Mechanisms of the Methanol-to-hydrocarbon (MTH) Conversion on Acidic Zeolite Catalysts

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History of methanol-to-hydrocarbon (MTH) conversion on zeolites

MTG (methanol-to-gasoline):

- 1982, Wesseling/Germany, demonstration plant, 6 870 t gasoline, H-ZSM-5, total process time 8 600 h, later modified to MTO process
- 1986, Maui field/New Zealand, commercial process, 600 000 t gasoline per year, H-ZSM-5, stopped after *ca.* 5 years

MTO (methanol-to-olefin):

- 1996, Norsk Hydro/Norway, demonstration unit, 0.5 t ethene and propene per year, H-SAPO-34
- 2005, Dalian/VR China, test unit, 10 000 t olefins per year
- 2005, Shaanxi/VR China, start of the construction of a commercial plant, 800 000 t olefins per year

Zeolite catalysts applied for the methanol conversion

H-ZSM-5: **Structure type MFI**

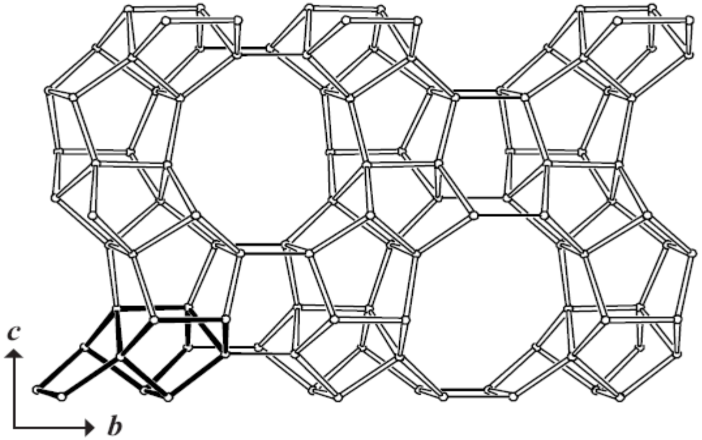
$H^+_n[Al_nSi_{96-n}O_{192}]$

crossing intersections at

interconnecting 10-ring channels

[100] 0.51 nm x 0.55 nm

[010] 0.53 nm x 0.56 nm



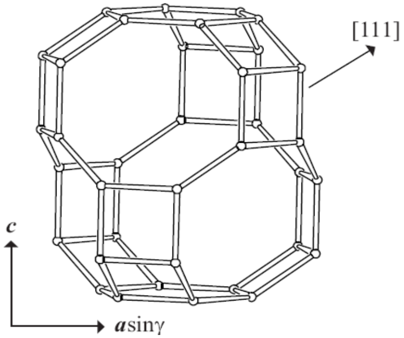
H-SAPO-34: **Structure type CHA**

$H^+_n[Al_{18}P_{18-n}Si_nO_{72}]$

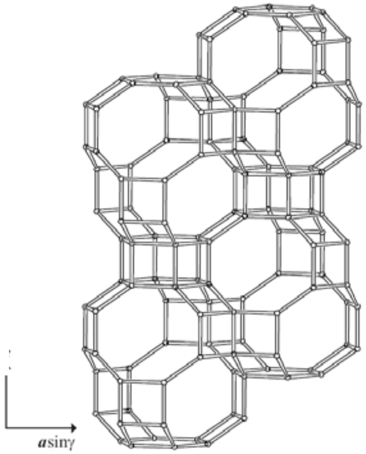
chabazite cages accessible by

8-ring windows perpendicular to

[001] 0.38 nm x 0.38 nm



chabazite cage



Periods in the life of an MTO catalysts

I: Induction period of the methanol conversion on zeolites

formation of first C-C bonds by decomposition of surface methoxy groups or alkylation of organic impurities

II: Steady-state of the methanol conversion on zeolites

methylation and dealkylation of organic compounds forming a catalytically active hydrocarbon pool

III: Catalyst deactivation during methanol conversion on zeolites

formation of inactive coke deposits affecting the methanol conversion and the selectivity to ethylene and propylene

I. The induction period of the MTO reaction on acidic zeolite catalysts

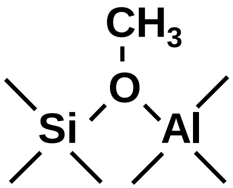
I: Induction period

formation of catalytically active organic deposits in zeolite pores (hydrocarbon-pool compounds):

- **impurities in the methanol feed may act as organic presursors**

- **formation of surface methoxy groups**

$$CH_3OH + ZOH \xrightarrow{-H_2O} ZOCH_3$$



- **decomposition of surface methoxy groups leads to first C-C bond formation and methylation of hydrocarbons**

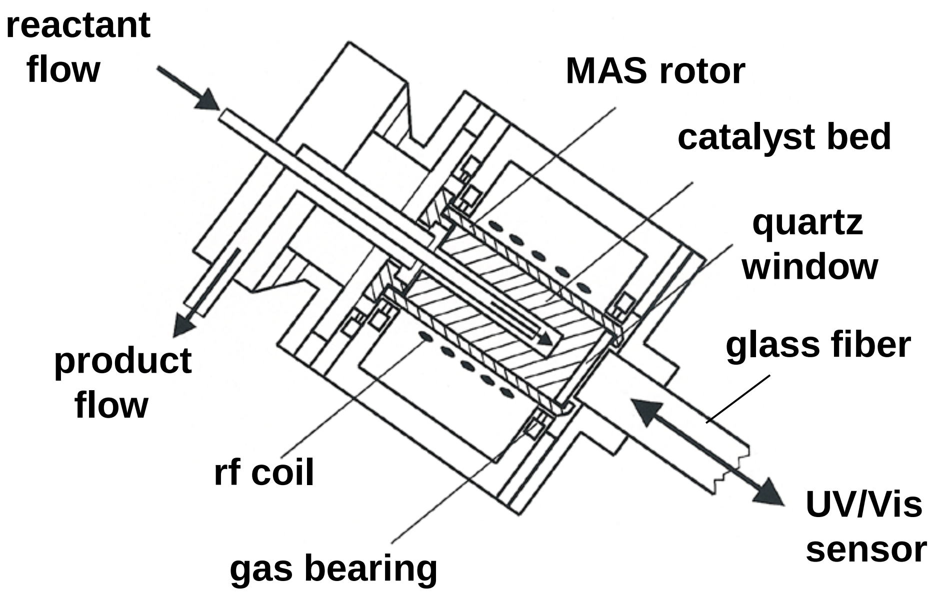
$$2\ ZOCH_3 \longrightarrow ZOCH_3 + ZOH + :CH_2 \longrightarrow ZOCH_2CH_3 + ZOH$$

- **alkylation of organic precursors leads to the formation of hydrocarbon-pool compounds (alkylated olefins and aromatics)**

I: Induction period

MAS NMR-UV/Vis studies of the decomposition of methoxy groups on H-Y and H-SAPO-34 formed by methanol

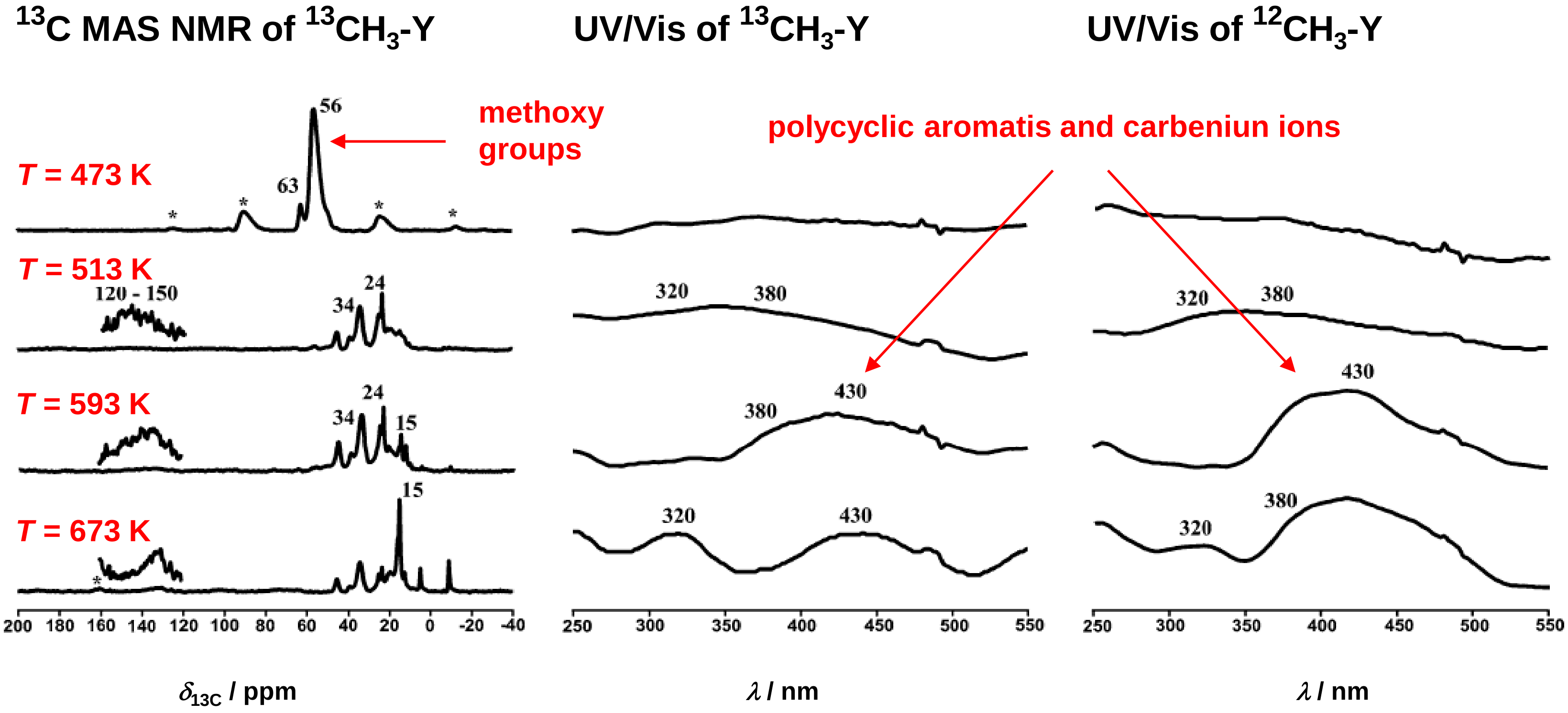
- **experimental technique:**
  M. Hunger, W. Wang, Chem. Commun. (2004) 584



- **preparation of methoxy groups by adsorption of ^{13}C-enriched methanol and highly purified (impurities < 30 ppm) $^{12}CH_3OH$ on H-Y and H-SAPO-34 and thermal treatment**

I: Induction period

in situ MAS NMR-UV/Vis study of the decomposition of methoxy groups



^{13}C MAS NMR of $^{13}CH_3$-Y

UV/Vis of $^{13}CH_3$-Y

UV/Vis of $^{12}CH_3$-Y

methoxy groups

polycyclic aromatis and carbeniun ions

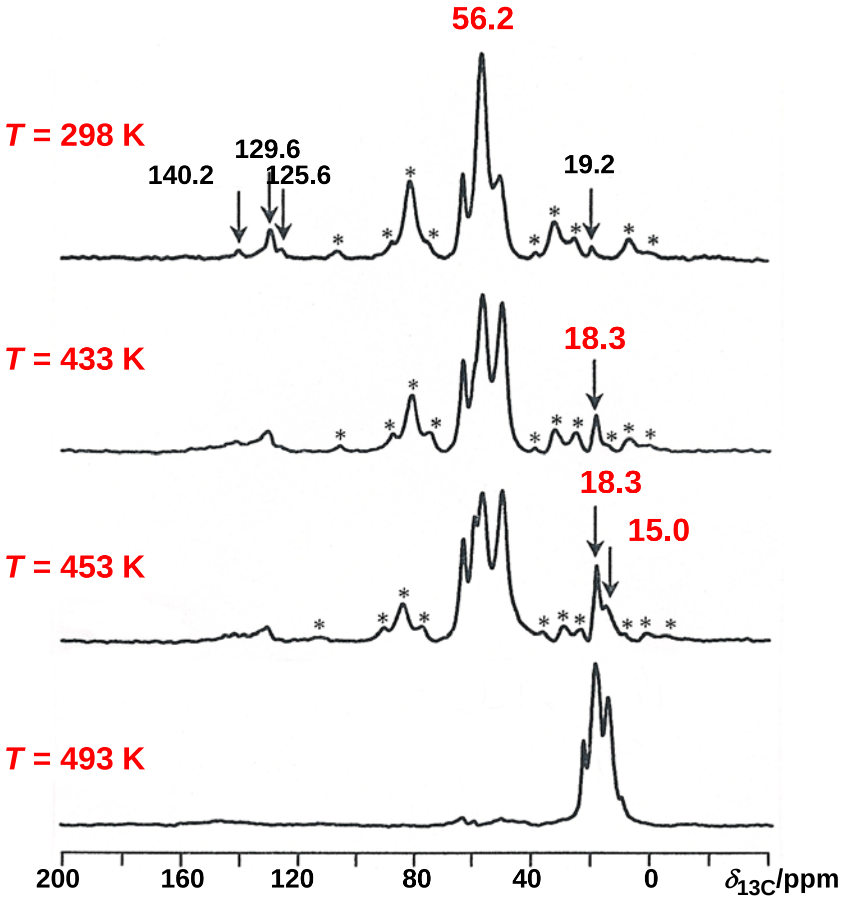
decomposition of methoxy groups formed by ^{13}C- enriched and highly purified (impurities < 30 ppm) methanol start at the same temperature and give similar UV/Vis-sensitive hydrocarbons

→ first hydrocarbons are also formed without contribution of impurities

I: Induction period

reaction of methoxy groups with toluene on zeolite H-Y

^{13}C stopped-flow MAS NMR



methoxy toluene

$\mathrm{Si(O^{13}CH_3)Al} + \mathrm{CH_3C_6H_5}$

56.2 ppm 19.2 ppm

$\rightarrow \mathrm{Si(OH)Al} + \mathrm{CH_3C_6H_4{}^{13}CH_3}$

18.3 ppm

xylene

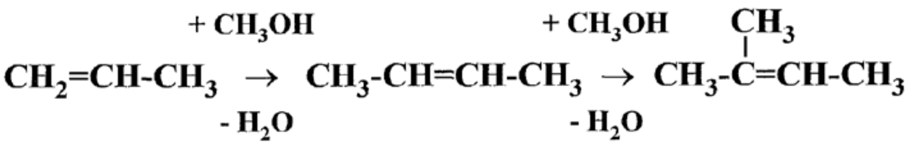
methoxy groups contribute to the alkylation of aromatic compounds

II. Steady-state of the methanol conversion on acidic zeolites

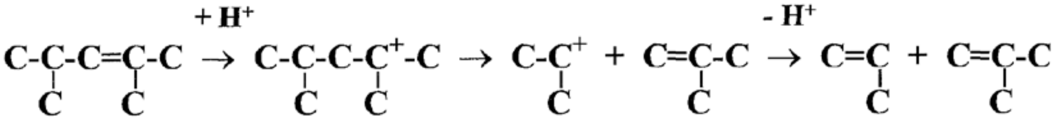
II: Steady-state conditions

most favored reaction mechanism is the hydrocarbon-pool mechanism:

- *via* olefinic compounds (H. Schulz, M. Wei, Microporous Mesoporous Mater. 29 (1999) 205)

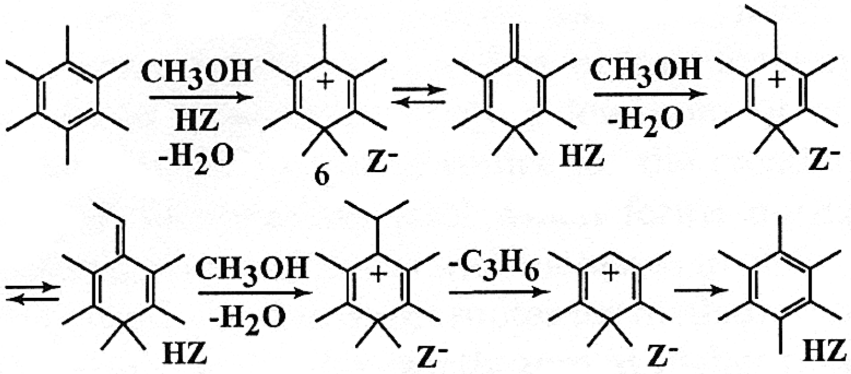


$$CH_2{=}CH{-}CH_3 \xrightarrow[-\,H_2O]{+\,CH_3OH} CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[-\,H_2O]{+\,CH_3OH} CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_3$$



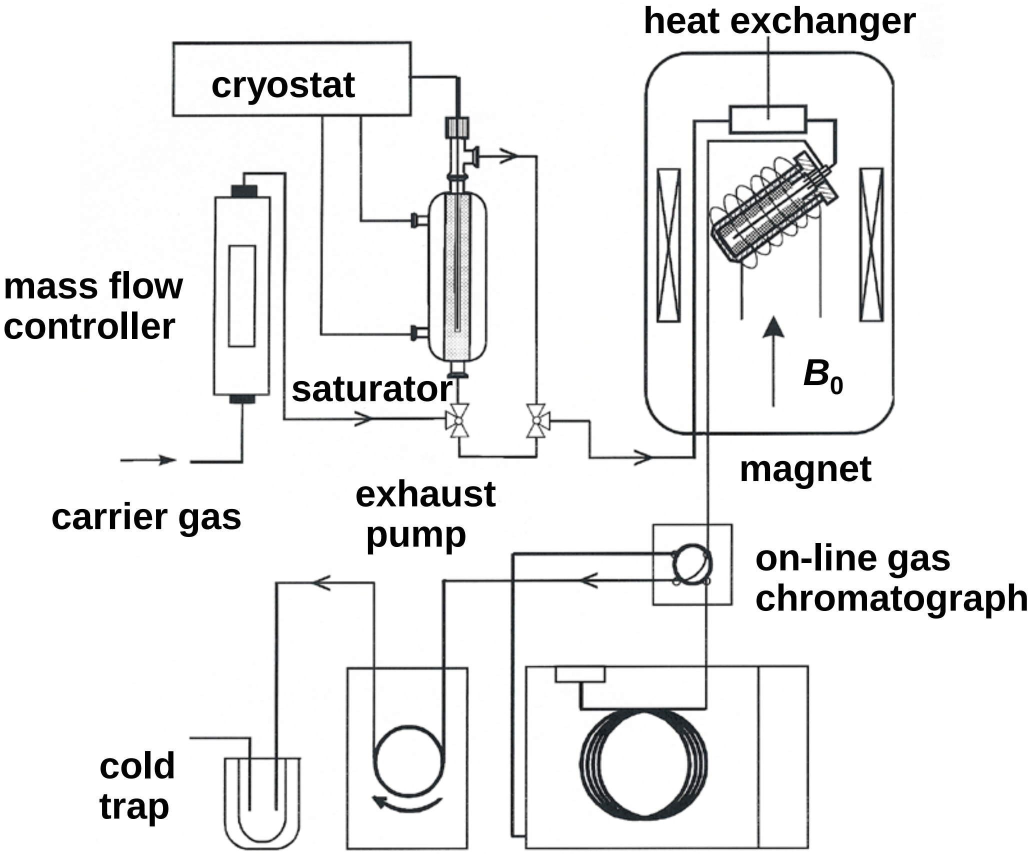
$$C{-}\underset{C}{\underset{|}{C}}{-}C{=}\underset{C}{\underset{|}{C}}{-}C \xrightarrow{+\,H^+} C{-}\underset{C}{\underset{|}{C}}{-}C{-}\underset{C}{\underset{|}{C^+}}{-}C \rightarrow C{-}\underset{C}{\underset{|}{C^+}} + C{=}\underset{C}{\underset{|}{C}}{-}C \xrightarrow{-\,H^+} C{=}\underset{C}{\underset{|}{C}} + C{=}\underset{C}{\underset{|}{C}}{-}C$$

- *via* polyalkylaromatics (J.F. Haw et al., Acc. Chem. Res. 36 (2003) 317)



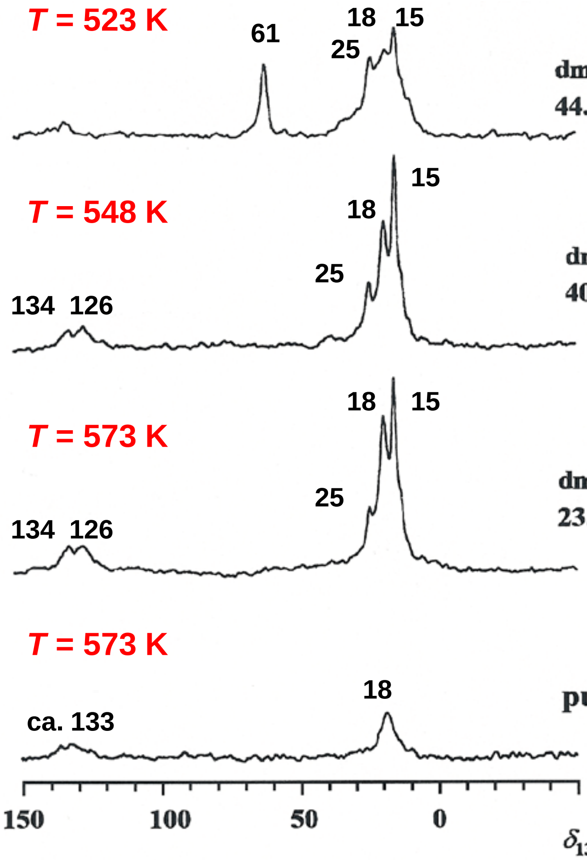
II: Steady-state conditions

MAS NMR technique for the study of hydrocarbon-pool compounds under *in situ* conditions



II: Steady-state conditions

in situ ^{13}C MAS NMR study of the hydrocarbon pool formed on H-ZSM-5



yields / %

dme	C_2=	C_3=	C_3	C_4=	C_4
44.3	2.7	1.4	0	0	0

dme	C_2=	C_3=	C_3	C_4=	C_4
40.2	3.6	3.6	0.6	0	0

dme	C_2=	C_3=	C_3	C_4=	C_4
23.8	12.5	13.0	1.6	9.9	1.8

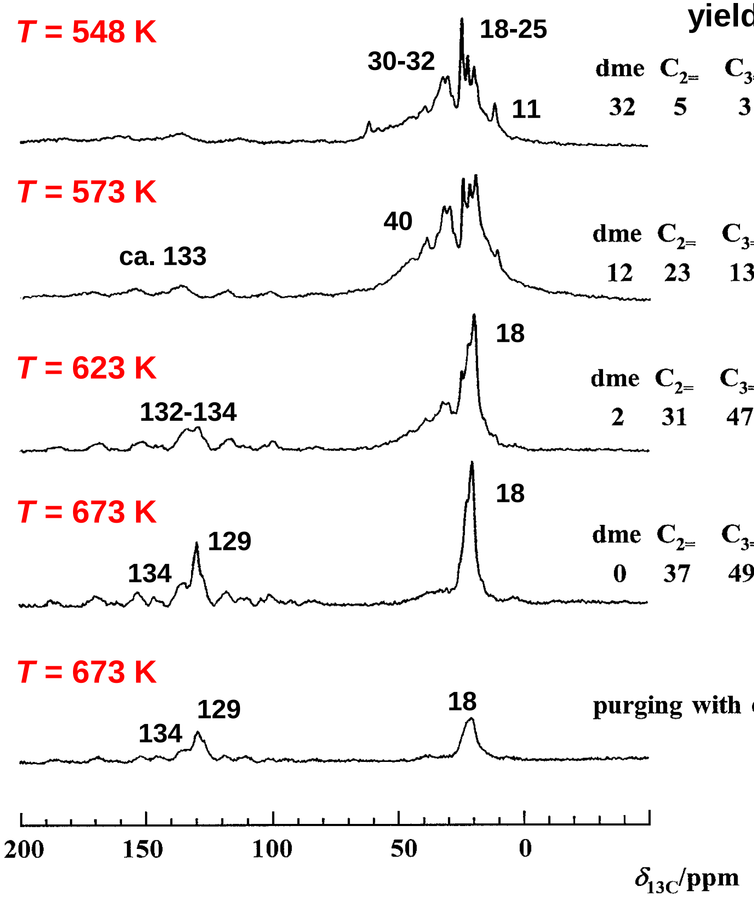
purging with dry nitrogen

mixture of olefinic and aromatic compounds, such as:
- 3-hexene (14.4, 25.9, 131.2 ppm)
- 2,4-hexadiene (17.2, 126.2, 132.5 ppm)
- ….
- hexamethylbenzene (17.6, 132.1 ppm)

polymethylaromatics remain after purging, such as:
- toluene (20.3, 128.5, 129.0 ppm)
- ….
- hexamethylbenzene (17.6, 132.1 ppm)

II: Steady-state conditions

in situ ^{13}C MAS NMR study of the hydrocarbon pool formed on SAPO-34



yields / %

	dme	$C_{2=}$	$C_{3=}$	$C_{4=}$	C_4
T = 548 K	32	5	3	2	2
T = 573 K	12	23	13	7	6
T = 623 K	2	31	47	9	10
T = 673 K	0	37	49	8	10
T = 673 K	purging with dry nitrogen				

$T \leq 573$ K:

mixture of olefinic and aromatic compounds, such as:

- 2-methyl-2-butene (9.3-22.5, 118.8, 131.8 ppm)
- 2,4-hexadiene (19.5, 132.5 ppm)
- ....
- tetramethylbenzene (18.9, 131.1, 134.0 ppm)

$T > 573$ K:

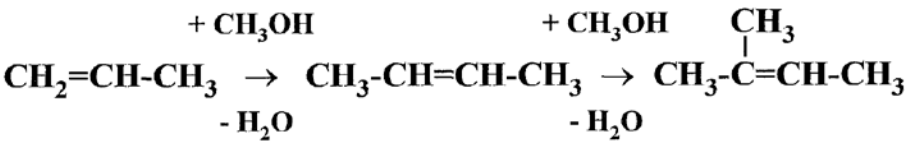
domination of polymethyl-aromatics, such as:

- toluene (20.3, 128.5, 129.0 ppm)
- ....
- trimethylbenzene (21.2, 127.4, 137.6 ppm)
- hexamethylbenzene (17.6, 132.1 ppm)

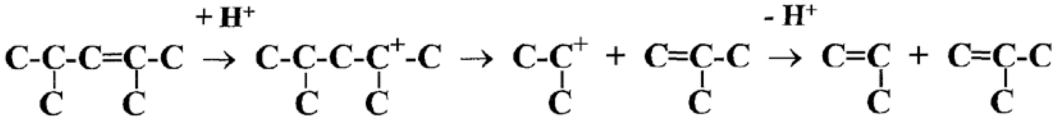
II: Steady-state conditions

most favored reaction mechanism is the hydrocarbon-pool mechanism:

- *via* olefinic compounds (H. Schulz, M. Wei, Microporous Mesoporous Mater. 29 (1999) 205)

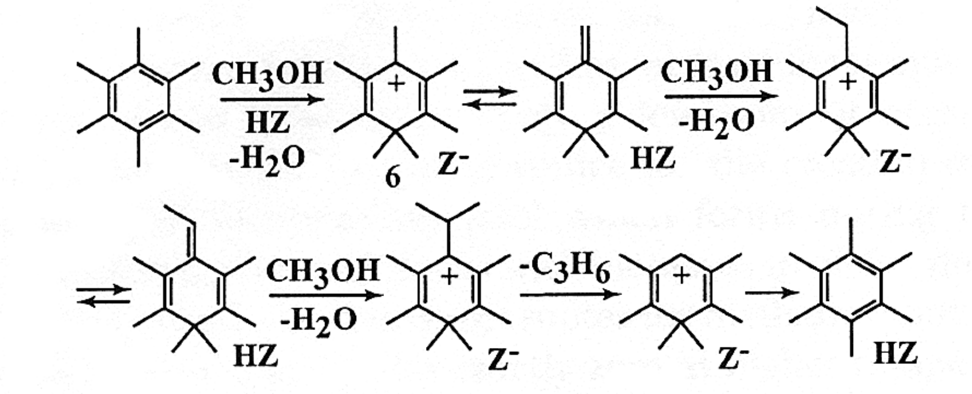


$$CH_2{=}CH{-}CH_3 \xrightarrow[-H_2O]{+CH_3OH} CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[-H_2O]{+CH_3OH} CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_3$$



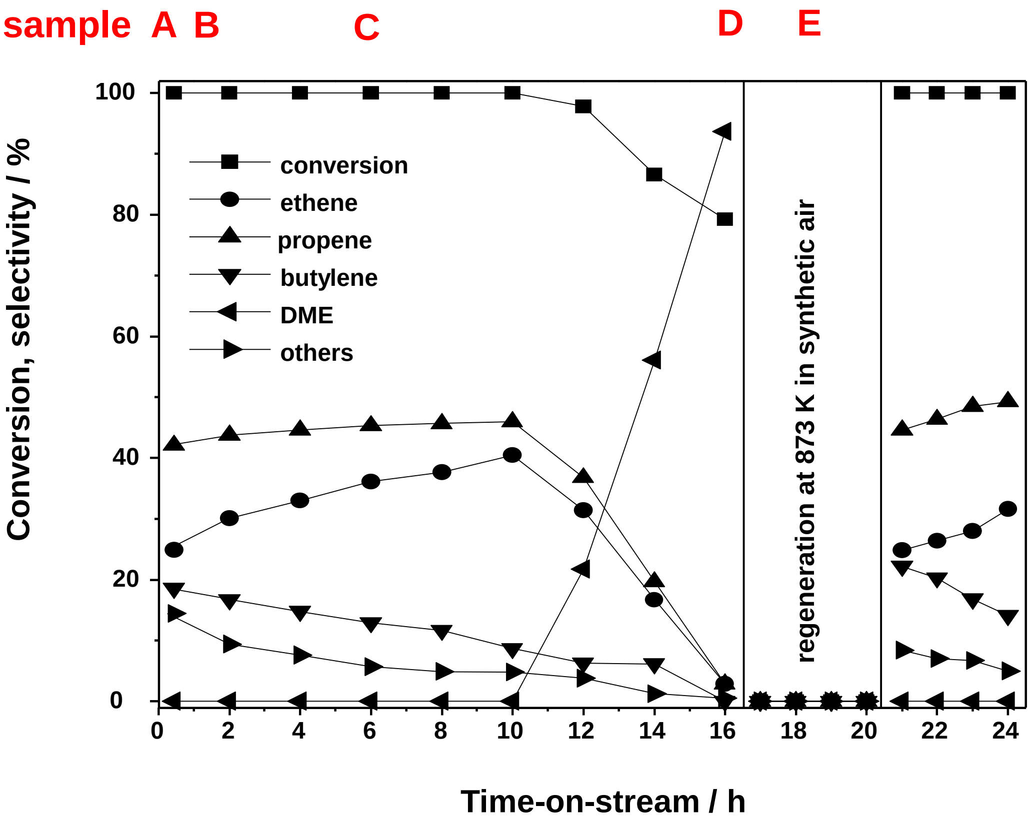
$$C{-}\underset{\underset{C}{|}}{C}{-}C{=}\underset{\underset{C}{|}}{C}{-}C \xrightarrow{+H^+} C{-}\underset{\underset{C}{|}}{C}{-}C{-}\underset{\underset{C}{|}}{C^+}{-}C \rightarrow C{-}\underset{\underset{C}{|}}{C^+} + C{=}\underset{\underset{C}{|}}{C}{-}C \xrightarrow{-H^+} C{=}\underset{\underset{C}{|}}{C} + C{=}\underset{\underset{C}{|}}{C}{-}C$$

- *via* polyalkylaromatics (J.F. Haw et al., Acc. Chem. Res. 36 (2003) 317)



II: Steady-state conditions

preparation of SAPO-34 catalysts (B, C, and D) loaded with hydrocarbon-pool compounds by MTO conversion in a fixed-bed reactor at *T* = 673 K (*WHSV* = 0.5 gh/mol)



A: calcined SAPO-34

B: 1 h used SAPO-34

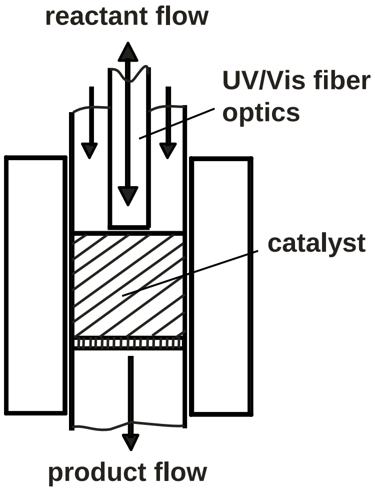
C: 6 h used SAPO-34

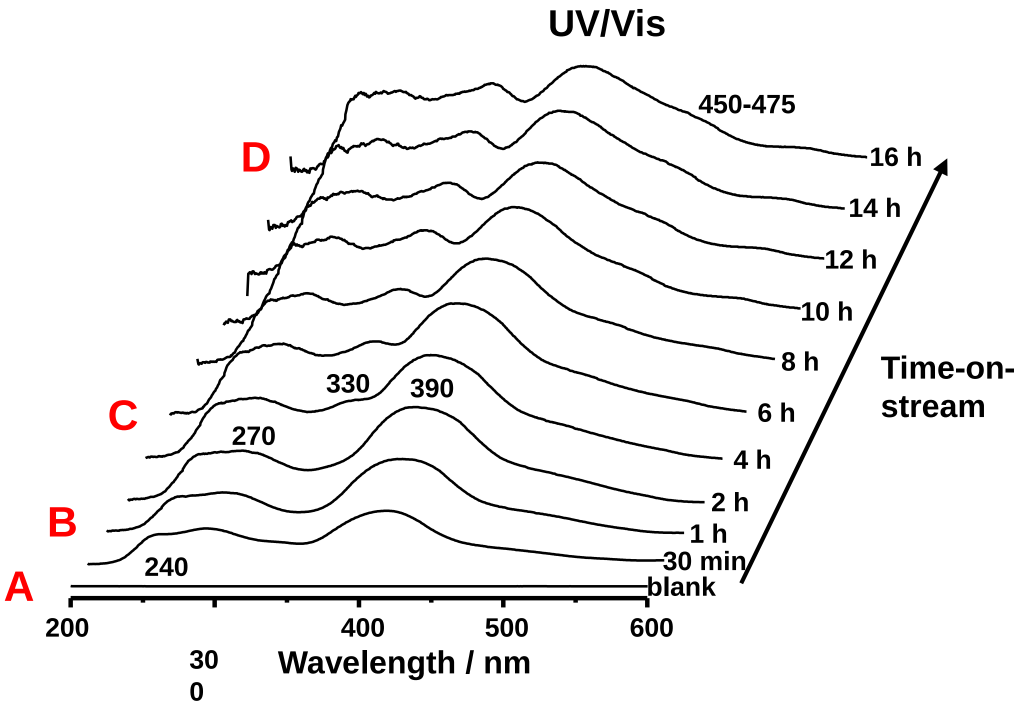
D: 16 h used SAPO-34

E: regenerated SAPO-34 (at 873 K in air)

II: Steady-state conditions

UV/Vis studies of SAPO-34 catalysts during MTO conversion in a fixed-bed reactor at 673 K (*W*/*F* = 25 gh/mol)





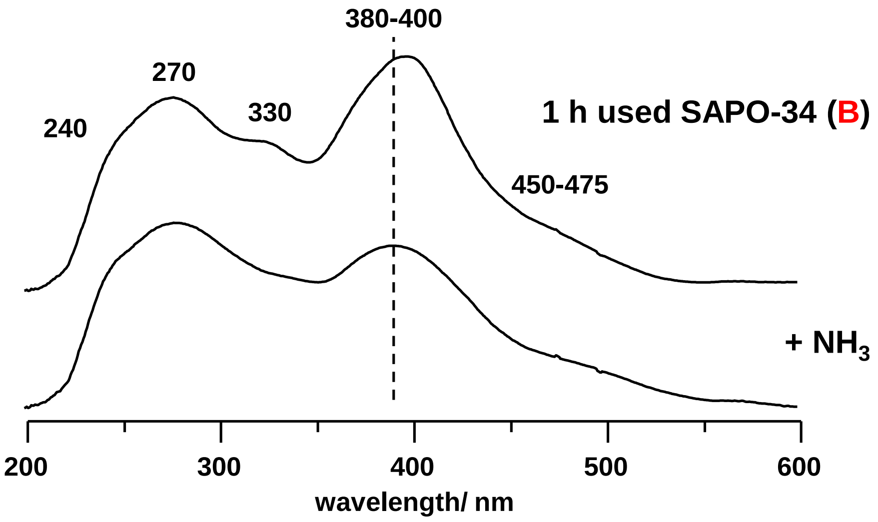
assignment of UV/Vis bands:

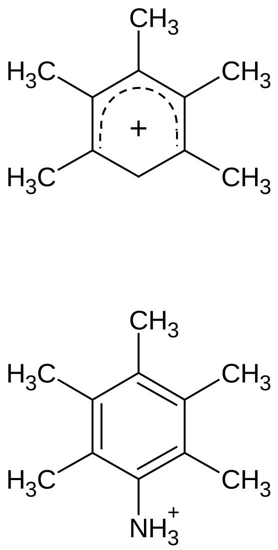
240 nm:	dienes	390 nm:	benzene-type carbenium ions
270 nm:	aromatics and polyalkylaromatics	450 nm:	trienylic carbenium ions
330 nm:	cyclohexadienyl carbenium ion	400-475 nm:	polycyclic aromatics

II: Steady-state conditions

UV/Vis spectra of SAPO-34 used as MTO catalyst for 1 h (sample B) and recorded before and after ammonia loading

UV/Vis





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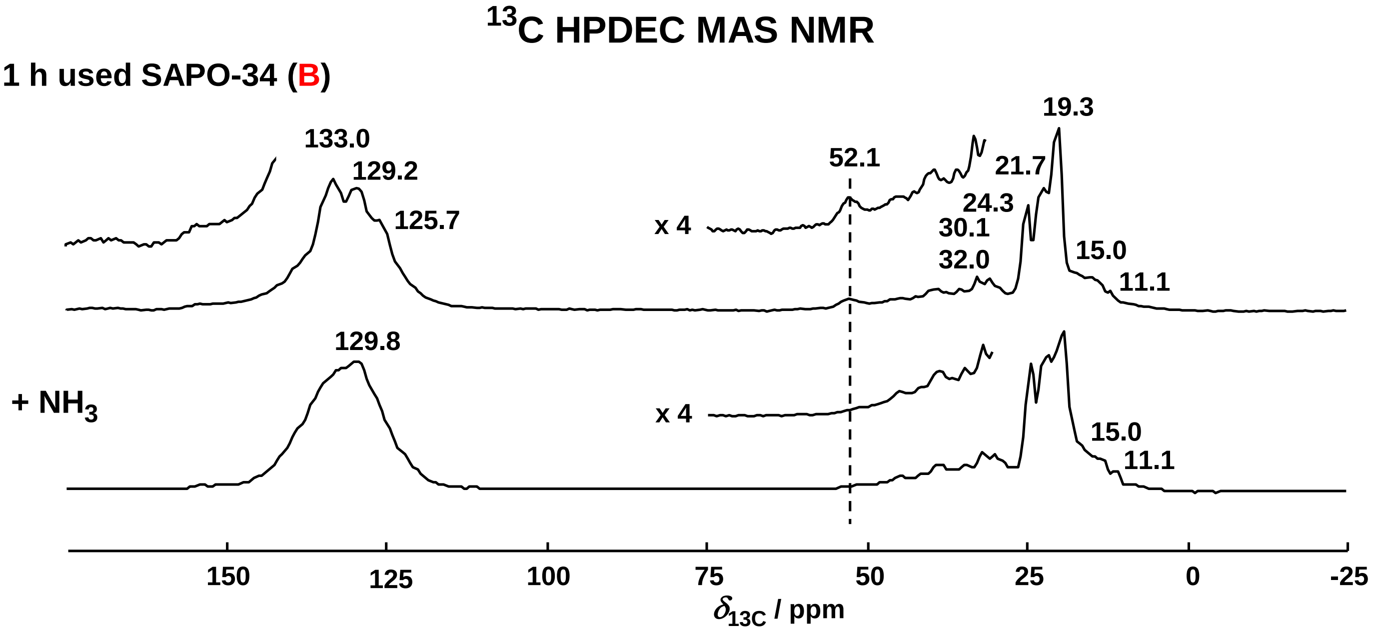
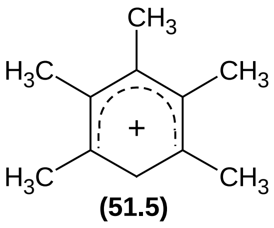
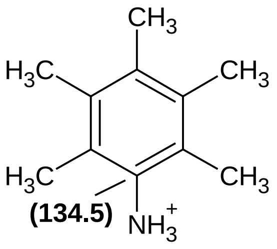
II: Steady-state conditions

^{13}C HPDEC MAS NMR spectra of SAPO-34 used as MTO catalyst for 1 h (sample B) and recorded before and after ammonia loading





(δ_{13C} = 16.1-17.5; 51.5; 131.9-134.6 ppm)



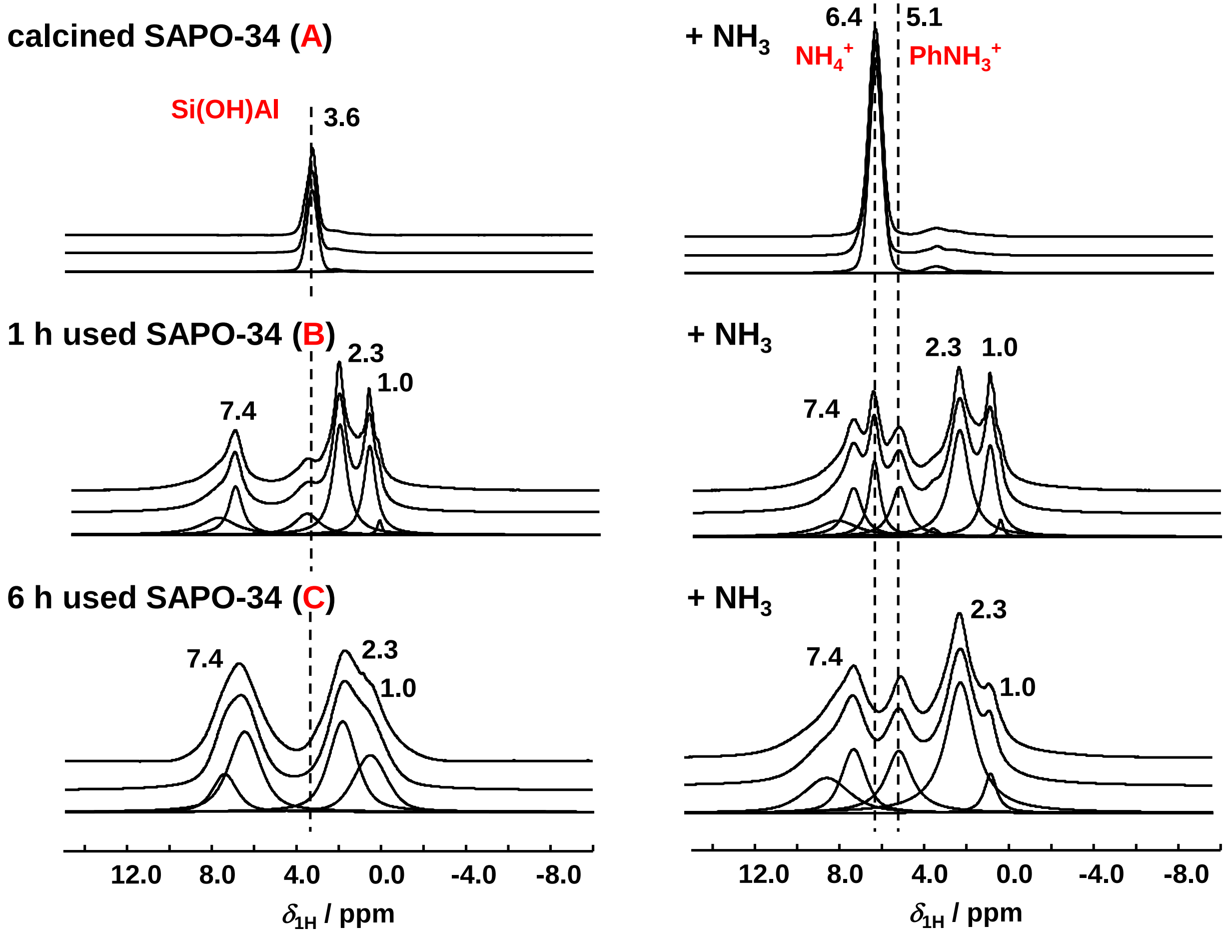
(δ_{13C} = 13.6-17.6; 129.8-134.6 ppm)

HNMR (CNMR) Predictor, Product Version 9.08, Advanced Chemistry Development Inc., 2006.

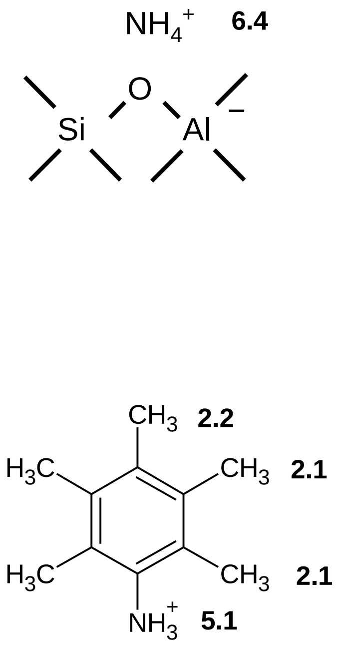
II: Steady-state conditions

^{1}H MAS NMR studies of SAPO-34 catalysts obtained upon MTO conversion in a fixed-bed reactor at 673 K (*W*/*F* = 25 gh/mol)

^{1}H MAS NMR spectra recorded with ν_{rot} = 25 kHz



^{1}H NMR shifts / ppm:



HNMR (CNMR) Predictor, Product Version 9.08, Advanced Chemistry Development Inc., 2006.

II: Steady-state conditions

numbers of bridging OH groups, n_{SiOHAl}, ammonium, n_{NH4+}, and polyalkylphenylammonium ions, n_{PhNH3+}, formed upon loading of ammonia on the calcined and used SAPO-34 catalysts

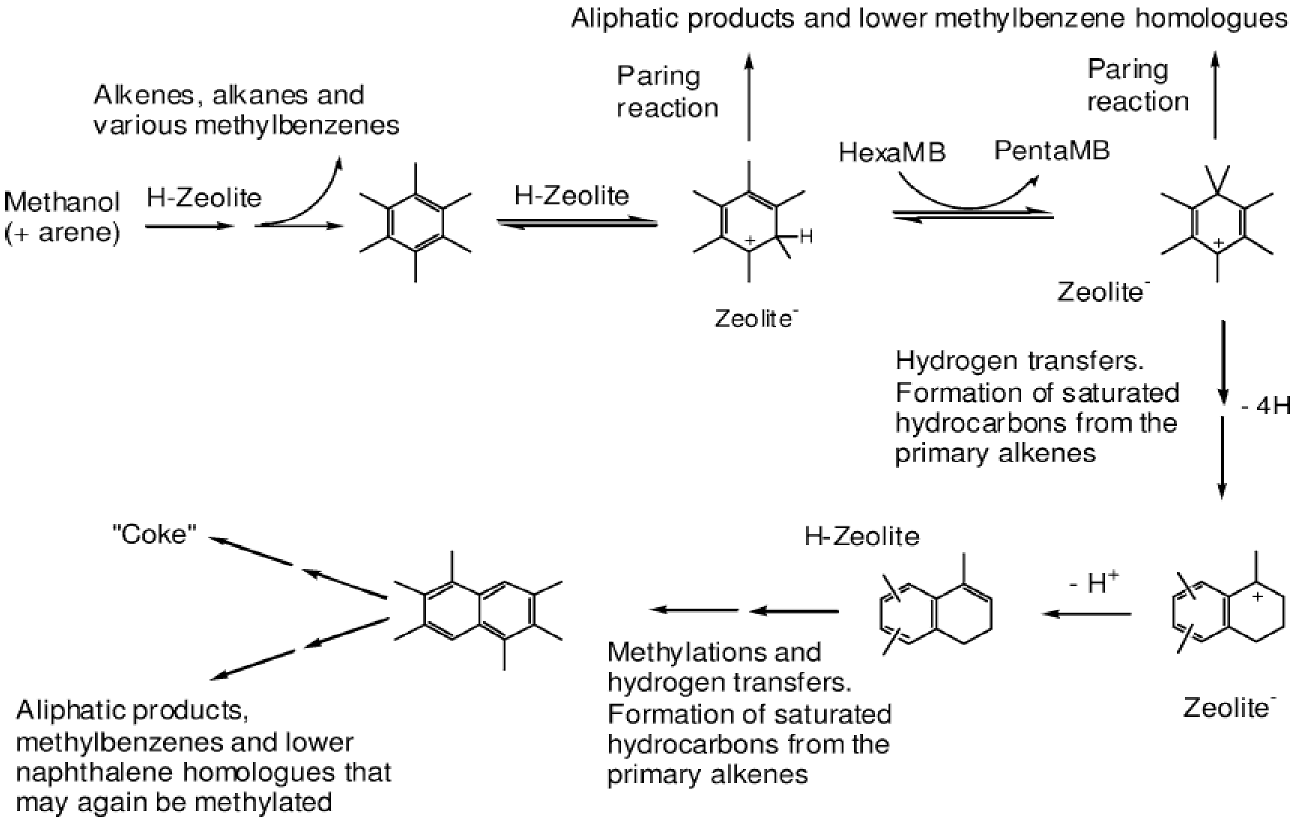
Catalyst samples	n_{SiOHAl} *)	n_{NH4+} *)	n_{PhNH3+} *)
calcined SAPO-34 (**A**)	**1.45 mmol/g**	0	0
calcined SAPO-34 (**A**) + NH_3	**0.15 mmol/g**	**1.30 mmol/g**	0
1 h used SAPO-34 (**B**)	**0.56 mmol/g**	0	0
1 h used SAPO-34 (**B**) + NH_3	**0.13 mmol/g**	**0.33 mmol/g**	**0.40 mmol/g**
6 h used SAPO-34 (**C**)	0	0	0
6 h used SAPO-34 (**C**) + NH_3	0	0	**0.82 mmol/g**

***) accuracy of ±10% for the numbers, n_i, determined by ^{1}H MAS NMR spectroscopy**

III. Deactivation of MTO catalysts by coke formation

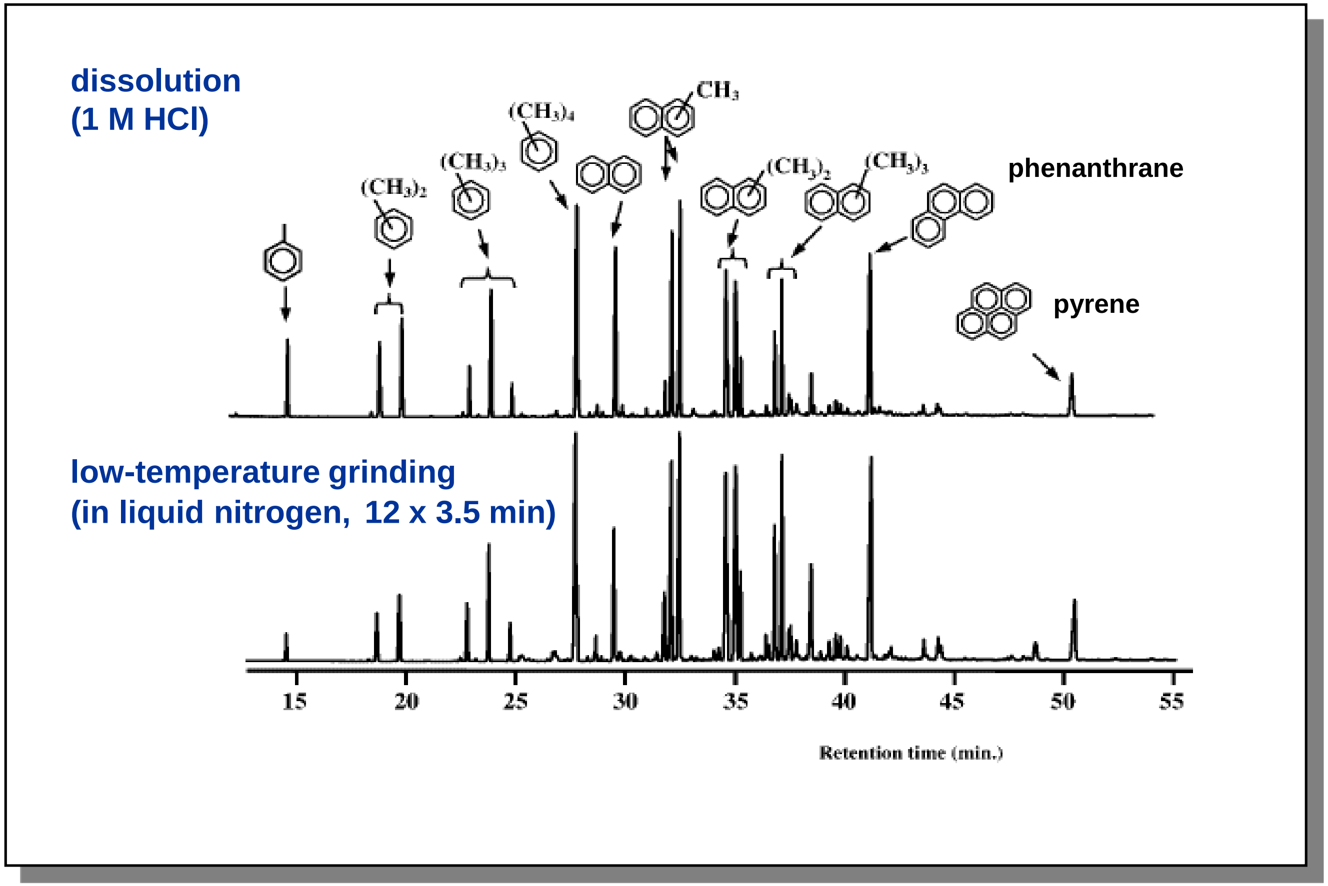
III: Catalyst deactivation

mechanism of coke formation studied by sequential conversion of hexamethylbenzene (M. Bjorgen *et al.,* J. Catal. 215 (2003) 30)



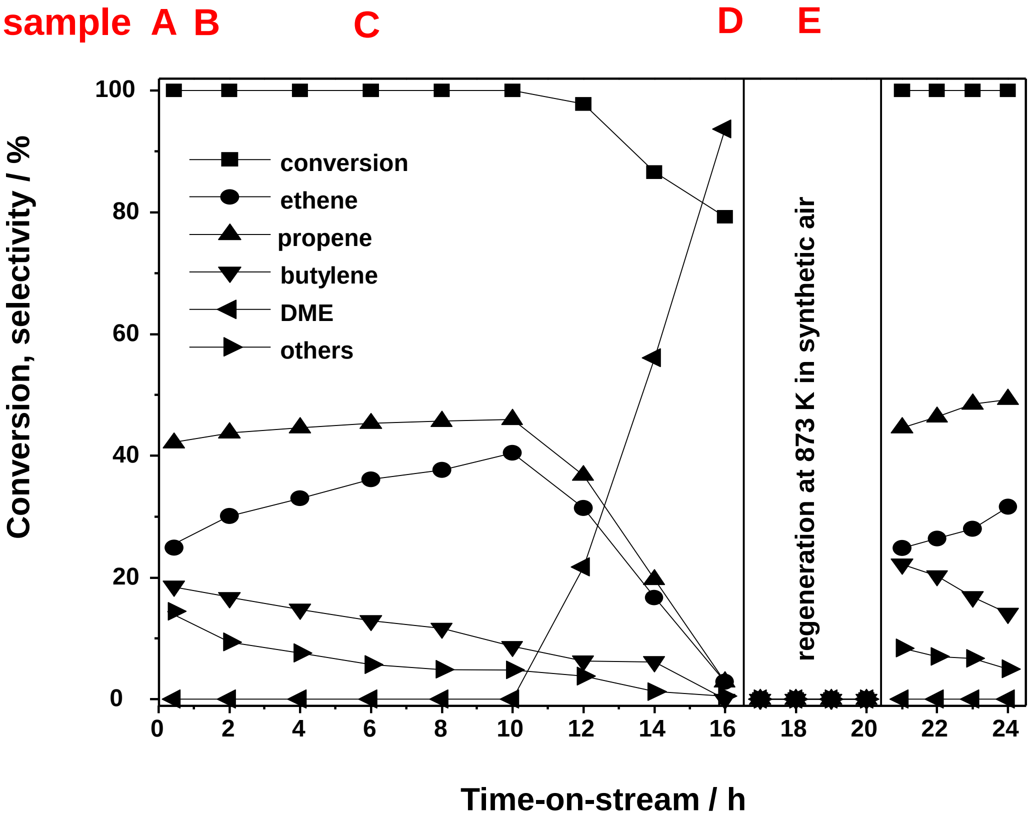
III: Catalyst deactivation

ex situ **study of coke deposits via dissolution and low-temperature grinding of used SAPO-34 catalysts (H. Fu *et al.*, Catal. Lett. 76 (2001) 89)**



II: Steady-state conditions

preparation of SAPO-34 catalysts (B, C, and D) loaded with hydrocarbon-pool compounds by MTO conversion in a fixed-bed reactor at T = 673 K ($WHSV$ = 0.5 gh/mol)



A: calcined SAPO-34

B: 1 h used SAPO-34

C: 6 h used SAPO-34

D: 16 h used SAPO-34

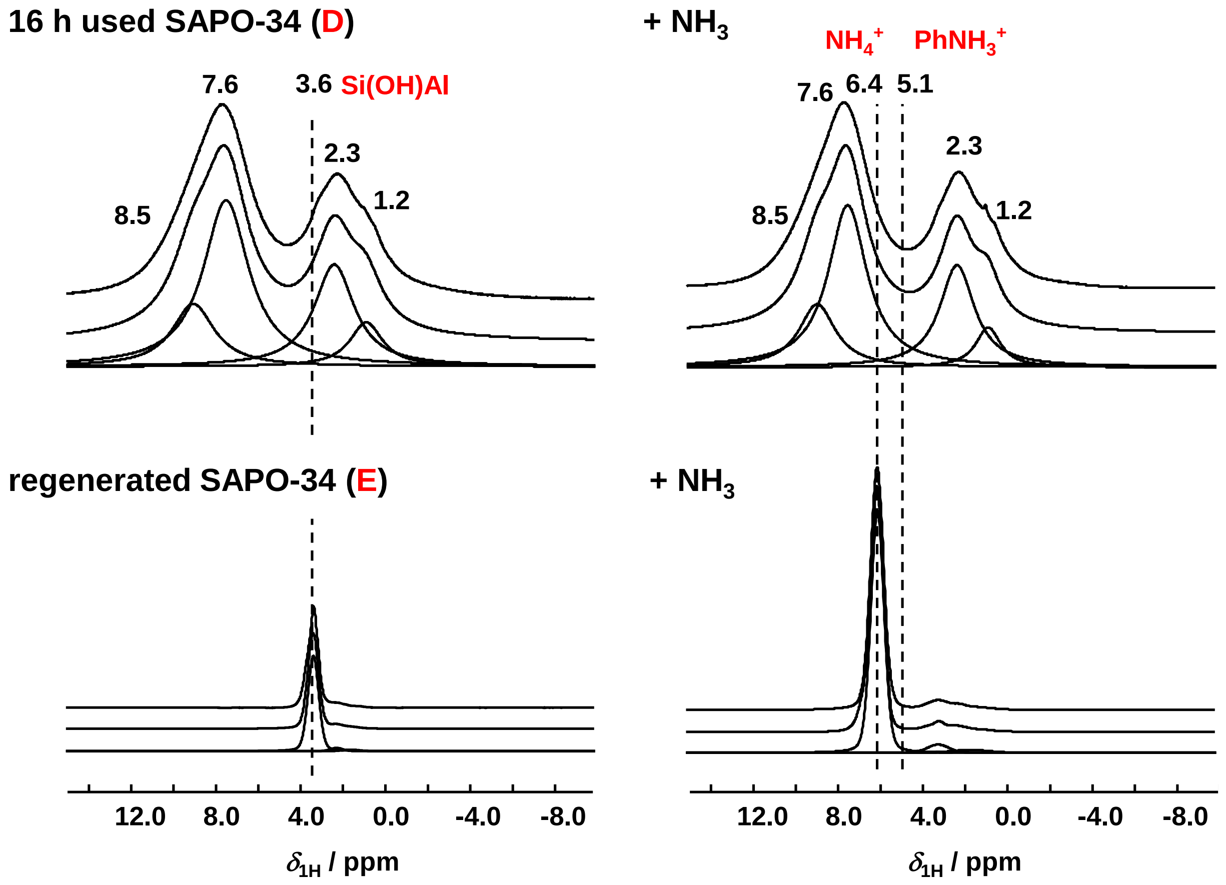
E: regenerated SAPO-34 (at 873 K in air)

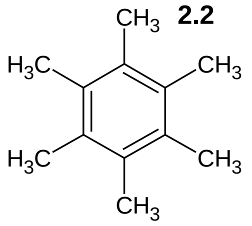
III: Catalyst deactivation

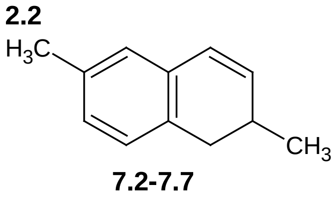
^{1}H MAS NMR studies of SAPO-34 catalysts obtained upon MTO conversion in a fixed-bed reactor at 673 K for 16 h (D) and after regeneration at 873 K in air (E)

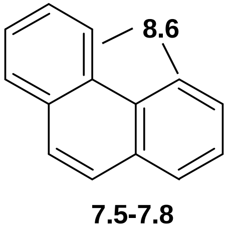
^{1}H MAS NMR spectra recorded with ν_{rot} = 25 kHz

^{1}H NMR shifts / ppm:









HNMR Predictor, Product Version 9.08, Advanced Chemistry Development Inc., 2006.

III: Catalyst deactivation

numbers of bridging OH groups, n_{SiOHAl}, ammonium, $n_{\mathrm{NH4+}}$, and polyalkylphenylammonium ions, $n_{\mathrm{PhNH3+}}$, formed upon loading of ammonia on the calcined (A), used (D), and regenerated SAPO-34 catalysts (E)

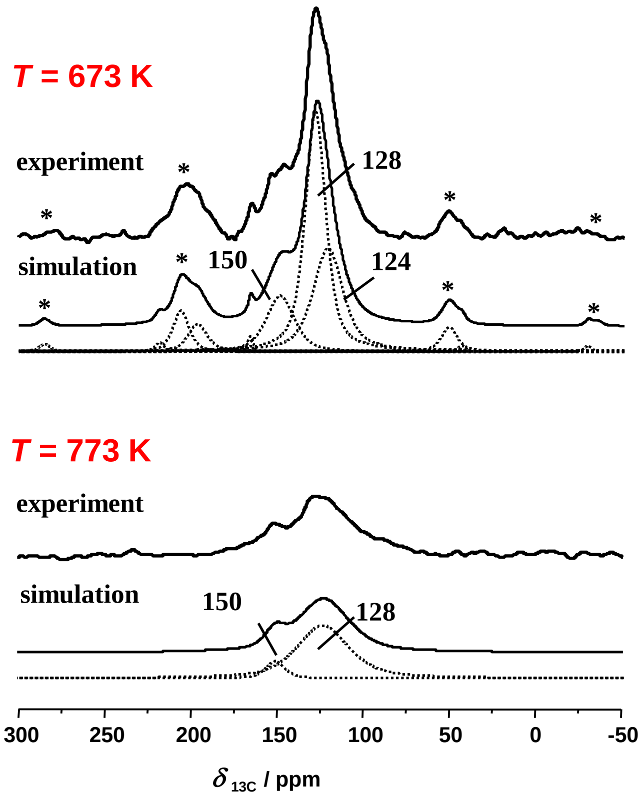
Catalyst samples	n_{SiOHAl} *)	$n_{\mathrm{NH4+}}$ *)	$n_{\mathrm{PhNH3+}}$ *)
calcined SAPO-34 (**A**)	**1.45 mmol/g**	0	0
calcined SAPO-34 (**A**) + NH_3	**0.15 mmol/g**	**1.30 mmol/g**	0
16 h used SAPO-34 (**D**)	0	0	0
16 h used SAPO-34 (**D**) + NH_3	0	0	0
regenerated SAPO-34 (**E**)	**1.25 mmol/g**	0	0
regenerated SAPO-34 (**E**) + NH_3	**0.10 mmol/g**	**1.15 mmol/g**	0

***) accuracy of ±10% for the numbers, n_i, determined by ^{1}H MAS NMR spectroscopy**

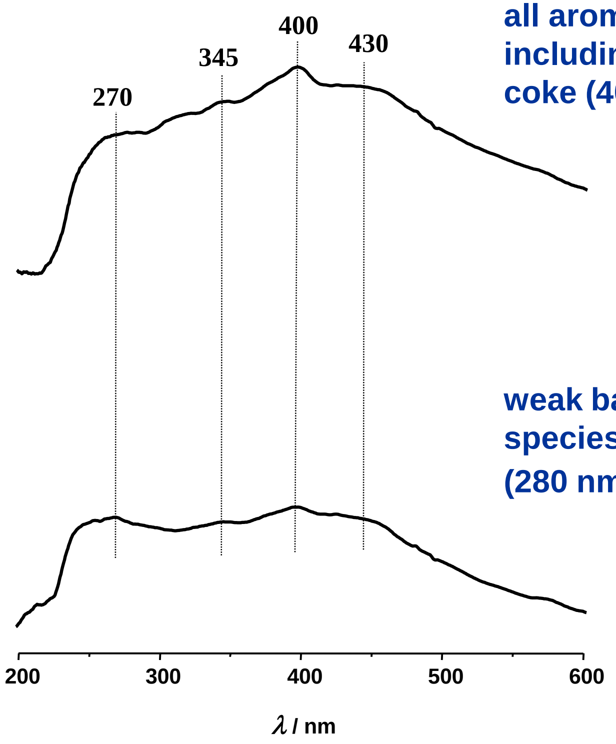
III: Catalyst deactivation

regeneration of coked H-SAPO-34 (like sample D) by purging with synthetic air (20 vol.-% O_2, 30 ml/min) at T = 673 and 773 K for 2 h

^{13}C MAS NMR



UV/Vis



decrease of all aromatics including polycyclic coke (400 nm)

weak band of phenolic species (280 nm)

III: Catalyst deactivation

evaluation of the ^{13}C MAS NMR spectra of coked SAPO-34 (like sample D) before and after regeneration in synthetic air for 2 h

Signal at δ_{13C} / ppm	Assignments	Number of ^{13}C atoms in mmol / g		
		reaction at 673 K	syn. air at 673 K	syn. air at 773 K
16-21	methyl groups bound to aromatics	0.53	-	-
14-15 and 22-29	ethyl groups bound to aromatics	0.16	-	-
125-137	alkylated and non-alkylated aromatic rings	3.33	0.17	0.05
145-155	carbon in aromatics bound to oxygen atoms	-	0.45	0.13

thermal destruction of all aromatics (UV/Vis bands at 280 nm and 400 nm), but formation of oxygenated species (270 nm)

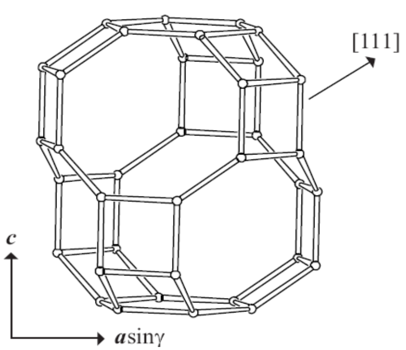
IV: Alternative catalysts

H-SAPO-34: Structure type CHA

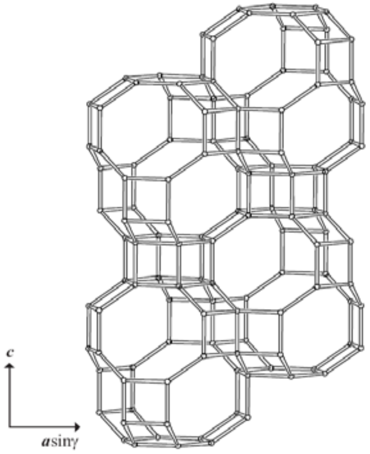
$H^{+}_{n}[Al_{18}P_{18-n}Si_{n}O_{72}]$

chabazite cages (diameter 0.94 nm)

8-ring windows perpendicular to [001] 0.38 nm x 0.38 nm



chabazite cage

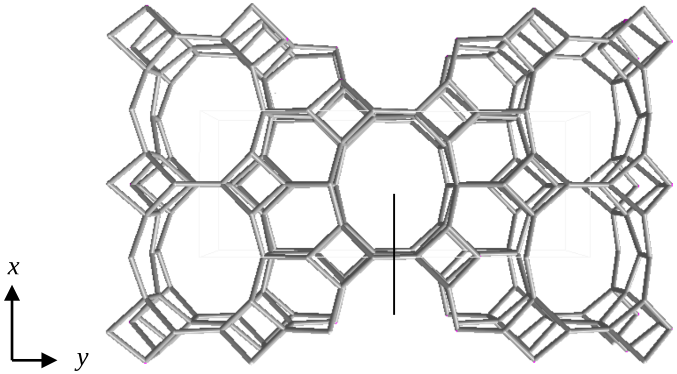


H-SAPO-41: Structure type AFO

$H^{+}_{n}[Al_{10}P_{10-n}Si_{n}O_{40}]$

one-dimensional 10-ring pores

[001] 0.43 nm x 0.70 nm

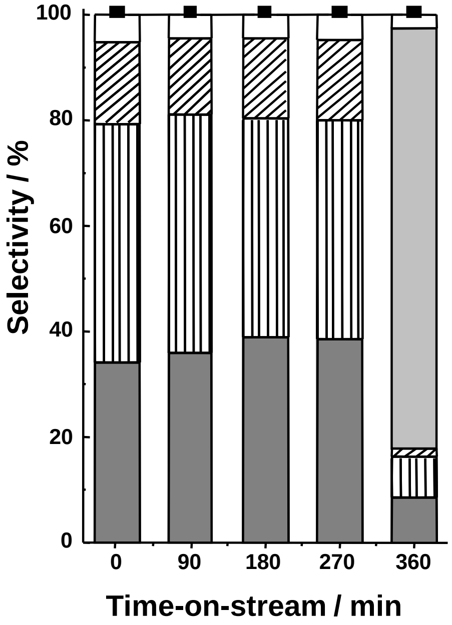


10-ring pores

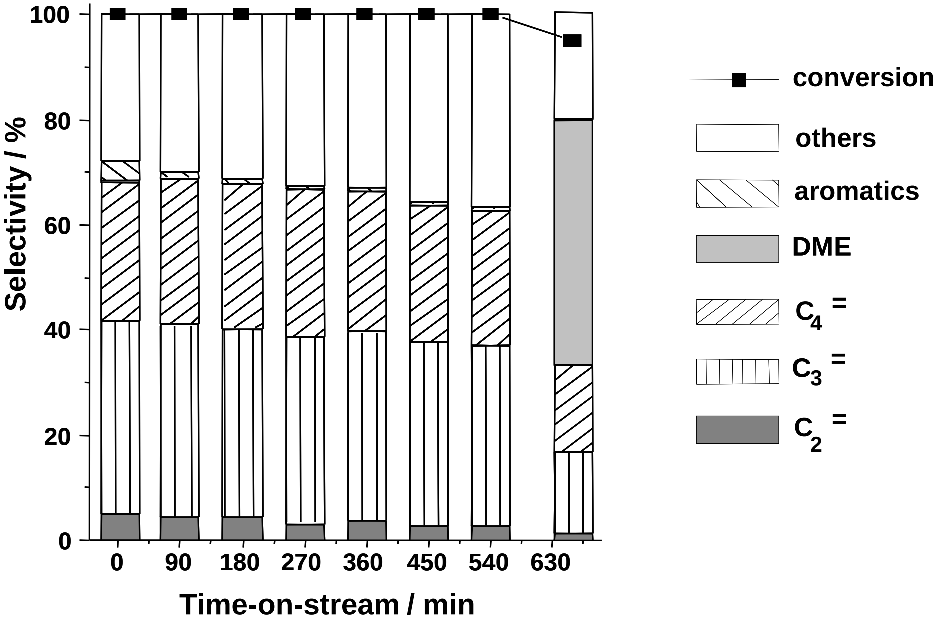
IV: Alternative catalysts

methanol conversion (*WHSV* = 1/h) in a fixed-bed reactor at *T* = 723 K

SAPO-34



SAPO-41



chemical compositions (ICP-AES):

$n_{Si}/(n_{Si}+n_{Al}+n_P) = 0.17$

$n_{Si}/(n_{Si}+n_{Al}+n_P) = 0.03$

number of available Brønsted acid sites (^{1}H MAS NMR):

n_{acOH} = 1.15 mmol/g

n_{acOH} = 0.25 mmol/g

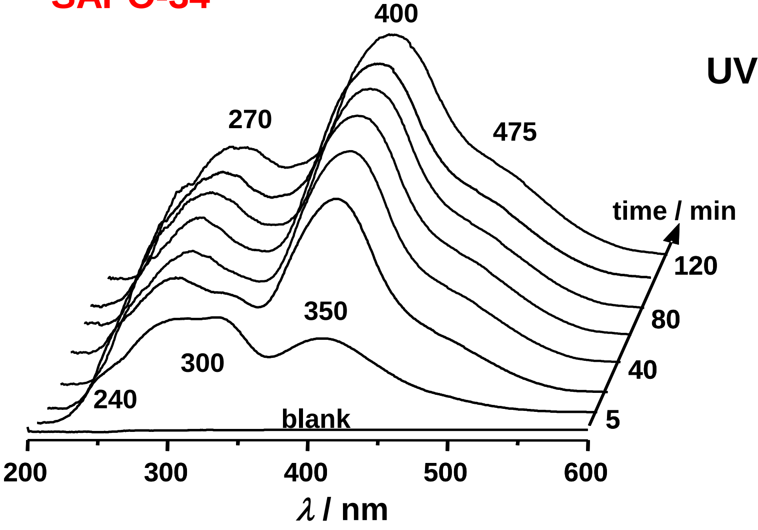
W. Dai et al., ACS Catal. (2011), accepted.

IV: Alternative catalysts

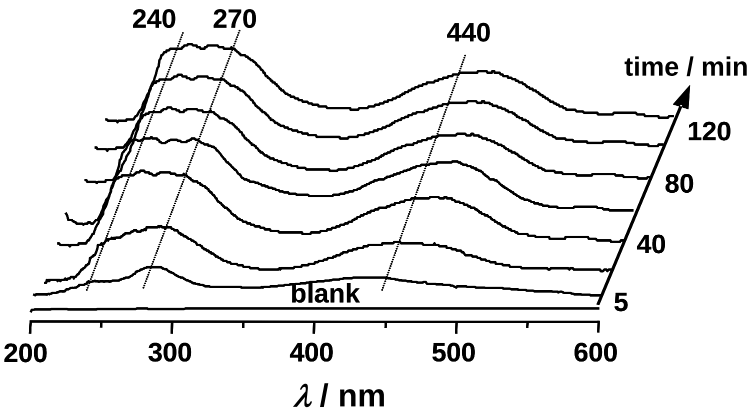
in situ UV/Vis studies of hydrocarbon-pool compounds and coke deposits formed by methanol conversion (_WHSV_ = 1/h) on SAPO-34 and SAPO-41 in a fixed-bed reactor at _T_ = 723 K

UV/Vis

SAPO-34



SAPO-41



occluded organic compounds (TG-DTA):

10.2 wt.-% **5.5 wt.-%**

W. Dai et al., ACS Catal. (2011), accepted.

Summary

depending on the level of impurities present in the methanol feed, methoxy groups may play a key role during the induction period

the composition of the hydrocarbon pool formed under steady-state conditions depends on the type of zeolites (H-ZSM-5: more olefinic species; SAPO-34: more polymethylaromatics) and the reaction parameters

adsorption of ammonia on used MTO catalysts gives information on number of accessible Brønsted acid sites and polyalkylbenzenium ions

optimized MTO catalyst lifetimes require further studies of microporous Solids with one-dimensional pore system and medium acid site density And acid strength (silicoaluminophosphates)

UV/Vis spectroscopy is an interesting tool for an *on-line* study of the hydrocarbon pool and coke formation on MTO catalysts

Thanks to …

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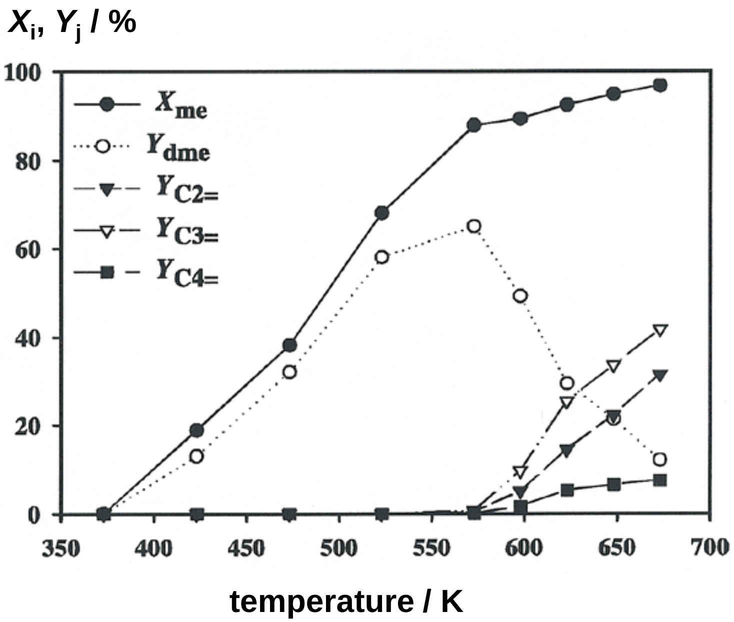
Comparison of MTH on H-ZSM-5 in standard fixed bed and rotor reactors, A. Buchholz, diploma thesis, University Stuttgart, 2000

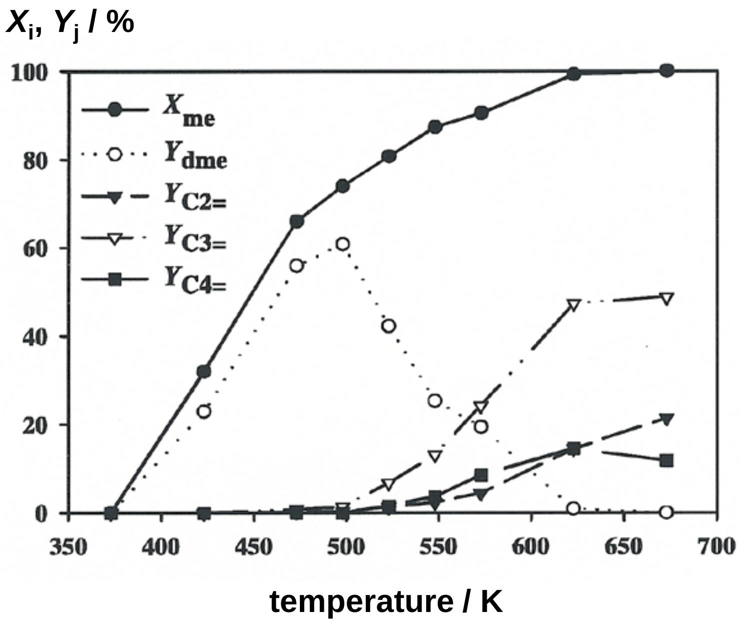
fixed-bed reactor

W_{cat}/F_{me} = 25 gh/mol



spinning (2 kHz) MAS NMR rotor

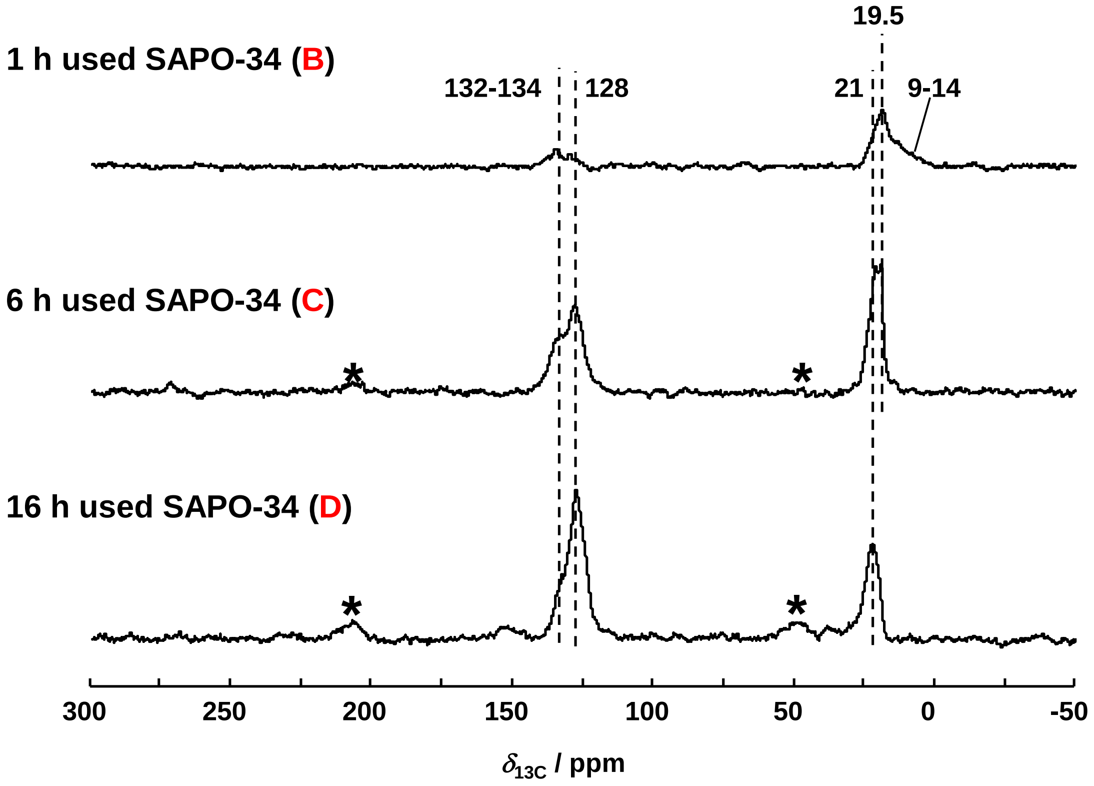
W_{cat}/F_{me} = 25 gh/mol



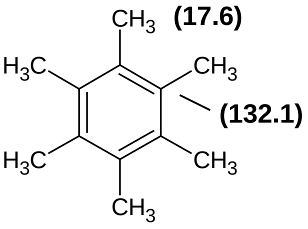
II: Steady-state conditions

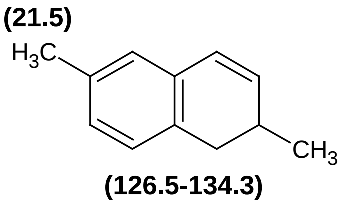
^{13}C MAS NMR studies of SAPO-34 catalysts obtained upon MTO conversion in a fixed-bed reactor at 673 K (*W*/*F* = 25 gh/mol)

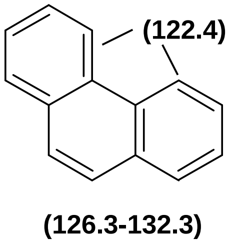
^{13}C MAS NMR spectra



^{13}C NMR shifts / ppm:







ACD/CNMR, Product Version 1.1, Advanced Chemistry Development Inc., 1995.

I: Induction period

assignments of UV/Vis bands (π-π^* transitions) observed during the methanol-to-olefin conversion on acidic zeolite catalysts

Bands at λ / nm	**Assignments**
240	dienes
270	aromatics and polyalkylaromatics
320	monoenyl carbenium ions
330	cyclohexadienyl carbenium ions
390	benzenium-type carbenium ions
400-475	polycyclic aromatics
450	trienylic carbenium ions

References:

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H. Foerster et al., J. Mol. Struct. 296 (1993) 61.
M. Bjørgen et al., J. Am. Chem. Soc. 125 (2003) 15863.