2007 Workshop Product:

BASIC RESEARCH NEEDS:
CATALYSIS FOR ENERGY
HEADLINE SUMMARY OF REPORT CONTENT

- **MOTIVATION**: CATALYSIS ESSENTIAL TO CONVERSION FOR FUELS & CHEMICALS, NEEDED FOR **FUTURE FEEDSTOCKS**
- FUTURE FEEDSTOCKS: **HEAVY FOSSIL** & also RENEWABALES: **BIOMASS**, ULTIMATELY **CO_2**
- NEED **NEW** CLASSES OF **CATALYSTS** DIFFERENT FROM THOSE DOMINATING TODAY'S TECHNOLOGY

2007 Workshop Product:

BASIC RESEARCH NEEDS:
CATALYSIS FOR ENERGY

Grand Challenges

1. **Understanding mechanisms & dynamics of catalytic transformations**
2. **Design & controlled synthesis of catalytic structures**

Priority Research Directions

1. **Understanding complex transformations of fossil fuel feedstocks**
2. **Understanding lignocellulosic biomass: chemistries of deconstruction and conversion to fuels**
3. **Photo- and electrochemical conversion of H_2O & CO_2**

Cross-Cutting Themes

1. **Advanced instrumentation for characterization of catalysts in working state**
2. **Advanced theoretical methods for the simulation of catalysts & catalytic processes**

INTEGRATION:

Grand Scientific Challenges in Catalysis

ELUCIDATE REACTION NETWORKS & MECHANISMS

UNDERSTAND DYNAMICS OF CATALYTIC REACTIONS (including changes in catalyst surfaces and bulk)

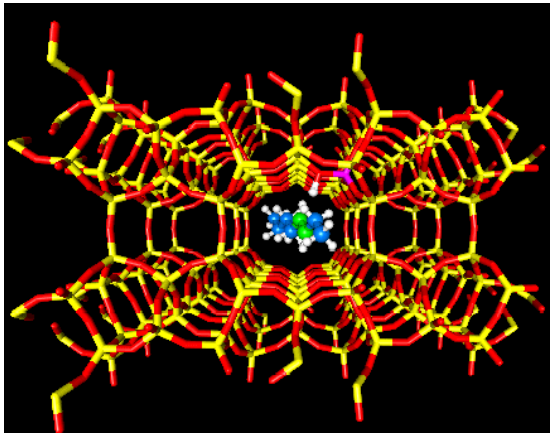
USE SPECTROSCOPY, IMAGING, & SIMULATION TO REPRESENT ELECTRONIC & GEOMETRIC STRUCTURES OF CATALYSTS—AS THEY FUNCTION

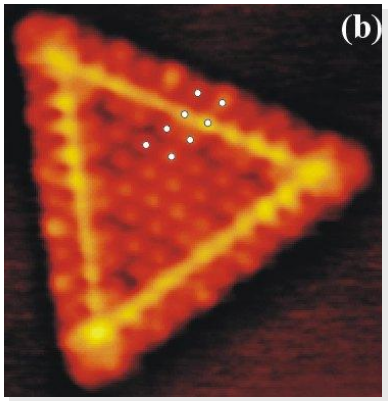
USE RESULTS AS BASIS FOR

PREDICTION OF CATALYTIC PROPERTIES & DEPENDENCE ON REACTION CONDITIONS

Grand Scientific Challenges in Catalysis

GAIN FUNDAMENTAL UNDERSTANDING FROM INVESTIGATION OF UNIFORM (“MOLECULAR”) STRUCTURES ON WELL-DEFINED SURFACES





INVESTIGATE POROUS MATERIALS WITH TAILORED PORE STRUCTURES, COMPOSITIONS, & NANO-ENVIRONMENTS FOR CATALYTIC SITES

INVESTIGATE CATALYSTS INSPIRED BY BIOLOGY

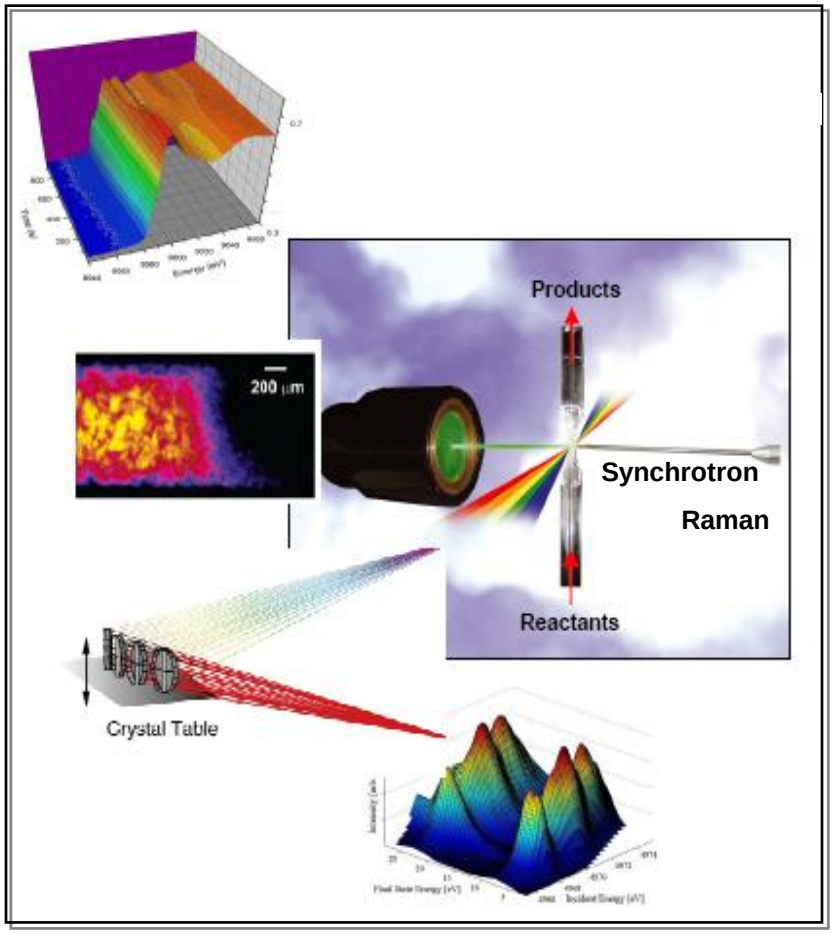
BUILD FROM UNDERSTANDING TO

CREATE **MULTIFUNCTIONAL CATALYSTS** WITH HIGH SELECTIVITIES & ACTIVITIES

SUCCESS REQUIRES:

Marked advances in instrumentation, theory, modeling, & simulation

Methods for application of complementary techniques in concert



Challenges:

Develop advanced instrumentation & methods for characterization of complex reactant/product mixtures & **working catalysts**

Use theory & computation in concert with experiment

SUMMARY:
SCIENTIFIC CHALLENGES

FUNDAMENTAL UNDERSTANDING FROM

- REAL-TIME SPATIALLY RESOLVED MEASUREMENTS OF OPERATING CATALYSTS
- UNDERSTANDING OF MECHANISMS & DYNAMICS OF CATALYZED REACTIONS, SEPARATING REACTIVE SPECIES FROM RED HERRINGS
- DESIGN & SYNTHESIS OF CATALYTIC STRUCTURES AT ATOMIC & NANO SCALES

MEETING THE CHALLENGES

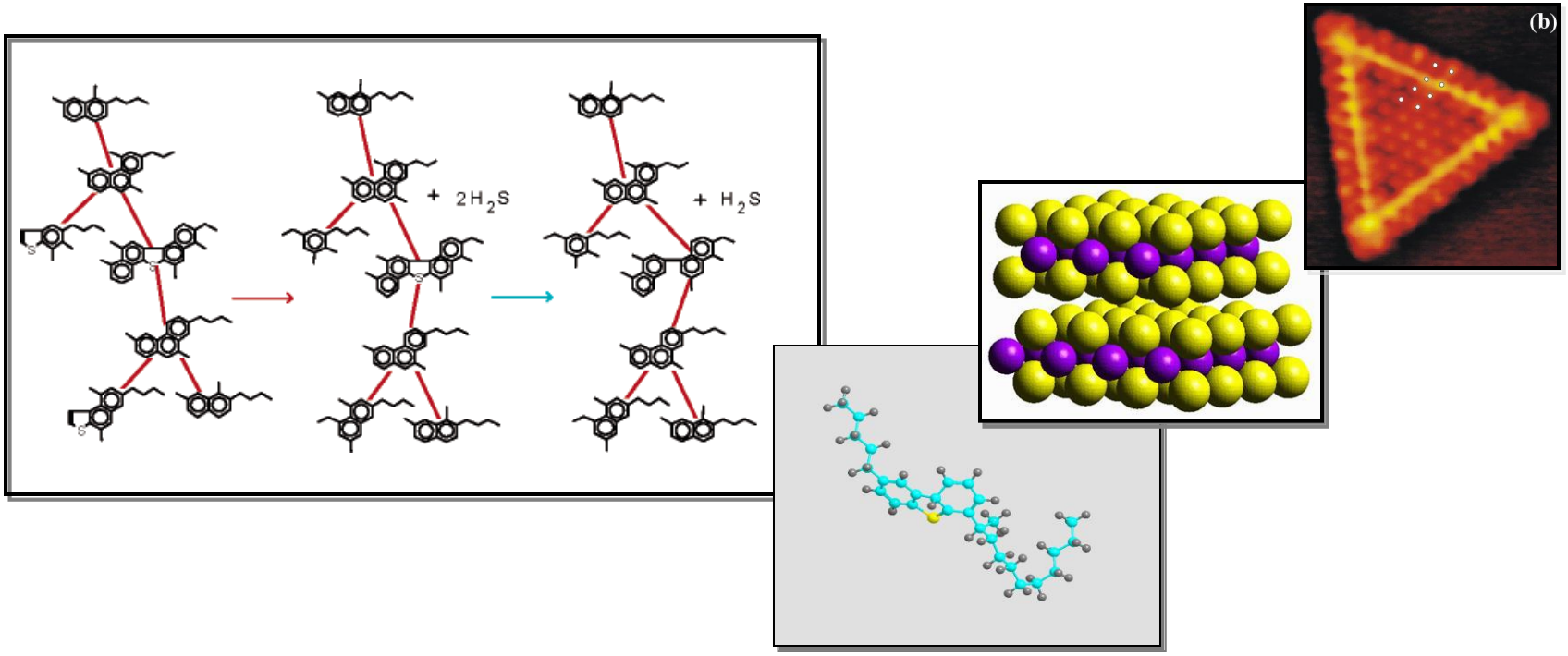
REQUIRES

- MUCH IMPROVED EXPERIMENTAL & COMPUTATIONAL TOOLS & THEORY
- CONCERTED APPLICATION OF COMPLEMENTARY TOOLS
- FOCUS ON FUNCTIONING CATALYSTS
- STRONG COMMITMENT OF RESOURCES

SUMMARY

- **MOTIVATION**: CATALYSIS ESSENTIAL TO CONVERSION FOR FUELS & CHEMICALS, NEEDED FOR **FUTURE FEEDSTOCKS**
- FUTURE FEEDSTOCKS: HEAVY FOSSIL, RENEWABALES: BIOMASS, ULTIMATELY CO_2
- REQUIRE CLASSES OF CATALYSTS DIFFERENT FROM THOSE DOMINATING TODAY'S TECHNOLOGY
- UNDERSTANDING REQUIRES CHARACTERIZATION OF FUNCTIONING CATALYSTS BY MULTIPLE TECHNIQUES INCLUDING SPECTROSCOPY, MICROSCOPY, & THEORY
- ROLE OF NEUTRONS?

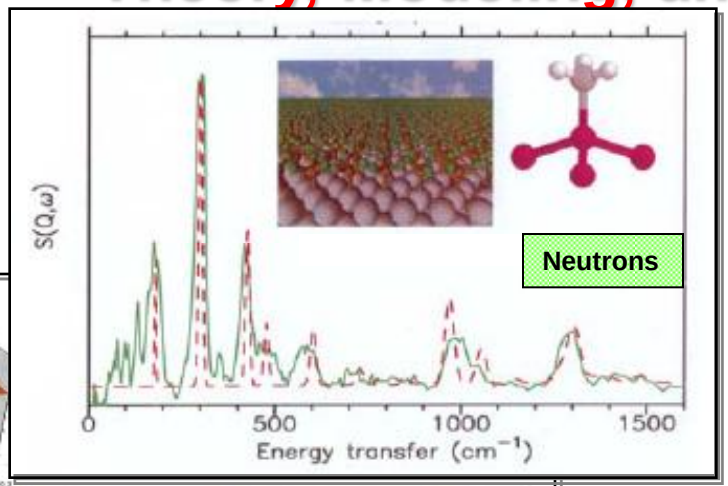
Cross-Cutting Themes: Advanced Instrumentation and Theory, Modeling, and Simulation

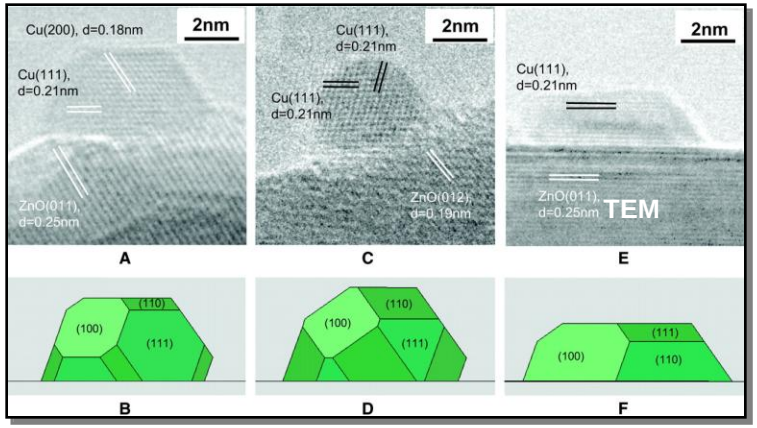


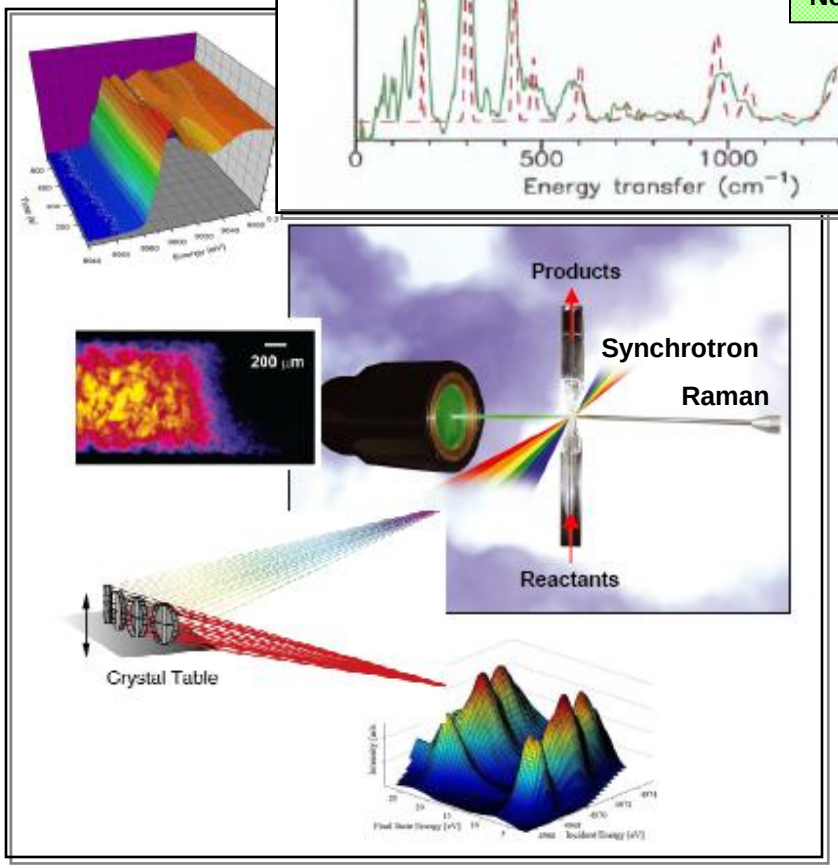
Challenge: Develop reliable theoretical methods for describing reactions of complex organic (**hydrogen-containing**) molecules including the effects of transport

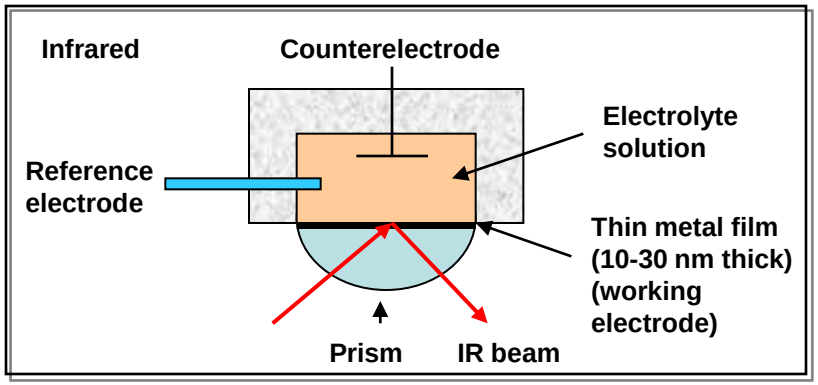
Challenge: Develop simulation strategies for describing complex systems of reactions occurring during processing of fossil & bio-derived feedstocks

Cross-Cutting Themes: Advanced Instrumentation and Theory, Modeling, and Simulation



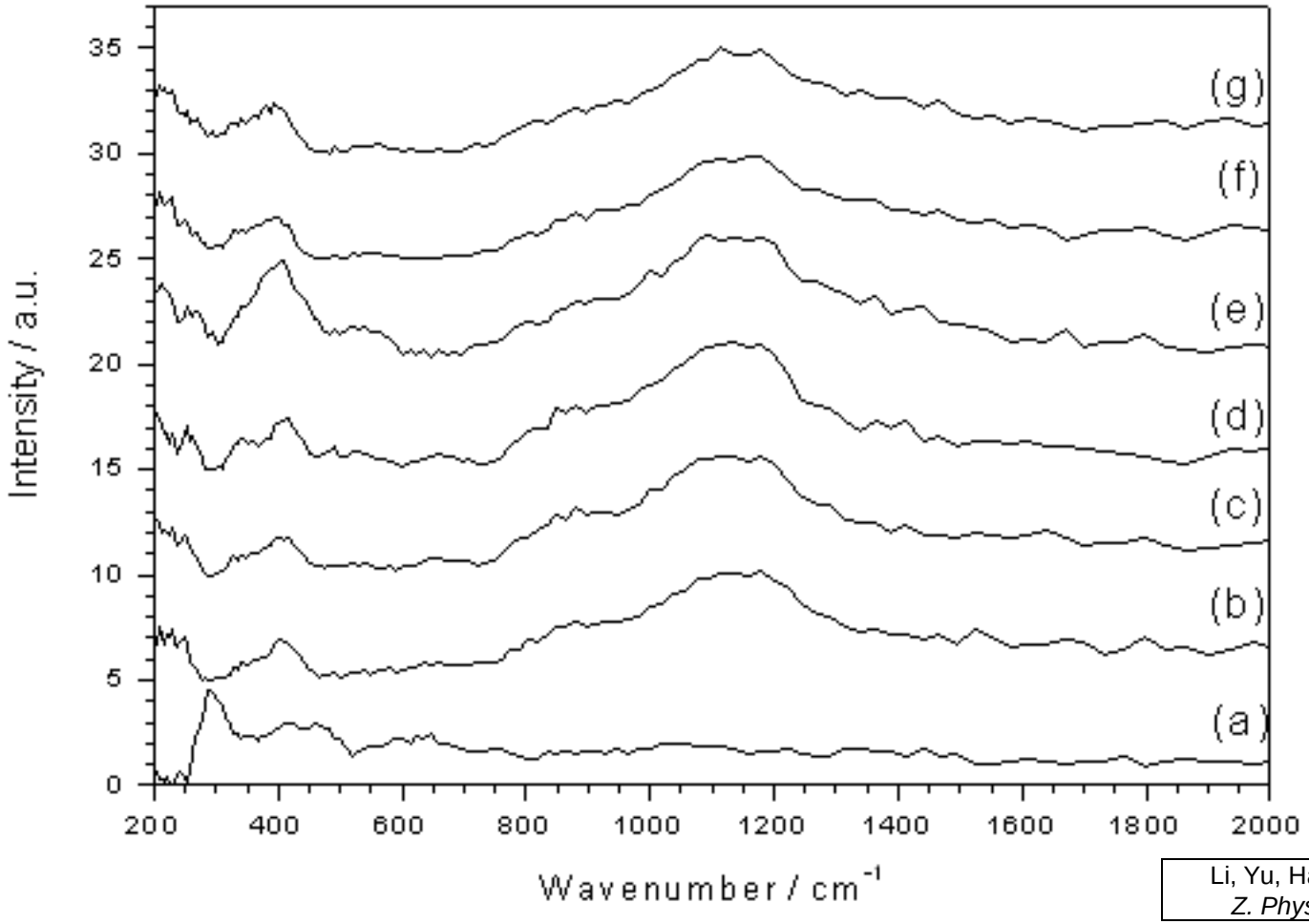






Challenge: instrumentation & methods for observation of functioning catalysts

IINS & ^{1}H NMR EVIDENCE OF HYDROGEN IN VARIOUS FORMS: ZEOLITE-SUPPORTED Ir_6 CLUSTERS



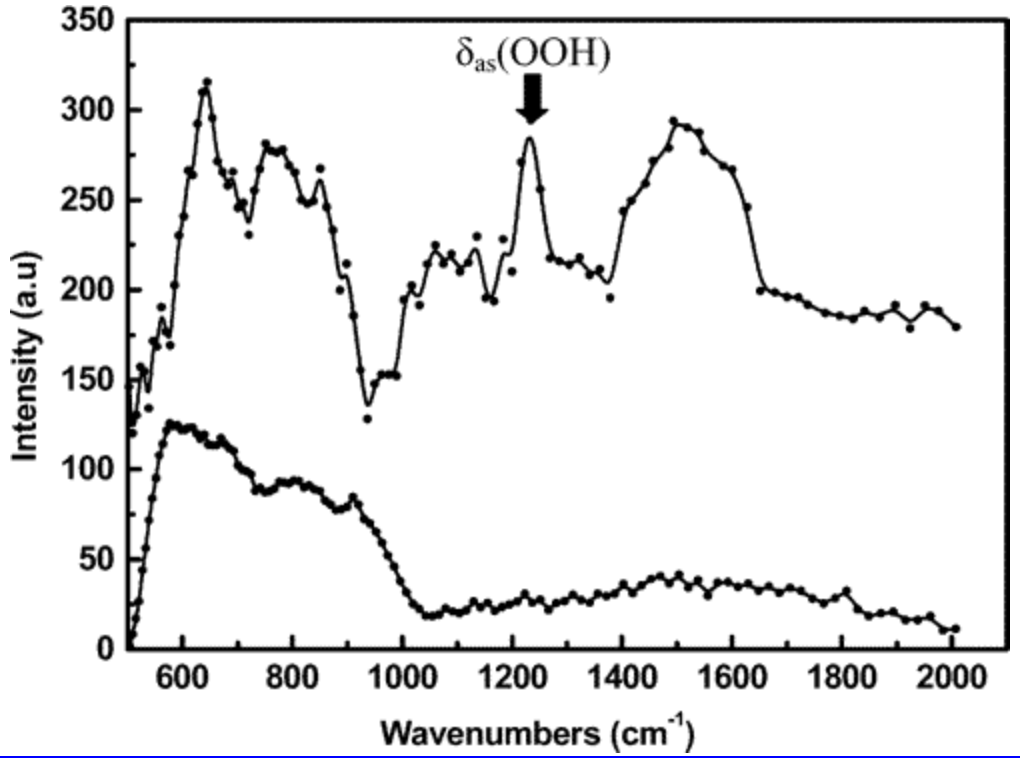
Li, Yu, Hartl, Daemen, Eckert, Gates, *Z. Phys. Chem.* **220**, 1553 (2006).

IINS: O–H (various), Ir–H BENDING, & CLUSTER DEFORMATION (RIDING MODES)

^{1}H NMR: O–H (various), IRIDIUM HYDRIDES

INCREASES IN BAND INTENSITIES RESULTING FROM H_2 TREATMENT

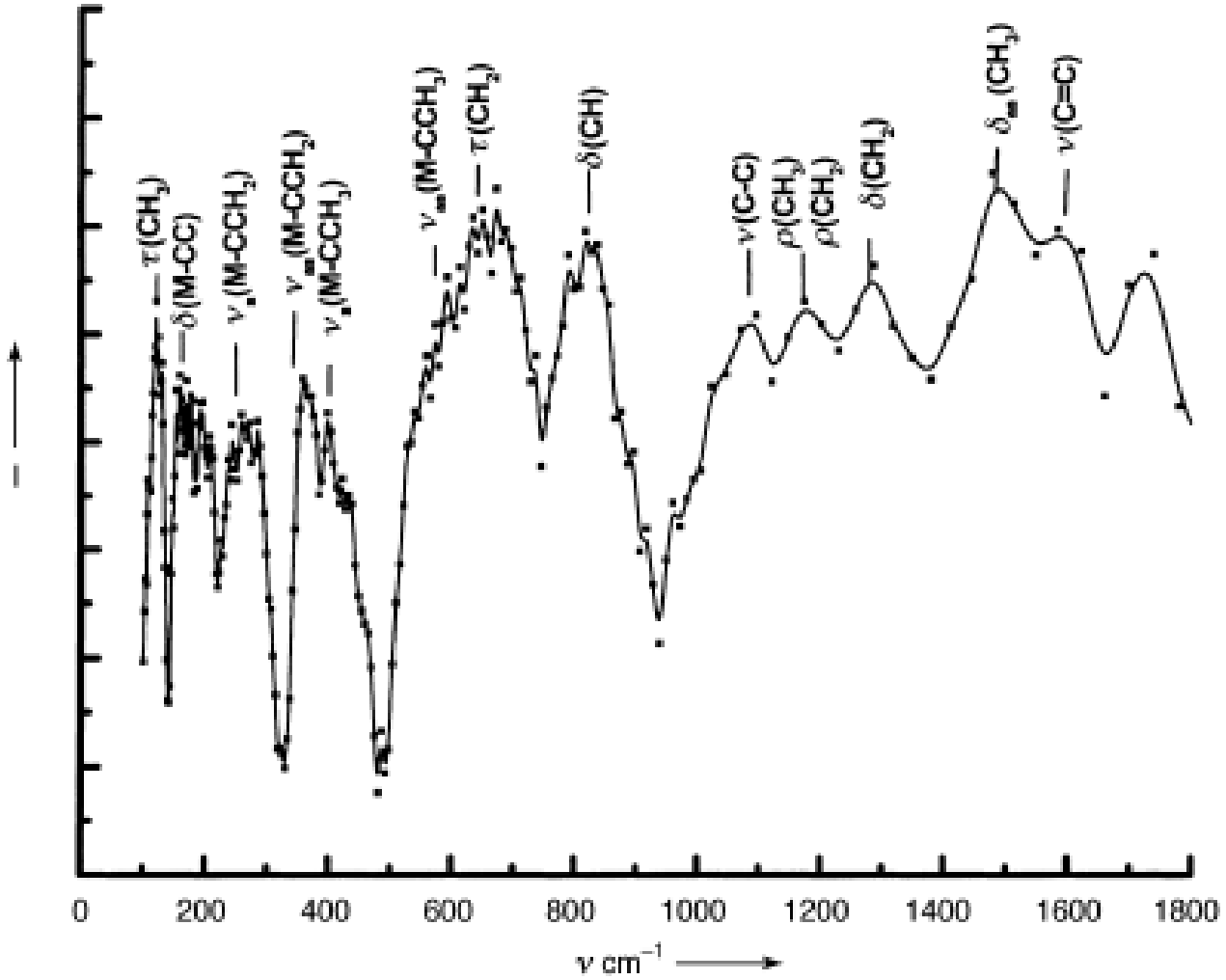
INNS EVIDENCE OF STABLE SURFACE REACTION INTERMEDIATE



SELECTIVE OXIDATION OF PROPYLENE ON SUPPORTED GOLD NANOCLUSTERS: EVIDENCE OF (SURFACE?) HYDROPEROXIDE REACTION INTERMEDIATE

Sivadinarayana, Choudhary, Daemen, Eckert, Goodman, *J. Am. Chem. Soc*. **126**, 38 (2004).

INNS EVIDENCE OF STABLE SURFACE REACTION INTERMEDIATE



CH_4 DECOMPOSITION ON Ru/Al_2O_3:
EVIDENCE OF ETHYLIDYNE, VINYLIDENE, & METHYLIDYNE

Chinta, Choudhary, Daemen, Eckert, Goodman, *Angew. Chem. Int. Ed.* **41**, 144 (2002).

OTHER EXAMPLES OF STABLE SURFACE SPECIES IDENTIFIED BY INS

- **METHYL GROUPS ON DEACTIVATED PALLADIUM HYDROGENATION CATALYST**
- **VARIOUS TYPES OF COKE ON SUPPORTED METAL CATALYSTS**
- **VARIOUS TYPES OF HYDROGEN ON FUEL CELL CATALYST**

DETAILS OF THESE & OTHERS: Albers & Parker, *Advan. Catal.* **51**, 100 (2007).

- UNDERSTANDING REQUIRES CHARACTERIZATION OF FUNCTIONING CATALYSTS BY MULTIPLE TECHNIQUES INCLUDING SPECTROSCOPY, MICROSCOPY, & THEORY

ROLE OF NEUTRONS?

SPECTROSCOPY OF WORKING CATALYSTS

- IR
- RAMAN
- EXAFS/XANES
- EPR
- UV-VISIBLE
- XRD
- MÖSSBAUER
- NMR
- IINS
- SUM FREQUENCY GENERATION
- GRAVIMETRIC METHODS
- PHOTOLUMINESCENCE
- XPS
- TEM
- STM
- MAGNETIC RESONANCE IMAGING

A NUMBER OF THESE TECHNIQUES NOW USED IN TANDEM

EPR/UV-vis
IR/XANES/EXAFS
XRD/EXAFS
&
IN TRANSIENT MODE

See Advan. Catal. **50** (2006)**, 51** (2007)**, 52** (2009).

OPPORTUNITIES TO DEVELOP ADVANTAGES OF IINS OF WORKING CATALYSTS

- **ADVANCE PROCEDURES FOR HIGH-PRESSURE EXPERIMENTS**
- **DEVELOP FLOW REACTORS/CELLS FOR STEADY-STATE EXPERIMENTS TO ALLOW DETERMINATION OF EFFECTS OF REACTANT COMPOSITION ON CATALYST STRUCTURE**
- **USE IINS IN CONCERT WITH COMPLEMENTARY TECHNIQUES—MATCH CONDITIONS IN COMPLEMENTARY EXPERIMENTS**