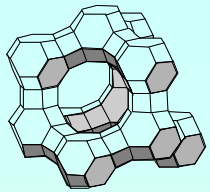

Mechanisms of the Methanol-to-hydrocarbon (MTH) Conversion on Acidic Zeolite Catalysts

Michael Hunger

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University of Stuttgart, Germany

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

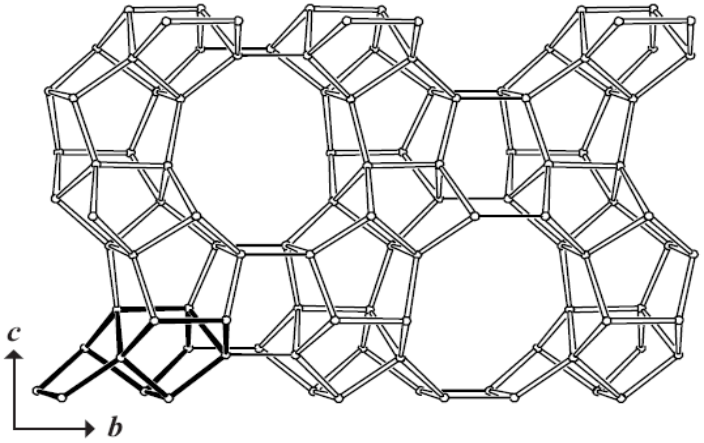
$H^+_n[Al_nSi_{96-n}O_{192}]$

crossing intersections at

interconnecting 10-ring channels

[100] 0.51 nm x 0.55 nm

[010] 0.53 nm x 0.56 nm



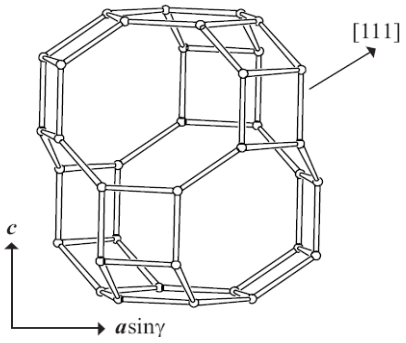
H-SAPO-34: Structure type CHA

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

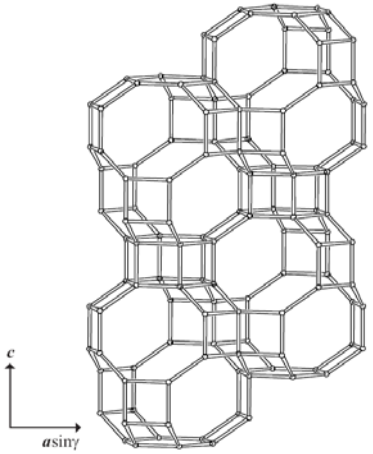
chabazite cages accessible by

8-ring windows perpendicular to

[001] 0.38 nm x 0.38 nm



chabazite cage



Periods of the methanol conversion on acidic zeolites

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 deposits forming a catalytically active hydrocarbon pool

III: Catalyst deactivation during methanol conversion on zeolites

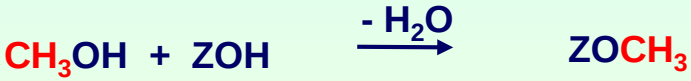
Formation of inactive coke deposits affecting the methanol conversion and the selectivity to ethylene and propylene

I. The induction period of the methanol conversion on acidic zeolites

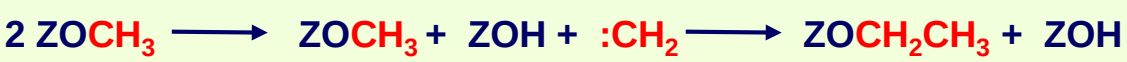
I: Induction period

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

- **formation of surface methoxy groups**



- **decomposition of surface methoxy groups leads to first C-C bond formation and organic precursors**

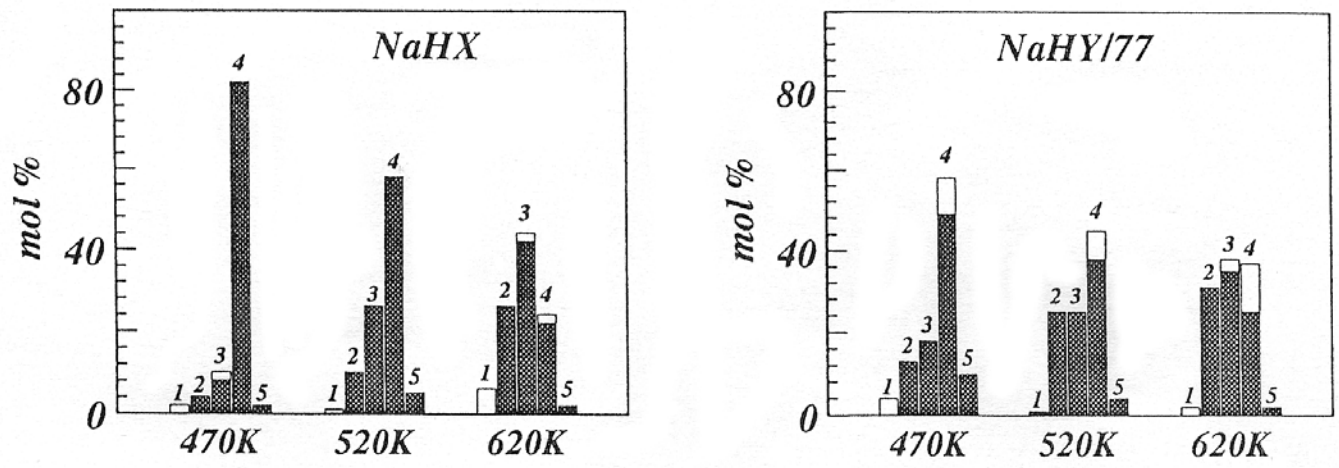


- **impurities in the methanol feed may act as organic presursors**

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

I: Induction period

Formation and decomposition of methoxy groups in zeolites H,Na-X and H,Na-Y, J. Datka et al., Proc. 12th Int. Zeolite Conf., 1998, p. 2601

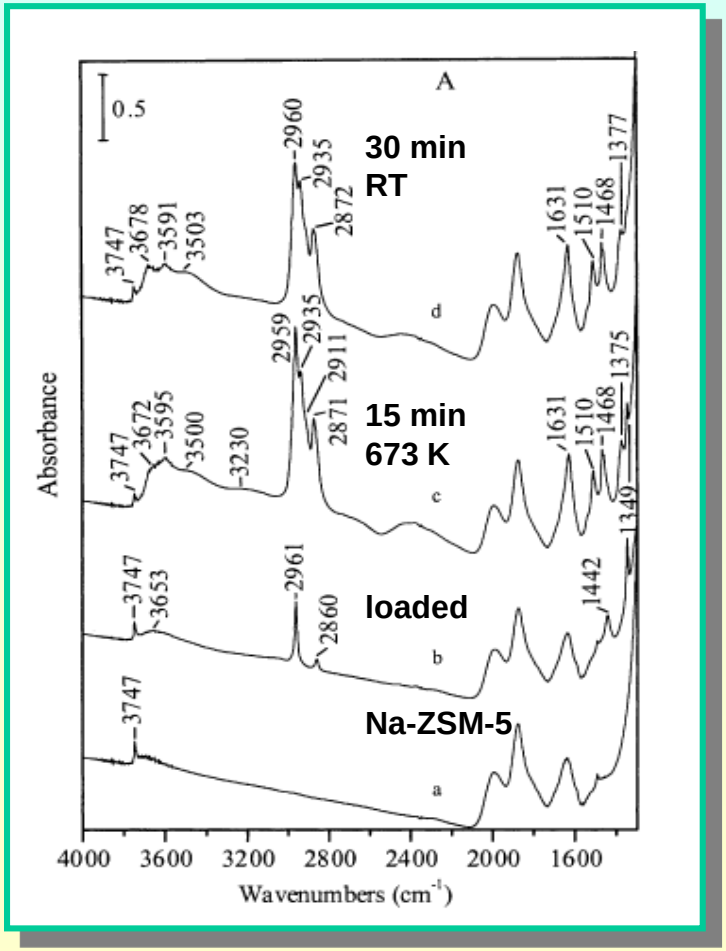


Products of the decomposition of methoxy groups as a function of temperature (1 – 5 = C_1 – C_5, ■ alkenes, □ alkanes)

→ **alkenes were found to be the primary products formed by the decomposition of methoxy groups on acidic zeolites**

I: Induction period

Catalytic conversion of chloromethane to higher hydrocarbons on zeolite Na-ZSM-5, D. Jaumain, B.L. Su, J. Mol. Catal. A 197 (2003) 263



bands at 2959 to 2961 cm^{-1}:
formation of methoxy groups

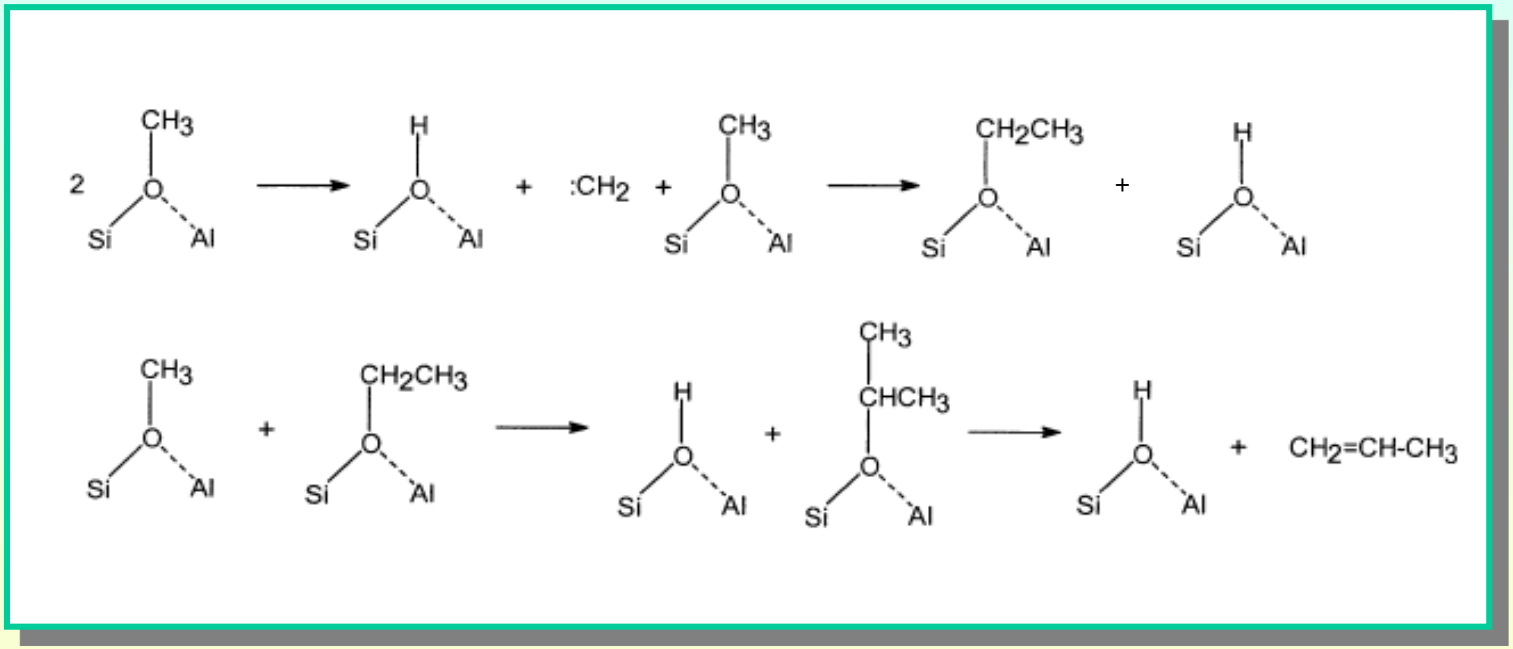
bands at 1377, 1468, 2935 cm^{-1}:
vibrations of -CH_2- groups

bands at 1631 cm^{-1}:
-C=C- vibrations

→ **C-C bonds occur and indicate the formation of higher hydrocarbons**

I: Induction period

Mechanism of the formation of higher hydrocarbons by methoxy groups, D. Jaumain, B.L. Su, J. Mol. Catal. A 197 (2003) 263



→ **first C-C bond formation occurs via a ylide transfer between neighboring methoxy groups and insertion in the C-H bonds of these surface species**

I: Induction period

Study of ylide formation via the H/D exchange between $ZOCD_3$, $ZOCH_3$, and ZOH

J. Novakova et al., J. Catal. 97 (1986) 277:

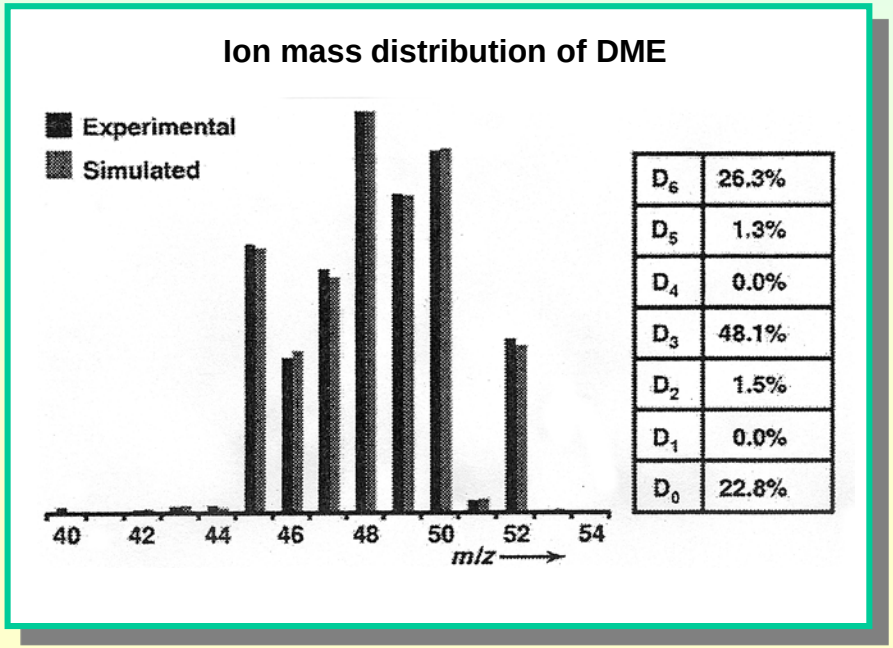
on H-ZSM-5 and at 520-640 K, hydrogen transfer takes place between methoxy groups as observed by mass spectrometry of desorbed products

D.M. Marcus et al., Angew. Chem. 45 (2006) 1:

on H-SAPO-34 and up to 623 K, no H/D exchange of $ZOCD_3$ and $ZOCH_3$ groups before these species react with adsorbed water to dimethylether (DME)

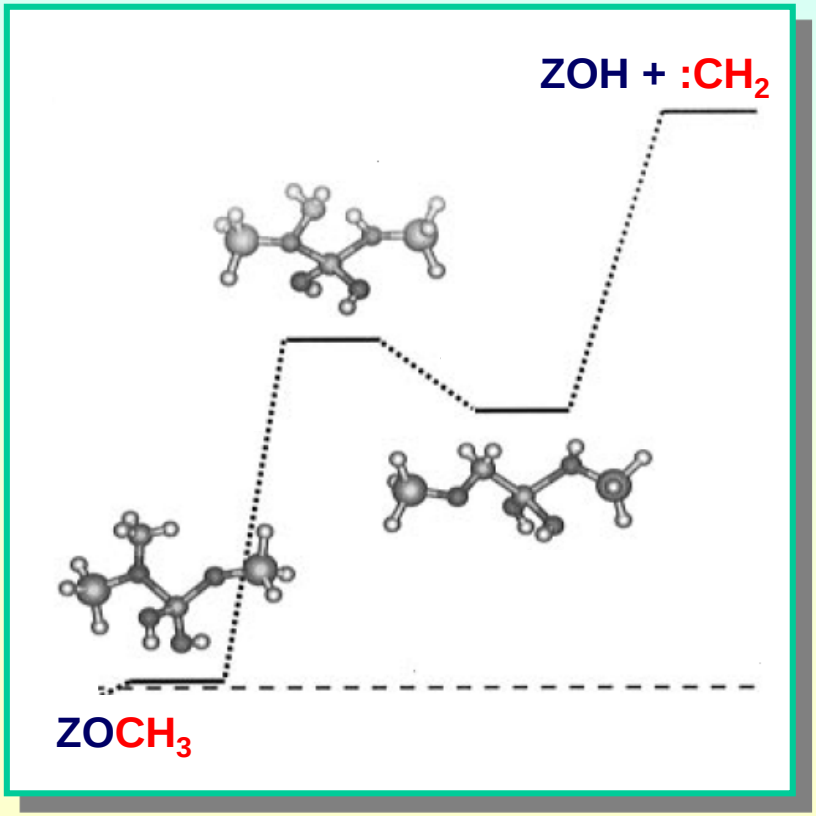
→ **formation of ylide ($:CH_2$) ?**

→ **role of impurities ?**



I: Induction period

Calculation of the activation barrier of the ylide (:CH_2) formation, P.E. Sinclair, C.R.A. Catlow, J. Phys. Chem. B 101 (1997) 295



activation barrier of 215-232 kJ/mol:

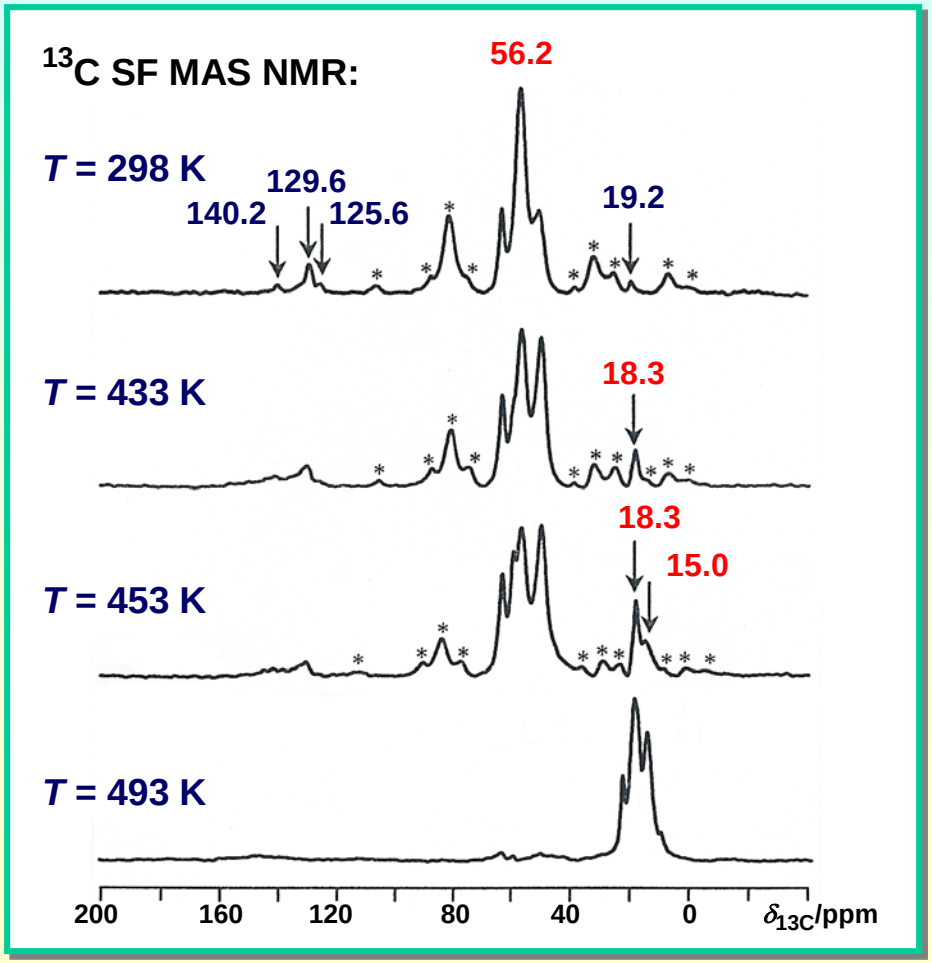
"deprotonation of methyl groups during the methanol to gasoline (MTG) conversion can occur to produce surface-stabilized carbenes"

D. Lesthaeghe et al., Angew. Chem. 118 (2006) 1746:

"This step was found to be highly activated" (242 kJ/mol) in comparison with reaction routes, where a contribution of organic impurities in the methanol feed is assumed

I: Induction period

reaction of methoxy groups with toluene on zeolite H-Y, W. Wang et al., J. Am. Chem. Soc. 125 (2003) 15260



methoxy toluene

$SiO(^{13}CH_3)Al + CH_3C_6H_5$

56.2 ppm 19.2 ppm

→ $SiOHAl + CH_3C_6H_4{}^{13}CH_3$

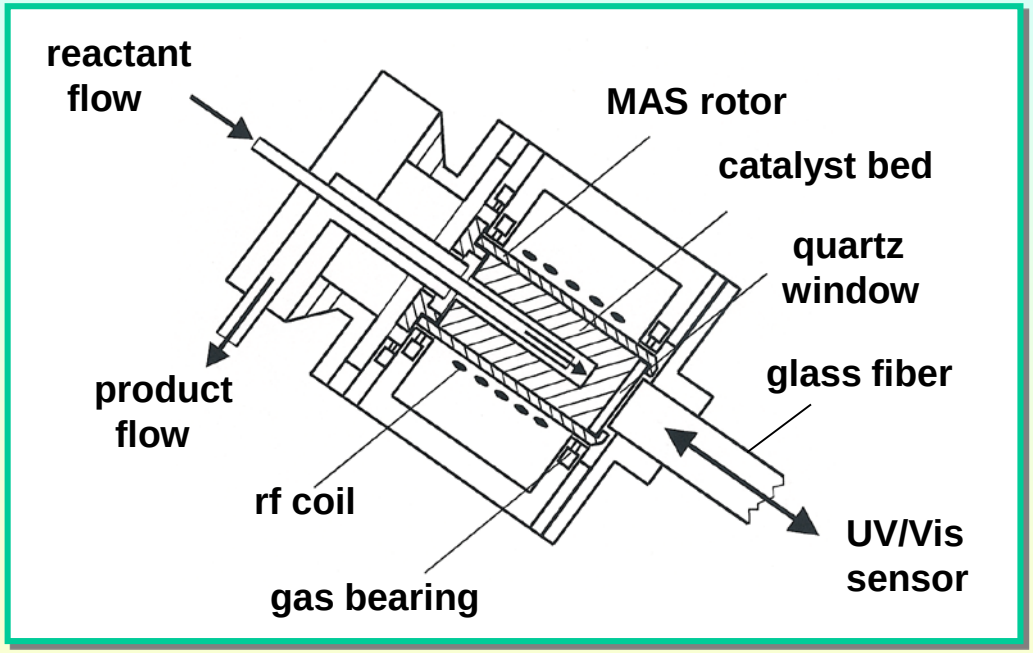
18.3 ppm

methoxy groups contribute to the alkylation of aromatic compounds

I: Induction period

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

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



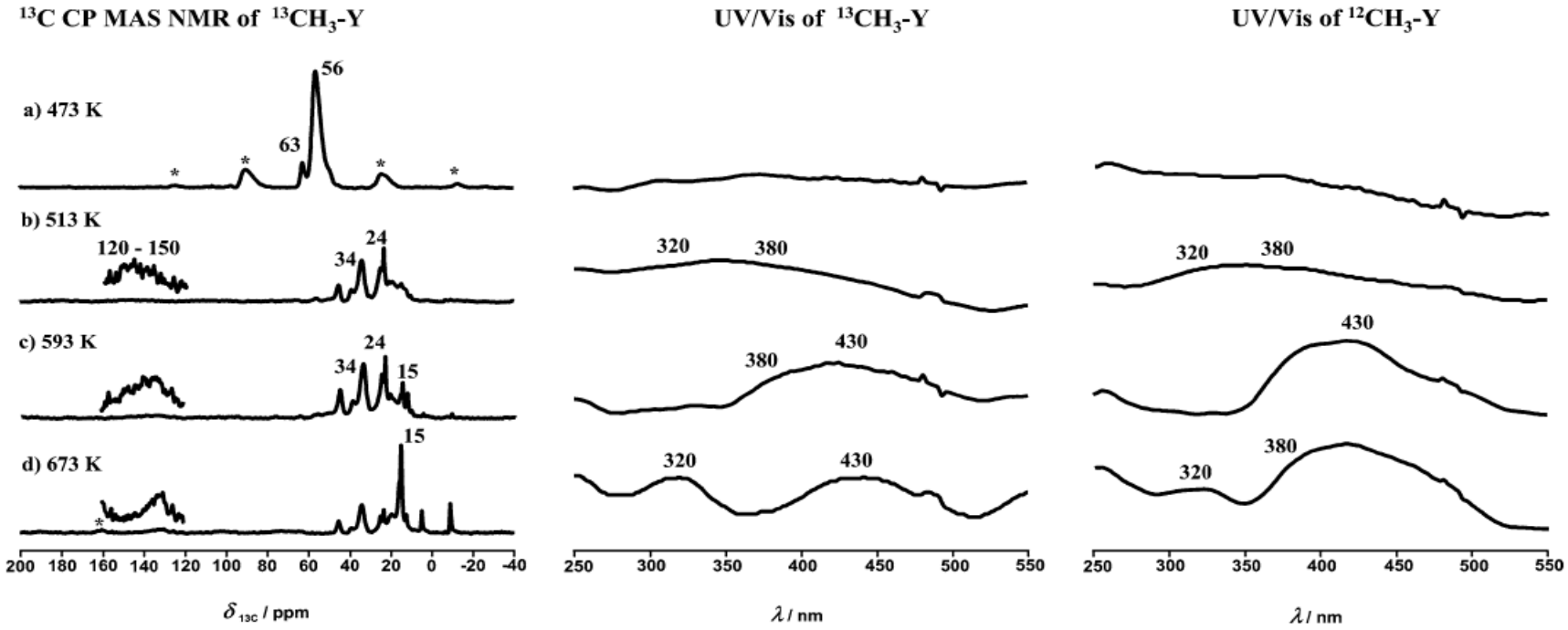
- **preparation of methoxy groups by adsorption of ^{13}C-enriched methanol and highly purified (impurities < 30 ppm) $^{12}CH_3OH$ on H-Y and H-SAPO-34 and thermal treatment**

I: Induction period

Modified 7 mm Doty MAS NMR probe equipped with an injection system and a quartz fiber optics

I: Induction period

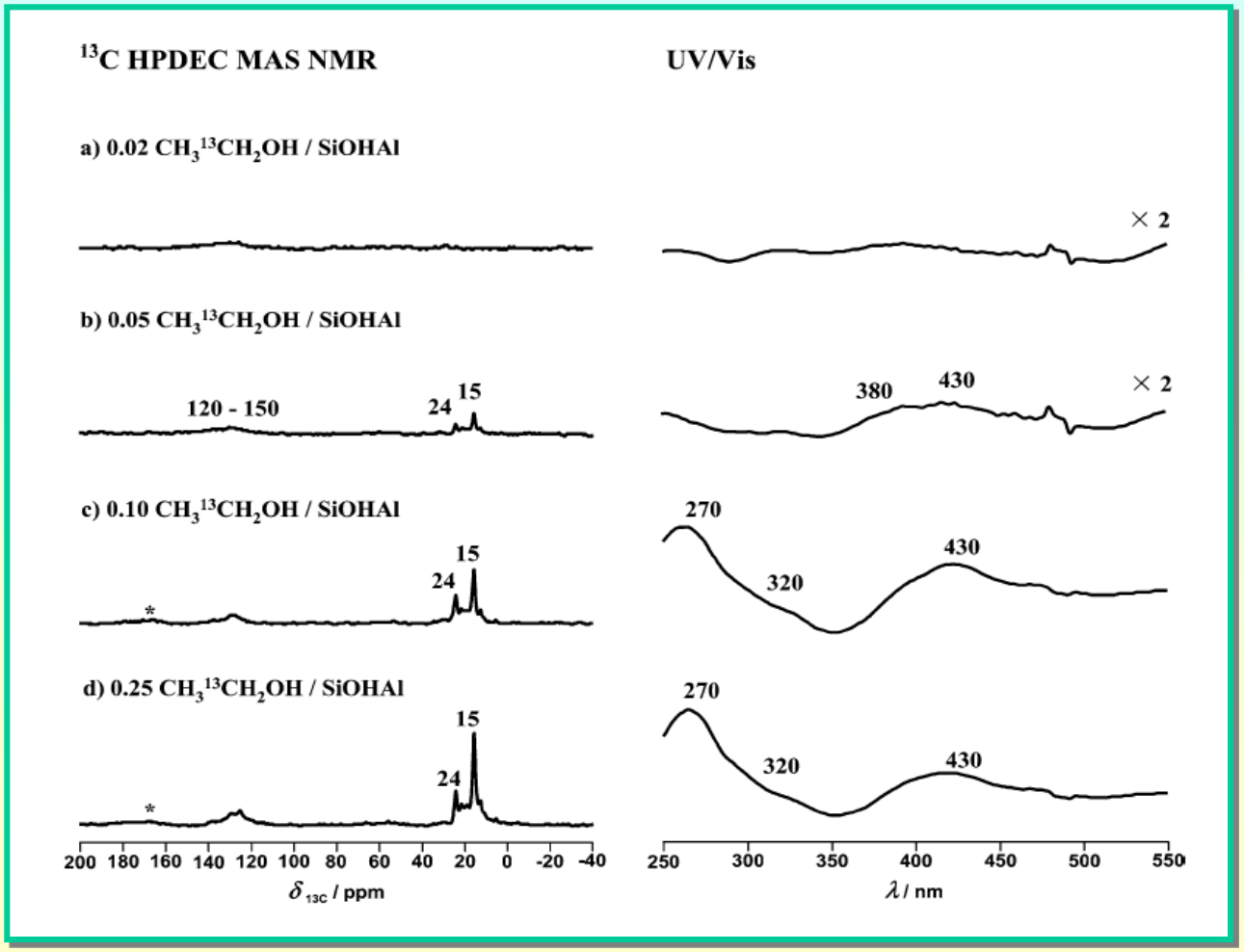
MAS NMR-UV/Vis study of the decomposition of methoxy groups, Y. Jiang et al., J. Catal. 238 (2006) 21



- decomposition of ^{13}C- enriched and highly purified (impurities < 30 ppm) methoxy groups start at the same temperature and give similar UV/Vis-sensitive hydrocarbons
- hydrocarbons were formed without contribution of impurities

I: Induction period

conversion of ethanol (most important impurity) on H-SAPO-34 at 673 K



similar UV/Vis sensitive hydrocarbons are formed

however, two orders higher ethanol loading is neccessary than maximum impurity content in methanol feed

I: Induction period

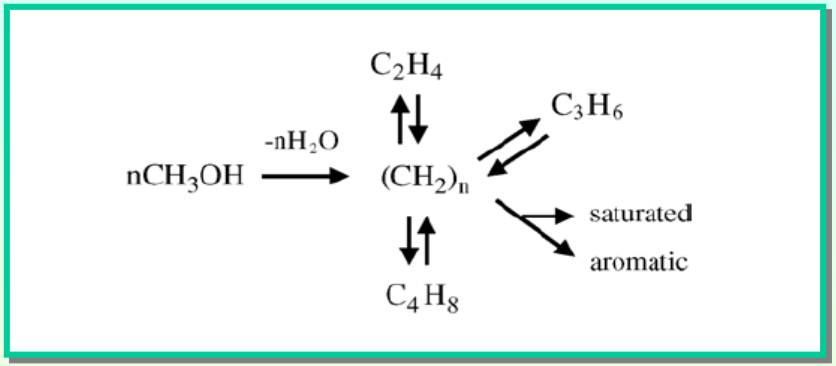
Possible reasons for the different reactivities of methoxy groups described in the literature:

- **different behaviors and distributions of surface sites of the catalysts**
- **different densities of methoxy groups (Y. Jiang et al.: 1.3 methoxy per chabazite cages, D.M. Marcus et al.: ca. 0.7 methoxy groups per chabazite cage)**
- **the temperature threshold was not reached, which is necessary to decompose organic surface compounds on the catalyst under study**
- **comparison of studies performed under batch conditions (first volatile products can not leave the catalyst) and in flow reactors (first volatile products are purged from the catalyst surface)**

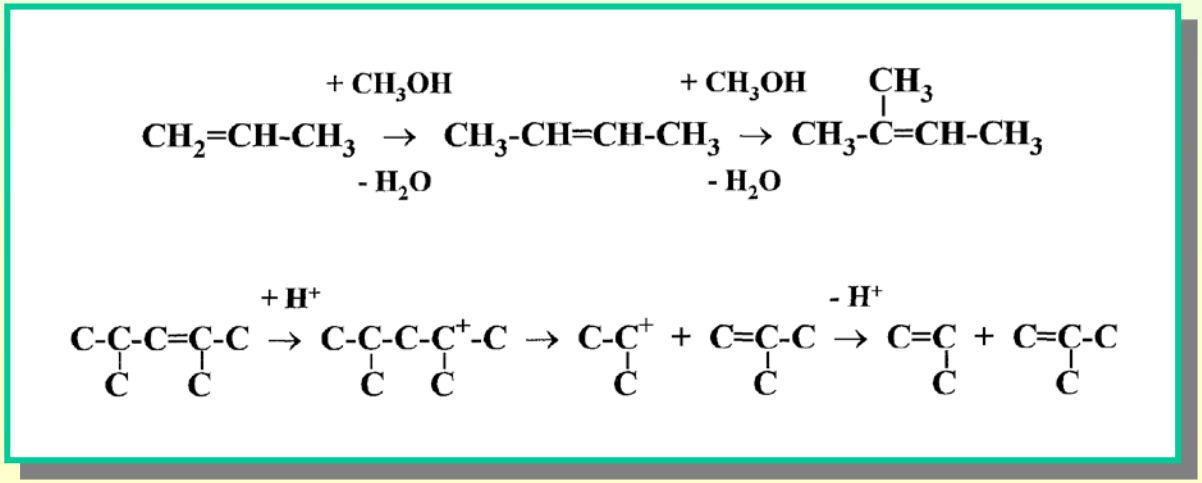
II. Steady-state of the methanol conversion on acidic zeolites

II: Steady-state conditions

Most favored mechanism is the hydrocarbon pool mechanism, L.M. Dahl, S. Kolboe, J. Catal. 149 (1994) 458

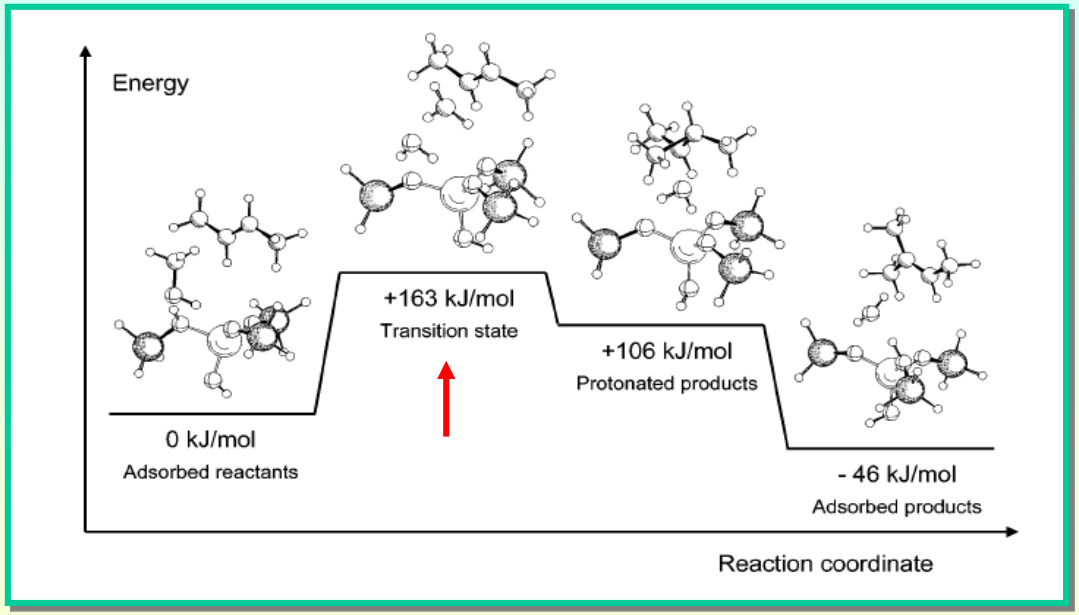


H. Schulz, M. Wei, Microporous Mesoporous Mater. 29 (1999) 205



II: Steady-state conditions

Theoretical studies of the methylation of alkenes (trans-2-butene), S. Svelle et al., J. Phys. Chem. B, 107 (2003) 9281

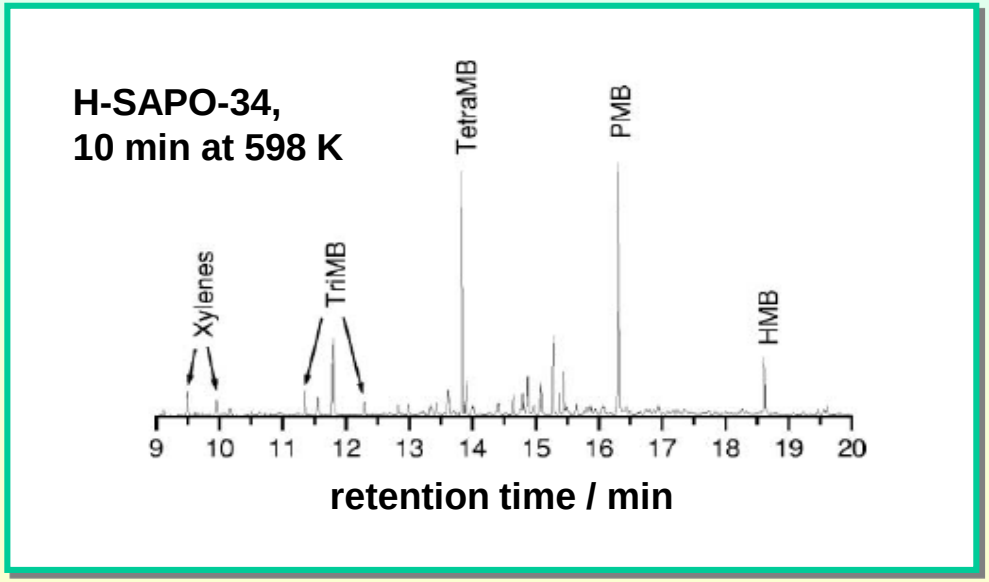


For the methylation of toluene and hexaMB, energy barriers of 191 kJ/mol and 171 kJ/mol, respectively, were calculated using the same hybrid density functional and basis set, B. Arstad et al., J. Phys. Chem. B, 106 (2002) 12726

II: Steady-state conditions

Study of the composition of the hydrocarbon pool on H-SAPO-34 by *ex situ* methods, B. Arstad et al., Catal. Lett. 71 (2001) 209

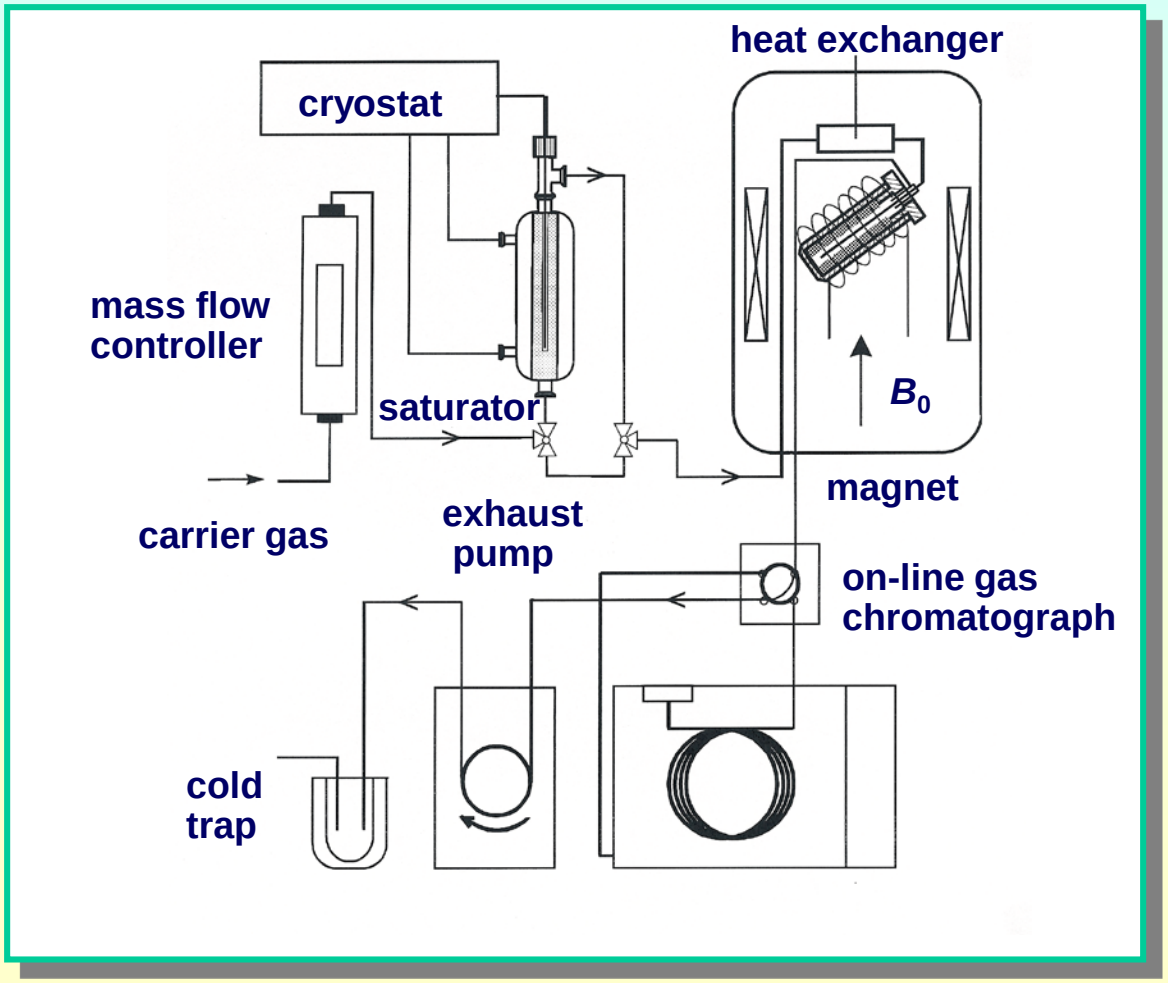
- **spent catalyst was dissolved in 1 M HCl, organic compounds are extracted with CCl_4**
- **CCl_4 solution was analyzed by GC-MS (HP 6890 with MSD 5973)**



→ **preferentially, polymethylaromatics were determined for H-SAPO-34**

II: Steady-state conditions

MAS NMR technique for the study of hydrocarbon pool compounds under *in situ* conditions, M. Hunger et al., Catal. Lett. 57 (1999) 199

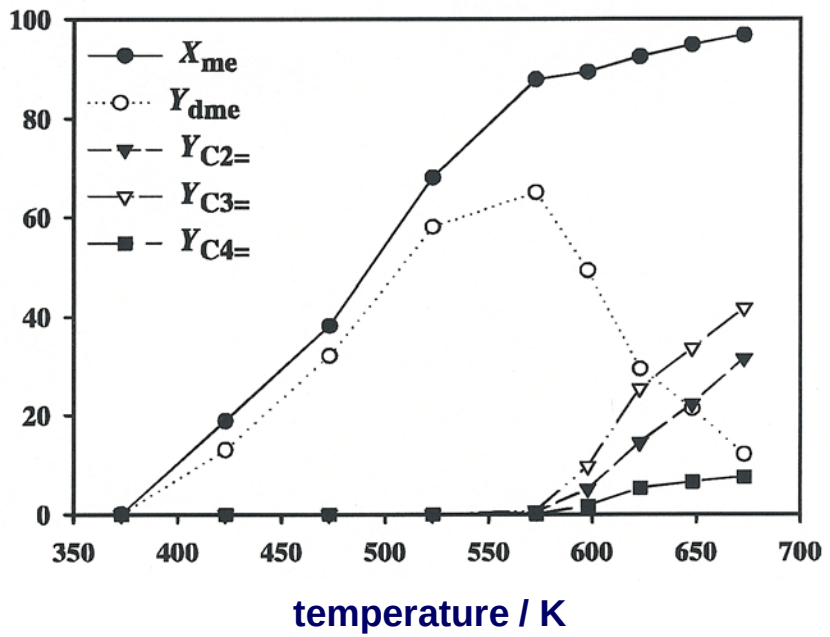


II: Steady-state conditions

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

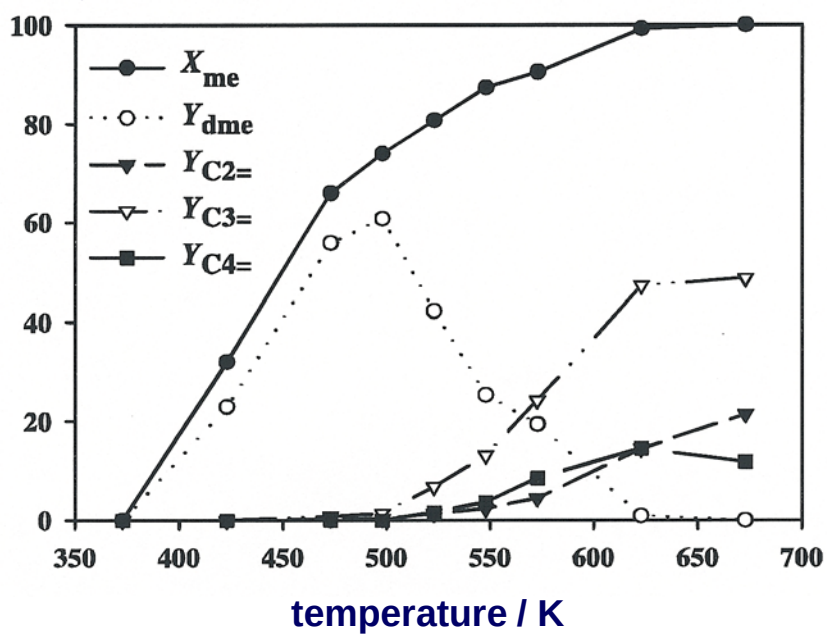
fixed-bed reactor

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



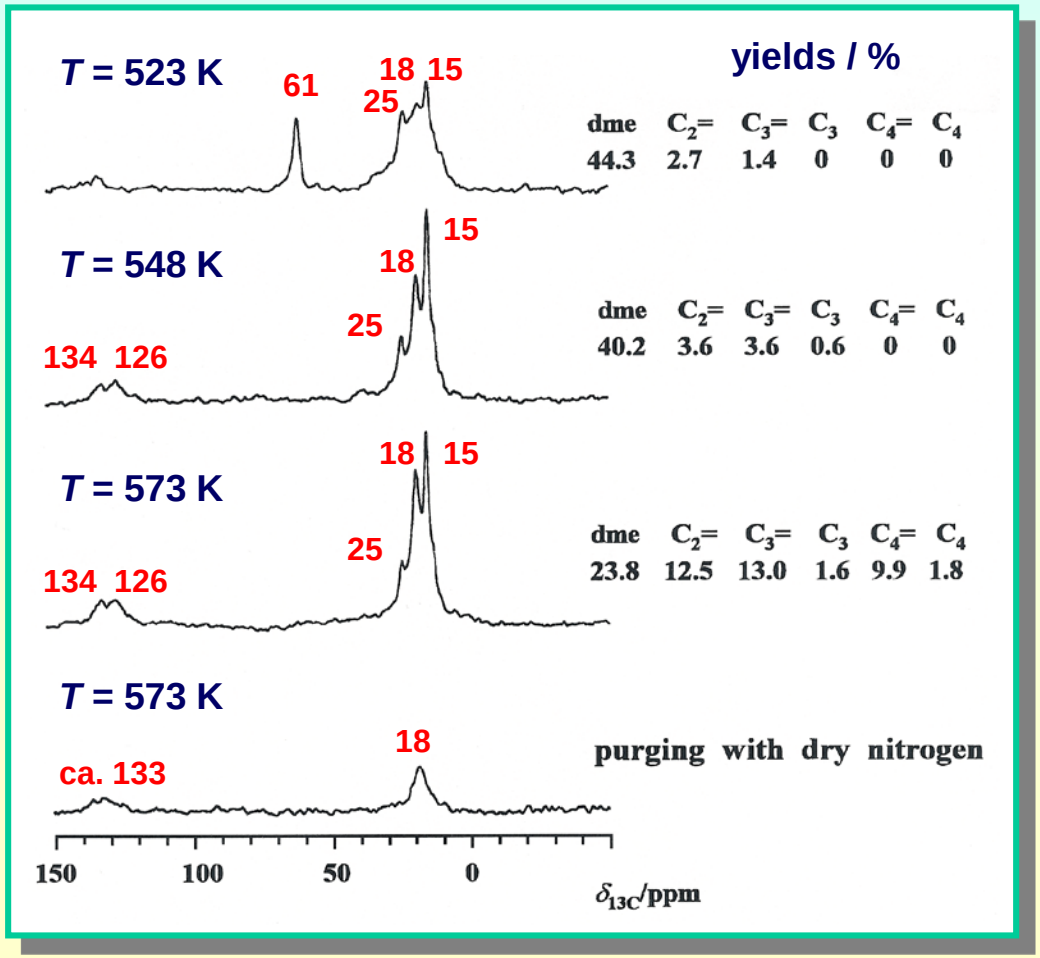
spinning (2 kHz) MAS NMR rotor reactor

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



II: Steady-state conditions

***In situ* ^{13}C MAS NMR study of the hydrocarbon pool on H-ZSM-5, M. Seiler et al., Catal. Lett. 62 (1999) 139**



→ **mixture of olefinic and aromatic compounds, e.g.:**

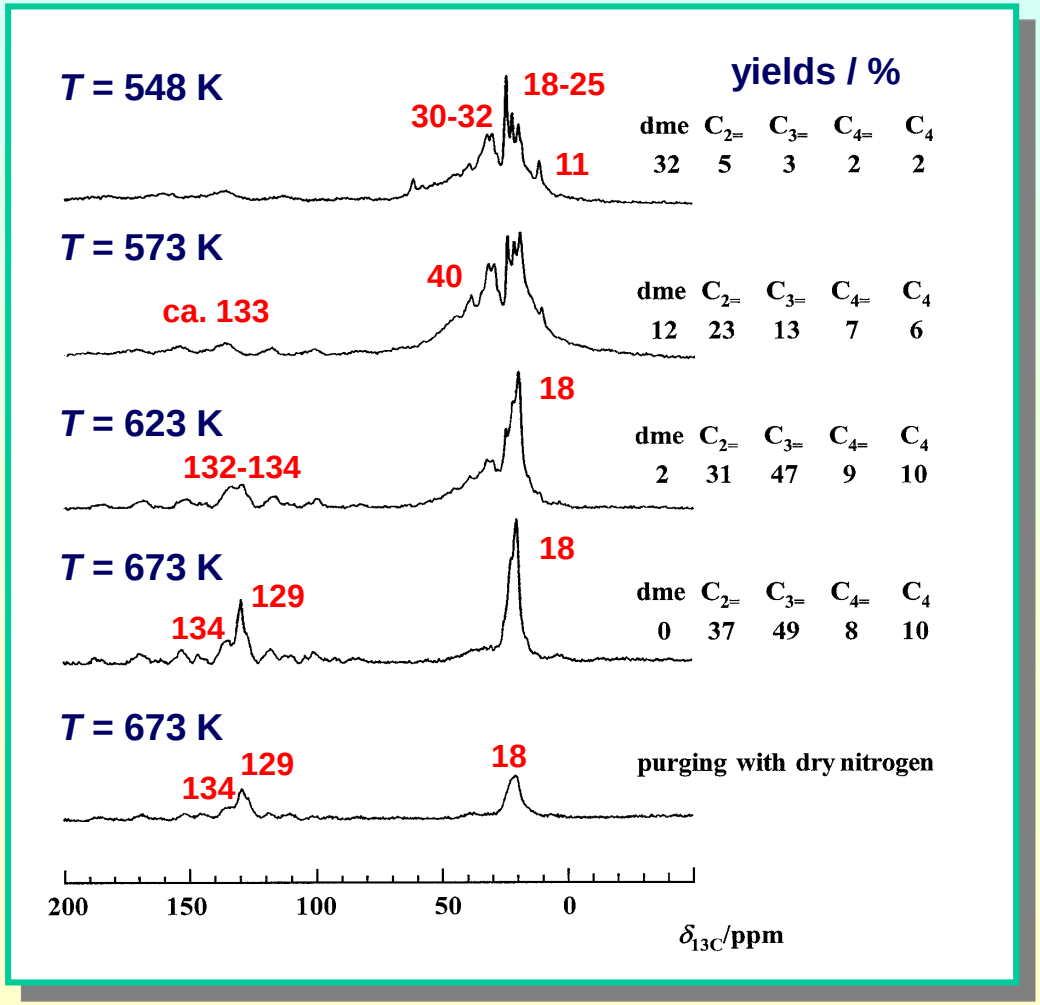
3-hexene (14.4, 25.9, 131.2 ppm)
2,4-hexadiene (17.2, 126.2, 132.5 ppm)
....
hexamethylbenzene (17.6, 132.1 ppm)

→ **polymethylaromatics remain after purging:**

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 on H-SAPO-34, M. Hunger et al., Catal. Lett. 1-2 (2001) 61



***T* ≤ 573 K:**

→ **mixture of olefinic and aromatic compounds, e.g.:**

- **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)**

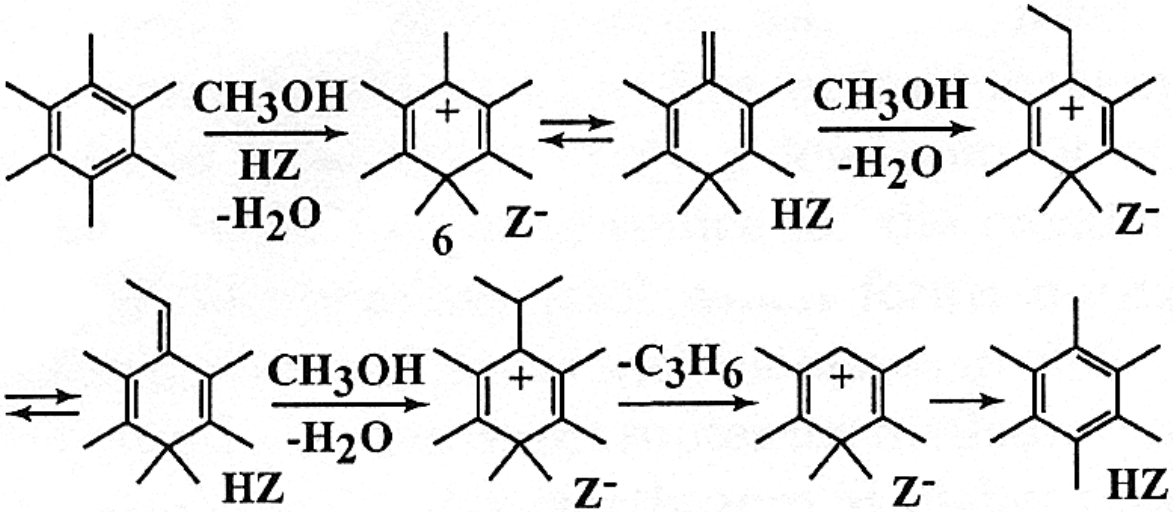
***T* > 573 K:**

→ **domination of polymethyl-aromatics:**

- **toluene (20.3, 128.5, 129.0 ppm)**
- **....**
- **tetramethylbenzene (18.9, 131.1, 134.0 ppm)**
- **hexamethylbenzene (17.6, 132.1 ppm)**

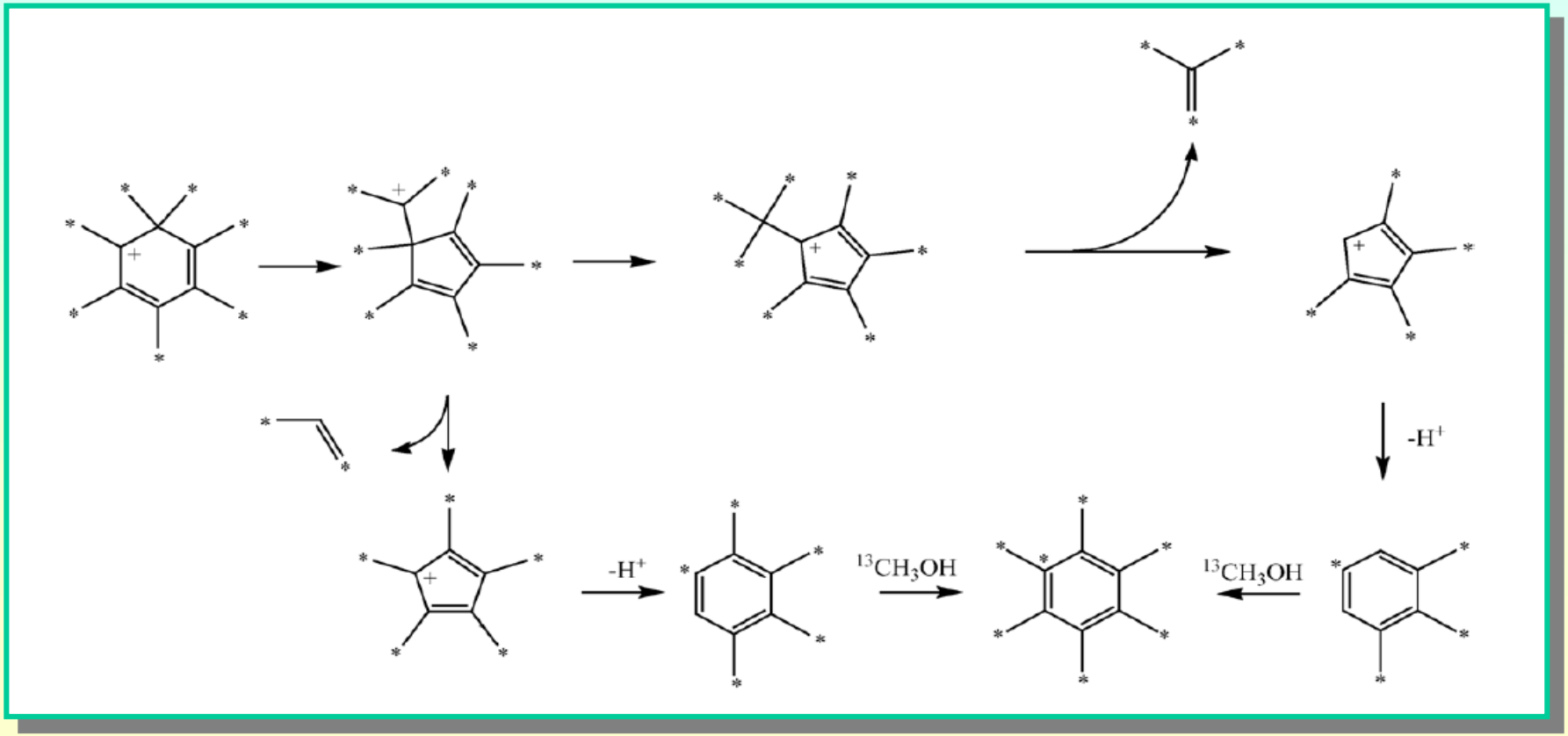
II: Steady-state conditions

Alkyl chain growing by exocyclic methylation reaction, J.F. Haw et al., Acc. Chem. Res. 36 (2003) 317



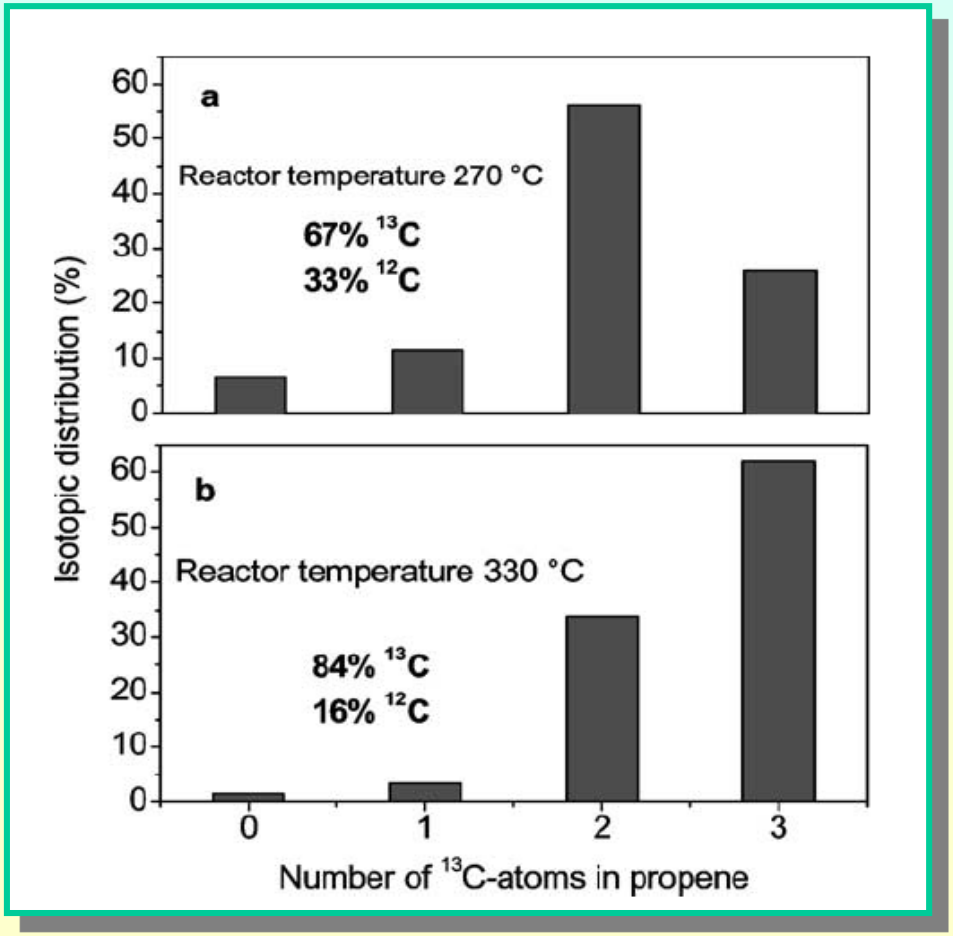
II: Steady-state conditions

Alkyl chain growing by paring reaction, M. Bjorgen et al., J. Catal. 221 (2004) 1:



II: Steady-state conditions

Co-reaction of $^{13}CH_3OH$ and $^{12}C_6H_6$ on zeolite H-Beta (12-ring channels), M. Bjorgen et al., J. Catal. 221 (2004) 1



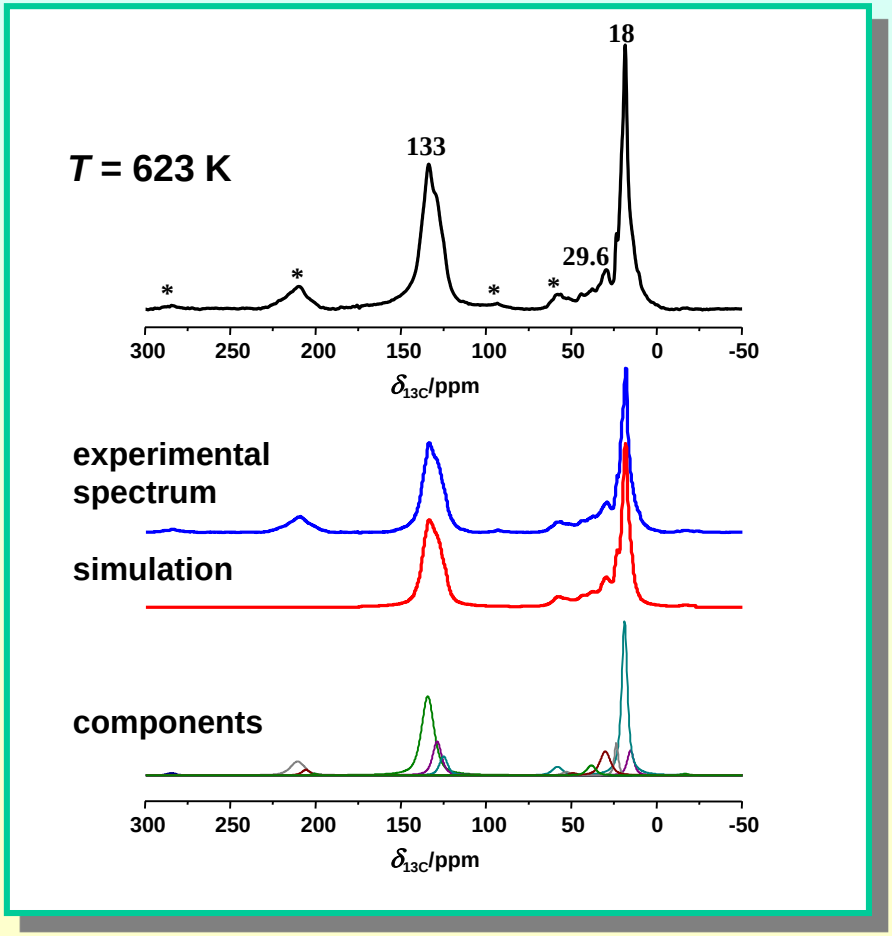
→

the majority of propene (and isobutene) product molecules contain ^{12}C atoms from non-enriched benzene rings

the isotopic distribution is in agreement with the paring reaction mechanism (on H-Beta)

II: Steady-state conditions

Evaluation of ^{13}C MAS NMR spectra recorded after sequential conversion of $^{12}CH_3OH$ for 6 h and $^{13}CH_3OH$ for 2 h on H-SAPO-34 (*W/F* = 25 gh/mol)



determination of the absolute number of ^{13}C atoms by spin-counting in comparison with an external intensity standard

relative intensities of ^{13}C atoms at 15-30 ppm and 125-135 ppm give distribution of carbon atoms in alkyl groups and aromatic rings, respectively

II: Steady-state conditions

Study of ^{13}C scrambling by sequential conversion of $^{12}CH_3OH$ for 6 h and $^{13}CH_3OH$ for 2 h on H-SAPO-34 (*W/F* = 25 gh/mol)

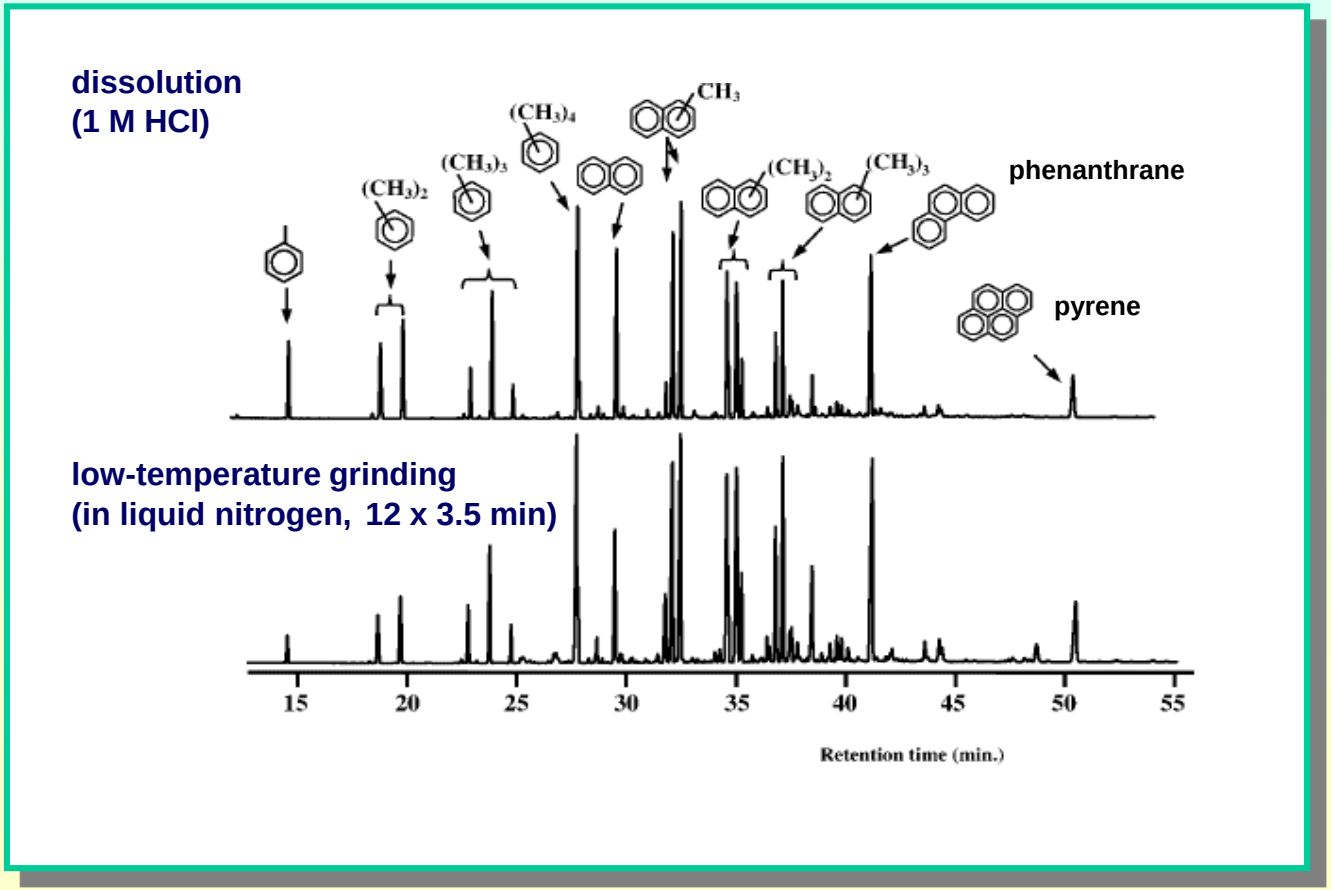
Reaction temperature and type of ^{13}C atoms	Number of ^{13}C atoms for continuous conversion of $^{13}CH_3OH$	Number of ^{13}C atoms for sequential conversion of $^{12}CH_3OH$ and $^{13}CH_3OH$	Comparison with continuous conversion of $^{13}CH_3OH$
T = 623 K in alkyl groups in aromatic rings	 2.74 mmol/g 3.28 mmol/g	 0.61 mmol/g 1.00 mmol/g	 22.3 % 30.5 %
T = 673 K in alkyl groups in aromatic rings	 0.69 mmol/g 3.33 mmol/g	 0.21 mmol/g 0.65 mmol/g	 30.4 % 19.5 %

→ **strong ^{13}C scrambling of carbon atoms in aromatic rings support paring mechanism on H-SAPO-34**

III. Deactivation of MTH catalysts by coke formation

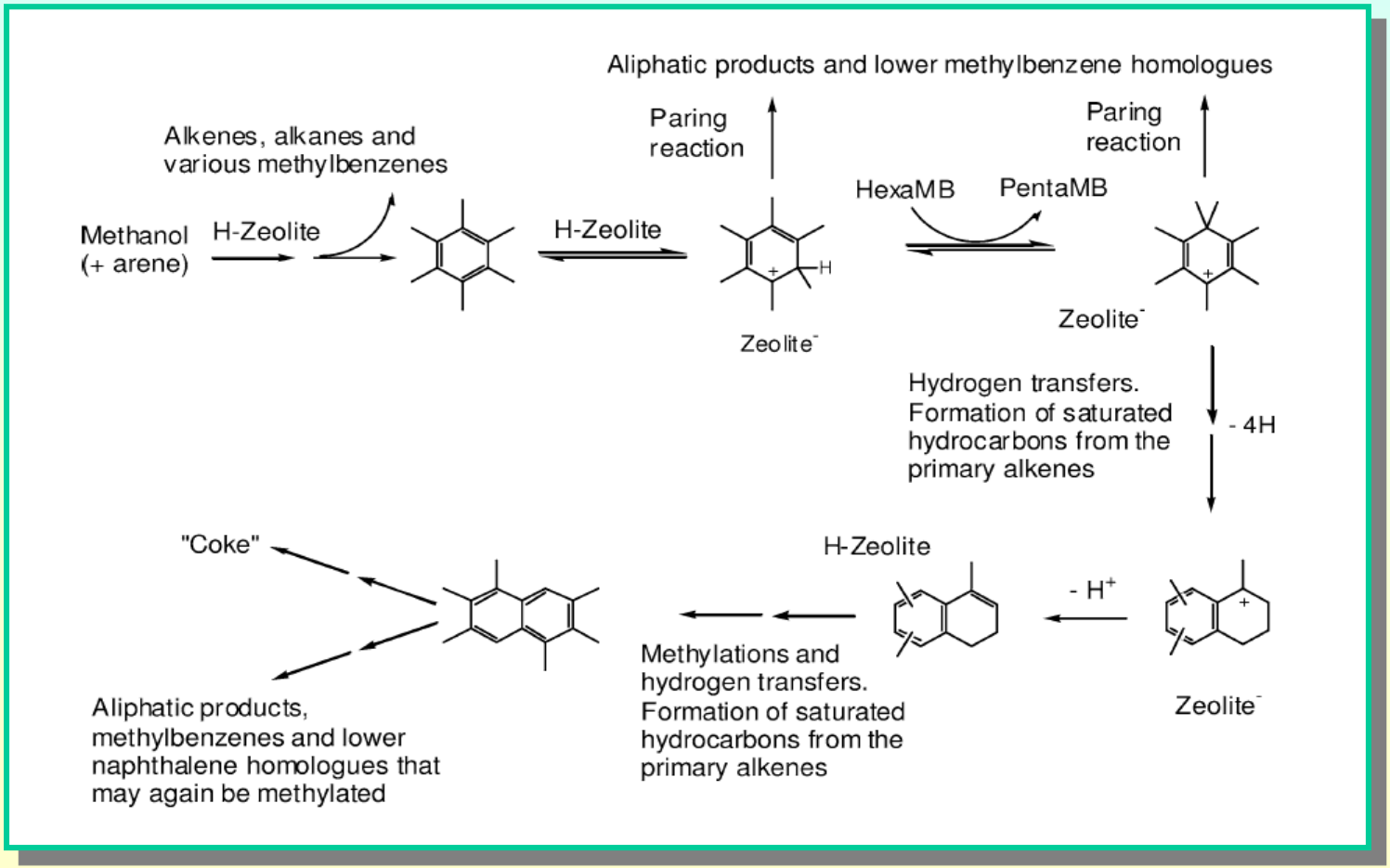
III: Catalyst deactivation

***Ex situ* study of coke deposits via dissolution and low-temperature grinding of used H-SAPO-34 (4 ml methanol at 673 K), H. Fu et al., Catal. Lett. 76 (2001) 89**



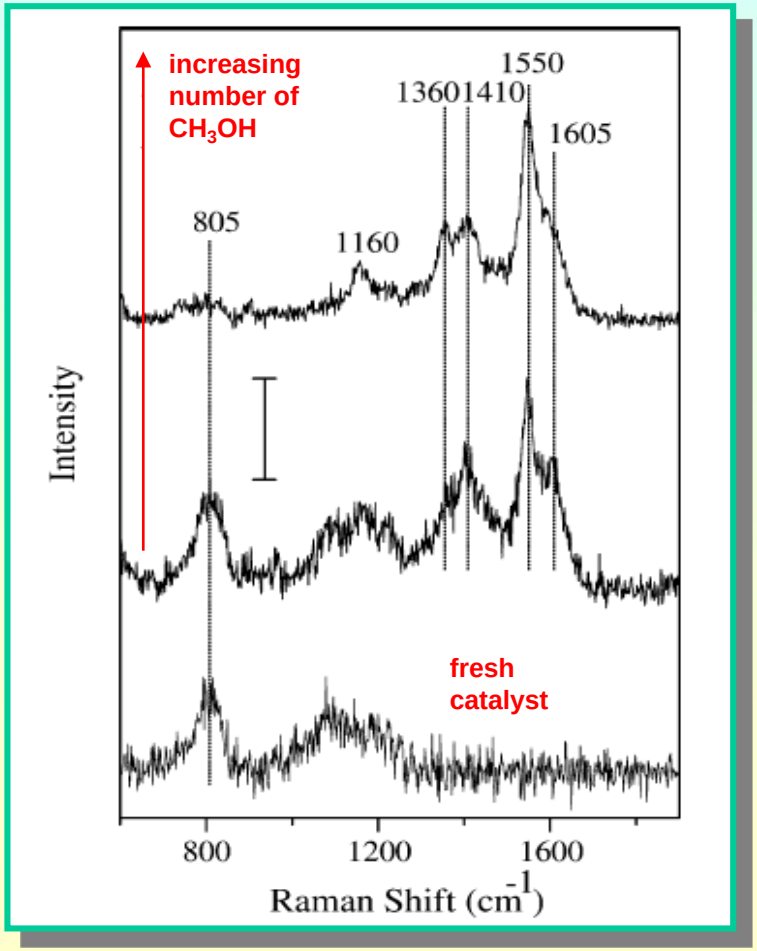
III: Catalyst deactivation

***Ex situ* study of coke formation by sequential conversion of hexamethyl-benzene on H-Beta at 598 K, M. Bjorgen et al., J. Catal. 215 (2003) 30**



III: Catalyst deactivation

In situ Raman investigation of coke formation on H-ZSM-5 at 473 K, Y.T. Chua et al., J. Catal. 213 (2003) 39



Raman band assignments of retained hydrocarbons

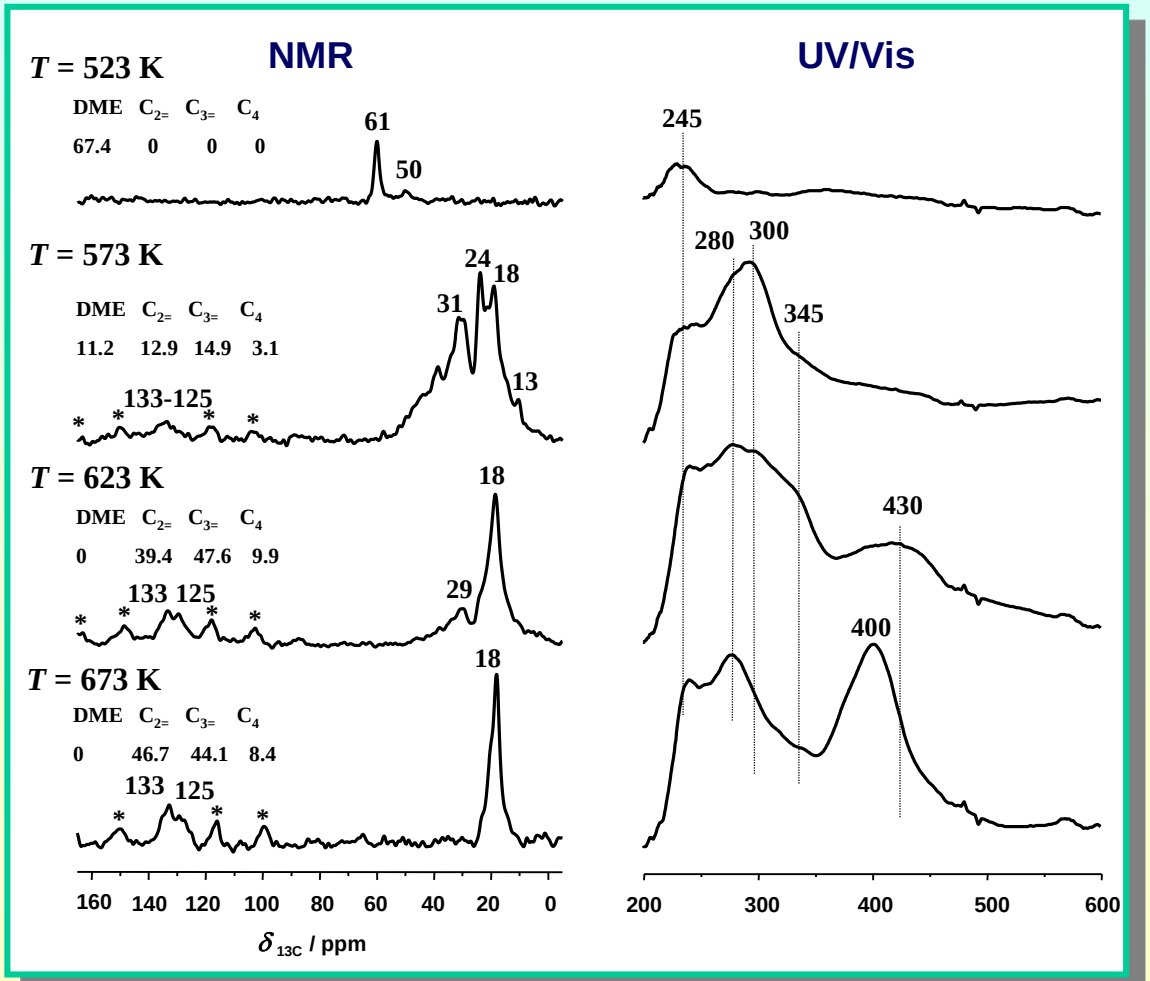
Raman shift (cm^{-1})	Raman band assignments
1605–1615	Ring stretches of polyaromatic species
1360–1410	Ring stretches of polyaromatic species
1200–1210	C–C stretches of polyaromatic species
1545–1550	C=C stretches of conjugated olefins
1483	In-phase C=C stretch of cyclopentadienyl

→ **polyolefins, cyclopentadienyl species, and polyaromatics were identified among the retained hydrocarbons**

→ **intensity distribution indicates formation of chain-like polyaromatics (anthracene, pentacene)**

III: Catalyst deactivation

In situ ^{13}C MAS NMR-UV/Vis spectroscopy of coke formation on H-SAPO-34 at 523 to 673 K for 3 h under continuous-flow conditions



NMR:

- quantitative evaluation
- separation of alkyl groups and aromatics
- rotor reactor comparable with fixed-bed reactor

UV/Vis:

- sensitive for carbenium cations
- separation of aromatics and polycyclic aromatics

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132-139.

III: Catalyst deactivation

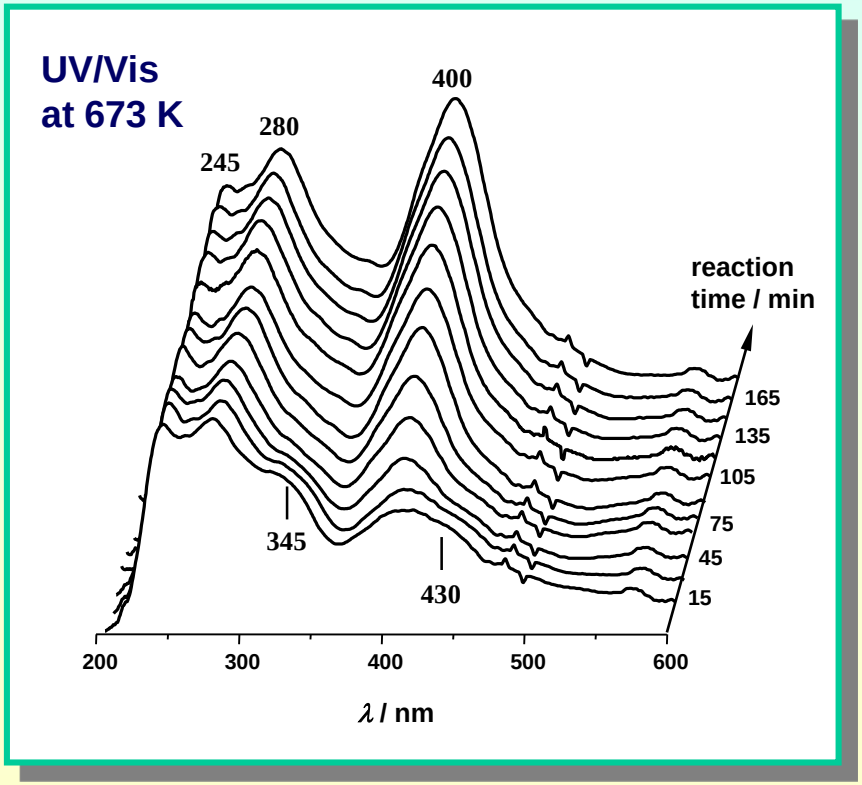
Assignments of UV/Vis bands (π-π^* transitions) observed during methanol-to-olefin conversion on H-SAPO-34 at 523-673 K:

Bands at ν / nm	Assignments
220-245	neutral dienes
254-280	neutral aromatics and polyalkylaromatics
270	neutral phenols
300-320	monoenylic carbenium ions
345-380	dienylic carbenium ions
390-410	neutral polycyclic aromatics
430-470	trienylic carbenium ions

Ref.: H.G. Karge et al., Stud. Surf. Sci. Catal. 49 (1989) 1327; J. Mohan, Organic Spectroscopy Principles and Applications, Alpha Science International Ltd., Harrow, U.K., 2002, p. 137; A.V. Demidov, Mater. Chem. Phys. 39 (1994) 13; I. Kirisci et al., Chem. Rev. 99 (1999) 2085; R. Ahmad et al., J. Catal. 218 (2003) 365-374.

III: Catalyst deactivation

***In situ* UV/Vis study of coke formation during methanol conversion on H-SAPO-34 at 673 K (*W/F* = 25 gh/mol):**



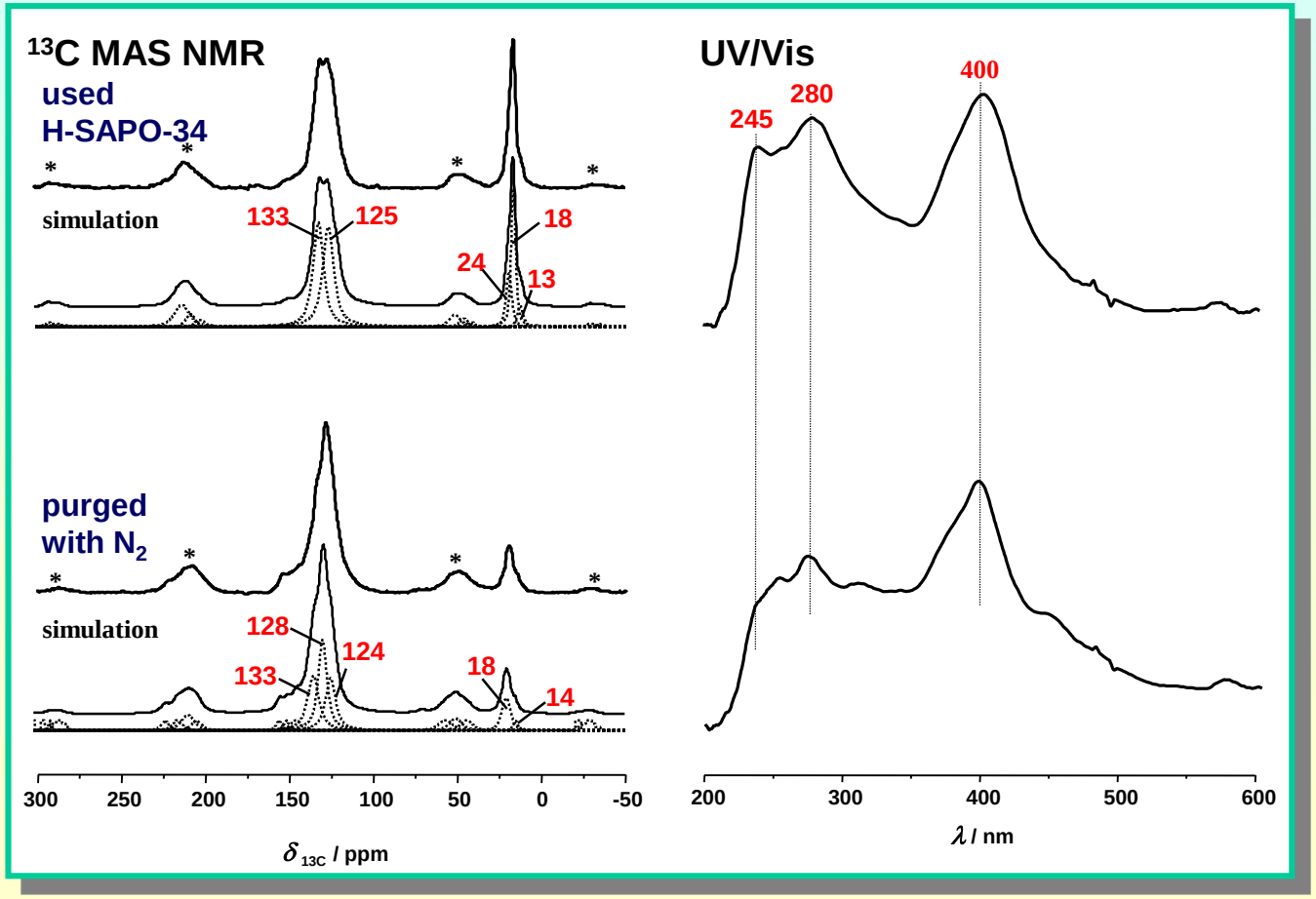
continuous increase of band at 400 nm indicates formation of polycyclic aromatics at 673 K

simultaneously, the bands of di- and trienylic carbenium ions decrease (345 nm, 430 nm)

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132-139.

Study of the stability of organic deposits

Occluded and stable organic deposits formed by conversion of methanol (*W/F* = 25 gh/mol) on H-SAPO-34 at 673 K for 3 h



decrease of dienes (245 nm) and polyalkylaromatics (280 nm)

stable polycyclic aromatics (400 nm)

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132-139.

III: Catalyst deactivation

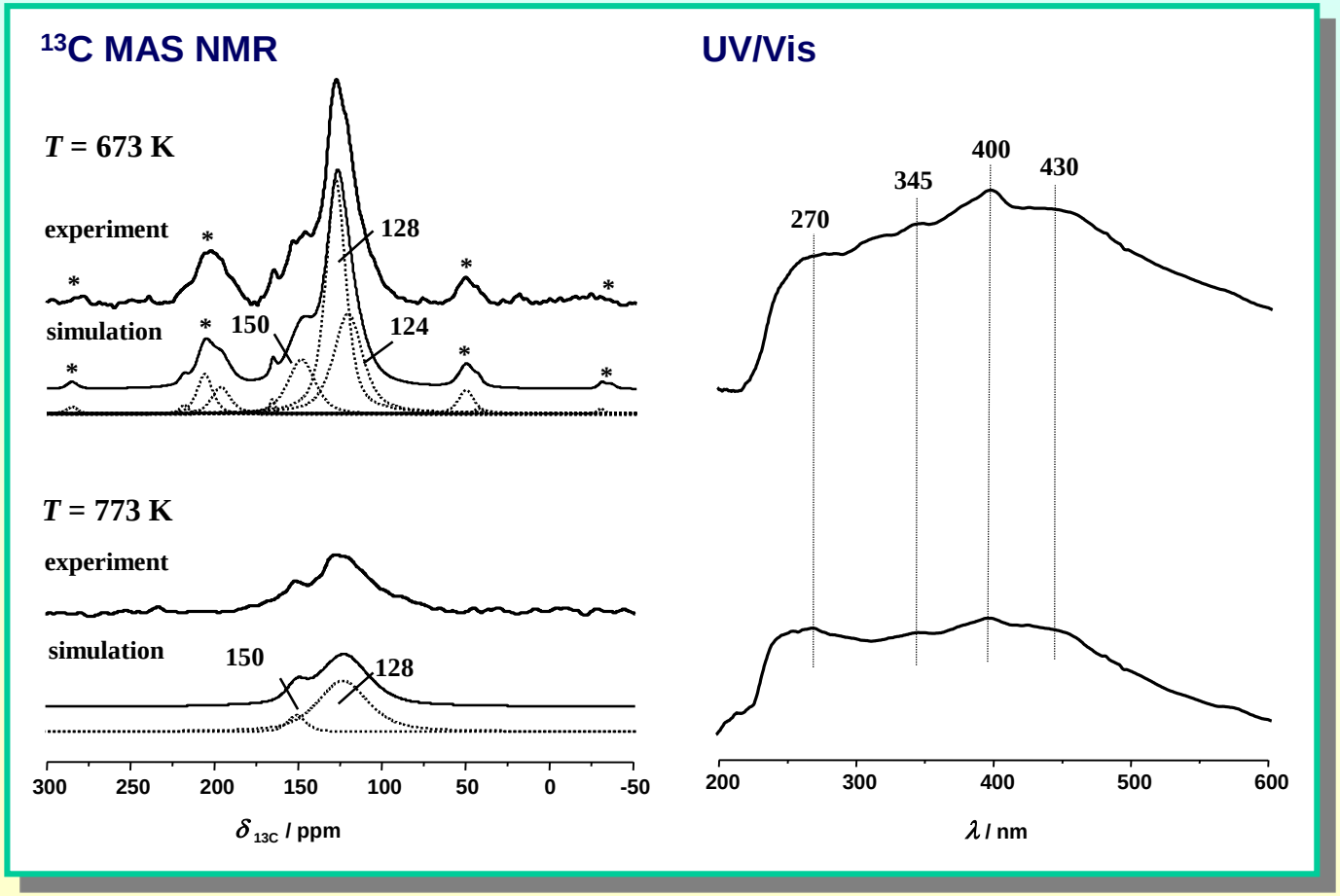
Quantitative evaluation of the ^{13}C MAS NMR spectra of used H-SAPO-34 before and after purging with N_2

Signal at δ_{13C} /ppm	Assignments	Number in mmol/g		
		reaction at 623 K	reaction at 673 K	purging with N_2 at 673 K
16-21	methyl groups bound to aromatics	1.87	0.53	0.31
14-15 and 22-29	ethyl groups bound to aromatics	0.21	0.08	0.03
23-24 and 33-37	isopropyl groups bound to aromatics	0.15	-	-
125-137	alkylated and non-alkylated aromatic rings	0.55	0.56	0.41

→ agrees with the stronger decrease of UV/Vis bands of alkylated aromatics (280 nm) than of polycyclic aromatics (400 nm)

III: Catalyst deactivation

Regeneration of the used (673 K) H-SAPO-34 by purging with synthetic air (20 vol.-% O_2, 30 ml/min) at 673 and 773 K for 2 h



decrease of all aromatics including polycyclic coke (400 nm)

new band of phenolic species (270 nm)

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132-139.

III: Catalyst deactivation

Quantitative evaluation of the ^{13}C MAS NMR spectra of used H-SAPO-34 regenerated by purging with synthetic air for 2 h

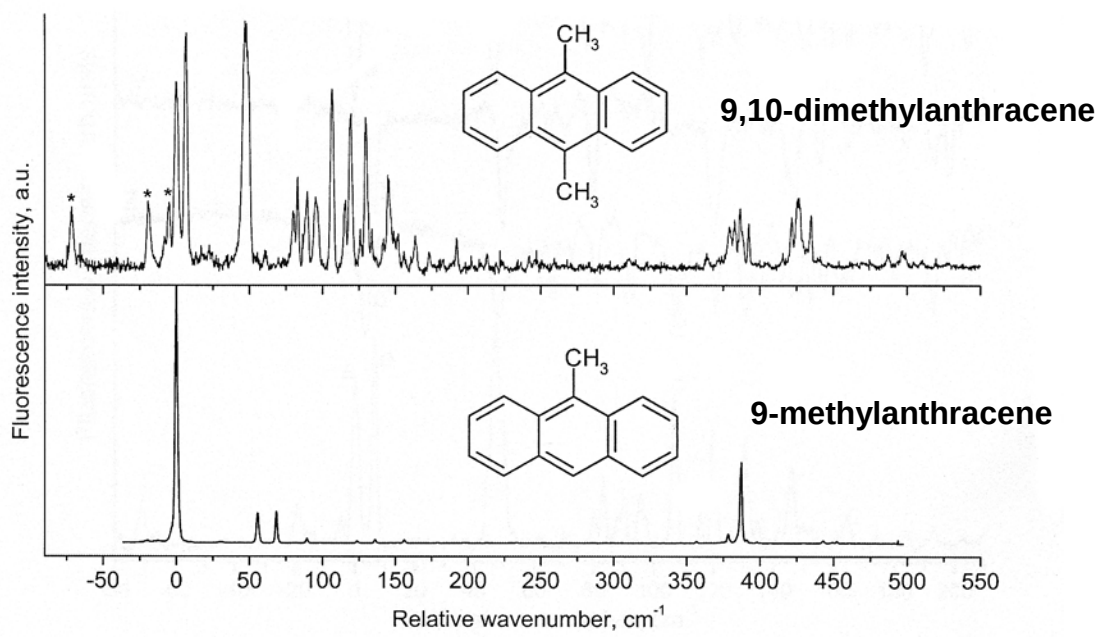
Signal at δ_{13C} /ppm	Assignments	Number in mmol/g		
		reaction at 673 K	syn. air at 673 K	syn. air at 773 K
16-21	methyl groups bound to aromatics	0.53	-	-
14-15 and 22-29	ethyl groups bound to aromatics	0.08	-	-
125-137	alkylated and non-alkylated aromatic rings	0.56	0.17	0.05
145-155	carbon in aromatics bound to oxygen atoms	-	0.45	0.13

→ nearly total removal of aromatics (UV/Vis bands at 280 nm and 400 nm), but formation of oxygenated spieces (270 nm)

III: Catalyst deactivation

Possible assignment of the coke band at ca. 400 nm, Y. Stepanenko et al., J. Mol. Spectrosc. 233 (2005) 15

Laser induced fluorenscence excitation spectra



chain-like polyaromatics

in agreement with assignment of Raman bands by Chua et al.

Summary

- depending on the level of impurities present in the methanol feed, methoxy groups play a key role during the induction period
- the composition of the hydrocarbon pool formed under steady-state conditions depends on the type of zeolite (H-ZSM-5: more olefinic species; H-SAPO-34: more polyalkylaromatics) and the reaction parameters
- the paring mechanism is the dominating reaction route of the formation of large alkyl compounds in H-SAPO-34 under steady-state conditions
- on H-SAPO-34, coke formation starts already at 673 K and consists mainly of chain-like polycyclic aromatics (UV/Vis band at 400 nm)
- UV/Vis spectroscopy could be an interesting tool for the *in situ* watching of coke formation on MTH catalysts in industrial processes

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