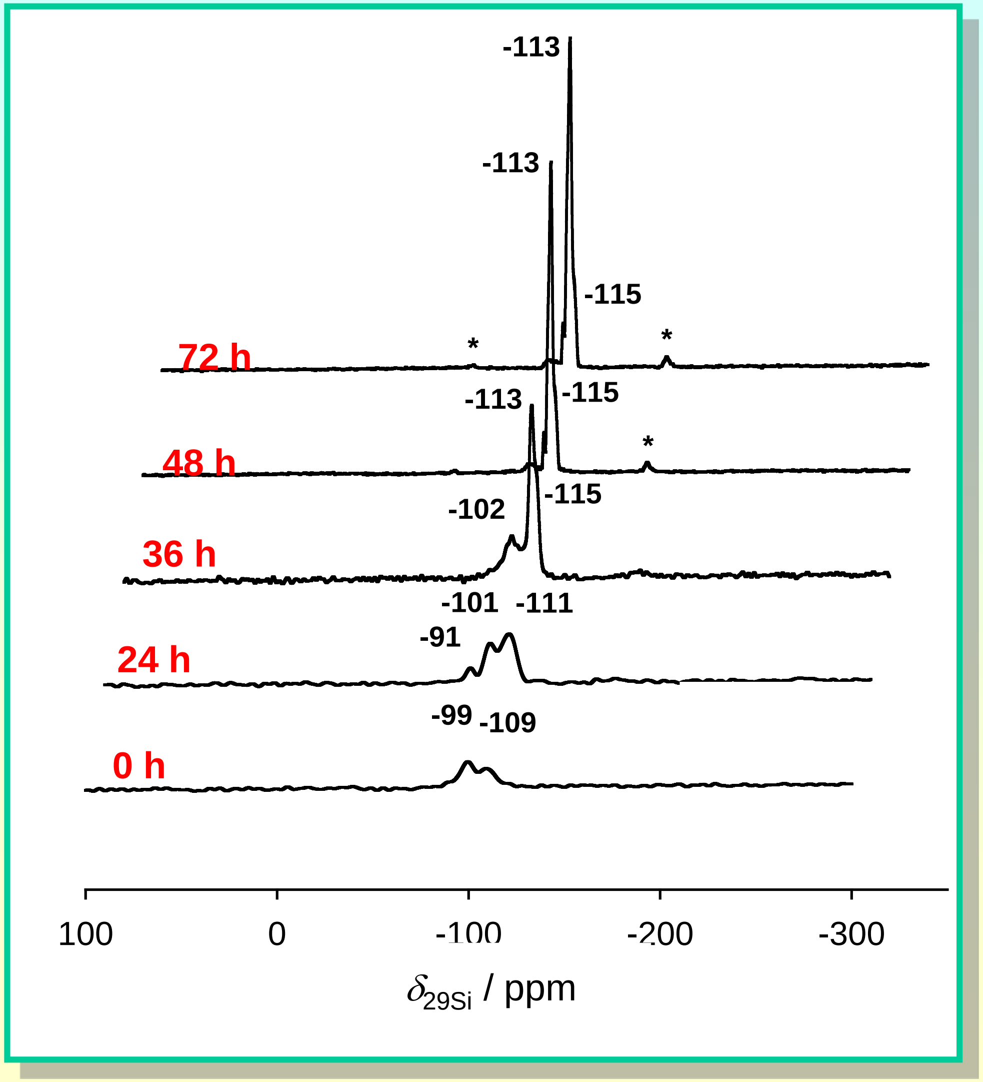
- ^{29}Si MAS NMR spectra recorded after different conversion times

- signals of MCM-41 domains:

  -91 ppm: Q^2 silicon
  -99 .. -101 ppm: Q^3 silicon
  -111 ppm: Q^4 silicon

- signals of ZSM-5 domains:

  -101 ppm: Q^3 silicon
  -113, -115 ppm: Q^4 silicon



^1H MAS NMR of MZH-t materials

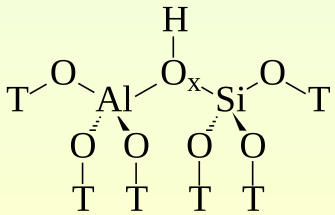
- types of hydroxyl groups:

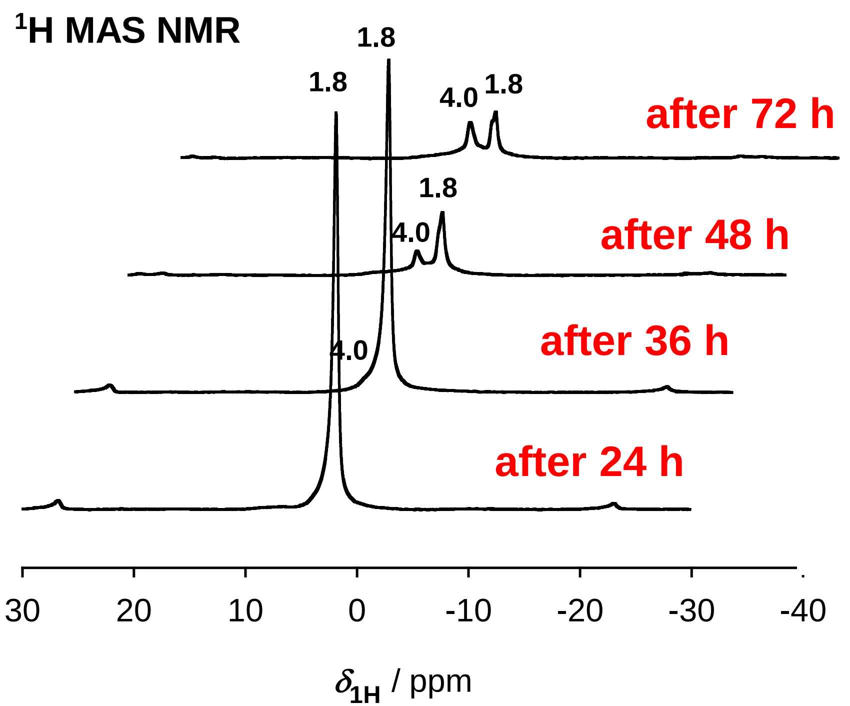
  1.8 ppm SiOH

  4.0 ppm SiOHAl

- behavior of SiOHAl groups:

  acidic OH groups of zeolite domains

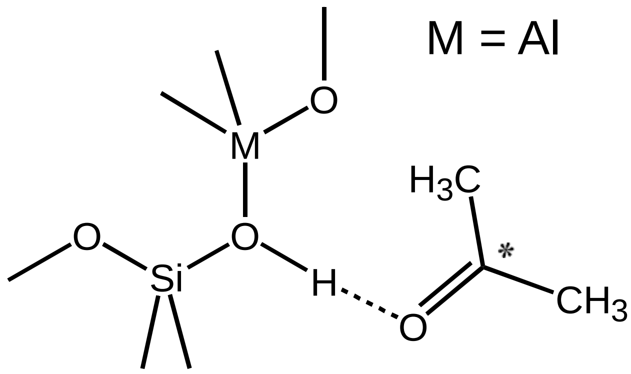




→ strong increase of SiOHAl groups with increasing dry-gel conversion time

Acid strength of the MZH-36h material

- adsorption of ^{13}C-2-acetone as probe molecule



Zeolite	δ_{13C} / ppm
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H-[Al]Beta	221
H-ZSM-5	223
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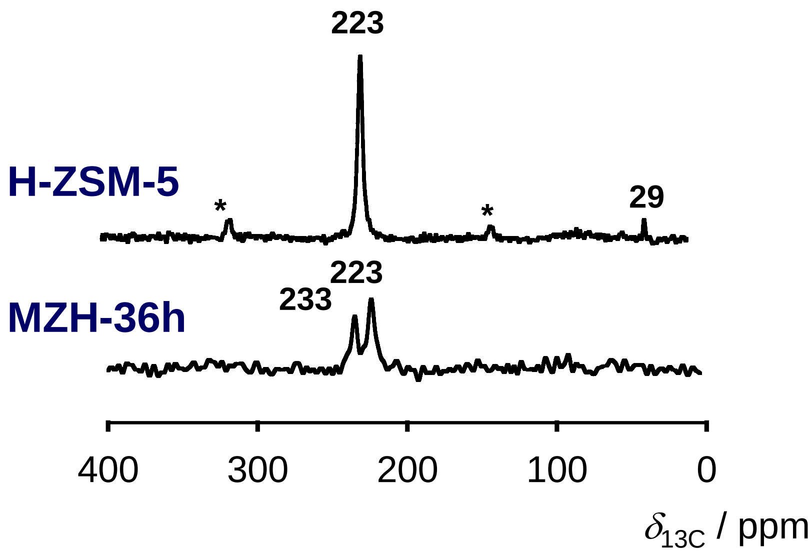
- ^{13}C MAS NMR shift as a measure of the acid strength



- ^{13}C MAS NMR signal at 233 ppm: adsorption of acetone at Lewis-acid sites

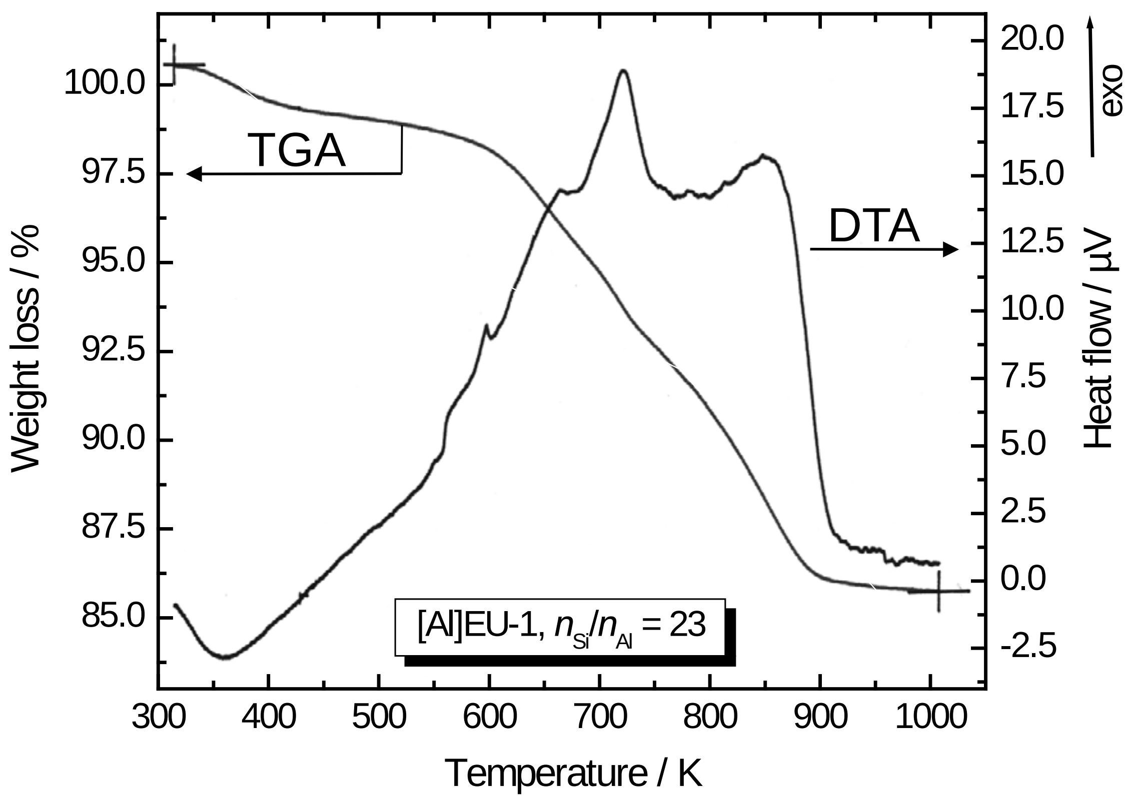
Conclusions: Potential and limitations of DGC

- **high effort of preparing the dry gel**
- **dry gel is chemically unstable**
- **amount of water in the autoclave is a sensitive parameter**
- **decrease of expensive structure-directing agents in the dry gel**
- **expansion of the range of chemical compositions of zeolites**
- **preparation mesoporous/microporous hybride materials**

References

- A. Arnold, S. Steuernagel, M. Hunger, J. Weitkamp, *Insight into the dry-gel synthesis of gallium-rich zeolite [Ga]Beta*, Microporous Mesoporous Mater. 62 (2003) 97-106.
- A. Arnold, M. Hunger, J. Weitkamp, *Dry-gel synthesis of zeolites [Al]EU-1 and [Ga]EU-1*, Microporous Mesoporous Mater. 67 (2004) 205-213.
- M. Xu, W. Wang, J. Weitkamp, M. Hunger, *Dry-gel synthesis of mesoporous MCM-41 materials with modified pore structure*, Z. Phys. Chem. 219 (2005) 877-890.

TGA / DTA of zeolite [Al]EU-1

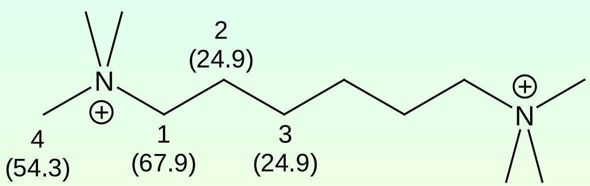


- ***T*** **< 573 K: desorption of water**
- ***T*** **= 673-773 K: decomposition of template molecules**
- ***T*** **= 823-950 K: decomposition of template molecules, adsorbed on acid sites**
- **weight loss of the calcined samples of ca. 15 %**
- **similar curves obtained for [Ga]EU-1 zeolites**

assignment of the DTA peaks:
R. Millini, L.C. Carluccio, A. Carati, W.O. Parker, Microporous Mesoporous Mater. 46 (2001) 191.

^{13}C MAS NMR of the template molecules

- **hexamethonium bromide (HMBr)**



- **formation of:**
  CH_3N^+-$(CH_2)_4$-CH=CH_2
  via Hofmann elimination