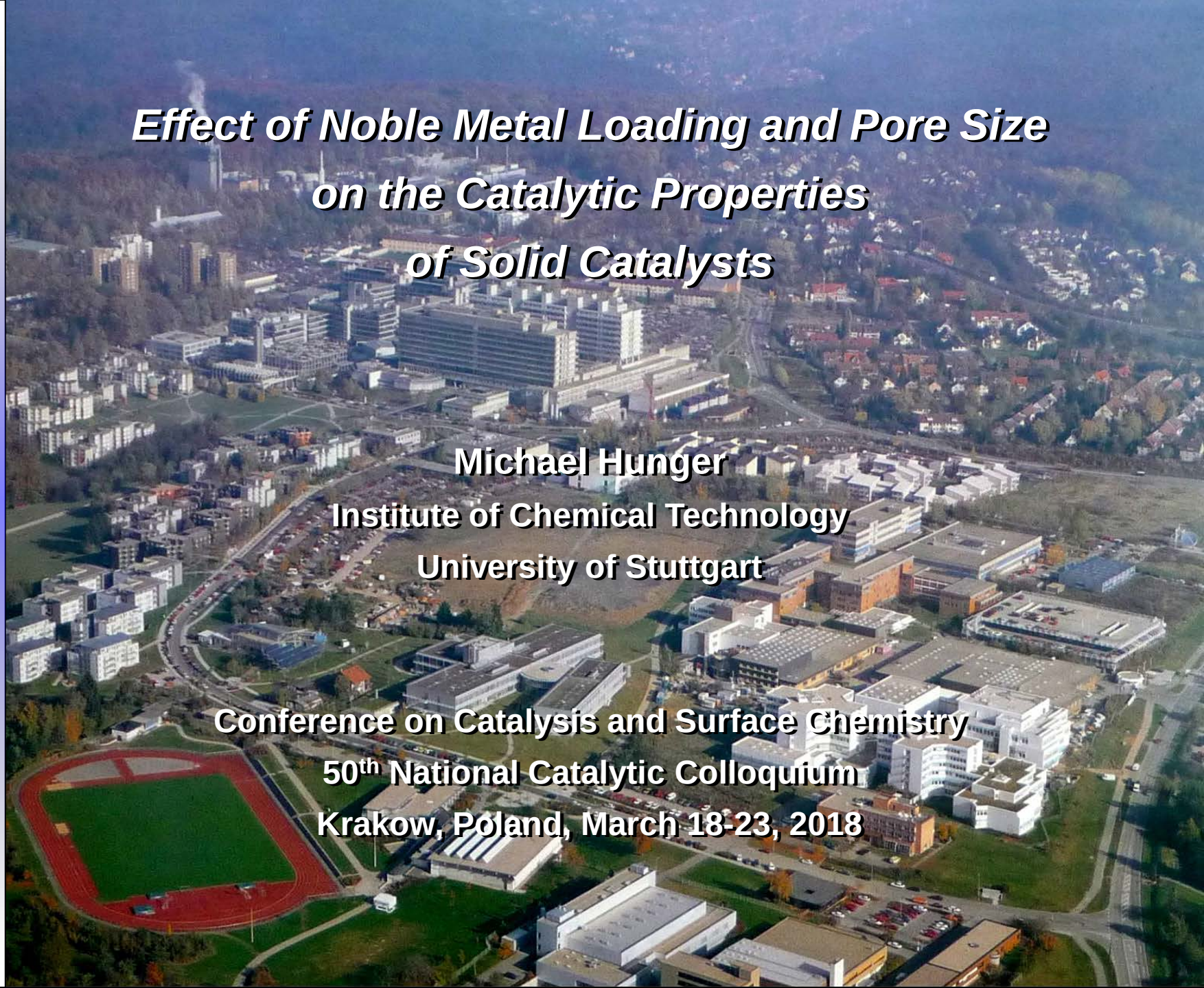


Effect of Noble Metal Loading and Pore Size on the Catalytic Properties of Solid Catalysts

Michael Hunger

Institute of Chemical Technology

University of Stuttgart

Conference on Catalysis and Surface Chemistry

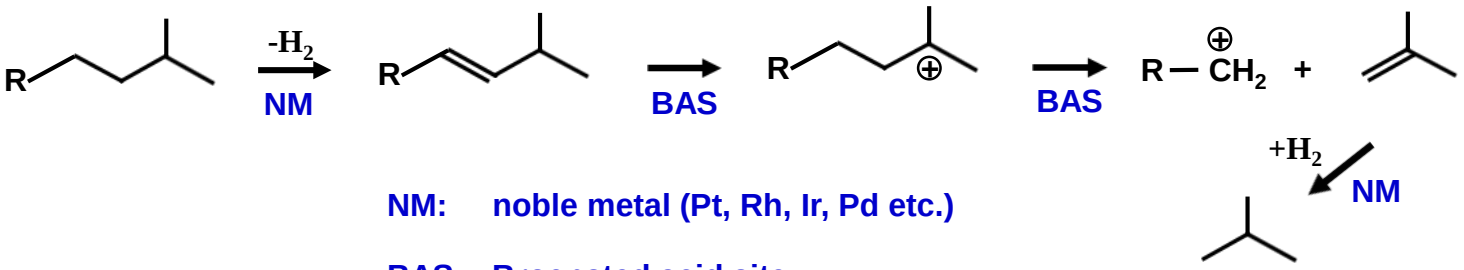
50th National Catalytic Colloquium

Krakow, Poland, March 18-23, 2018

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

Examples for applications of noble metal containing solid catalysts

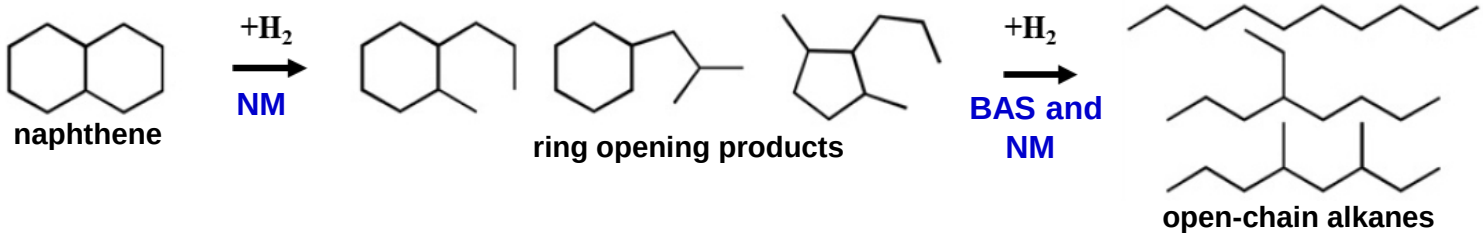
- **hydrocracking of alkanes [1]**



NM: noble metal (Pt, Rh, Ir, Pd etc.)

BAS: Broensted acid site

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



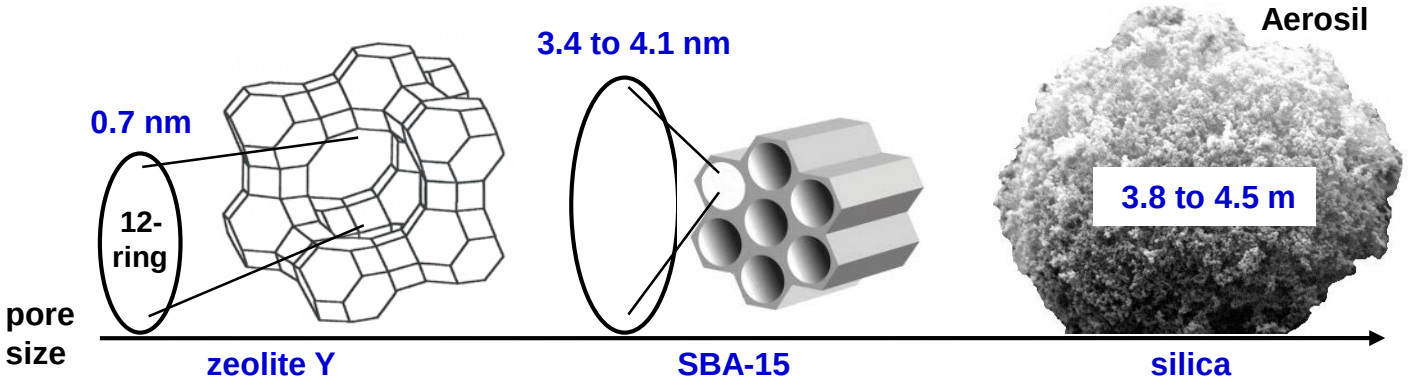
[1] J. Scherzer, A.J. Gruia, Hydrocracking Science and Technology, Marcel Dekker, New York, USA, 1996.

[2] A. Galadina, O. Muraza, Ring opening of hydrocarbons for diesel and aromatics production: Design of heterogeneous catalytic systems, Fuel 181 (2016) 618-629.

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 $RhCl_3 \cdot x\,H_2O$, $[Ir(NH_3)_5Cl]Cl_2$, $[Pd(NH_3)_4]Cl_2$, 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 →

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.

Investigation of Broensted acid sites on noble metal containing zeolites Y

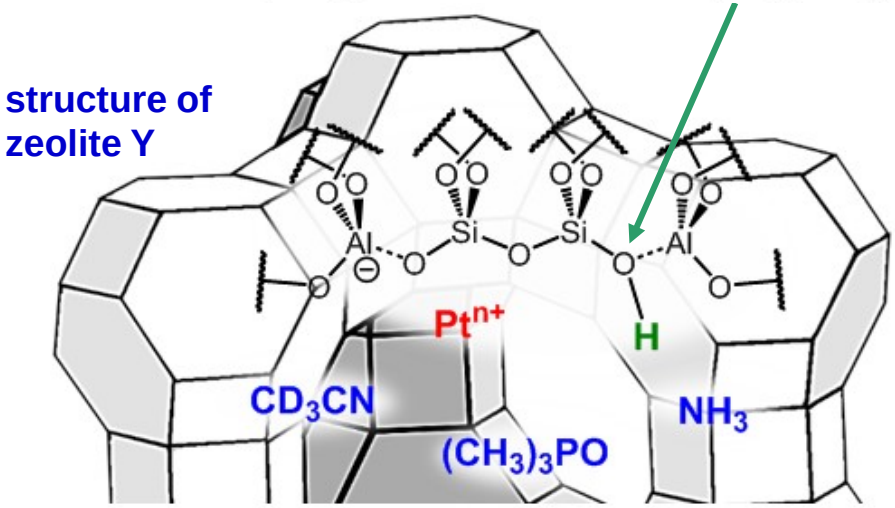
Generation of Broensted acid sites on noble metal containing zeolites Y

suggested mechanism for the formation of catalytically active sites of zeolite H,Na-Y (e.g. n_{Si}/n_{Al} = 2.7) loaded with Pt complexes [1]

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

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

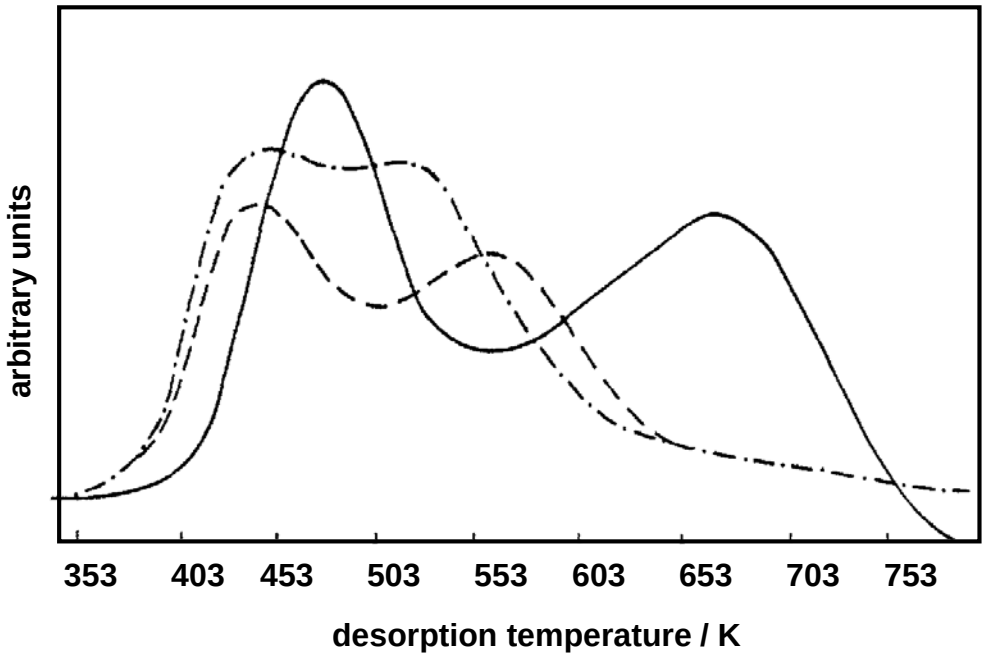
reduction $Pt^{2+}(ZO^-)_2 \xrightarrow{H_2,\ 623\ K} Pt^0(H^+)_2(ZO^-)_2$



[1] P. Gallezot, in: Molecular Sieves: Post-Synthesis Modification I, Springer-Verlag, Berlin, 2002, p. 257-305.

Characterization of the Broensted acid site density of noble metal containing zeolites Y

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

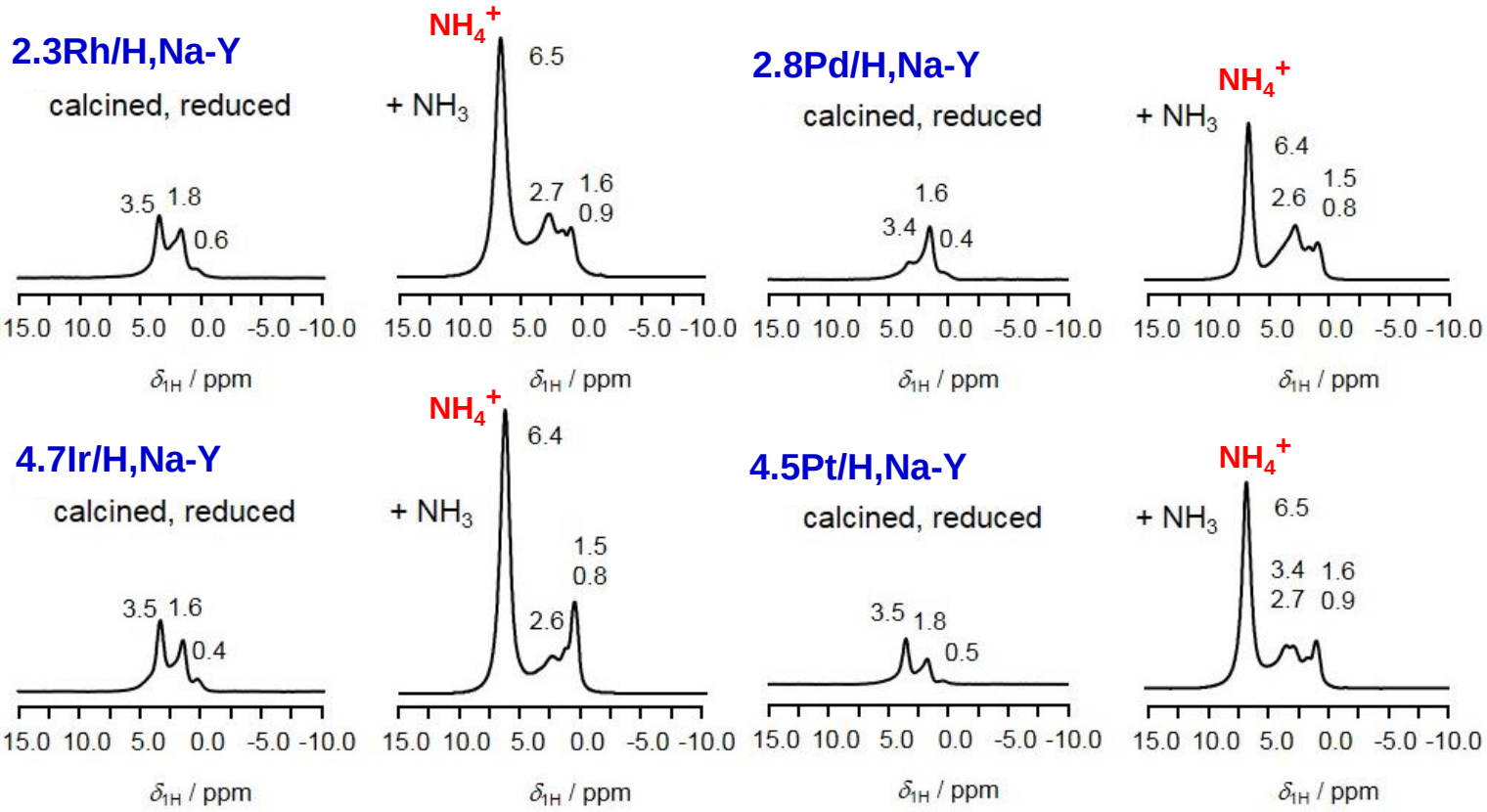


adapted ^{1}H MAS NMR method:

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

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

^{1}H MAS NMR studies of the Broensted acid site density of noble metal containing zeolites Y



metal OH: **0.4 – 0.9 and 2.6 – 2.7 ppm**

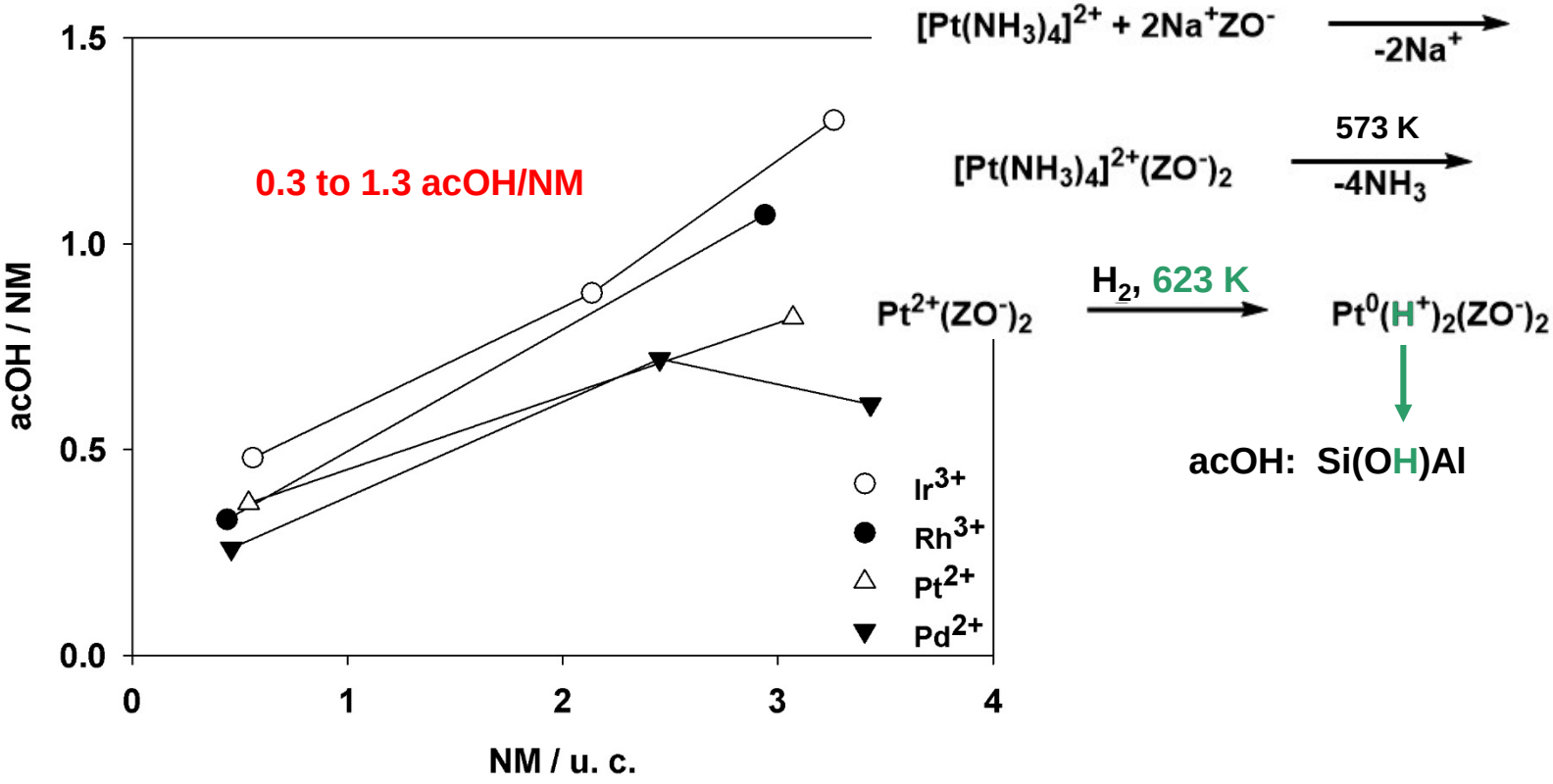
SiOH: **1.5 – 1.8 ppm**

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

[1] U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254.

^{1}H MAS NMR studies of the Broensted acid site density 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 [1]

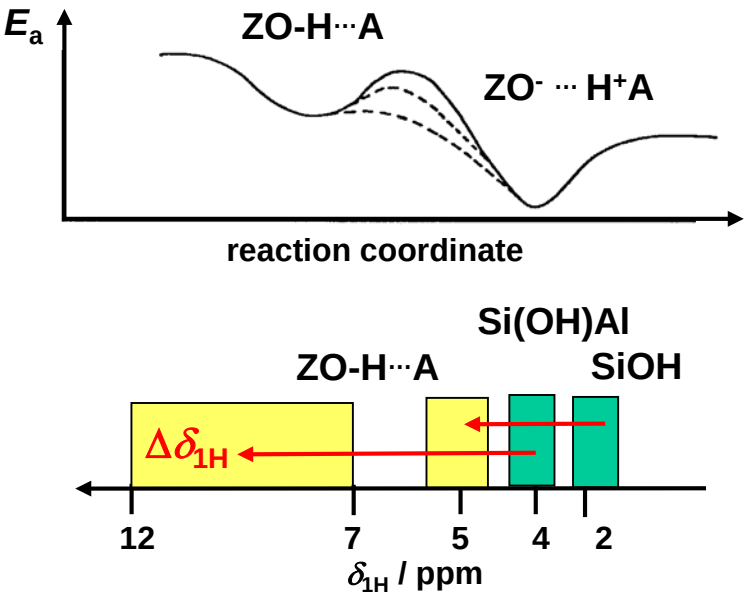


[1] U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254.

^{1}H MAS NMR studies of the Broensted acid strength of 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) [1, 2]:

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

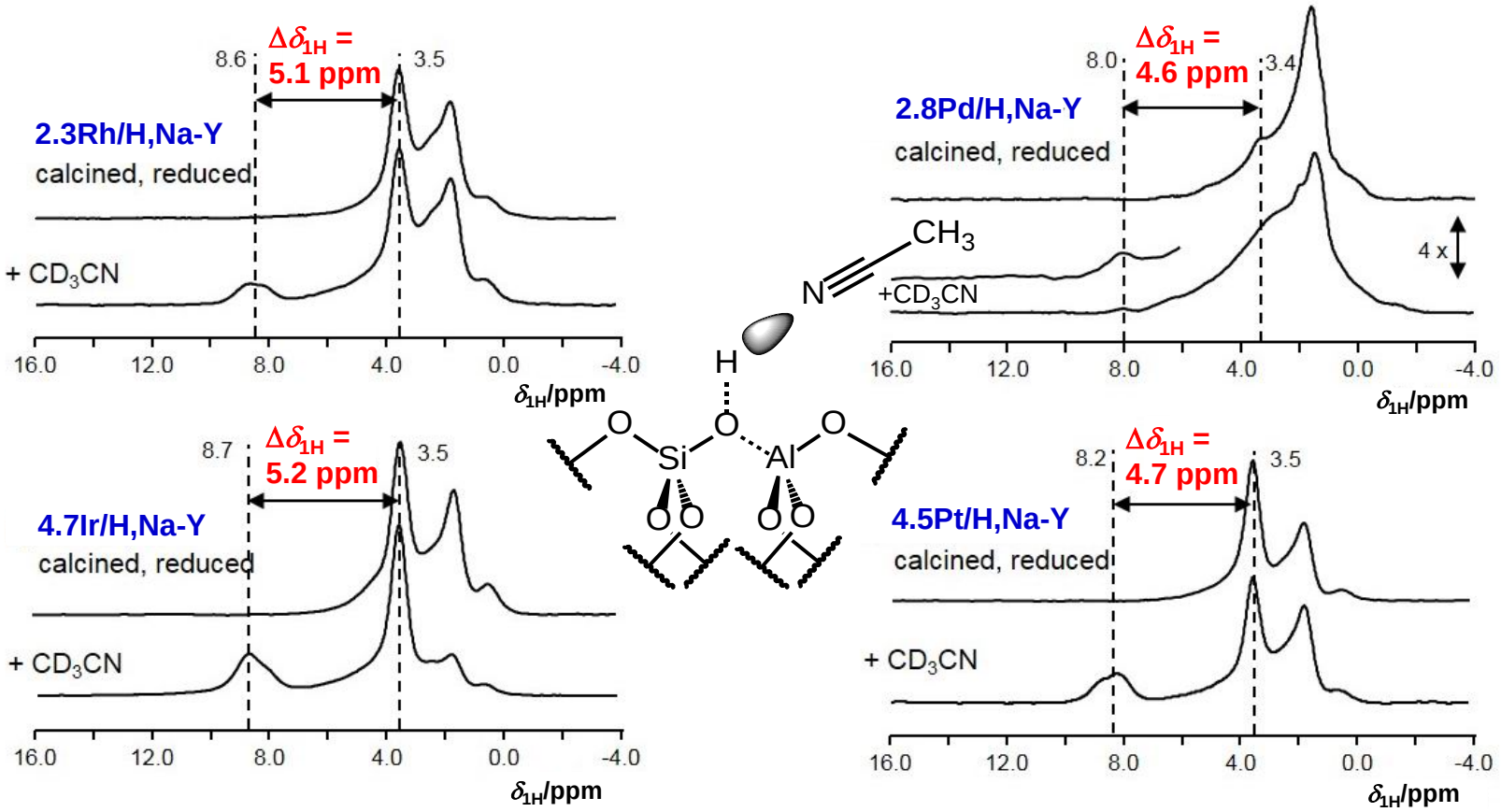
[1] J. Jaenchen, J.H.M.C. van Wolput, L.J.M. van de Ven, J.W. de Haan, R.A. van Santen, Catal. Lett. 39 (1996) 147.

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

^{1}H MAS NMR studies of the Broensted acid strength of noble metal containing zeolites Y

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

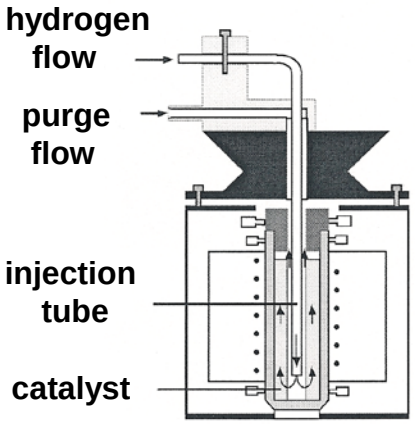
for comparison: 0.2H,Na-Y has $\Delta\delta_{1H}$ = 5.2 ppm [1]

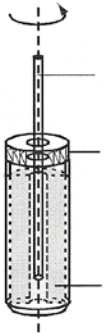


[1] U. Obenaus et al., J. Phys. Chem. C 119 (2015) 15254.

Hydrogenation activity of noble metal containing porous solids

Experimental technique of in situ MAS NMR spectroscopy under flow conditions

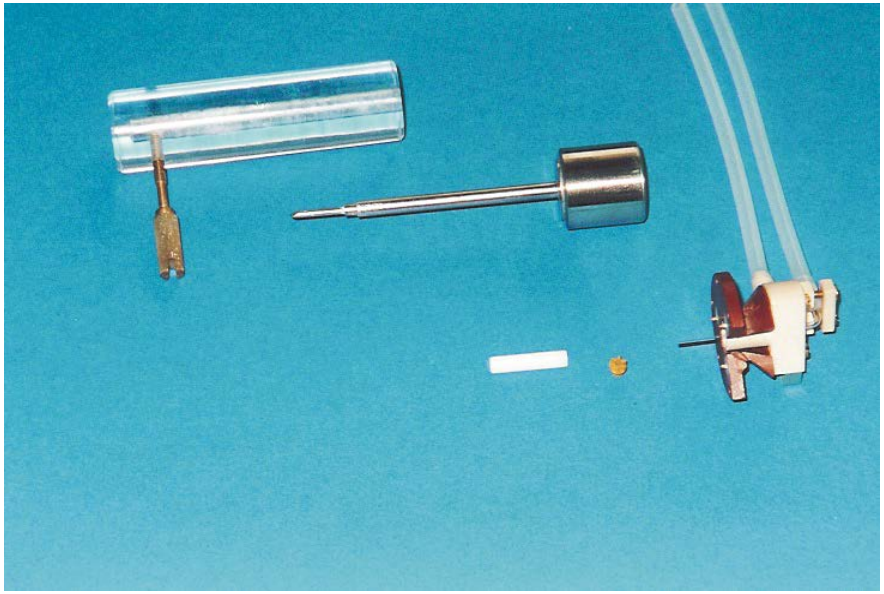




modified 4 mm Bruker MAS NMR probe

equipped with an injection system

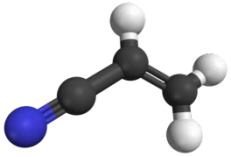
tools for the preparation of the catalyst bed (hollow cylinder) inside the MAS NMR rotor [1, 2]

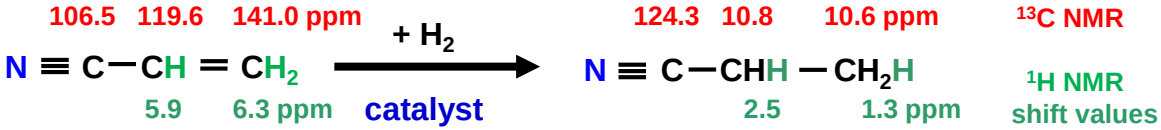


[1] A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.
[2] M. Hunger, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105.

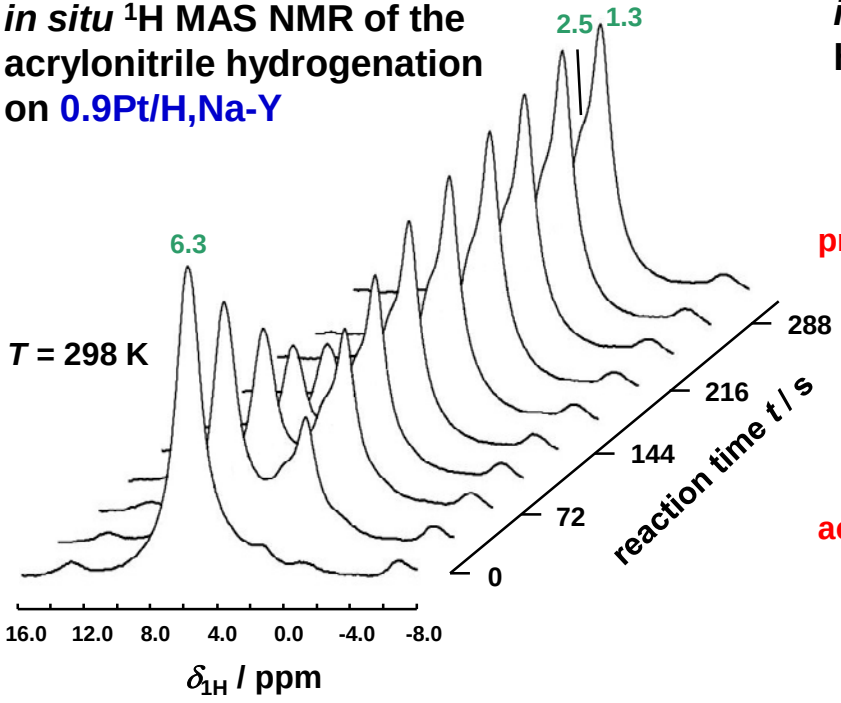
Intrinsic hydrogenation activity of noble metal containing porous solids

hydrogenation of pre-adsorbed acrylonitrile to propionitrile [1]

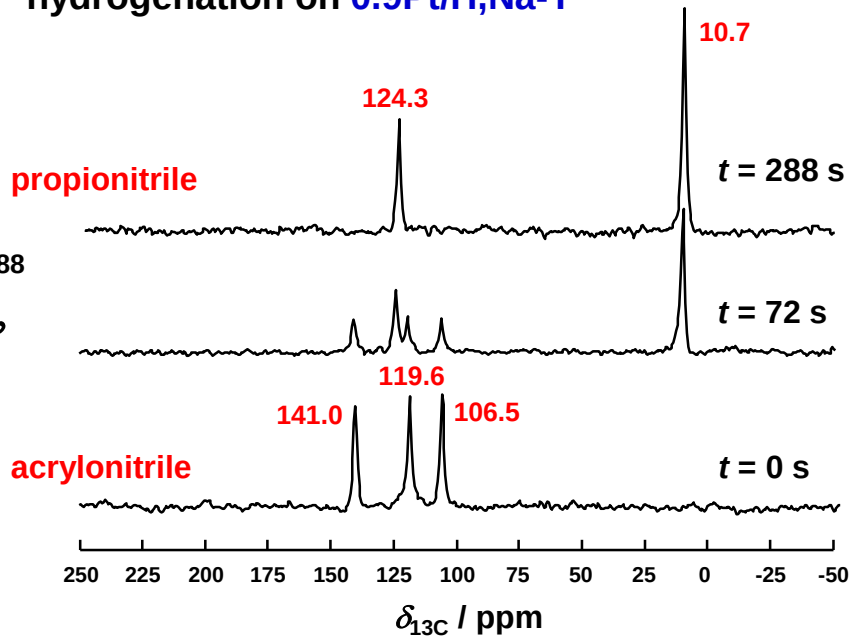




***in situ* ^{1}H MAS NMR of the acrylonitrile hydrogenation on 0.9Pt/H,Na-Y**



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



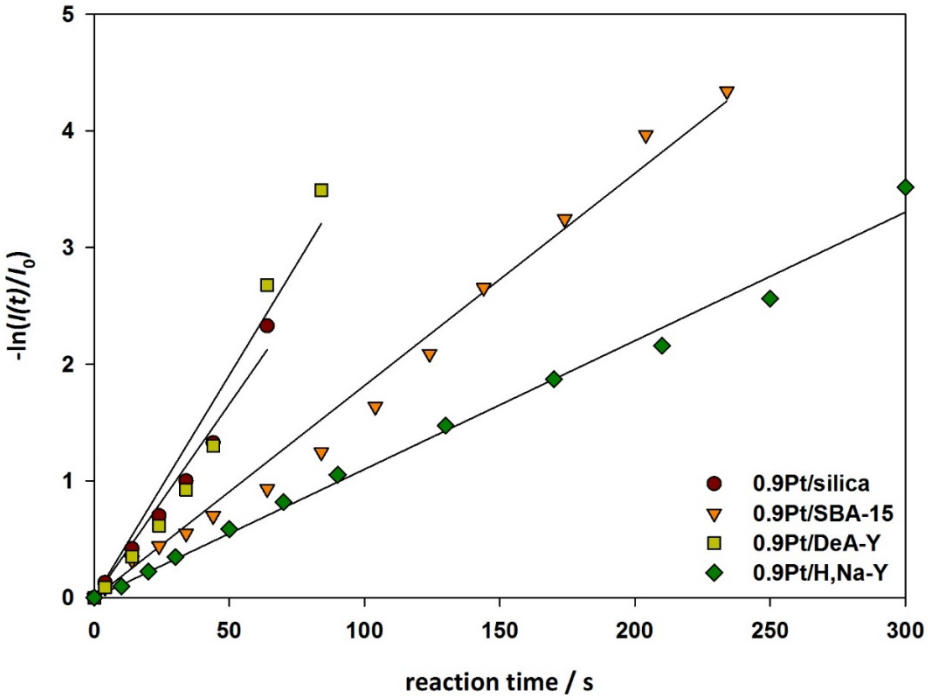
Bruker Avance III 400WB spectrometer, modified 7 mm MAS NMR probe, ν_{rot} ca. 2 kHz, 1 FID per spectrum, D1 = 6 s

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

Intrinsic hydrogenation activity of noble metal containing porous solids

catalyst	n_{Si}/n_{Al}	noble metal content / wt %	disper-sion / %
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 [1]



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

[1] U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284.

Intrinsic hydrogenation activity of noble metal containing porous solids

velocity constants *k* and reaction rates *r* for the intrinsic hydrogenation of acrylonitrile

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.

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

Dehydrogenation activity of noble metal containing zeolites Y

dehydrogenation of propane to propene in a fixed-bed reactor (*T* = 828 K, atmospheric pressure, propane/N_2 mixture of 2 : 1, $WHSV_{C3}$ = 3 h^{-1}, TOS = 35 min) [1]

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 turn-over-frequencies *TOF* of the dehydrogenation of propane:**

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

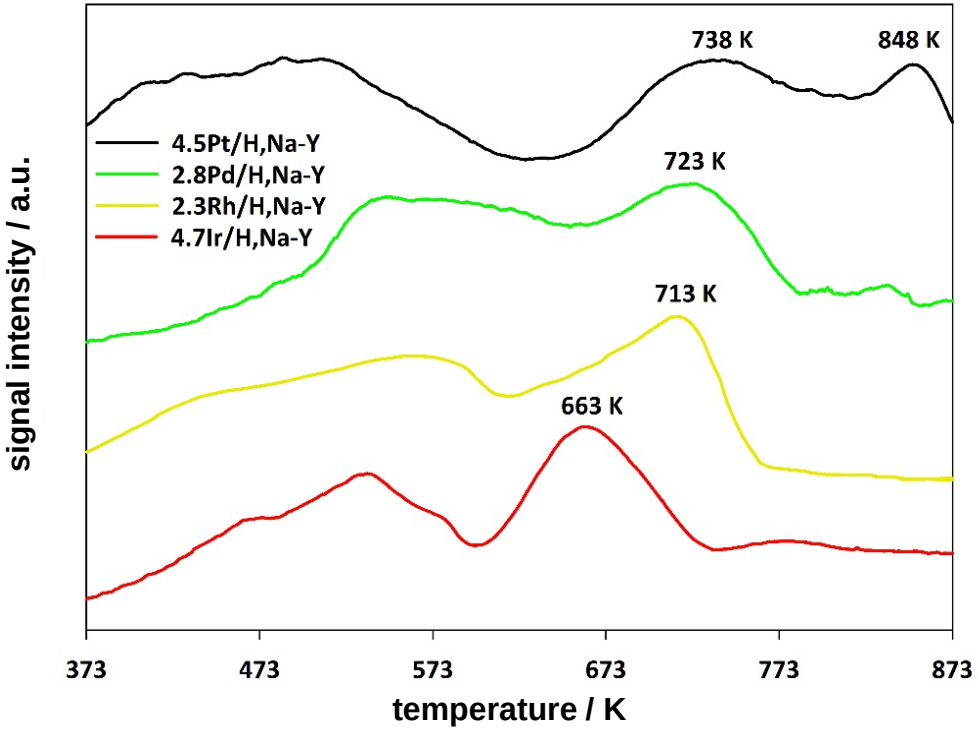
  2.8Pd/H,Na-Y = 2.3Rh/H,Na-Y < 4.7Ir/H,Na-Y < 4.5 Pt/H,Na-Y

- **sequence of *r* values of the hydrogenation of acrylonitrile:**

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

[1] U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284.

Strength of hydrogen chemisorption on noble metal containing zeolites Y



- high-temperature peaks T_{HT} of H_2 desorption (TPD) [1]:

  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 hydrogen chemisorption between Pt atoms

[1] U. Obenaus et al., J. Phys. Chem. C 120 (2016) 2284 (Supporting Information).

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

- turn-over-frequencies ***TOF*** of the **dehydrogenation** of propane:

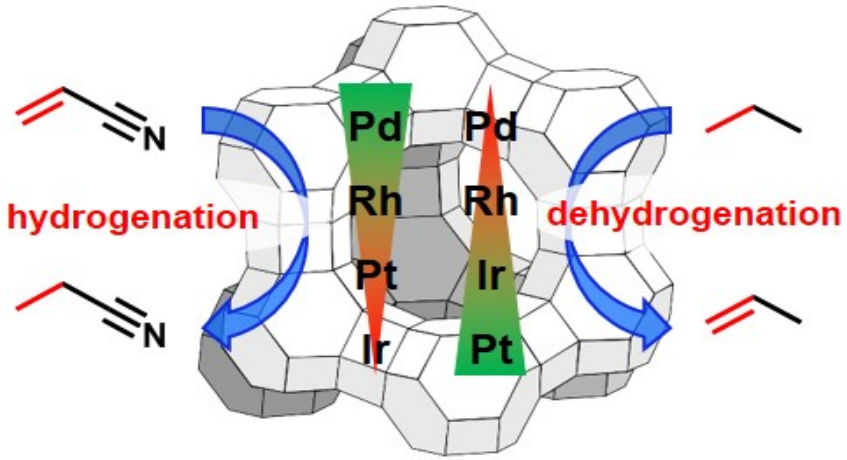
  Pd/H,Na-Y < Rh/H,Na-Y < Ir/H,Na-Y

- reaction rates ***r*** of the **hydrogenation** of acrylonitrile:

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

- positions T_{HT} of high-temperature peaks of H_2-TPD:

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



strong hydrogen chemisorption has:

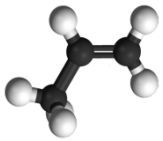
- **negative effect on dehydrogenation (hindered hydrogen desorption)**
- **positive effect on hydrogenation (hydrogen reservoit at noble metals)**

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

Formation of parahydrogen induced polarization (PHIP) on noble metal containing porous solids

Principles of parahydrogen induced polarization (PHIP)

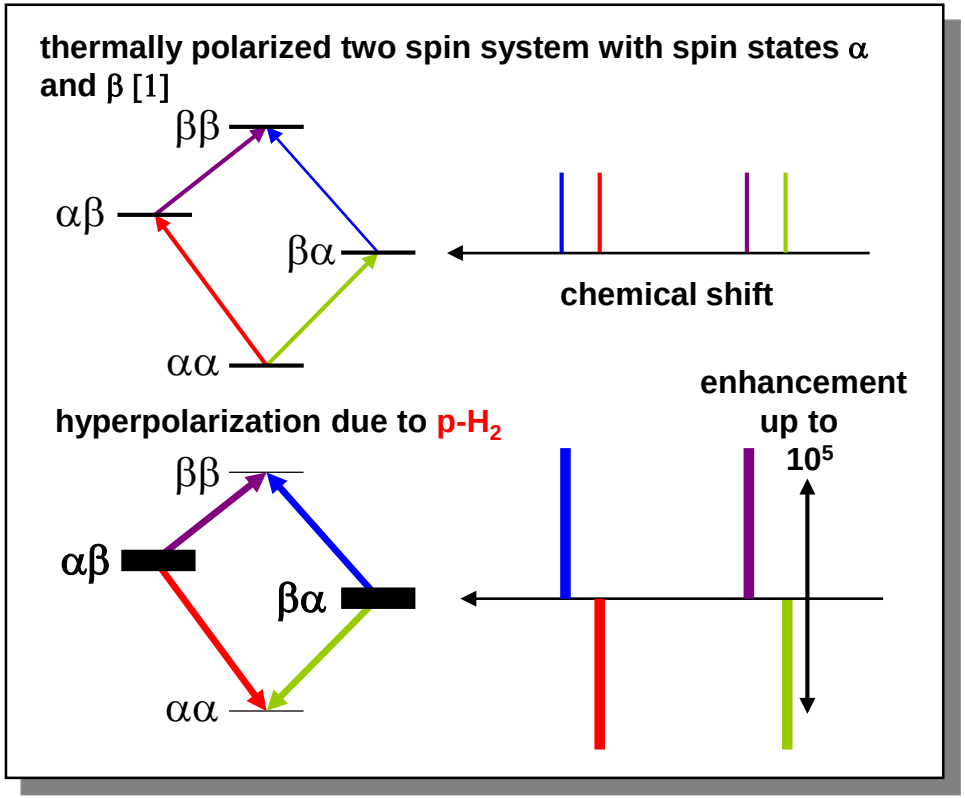
hydrogenation of propene with para-enriched H_2 p-H_2:



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

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

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

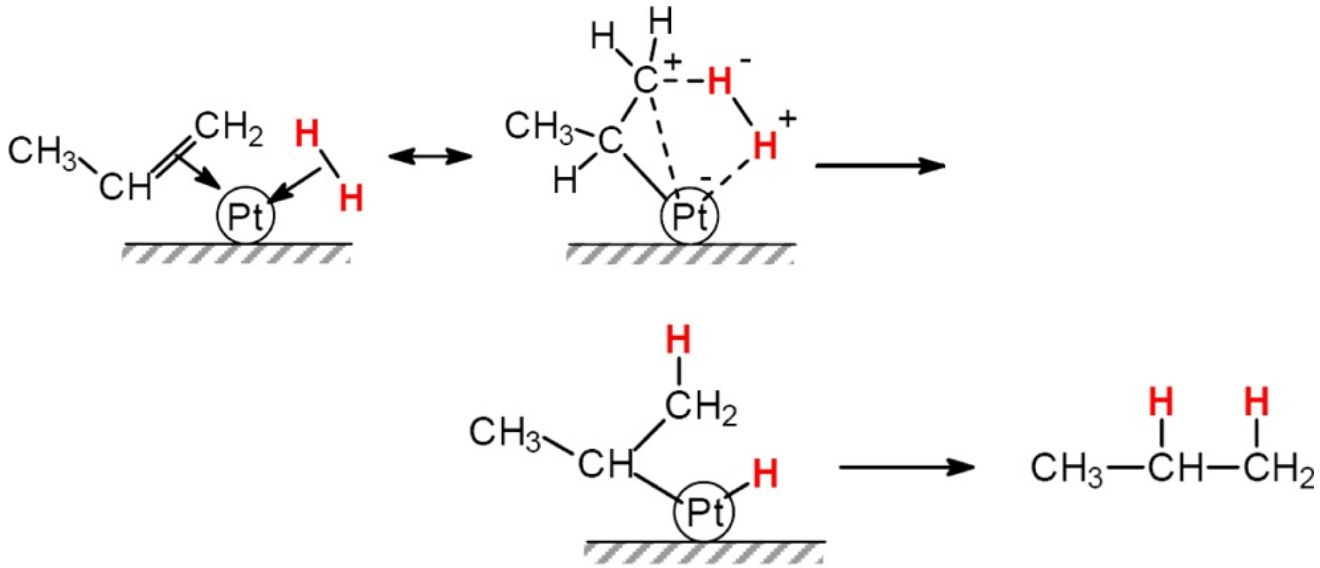


PASADENA: Parahydrogen And Synthesis Allow Dramatically Enhanced Nuclear Alignment (p-H_2 incorporation inside a strong B_0 field)

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

Suggested transition state for PHIP formation

PHIP requires pairswise incorporation of p-H_2 into the reactant (Scheme 1 of Ref. [1])

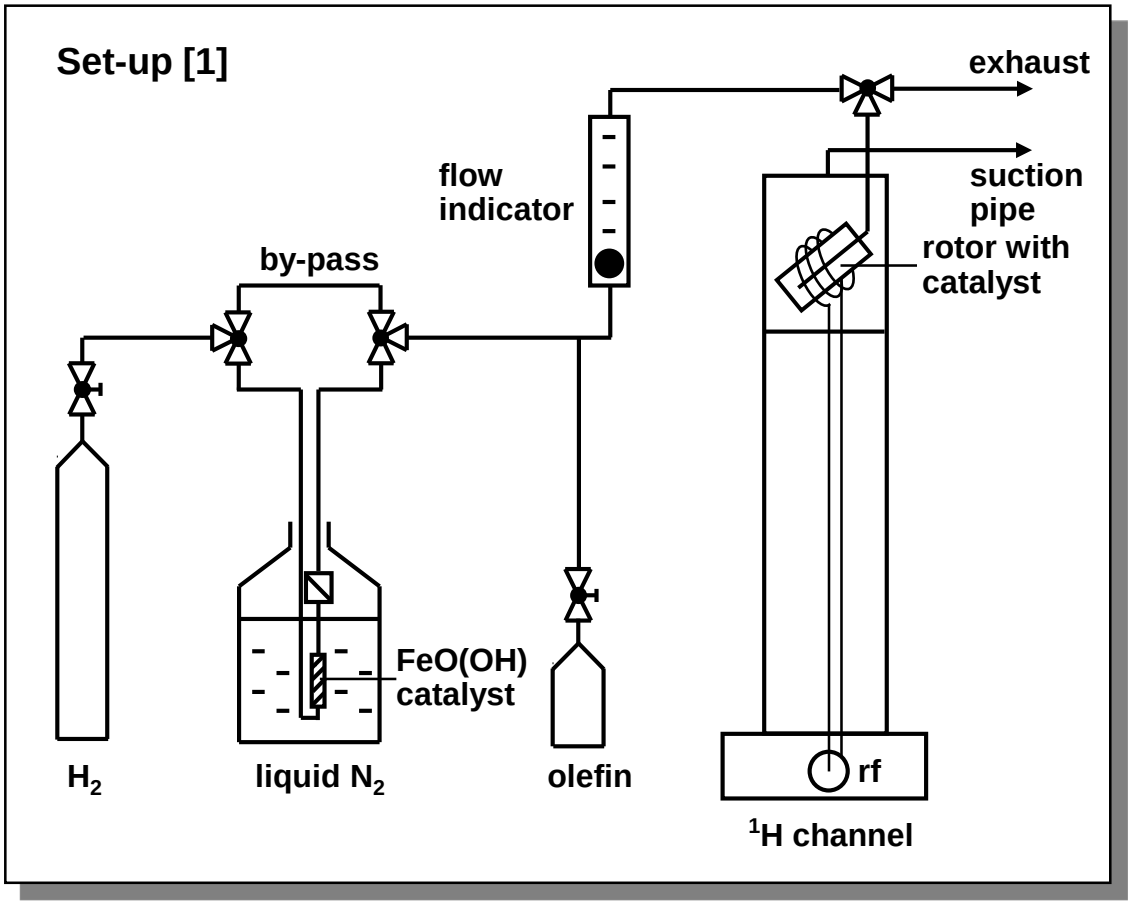


[1] S.S. Arzumanov, A.G. Stepanov, J. Phys. Chem. C 117 (2013) 288-2892.

Experimental set-up utilized for PHIP formation

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

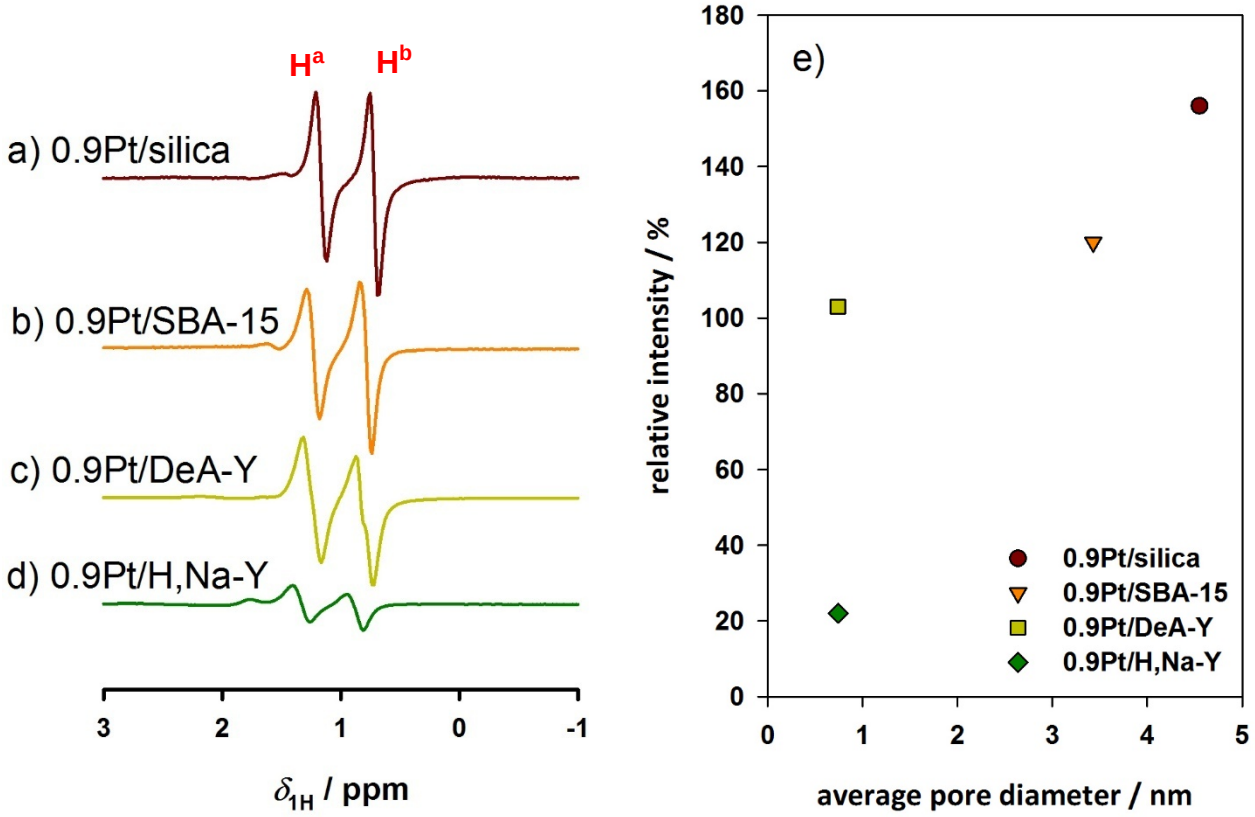
- **modified 4 mm Bruker MAS NMR probe**
- **at ν_0 = 400.13 MHz, ν_{rot} ca. 4 kHz, $\pi/4$ pulses, *NS* = 96, D1 = 0.1 s**
- **para : ortho ratio of 1 : 1 (p-H_2) obtained by contact with FeO(OH) (Sigma-Aldrich) placed in liquid nitrogen**
- **propene and p-H_2 flows of 40 and 30 ml/min, respectively**



[1] H. Henning, M. Dyballa, M. Scheibe, E. Klemm, M. Hunger, Chem. Phys. Lett. 555 (2013) 258.

Parahydrogen induced polarization (PHIP) on porous solids

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



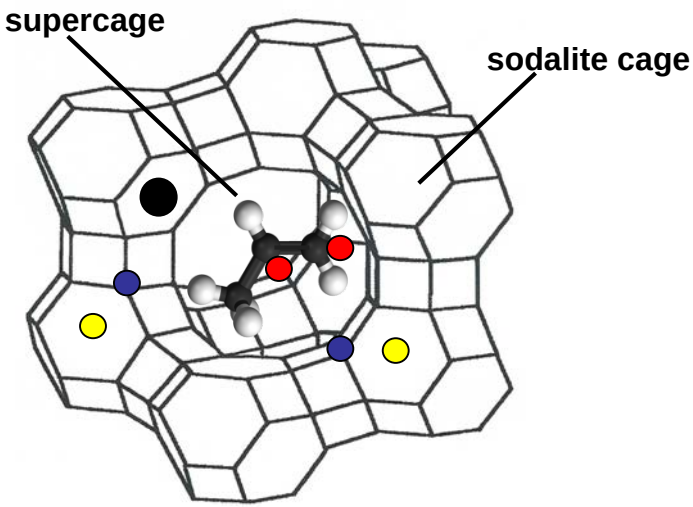
- **intensities of the anti-phase signals moderately depend on pore size and strongly on the presence of framework Al and Na^+ cations**

[1] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, J. Phys. Chem. C 121 (2017) 9953-9962.

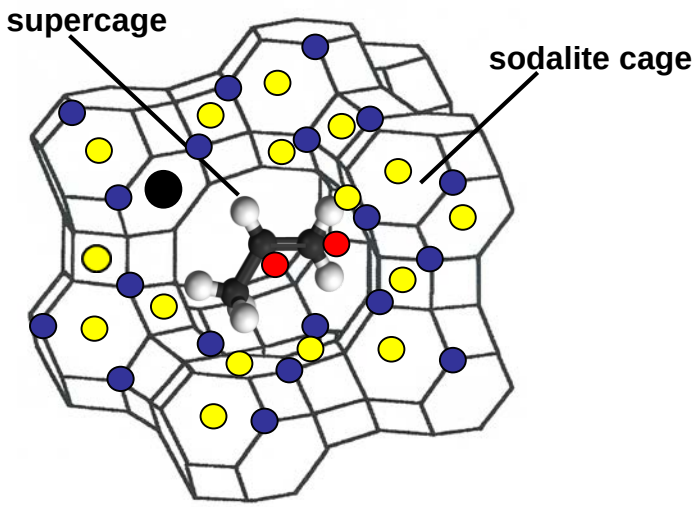
Relaxation of PHIP on noble metal containing zeolites Y

possible spin interactions of hyperpolarized propane in zeolite Y

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



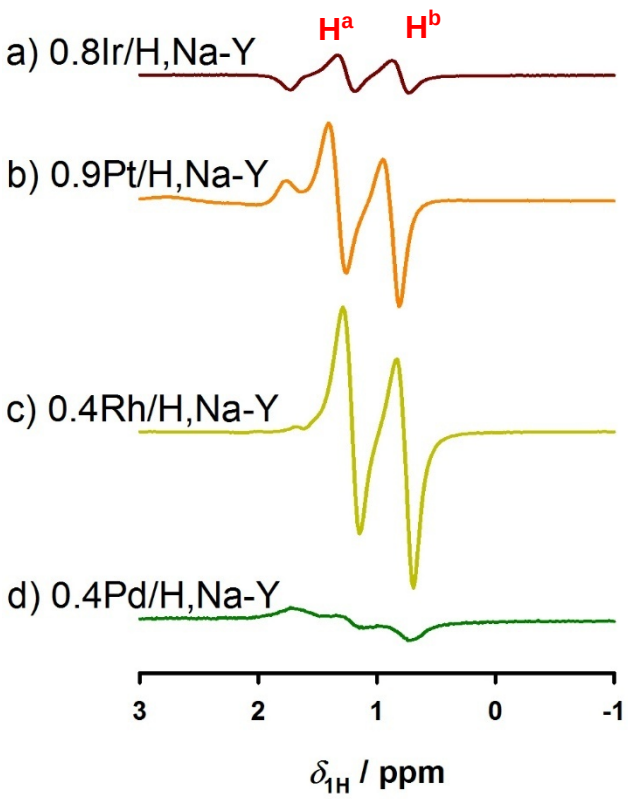
0.9Pt/H,Na-Y (n_{Si}/n_{Al} = 2.7)

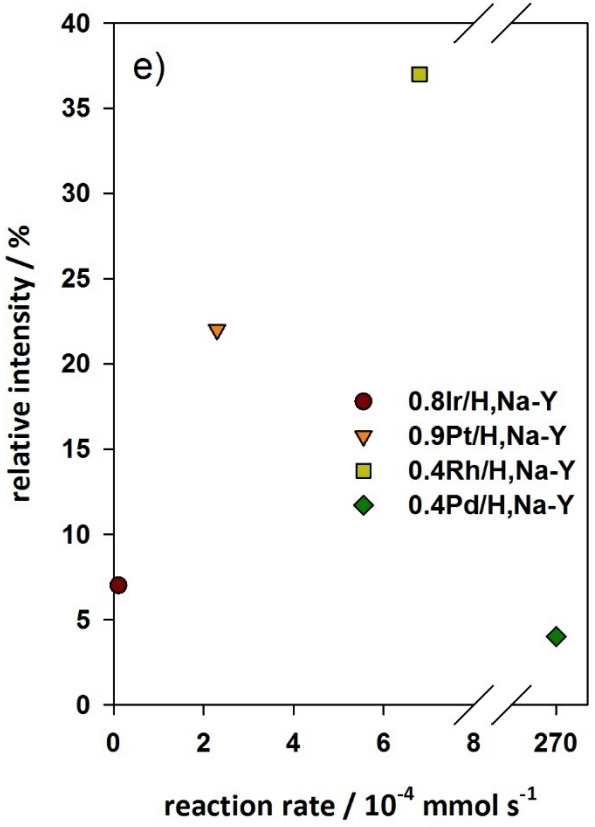


- hyperpolarized H atom
- Pt atom (I = 1/2, 34 %)
- Al atom (I = 5/2, 100 %)
- Na^+ cation (I = 3/2, 100 %)

Parahydrogen induced polarization (PHIP) on zeolites H,Na-Y

***in situ* ^{1}H MAS NMR investigation of PHIP on zeolites H,Na-Y loaded with same numbers of different noble metals [1]**





- **moderately active catalysts (0.9Pt/H,Na-Y, 0.4Rh/H,Na-Y) form PHIP, while a too high activity (0.4Pd/H,Na-Y) suppresses a pairwise p-H_2 incorporation**

[1] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, J. Phys. Chem. C 121 (2017) 9953-9962.

Summary

- reduction of noble metals in zeolites Y at optimum temperature of 623 K causes formation of 0.3 to 1.3 acOH/NM with decreased acid strength for Pd/ and Pt/H,Na-Y

- hydrogenation rates *r* on noble metal containing zeolites Y have sequence:
  Pd/H,Na-Y > Rh/H,Na-Y > Ir/H,Na-Y

- *TOF* values of dehydrogenation have opposite sequence of:
  Pd/H,Na-Y < Rh/H,Na-Y < Ir/H,Na-Y

- sequence of the positions T_{HT} of high-temperature peaks of H_2-TPD is:
  Pd/H,Na-Y > Rh/H,Na-Y > Ir/H,Na-Y

- strong hydrogen chemisorption has a negative effect on dehydrogenation (hindered hydrogen desorption) and a positive effect on hydrogenation (hydrogen reservoit at noble metals)

- formation of parahydrogen induced polarization (PHIP) indicates that:
  pairswise incorporation of p-H_2 occurs for Rh and Pt containing zeolites Y, but much less on Ir (low activity) and Pd (too high activity) containing catalysts

- moderate influence 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 ….

co-workers:

Utz Obenaus
Harald Henning
Bejoy Thomas
Jörg Frey
Swen Lang
Weili Dai
Zichun Wang
Mingcan Xu
Jiang Jiao
Jun Huang
Yijiao Jiang
Arne Bressel
Reddy Marthala

financial support:

Deutsche Forschungs-Gemeinschaft (HU533/13-1)

National Natural Science Foundation of China

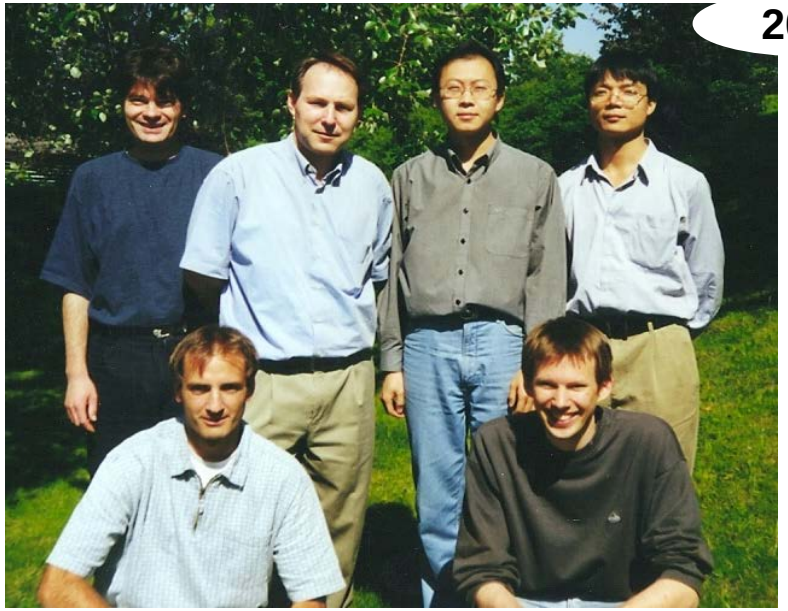
Volkswagen-Stiftung

DECHEMA e.V.

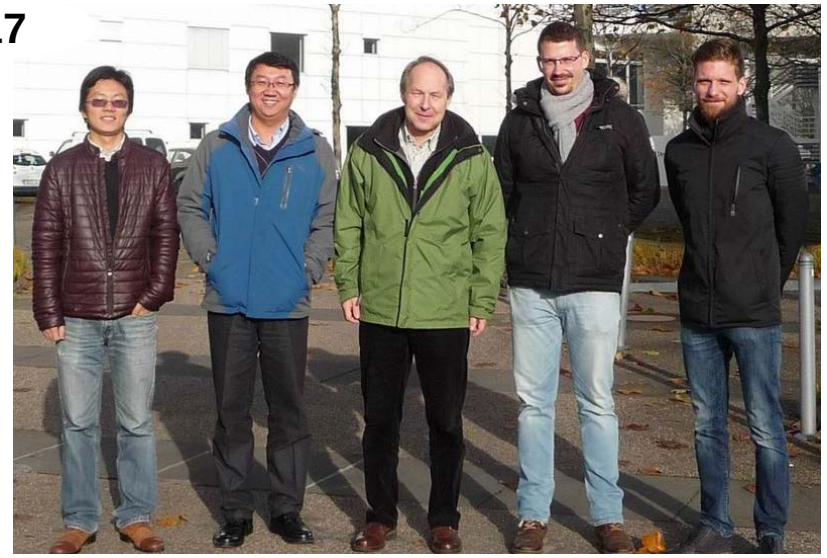
Alexander von Humboldt-Stiftung

Thanks to ….

2001

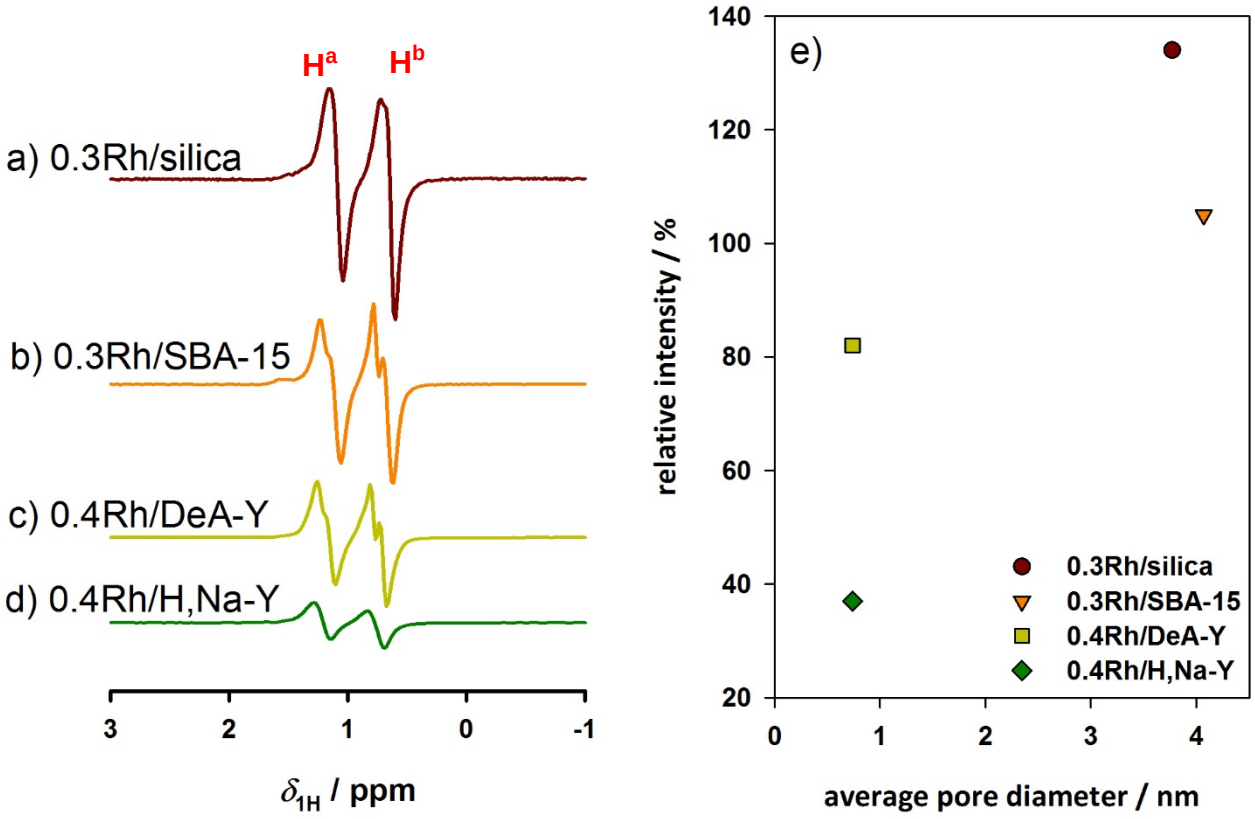


2017



Parahydrogen induced polarization (PHIP) on porous solids

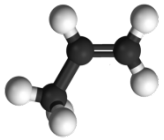
***in situ* ^{1}H MAS NMR investigation of PHIP on Rh containing porous solids [1]**

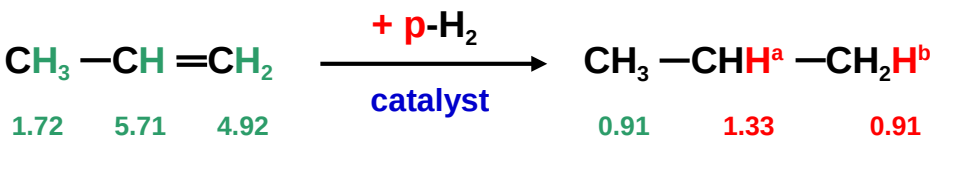


- **intensities of the anti-phase signals depend slightly on pore size and strongly on presence of relaxation centers (framework Al, Na^+ cations)**

[1] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, J. Phys. Chem. C 121 (2017) 9953-9962.

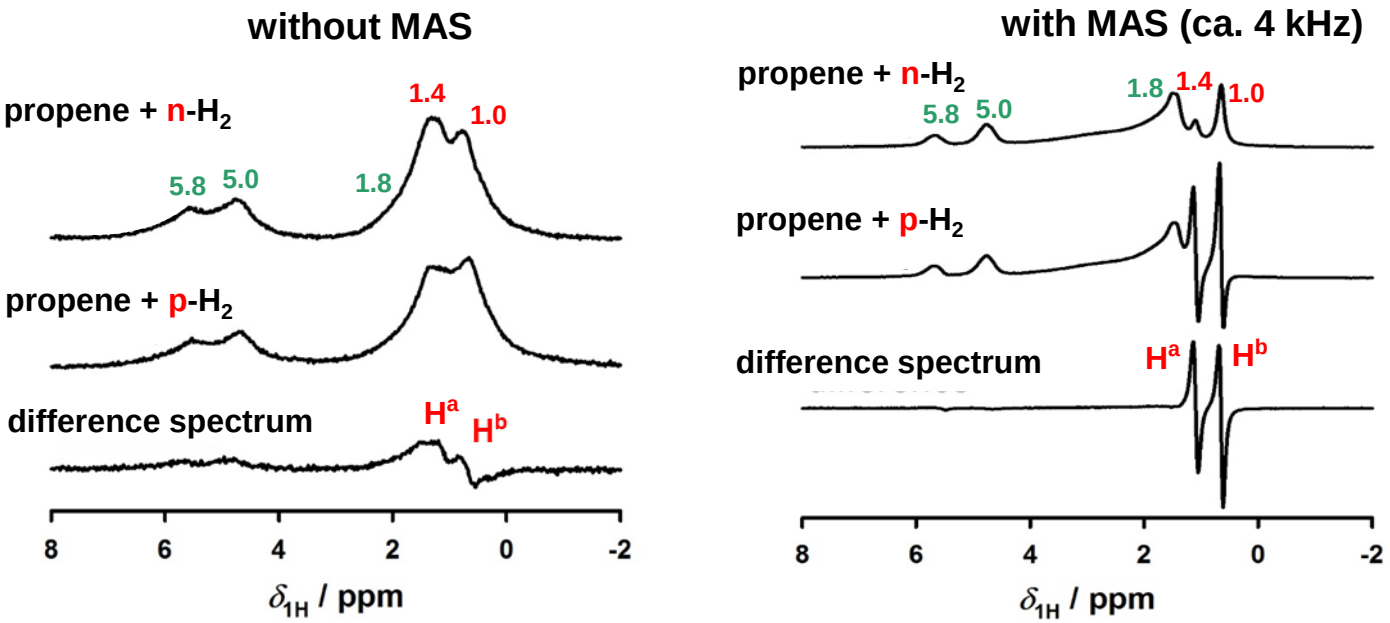
Parahydrogen induced polarization (PHIP) on porous solids





^{1}H NMR shift values (literature)

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



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

[1] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, J. Phys. Chem. C 121 (2017) 9953-9962.

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 ($\rightarrow$ 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)