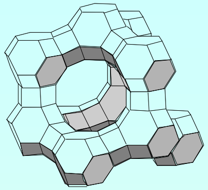


In situ MAS NMR and UV/VIS spectroscopic studies of hydrocarbon-pool compounds and coke deposits formed in the methanol-to-olefin conversion on H-SAPO-34

15th IZC, August 12-17, 2007, Beijing, China

Y. Jiang, J. Huang, J. Weitkamp, M. Hunger

History of methanol-to-hydrocarbon conversion on acidic 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/China, test unit, 10 000 t olefins per year**
- **2005, Shaanxi/China, start of the construction of a commercial plant, 800 000 t olefins per year**

Periods of the methanol conversion on acidic zeolites

I: Induction period of the methanol conversion on zeolite catalysts

Formation of first C-C bonds by reaction of surface methoxy groups and alkylation of organic impurities

II: Steady-state of the methanol conversion on zeolite catalysts

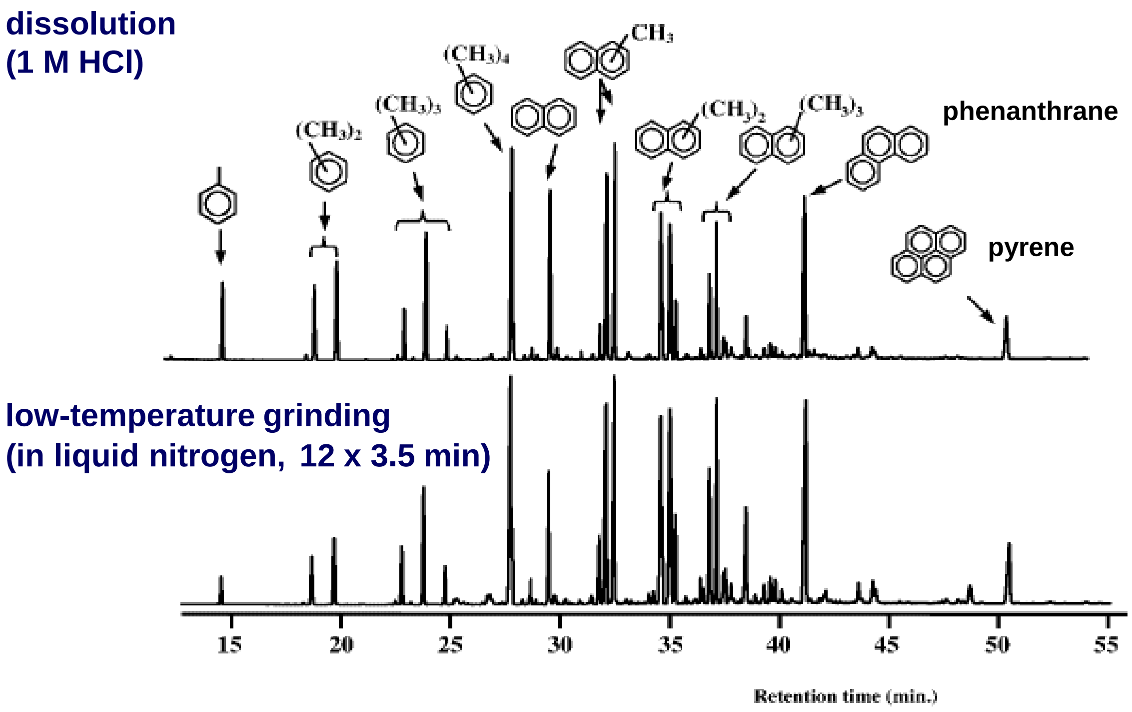
Formation of light olefins by methylation and dealkylation of catalytically active hydrocarbon-pool compounds (olefinic and aromatic deposits)

III: Catalyst deactivation during methanol conversion on zeolites

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

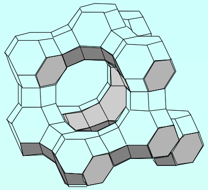
Ex situ study of coke compounds

***Ex situ* GC-MS study of coke deposits upon dissolution and low-temperature grinding of used H-SAPO-34 (4 ml methanol on 300 mg catalyst at 673 K, H. Fu *et al.*, Catal. Lett. 76 (2001) 89)**



dissolution
(1 M HCl)

low-temperature grinding
(in liquid nitrogen, 12 x 3.5 min)

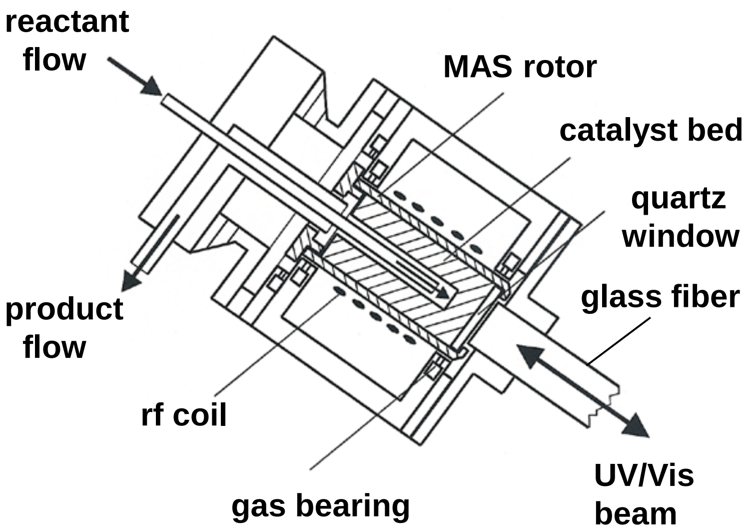


Experimental technique and catalyst material

Technique of MAS NMR-UV/Vis spectroscopy

- a flow MAS NMR probe (modified 7 mm MAS rotor with quartz glass window) was equipped with an UV/Vis glass fiber at the bottom of the MAS stator
- comparison with standard fixed-bed reactor

MAS NMR-UV/Vis probe



reactant flow

MAS rotor

catalyst bed

quartz window

glass fiber

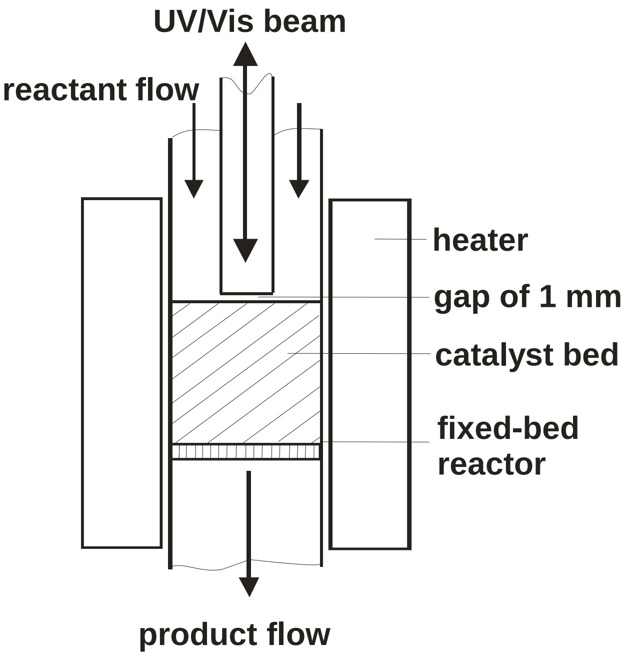
product flow

rf coil

gas bearing

UV/Vis beam

fixed-bed reactor



UV/Vis beam

reactant flow

heater

gap of 1 mm

catalyst bed

fixed-bed reactor

product flow

Technique of MAS NMR-UV/Vis spectroscopy

Modified 7 mm Doty MAS NMR probe equipped with an injection system and an UV/Vis glass fiber

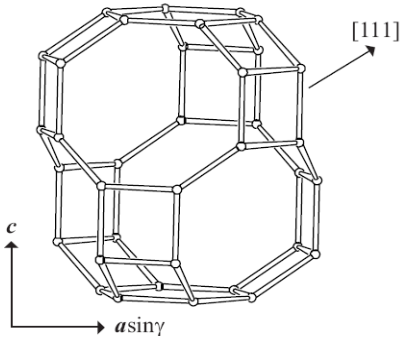
Catalyst material

H-SAPO-34:

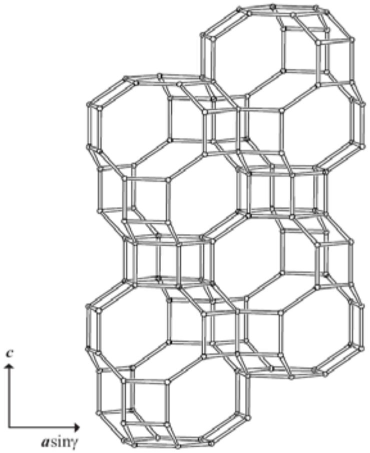
Structure type CHA

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

chabazite cages accessible by 8-ring windows perpendicular to [001] 0.38 nm x 0.38 nm



chabazite cage



- **sample preparation and catalysis:**
  - **synthesis of SAPO-34 with $n_{Si}/(n_{Al}+n_{P}+n_{Si})$ ratio of 0.11 according to Ref. [1]**
  - **calcination at 873 K for 6 h in synthetic air (20 vol. oxygen, 60 l/h)**
  - **100 mg of calcined catalyst in fixed-bed or MAS NMR rotor reactor**
  - **modified residence time of W_{cat}/F_{me} = 25 gh/mol**

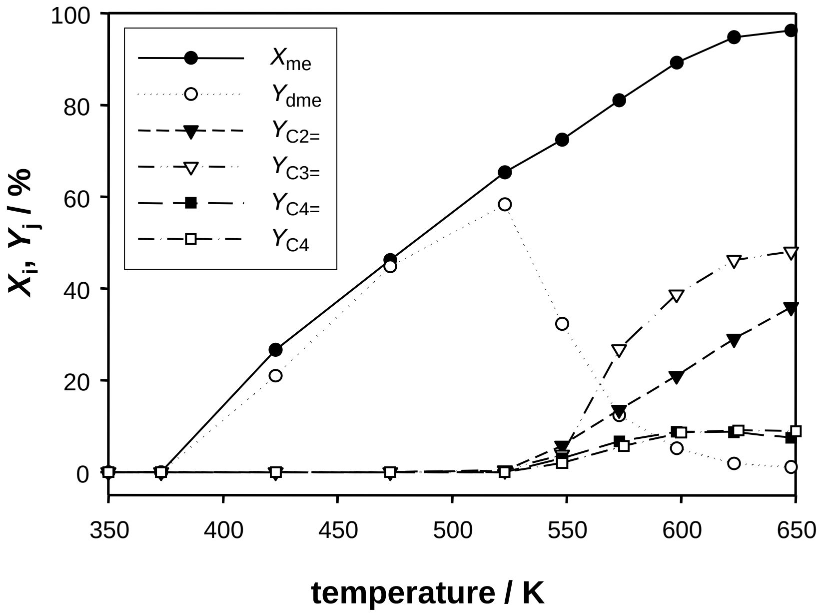
[1] M. Kang, T. Inui, J. Mol. Catal. A: Chemicals 140 (1998) 55.

On-line GC study of the MTO reaction in different reactors

Comparison of methanol conversion on H-SAPO-34 in an MAS NMR rotor reactor (left) and a standard fixed-bed reactor (right)

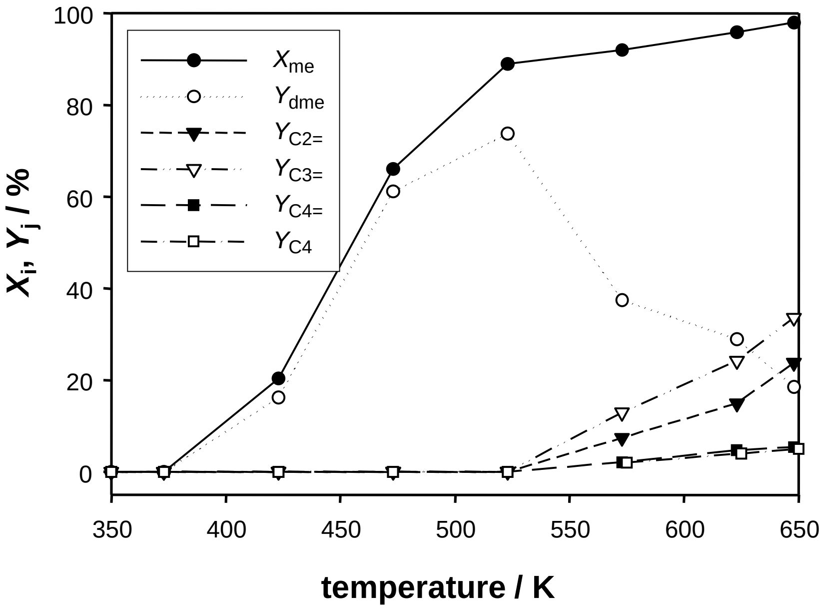
spinning (2 kHz) MAS NMR rotor reactor

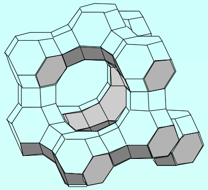
W_{cat}/F_{me} = 25 gh/mol



fixed-bed reactor

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

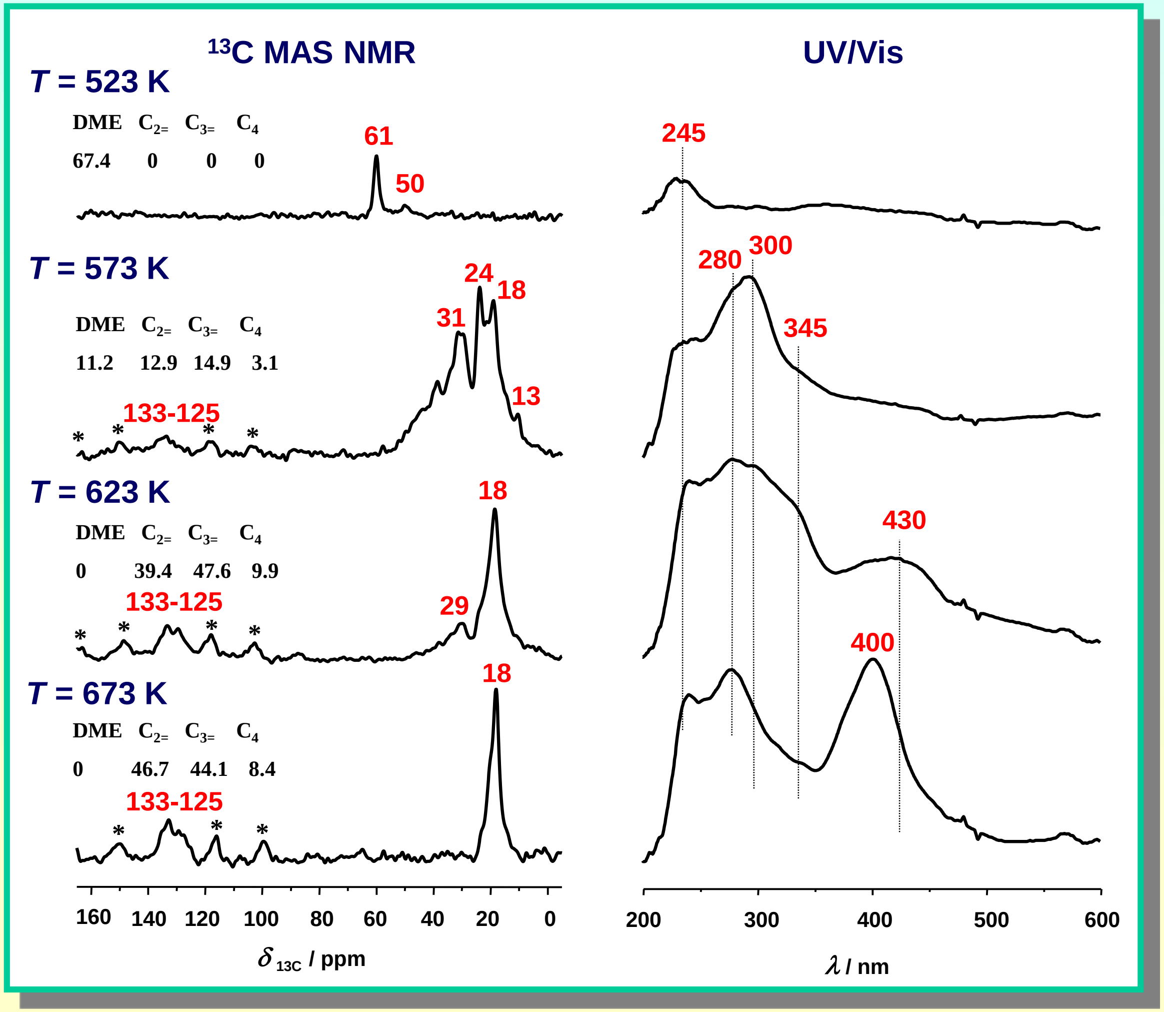




In situ MAS NMR-UV/Vis investigations of organic deposits formed during the MTO reaction on H-SAPO-34

In situ MAS NMR-UV/Vis study of the formation of organic deposits

In situ ^{13}C MAS NMR-UV/Vis spectroscopy of deposit formation on H-SAPO-34 at 523 to 673 K for 3 h under continuous-flow conditions (W_{cat}/F_{me} = 25 gh/mol)



NMR:

- separation of alkyl groups (13-31) and aromatic compounds (125-133)

UV/Vis:

- sensitive for carbenium cations (300, 345, 430 nm)
- separation of aromatics (280 nm) and polycyclic aromatics (400 nm)

On-line GC:

- determination of volatile reaction products

Assignment of UV/Vis bands

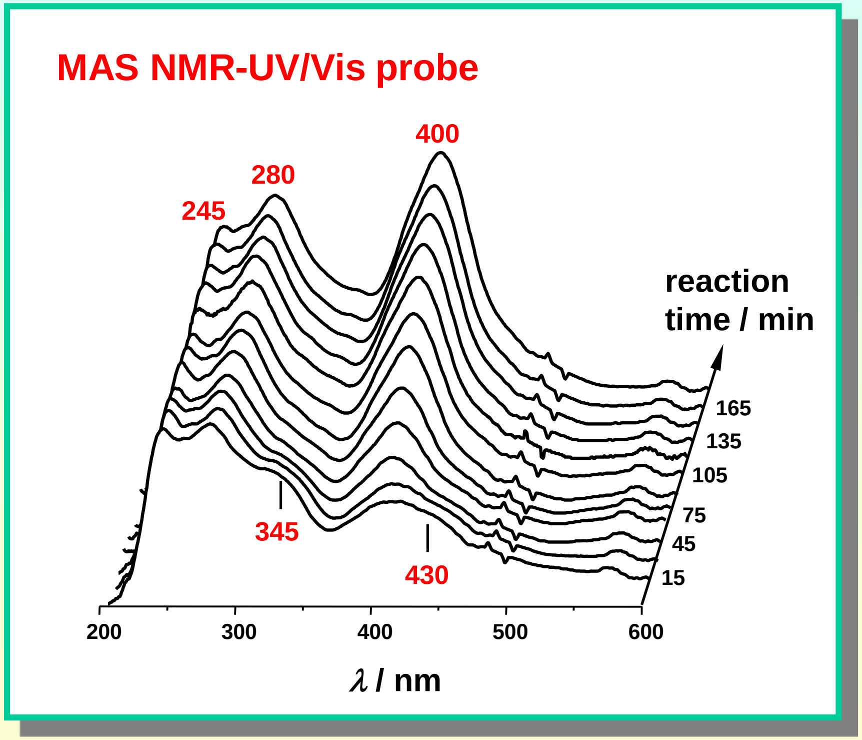
Assignments of UV/Vis bands (π-π* transitions) observed during the methanol-to-olefin conversion on H-SAPO-34 at 523 to 673 K

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

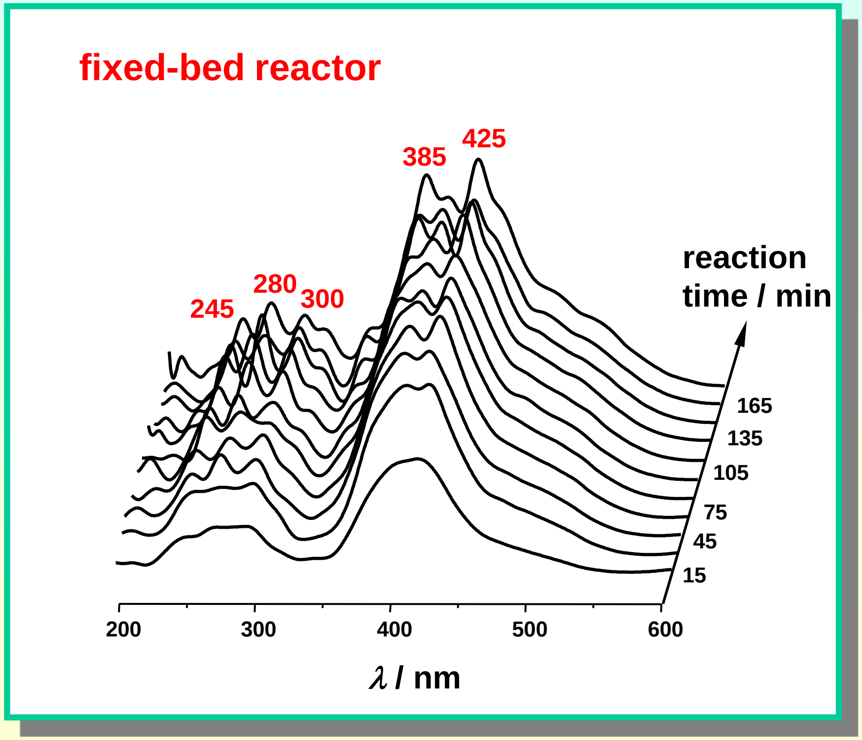
Refs.: H.G. Karge *et al.,* Stud. Surf. Sci. Catal. 49 (1989) 1327; J. Mohan, Organic Spectroscopy Principles and Applications, Alpha Science International Ltd., Harrow, U.K., 2002, p. 137; A.V. Demidov, Mater. Chem. Phys. 39 (1994) 13; I. Kirisci *et al.,* Chem. Rev. 99 (1999) 2085; R. Ahmad *et al.,*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

UV/Vis study of the formation of organic deposits in different reactors

***In situ* UV/Vis studies of deposit formation during methanol conversion on H-SAPO-34 at 673 K (W_{cat}/F_{me} = 25 gh/mol)**



MAS NMR-UV/Vis probe



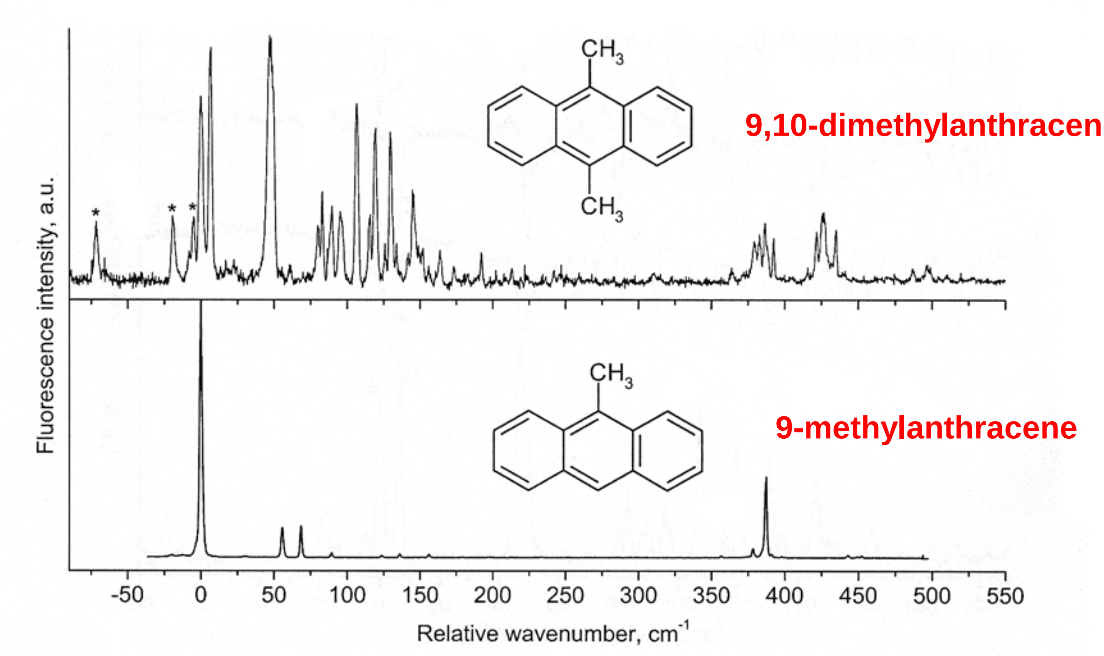
fixed-bed reactor

- **continuous increase of the band at *ca.* 400 nm indicates formation of polycyclic aromatics**
- **simultaneously, the bands of di- and trienylic carbenium ions decrease (345 nm, 430 nm)**

Assignment of the coke band

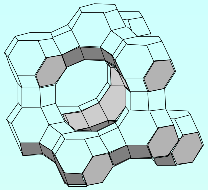
Possible assignment of the coke band at *ca.* 400 nm,
(Y. Stepanenko *et al.,* J. Mol. Spectrosc. 233 (2005) 15)

Laser-induced fluorenscence excitation spectra



chain-like polyaromatics correspond to:

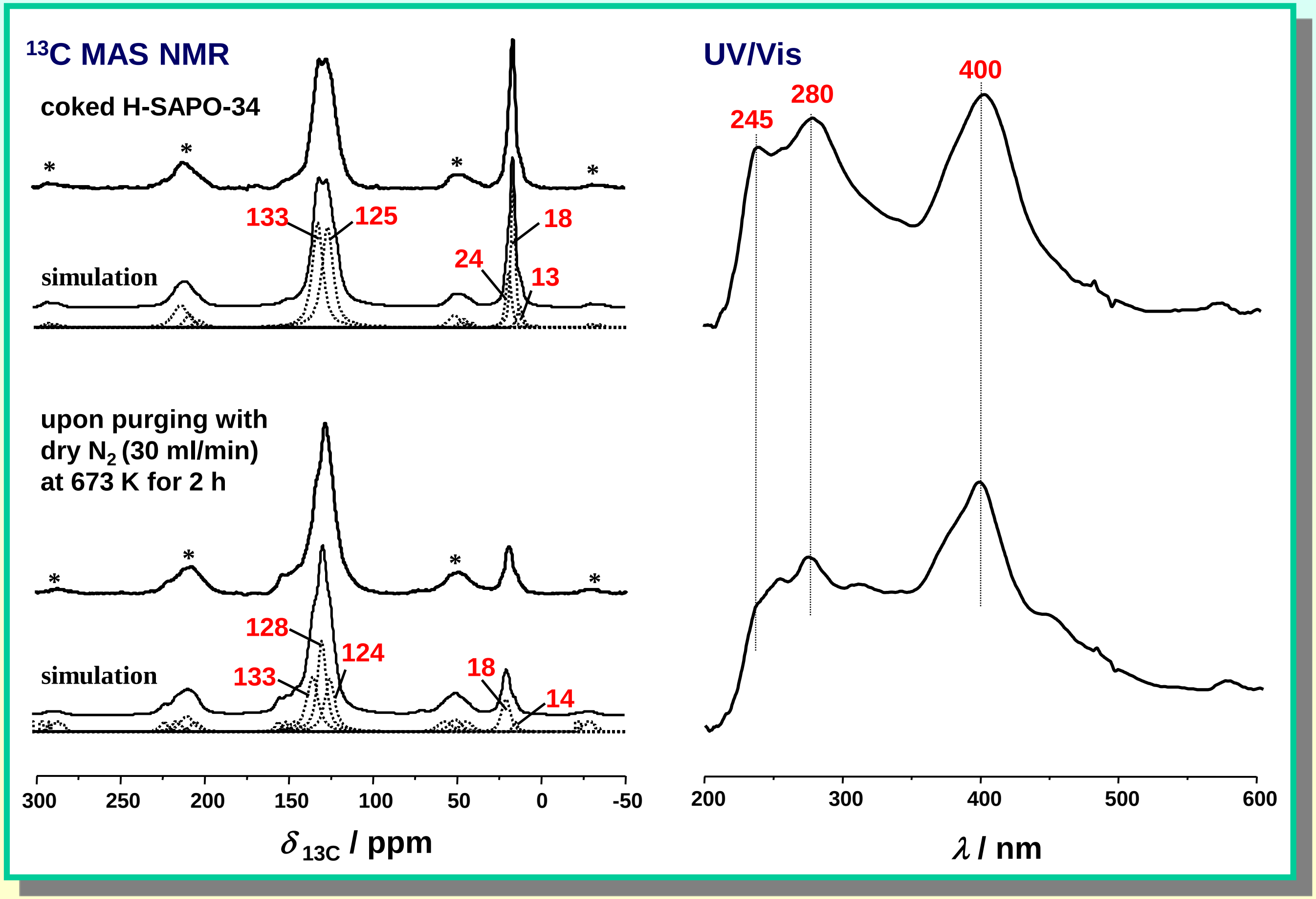
polymethyl-anthracenes



Regeneration of the coked H-SAPO-34 catalyst

Purging of the coked MTO catalyst

Study of the stability of organic deposits formed by conversion of methanol (W_{cat}/F_{me} = 25 gh/mol) on H-SAPO-34 at 673 K for 3 h



decrease of dienes (245 nm) and polyalkyl-aromatics (280 nm)

stable band of polycyclic aromatics (400 nm)

Y. Jiang et al., Microporous Mesoporous Mater. (2007) accepted.

Results of the quantitative evaluation

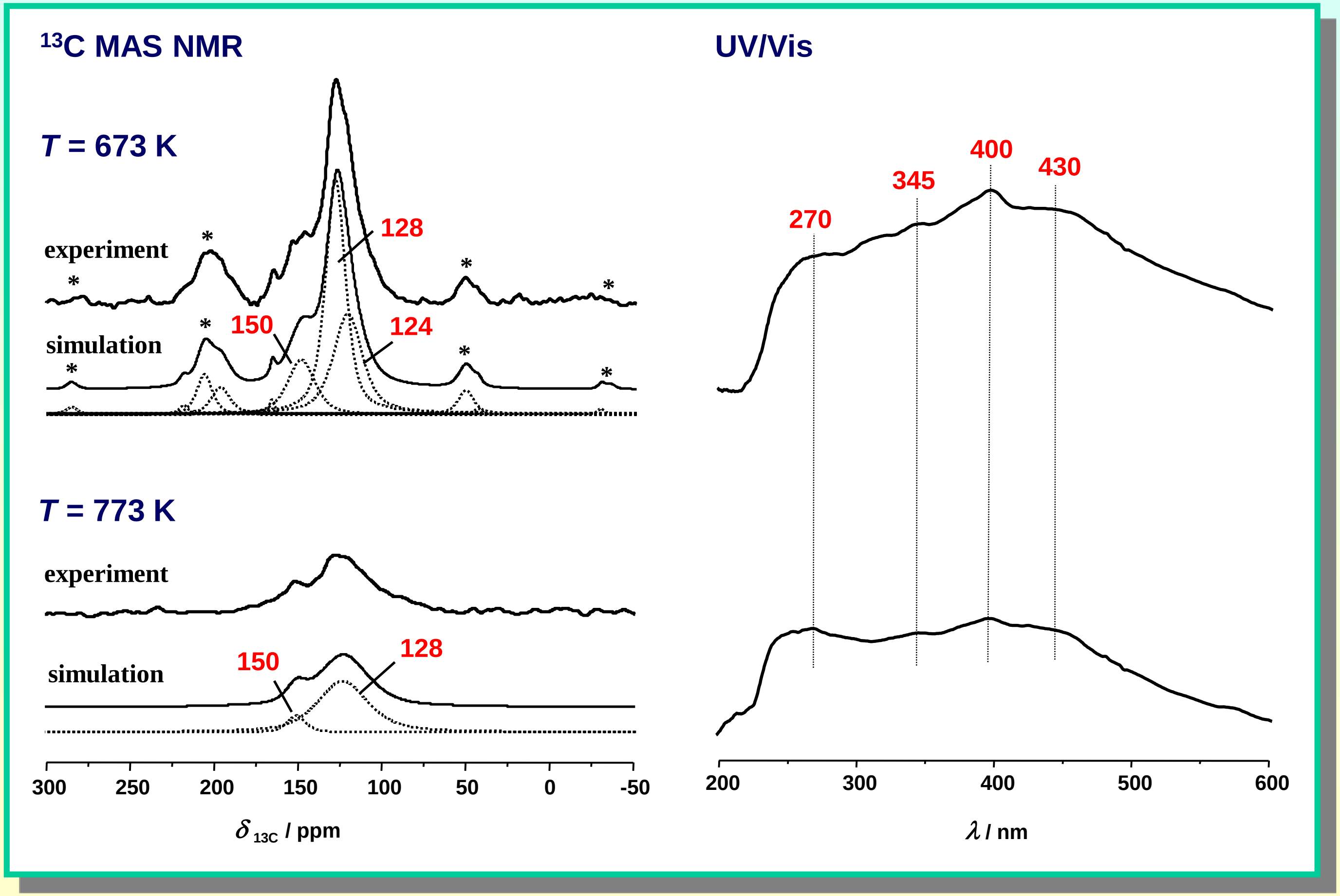
Quantitative evaluation of the ^{13}C MAS NMR spectra of coked H-SAPO-34 before and after purging with dry N_2 (30 ml/min, at 673 K, 2 h)

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

→ **change of ^{13}C MAS NMR intensities agrees with stronger decrease of UV/Vis band of aromatics at 280 nm than that of polycyclic aromatics at 400 nm**

Regeneration of coked MTO catalyst

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



decrease of all aromatics including coke compounds (400 nm)

new band of phenolic species (270 nm)

Results of the quantitative evaluation

Quantitative evaluation of the ^{13}C MAS NMR spectra of coked H-SAPO-34 regenerated by burning with synthetic air at 673 and 773 K 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 coke compounds (UV/Vis band at 400 nm), but formation of phenolic species (145-155 ppm, 270 nm)**

Summary

- formation of polycyclic aromatics during MTO on H-SAPO-34 occurs already at 673 K
- UV/Vis band at 400 nm indicates formation of chain-like polycyclic aromatics, such as polymethylanthracenes
- quantitative solid-state NMR indicates that these polycyclic aromatics are totally removed by burning with air at 773 K, but a low content of phenolic species is formed
- *in situ* MAS NMR-UV/Vis spectroscopy combines high sensitivity for alkylated compounds and quantitative evaluation with high sensitivity for aromatic compounds and carbenium ions
- UV/Vis spectroscopy could be an interesting tool for the *in situ* watching of coke formation on industrial MTO catalysts

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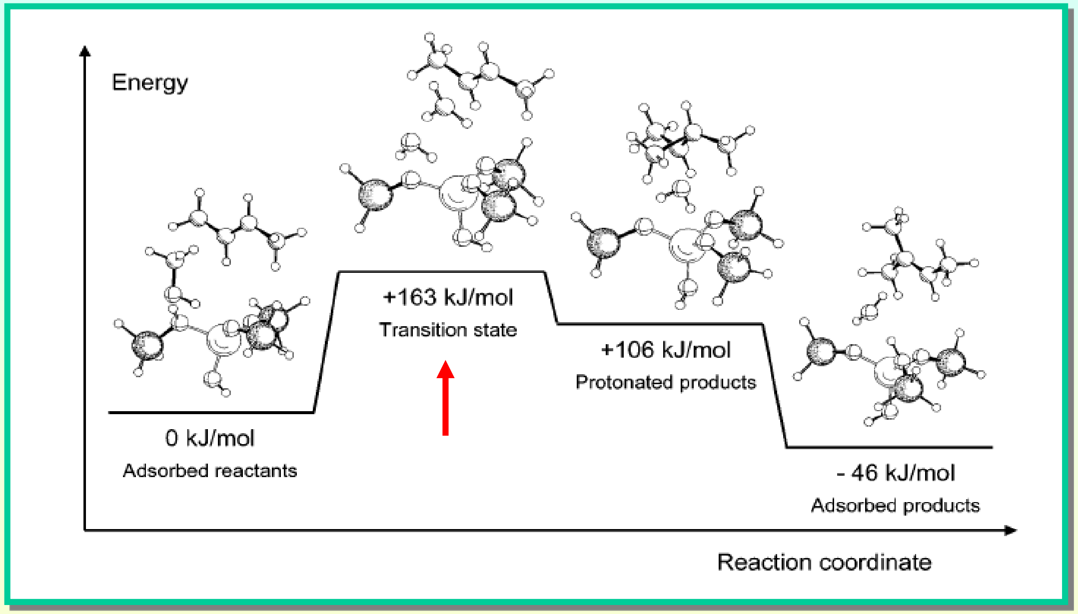
Fonds der Chemischen Industrie

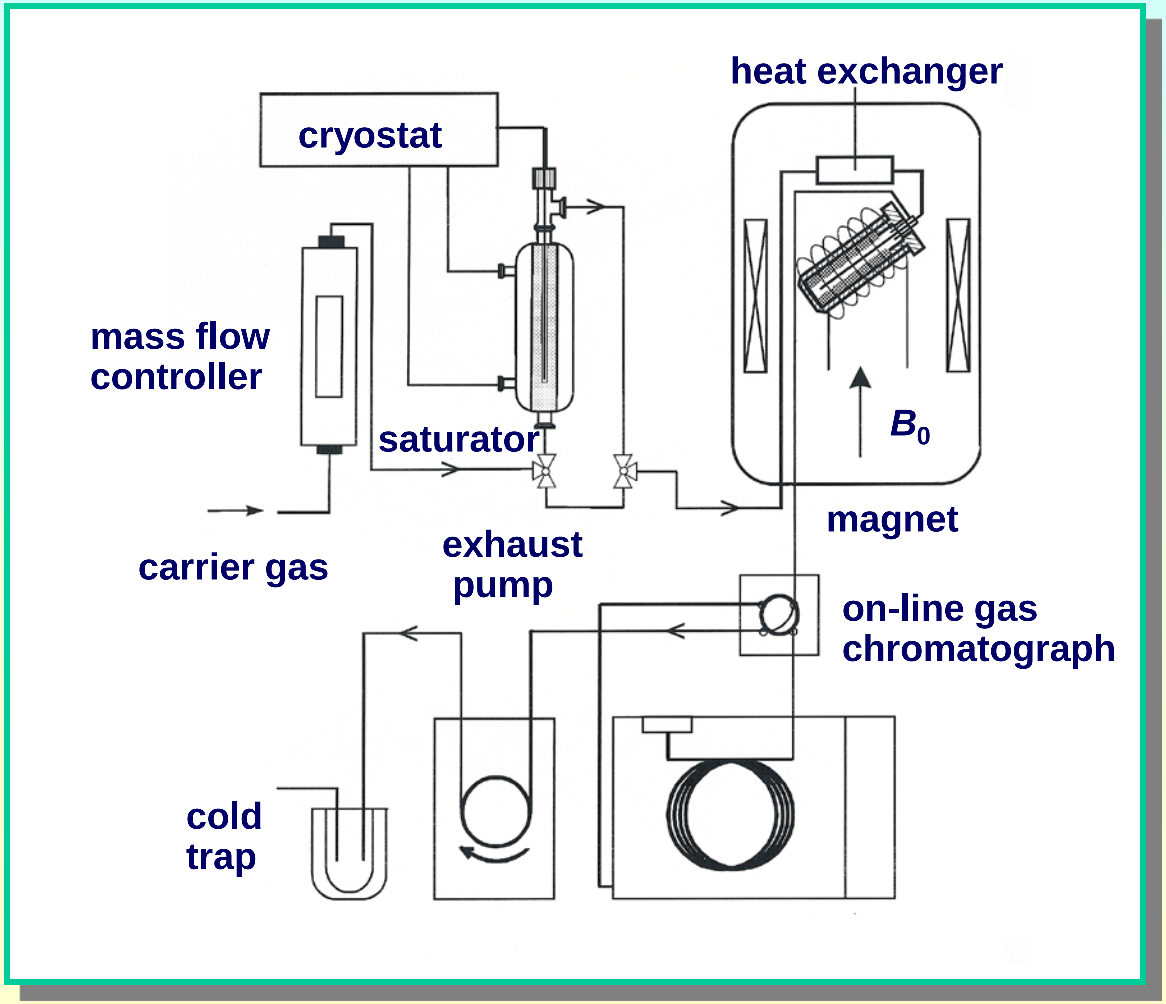
Function of the hydrocarbon pool compounds

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

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



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