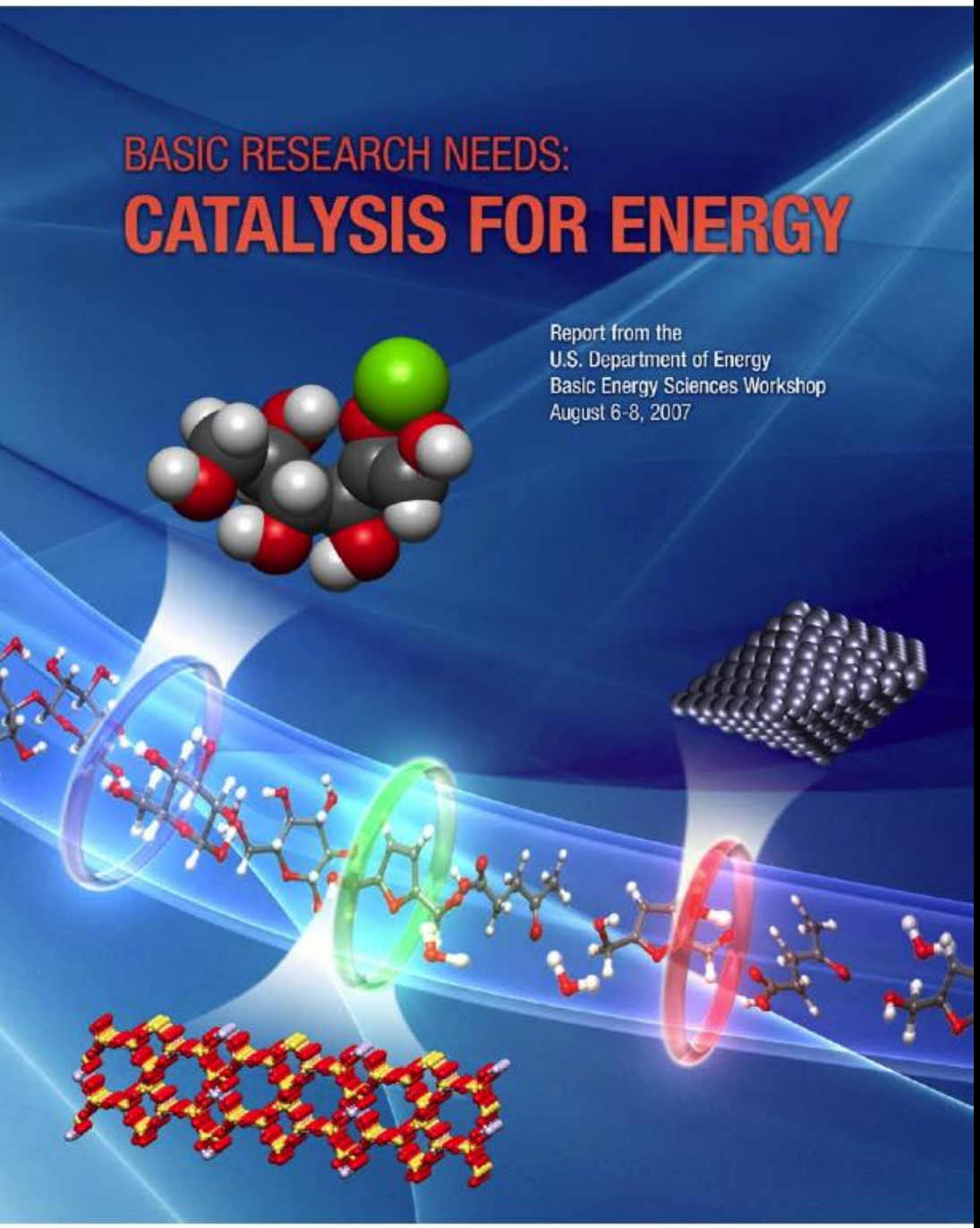


Neutrons for Catalysis

Neutrons as Microscopic Probes in Heterogeneous Catalysis

Juergen Eckert

Materials Research Laboratory
University of California Santa Barbara

Grand Challenges for Catalysis Research

1. Understanding mechanisms and dynamics of catalyzed transformation

   Catalytic reaction rates and selectivity

   ⇩

   Kinetics, energetics and dynamics of individual elementary steps

   ⇩

   Structure and dynamics of catalytic sites

2. Design and controlled synthesis of catalytic structures

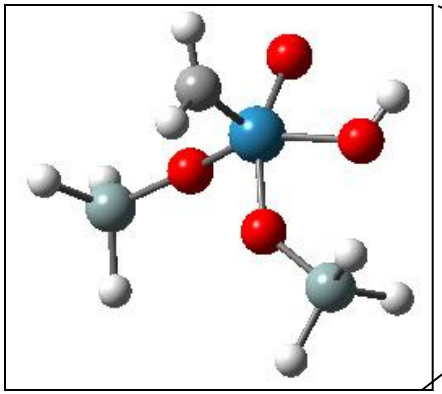
   theory as predictive design tool

   systematic approaches to construct and characterize at an atomic level molecules and materials designed

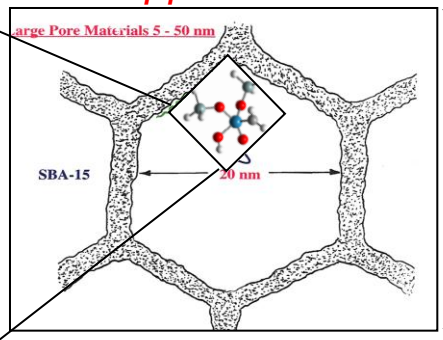
   control and direct chemical reactions in complex media

Hierarchical integration:
From active sites to catalytic materials

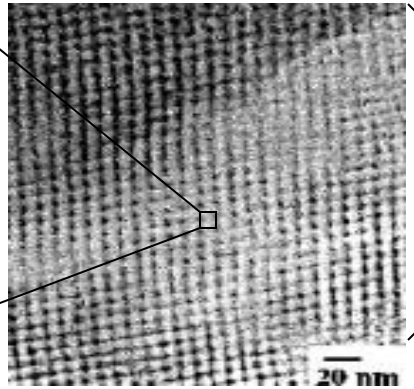
active site



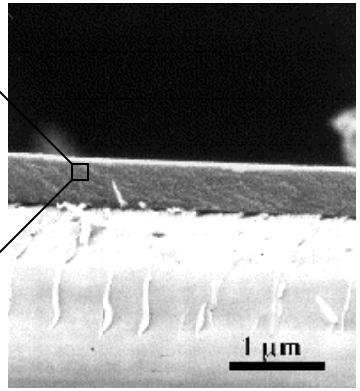
metal-support interaction



support design



cast film



bench scale

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

in-situ reactor for neutron scattering

→

pilot plant

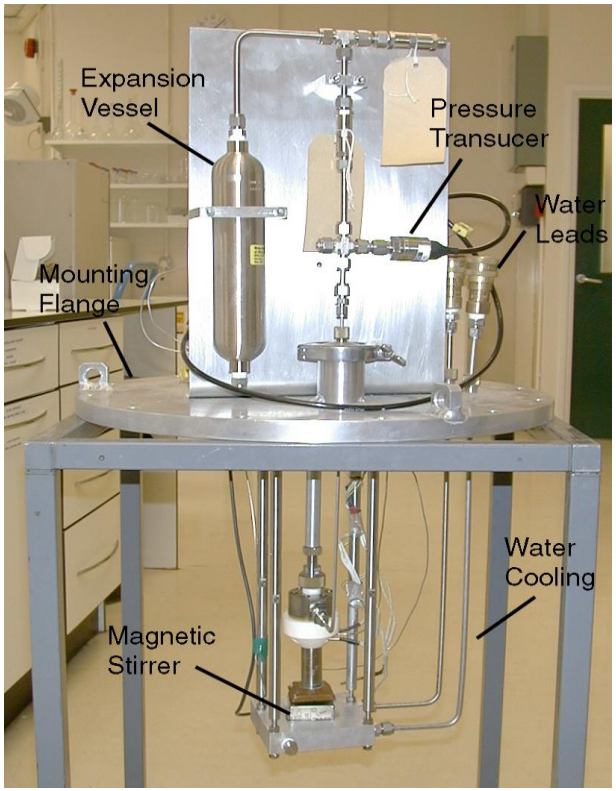
QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

→

new products and processes

In-situ (or '*semi in-situ*') Neutron Scattering Studies: no "windows" necessary!

INS* (Goodman et al.)
on
quenched catalytic reactions



In-situ gas-loading cells are available for neutron scattering:
sorption complexes (structure, dynamics*)
molecular diffusion

*low-T is generally preferred for INS: "better" spectra, hence "semi in-situ"

any T, P: diffraction,SANS, QENS, in-situ possible

not widely available: standard equipment to monitor catalytic reactions

Diffraction Study (O'Hare):

in-situ hydrothermal crystallization cell (ISIS) at elevated T and P

Selected items from the BES report relevant to the use of neutrons:

1. Reaction Mechanism:
(Sequence of elementary steps by which reactants can be converted to products)

Need to determine:

- geometric structure (atomic positions) energies and electronic structure of the initial state (reactant), final state (product) and transition state at each step, all with high spatial (every type of active site!) and temporal resolution

- dynamics of their interconversion

- dependence on the details of the dynamic structure of the active site, surroundings and reaction media

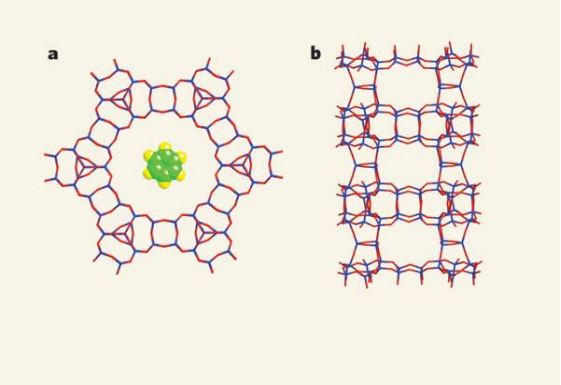
- this on time scales: 10^{-18} to 10^{4} s

- accurate measurements of selected model systems: benchmarks for theory development

- theory to develop true predictive capability, and optimize catalyst structure

Selected items from the BES report relevant to the use of neutrons:

2. Design and Controlled Synthesis of Catalytic Structures

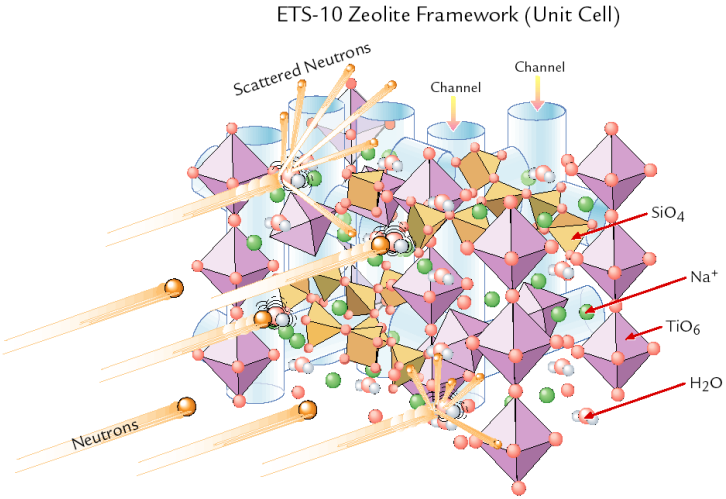


uniform catalyst structure ⇒ better selectivity

evolution of catalyst structure in reactive environment: deactivation

design of 3-D nanostructured catalysts (e.g. large pore zeolites, ITQ-33)

- for high degree of selectivity
- wider array of porous structures (hybrids, oxide structures)
- high degree of stability
- include multiple catalytic centers (cascade reaction schemes)



learn from enzymes: biomimetic catalysts

rational catalyst design ⇔ process development

development of non-precious metal catalysts with superior performance

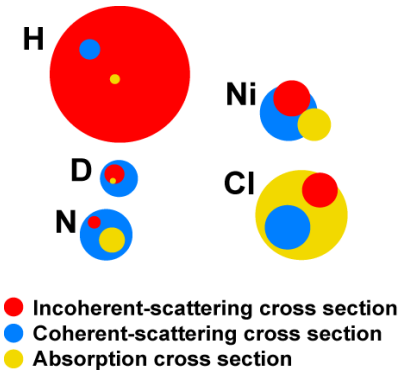
Neutrons as microscopic probes in heterogeneous catalysis

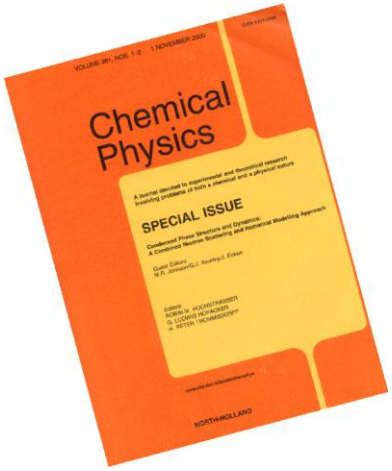
Both elastic and inelastic scattering of neutrons can be detected:

⇒ determine structure AND dynamics

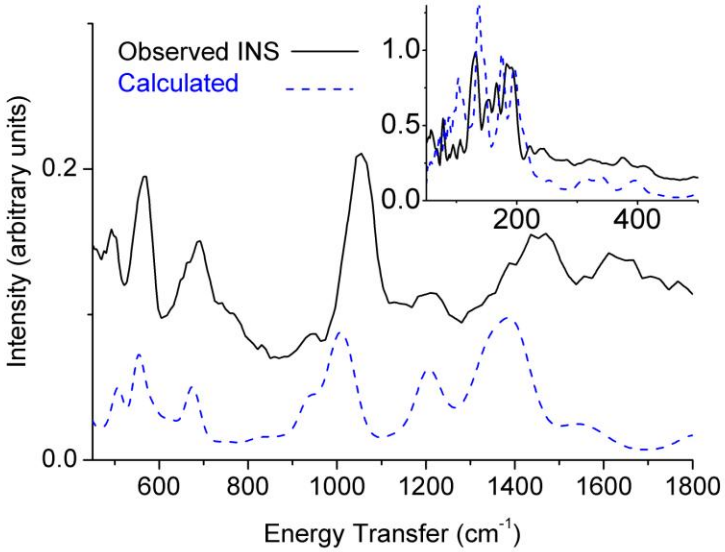
Neutrons are scattered by atomic nuclei, not electrons:

- low absorption cross-sections (sample containers!)
- isotope-dependent scattering (H/D; Fe, Ti, others)
- ease of complementary computational studies





"Condensed phase structure and Dynamics:
a combined neutron scattering and numerical modeling approach",
Chem. Phys. **261**, issue 1/2, 2000.



INS spectra of Tetraacetylethane; calc. MD/DFT
J. Stare, G. J. Kearley, J. Eckert, L. L. Daemen, M. Hartl, D. Hadzi
(unpublished)

Some (old) **examples** of what has been done:
⇒ basis for where to go in the future

Structure of the active site: TS-1

Binding of reactants:

water; chloroform in zeolites

hydrogen on metal particles

Diffusion (reactants, products…)

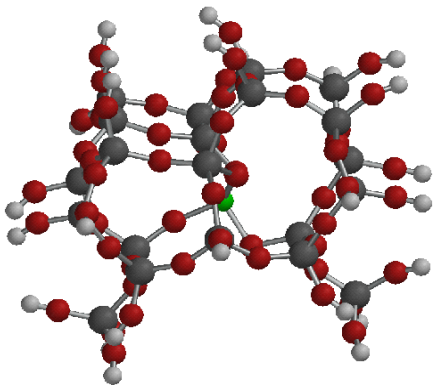
Reaction mechanism by INS(?): what are the intermediates, products?

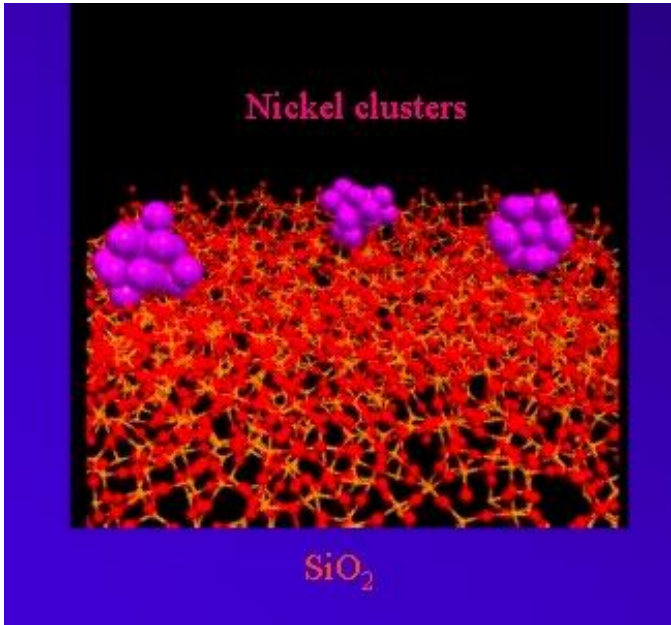
oxidative addition of H_2 to a metal

propylene epoxidation in TS-1, on Au/TiO_2

catalytic decomposition of CH_4

Examples of active sites

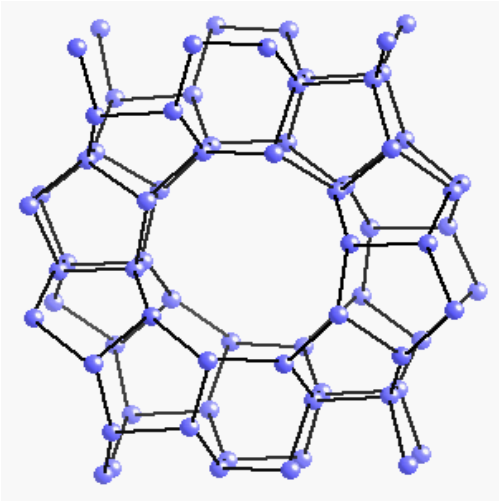




Micro-, Mesoporous and Model Ti-silicates

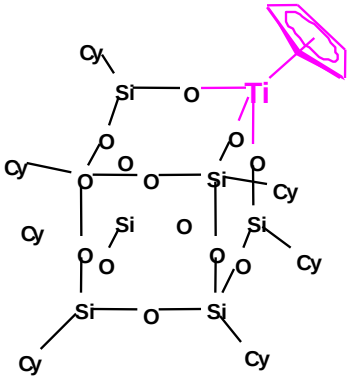
TS-1

- Ti-silicalite with 5.5 Å openings



Ti-MCM-41

- amorphous silica with 20 - 30 Å pores

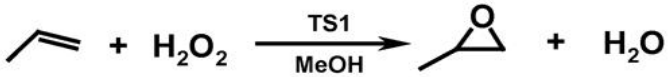


- Cyclopentadienyl Ti-silsesquioxane

Molecular-level investigations in Heterogeneous Catalysis by Spectroscopy*, Diffraction, and Computation

Example: we have the following reaction catalyzed by “TS-1”:

Propene oxidation with H_2O_2 / TS1



What are some of things we would like to learn about this reaction, how and why?

1. Catalyst:

   What is the active site, and its structure ?

   Origin of the reactivity, selectivity, efficiency ?

   Can this be improved ?

   How does the catalyst deactivate ?

2. Reaction:

   How does the reaction proceed (step-by-step) ?

   What exactly is the role of the catalyst, the active site ?

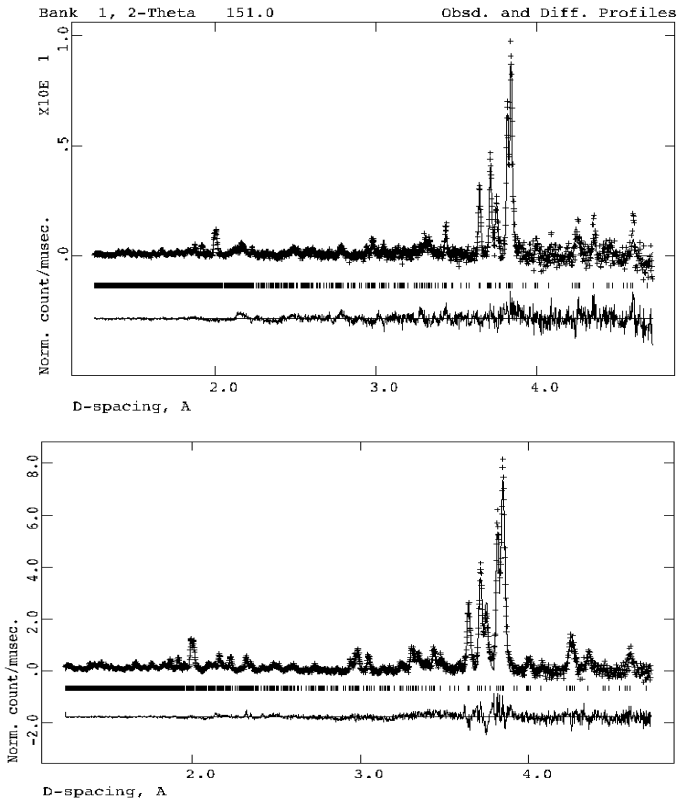
   Identity of intermediates, desirable and undesirable products ?

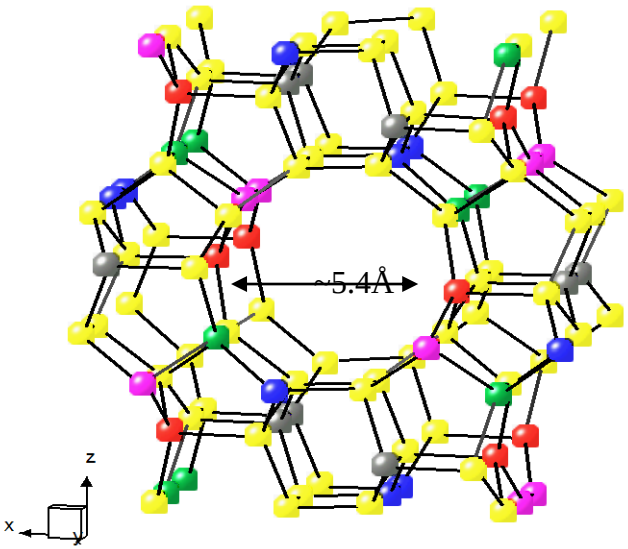
We can answer many of these questions by a combination of the above techniques

* IR, Inelastic neutron scattering, NMR and EXAFS

Locate a very small amount of Ti or Fe in ZSM-5 by a Powder Diffraction Experiment - Neutrons or X-rays ?

- x-rays
  - Atomic scattering lengths based on atomic number (electrons): Ti is fairly similar to Si
- Neutrons
  - scattering cross-section is a complex function of nuclear properties; Ti is very different from Si (Ti: -3.4, Si: +4.1 fm)



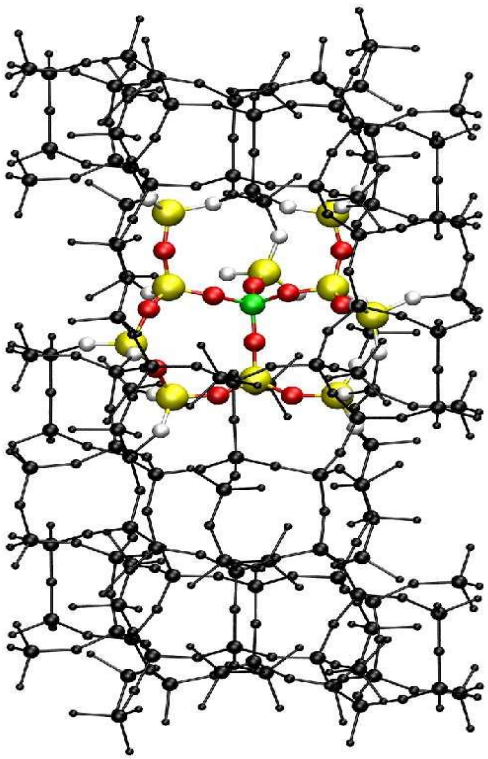


T3 - red (4% Ti)
T7 - blue (4% Ti)
T8 - green (12% Ti)
T10 - gray (5% Ti)
T12 - magenta (6% Ti)

Neutron Powder Diffraction Pattern of TS-1 (bottom) and FeS-1 (top)

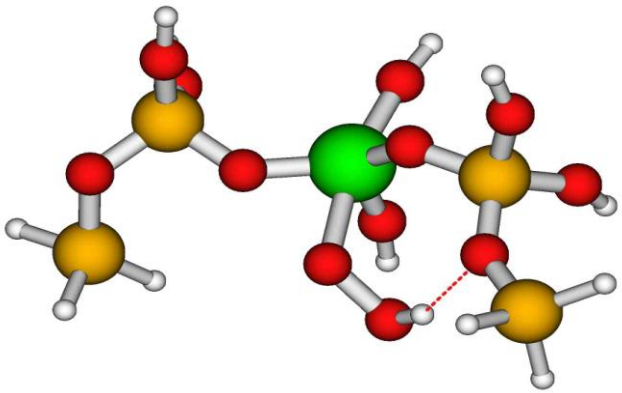
Reaction mechanism* is amenable to computational study: Propene Epoxidation by aq. H_2O_2

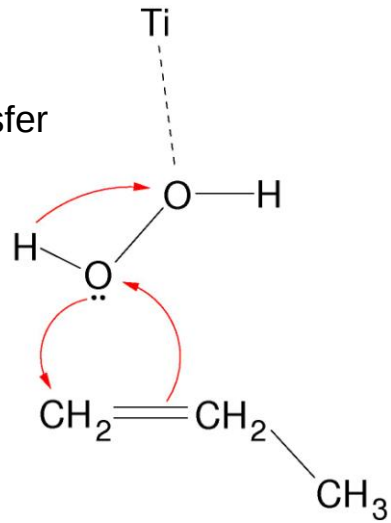
(J. Stare, N. J. Henson, and J. Eckert , J. Chem. Info. and Modeling, **49**, 833, 2009)



QM/MM

H_2O (not shown) assists in proton transfer

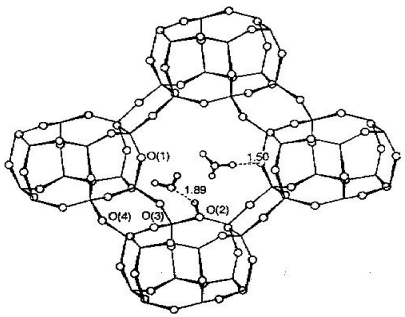


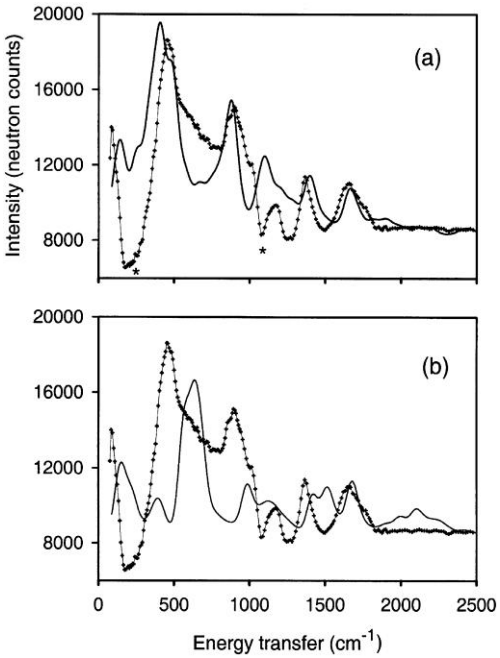


INS spectra (at various steps, T) have been collected…
computational studies (fully periodic)will continue on “Coyote”

How can we use INS Vibrational Spectroscopy to solve structural problems ?

A somewhat old (but important) example: how does a water molecule bind to the active site in acid zeolites?
Does the proton transfer or not upon binding?





Neutron Diffraction: Water in H-SAPO-34

: both binding modes present

L. Smith et al., Science 271, 799, 1996

INS and theory: water in H-ZSM-5

: no proton transfer

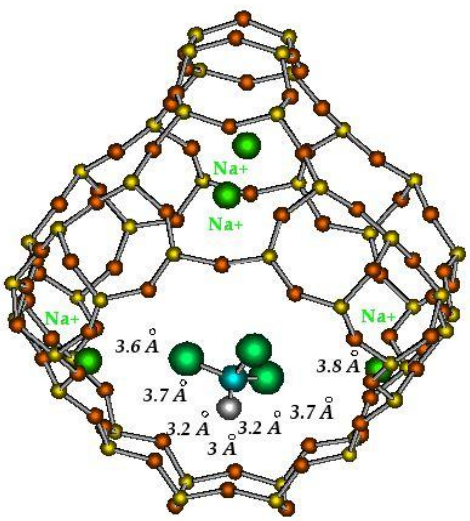
H. Jobic et al., J. Phys. Chem. 100, 19545, 1996

Binding of Chloroform in Faujasite Type Zeolites

C. F. Mellot. A. Davidson, J. Eckert and A. K. Cheetham, J. Phys. Chem. **102**, 2530, 1998.

Molecular Mechanics approach:
Monte Carlo Docking

Monte Carlo docking of a chloroform molecule in NaY leads to a preferred location in the 12ring window, the **CH bond pointing towards the framework**. This orientation would be stabilized through weak hydrogentype bond.



Predicted adsorption energy ~ 40 kJ/mol
electrostatic contribution ~ 80% dispersion ~ 20%

INS spectra (FDS/Lujan Center)

C-H bending mode (ν_4) is at higher frequency

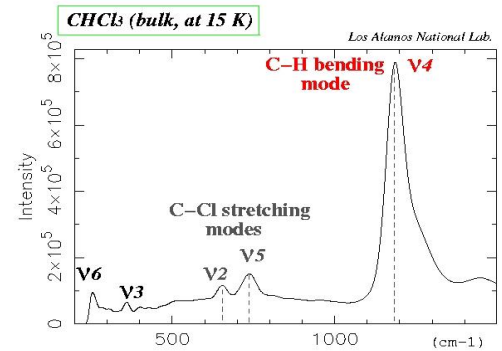
for adsorbed chloroform (bottom)

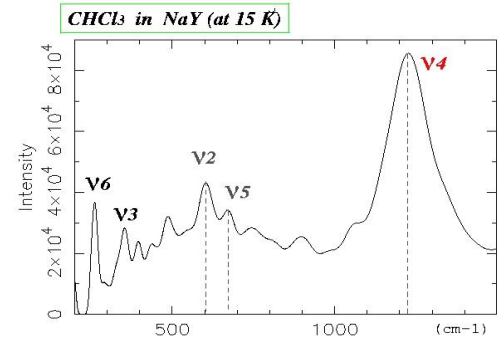
relative to bulk (top)

➔**formation of H-bond**

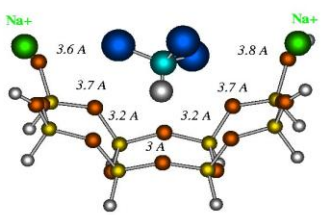
C-H….O(framework)

Inelastic Neutron Scattering





2 **CHCl3 orientation from Monte Carlo calculations involving hydrogen–bond with the framework**



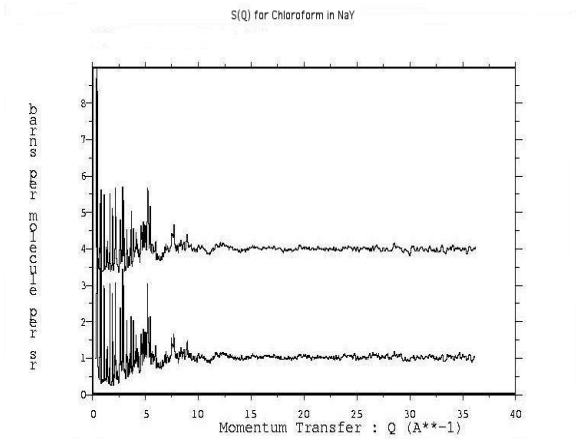
ΔE(interaction)= – 49.4 kJ/mol

QM cluster calculations also favor this orientation by 35 kJ/mol

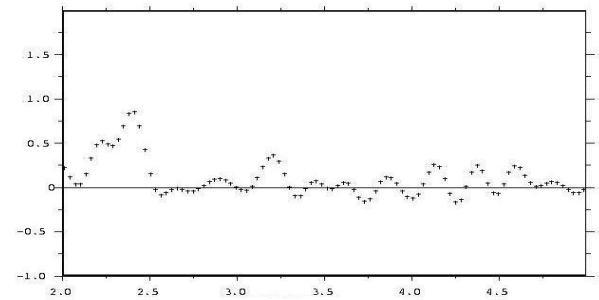
Binding of Chloroform in Faujasite Type Zeolites

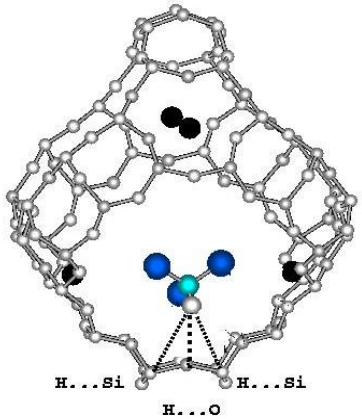
Differential (H/D) pdf analysis of Neutron Diffraction Data

(J. Eckert, C. Mellot-Draznieks and A. K. Cheetham, J. Am. Chem. Soc. **2002**, *124*, 170)



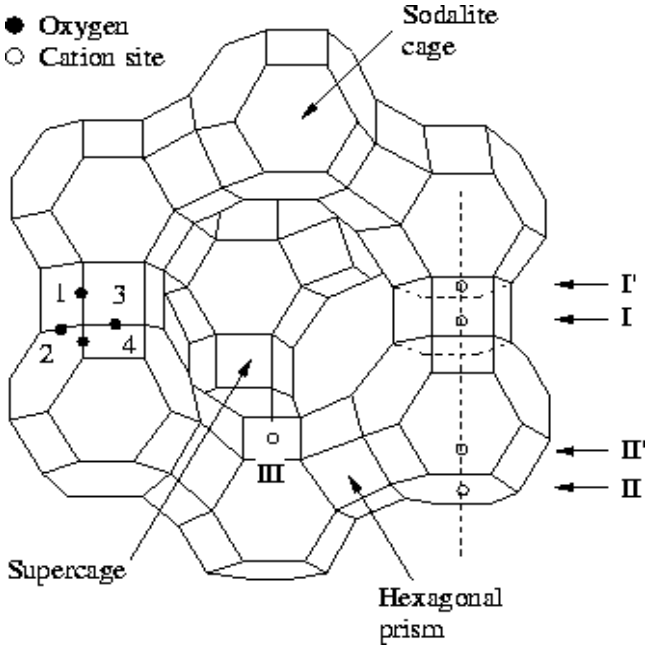
S(Q)for H and D-chloroform in NaY
(GLAD/IPNS/ANL)





Direct evidence for formation
of a C-H….O(framework) hydrogen bond

Schematic showing guest-host distances observed in H-pdf(top) : H…O at 2.25 Å and H….Si at 3.5 Å. Peak at 2.4 Å is the intramolecular H…Cl distance.



Probing the Nature of Acetylene Bound to the Active Site of a NiNa–Zeolite Y Catalyst by in situ Neutron Scattering

John F. C. Turner, Chris J. Benmore, Carolyn M. Barker, Nikolas Kaltsoyannis, John Meurig Thomas, William I. F. David, and C. Richard A. Catlow

NiNa-Y has both Ni and Na cations for charge compensation (of Al in the Framework)

Ni sites are likely to be much more active

Where and how does acetylene bind?

A small molecule can “get lost” in a large cavity in conventional structure refinement

Use Neutron Diffraction and PDF analysis

Collect diffraction data on

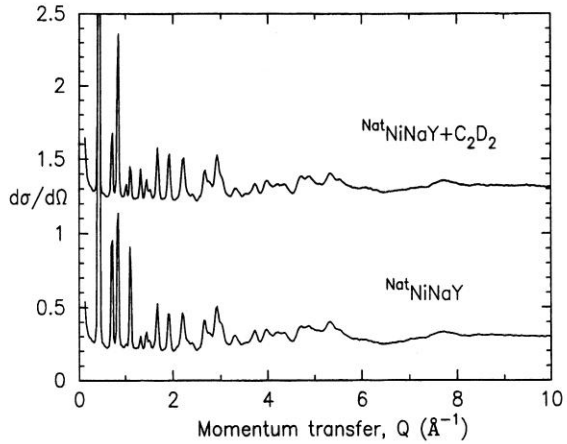
^{Nat}NiNa-Y

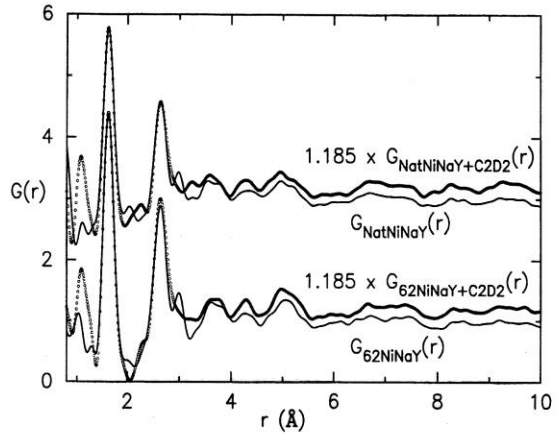
^{Nat}NiNa-Y + C_2D_2

^{62}NiNa-Y

^{62}NiNa-Y + C_2D_2

take various differences
obtain Ni partial PDF's with and without acetylene bound





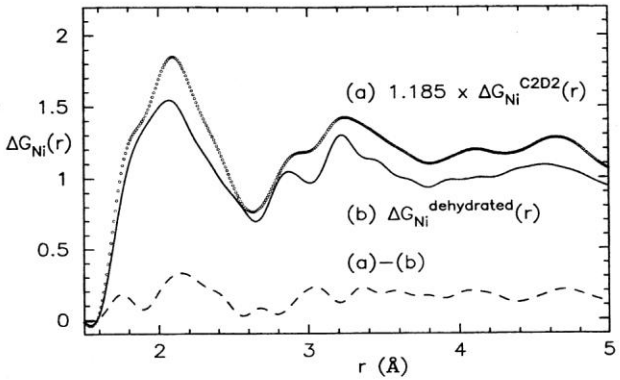


Figure 4. Real space Ni environment in NiNaY, measured with (circles), and without (solid line) the presence of acetylene (the NiNaY + C_2D_2 difference has been scaled by a factor of 1.185, see text).

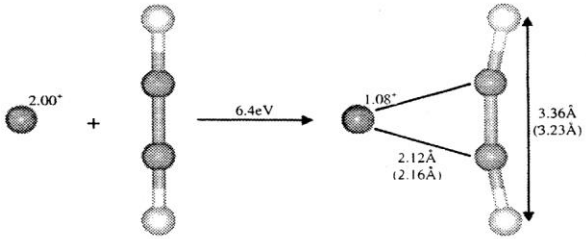
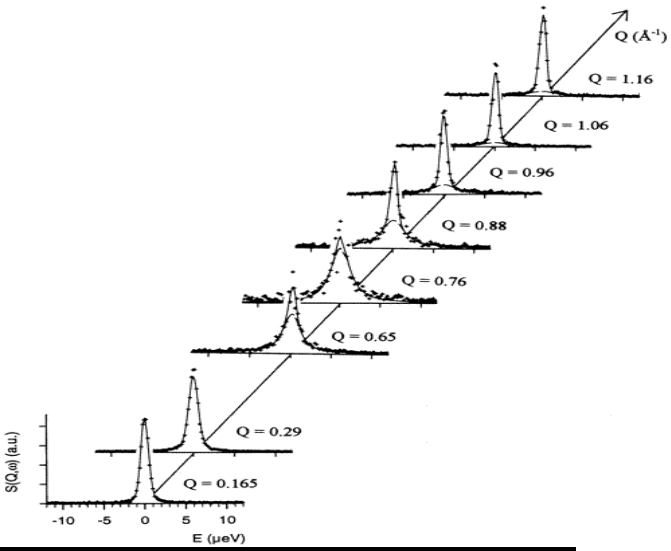


Figure 5. BLYP/DNP optimized geometries, Ni charge, and binding energy for the interaction of one molecule of acetylene with a bare Ni^{II} ion. Distances obtained from neutron scattering data in brackets.

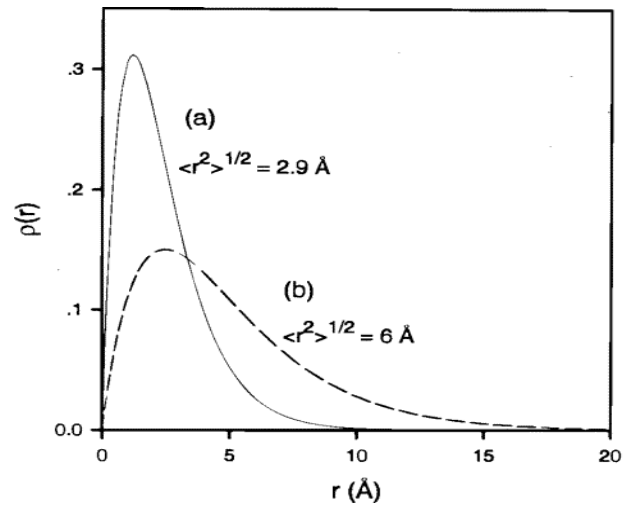
result checked against computation

Diffusion of Benzene by Quasielastic Neutron Scattering

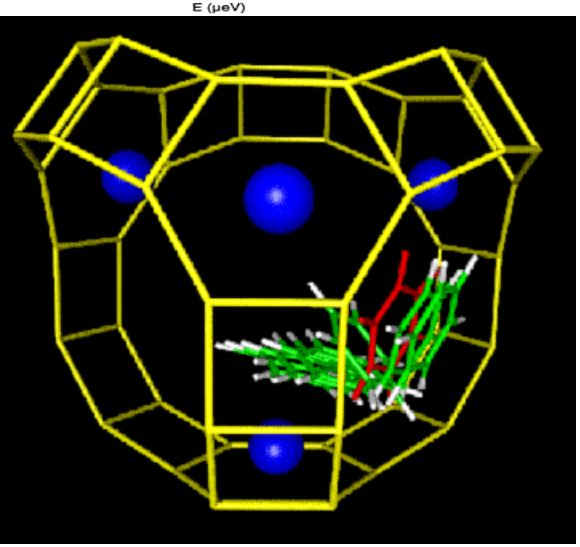
ILL: Jobic et al. J. Phys. Chem. B 2000, 104,

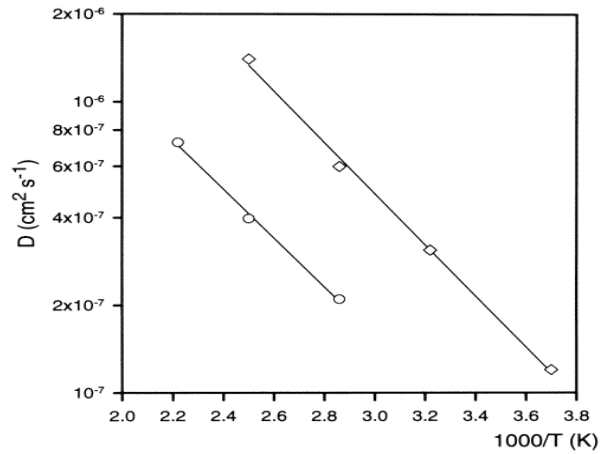


Quasielastic Neutron Scattering Spectra, 350K
1.5 Benzene/supercage



QENS provides both **time and spatial** information:
jump distance distributions (top) and
diffusion constants (bottom)

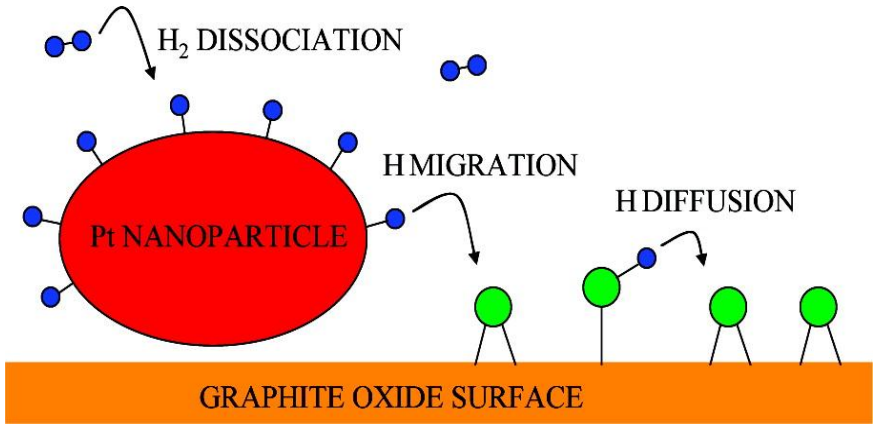




Simulations: Auerbach et al.,

“Hydrogen Spillover” : significant increases in Hydrogen Capacities

see, for example, L. Wang and R. T. Wang, Energ. Environ. Sci. 2008, 1, 268



Process has been known for some time in Catalysis, e.g. hydrogenation reactions

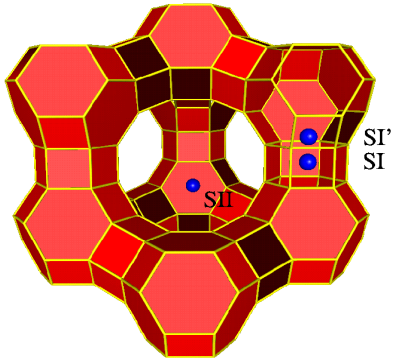
Details are poorly understood

But, it is now applied to Hydrogen Storage Materials

Storage increases seem to be based on these:

H atoms can be more densely packed than molecules

H atoms can migrate, diffuse to many places on/in the support/host material which are inaccessible to H_2.



Ir_6 clusters in Faujasites: H_2 Spillover*: INS studies

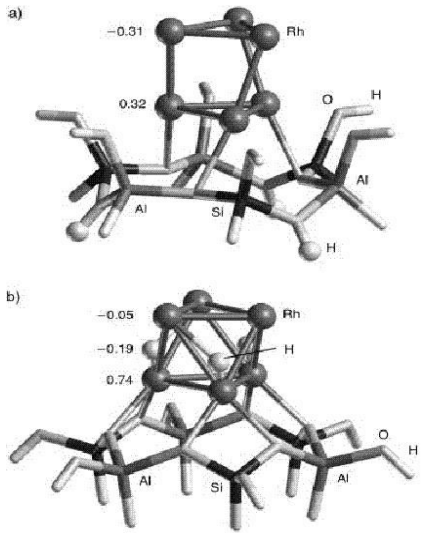
F. L. Ping, M. Hartl, L. L. Daemen, J. Eckert, and B. C. Gates, Z. Phys. Chemie, **220**, 1553, 2006.

dispersed Metal Clusters are important Industrial Catalysts
role of support is still not well understood

interaction between metal cluster and support
includes -OH groups on the support

molecular H_2 apparently dissociates on the metal cluster and "spillover" onto the support, forming OH groups.

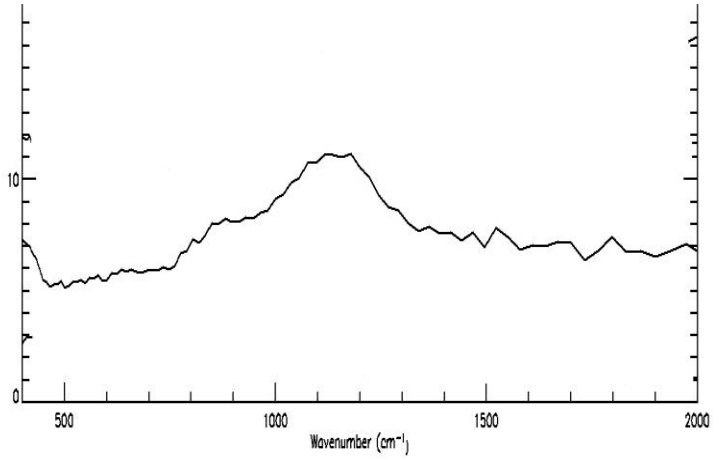
the metal is oxidized in this process



Sample:

4g of zeolite NaY w/ 2 mmol Ir
appr. 4mmol of -OH left after calci
total H on Ir clusters ~ 1-2 mmol

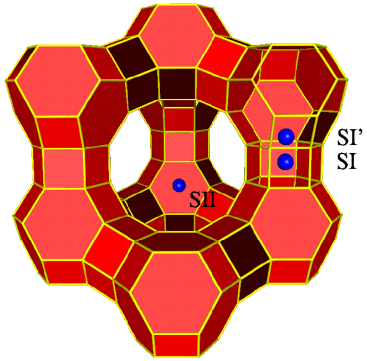
INS spectrum (below, NaY "blank" subtracted) c
sample clearly shows
d(IrH) at ~ 875 cm-1
d(OH) at ~ 1100 cm-1.



Computation (Rh_6 cluster, left) finds **"reverse spillover"** from surface -OH, 3H per cluster

Vayssilov et al., Angew. Chem. Int.'l Ed. **2003**, 42, 1391.

*Related experiment: P. C. H. Mitchell et al. , J. Phys. Chem.B 2003, 107, 6838

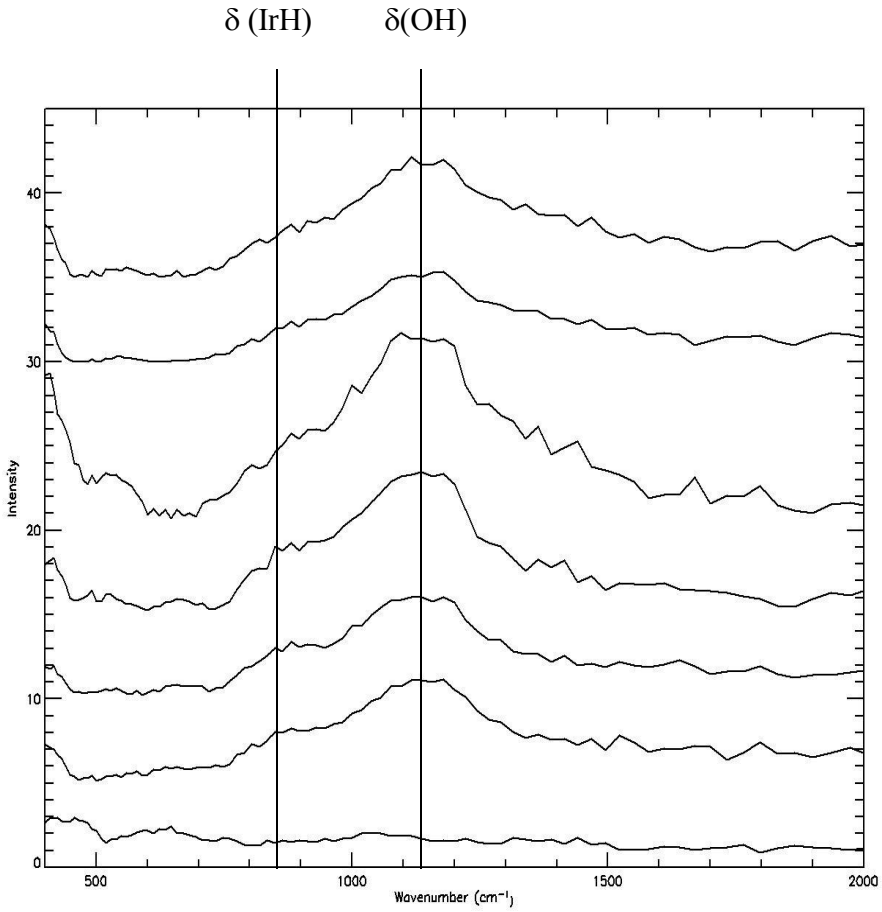


Ir_6 clusters in Faujasites: H_2 Spillover: INS studies

(F. L. Ping, M. Hartl, L. L. Daemen, J. Eckert, and B. C. Gates, Z. Phys. Chemie, **220**, 1553, 2006)

Reaction steps all carried out **in-situ** on the spectrometer, same sample (bottom up):

7. Re-exchanged with H_2 at RT
6. Exchanged with D_2 at 200°C
5. H_2 adsorbed at 200°C
4. H_2 adsorbed at RT
3. Previous sample evacuated
2. Ir6/NaY "as-prepared"
1. bare, calcinedNaY zeolite

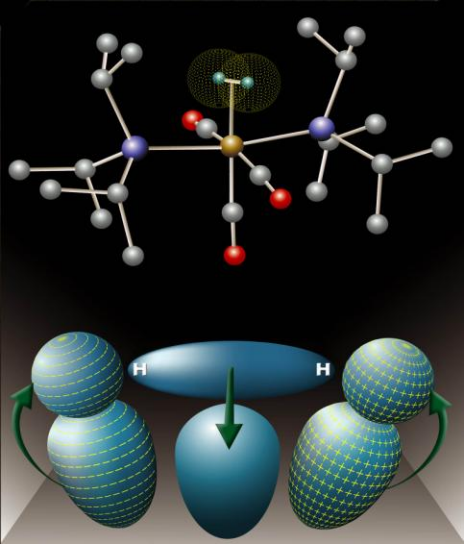


Notes: Exchange carried out at at 80 torr, several adsorption/evacuation cycles
Also observe H-Ir "riding modes" at low frequency (< 150 cm^{-1})

Reaction Coordinate for Molecular Hydrogen

(Oxidative Addition to the Metal):

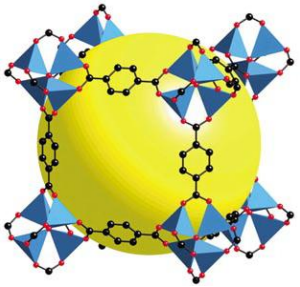
Each Step is Represented by a Different $M(H_2)$ Complex

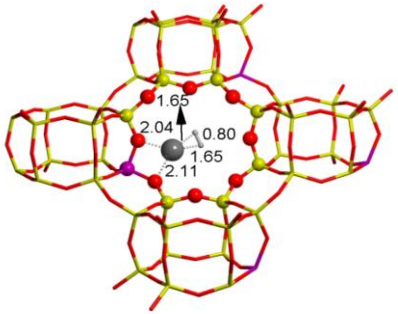


The Kubas Complex,

$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$

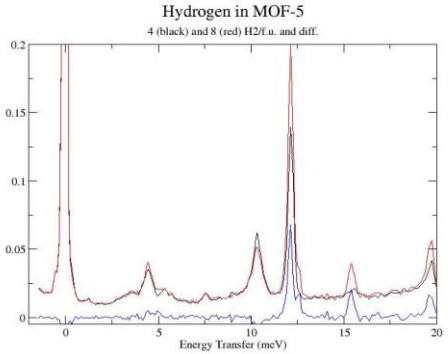
Free molecule	-	free rotor (120 cm^{-1})
Physisorbed Hydrogen	-	(weakly) hindered rotor (85 cm^{-1}, MOF-5)
		two degrees of freedom
Chemically bound	-	~ planar rotation (1 cm^{-1}, Cu-ZSM-5)
(dihydrogen ligand)		
Hydride (H)	-	no molecular rotation

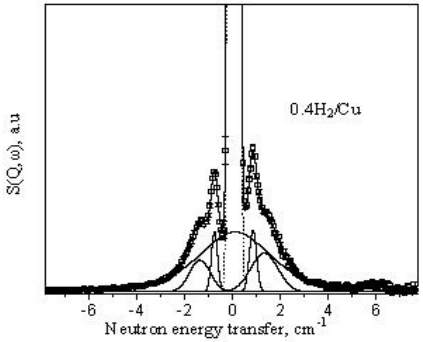




H_2-CuCHA(IV)

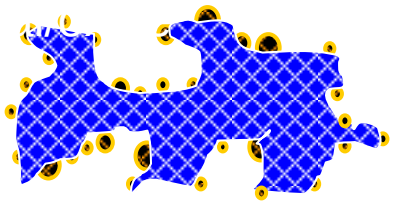
Rotational tunneling frequencies of hydrogen or dihydrogen probes the interaction with the host material





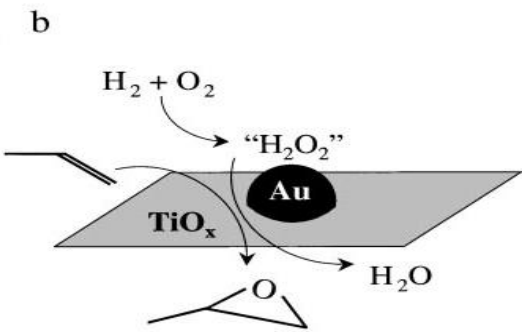
Current hydrogen storage materials are at the extreme ends of this range: either carbon, MOF's, etc.
or metal hydrides, chemical hydrides
"intermediates" only as organometallics

Inelastic Neutron Scattering Experiments: propene epoxidation



Surface Area = ~100 m^2/g

High Surface area oxide-supported metal catalysts



- **Catalyst**

  appr. 3g of Au (1% wt.) on TiO_2

- **Technique:**

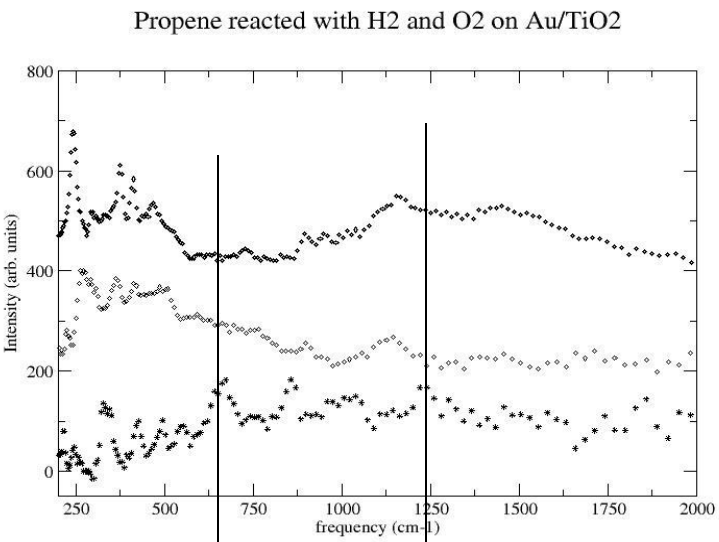
  Flow a gas mixture (70% He, 10 % H_2, 10 % O_2, 10% propene) over the catalyst in reactor at a 150 C for 3 hours

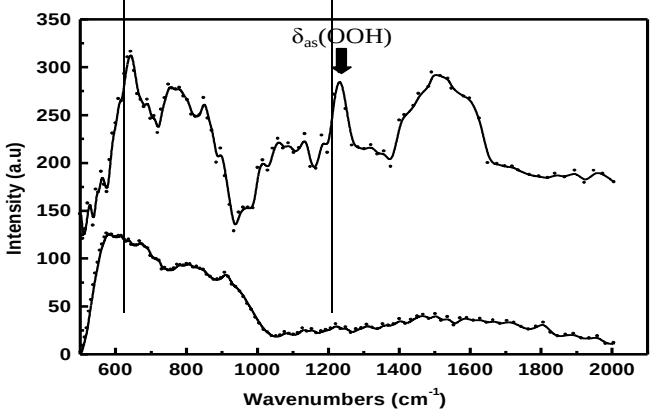
  Quench the reaction in liquid nitrogen (77 K); keep reactor cold

  Collect INS spectrum at 30 K

- **Identify reaction intermediates and products at the surface of the catalyst by their vibrational spectra**

Propene reacted with H_2 and O_2





Comparison (top) of INS spectra of:
bulk PO
PO adsorbed on Au/TiO_2
propene reacted (H_2/O_2)

and (below left),

spectrum of H_2/O_2 reacted over Au/TiO_2

PO skeletal modes strongly affected by binding to catalyst upon formation

peaks at 630, 850, 1230cm^{-1} are from reaction products: coordinated water, H_2O_2

Why is this not yet published?
$\Rightarrow$ need extensive computational studies to sort out this mess!

Catalytic Decomposition of Methane for H_2 Production

Ni on SiO_2 and Ru on Al_2O_3;

metal loading was 10%; measured specific area ~ 5 m^2/g.

- Flow a 10% mixture of CH_4 in Ar over the catalyst contained in a small reactor at a fixed temperature for 4 hours; flow rate 0.9 L /min.
- Quench the reaction by dropping the reactor in liquid nitrogen (77 K);
- Mount the reactor on closed-cycle refrigerator cold finger and cool to 20 K, collect INS spectrum.

can we learn details of the reaction mechanism by this approach ??

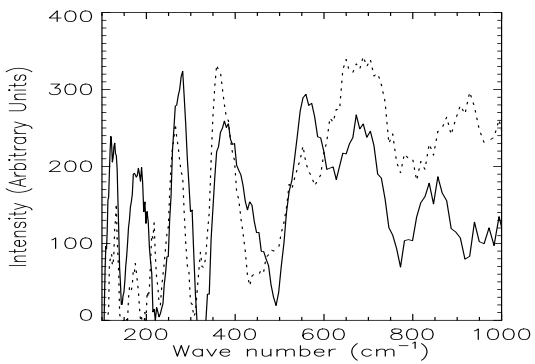
Species well known from EELS/Single Crystal Surface model studies - now on a real catalyst; examples (assignments made the "usual" way):

methylidyne(CH) ~ 830 cm^{-1}

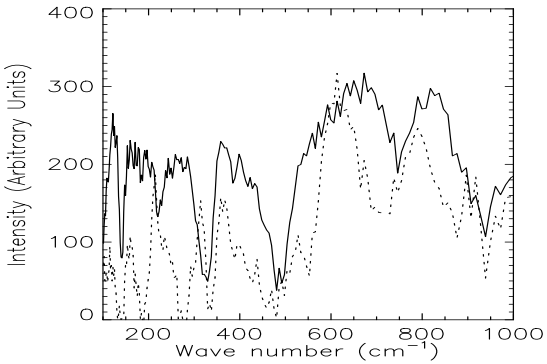
ethylidyne $\nu(MCCH_3)$ ~ 410 cm^{-1}

vinylidene $\tau(CH_2)$ ~ 670 cm^{-1}

Ni on SiO_2



Ru on Al_2O_3



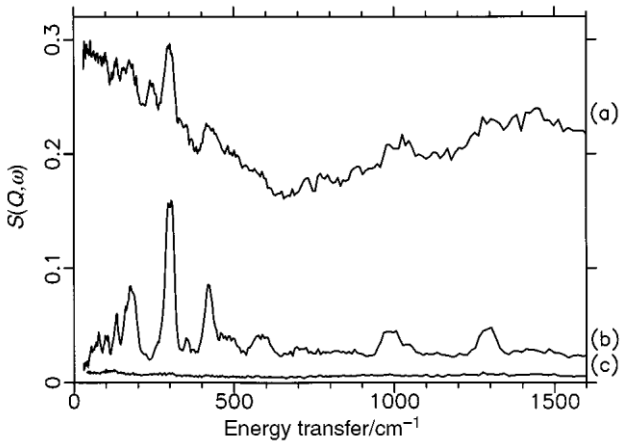
T=325 °C (dashed), =250 °C (solid)

Computational studies are required for proper identification of Intermediates, products and reaction mechanism

C. Sivadinarayana, T. V. Choudhary, L. L. Daemen, J. Eckert and D. W. Goodman, Angew. Chem. Int.'l Ed. **41**, 144, (2002).

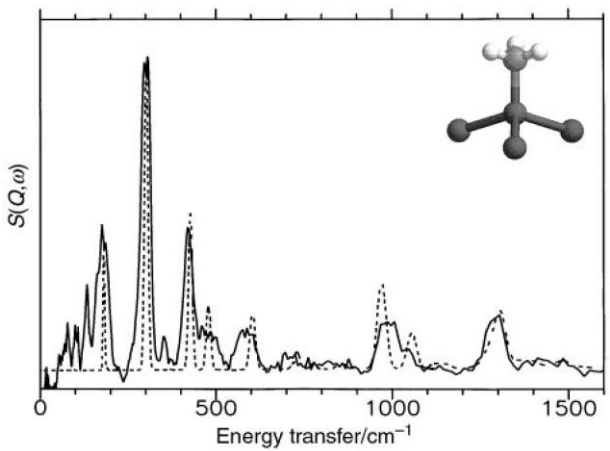
Poisoning of a Pd Catalyst Studied by INS*

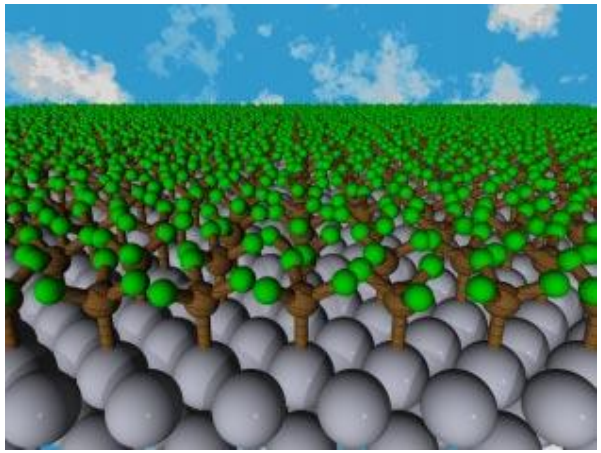
ISIS Facility (UK): Albers (Degussa-Huls) et al., Chem. Com. **1999**, 1619



Deactivated catalyst before (a) and after (b) solvent extraction. Active catalyst after extraction (c)

Identification of species poisoning the catalyst
Comparison of observed and calculated INS spectrum for on-top methyl group





*** and computations**

Grand Challenges for Catalysis Research:

Where do go from here ? Some random thoughts:

Go to a workshop at SNS !

Plan new experiments (Hydrogenation on a new, high surface area MoN catalyst (Lujan Center, LANL)

Neutrons:

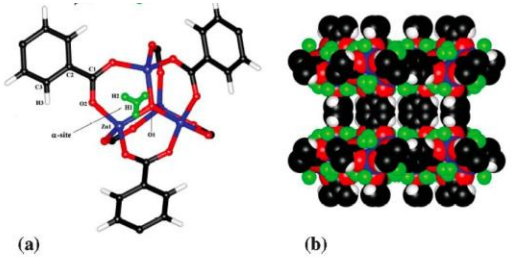
Experiments on real catalysts under reaction conditions (T, P) - if appropriate equipment, sample environments, labs are available

Hydrogen

Detailed characterization of model systems for theory Validation - especially for crystalline systems.

Structure-function: new catalysts vs. old

Molecular diffusion, dynamics, in concert with computational studies of detailed reaction mechanisms may provide insight in the latter



Example: H_2 in MOF-5: only single X-tal neutron diffraction study !

*E.C. Spencer et al. Chem Comm 2006, 276