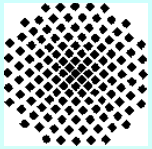
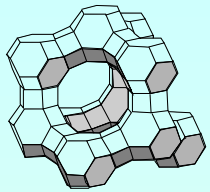
University of Stuttgart

Institute of
Chemical Technology





In situ solid-state NMR investigations of the conversion of methanol on acidic zeolites

Michael Hunger

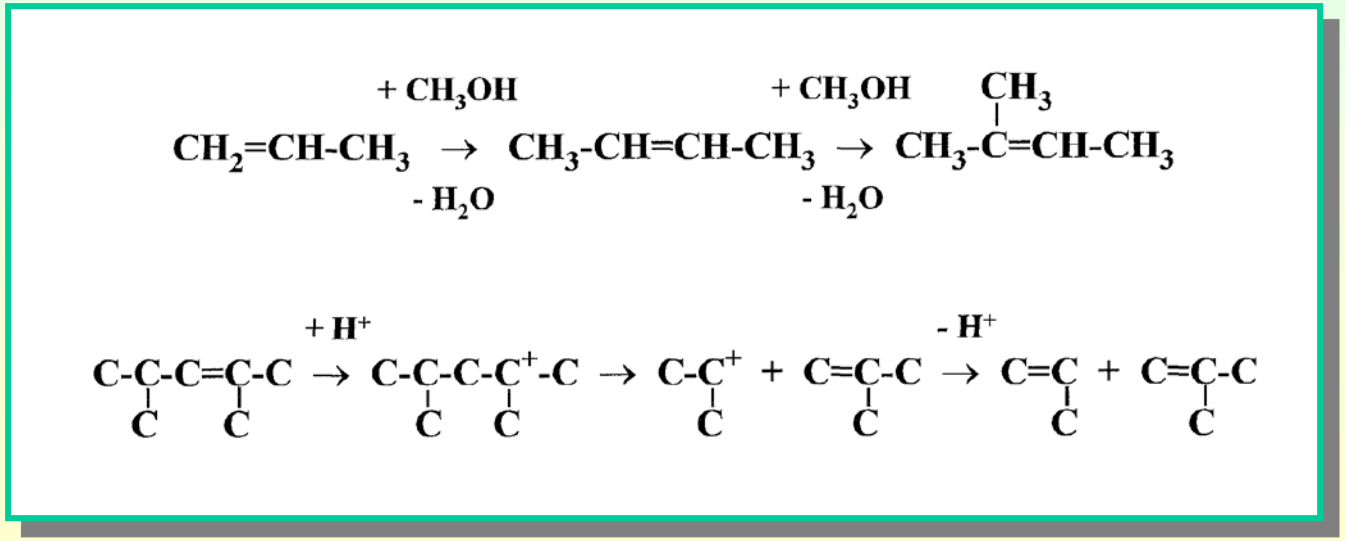
Institute of Chemical Technology

University of Stuttgart, Germany

Methanol to olefin (MTO) conversion on acidic zeolites

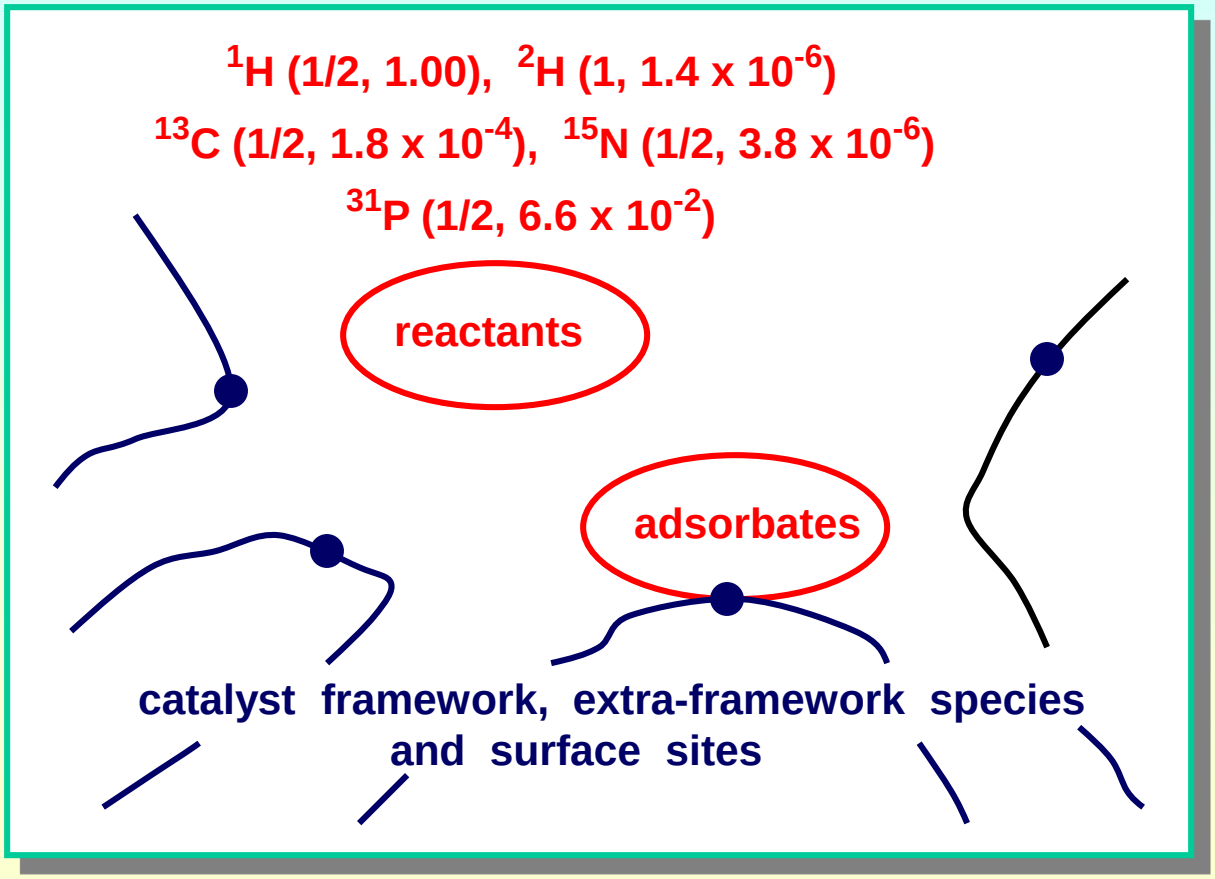
reaction mechanisms proposed in the literature:

- **carbene mechanism (Swabb and Gates)**
- **oxonium ylide mechanism (Berg and Olah)**
- **carbon-pool mechanism (Haag, Hoelderich, Kolboe)**



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

Examples of nuclei accessible for in situ NMR in heterogeneous catalysis



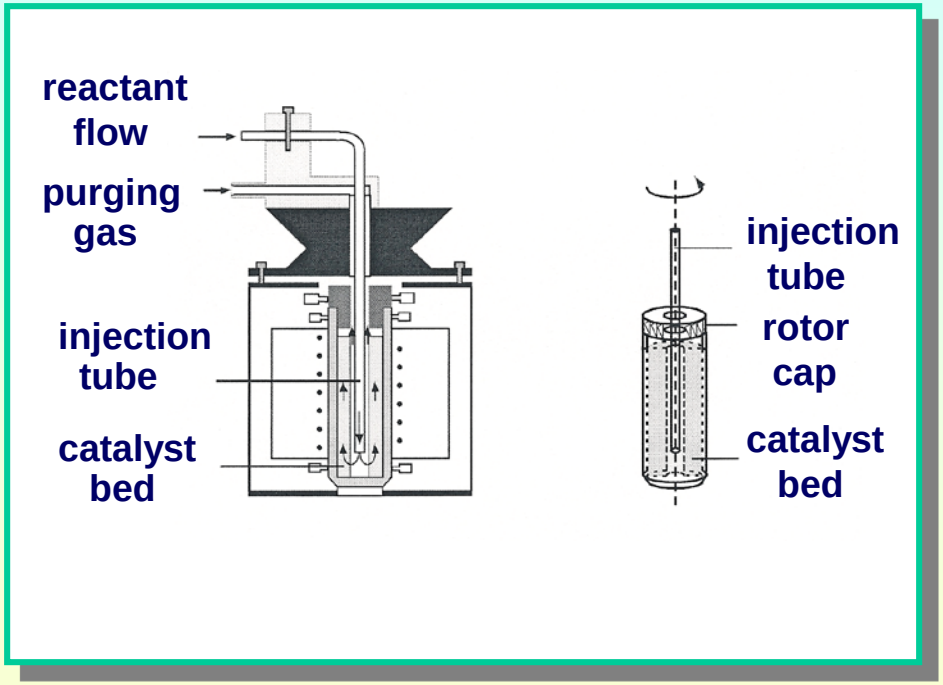
^{7}Li (3/2, 0.27)
^{11}B (3/2, 0.13)
^{17}O (5/2, 1.1 x 10^{-5})
^{23}Na (3/2, 9.2 x 10^{-2})
^{27}Al (5/2, 0.21)
^{29}Si (1/2, 3.7 x 10^{-4})
^{31}P (1/2, 6.6 x 10^{-2})
^{51}V (7/2, 0.38)
^{67}Zn (5/2, 1.2 x 10^{-2})
^{71}Ga (3/2, 5.6 x 10^{-2})
^{133}Cs (7/2, 4.7 x 10^{-2})

isotope (nuclear spin, relative sensitivity in comparison with ^{1}H)

Contents

- technique of continuous-flow (CF) MAS NMR spectroscopy
- investigation of the methanol conversion on acidic zeolites under steady state conditions
- role of Broensted acid sites during methanol conversion
- reactivity of surface methoxy groups studied by stopped-flow experiments
- CF MAS NMR/UV Vis spectroscopic studies of the initiation of the methanol to hydrocarbon conversion

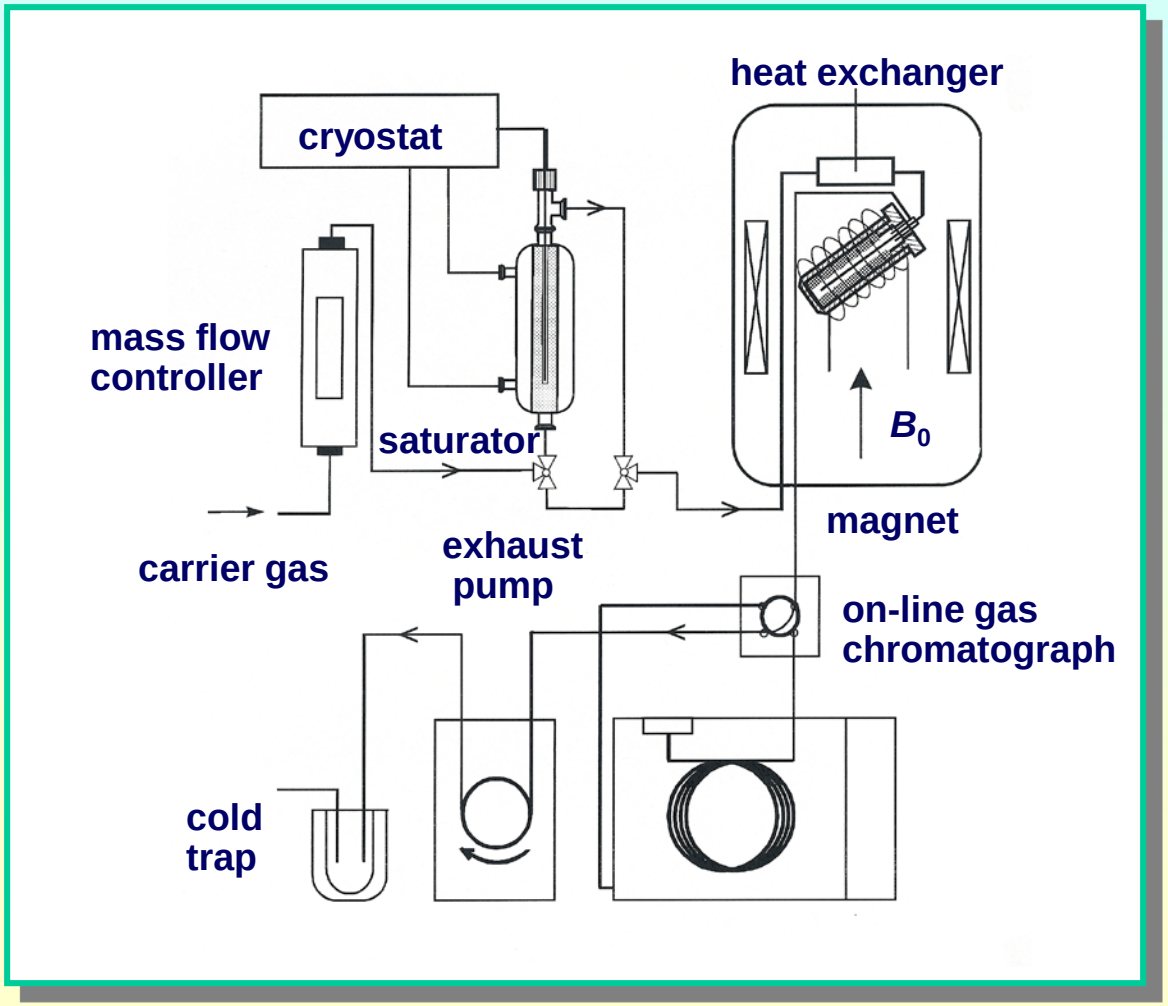
Continuous-flow (CF) MAS NMR technique



- **continuous injection of reactants into a spinning MAS NMR rotor reactor (*T* < 923 K)**

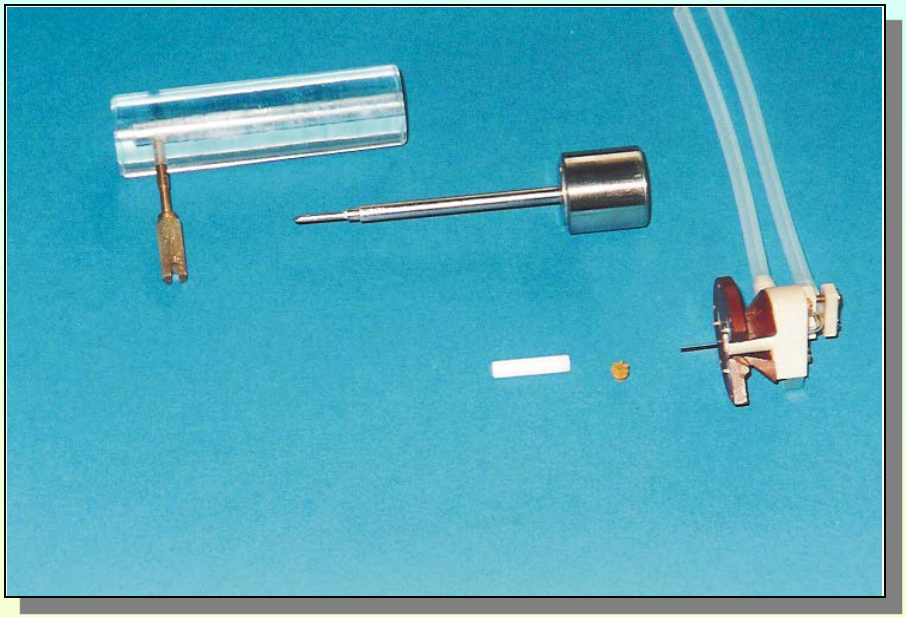
M. Hunger, T. Horvath, J. Chem. Soc., Chem. Commun. (1995) 1423.

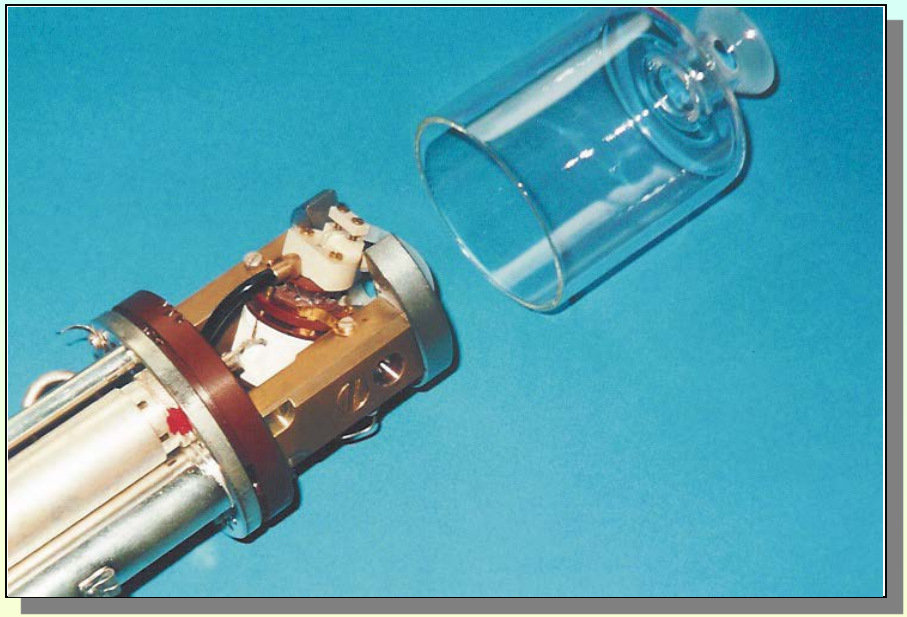
Coupling of in situ CF MAS NMR and on-line gas chromatography



M. Hunger et al., Catal. Lett. 57 (1999) 199.

Continuous-flow (CF) MAS NMR technique



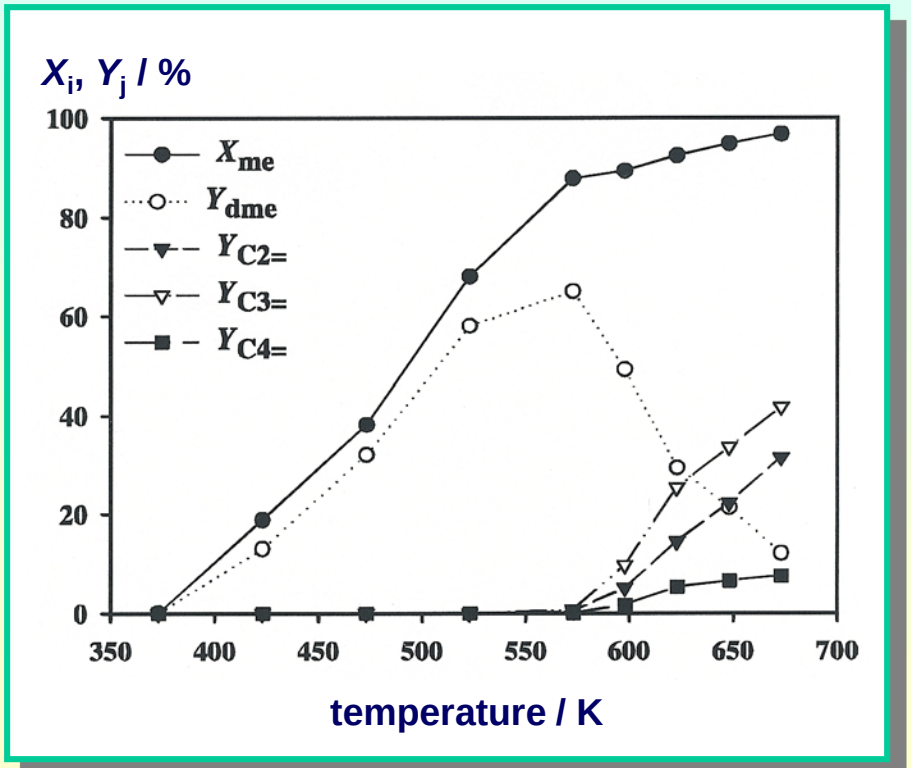


A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.

Conversion of methanol on H-ZSM-5 in a fixed-bed and in an MAS NMR rotor reactor

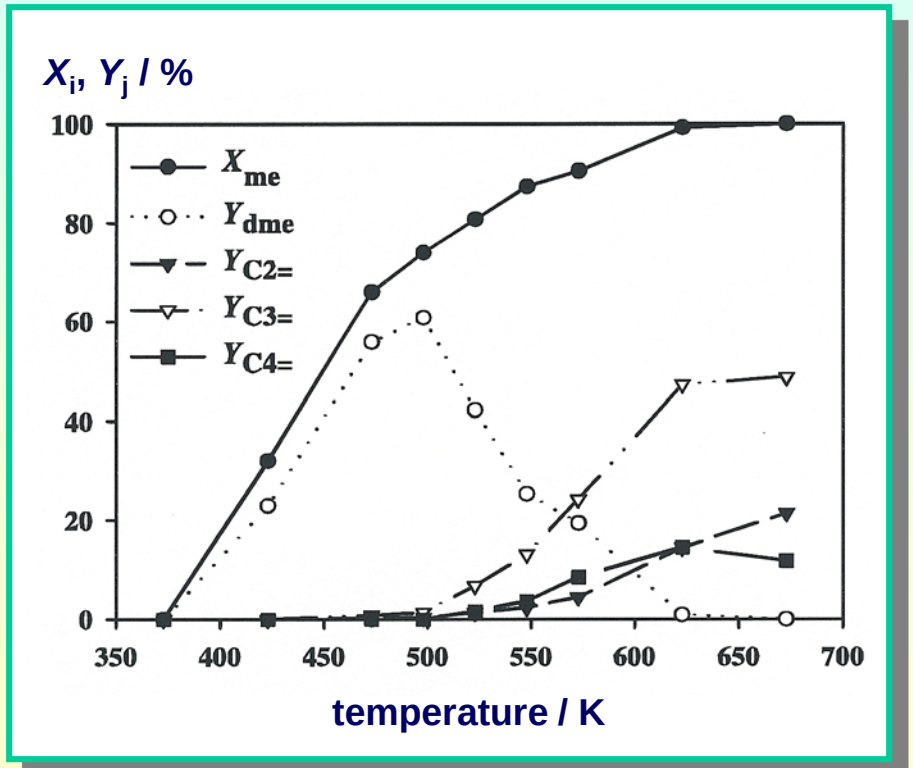
fixed-bed reactor

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



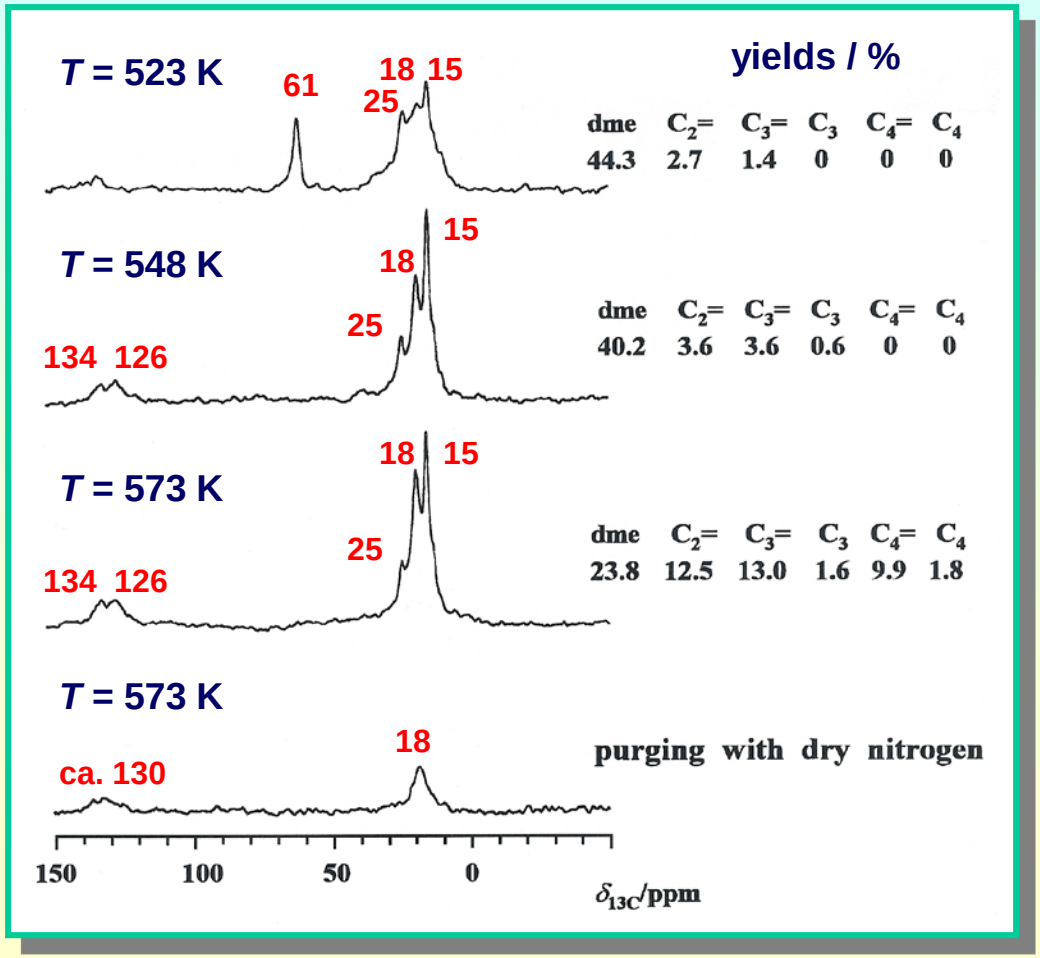
spinning (2 kHz) MAS NMR rotor reactor

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



A. Buchholz, diploma thesis, University Stuttgart, 2000.

Conversion of methanol on H-ZSM-5 studied by in situ ^{13}C CF MAS NMR



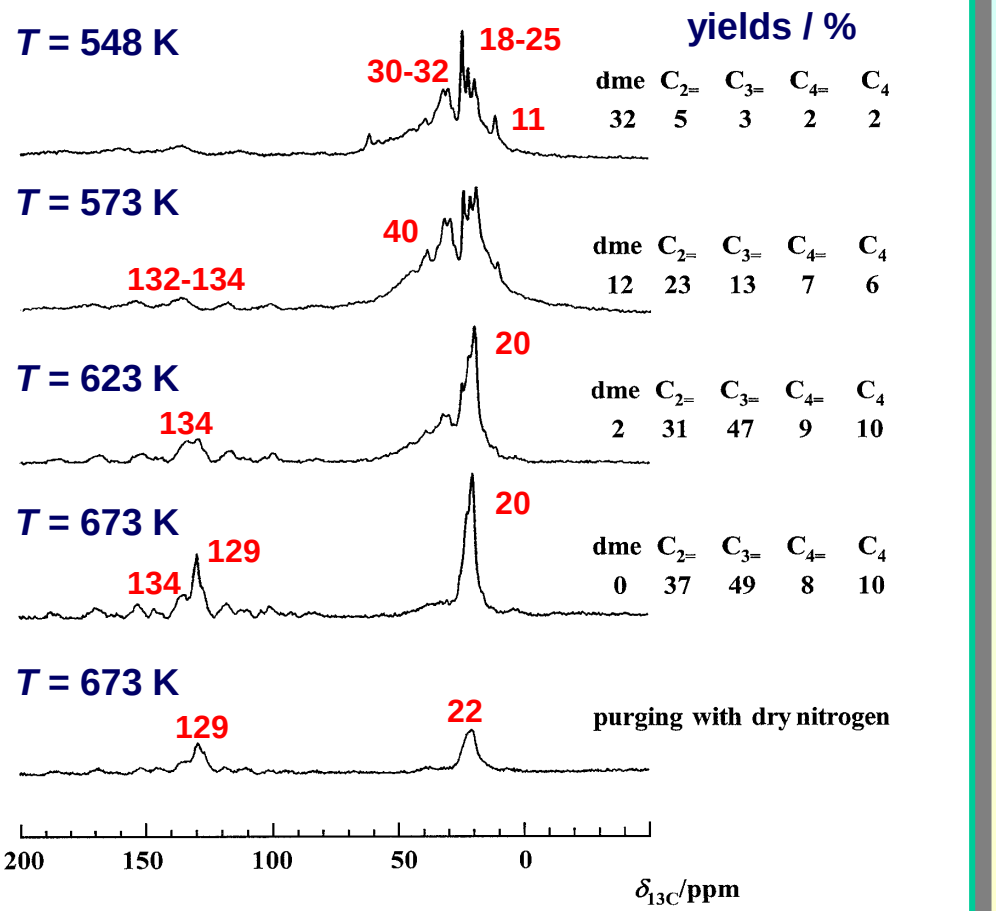
→ **aliphatic intermediates, e.g.:**
3-hexene (14.4, 25.9, 131.2 ppm)
2,3-hexadiene (17.5, 126.2, 132.5 ppm)
....

→ **olefin pool with carbon numbers of *n* > 6**

→ **aromatic adsorbates remain after purging:**
benzene (128.6 ppm)
....
hexamethylbenzene (17.6, 132.1 ppm)

M. Seiler, et al., Catal. Lett. 62 (1999) 139.

Conversion of methanol on H-SAPO-34 studied by in situ ^{13}C CF MAS NMR



***T* < 623 K:**

→ **mixture of aliphatic compounds:**

3-hexene (14.4, 25.9, 131.2 ppm)

2,3-hexadiene (17.5, 126.2, 132.5 ppm)

....

***T* > 623 K:**

→ **domination of aromatic compounds:**

benzene (128.6 ppm)

toluene (20.3, 128.5, 129.0 ppm)

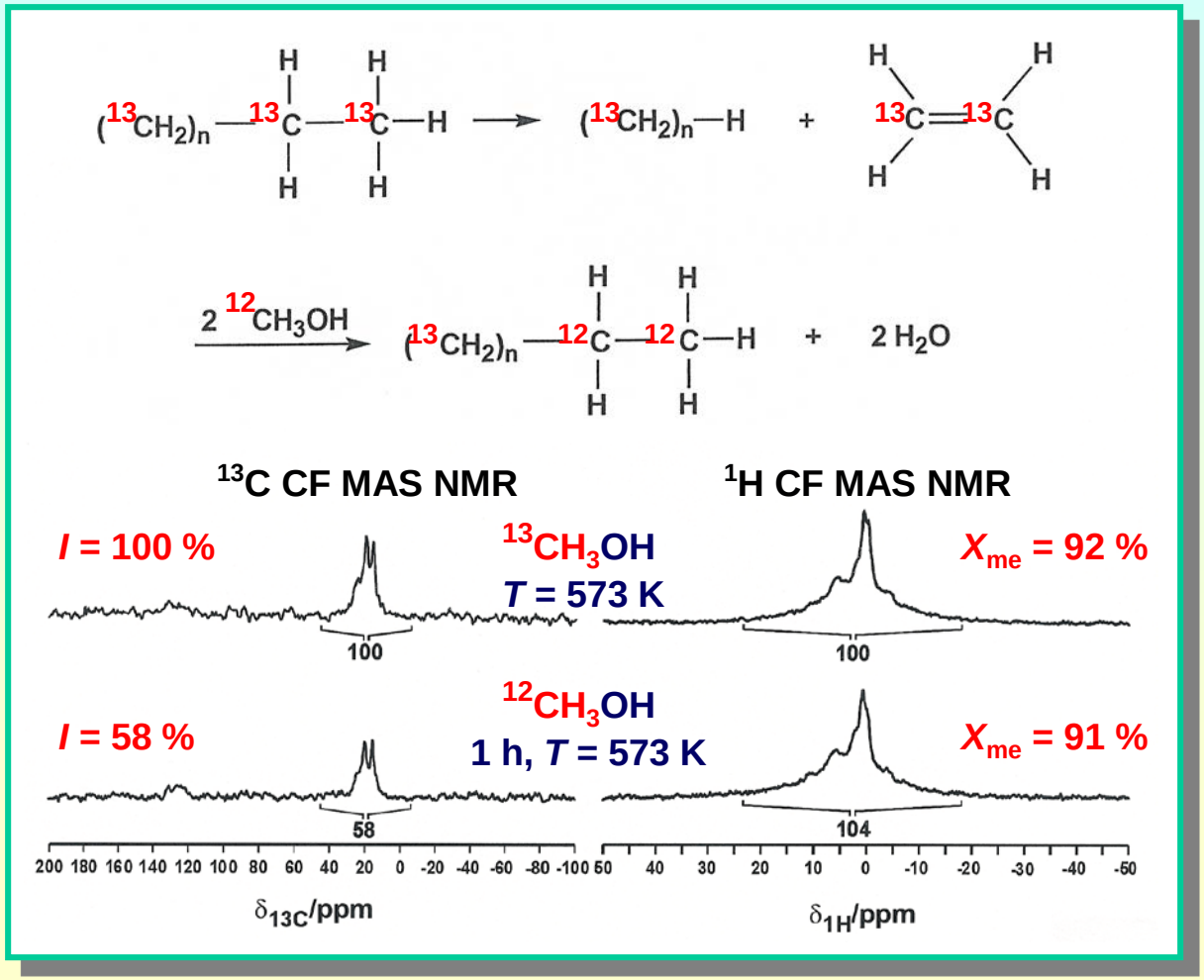
....

tetramethylbenzene (18.9, 131.1, 134 ppm)

hexamethylbenzene (17.6, 132.1 ppm)

M. Hunger, et al., Catal. Lett. 1-2 (2001) 61.

Role of the carbon pool in the MTO process on H-ZSM-5



switching of the reactant flow induces a decrease of the ^{13}C-isotopes in the alkyl groups:

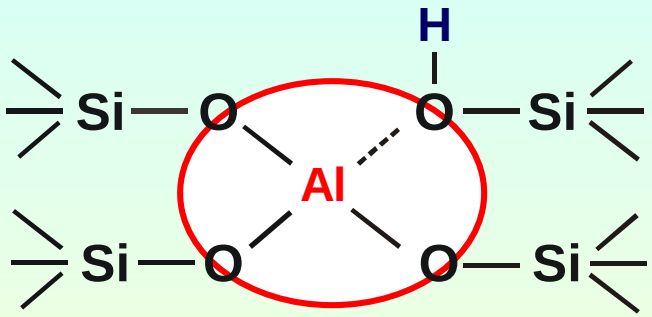
→ **alkyl groups are involved in the formation of olefins**

→ **carbon pool plays an active role in the MTO process**

M. Seiler et al., Catal. Lett. 88 (2003) 187.

State of SiOHAl groups in H-ZSM-5 during the MTO process

reactant / adsorbat



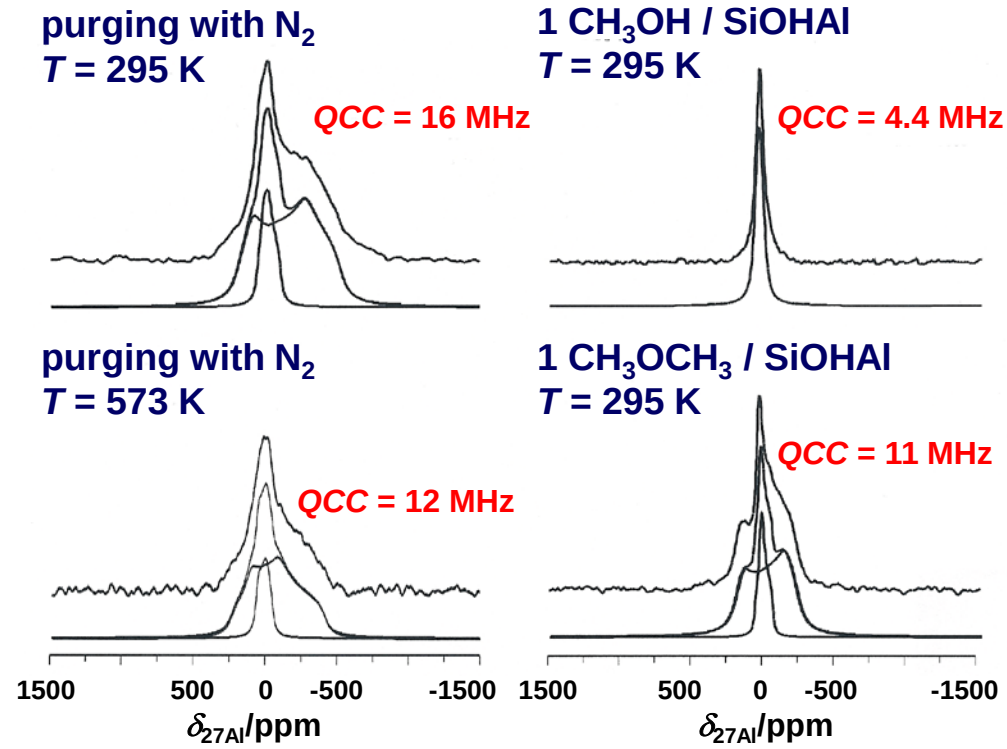
- electric field gradient :

$$V_{zz} = eq$$

- quadrupole coupling constant:

$$QCC = \frac{e^2qQ}{h}$$

^{27}Al spin-echo NMR experiments



M. Seiler et al., J. Phys. Chem. B 105 (2001) 8143.

NMR parameters of ^{27}Al nuclei during the MTO process

reactant / adsorbate	*QCC*	$\Delta\nu_{1/2}^{MAS}$*
calcined H-ZSM-5	16 MHz	36 kHz / 350 ppm
methoxy/H-ZSM-5	13 MHz	25 kHz / 235 ppm
1 CH_3OCH_3/SiOHAl	11 MHz	17 kHz / 165 ppm
1 CH_3OH/SiOHAl	4.4 MHz	2.8 kHz / 26.5 ppm
n H_2O/H-ZSM-5	2.0 MHz	0.6 kHz / 5.5 ppm

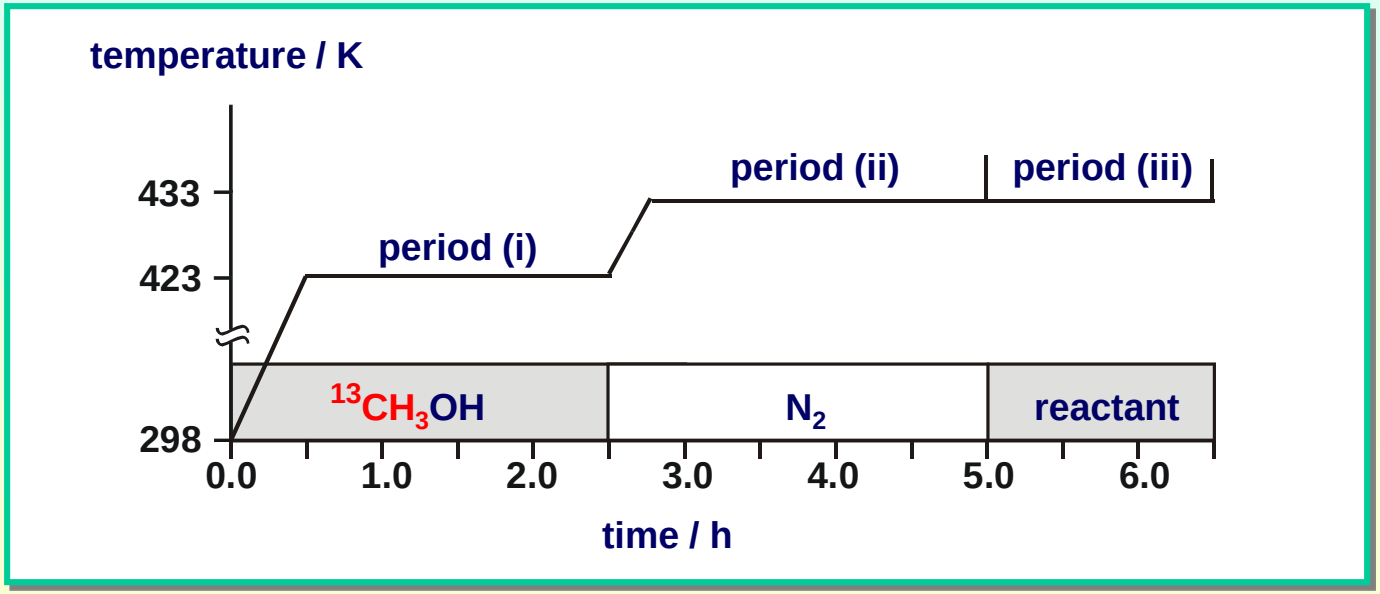
*: B_0 = 9.4 T

→ absence of narrow ^{27}Al MAS NMR signals indicates that no adsorption of CH_3OH and H_2O occurs at SiOHAl groups under reaction conditions

M. Seiler et al., J. Phys. Chem. B 105 (2001) 8143;
Wang et al., Chem. Phys. Lett. 370 (2003) 88.

Study of surface methoxy groups by in situ SF (stopped-flow) MAS NMR

- **selective preparation of adsorbate complexes by purging the volatile reactants in period (ii)**

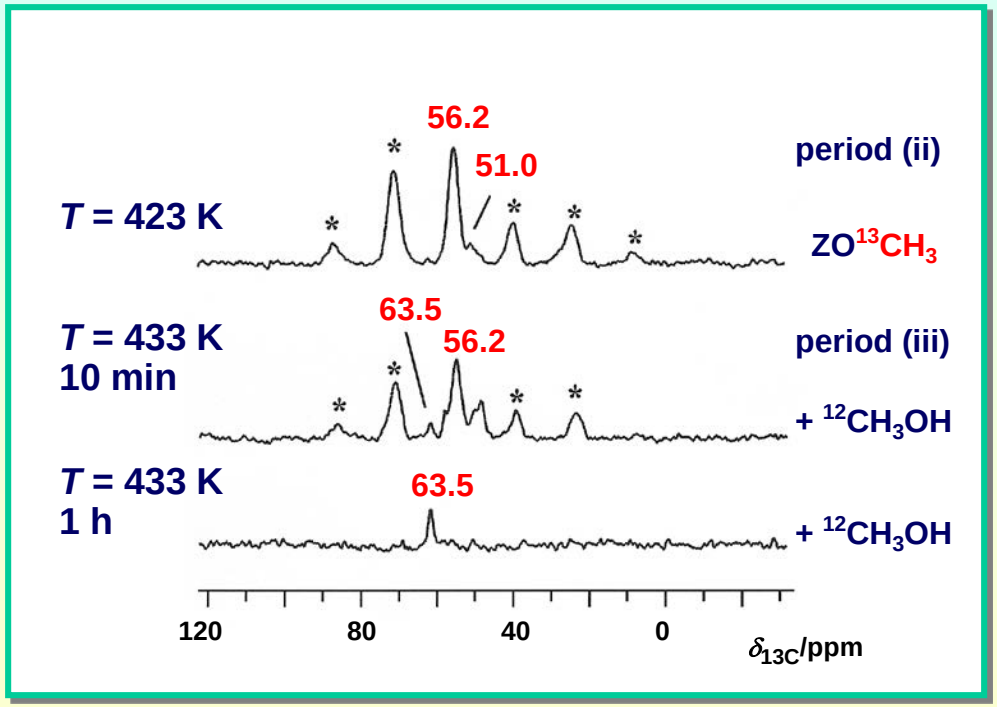


→ **investigation of the reactivity of intermediates**

W. Wang et al., J. Phys. Chem. B 105 (2001) 12553.

Reaction of methoxy groups with methanol on acidic zeolites

- ^{13}C SF MAS NMR investigation of methoxy groups on zeolite H-Y



methanol

$^{13}CH_3OH + ZOH$

49.0 ppm

$- H_2O$ →

methoxy

$ZO^{13}CH_3$

56.2 ppm

$+ {}^{12}CH_3OH$ →

$- H_2O$

dme

$^{12}CH_3OH^{13}CH_3$

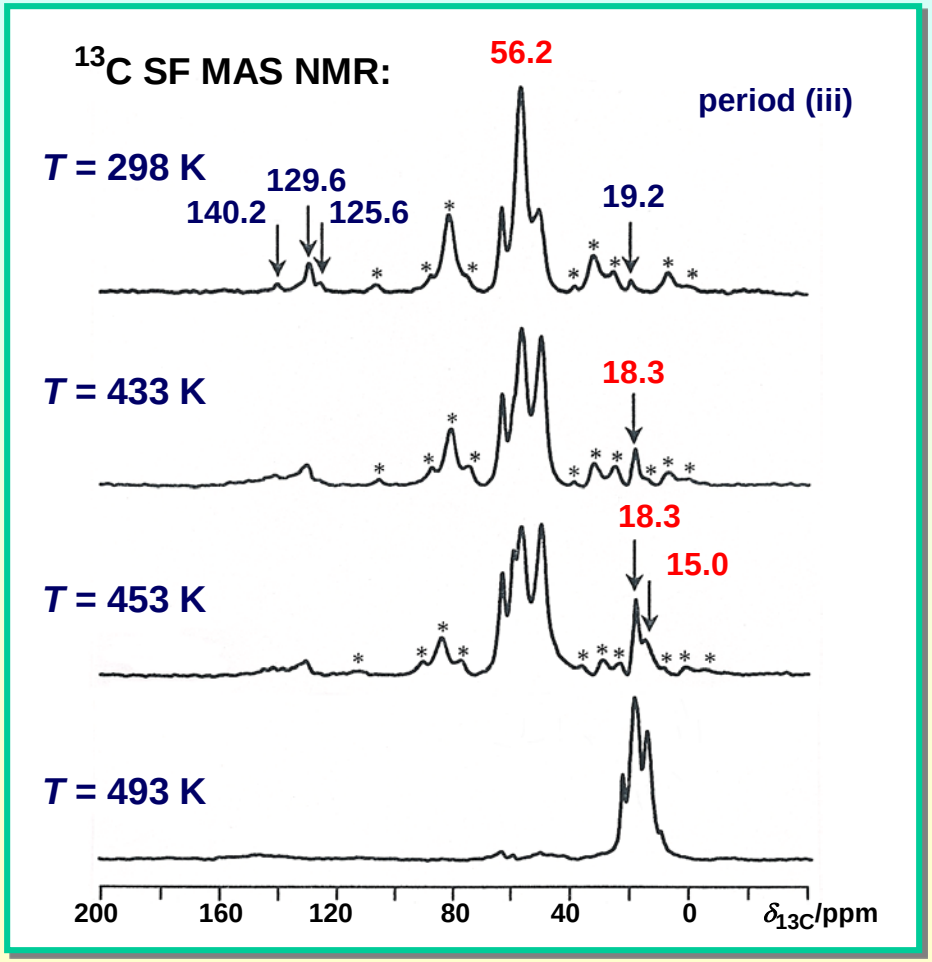
63.5 ppm

→ ^{13}C-labelled methoxy groups contribute to the formation of dimethyl ether

W. Wang et al., J. Phys. Chem. B 105 (2001) 12553.

Methylation of aromatics by surface methoxy groups

reaction of methoxy groups with toluene on zeolite H-Y



methoxy toluene

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

56.2 ppm 19.2 ppm

→ $SiOHAl + CH_3C_6H_4{}^{13}CH_3$

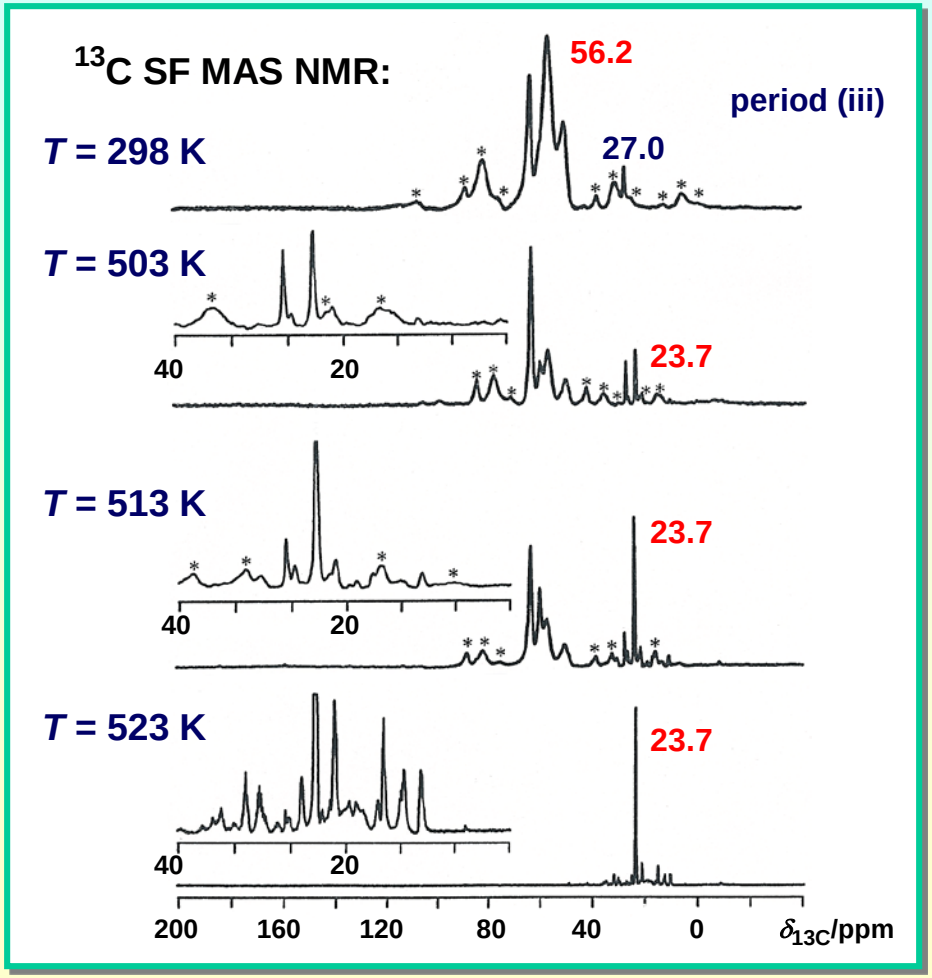
18.3 ppm

- methylation of aromatics by surface methoxy groups starts at *T* = 433 K

W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc. 125 (2003) 15260.

Methylation of alkanes by surface methoxy groups

reaction of methoxy groups with cyclohexane on zeolite H-Y



methoxy cyclohexane

$SiO(^{13}CH_3)Al + C_6H_{12}$

56.2 ppm 27.0 ppm

→ $SiOHAl + {}^{13}CH_3C_6H_{11}$

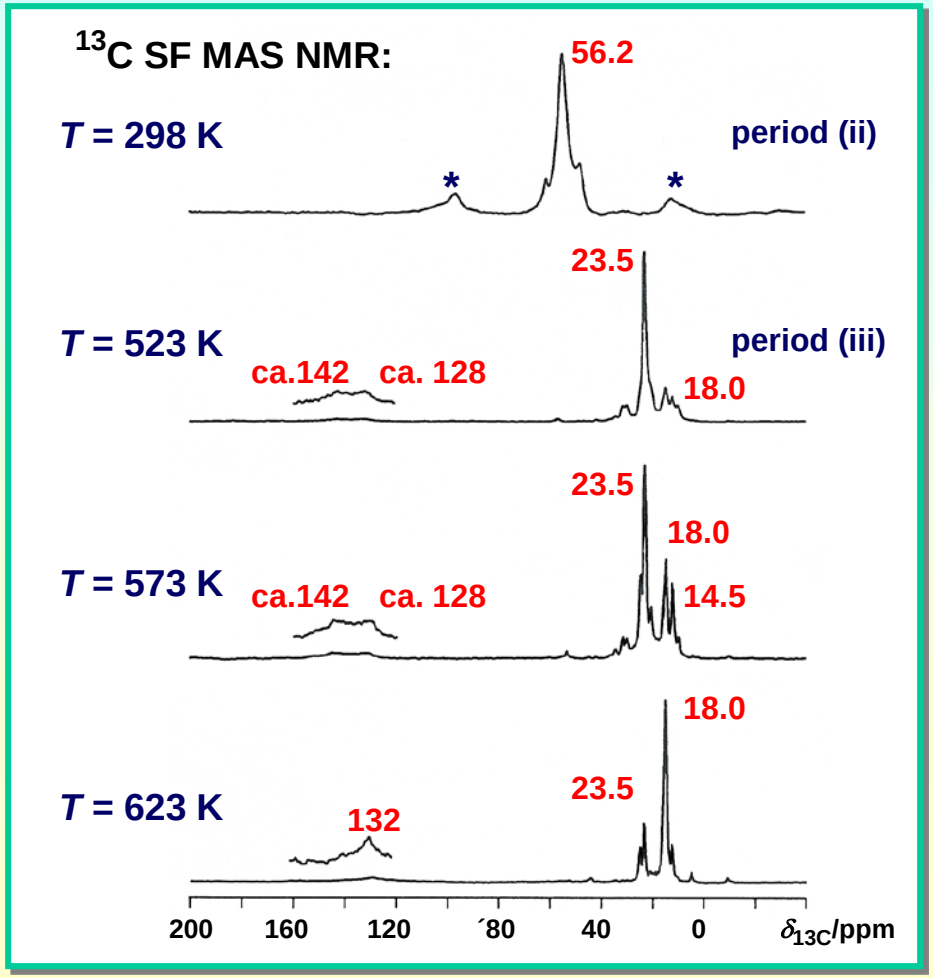
23.7 ppm

- methylation of alkanes by surface methoxy groups starts at T = 503 K
- intermediates of ylide or carbene nature

W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc. 125 (2003) 15260.

Initiation of the MTO process by surface methoxy groups on acidic zeolites

- **stopped-flow conversion of methoxy groups on zeolite H-Y**



- **initiation of the hydrocarbon formation at *T* = 523 K**

- **formation of aliphatics:**

→ **isobutane (23.3, 24.6 ppm)**
isobutene (23.7, 119.5, 141.4 ppm)
dimethylbutadiene (20.1, 111.3, 142.1 ppm)
....

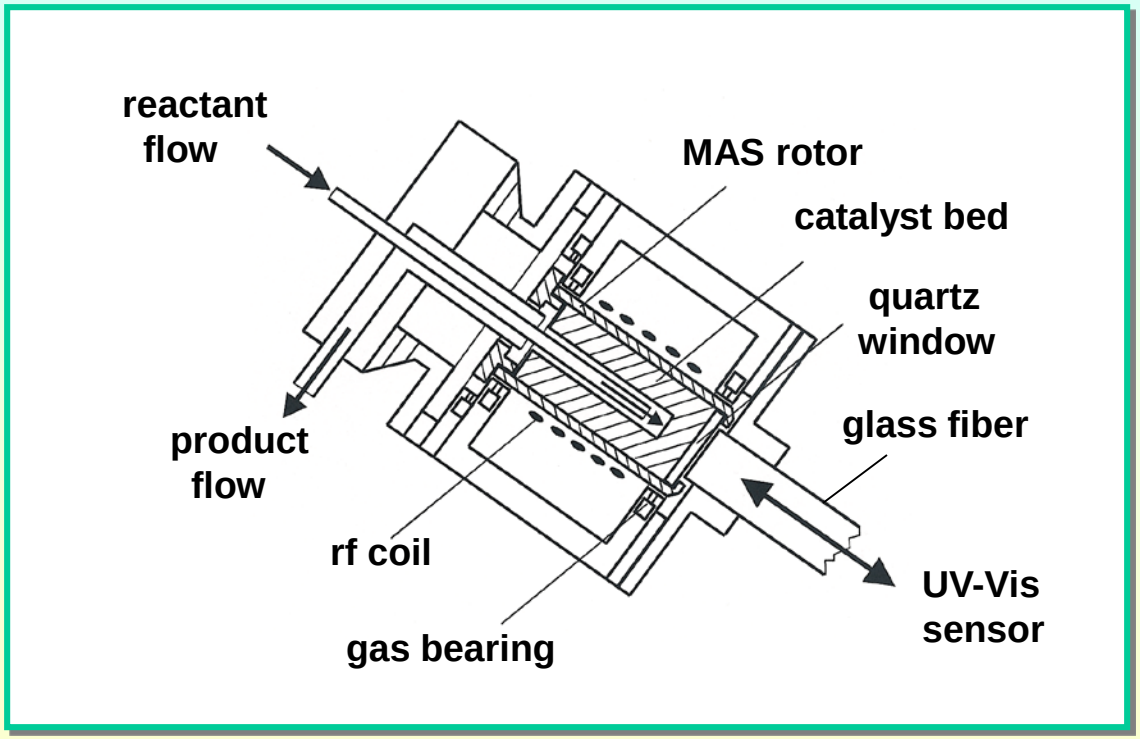
and aromatic compounds:

→ **benzene (128.6 ppm)**
....
hexamethylbenzene (17.6, 132.1 ppm)

W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc. 125 (2003) 15260.

MAS NMR/UV-Vis coupling

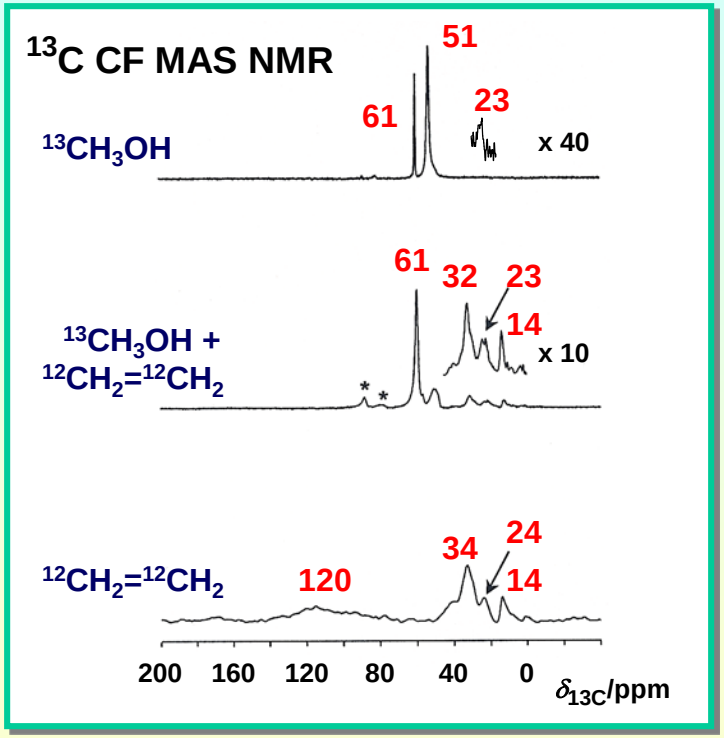
installation of a quartz fiber optic at the bottom of a CF MAS NMR turbine

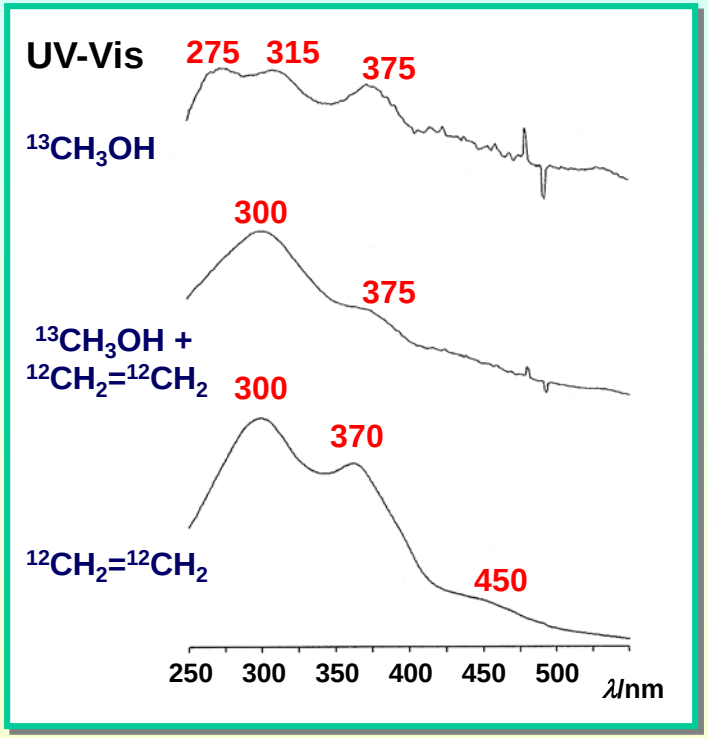


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

MAS NMR/UV Vis coupling

conversion of $^{13}CH_3OH$ on dealuminated H-ZSM-5 at 423 K





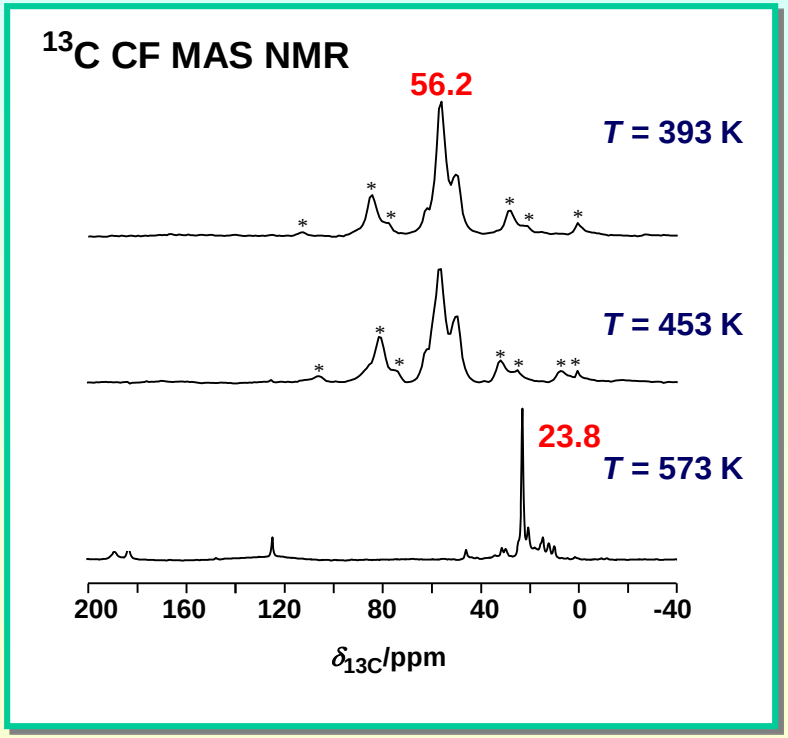
→ **275 nm:** neutral aromatic compounds
315 nm: monoenyl carbenium ions

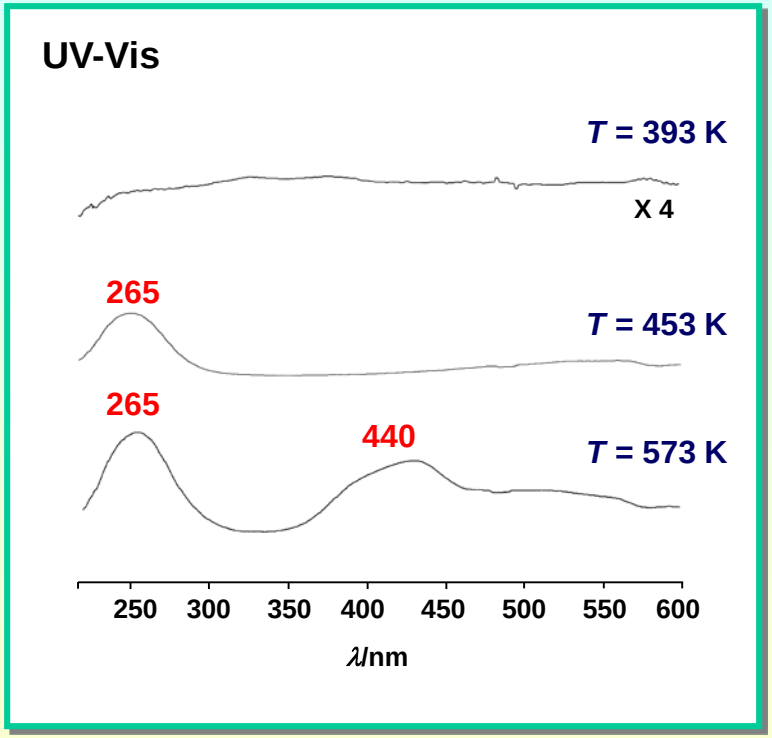
375 nm: dienyl carbenium ions
450 nm: polyaromatic compounds

M. Hunger, W. Wang, Chem. Commun. (2004) 584.

MAS NMR/UV Vis coupling

conversion of surface methoxy groups on zeolite H-Y





→ **23.8 ppm: isobutane**
ca. 130 ppm: aromatics

265 nm: neutral aromatic compounds
440 nm: polyaromatic compounds

Conclusions

Study of the MTO process on zeolites by *in situ* NMR spectroscopy:

- **a mixture of large olefins and aromatic compounds is formed under steady state conditions**
- **composition of this hydrocarbon pool depends on the reaction conditions and the catalyst**
- **alkyl groups of the hydrocarbon pool contribute to the conversion of methanol**
- **surface methoxy groups may be responsible for the formation of first hydrocarbons during the induction period of the MTO process**
- **aromatics are formed immediately after starting the conversion of methanol and methoxy groups on acidic zeolites**

Acknowledgements

Jens Weitkamp

Thomas Horvath
Udo Schenk
Michael Seiler
Wei Wang
Andreas Buchholz
Mingcan Xu
Jian Jiao

Irina Ivanova
Alexander Stepanov
Ago Samoson

Deutsche Forschungs-gemeinschaft

Volkswagen-Stiftung Hannover

Max-Buchner-Forschungs-stiftung

Fonds der Chemischen Industrie