Applications of Neutron Scattering Methods in Heterogeneous Catalysis

B. (More) Examples:

Propylene Epoxidation

Methane Decomposition

Hydrogen Spillover

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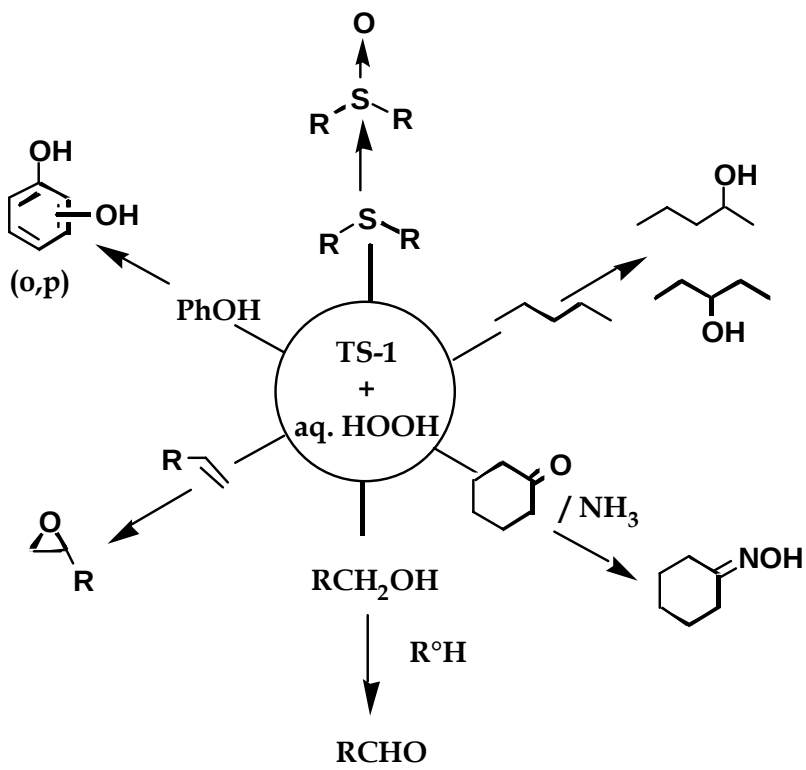
Epoxidation in Titanosilicate

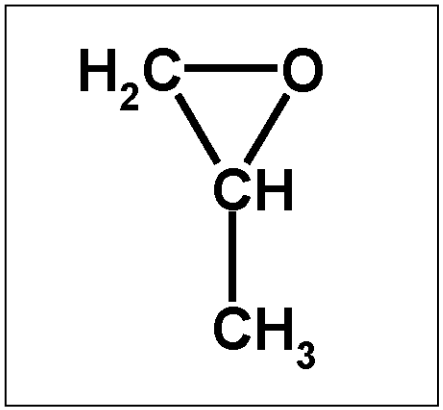
- TS-1 -- utilizes aqueous hydrogen peroxide as oxidant[1]
- Benign coproduct (H_2O)
- Commercial interest for catechol/hydroquinone and alkene oxide production
- Ethylene oxide (6 billion lbs/y US) - ethylene glycol, polyesters, polyethers, polyols, ...
- Propylene oxide (3 billion lbs/y US) - polyols, polyethers, ...

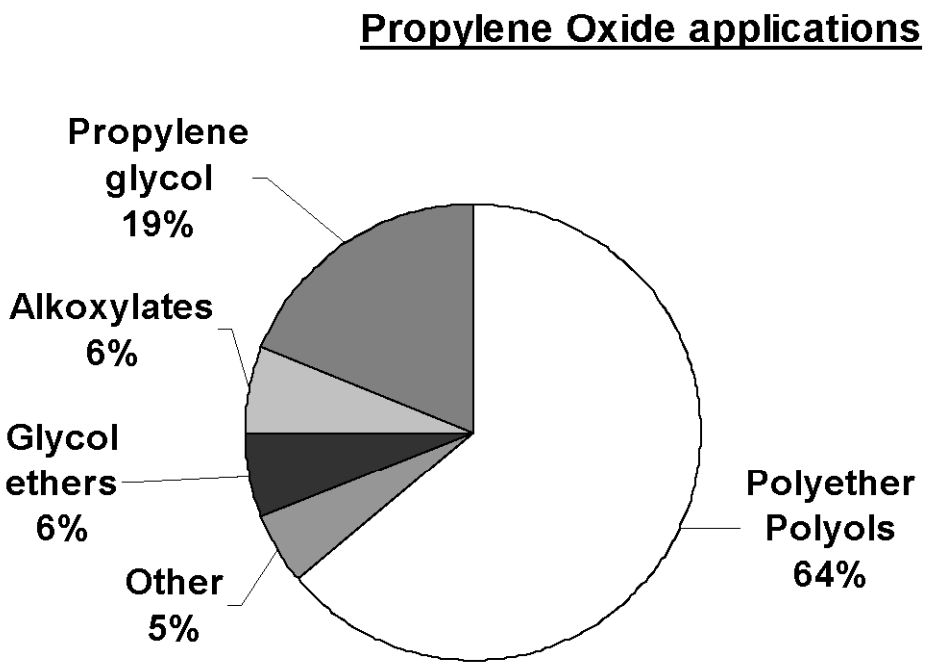


1. Taramaso, Perego, and Notari USP 4,410,501 (1983)

Propylene Oxide

Applications

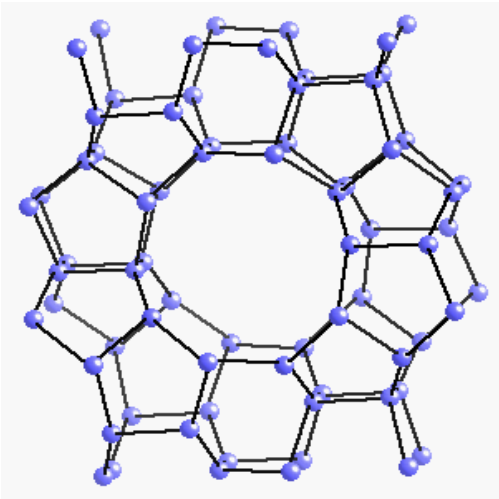




Micro-, Mesoporous and Molecular Ti-silicates

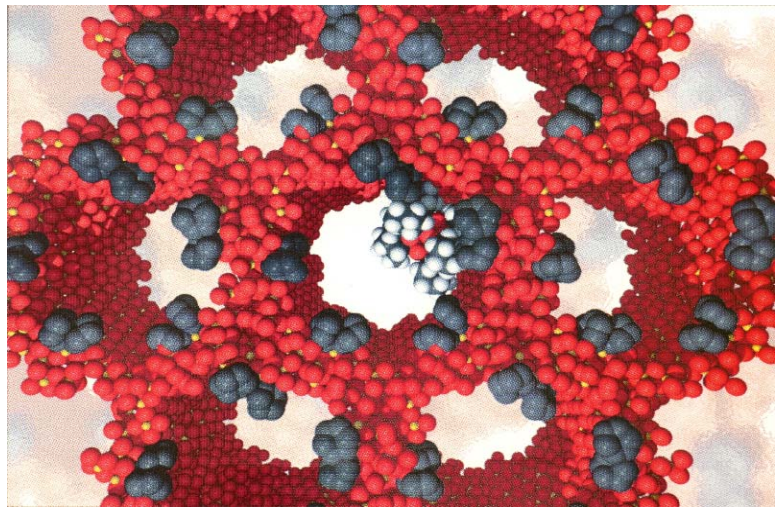
TS-1

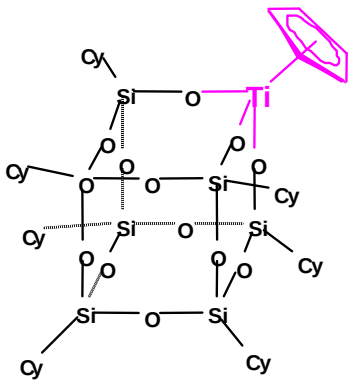
- Ti-silicalite with 5.5 Å openings



Ti-MCM-41

- amorphous silica with 20 - 30 Å pores

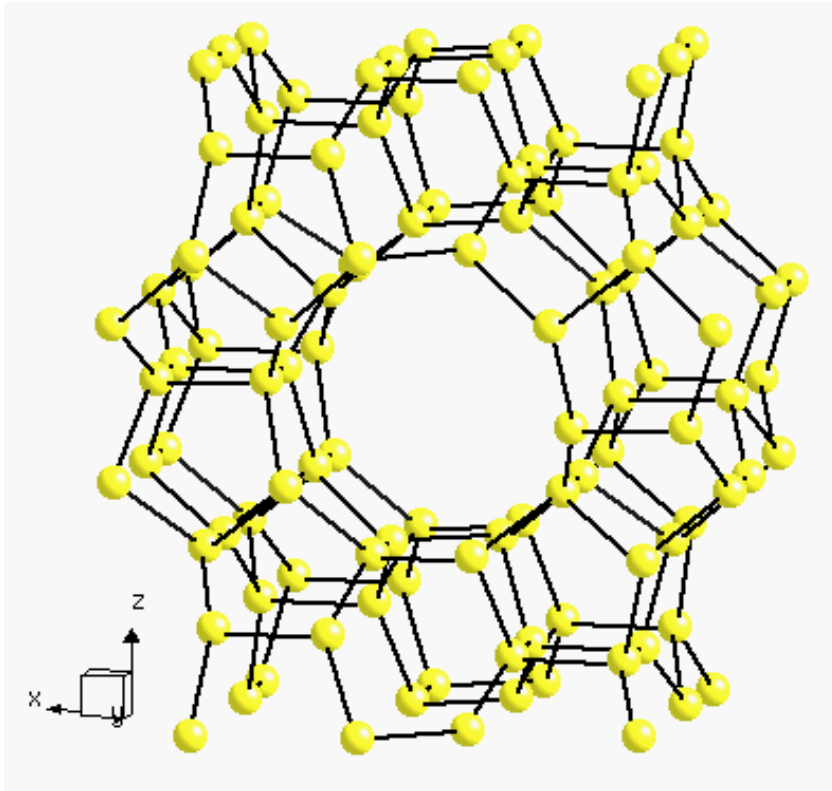




- Cyclopentadienyl Ti-silsesquioxane

MFI Framework Structure

- channels along y-axis and staggered channels follow the x-axis
  - 3D connectivity ZSM-5 structure
- Straight
  - channel openings are ~5.5 Å in diameter
- Orthorhombic (at RT), P*nma*
  - 12 different T sites
  - 26 Oxygen sites



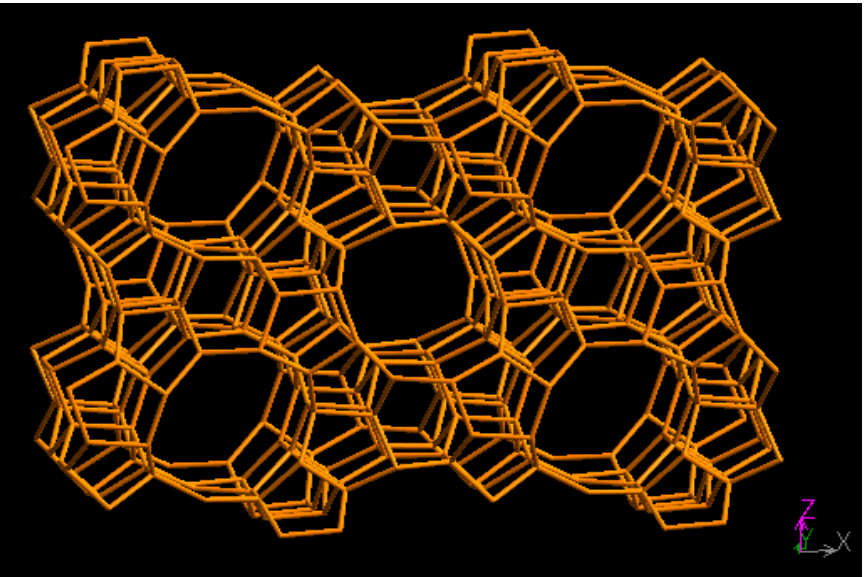
Silicon atoms
Oxygen atoms located between Si's

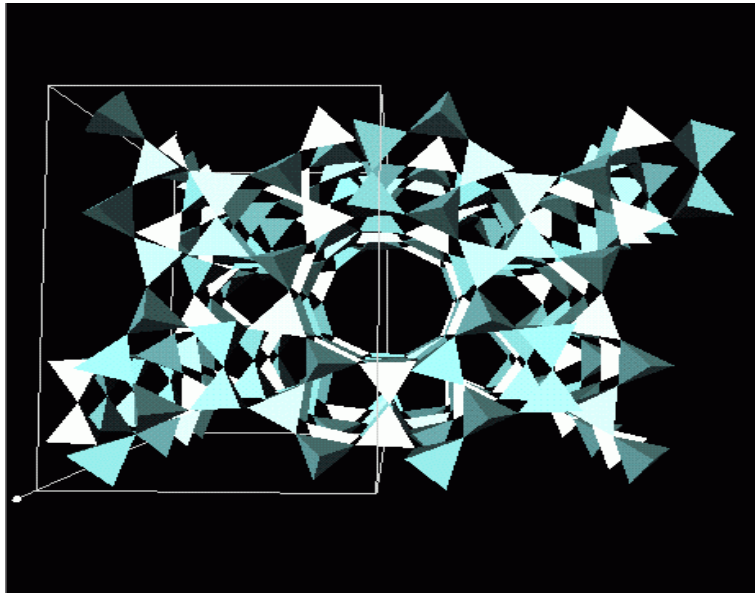
Titanium Silicalite-1 (TS-1): Structure

- Start with silicon-oxygen MFI framework
- Substitute 0–3% of the silicon with titanium
  - Site isolated Ti centers for catalysis
  - Presence of Ti in framework determined by EXAFS, powder X-ray diffraction, XANES, DRUV-Vis, XPS, and MAS-NMR
  - No direct evidence of Ti position or if Ti has preference for certain Si sites
- Study correlation between Ti environment in framework and catalytic properties

Iron Silicalite-1 (FeS-1)

- Iron replaces a small amount (<5%) of Silicon
  - same as TS-1, MFI structure
- Fe^{3+} vs. Si^{4+}
  - framework will be negatively charged
  - Na^{+} or H^{+} in channels to balance charge
- Determine if Fe occupies the same sites as Ti using neutron diffraction





Some Theoretical Predictions for TS-1

Ti Siting in TS -1	Researchers	Method
Random	Millini et al.	molecular mechanics & quantum chemical calculations
T8	Oumi et al. with Perego et al.	molecular dynamics paired w/lattice expansions
T12	Oumi et al. with Millini et al.	molecular dynamics paired w/lattice expansions
T2 and T12	Njo et al.	mmc & molecular mechanics

Neutron Diffraction Data

- Collected neutron diffraction data at Los Alamos Neutron Science Center (LANSCE)
  - used HIPD at the Manuel Lujan Neutron Scattering Center
  - at room temperature
  - three TS-1 samples with Si:Ti mole ratios of
    - 20:1 (A)
    - 30:1 (B & C)
  - one FeS-1 sample with Si:Fe mole ratio of
    - 70:1 (D)

Note - neutron scattering lengths (fm = 10^{-15}m):

Si 4.15	
Fe (natural) 9.45	(isotopes) 2.3 to 15
Ti -3.44 (natural)	(isotopes) -6.08 to 6.18

Structural Disorder

- Ti–O and Fe–O have longer bond lengths than Si–O
  - oxygens connected to Ti's will move off ideal locations to lengthen the bonds
  - cause disorder of these oxygens in a crystal structure
- Ti/Fe/Si–OH bonds
  - for charge compensation owing to Fe^{+3} or to cation vacancies
  - move oxygens off ideal sites and add extra atoms into structure
- Thermal parameters of both Si and O's ranged widely
  - from negative to large positive values
  - refined isotropic thermal parameters by type
    - all O's equivalent
    - all Si's equivalent

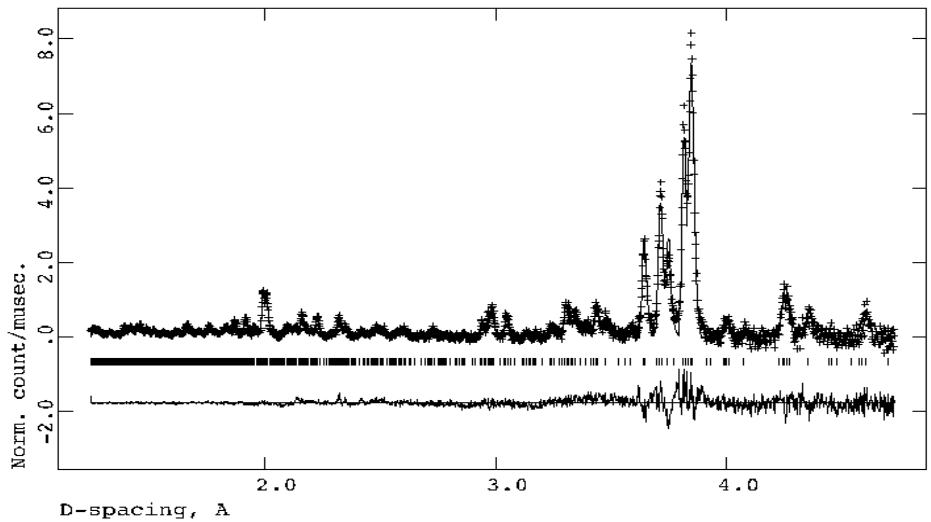
Structure Refinement

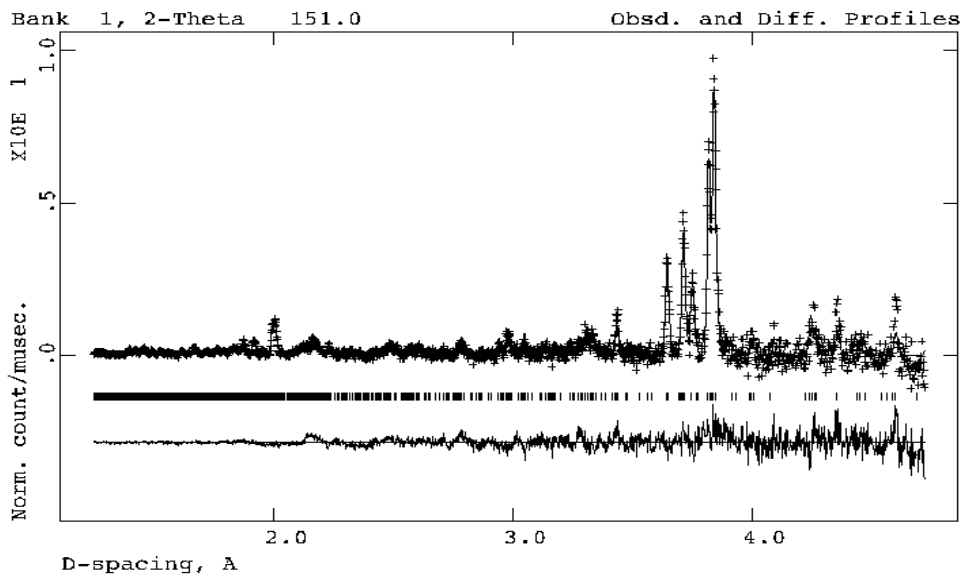
- Used General Structure Analysis System (GSAS) software package for structure refinement
- Starting atomic positions were from the X-ray crystal structure of H-ZSM-5 determined by Van Koningsveld
  - titanium and iron were not included in the initial models
- Atomic positions and thermal parameters were held at their original values and occupancies for Si were refined
  - if occ <1.0, Ti was placed on that site for samples A-D
  - if occ >1.0, Fe was placed on that site for sample E

Refinement Statistics

Sample	A	B	C	D
Space Group	P*nma*	P*nma*	P*nma*	P*nma*
Z	8	8	8	8
a	20.044(4)	20.062(10)	20.086(8)	20.014(17)
b	19.866(4)	19.880(10)	19.903(8)	19.885(17)
c	13.369(8)	13.387(8)	13.399(7)	13.361(14)
V	5323.3(36)	5339.3(49)	5356.2 (41)	5317.3(86)
#refl	3497	3519	3634	3529
#var	174	180	181	171
R_P	0.0164	0.0171	0.0139	0.0088
R_{wP}	0.0270	0.0278	0.0225	0.0142
χ^2	3.115	2.975	3.158	3.704

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





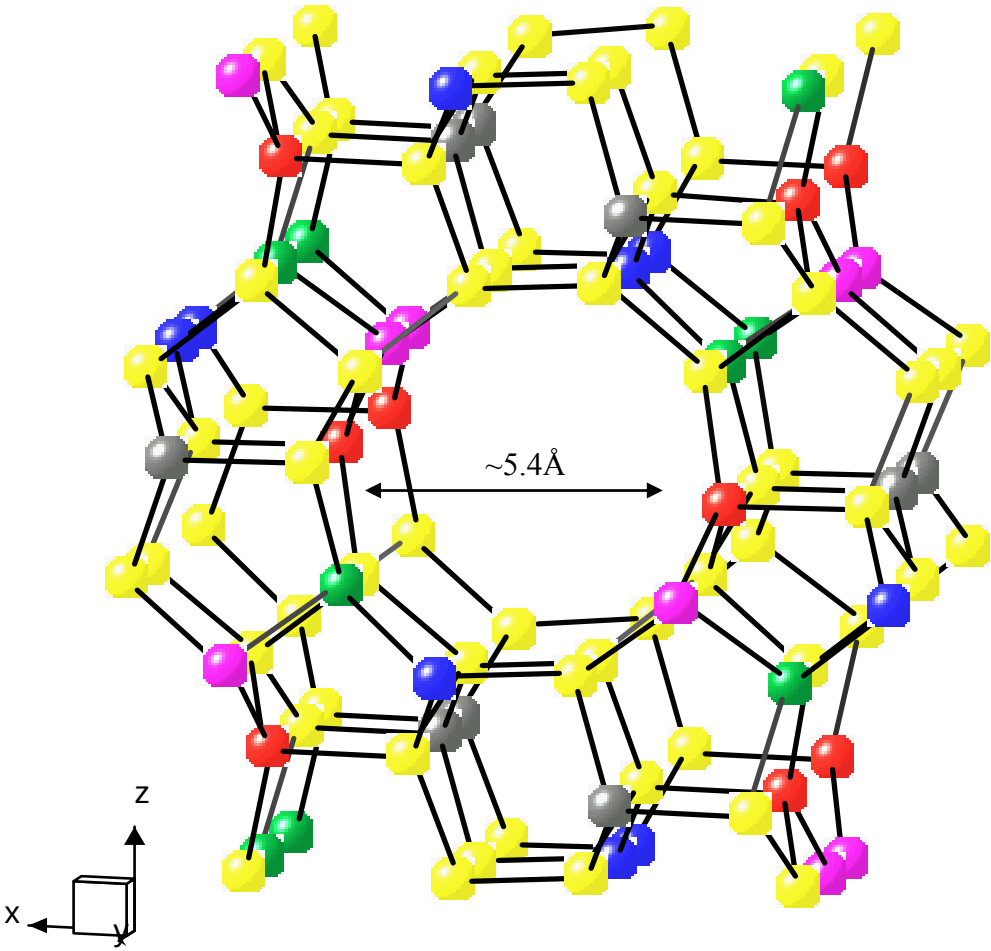
Titanium Siting

- Five of the twelve sites were found to contain Ti or Fe
- Total Ti occupancies were constrained to maximum amount for TS-1 (2.5%) and for Fe, based on chemical analysis
- T8 was found to contain the most Ti/Fe for each sample

T-site occupancies (%) in TS-1 and FeS-1

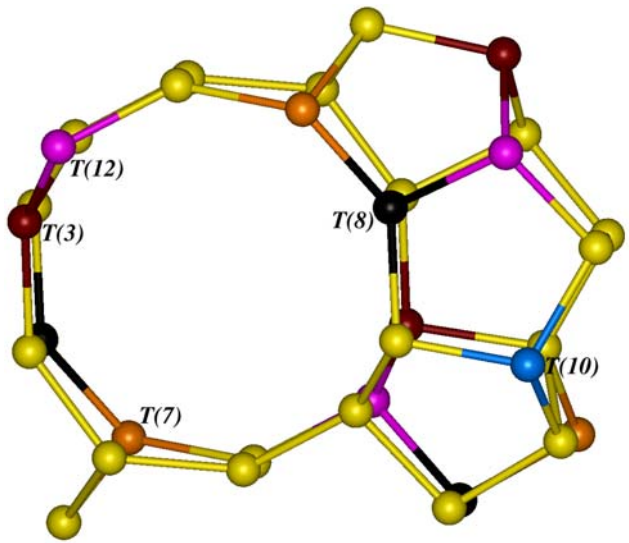
Sample	Metal	T3	T7	T8	T10	T12	Total Metal/ Unit Cell
A	Ti	6.7	0	10.2	4.0	10.6	2.52
B	Ti	3.8	4.3	11.5	5.1	6.2	2.47
C	Ti	7.1	0	12.1	6.1	5.9	2.49
D	Fe	0	0	19	0	0	1.52

TS-1 with Ti Sites

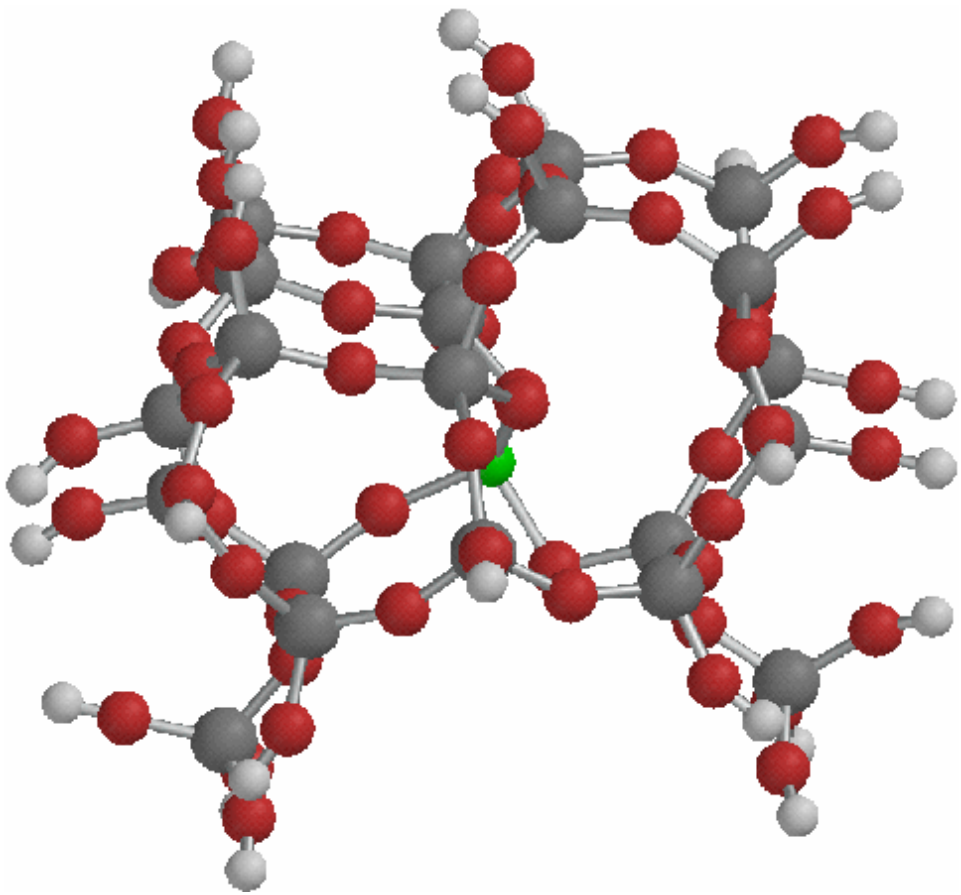


T3	- red	(4% Ti)
T7	- blue	(4% Ti)
T8	- green	(12% Ti)
T10	- gray	(5% Ti)
T12	- magenta	(6% Ti)

- Ti siting in TS-1 and Fe siting in FeS-1 is not random
  - the Ti, Si, and oxygen form 6-membered ring clusters
  - these clusters are ordered within the MFI structure
  - T8 is the preferred site for both Ti and Fe
- Ti is mainly located at the channel intersections
  - close to the TPA^+ templating agent
  - more room available for H_2O_2 and for reactants
  - Preferred siting is reminiscent of proposed precursor (Jacobs et al.) observed during synthesis
  - Later experiments all find (somewhat) different, but always non-randow distribution of Ti
  - Suggests that Ti incorporation is under kinetic influence

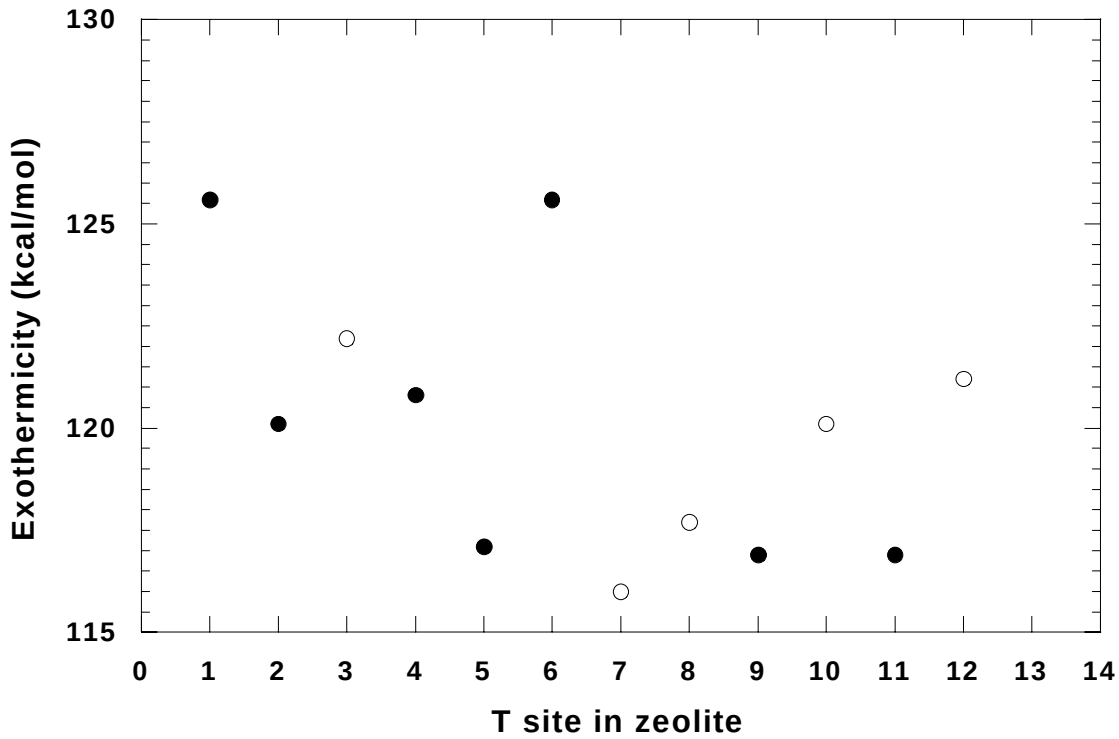


Cluster Used for Semiempirical QM Studies



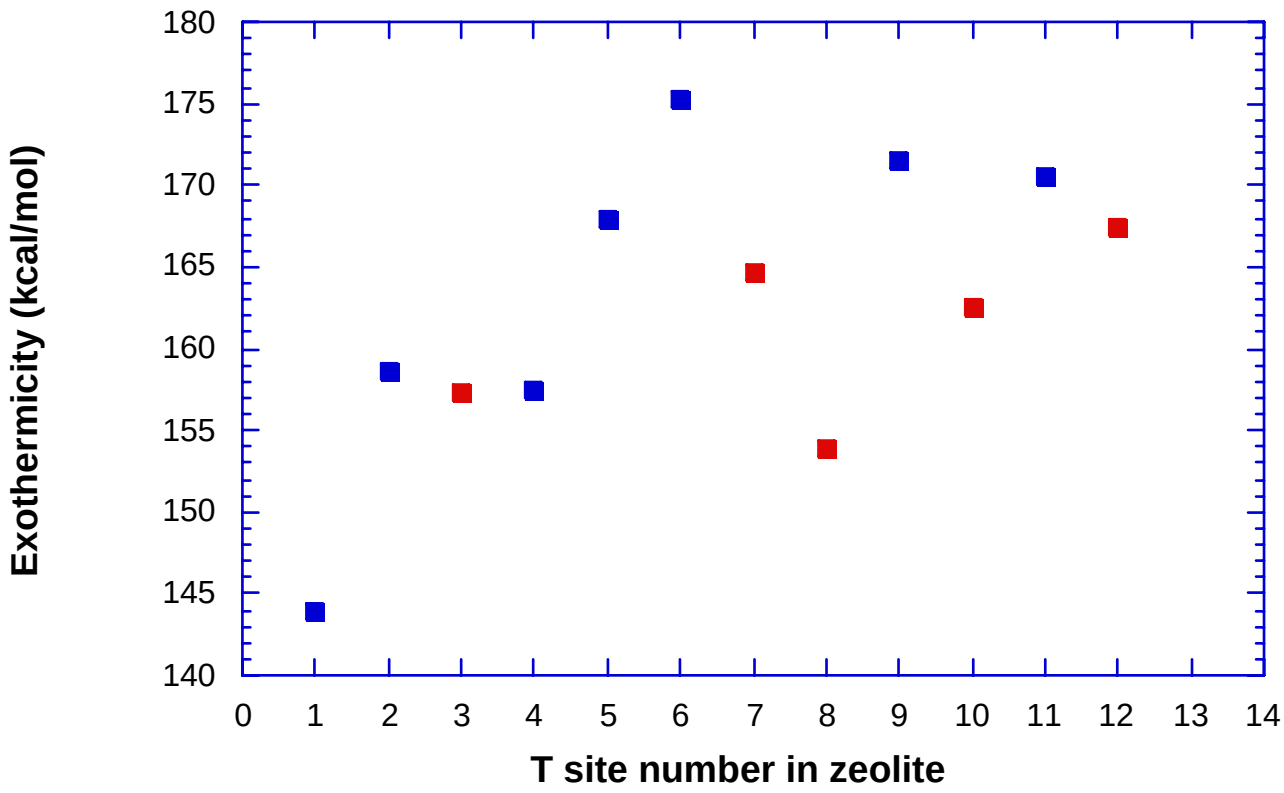
Ti green Si gray O red H white

Calculated Ti Substitution Energies at Various T Sites in TS-1



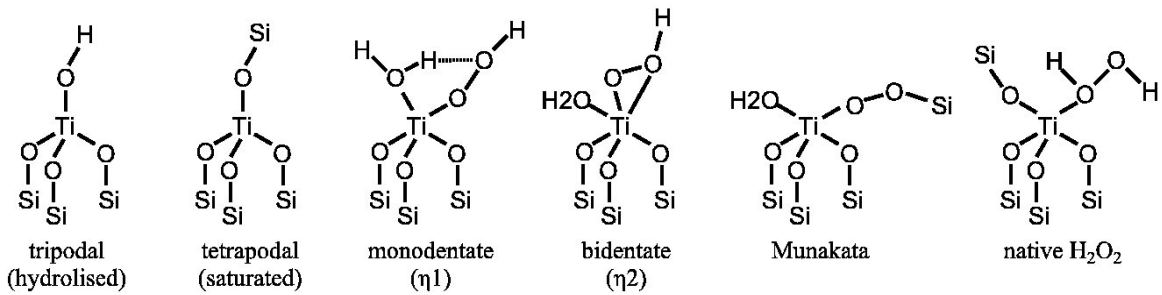
○ - Sites found by neutron diffraction to be occupied by Ti.

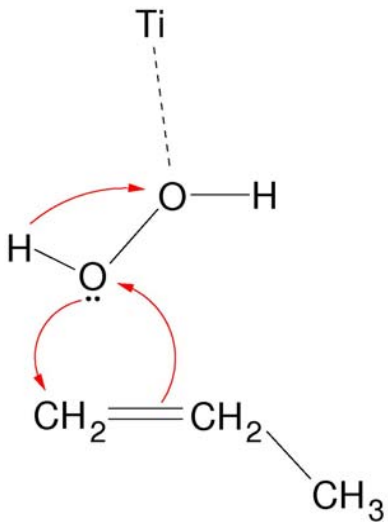
Ti Site Preferences in TS-1 Zeolite Template - Defect Binding Energies

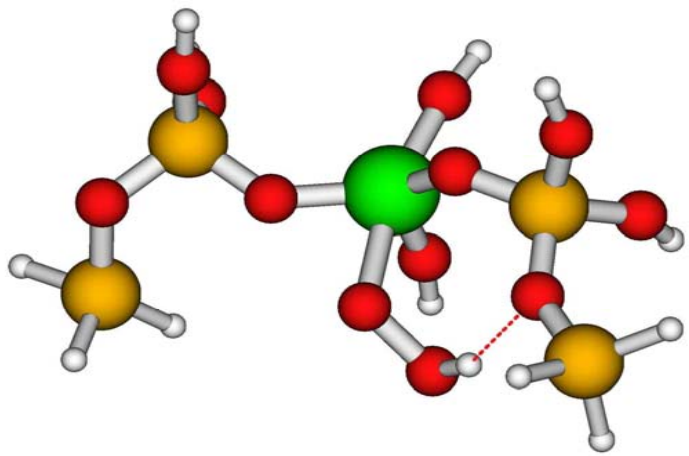
- Calculated Ti - OH^- NMe_4^+ Binding Energies (kcal/mol)
- **red squares denote observed sites**
- 

New Calculations on Propylene Epoxidation with H_2O_2: Effect Of the Presence of Water and of the System Size (Stare, Henson, Eckert)

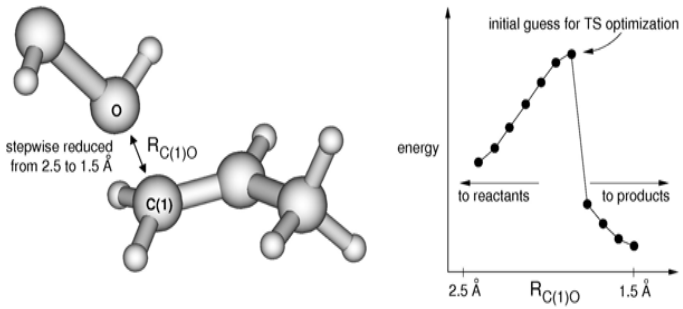
Conventional cluster calculation

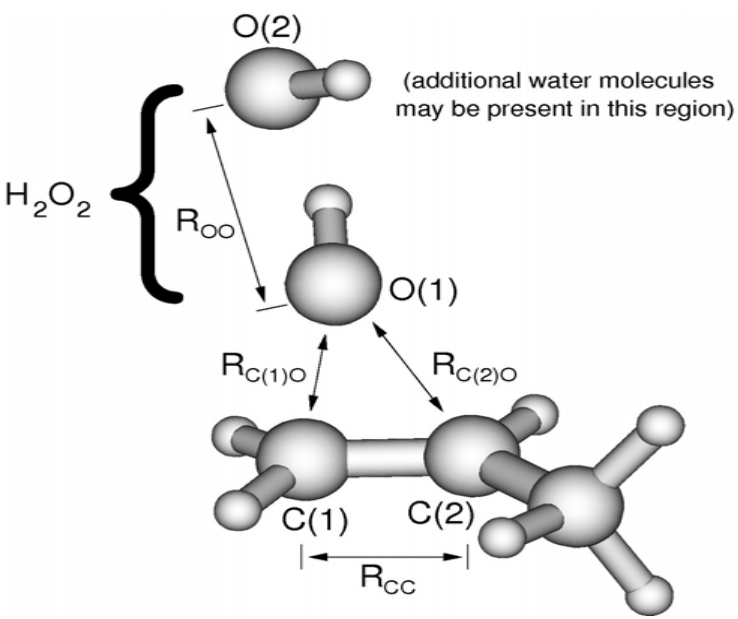


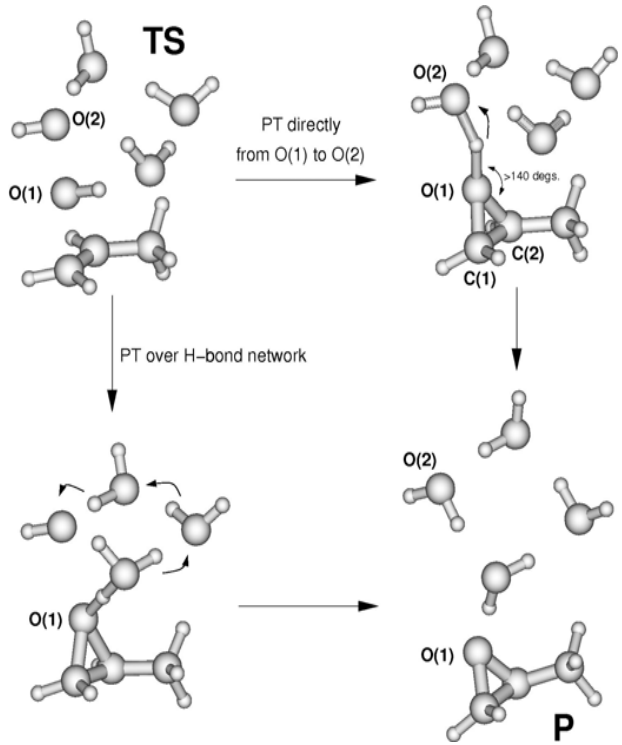




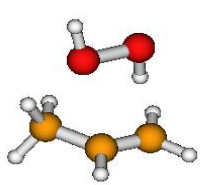
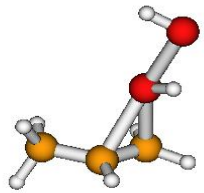
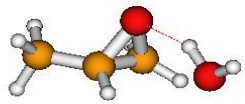
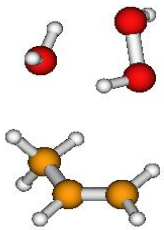
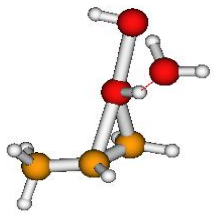
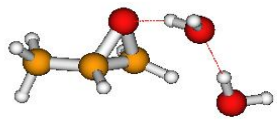
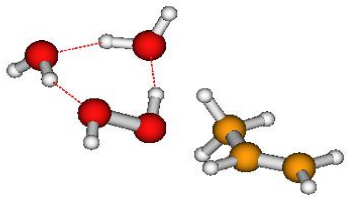
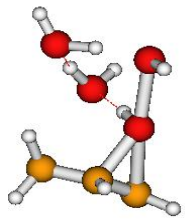
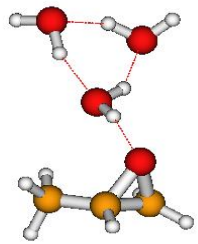
"Gas Phase" Calculation







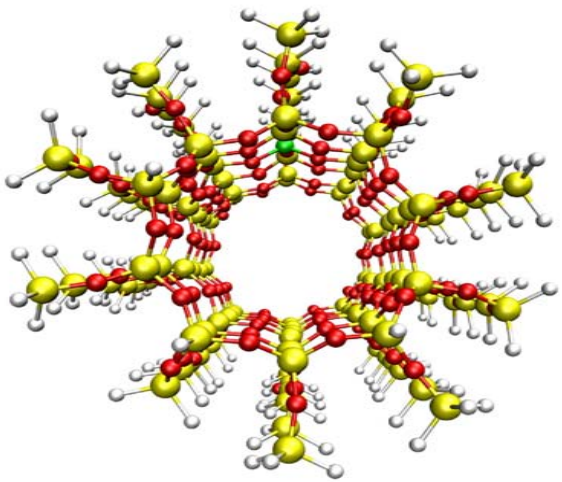
Propene epoxidation by hydrogen peroxide in the gas phase: influence of additional water molecules (all calculations are B3LYP/6-31G)**

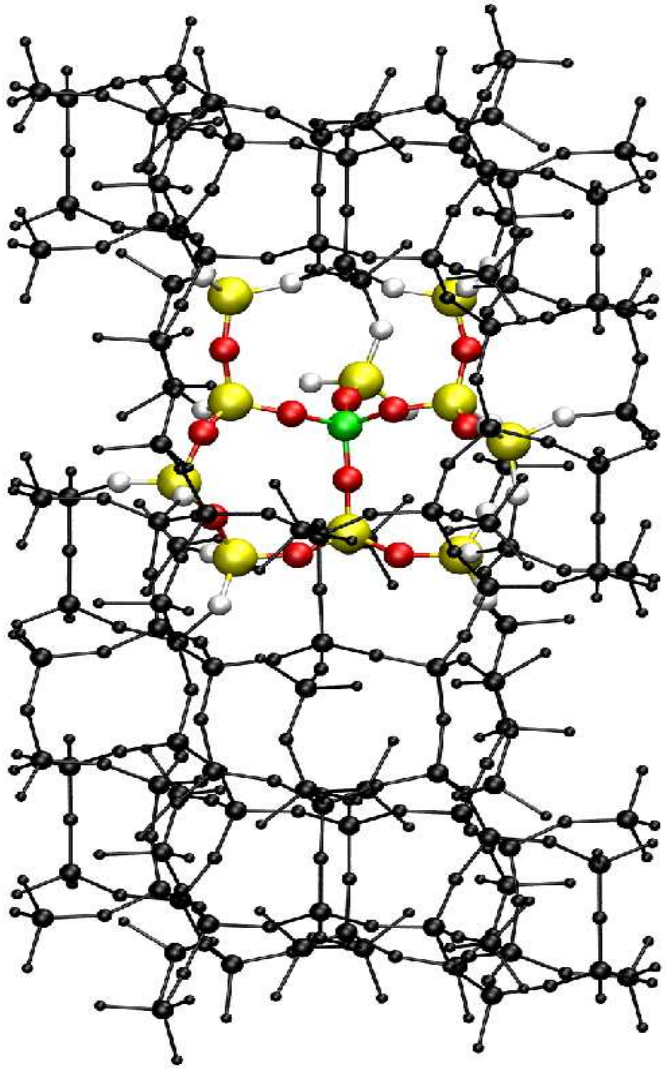
	Reactants	Transition State	Products	Activation barrier [kcal/mol]	Reaction energy [kcal/mol]
NO additional water molecules				**32.8**	**-40.2**
ONE additional water molecule				**21.3**	**-46.2**
TWO additional water molecules				**17.5**	**-41.9**

While additional water molecules have very small effect on the reaction energy, they significantly lower the activation barrier by providing a proton transfer pathway from the abstracted oxygen atom of H_2O_2 back to the distant one, a process resulting in formation of a water molecule.

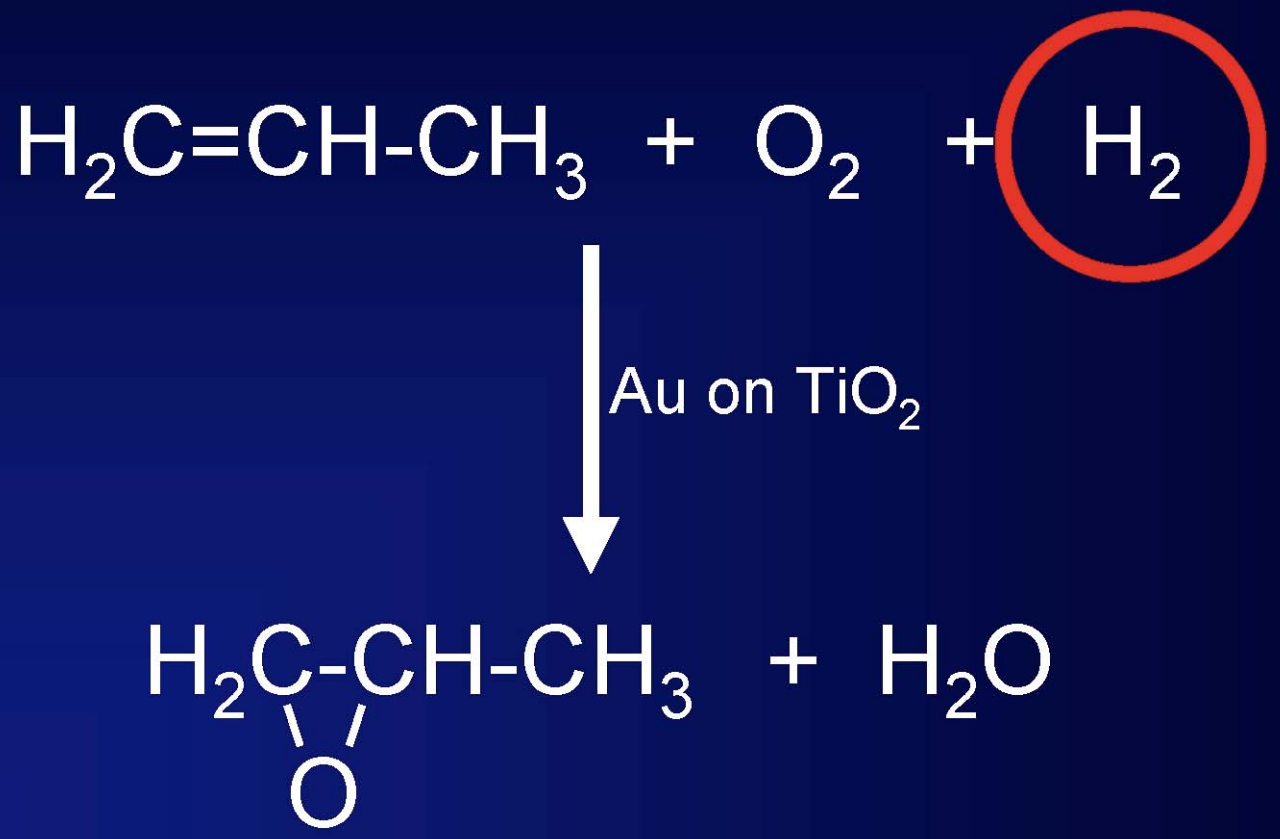
Size matters!

Use ONIOM embedding scheme (QM/MM) to treat a more realistic model.





Propene epoxidation: Gold on Titania catalysts



Discovered about 10 years ago by Haruta *et al.*

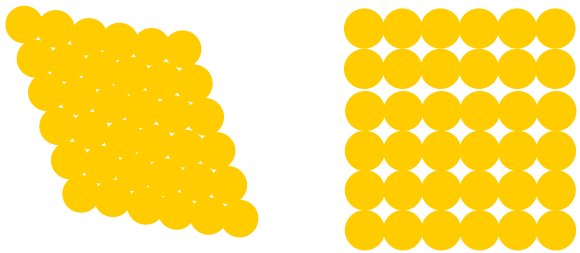
Gold on titanium catalysts

- Highly disperse gold catalysts developed for low-temperature CO oxidation
- Only epoxidation activity with hydrogen and oxygen
- Metallic gold inactive in epoxidation (and CO oxidation)
- Titania inactive in epoxidation using oxygen/hydrogen (active using hydrogen peroxide)

→ **Catalyst activity based on phase-cooperation between gold and titanium**

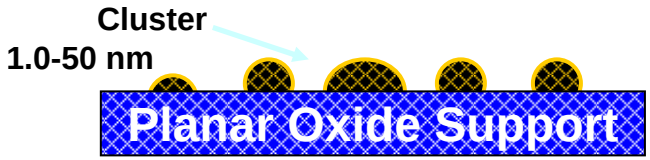
Mechanism ?

TYPES OF METAL CATALYSTS



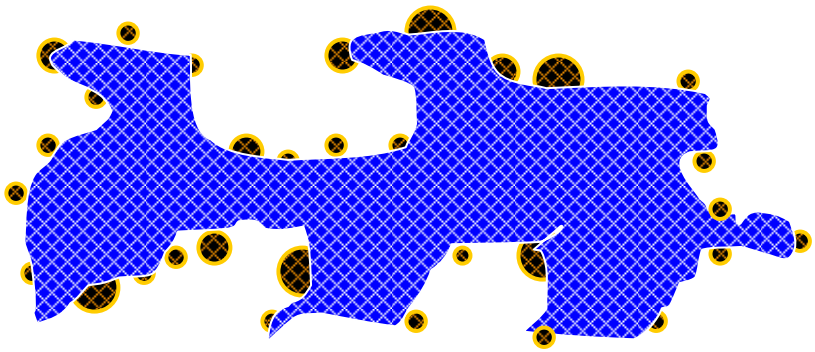
Surface Area = ~1 cm^2

A: Metal Single Crystals



Surface Area = ~0.1 cm^2

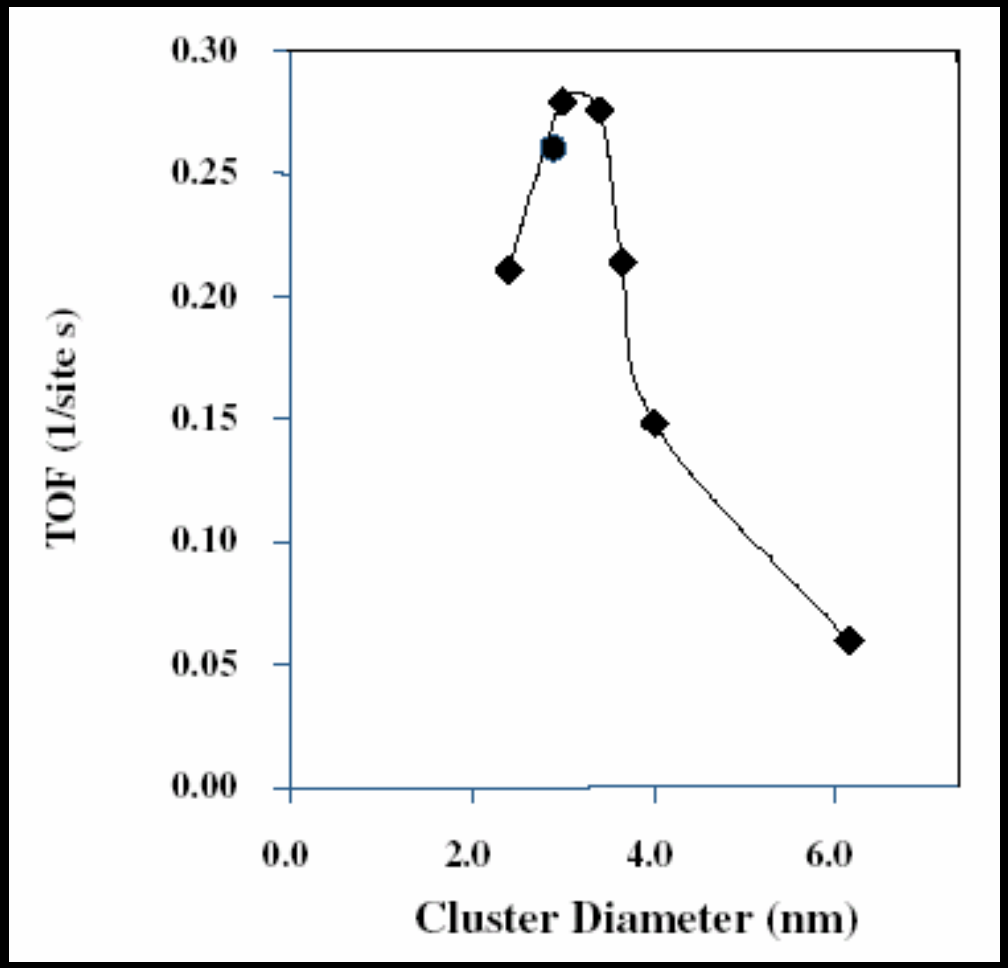
B: Planar oxide-supported metal catalysts



Surface Area = ~100 m^2/g

C: High Surface area oxide-supported metal catalysts

CO-OXIDATION ACTIVITY AS A FUNCTION OF CLUSTER SIZE



Goodman, et. al Science (1998) Catal. Lett (1998)

PREPARATION of nano-Au CATALYSTS

- **Catalyst Synthesis (DP)**

  Gold Precursor : $Au_6(PPh_3)_6(BF_4)_2$

  Solvent : Di-chloromethane

  Support : TiO_2 (P-25, Degussa); 78% anatase

- **Pre-treatment Procedure**

  Calcination @ 400° C (LTC)

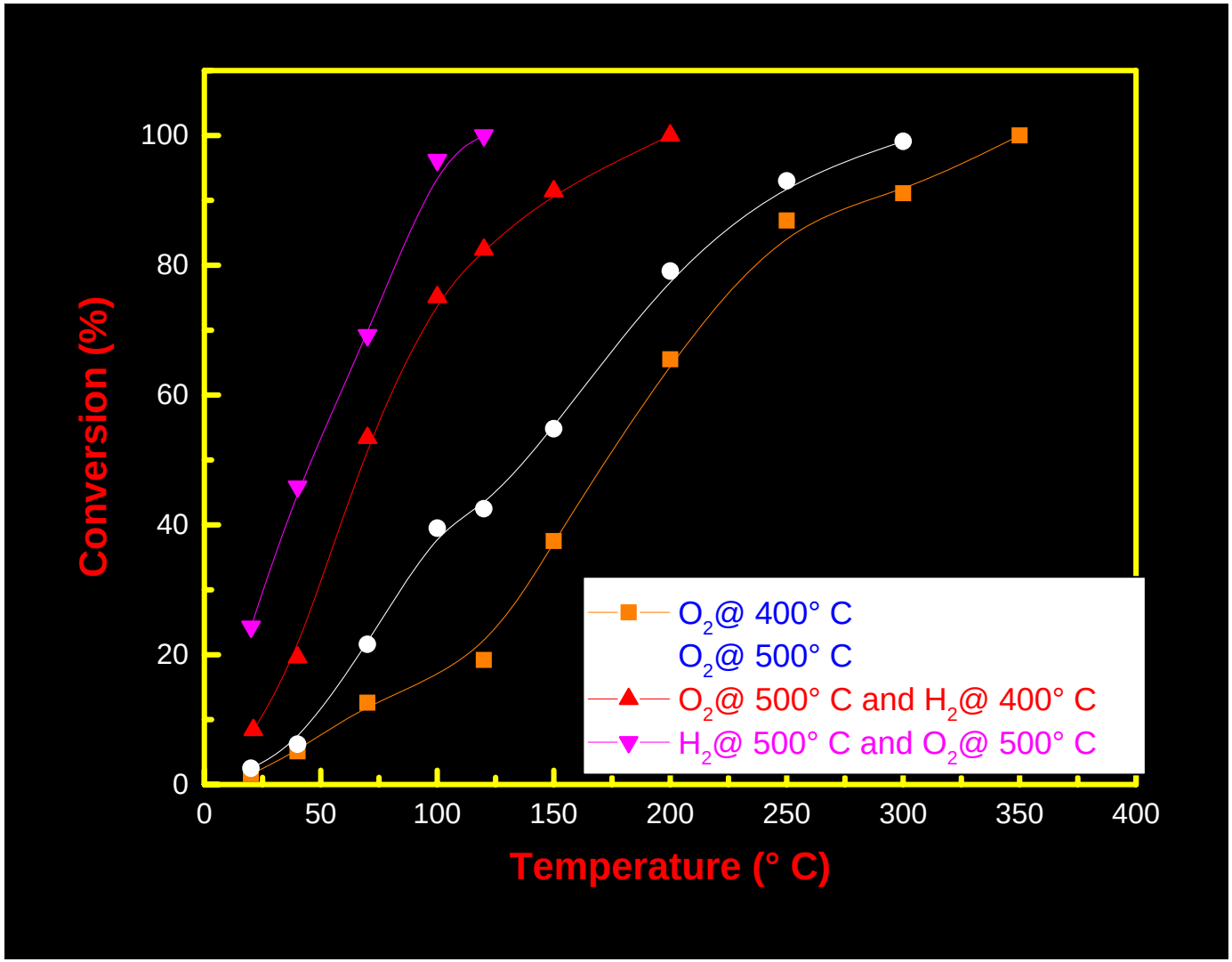
  Calcination @ 500° C (HTC)

  Reduction@ 500° C ; calcination@400° C (HTR/LTC)

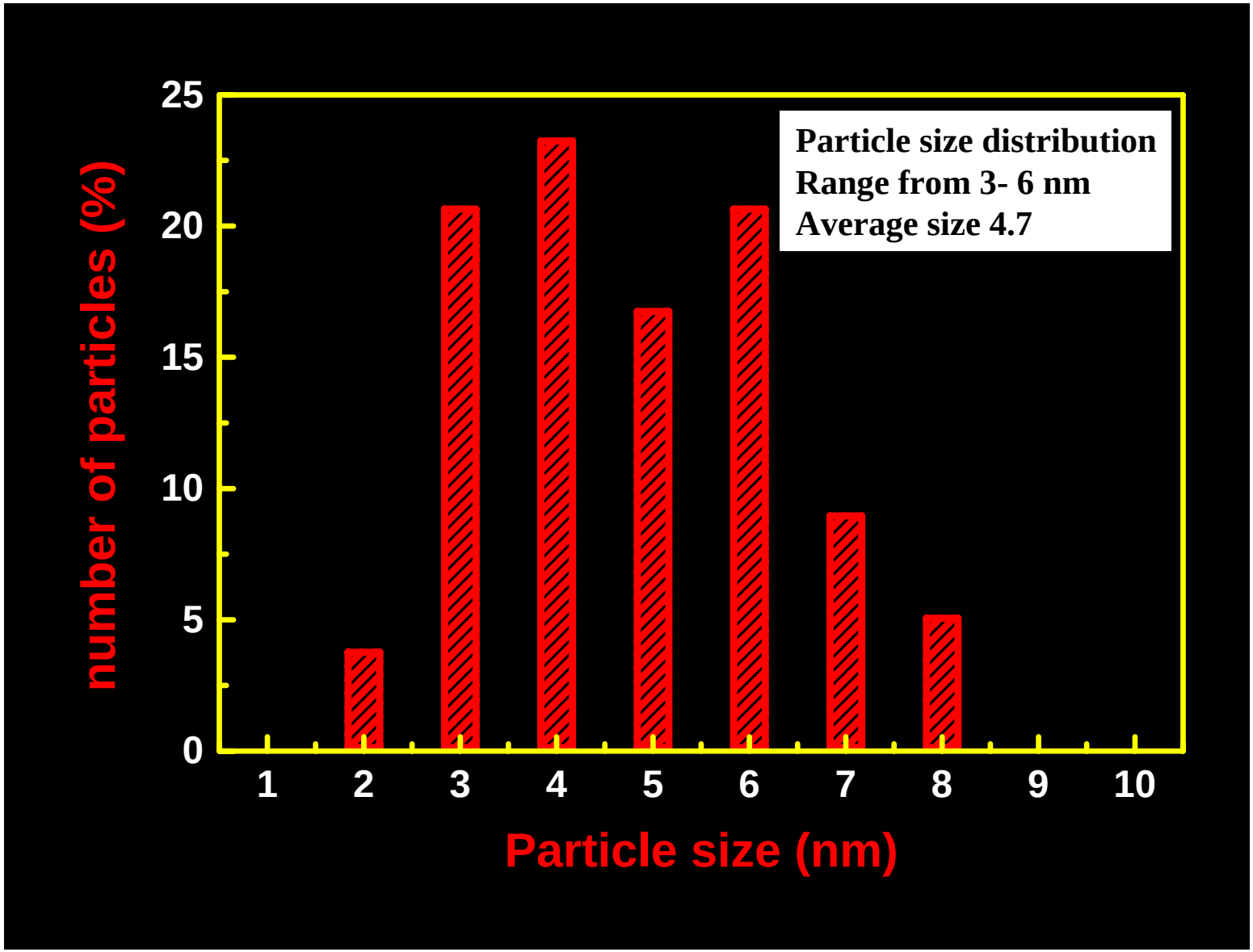
  *Calcination @ 500° C; reduction@ 400° C (HTC/LTR)

EFFECT OF PRE-TREATMENT: Au_6/TIO_2

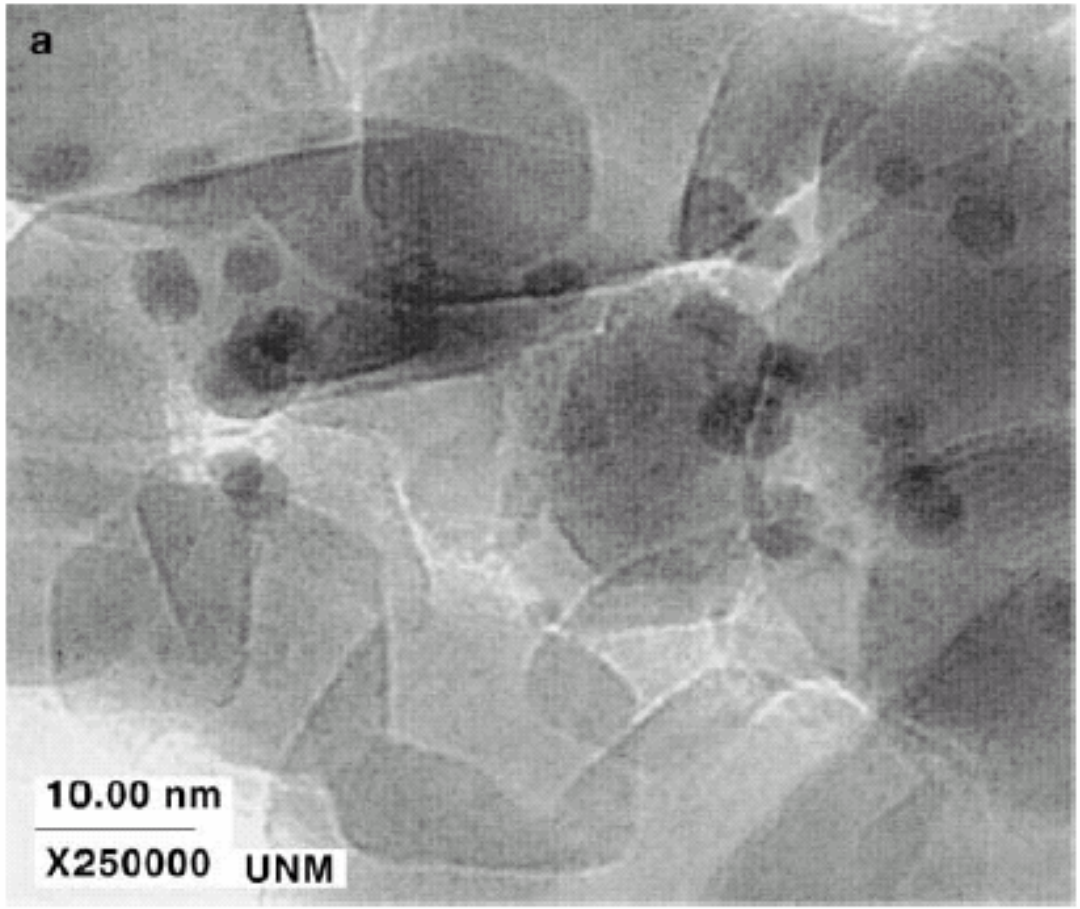
CO conversion: Sivadinarayana etal and Goodman Catal. Lett. (1999); J. Catal (2000)



EFFECT OF PARTICLE SIZE WITH HTR/LTC



TEM of 1% Au_6/ TiO_2 WITH HTR/LTC



Inelastic Neutron Scattering Experiments: propene epoxidation

- **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**

Inelastic neutron Scattering Experiments

-bare Au (1% wt.)/TiO_2 catalyst

-this spectrum was subtracted from all of the following:

-propene on Au/TiO_2; RT gas flow

-propene reacted with H_2 and O_2 in He, gas flow, 150 C, 3hrs.

-H_2, O_2, in He reacted over Au/TiO_2; gas flow, 150 C, 4 hrs.

-**Reference Spectra:**

-bulk solids (propene, propene oxide)

-in lieu of gas phase spectra

-adsorbate (propene on TS-1)

-possible products adsorbed on Au/TiO_2:

-water

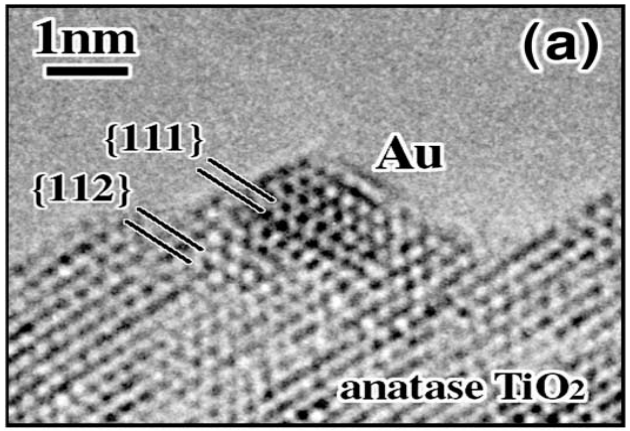
-propene oxide

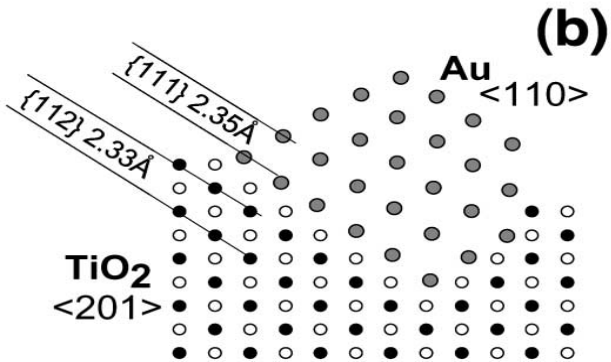
-proprionaldehyde

-acrolein

-acetaldehyde

Catalysis by Gold nanoparticles on metal oxide supports

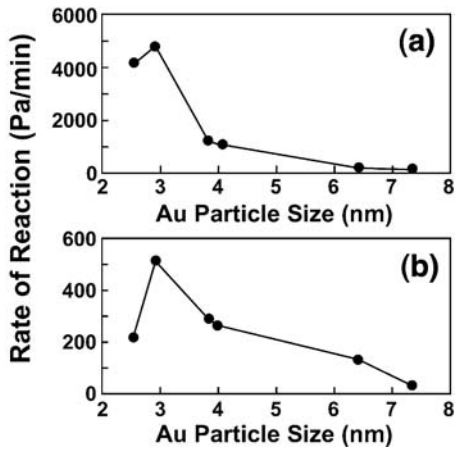




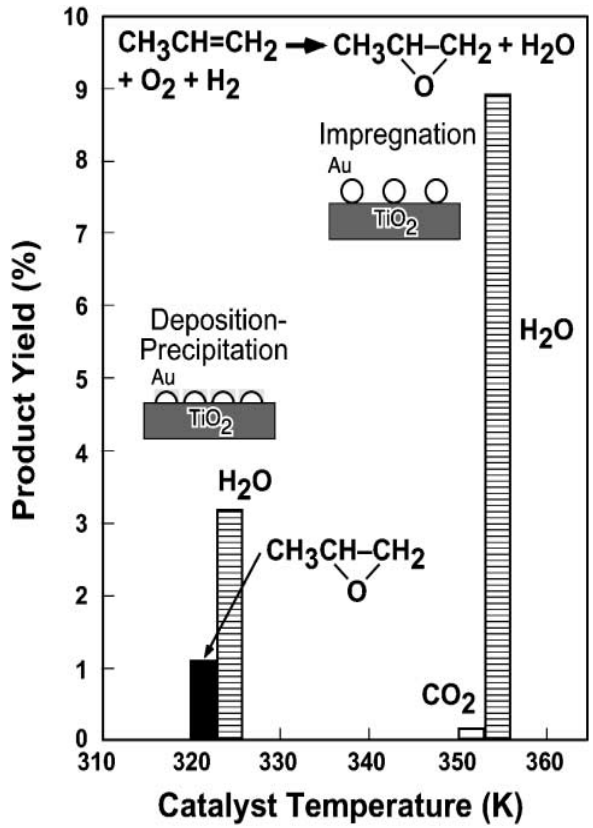
Small particles (~ 3nm) of Au supported on TiO_2 show significant catalytic activity and selectivity

Examples: oxidation of CO (top; below)
oxidation of propylene

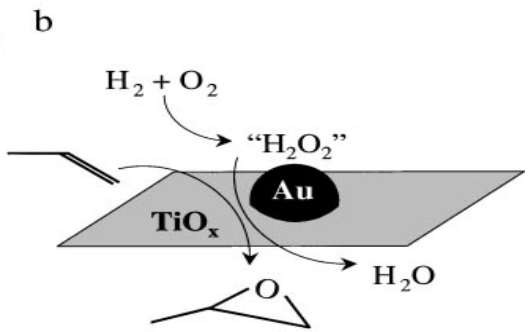
(Haruta, M. *Cattech* 2002, *6*, 102)



Catalysis by supported Au nanoparticles



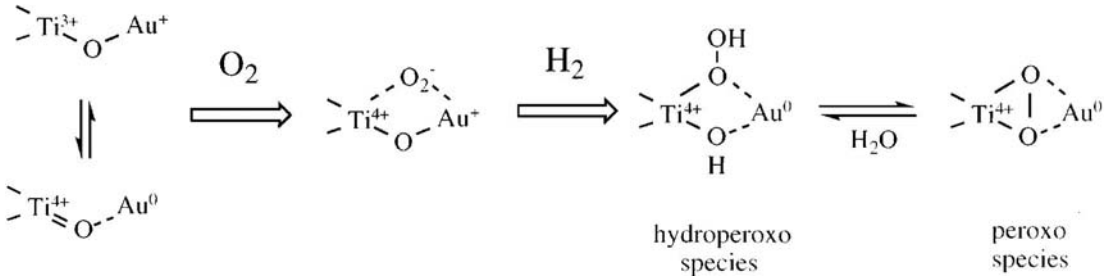
- Why consider Au for catalysis ?
- **Au surfaces are catalytically inactive!**
- **But, small, hemispherical Au particles show surprising activity AND selectivity in oxidation (e.g. of propylene) at low T**
- **And, Au is less expensive than Pt**
- What is the active site/species?



Suggests that Au/TiO_2 interface is important

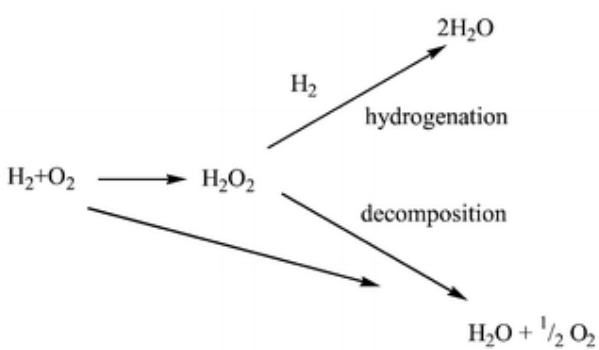
Reaction of hydrogen and oxygen over Au/TiO_2

What is the active species in propene epoxidation?



proposal for hydroperoxy species by Haruta and others

React just H_2 and O_2 over Au/TiO_2 (He, 150 C); INS

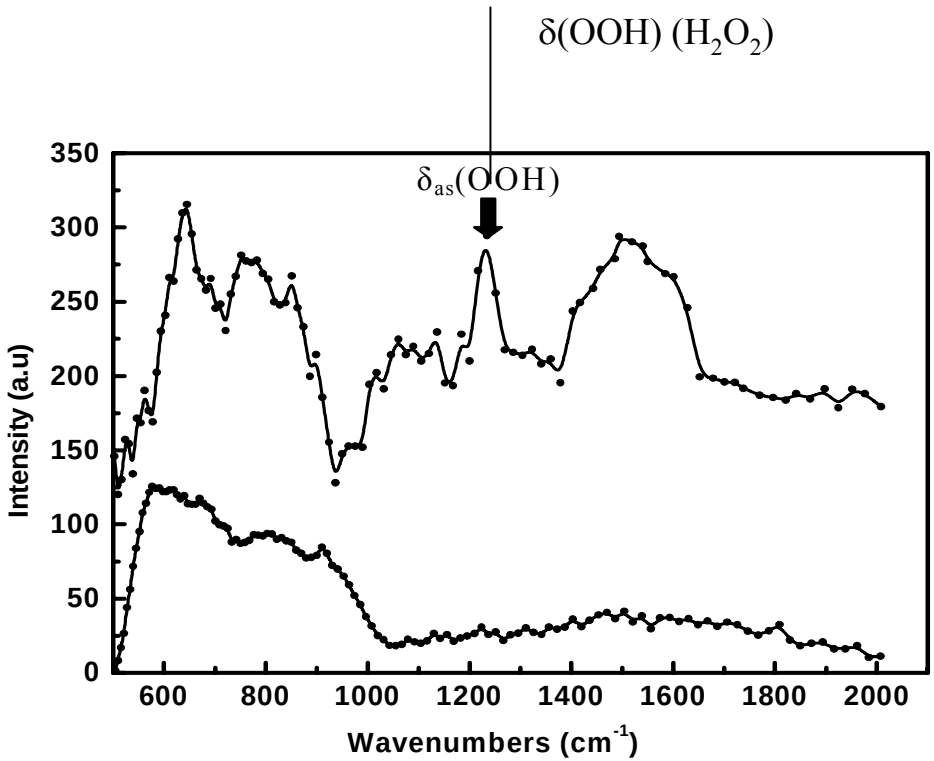


Landon et al. Chem Comm.**2002**, 2058
- formation of H_2O_2 over Au/Al_2O_3 (n methanol, 2C)

Reaction of hydrogen and oxygen over Au/TiO_2

INS spectra (20 K) of quenched reaction; adsorbed water for reference (arb., scaling) (bare catalyst spectrum subtracted)

Note: INS spectrum dominated by modes involving large amplitude H motion



possible intermediates, products:

Water
Hydrogen peroxide
Hydroperoxy species;
bound, or complexed

Identification ?

Reaction of hydrogen and oxygen over Au/TiO_2

Tentative identification of INS spectral features using literature data -experiment and calculations:

- -hydrogen peroxide (matrix isolation study: Petterson et al.)
- -peroxy radical (matrix isolation study; Nelander)
- -peroxy radical/water complex (calc.; Aloisio and Francisco*)
- -water on oxide surfaces (numerous INS studies)

Assignments:

Water librations: 630, 770, 835 cm^{-1}

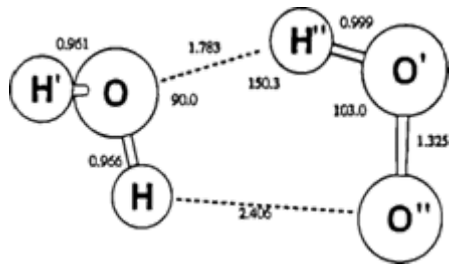
O_2H… $\nu(OO) \sim 1065\ cm^{-1}$

$\delta(OOH)$ 1505 cm^{-1}

H_2O_2: $\nu(OO) \sim 900\ cm^{-1}$

$\delta_a(OOH)$ 1230 cm^{-1}

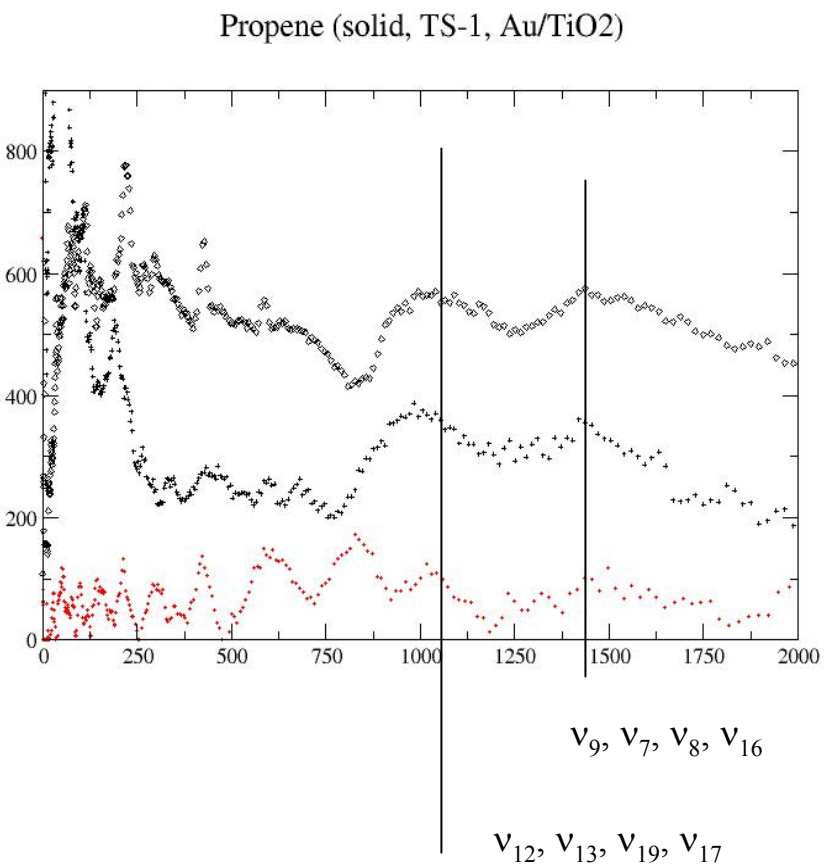
$\delta_s(OOH)$ 1440 cm^{-1}



* Peroxy radical/water complex
J. Phys Chem A **1998**, 102, 1899

Propene adsorbed under RT gas flow conditions

propene/He mixture, STP, at RT ,250 mL/min., 45 min., LN_2 quench



What spcies might we expect under these conditions?

On TiO_2:

physisorbed propene, H-bonded?

On Au:

π-or di-σ bonded propene

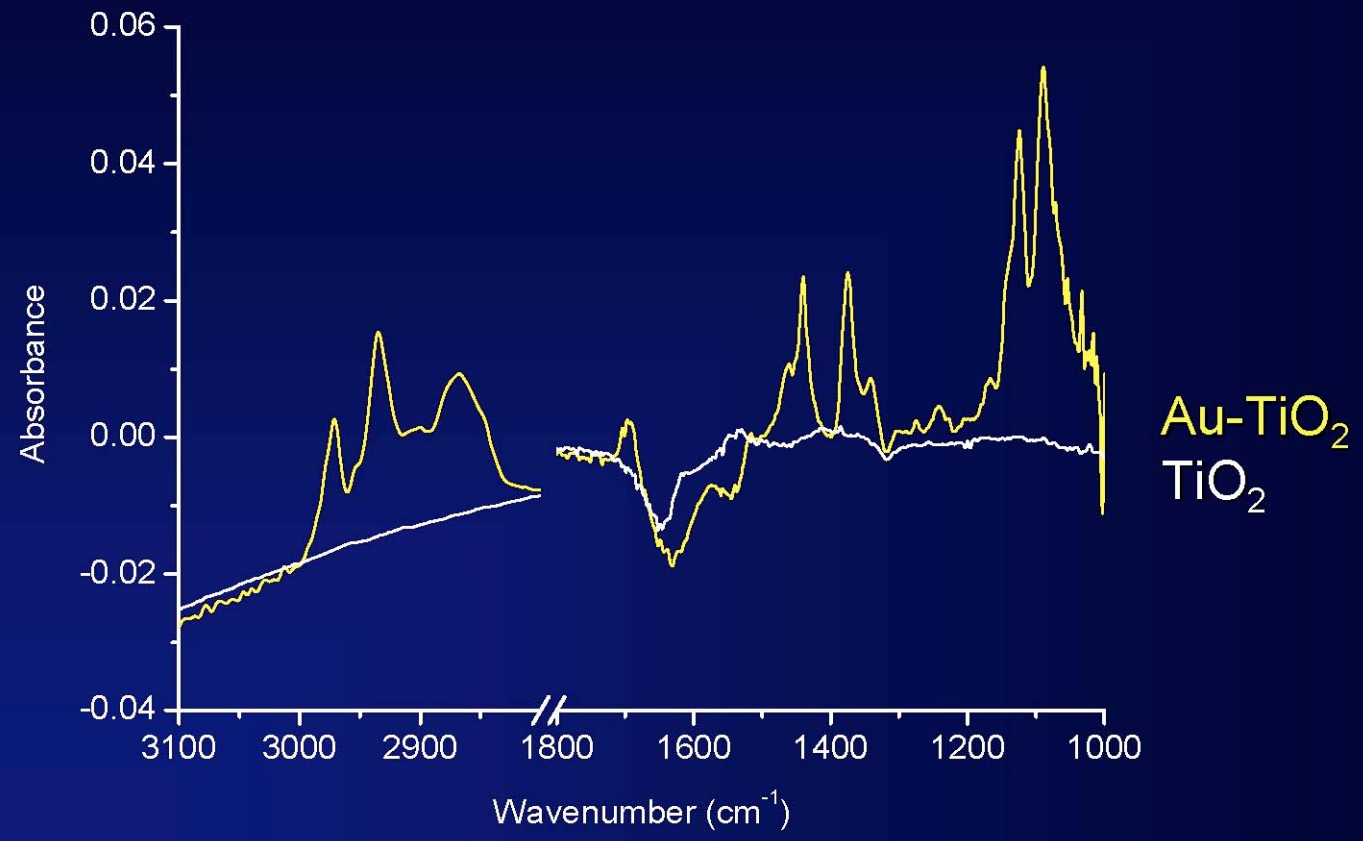
INS spectrum is a superposition of modes from all species present. reflects relative numbers.

Hi-frequency region contains too many modes, inadequate resolution - is for IR, Raman ?

Low-frequency region good for INS !!

Propene adsorption – desorption

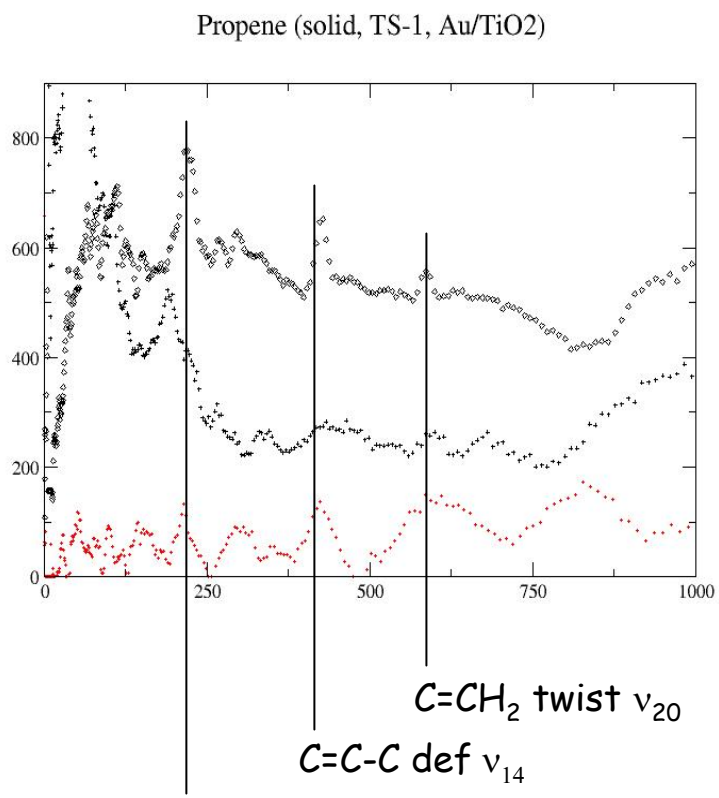
Titania *versus* Au-TiO_2

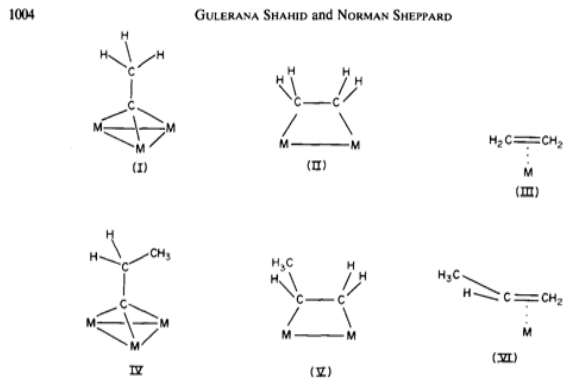


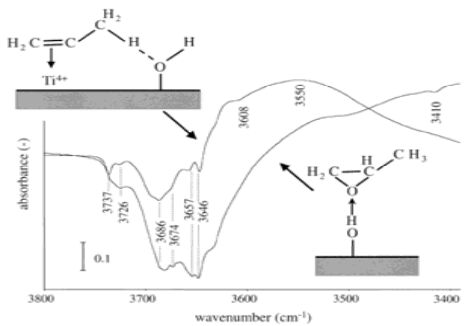
Presence of gold causes interaction / reaction between propene and Ti(O/OH)

Propene adsorbed under RT gas flow conditions

propene/He mixture, STP, at RT ,250 mL/min., 45 min., LN_2 quench





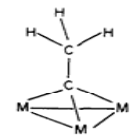


Note bands at 265, 290, ~350, 600, 825, etc. : 2nd species
Correspond to d-σ Os_2 complex (N. Sheppard et al.), or…
Need computational studies !!!

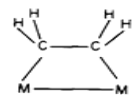
TABLE 2

Fundamental Frequencies of Free and Complexed Propenes (−190°C, cm^{-1} Units)

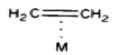
Modes[a]	$CH_{3CH}{=}CH_2$	$CD_3CD{=}CD_2$	$CD_3CH{=}CH_2$	$CH_3CH{=}CH_2$/Ni	$CD_3CD{=}CD_2$/Ni	$CD_3CH{=}CH_2$/Ni
Stretch(CH_2)	3073	2315	3095	3044	2300	3095
Stretch(CH)	3010	2245	3010	2996	2220	3010
Stretch(CH_2)	2990	2200	2984	2956	2195	2984
Stretch(CH_3)	2935	2230	2226	2931	2220	2226
Stretch(CH_3)	2880	2120	2070	2876	2110	2070
Stretch(CC)	1640	1582	1642	1242	1423	1242
Bend(CH_3)	1456	1040	1038	1448	1040	1038
Bend(CH_2)	1430	1013	1418	1516	995	1510
Bend(CH_2)	1367	1040	1060	1388	1040	1060
Bend(CH)	1290	960	1296	1361	911	1346
Stretch(CC)	1164	1142	1157	1154	1137	1115
Rock(CH_3)	936	710	777	933	709	777
Rock(CH_2)	930	777	860	930	777	860
Bend(CCC)	424	350	390	468	350	390
Stretch(CH_3)	2960	2200	2195	2901	2195	2195
Bend(CH_3)	1440	1040	1050	1432	1040	1050
Wag(CH_3)	1040	870	872	1032	846	826
Wag(CH)	995	732	1000	992	730	996
Wag(CH_2)	906	710	913	883	710	913
Twist(CH_2)	577	437	530	581	440	530
Twist(CH_3)	—	—	—	—	—	—
Stretch(M–C)	—	—	—	426	420	—
Stretch(M–C)	—	—	—	359	337	350



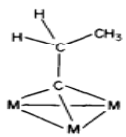
(I)



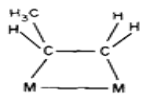
(II)



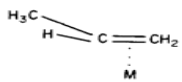
(III)



IV

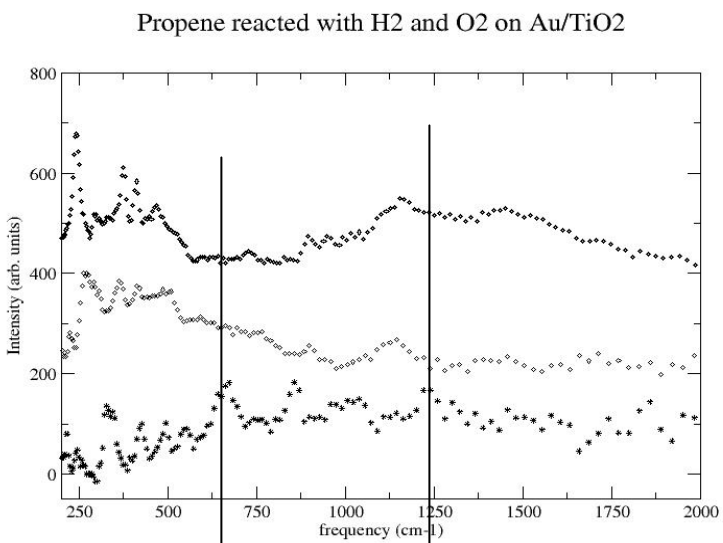


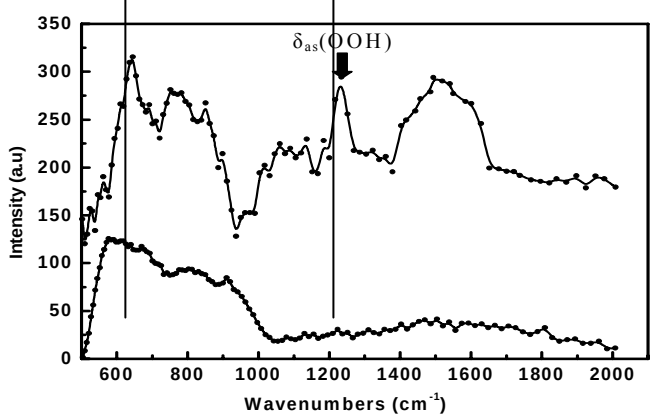
(V)



(VI)

Propene reacted with H_2 and O_2





Comparison (top) of INS spectra of:

bulk PO

PO adsorbed on Au/TiO_2

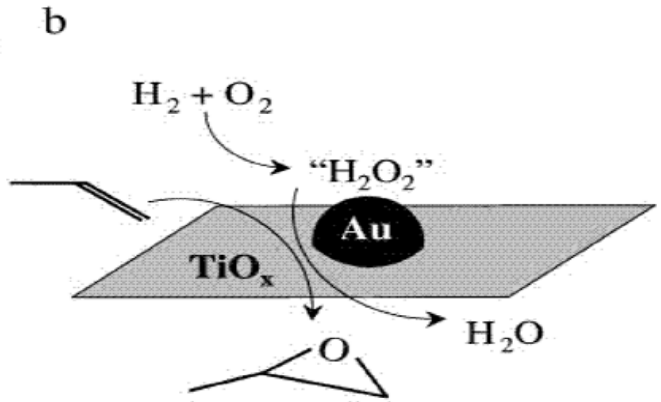
propene reacted (H_2/O_2)

and (below left),

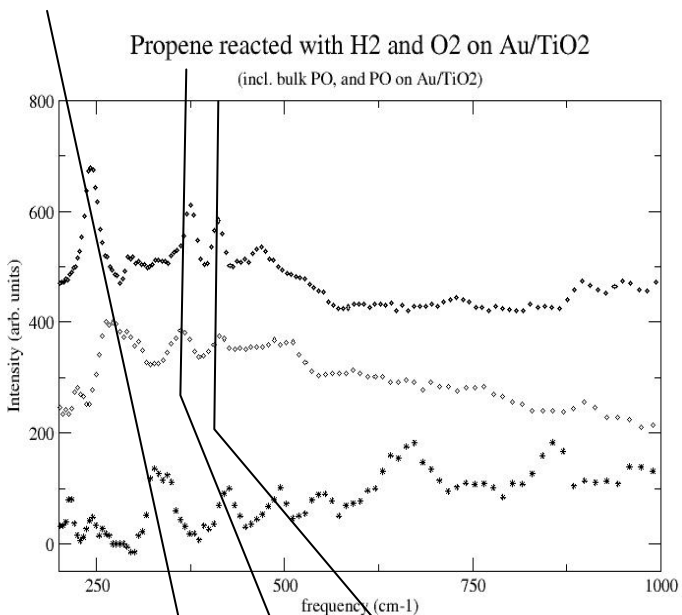
spectrum of H_2/O_2 reacted over Au/TiO_2

Reaction conditions should not have produced appreciable quantities of other products(e.g. propanal, acetone, ethanal)

Propene reacted with H_2 and O_2



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



C7-C3 deformations PO

PO torsion shifts - splits, or new mode (formation of oxometallocycle?)

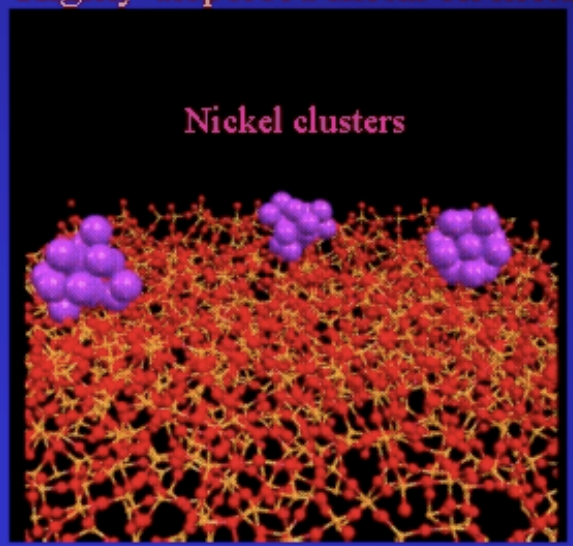
PO skeletal modes strongly affected by binding to catalyst upon formation

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

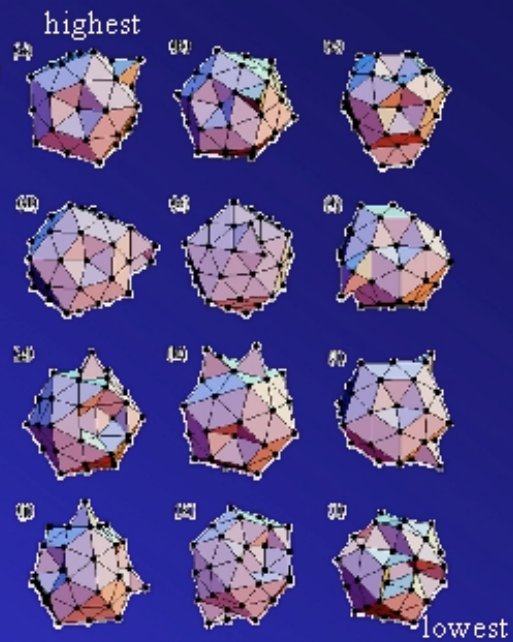
Computational studies could resolve remaining questions

Supported Catalyst

Highly dispersed metal on metal oxide



SiO_2



55 atom cluster surface energy minimization

http://brian.ch.cam.ac.uk/~jon/PhD2/node19.html

Catalytic Decomposition of Methane for H_2 Production

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

- Economical (and clean) Hydrogen production is one of the most critical issues for the "Hydrogen Economy" - for use in fuel cells (produce no CO_2)
- Hydrogen is abundant in nature as methane (CH_4), but conversion processes to H_2 either produce CO_2 or are costly for production H_2 of sufficient purity (< 1.5% CO in H_3PO_4 fuel cells)
- Catalytic decomposition of CH_4 into carbon and hydrogen may be an attractive solution.
- A process based on catalysts presents a number of problems (e.g., production of CO by reaction of C with O in the metal-oxide support).

⇨ Investigate methane decomposition on Ni- and Ru-supported catalysts as a method for the production of CO-free (< 50 ppm) hydrogen

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Catalytic Decomposition of CH_4

- Materials studied: Ni on SiO_2 and Ru on Al_2O_3; metal loading was 10%; measured specific area was about 5 m^2/g.

- Technique:
  - Flow a 10% mixture of CH_4 in Ar over the catalyst contained in a small reactor at a fixed temperature for 4 hours; the flow rate was 0.9 L per minute.
  - 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 vibrational spectrum.

- Identify with neutrons the set of intermediate chemical species at the surface of the catalyst.

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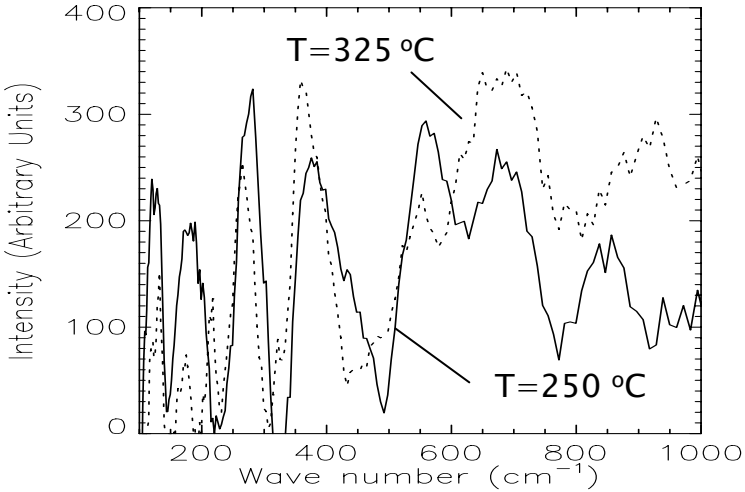
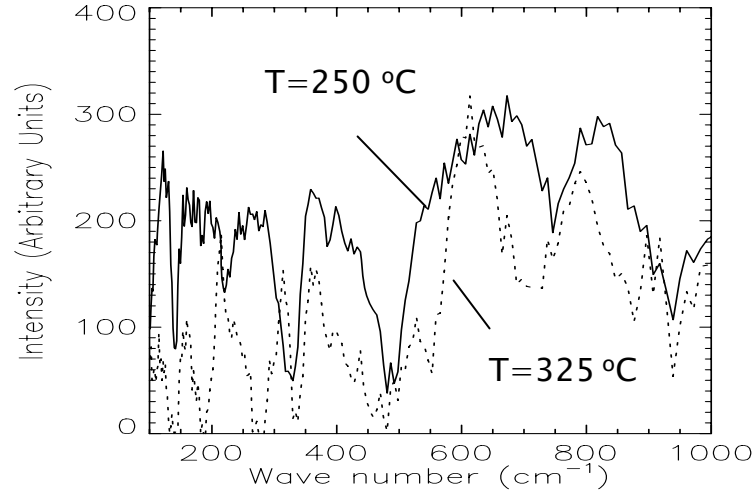
Results

Ni on SiO_2



Ru on Al_2O_3



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

≡CH (methylidyne) $\delta(CH) \sim 830\ cm^{-1}$

≡C —CH_3 (ethylidyne) $\nu(MCCH_3) \sim 410\ cm^{-1}$

═C ═CH_2 (vinylidene) $\tau(CH_2) \sim 670\ cm^{-1}$

RESULTS

- Methylidyne is clearly present: most stable decomposition product.
- Evidence for C agglomeration, namely C2 species ethylidyne and vinylidene. This is only the second time that ethylidyne has been observed on Ni. (It does not appear to occur on Ni single crystal surfaces used in HREELS studies.) *
- The higher reaction temperature (T=325 ^{o}C) produces less of ethylidyne species.
- Computational studies needed for more definitive species identification
- Feasibility of quenching catalytic reactions for the determination of intermediate and product species by INS vibrational spectroscopy

* The carbon produced could in fact be useful

Some assignments

Ni @ 250 °C (cm^{-1})	Ni @ 325 °C (cm^{-1})	Ru @ 250 °C (cm^{-1})	Ru @ 325 °C (cm^{-1})	Tentative assignment
		270		$\nu(MCCH_2)_s$ V
		380		$\nu(MCCH_2)_{as}$ V
		410		$\nu(MCCH_3)_s$ E
570		560		$\nu(MCCH_3)_{as}$ E
670	650/700*	670		$\tau(CH_2)$ V
840	900*	830	790	$\delta(CH)$
1020		(broad)	1040	$\nu(C\text{-}C)$ E; $\rho(CH_3)$ E
1190	1230	1220	1250	$\rho(CH_2)$ V
1300		1300		$\delta(CH_2)$ V
1470	1460	1485		$\delta(CH_3)$ E
1550	1550	1600		$\nu(C{=}C)$ V

Notes: (1) $\nu(MC)$ for CH should also be contained in the bands below 600 cm^{-1} – calculations are needed to help with mode assignment.

(2) E = ethylidyne; V = vinylidene; M = metal (Ni or Ru)

* The origin of the splitting is not clear.

$\equiv CH$ (methylidyne) $\equiv C-CH_3$ (ethylidyne) $=C=CH_2$ (vinylidene)

Hydrogen Spillover

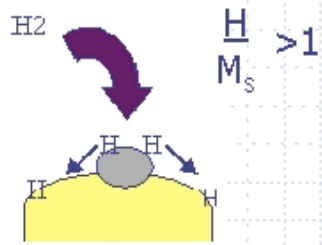
Traditional Conceptualization of Hydrogen Spillover

Dependent Upon:

- Metal Dispersion and Loading
- Metal-Carbon Interface
  - Chemical Nature
  - Interfacial Transfer Area
- Carbon
  - Acceptor sites
- Temperature
  - Activation
- Pressure
  - $f(P) = P^{0.5}$ (???)
  - Measured at $P \leq 1$ bar

Evidence for / Suggestions of...

- Dynamic Surface Restructuring at...
  - Carbon Nanotubes
  - High Pressure
  - Upon Metal Doping
  - Chemisorption

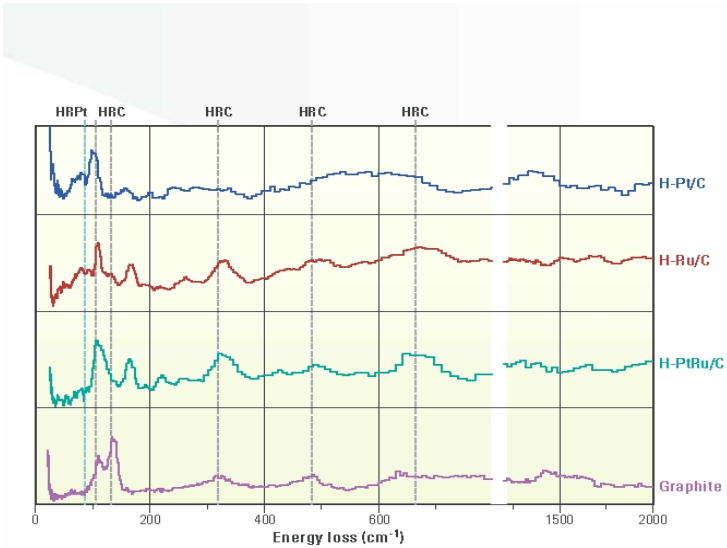


$$\frac{H}{M_s} > 1$$

From A. D. Lueking (ACS 2005)

Hydrogen Spillover on Supported Metal Catalysts

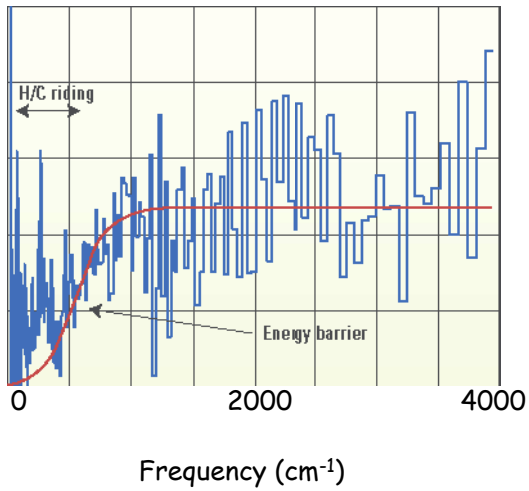
(C. H. tchell et al. , J. Phys. Chem.B 2003, 107, 6838)



C-supported Pt, Ru and Pt/Ru fuel cell catalysts
(Johnson/Matthey)

INS spectra collected on samples with:
(1) Fast H_2 uptake at RT, 10-30min.
(2) Slow H_2 uptake at 500K, several days

"Spillover" H (mobile) - (2)



Types of H observed:

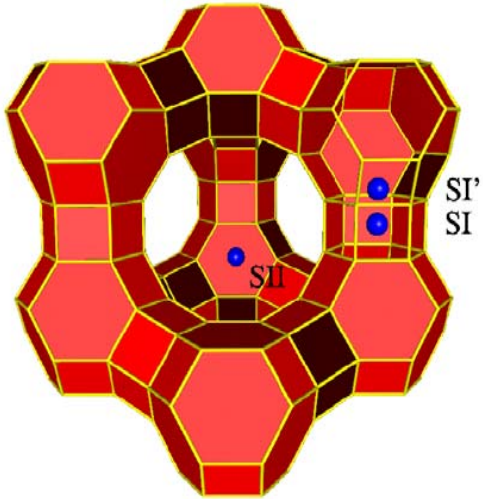
H "riding" on C - bound to edge sites
(comparison with coronene spectrum)

H "riding" on Pt, Ru

"spillover" H - weakly bound, diffusing

Ir_6 clusters in Faujasites: H_2 Spillover

(Bruce Gates, Fen Li, UCD)



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

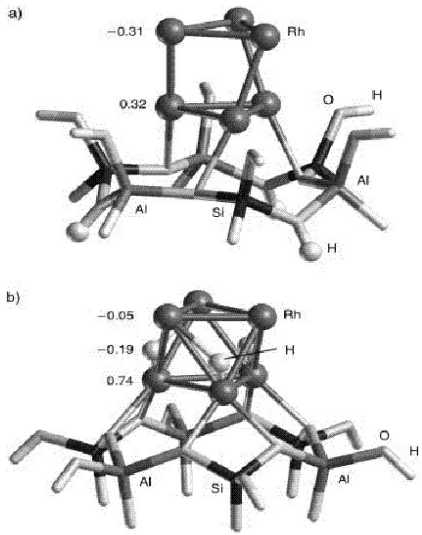
interaction between metal cluster and support
includes -OH groups on the support

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

the metal is oxidized in this process

use INS and D_2/H_2 exchange to observe details of hydrogen spillover

Note: this experiment was first attempted some time (?!) ago on BT-4 (NIST reactor).



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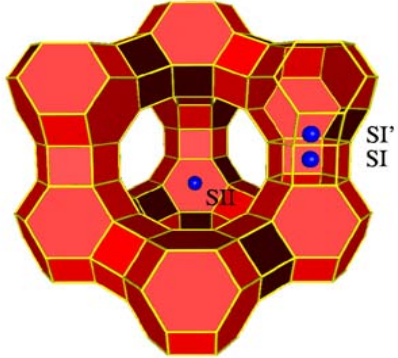
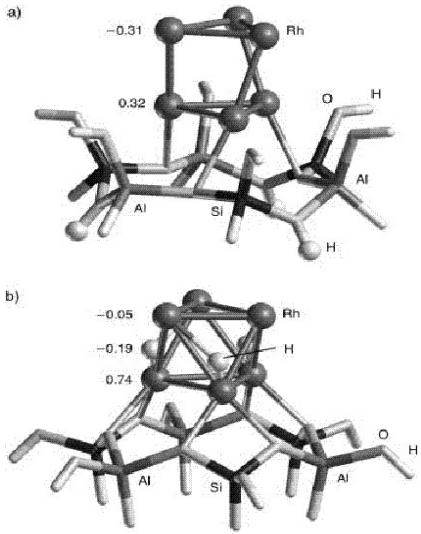


Ir_6 clusters in Faujasites: H_2 Spillover: INS studies

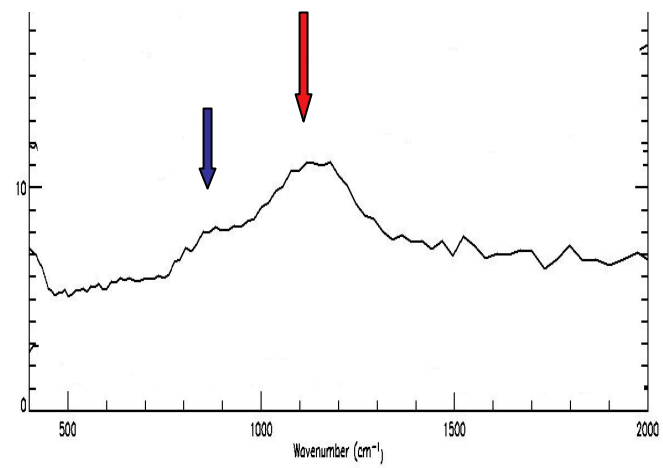
(Fen Li, Bruce Gates UCD; L. Daemen, M. Hartl, and J. Eckert, LANL)

Sample:

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

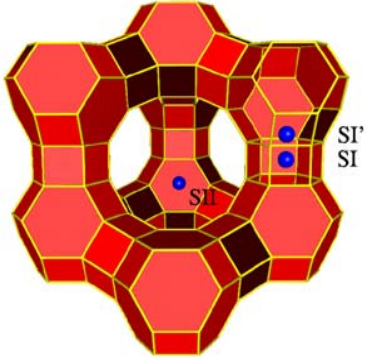


INS spectrum (below, NaY "blank" subtracted) of "as-prepared" sample clearly shows
δ(IrH) at ~ 875 cm^{-1}
δ(OH) at ~ 1100 cm^{-1}.



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

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

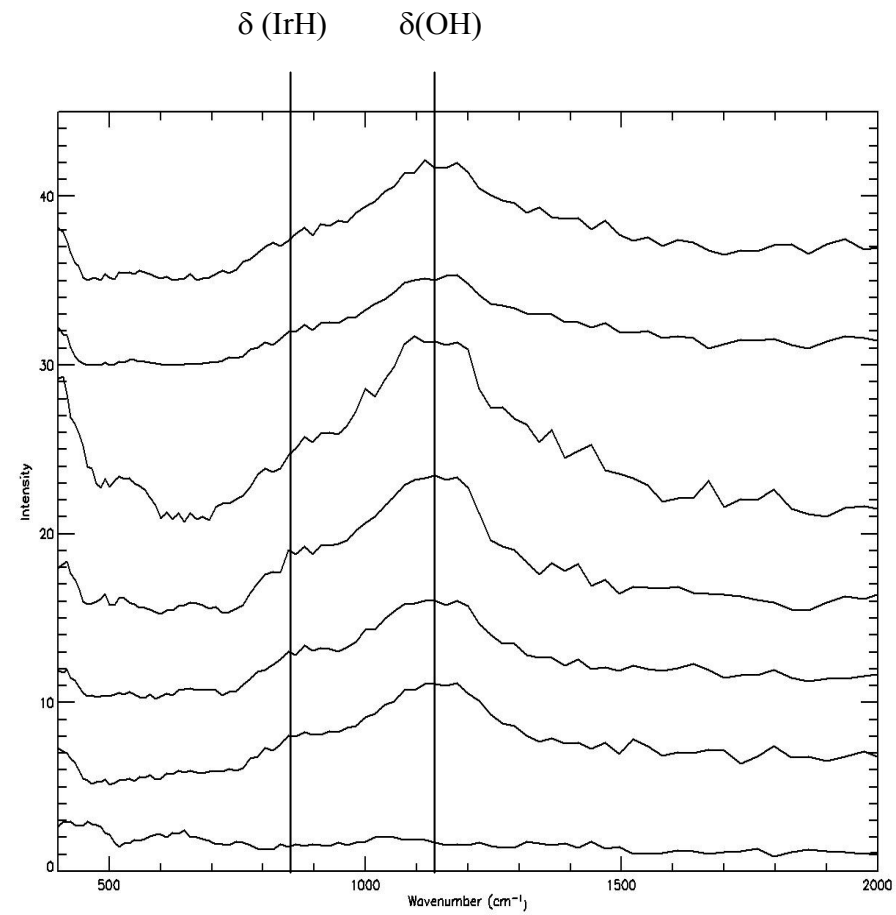


Ir_6 clusters in Faujasites: H_2 Spillover: INS studies

(Fen Li, Bruce Gates (UCD); Luke Daemen, Monika Hartl, and Juergen Eckert, Z. Phys. Chem., in press)

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})