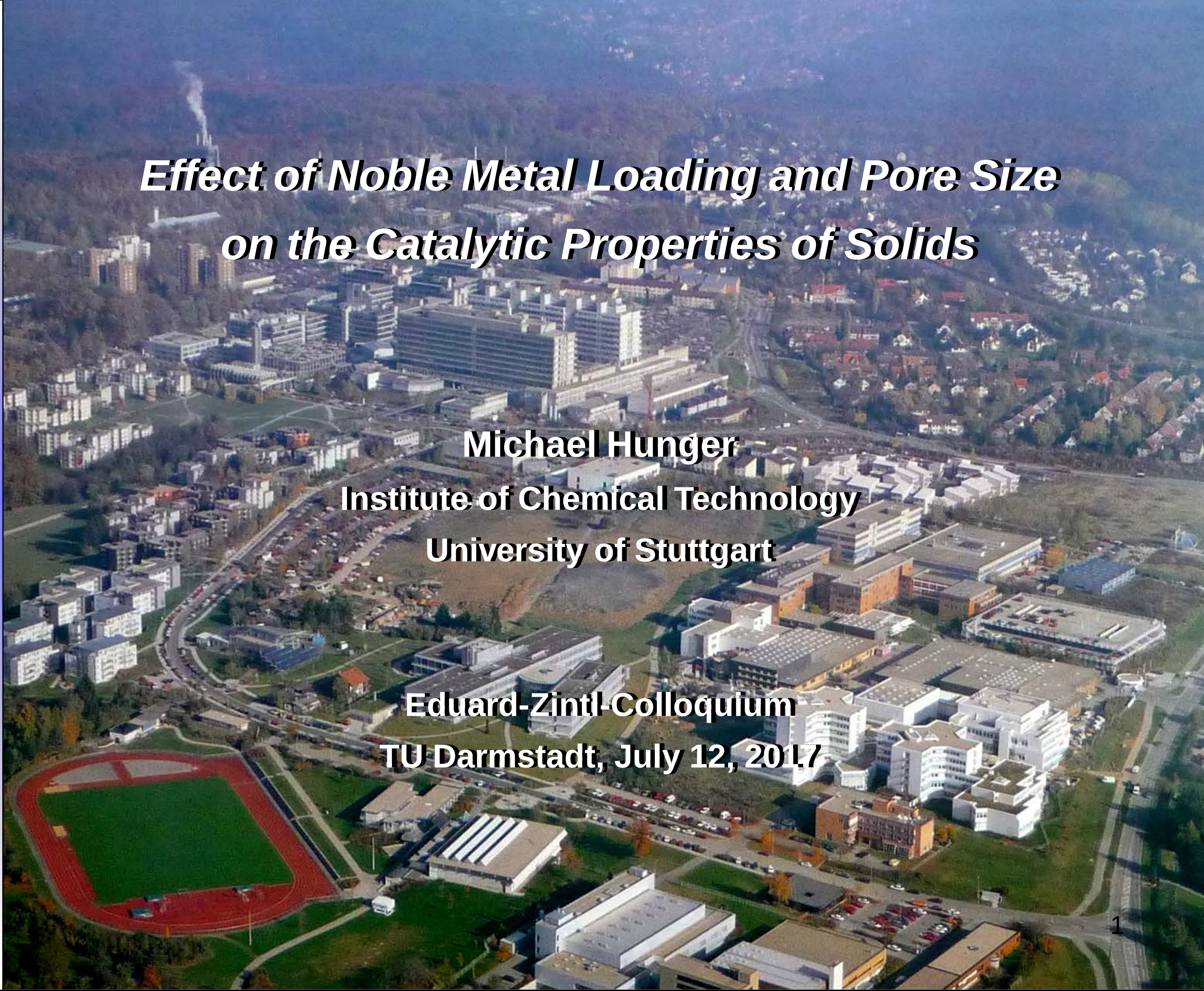

Effect of Noble Metal Loading and Pore Size on the Catalytic Properties of Solids

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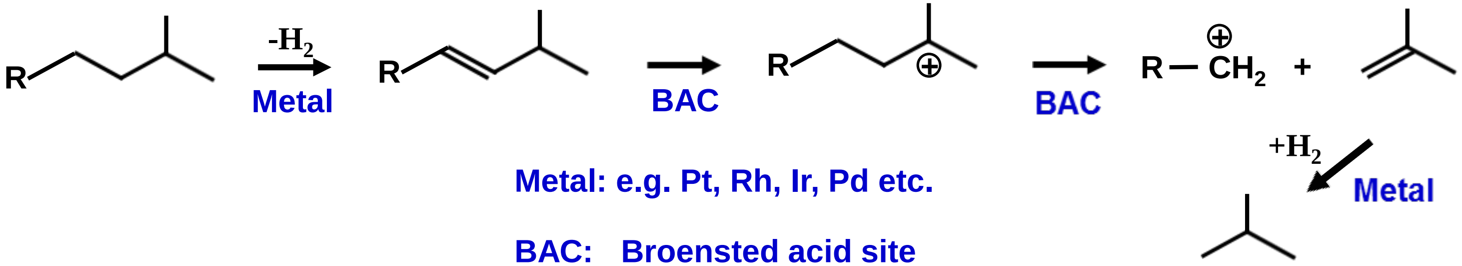
Institute of Chemical Technology
University of Stuttgart

Eduard-Zintl-Colloquium
TU Darmstadt, July 12, 2017

Effect of noble metal loading and pore size on the catalytic properties of solids

Examples for applications of noble metal containing solid catalysts

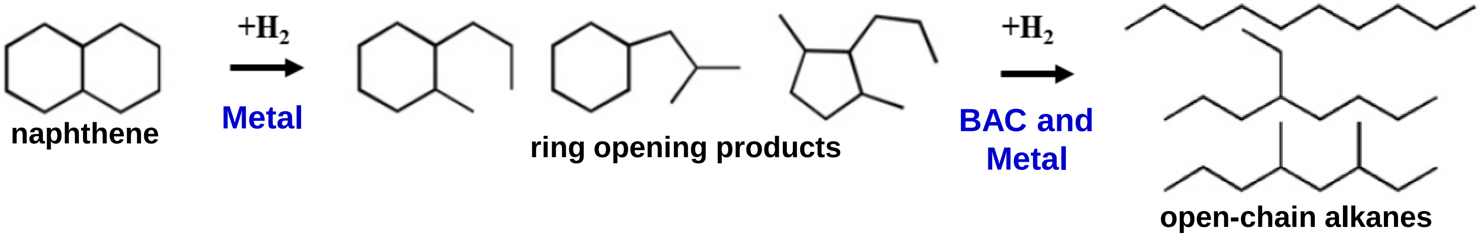
- **hydrocracking of alkanes [1]**



Metal: e.g. Pt, Rh, Ir, Pd etc.

BAC: Broensted acid site

- **ring-opening of naphthenes to open alkanes by hydrogenolysis [2]**



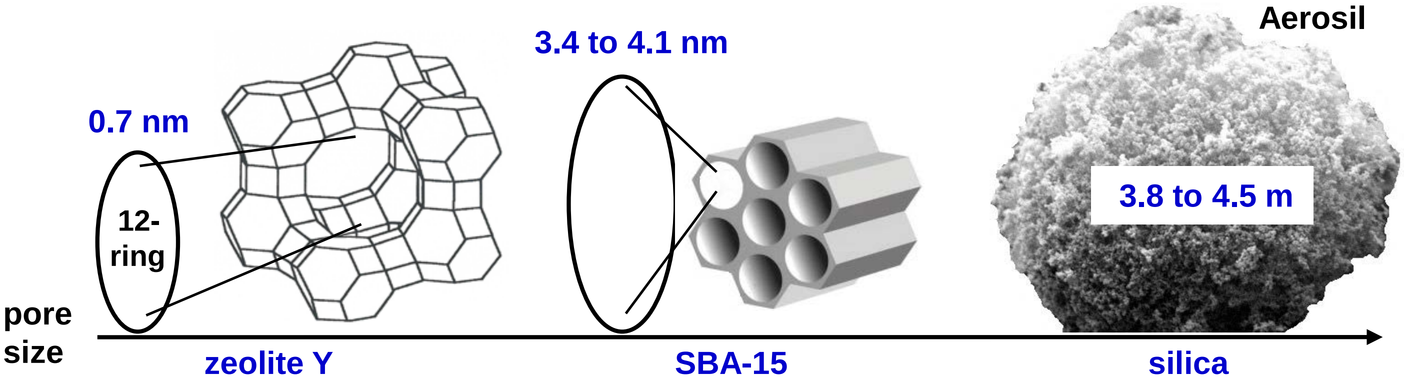
[1] J. Scherzer, A.J. Gruia, Hydrocracking Science and Technology, Marcel Dekker, New York, USA, 1996.

[2] S. Rabl et al., Ring Opening of Cis-decalin on Bifunctional Ir/- and Pt/La-X Zeolite Catalysts, Appl. Catal. A: General 400 (2011) 131-141.

Effect of noble metal loading and pore size on the catalytic properties of solids

Catalysts under study:

- parent and dealuminated zeolite Y, mesoporous SBA-15, amorphous silica



- loading of Rh$Cl_3 \cdot x\, H_2O$, [Ir$(NH_3)_5Cl]Cl_2$, [Pd$(NH_3)_4]Cl_2$, and [Pt$(NH_3)_4]Cl_2$

zeolite Na-Y, n_{Si}/n_{Al} = 2.7, Degussa AG Hanau → aqueous ion exchange at 353 K for 12 h → calcination in synthetic air at 573 K for 3 h, reduction in flowing hydrogen at 623 K for 2 h

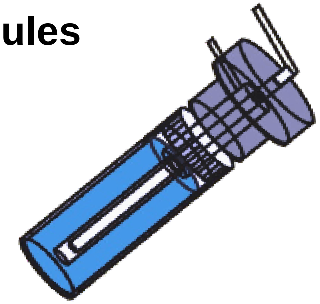
zeolite DeA-Y, n_{Si}/n_{Al} = 93, Degussa AG Hanau
SBA-15, n_{Si}/n_{Al} = 199, synthesis according to [1]
Aerosil 300, Degussa AG Hanau
→ aqueous wetness impregnation, evacuation at 313 K → calcination in synthetic air at 573 K for 3 h, reduction in flowing hydrogen at 623 K for 2 h

[1] D. Zhao et al., Science 279 (1998) 548-552.

Effect of noble metal loading and pore size on the catalytic properties of solids

Analytical methods

- NMR spectroscopy of surface sites using probe molecules
- hydrogenation of acrylonitrile studied by *in situ* ^{1}H MAS NMR spectroscopy



- dehydrogenation of propane in a standard fixed-bed reactor with on-line GC analysis under continuous flow conditions
- hydrogenation of propene with para-hydrogen studied by *in situ* ^{1}H MAS NMR spectroscopy under continuous flow conditions

Sample treatment before solid-state NMR studies

- evacuation at vacuum line after reduction and subsequent sealing in glass tubes
- loading of ammonia, acetonitrile, and acrylonitrile at vacuum line and subsequent evacuation at 453 K (ammonia) or 295 K (others)
- addition of solid trimethylphosphine and heating at 433 K for 2 h
- transfer of pretreated samples into MAS rotors inside glovebox purged with N_2

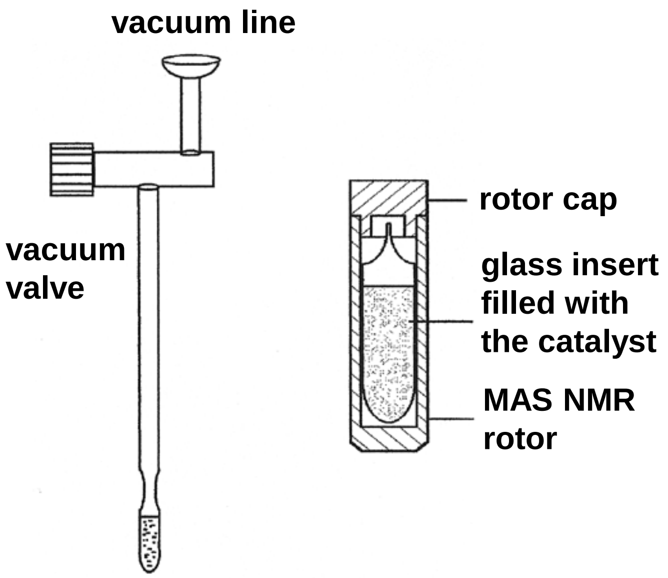
Preparation of dehydrated catalyst samples for MAS NMR studies

vacuum line for dehydration of catalyst samples in glass tubes at elevated temperatures (often 673 K)

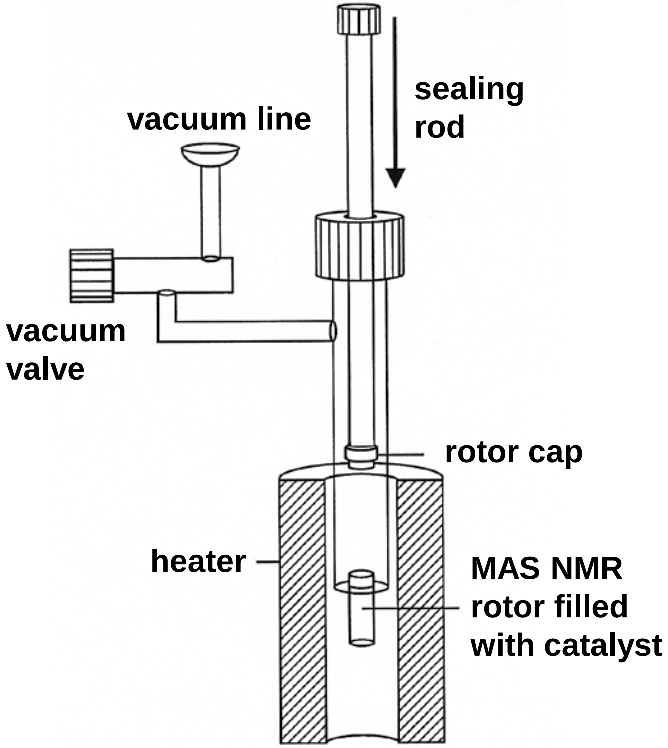
transfer of the dehydrated catalyst samples from glass tubes into MAS rotors inside a glove box (dry nitrogen)

Preparation of activated catalysts loaded with probe molecules or reactants

dehydration and loading of the catalyst inside the glass insert (e.g. commercial Wilmad MAS NMR inserts for 4 mm and 7 mm rotors)



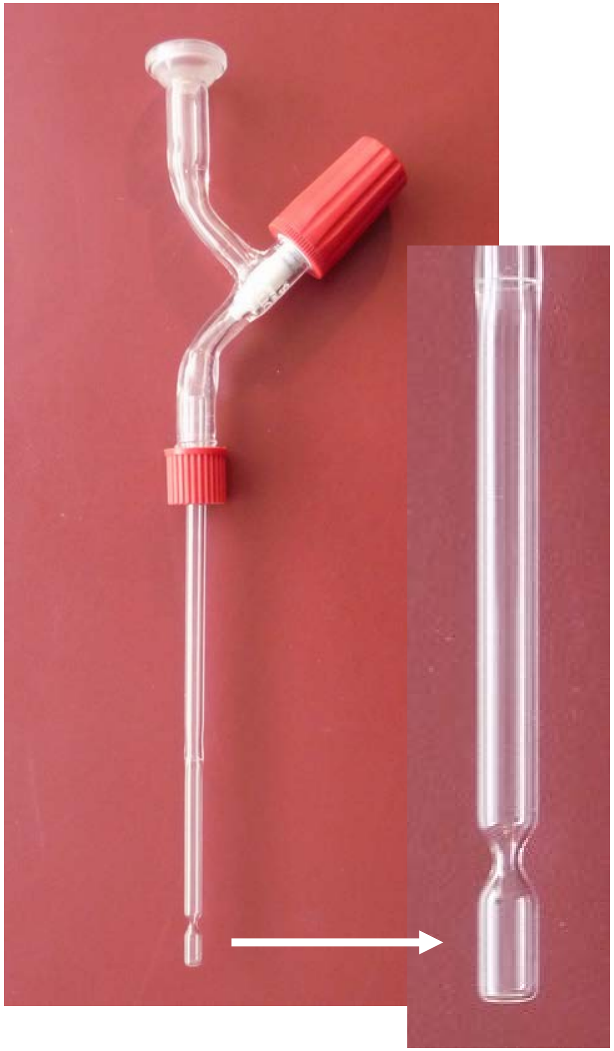
dehydration, loading, and sealing of the catalyst filled in an MAS NMR rotor inside a vacuum equipment

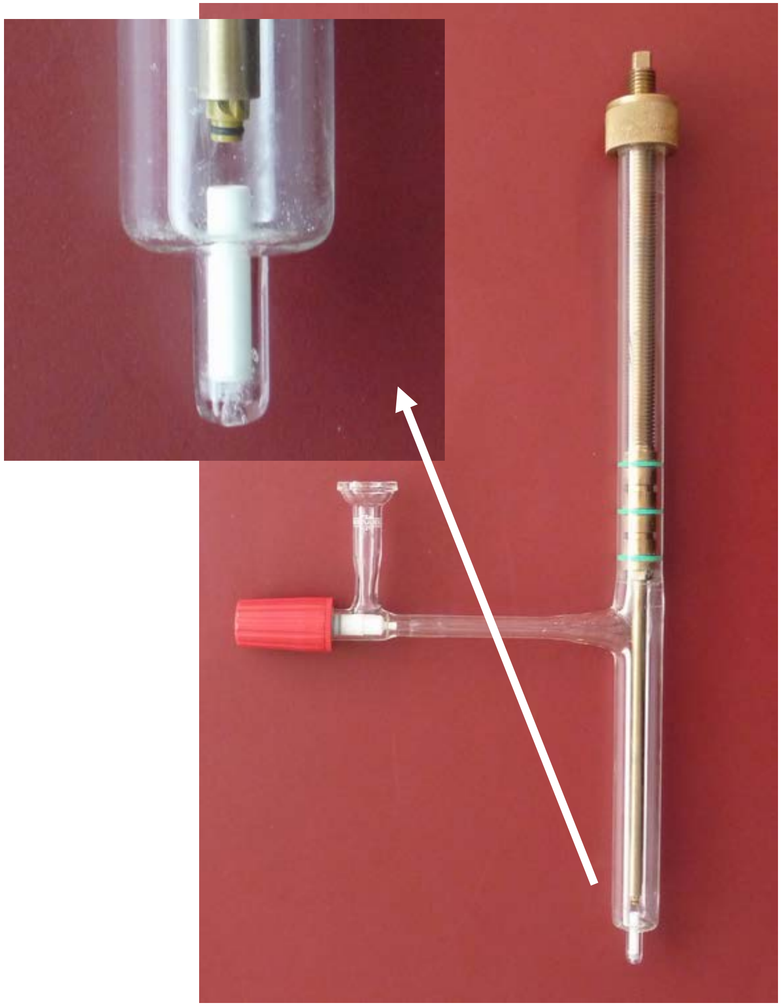


M. Hunger et al., in: B.M. Weckhuysen (ed.), *In situ Spectroscopy of Catalysts*, American Scientific Publishers, Stevenson Ranch, California, 2004, p. 177-218.

Preparation of activated catalysts loaded with probe molecules or reactants

Wilmad insert for 7mm Bruker rotors





selfmade equipment for rotor sealing

Investigation of surface sites on bifunctional noble metal containing zeolites

Generation of catalytically active surface sites on noble metal containing zeolites

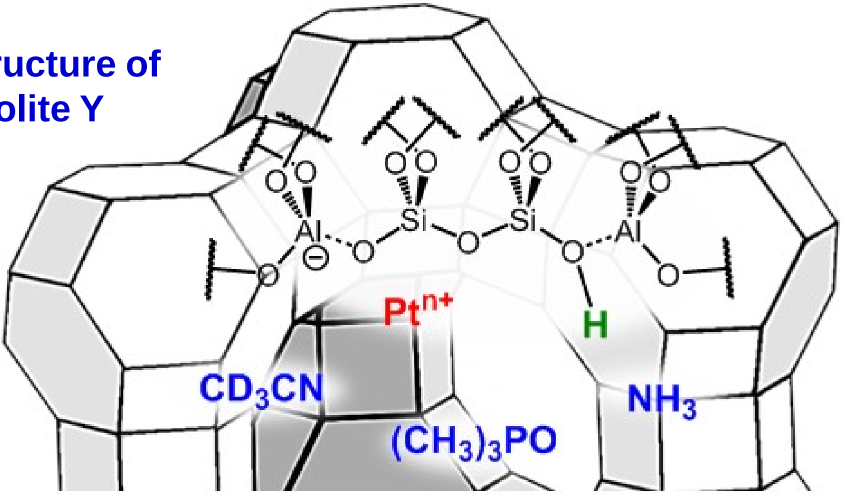
zeolites H,Na-Y (n_{Si}/n_{Al} = 2.7) loaded with calculated amounts of Rh, Ir, Pd, and Pt

exchange $[Pt(NH_3)_4]^{2+} + 2Na^+ZO^- \xrightarrow[-2Na^+]{}$

calcination $[Pt(NH_3)_4]^{2+}(ZO^-)_2 \xrightarrow[-4NH_3]{573\ K}$

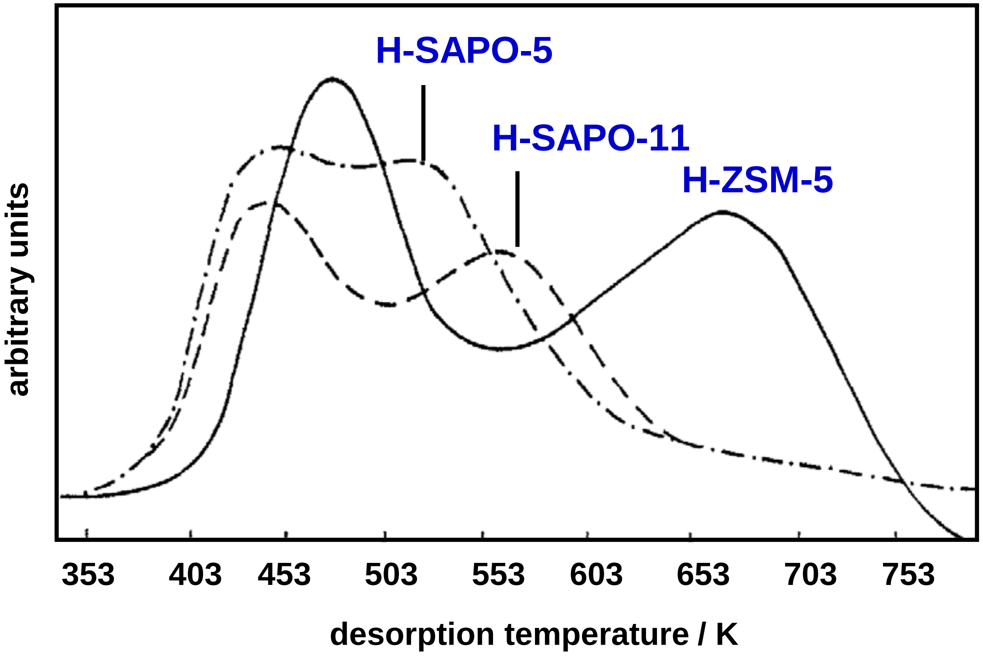
reduction $Pt^{2+}(ZO^-)_2 \xrightarrow{H_2,\ 623\ K} Pt^0(H^+)_2(ZO^-)_2$

structure of zeolite Y



^{1}H MAS NMR studies of the hydroxyl coverage of noble metal containing zeolites Y

temperature-programmed desorption of ammonia (TPD-A) in flowing helium [1]

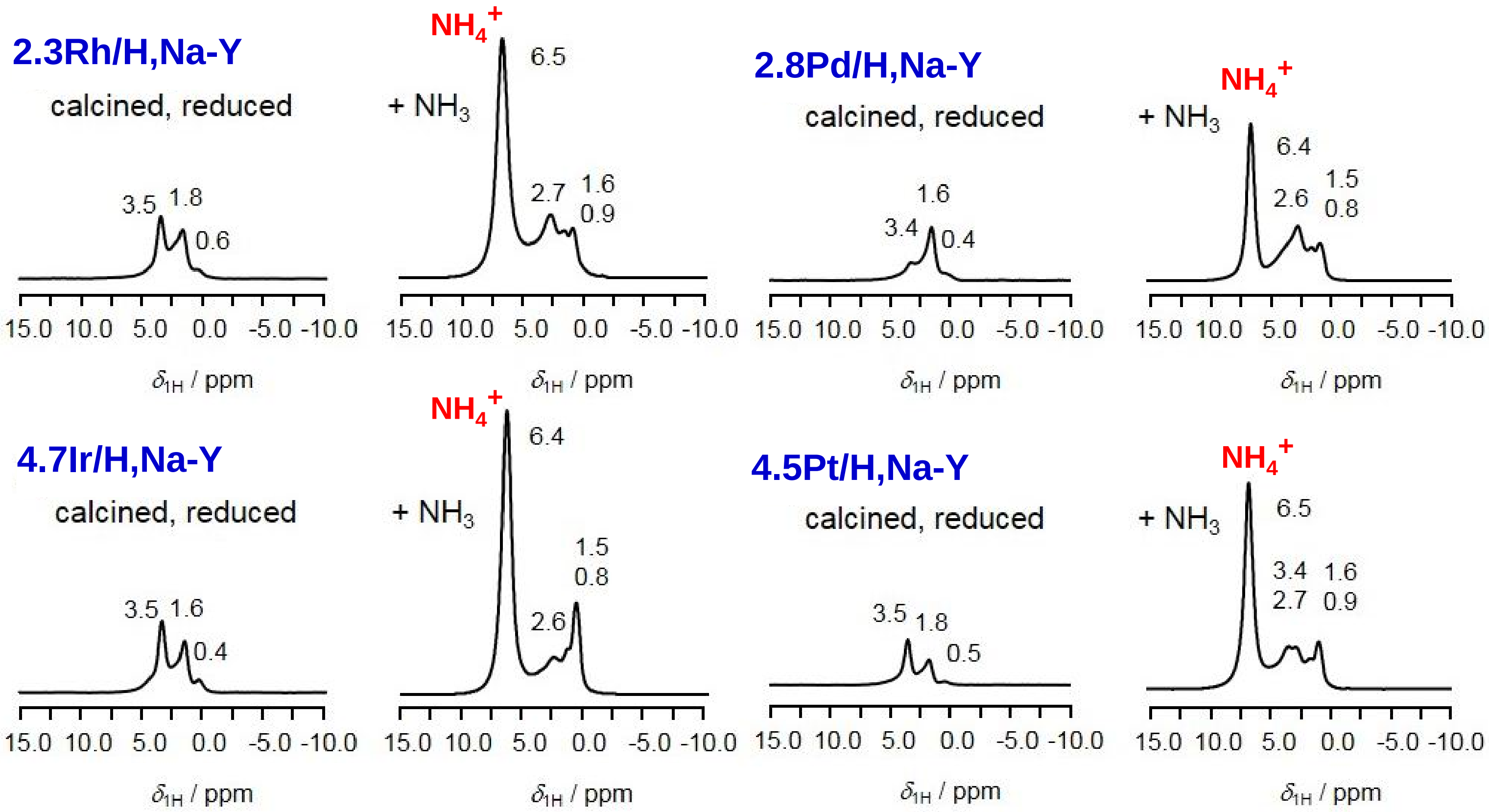


adapted ^{1}H MAS NMR measurement:

- **loading of dehydrated (623 K, vacuum) catalysts with ammonia (100 mbar, 10 min)**
- **evacuation of physisorbed ammonia at 453 for 2 h**

[1] L. Yang et al., Appl. Catal. A 67 (1991) 169.

^{1}H MAS NMR studies of the hydroxyl coverage of noble metal containing zeolites Y



metal OH: 0.4 – 0.9 and 2.6 – 2.7 ppm

SiOH: 1.5 – 1.8 ppm

Si(OH)Al: 3.4 – 3.5 ppm **+ NH_3 → NH_4^+: 6.4 – 6.5 ppm**

U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254-15262.

^{1}H MAS NMR studies of the hydroxyl coverage of noble metal containing zeolites Y

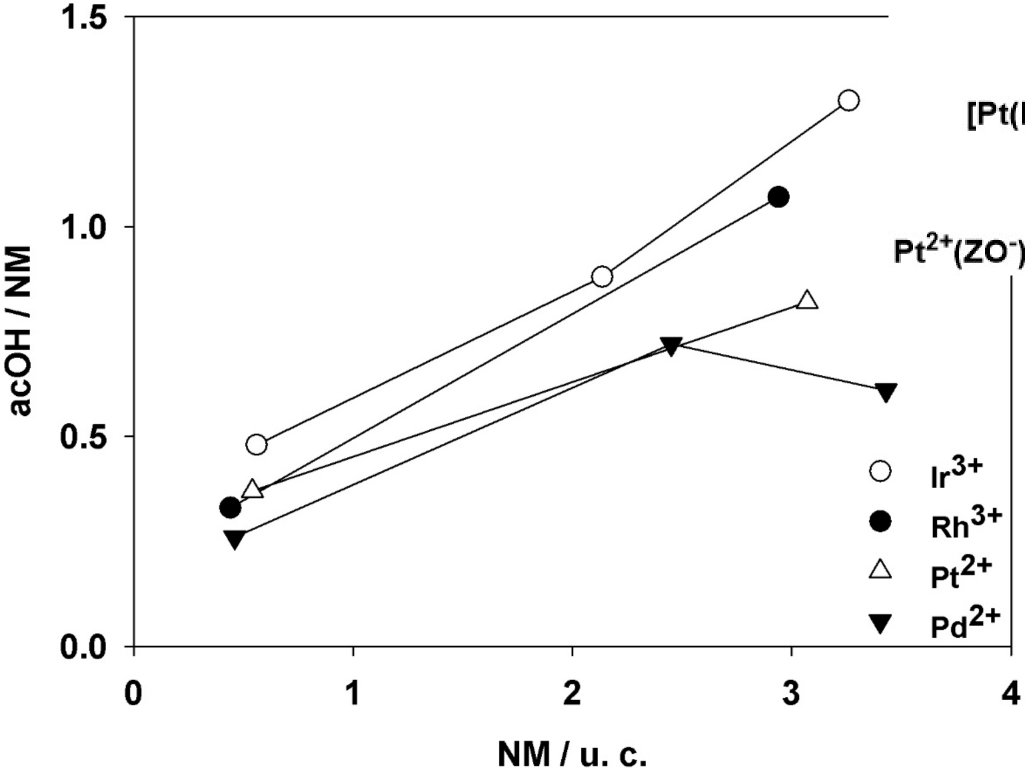
noble metal (NM) loading, noble metal dispersion (*D*), density of acidic OH groups (acOH), and number of acidic OH groups per noble metal atom (acOH/NM)

Samples	NM loading / wt.%	NM loading [a] / u.c.$^{-1}$	*D* / %	Density of acOH / u.c.$^{-1}$	acOH/NM
0.4Rh/H,Na-Y	0.36	0.44	54	0.15	0.3
2.3Rh/H,Na-Y	2.32	2.94	80	3.14	1.1
0.8Ir/H,Na-Y	0.83	0.56	121	0.27	0.5
3.1Ir/H,Na-Y	3.12	2.13	129	1.88	0.9
4.7Ir/H,Na-Y	4.68	3.26	130	4.24	1.3
0.4Pd/H,Na-Y	0.38	0.46	19	0.12	0.3
1.9Pd/H,Na-Y	2.00	2.45	48	1.76	0.7
2.8Pd/H,Na-Y	2.78	3.43	43	2.10	0.6
0.8Pt/H,Na-Y	0.82	0.54	73	0.20	0.4
4.5Pt/H,Na-Y	4.48	3.07	92	2.54	0.8

U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254-15262.

^{1}H MAS NMR studies of the hydroxyl coverage of noble metal containing zeolites Y

ratios of the numbers of acidic Si(OH)Al groups (acOH) and noble metal atoms (NM) for noble metal containing zeolites Y



$[Pt(NH_3)_4]^{2+} + 2Na^+ZO^- \xrightarrow[-2Na^+]{}$

$[Pt(NH_3)_4]^{2+}(ZO^-)_2 \xrightarrow[-4NH_3]{300°C}$

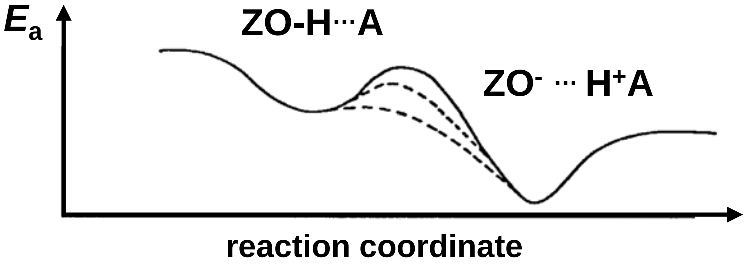
$Pt^{2+}(ZO^-)_2 \xrightarrow{H_2,\ 350°C} Pt^0(H^+)_2(ZO^-)_2$

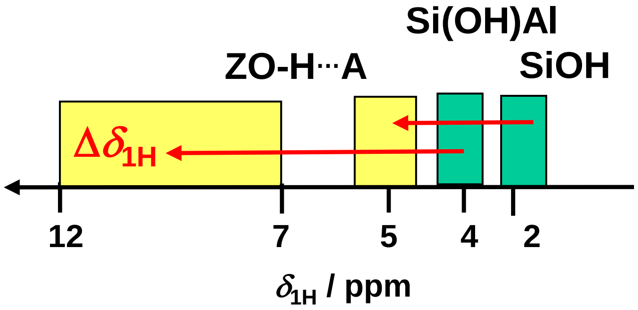
U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254-15262.

^{1}H MAS NMR studies of the acid strength of Si(OH)Al groups in noble metal containing zeolites Y

evaluation of the CD_3CN-induced low-field shift $\Delta\delta_{1H}$ of ^{1}H MAS NMR signals

energy profile of proton transfer reactions





low-field shift $\Delta\delta_{1H}$ of the ^{1}H MAS NMR signal of SiOHAl groups upon adsorption of acetonitrile (CD_3CN):

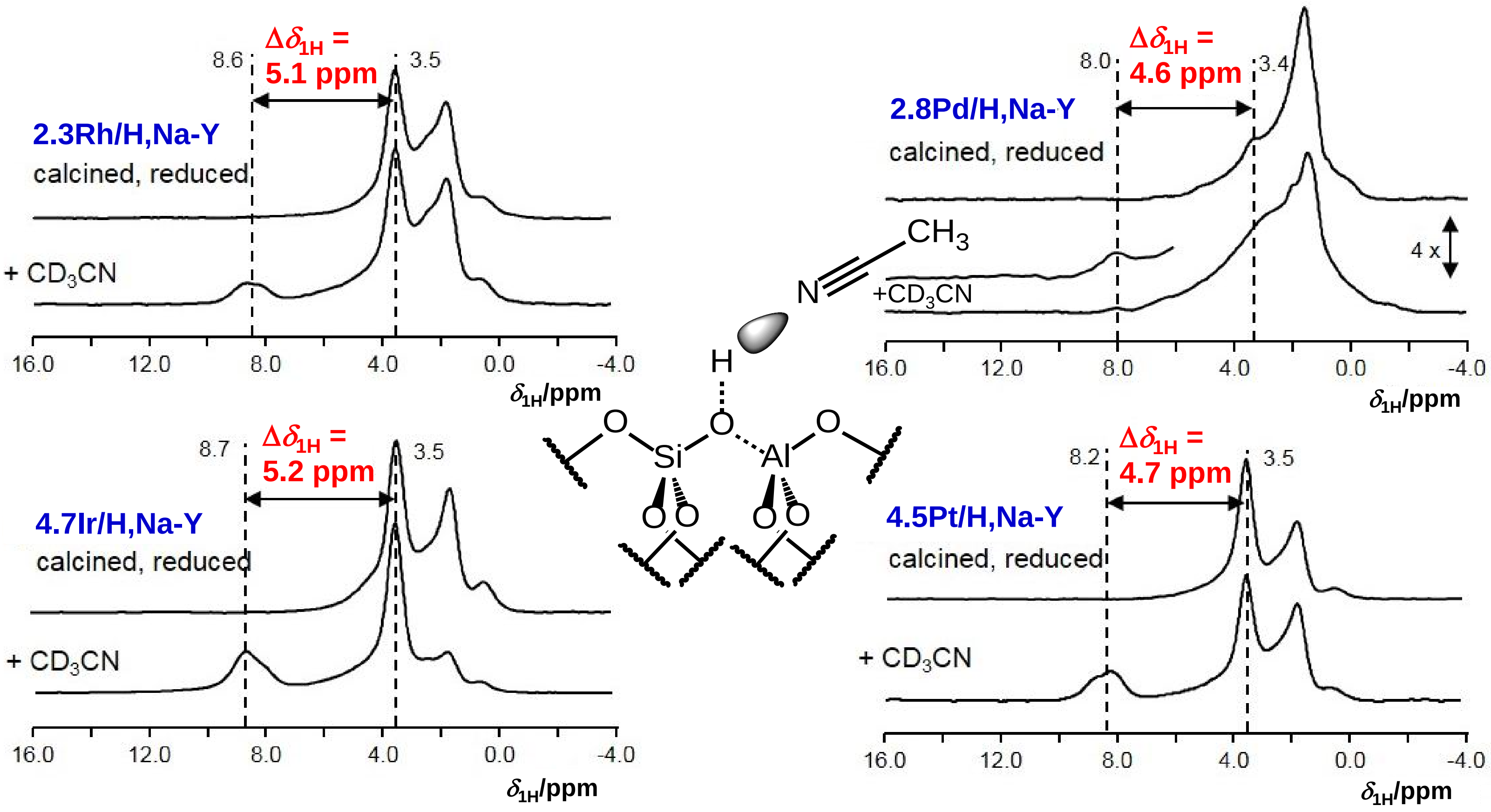
sample	$\Delta\delta_{1H}$ / ppm
AlOH	1.2
SiOH	3.0
Si(OH)Al:	
H,Na-X (n_{Si}/n_{Al} = 1.3)	3.6
H,Na-Y (n_{Si}/n_{Al} = 2.7)	5.1
Al,Na-Y (n_{Si}/n_{Al} = 2.7)	5.3
H,Na-Y (n_{Si}/n_{Al} = 5)	6.4
H-MOR (n_{Si}/n_{Al} = 10)	6.7
H,Na-Y(n_{Si}/n_{Al} = 18)	7.0
H-ZSM-5 (n_{Si}/n_{Al} = 19)	7.2
H-ZSM-5 (n_{Si}/n_{Al} = 26)	7.9

Y. Jiang, J. Huang, W. Dai, M. Hunger, Solid State Nucl. Magn. Reson. 39 (2011) 116-141.

^{1}H MAS NMR studies of the acid strength of Si(OH)Al groups in noble metal containing zeolites Y

evaluation of the CD_3CN-induced low-field shift $\Delta\delta_{1H}$ of ^{1}H MAS NMR signals

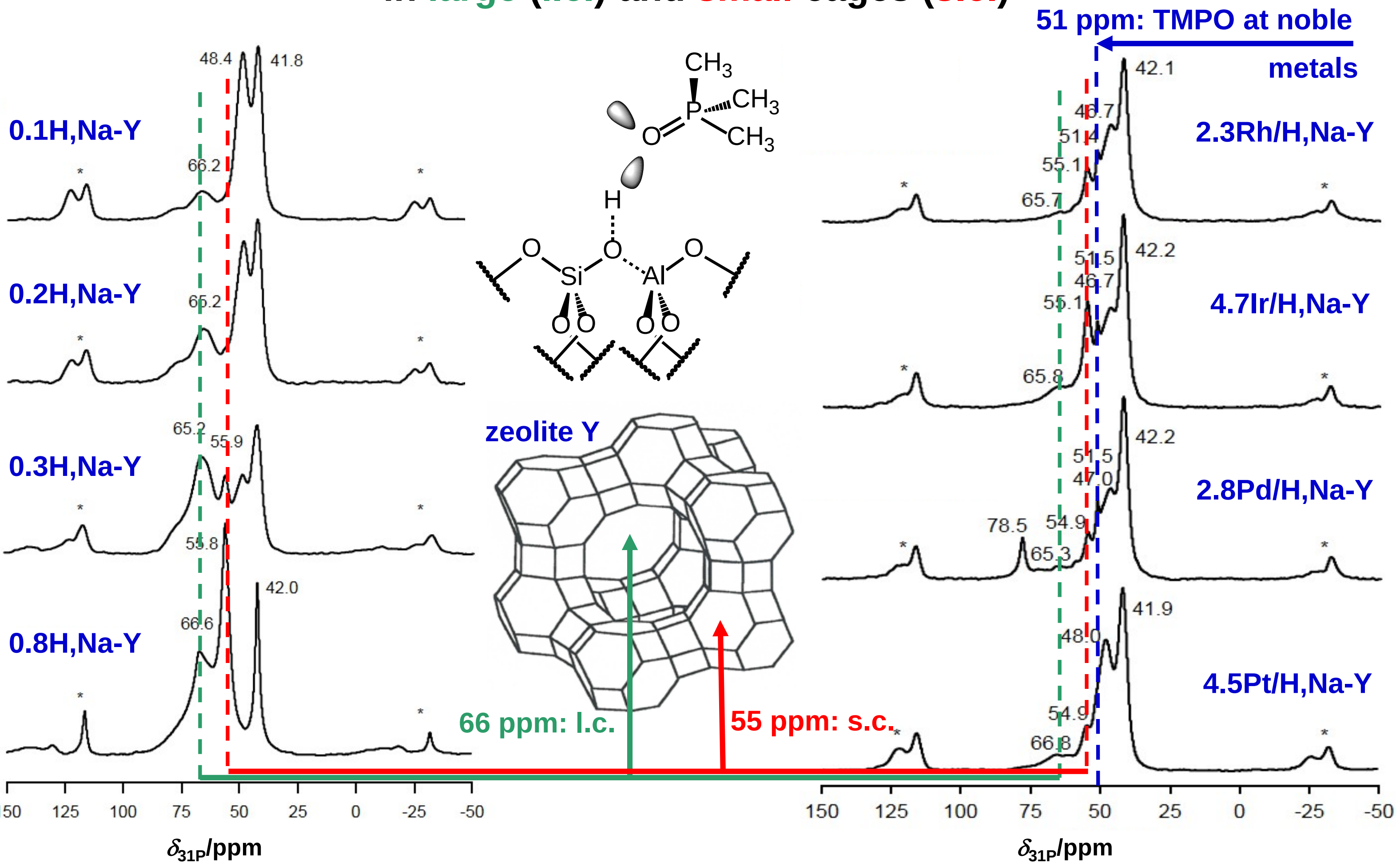
for comparison: 0.2H,Na-Y has $\Delta\delta_{1H}$ = 5.2 ppm



U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254-15262.

^{31}P MAS NMR studies of the surface site location in noble metal containing zeolites Y

interaction of trimethylphosphine oxide (TMPO) with Si(OH)Al groups in large (l.c.) and small cages (s.c.)



51 ppm: TMPO at noble metals

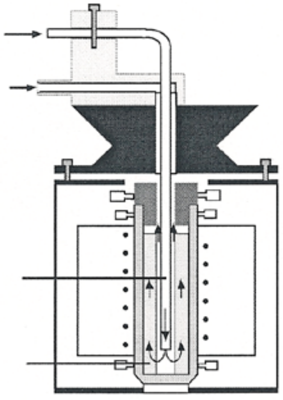
66 ppm: l.c.

55 ppm: s.c.

U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254-15262.

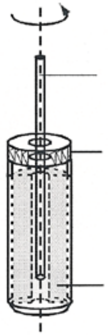
Intrinsic hydrogenation activity investigated by *in situ* MAS NMR spectroscopy

Experimental technique of in situ MAS NMR spectroscopy under flow conditions



reactant flow

purge flow



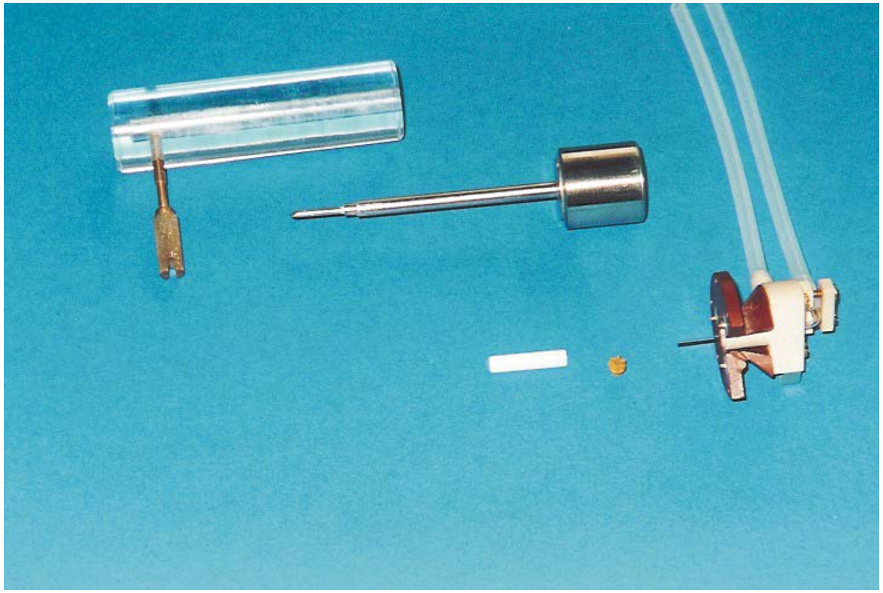
injection tube

rotor cap

catalyst bed

modified 4 mm Bruker MAS NMR probe equipped with an injection system

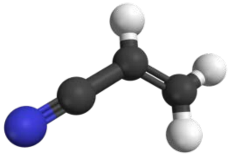
tools for the preparation of the catalyst bed (hollow cylinder) inside the MAS NMR rotor



A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.
M. Hunger, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105-127.

Study of the intrinsic acrylonitrile hydrogenation rate on noble metal containing porous solids

hydrogenation of pre-adsorbed acrylonitrile with H_2 at T = 298 K

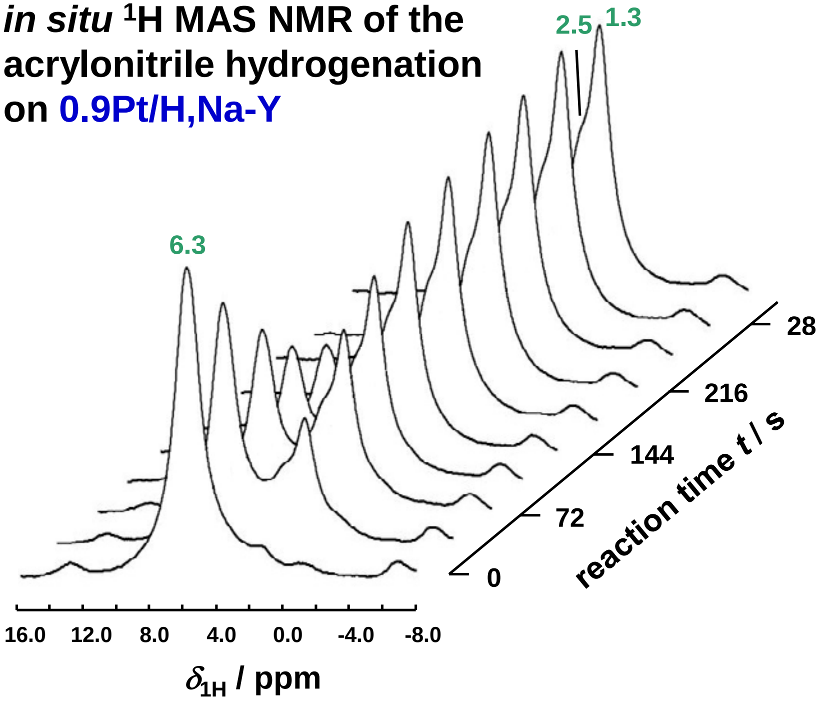


$$\underset{}{N \equiv \overset{106.5}{C} - \overset{119.2}{C}\underset{5.9}{H} = \overset{141.5\ \text{ppm}}{C}\underset{6.3\ \text{ppm}}{H_2}} \xrightarrow[\text{catalyst}]{+ H_2} N \equiv \overset{120.8}{C} - \overset{10.8}{C}H\underset{2.5}{H} - \overset{10.6\ \text{ppm}}{C}H_2\underset{1.3\ \text{ppm}}{H}$$

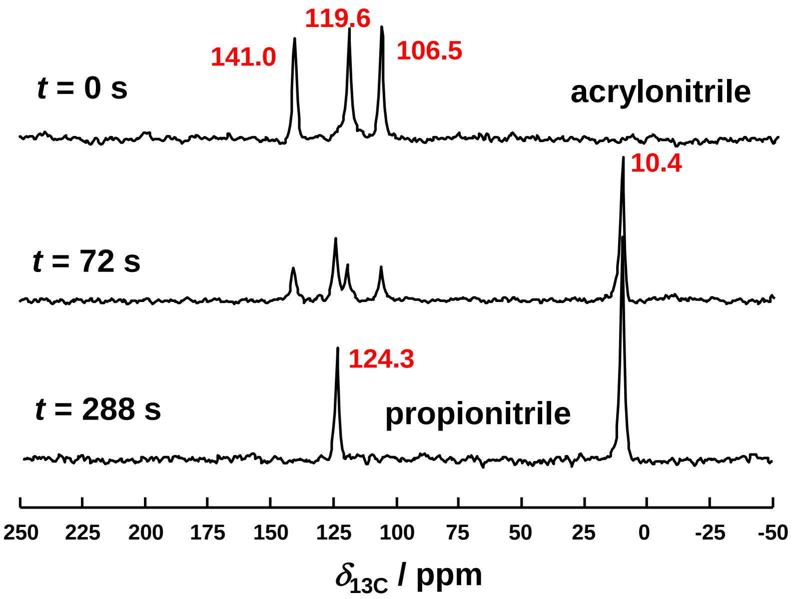
^{13}C NMR

^{1}H NMR shift values

in situ ^{1}H MAS NMR of the acrylonitrile hydrogenation on 0.9Pt/H,Na-Y



in situ ^{13}C MAS NMR of the acrylonitrile hydrogenation on 0.9Pt/H,Na-Y

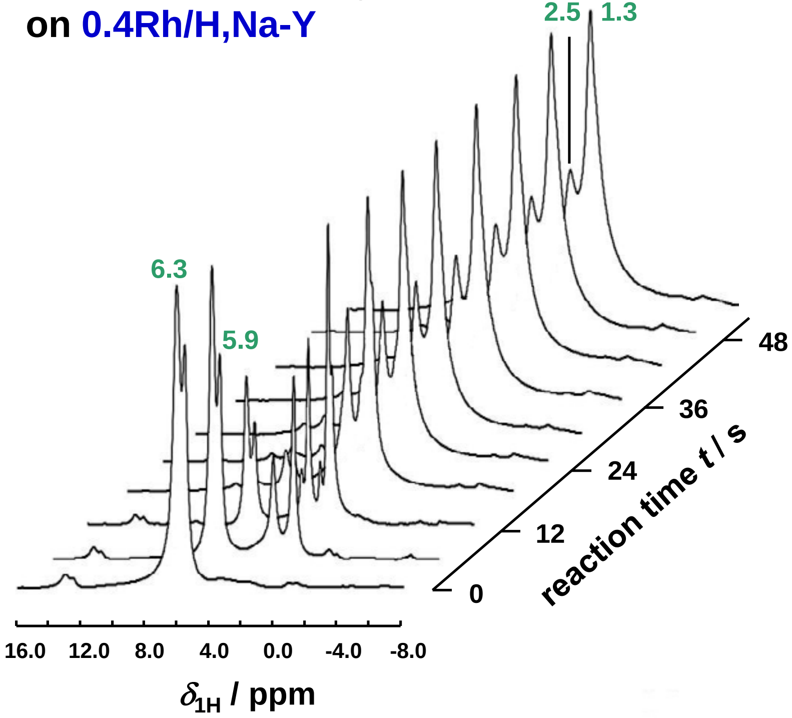


Bruker Avance III 400WB spectrometer, modified 7 mm MAS NMR probe, ν_{rot} ca. 2 kHz, 1 FID per spectrum, D1 = 6 s

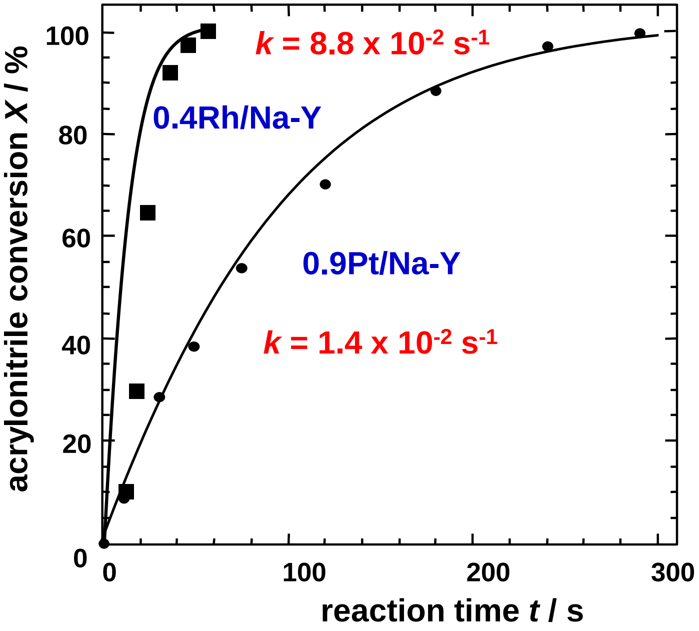
H. Henning et al., Micropor. Mesopor. Mater. 164 (2012) 104.

Study of the intrinsic acrylonitrile hydrogenation rate on noble metal containing porous solids

***in situ* ^{1}H MAS NMR of acrylonitrile hydrogenation on 0.4Rh/H,Na-Y**



determination of the velocity constants *k* of the intrinsic hydrogenation of acrylonitrile

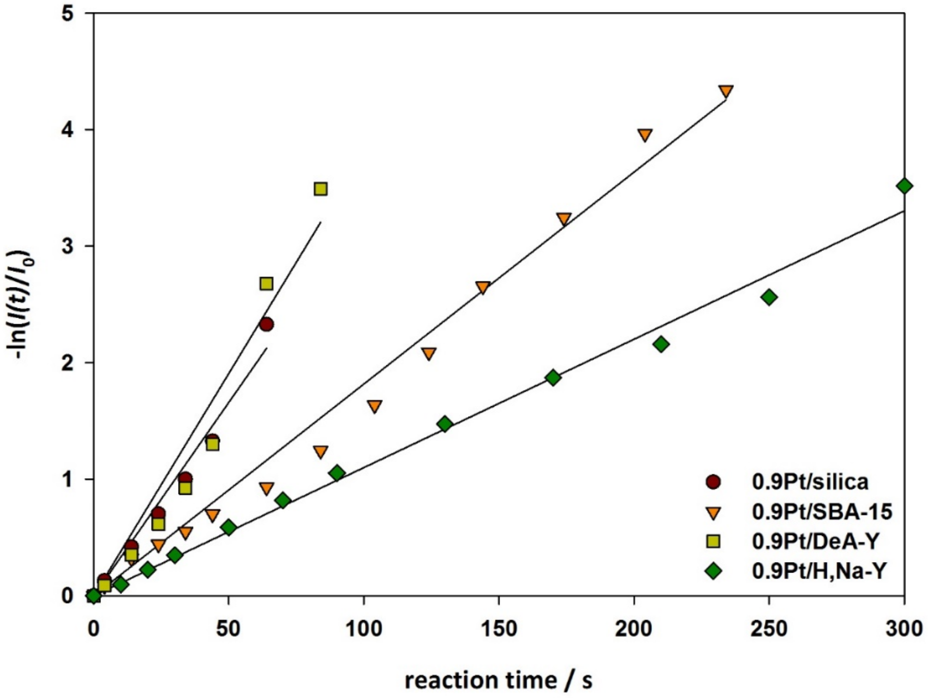


H. Henning et al., Micropor. Mesopor. Mater. 164 (2012) 104.

Study of the intrinsic acrylonitrile hydrogenation rate on noble metal containing porous solids

catalyst	n_{Si}/n_{Al}	noble metal content / wt %	dispersion / %
0.9Pt/silica	∞	0.85	83
0.9Pt/SBA-15	199	0.78	68
0.9Pt/DeA-Y	93	0.96	72
0.9Pt/H,Na-Y	2.7	0.82	73
0.3Rh/silica	∞	0.29	59
0.3Rh/SBA-15	209	0.33	60
0.4Rh/DeA-Y	112	0.37	68
0.4Rh/H,Na-Y	2.7	0.42	63
0.8Ir/H,Na-Y	2.7	0.84	121
0.4Pd/H,Na-Y	3.0	0.40	43

determination of the velocity constants *k* of the intrinsic hydrogenation of acrylonitrile on Pt containing solid catalysts



Bruker Avance III 400WB spectrometer, modified 4 mm MAS NMR probe, ν_{rot} ca. 4 kHz, 1 FID per spectrum, D1 = 6 s

U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284-2291.

Study of the intrinsic acrylonitrile hydrogenation rate on noble metal containing porous solids

velocity constants *k* and reaction rates *r* of the intrinsic hydrogenation of acrylonitrile on noble metal containing solid catalysts

catalyst	acrylonitrile / mmol	*k* / s^{-1}	*r* / mmol s^{-1}
0.9Pt/silica	0.023	$(3.3 \pm 0.3) \times 10^{-2}$	**$(7.6 \pm 1.1) \times 10^{-4}$**
0.9Pt/SBA-15	0.018	$(1.8 \pm 0.2) \times 10^{-2}$	**$(3.2 \pm 0.5) \times 10^{-4}$**
0.9Pt/DeA-Y	0.018	$(3.8 \pm 0.4) \times 10^{-2}$	**$(6.8 \pm 0.9) \times 10^{-4}$**
0.9Pt/H,Na-Y	0.021	$(1.1 \pm 0.1) \times 10^{-2}$	**$(2.3 \pm 0.3) \times 10^{-4}$**
0.4Rh/H,Na-Y	0.020	$(3.4 \pm 0.3) \times 10^{-2}$	**$(6.8 \pm 1.0) \times 10^{-4}$**
0.8Ir/H,Na-Y	0.017	$(6.7 \pm 0.7) \times 10^{-4}$	**$(0.11 \pm 0.02) \times 10^{-4}$**
0.4Pd/H,Na-Y	0.027	1.1 ± 0.3	**$(270 \pm 50) \times 10^{-4}$**

- **same kind and numbers of noble metals on different porous support materials lead to similar hydrogenation rates (same order of magnitude)**
- **sequence of *r* values catalysts (H,Na-Y) loaded with different noble metals:**

0.4Pd/H,Na-Y > 0.4Rh/H,Na-Y > 0.9Pt/H,Na-Y > 0.8Ir/H,Na-Y

U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284-2291.
U. Obenaus et al., J. Phys. Chem. C 121 (2017) 9953-9962.

Comparison of the hydrogenation and dehydrogenation activities of noble metal containing zeolites Y

Comparison of the hydrogenation and dehydrogenation rates of noble metal containing zeolites Y

dehydrogenation of propane in a standard fixed-bed reactor at 828 K, under atmospheric pressure, propane/N_2 mixture of 2:1, $WHSV_{C3}$ = 3 h^{-1} and after TOS = 35 min

catalyst	X_{C3} / %	$S_{C3=}$ / %	$Y_{C3=}$ / %	*TOF* / s^{-1}
0.4Pd/H,NaY	2	49	1	**1.03**
0.4Rh/H,NaY	2	73	1	**1.13**
0.8Pt/H,NaY	18	69	12	**8.39**
0.8Ir/H,NaY	6	63	4	**2.68**
2.8Pd/H,NaY	3	62	2	**0.20**
2.3Rh/H,NaY	3	80	2	**0.20**
4.5Pt/H,NaY	33	51	17	**2.71**
4.7Ir/H,NaY	8	57	5	**0.67**

- **sequence of *r* values (hydrogenation of acrylonitrile):**

  0.4Pd/H,Na-Y > 0.4Rh/H,Na-Y > 0.9Pt/H,Na-Y > 0.8Ir/H,Na-Y

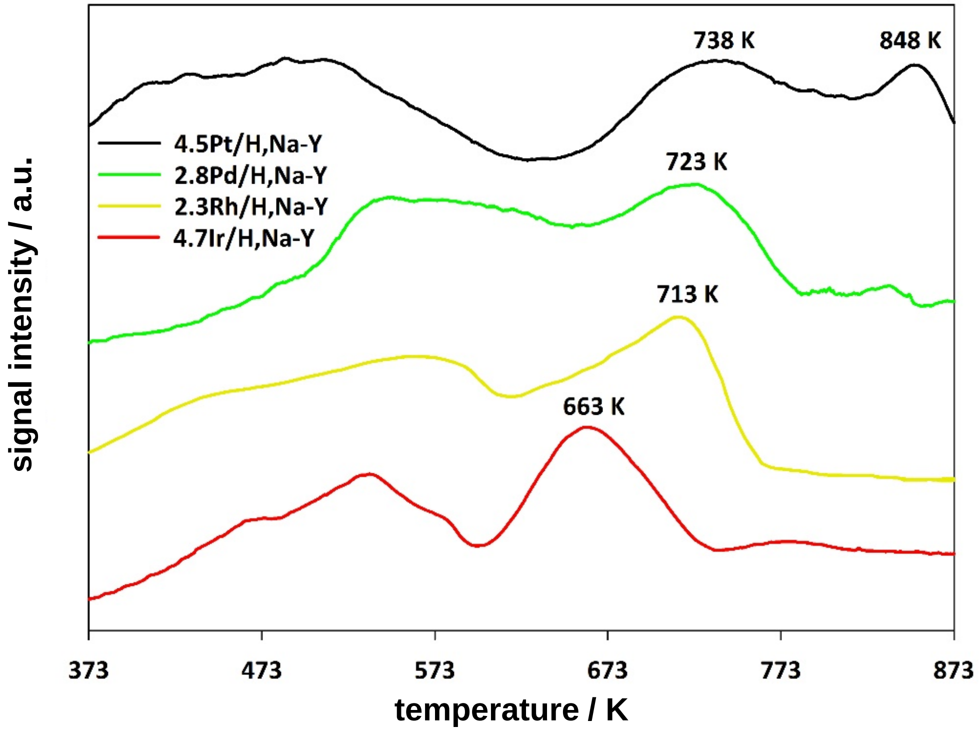
- **sequence of turn-over-frequencies *TOF* (dehydrogenation of propane):**

  0.4Pd/H,Na-Y ≤ 0.4Rh/H,Na-Y < 0.8Ir/H,Na-Y < 0.8Pt/H,Na-Y

  2.8Pd/H,Na-Y = 2.3Rh/H,Na-Y < 4.7Ir/H,Na-Y < 4.5 Pt/H,Na-Y

U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284-2291.

Comparison of the hydrogenation and dehydrogenation rates of noble metal containing zeolites Y



- **high-temperature peaks T_{HT} of H_2 desorption (TPD):**

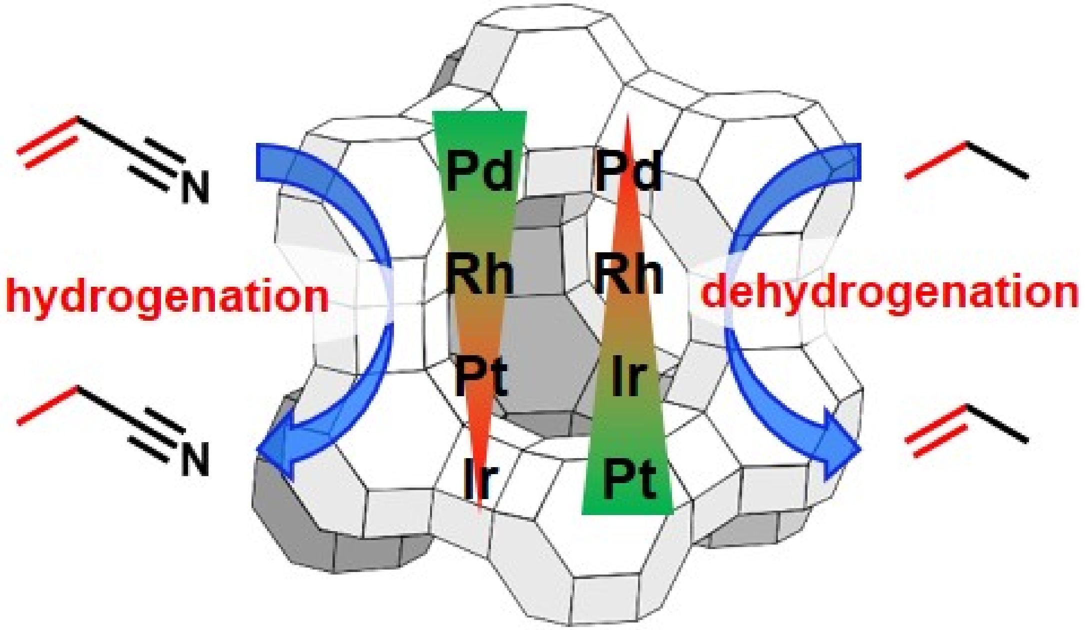
  Pd/H,Na-Y (T_{HT} = 723 K) > Rh/H,Na-Y (T_{HT} = 713 K) > Ir/H,Na-Y (T_{HT} = 663 K)

- **T_{HT} = 738 K and 848 K for Pt/H,Na-Y:**

  may be explained by strong H chemisorption inside Pt clusters

U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284-2291 (Supporting Information).

Comparison of the hydrogenation and dehydrogenation rates of noble metal containing zeolites Y



- high-temperature peaks T_{HT} of H_2 desorption (TPD):

  Pd/H,Na-Y (T_{HT} = 723 K) > Rh/H,Na-Y (T_{HT} = 713 K) > Ir/H,Na-Y (T_{HT} = 663 K)

- T_{HT} = 738 K and 848 K for Pt/H,Na-Y:

  strong H chemisorption inside Pt clusters may enhance dehydrogenation

U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284-2291.

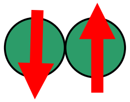
Parahydrogen induced polarization in porous solids studied by *in situ* MAS NMR spectroscopy

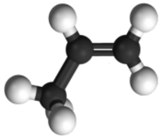
Parahydrogen induced polarization (PHIP) on porous solids

PASADENA: Parahydrogen And Synthesis Allow Dramatically Enhanced Nuclear Alignment (p-H_2 incorporation inside a strong B_0 field)

hydrogenation of propene with para-enriched H_2

p-H_2:

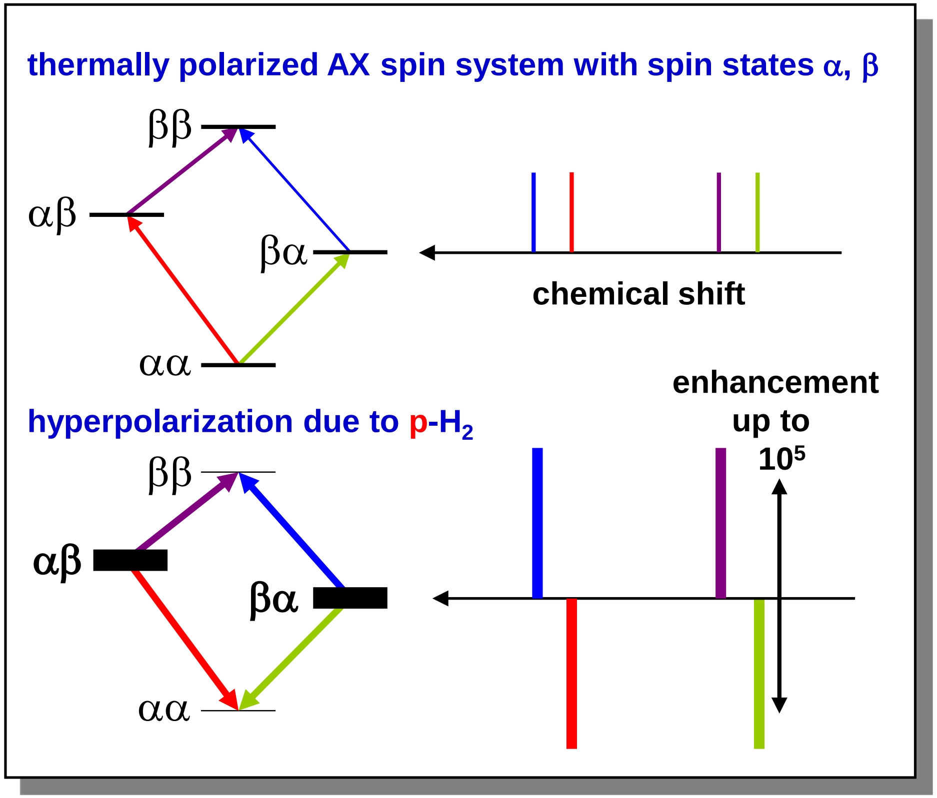




$$CH_3-CH=CH_2 \xrightarrow{+\ p\text{-}H_2} CH_3-CHH_{(A)}-CH_2H_{(X)}$$

- **pairwise incorporation of the two H atoms of p-H_2 causes large non-equilibrium spin polarization**

- **^1H MAS NMR signals due to a pairwise incorporation of p-H_2 into reactants have typical anti-phases (bottom)**

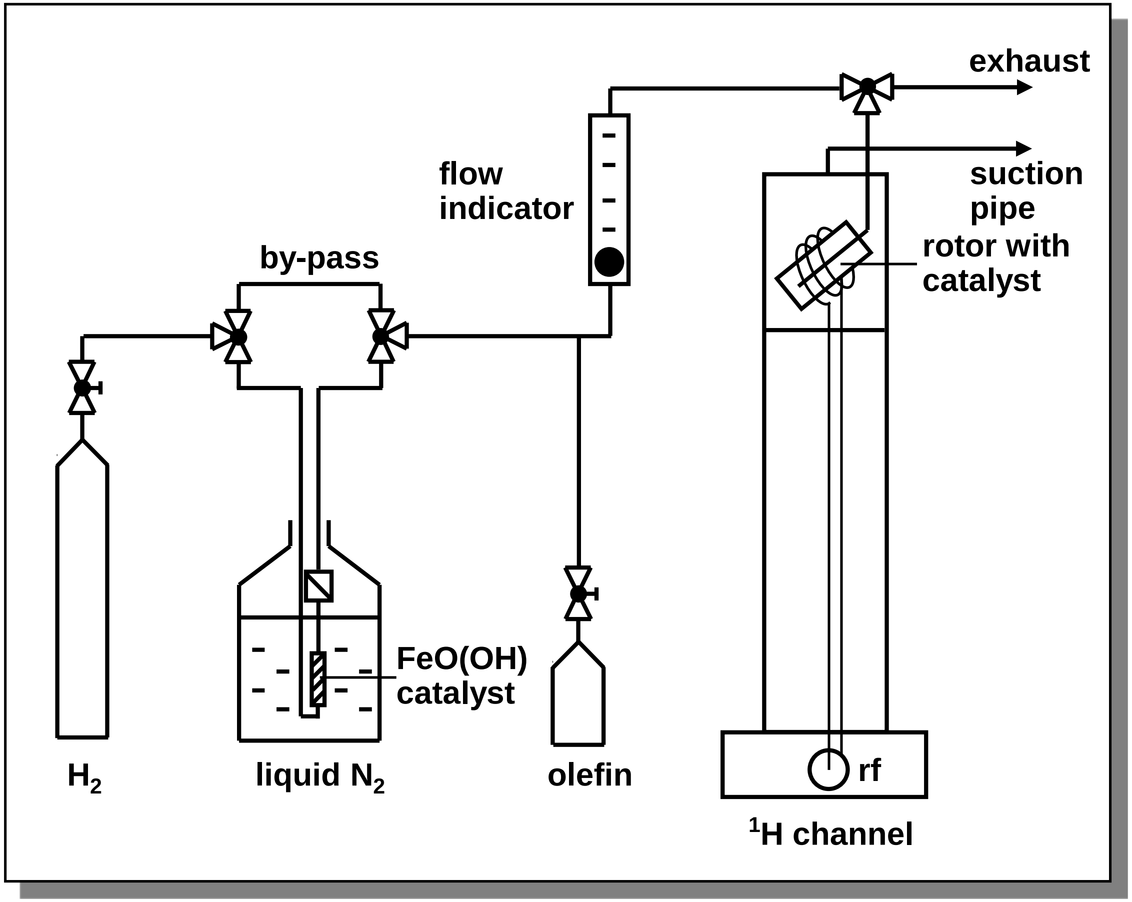


J. Natterer, J. Bargon, Prog. Nucl. Magn. Reson. Spec. 31 (1997) 293.

Parahydrogen induced polarization (PHIP) on porous solids

in situ **^{1}H MAS NMR studies of PHIP:**

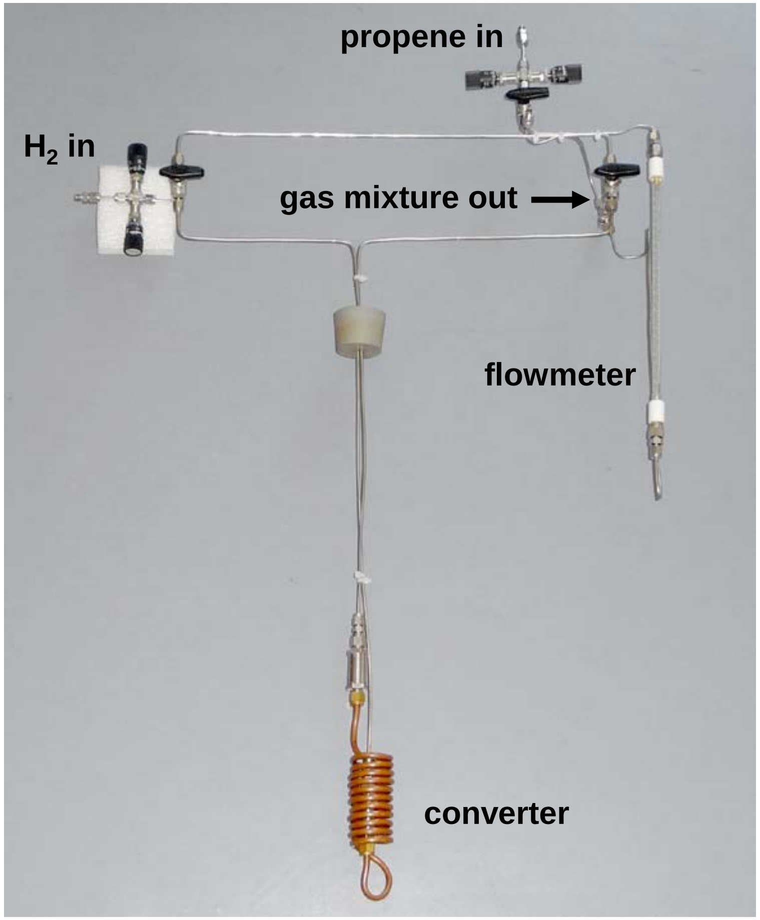
- **modified 4 mm Bruker MAS NMR probe**
- **at ν_0 = 400.13 MHz, ν_{rot} ca. 4 kHz, π/4 pulses, *NS* = 96, D1 = 0.1 s**
- **para : ortho ratio of 1 : 1 (p-H_2) obtained by contact with FeO(OH) (Sigma-Aldrich) placed in liquid nitrogen**
- **propene and p-H_2 flows of 40 and 30 ml/min, respectively**



U. Obenaus et al., J. Phys. Chem. C 121 (2017) 9953-9962.

Parahydrogen induced polarization (PHIP) on porous solids

equipment utilized for *in situ* ^{1}H MAS NMR studies of PHIP:



p-H_2 converter and gas mixing system

flow MAS NMR probe

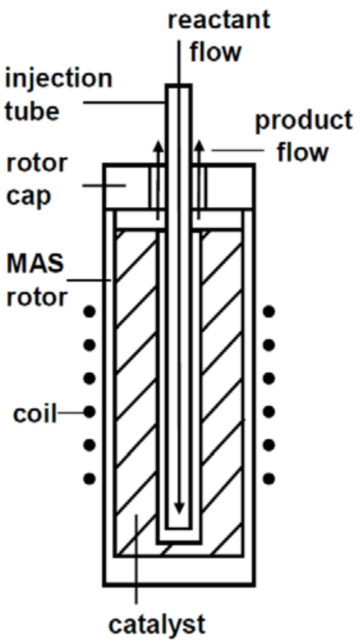
Parahydrogen induced polarization (PHIP) on porous solids

hydrogenation catalysts

catalyst	n_{Si}/n_{Al}	noble metal content / wt %	BET surface / $m^2\ g^{-1}$	total pore volume / $cm^3\ g^{-1}$	pore size / nm
0.9Pt/silica	∞	0.85	277	0.31	**4.55** [a]
0.9Pt/SBA-15	199	0.78	420	0.36	**3.43** [a]
0.9Pt/DeA-Y	93	0.96	721	0.42	**0.74** [b]
0.9Pt/H,Na-Y	2.7	0.82	937	0.47	**0.74** [b]
0.3Rh/silica	∞	0.29	282	0.27	**3.77** [a]
0.3Rh/SBA-15	209	0.33	690	0.72	**4.07** [a]
0.4Rh/DeA-Y	112	0.37	749	0.39	**0.74** [b]
0.4Rh/H,Na-Y	2.7	0.42	1012	0.54	**0.74** [b]
0.8Ir/H,Na-Y	2.7	0.84	1050	0.52	**0.74** [b]
0.4Pd/H,Na-Y	3.0	0.40	913	0.45	**0.74** [b]

a) **average pore size determined by N_2 adsorption**

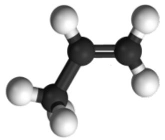
b) **crystallographic pore size**



ca. 40 mg catalyst
filling factor ca. 80 %

U. Obenaus et al., J. Phys. Chem. C 121 (2017) 9953-9962.

Parahydrogen induced polarization (PHIP) on porous solids



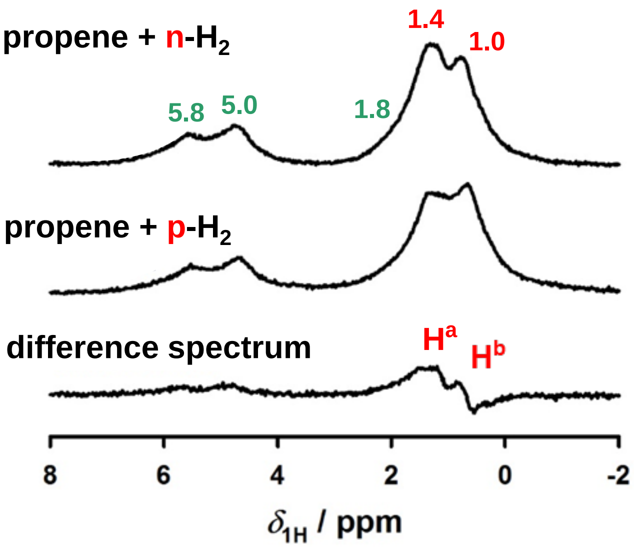
$CH_3-CH=CH_2 \xrightarrow[\text{catalyst}]{+\ p\text{-}H_2} CH_3-CHH^a-CH_2H^b$

CH_3	CH	CH_2		CH_3	CHH^a	CH_2H^b
1.72	5.71	4.92		0.91	1.33	0.91

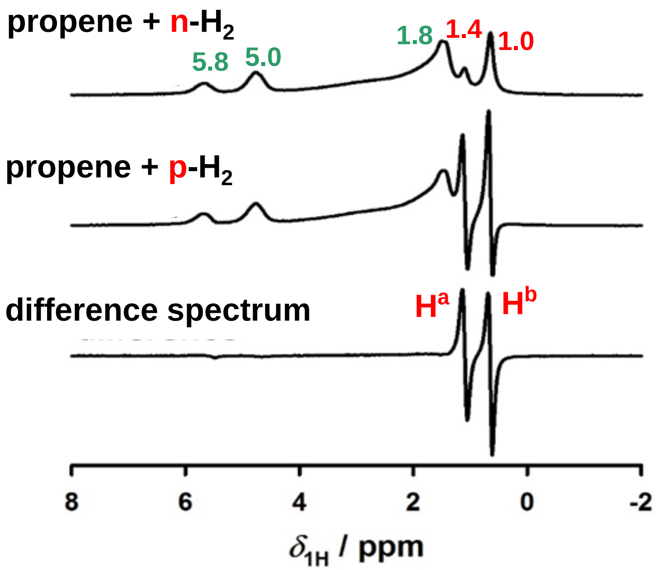
^1H NMR shift values (literature)

in situ ^1H MAS NMR investigation of PHIP on 0.9Pt/silica at T = 298 K

without MAS



with MAS (ca. 4 kHz)

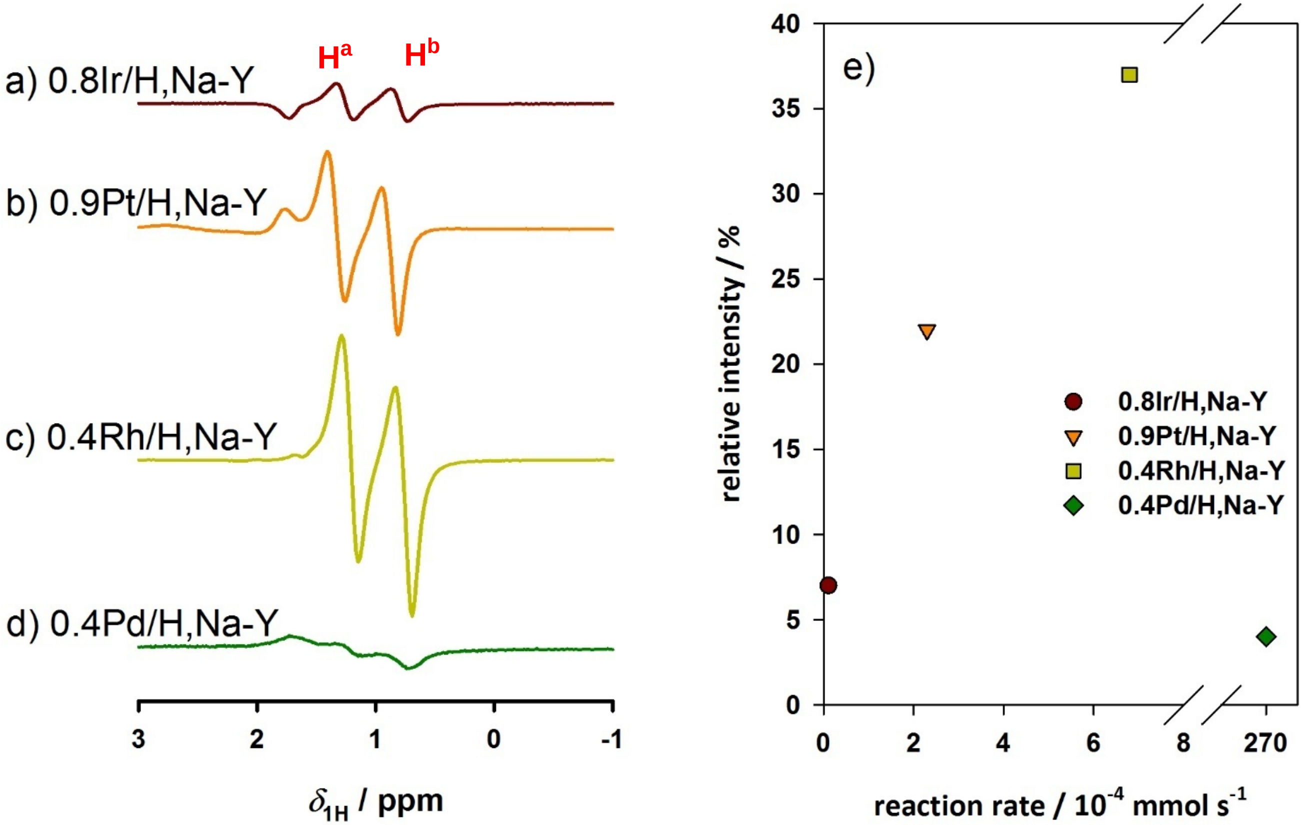


- anti-phase signals indicate pairwise incorporation of p-H_2 into propene
- signal narrowing by MAS hints at dipolar interactions of reactants inside pores

U. Obenaus et al., J. Phys. Chem. C 121 (2017) 9953-9962.

Parahydrogen induced polarization (PHIP) on porous solids

in situ **^{1}H MAS NMR investigation of PHIP on zeolite H,Na-Y**

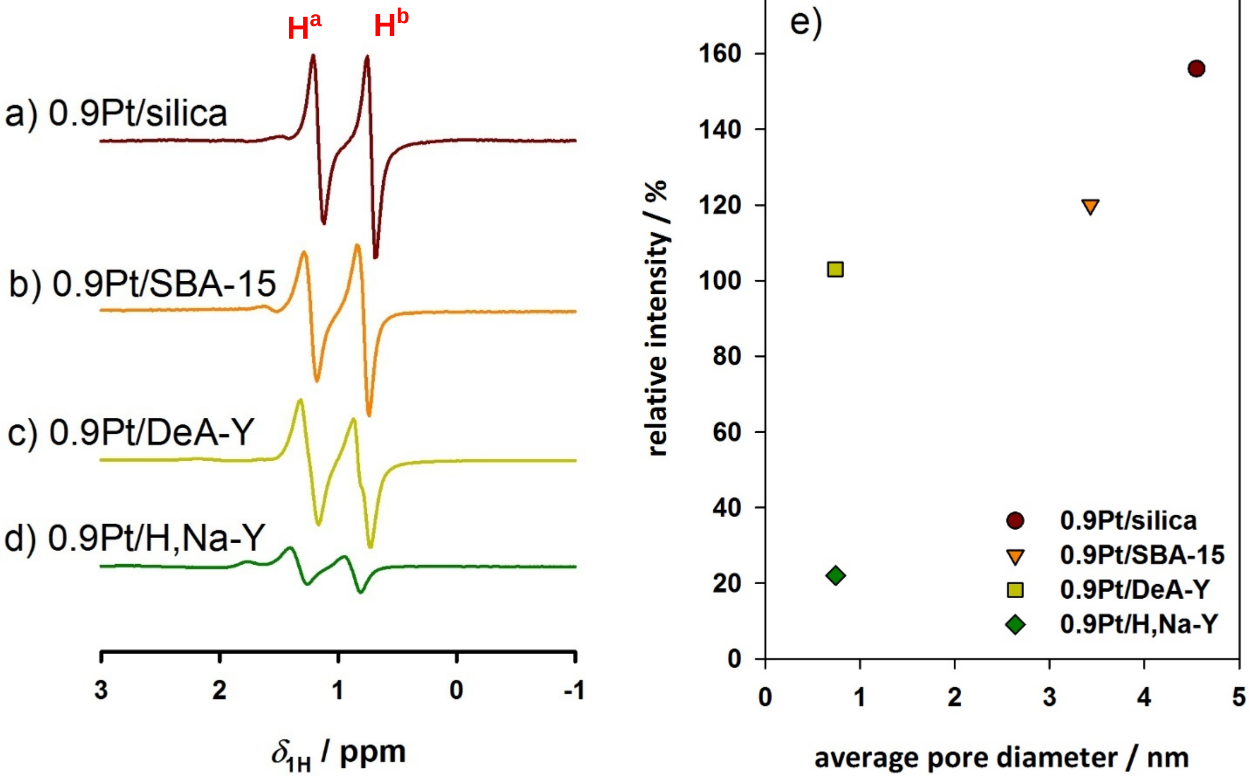


- **moderate hydrogenation activities (acrylonitrile) are suitable for PHIP formation, while a too high activity (0.4Pd/H,Na-Y) suppresses the pairwise p-H_2 incorporation**

U. Obenaus et al., J. Phys. Chem. C 121 (2017) 9953-9962.

Parahydrogen induced polarization (PHIP) on porous solids

in situ **^{1}H MAS NMR investigation of PHIP on Pt containing porous solids**



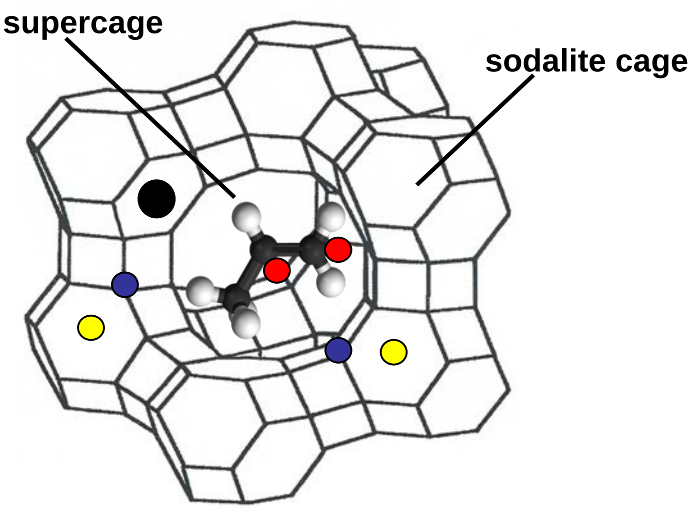
- **intensities of the anti-phase signals depend slightly on pore size and strongly on presence of framework Al and Na^+ cations**

U. Obenaus et al., J. Phys. Chem. C 121 (2017) 9953-9962.

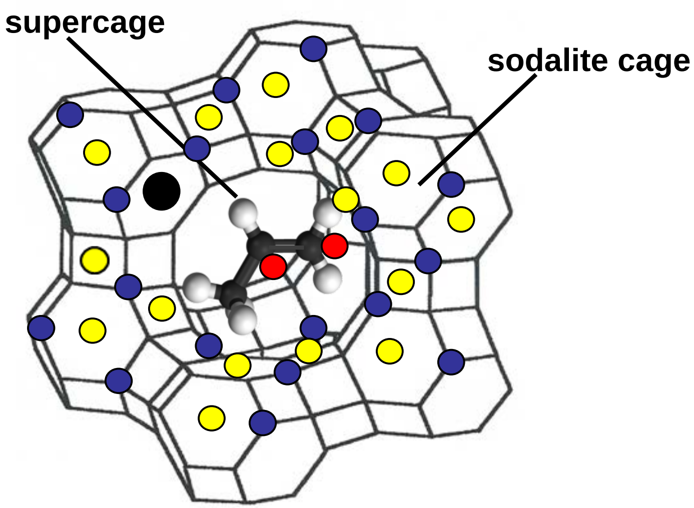
Parahydrogen induced polarization (PHIP) on porous solids

possible spin interactions of hyperpolarized propane in zeolite Y

0.9Pt/DeA-Y (n_{Si}/n_{Al} = 93)



0.9Pt/H,Na-Y (n_{Si}/n_{Al} = 2.7)

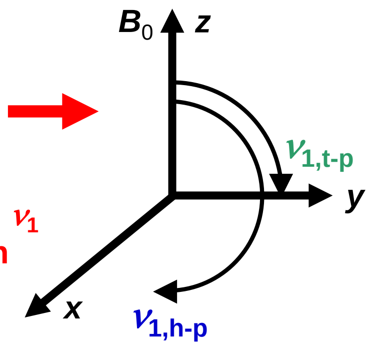


- ● **hyperpolarized H atom**
- ● **Pt atom (*I* = 1/2, 34 %)**
- ● **Al atom (*I* = 5/2, 100 %)**
- ○ **Na$^+$ cation (*I* = 3/2, 100 %)**

Parahydrogen induced polarization (PHIP) on porous solids

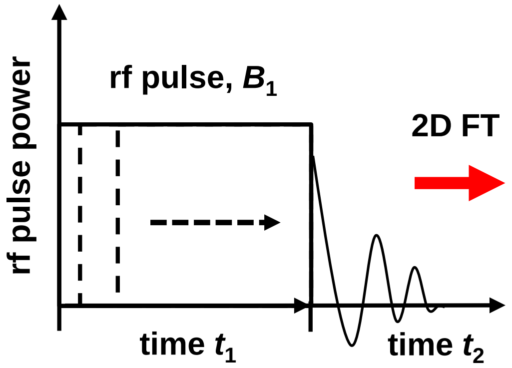
optimum excitation of thermally polarized spins: $\pi/2$ **pulse (**$\nu_{1,\text{t-p}}$**)**

optimum excitation of hyperpolarized spins [1]: $\pi/4$ **pulse (**$\nu_{1,\text{h-p}}$**)**

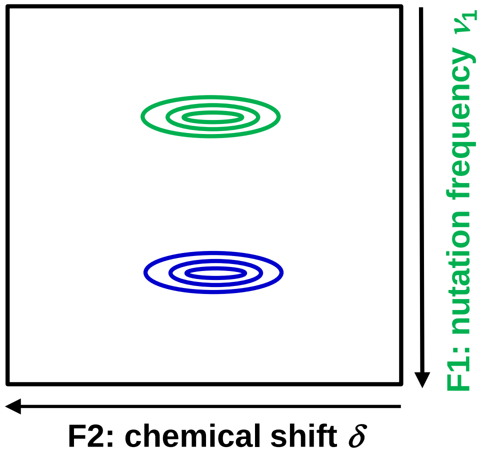


different nutation frequencies ν_1 in the rf field during excitation

2D nutation NMR experiment [2]



2D nutation spectrum



2D nutation analysis of chemically induced dynamic nuclear polarization in Ref. [3]

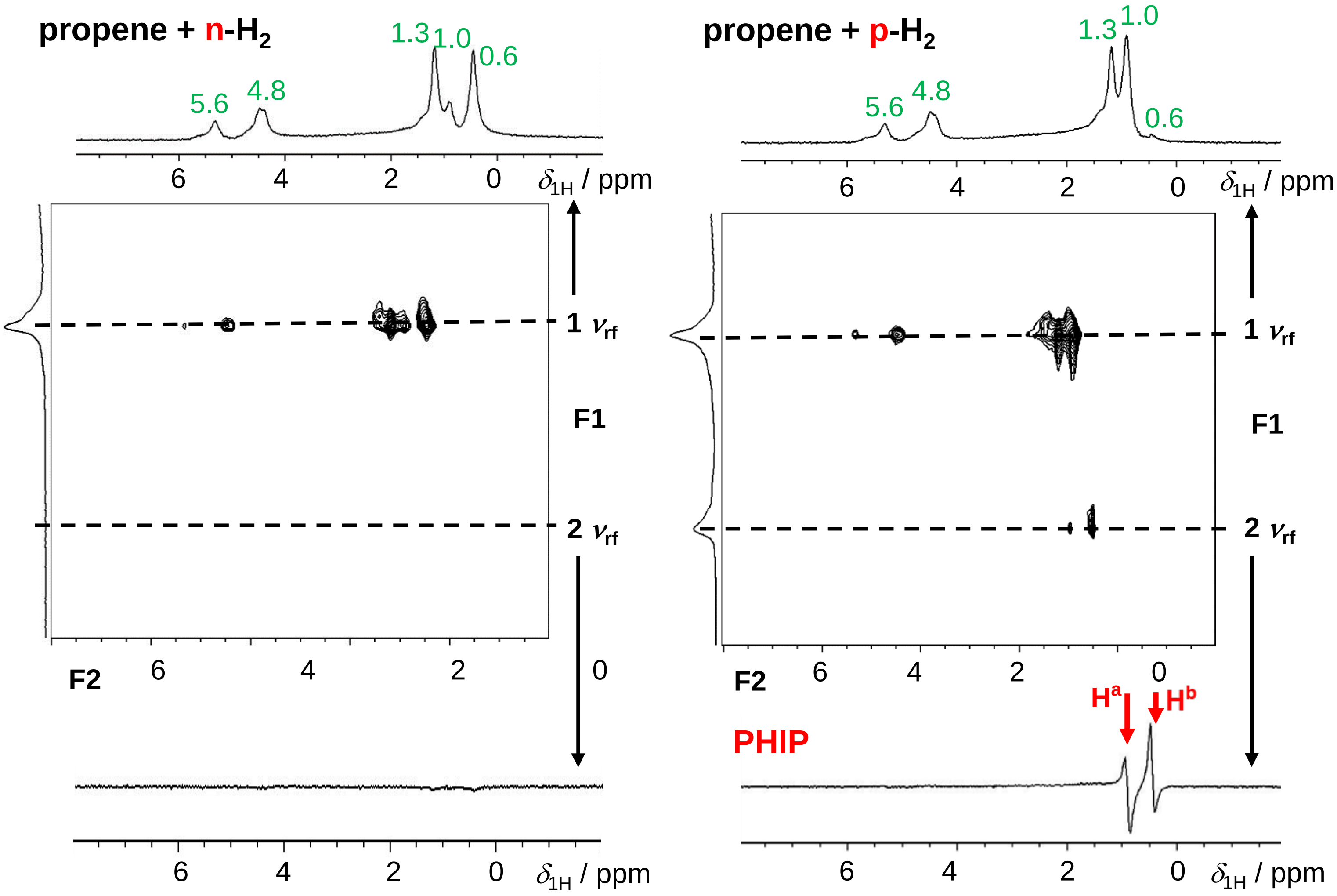
[1] D. Canet et al., Concepts in Magnetic Resonance A, 28 (2006) 321-330.

[2] G.A.H. Tijink et al., J. Am. Chem. Soc. 109 (1987) 7301-7303.

[3] H.-M. Vieth and co-workers, Z. Phys. Chem. 217 (2003) 1641-1659 and 227 (2013) 929-953.

Parahydrogen induced polarization (PHIP) on porous solids

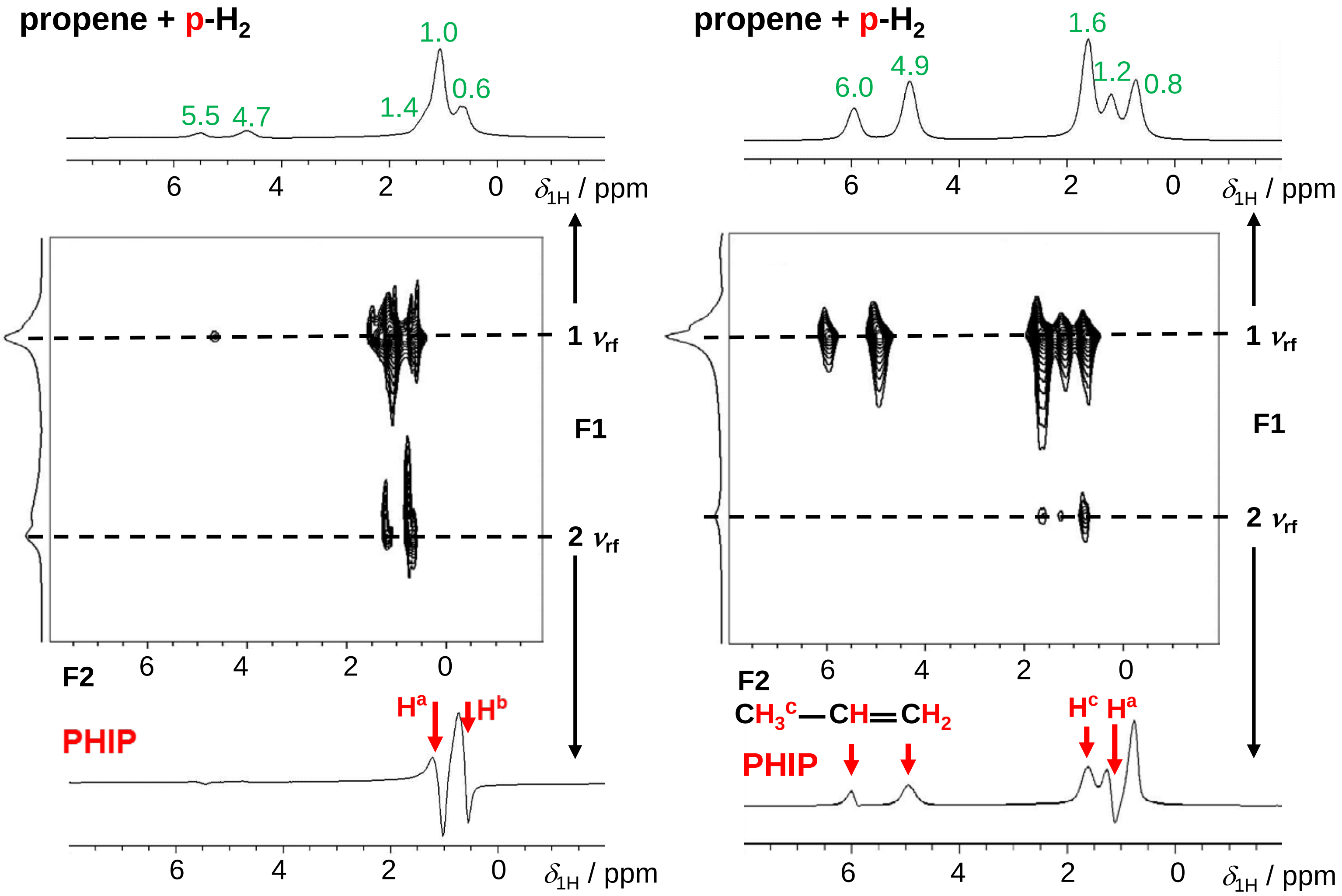
***in situ* 2D ^{1}H nutation MAS NMR on 0.9Pt/silica**



U. Obenaus et al., ChemPhysChem 18 (2017) 455-458.

Parahydrogen induced polarization (PHIP) on porous solids

***in situ* 2D ^{1}H nutation MAS NMR on 0.9Pt/DeA-Y (left) and 0.9Pt/H,Na-Y (right)**



U. Obenaus et al., in preparation.

Effect of noble metal loading and pore size on the hydrogenation behaviour of solid catalysts

Summary

- reduction of noble metals (NM) in H_2 at 623 K leads to formation 0.3 to 1.3 acOH/NM, which are characterized by a medium acid strength for Pd- and Pt-loaded zeolites Y

- intrinsic hydrogenation rates *r* of noble metal containing zeolites Y:

  Pd/H,Na-Y > Rh/H,Na-Y > Pt/H,Na-Y > Ir/H,Na-Y

- dehydrogenation rates (*TOF*) have opposite sequence:

  Pd/H,Na-Y ≤ Rh/H,Na-Y < Ir/H,Na-Y << Pt/H,Na-Y

- H_2-TPD indicates a positive effect of a hydrogen reservoit on the noble metals for the hydrogenation (T_{HT} = 738 K and 848 K for Pt/H,Na-Y, H sink in Pt clusters?):

  Pd/H,Na-Y (T_{HT} = 723 K) > Rh/H,Na-Y (T_{HT} = 713 K) > Ir/H,Na-Y (T_{HT} = 663 K)

- Rh and Pt containing porous solids are suitable catalysts for the formation of parahydrogen induced polarization (PHIP):

  i.e. pairswise incorporation of p-H_2, in contrast to Pd containing catalysts

- weak effect of the pore size (0.7 to 4.5 nm) on the formation of PHIP, but strong decrease of PHIP in the presence of potential relaxation centers

Thanks to ….

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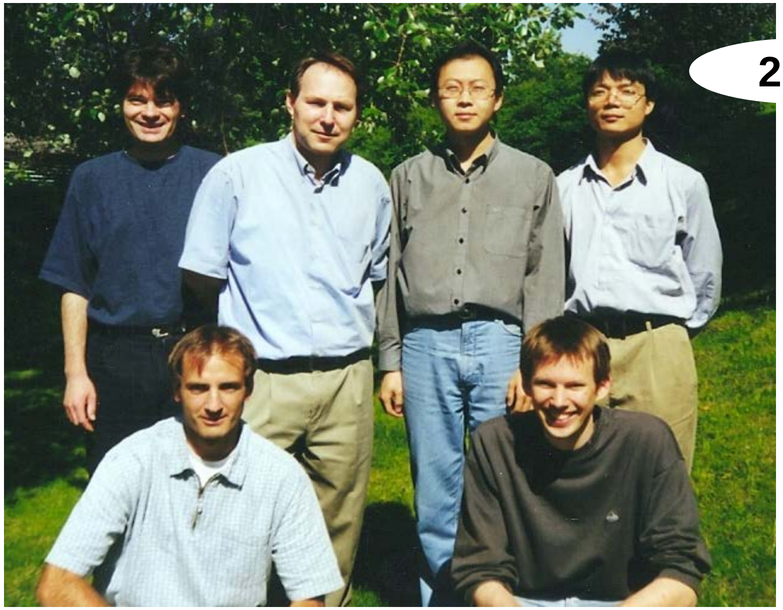
Thanks to ….



2001

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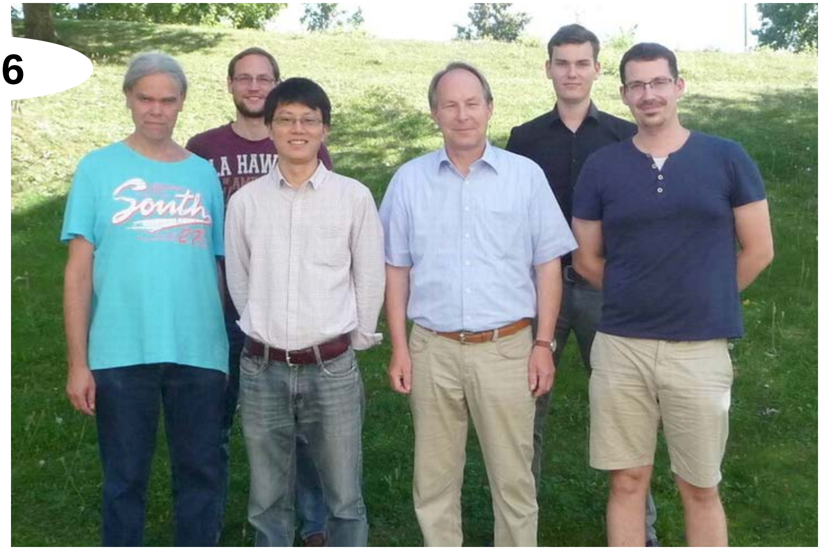
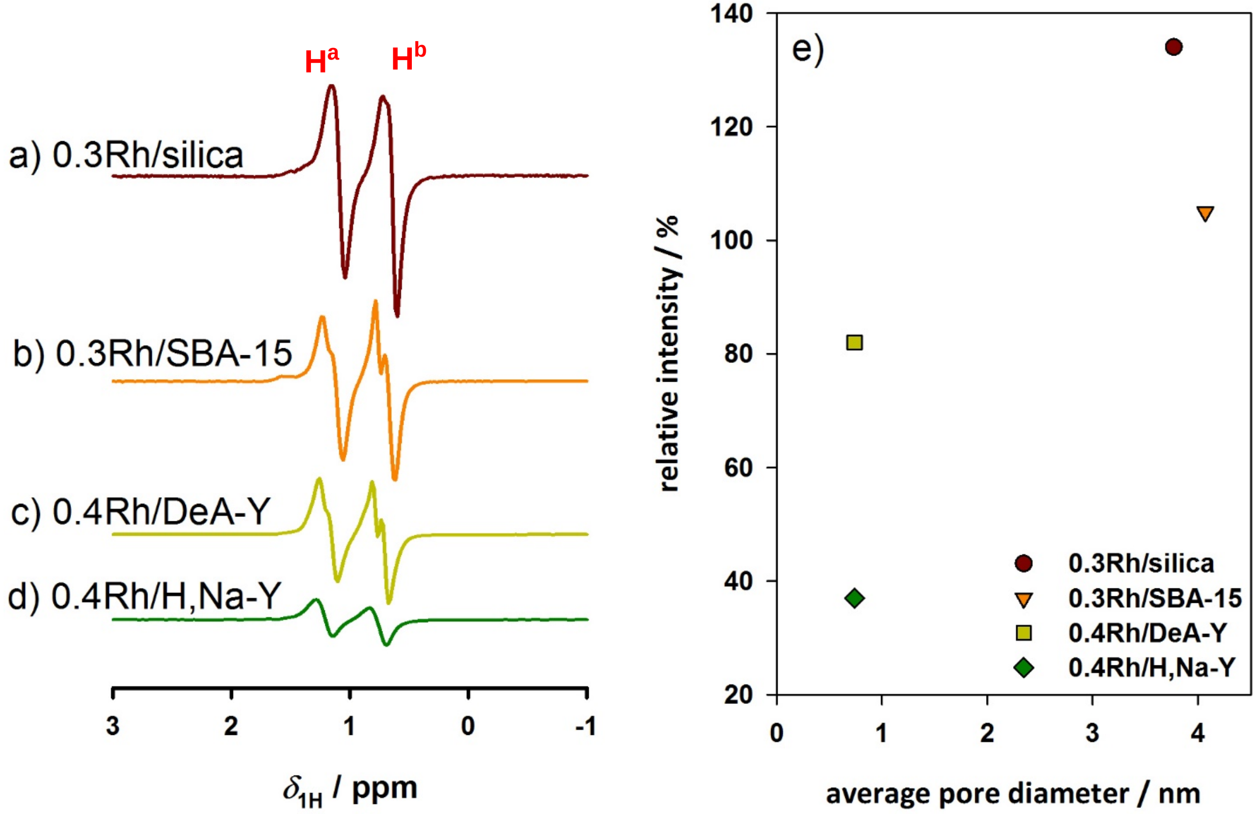


Parahydrogen induced polarization (PHIP) on porous solids

in situ **^{1}H MAS NMR investigation of PHIP on Rh-containing porous solids**



- **intensities of the anti-phase signals depend slightly on pore size and strongly on presence of relaxation centers (framework Al, Na^+ cations)**

U. Obenaus et al., J. Phys. Chem. C (2017), DOI: 10.1021/acs.jpcc.7b01899.

Conditions of optimum PASADENA experiments

- pairwise incorporation of p-H_2 into the reactants is required for reaching hyperpolarization (isolated hydrogenation sites?),
- highly mobile product molecules having low relaxation rate (→ low number of strong adsorption sites; large pores; sites at outer particle surface; elevated temperature?),
- the A_2 spin system must be converted into an AX spin system (chemically non-equivalent ($\Delta\nu$) H atoms),
- high ratio of $\Delta\nu$ /J improves the observability of the anti-phase signals,
- excitation by $\phi = \pi/4$ pulses because of the density operator

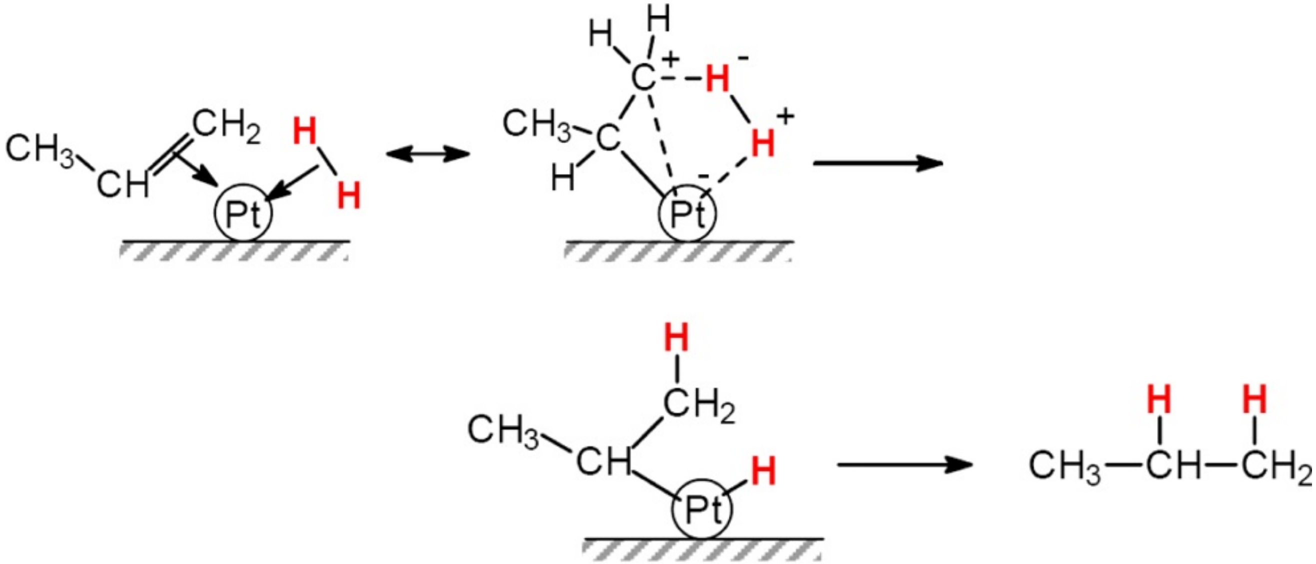
  $$\rho(\phi) \propto \cos(\phi)\sin(\phi) \cdot \mathcal{F}(I_1,I_2)$$
- no gaseous oxygen in the flow system (O_2 is paramagnetic; causes p-H_2 to o-H_2 conversion; relaxation of hyperpolarized reactants),
- p-H_2 : reactant ratio of > 1 and elevated temperature may accelerate hydrogenation with p-H_2,
- signal intensity has no explicite dependence on *T* inside the NMR probe since the enhancement factor

  $$\eta = kT\,(1 - 4a)\,/\,(6\gamma_{det}\,\hbar\,B_0)$$

  leads to an intensity proportional to $N\gamma_{det}^{3/2}B_0^{1/2}$ (a: p-H_2 content, γ_{det}: γ of detected nuclei)

Suggested transition state

Pairswise incorporation of p-H_2 into propene at Pt clusters after Scheme 1 of Ref. [1]



[1] S.S. Arzumanov, A.G. Stepanov, J. Phys. Chem. C 117 (2013) 288-2892.