Review of DRIFTS and Raman instruments and examples of applications

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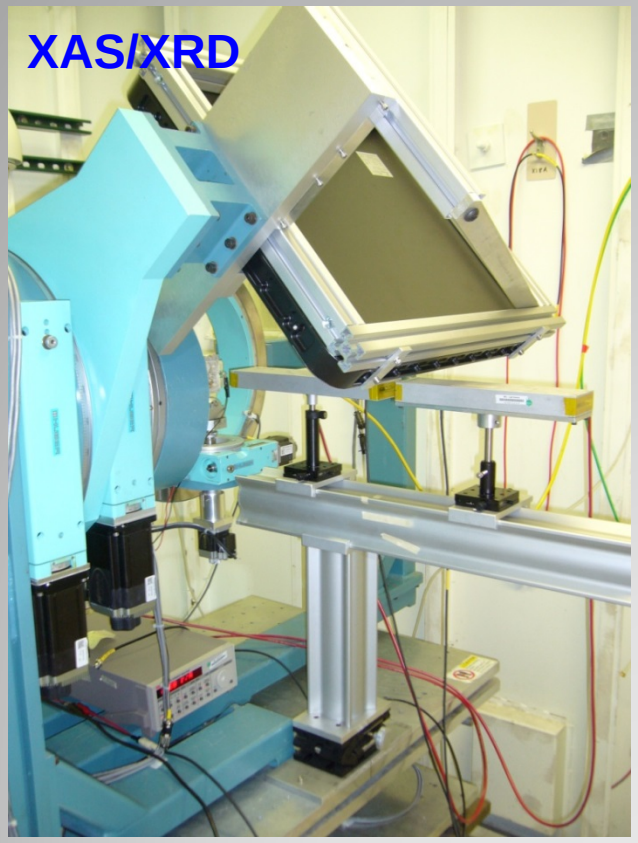
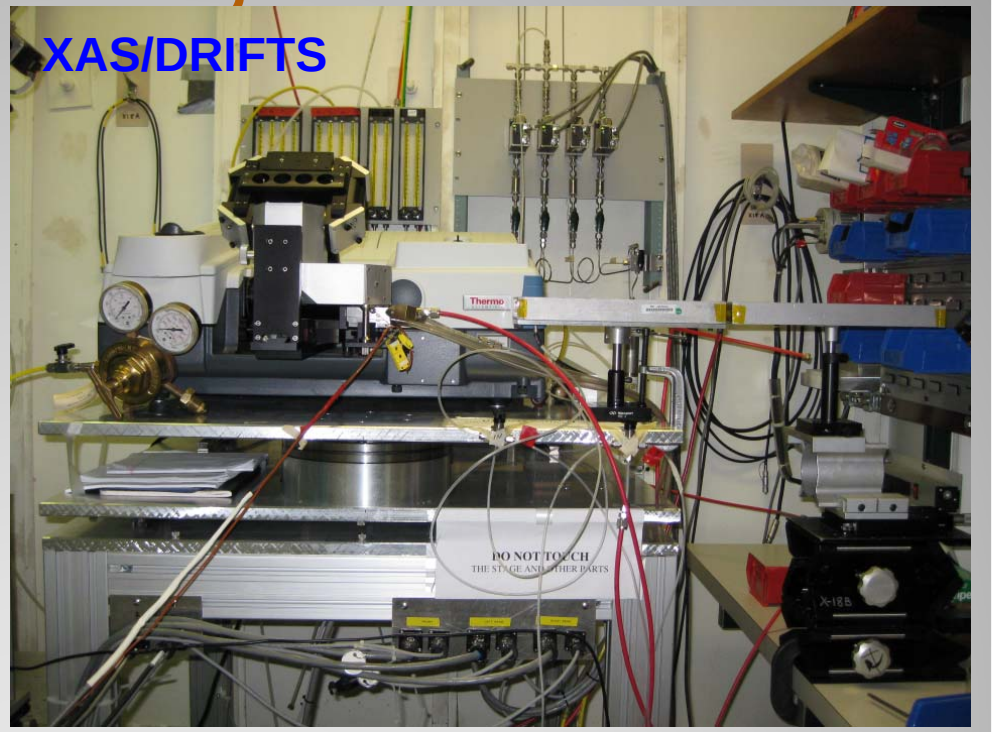
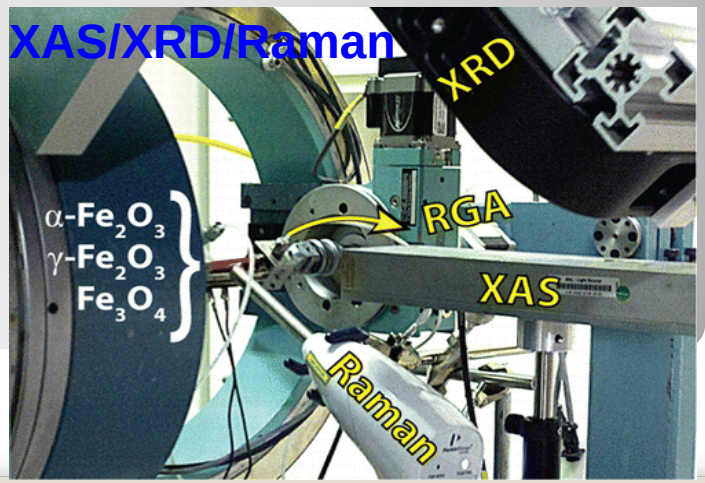
Combining XAS with vibrational techniques

- Overview of vibrational techniques at SCC
- Operation principles
- Importance in catalysis
- Applications

Hutch Interior, X18A







Hutch equipped for XAS, XRD and mass spectrometer (RGA).

Raman or DRIFTS instruments are moved into the hutch when needed. They can be also used as stand-alone techniques.

Supporting Equipment: Nanomaterial handling stations

Preparation of nanomaterials are done in Nano-hood and Nano-glove box.

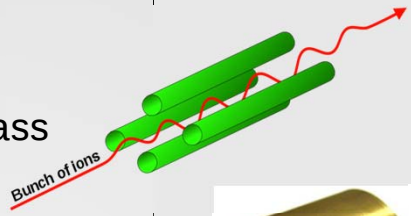
Equipment for heterogeneous catalysis: MFC/RGA

Mass Flow Controllers and Residual Gas Analyzer may be used with DRIFTS and Raman instruments for synchrotron ex-situ trials.

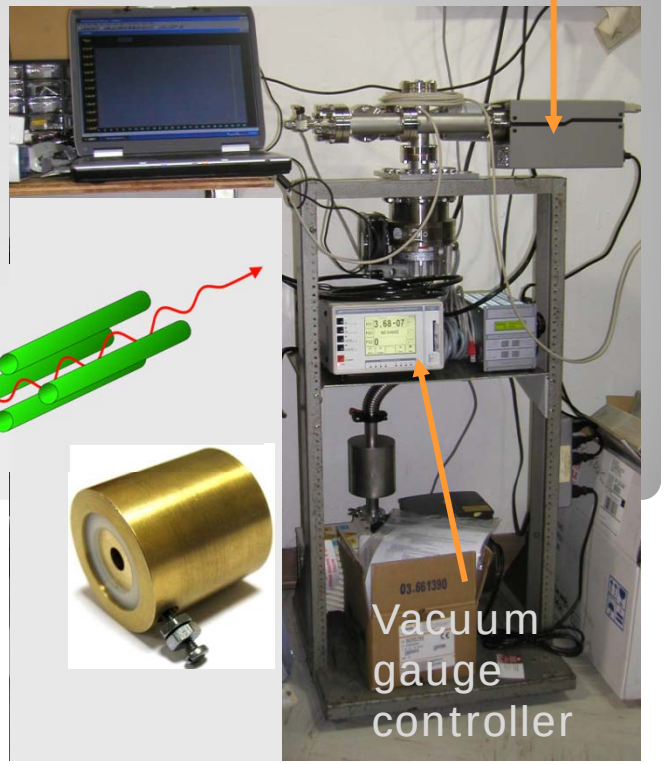
CO O_2 H_2 He

MFC:
He-calibrated
5 – 50 mL /min
4 inputs, 1 output

RGA:
1-200 amu
Quadruple mass spectrometric detection by Faraday cup;
50 μm ID capillary;
Chamber pressure ~1 x 10^{-6} torr (He);
Sensitivity to ~10^{-10} torr.



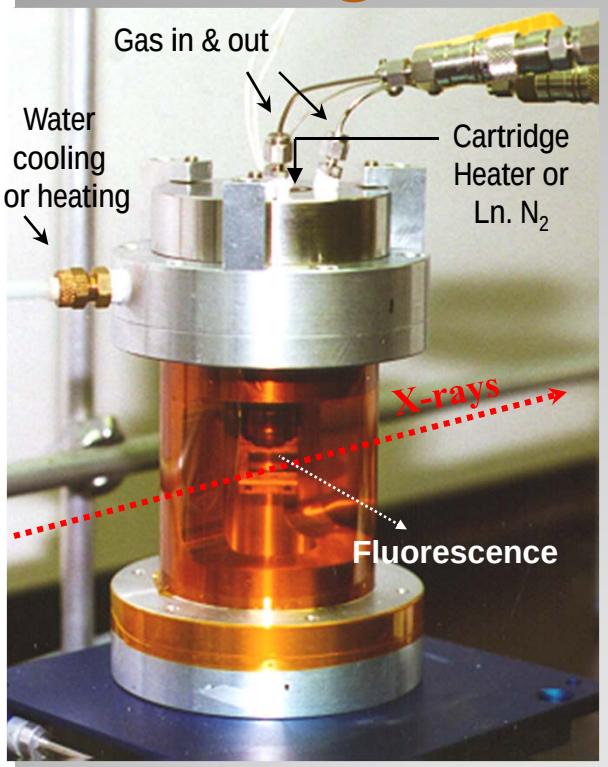
Mass spectrometer

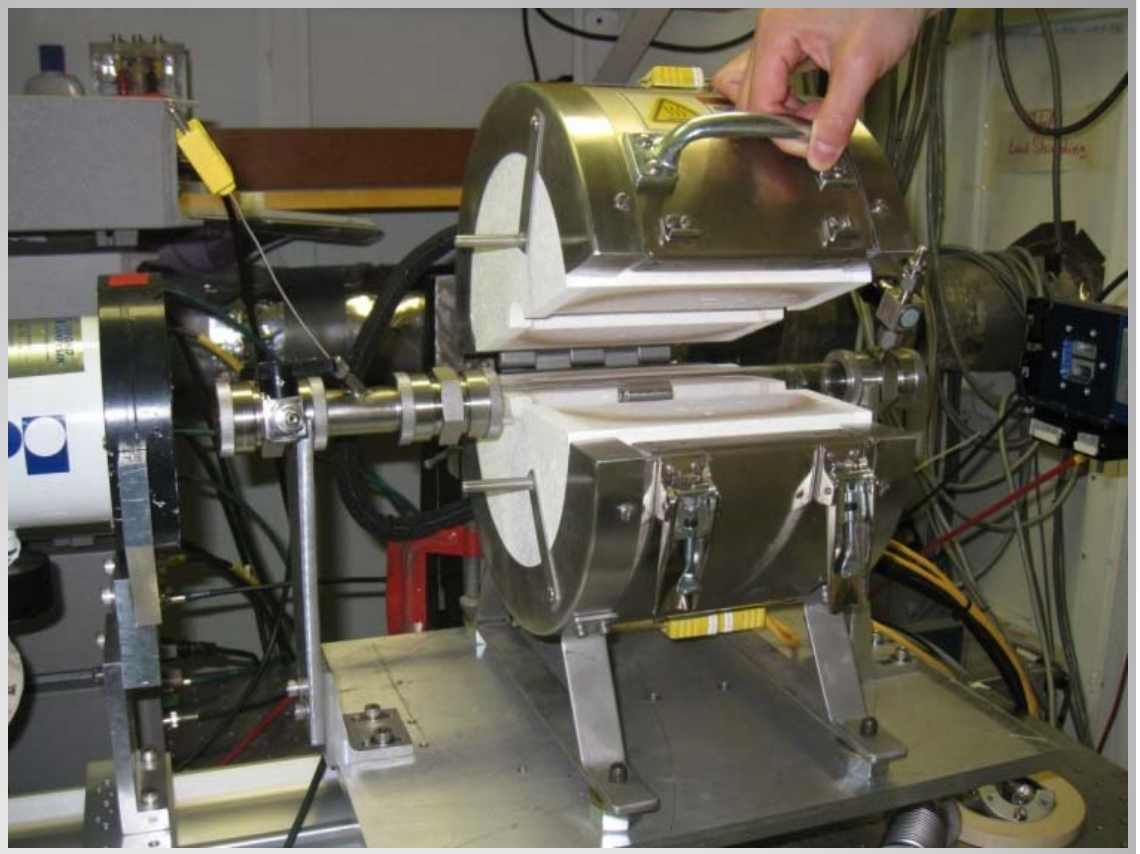


Gas reaction inlet: MFCs

Gas reaction outlet technique: RGA

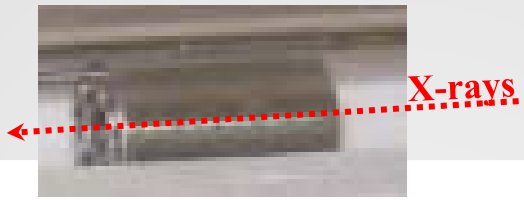
Large-volume Reactor Cells





Large reactor cell

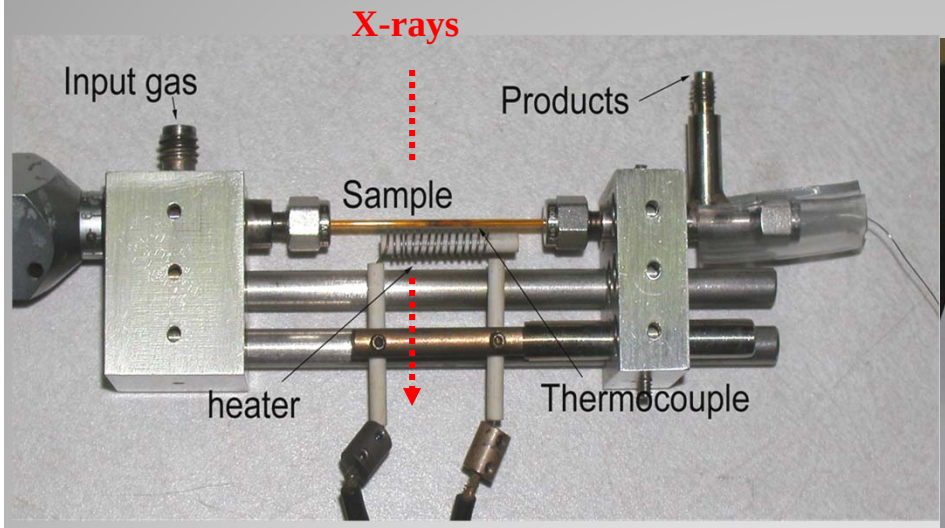
- In-situ XAS transmission or fluorescence
- Temp. range -200 – 500 ^{o}C with Ln. N_2
- Pellet catalyst sample
- Products analysis (RGA)
- Large reaction vessel

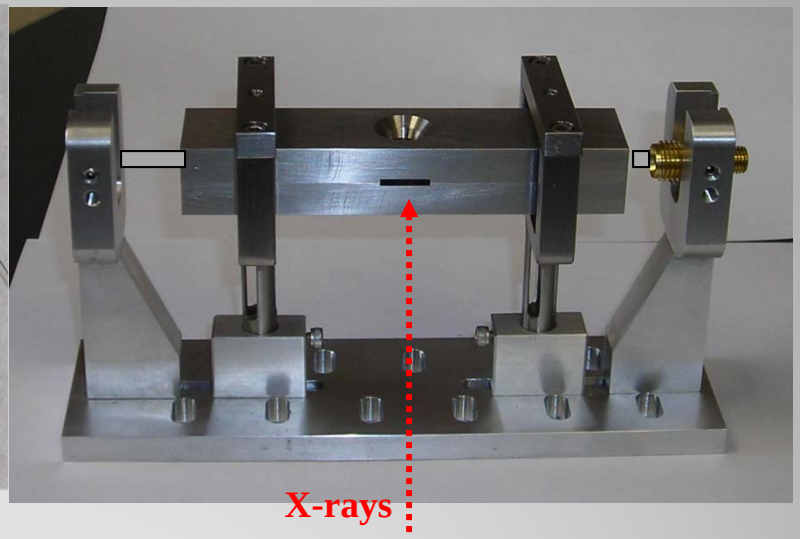


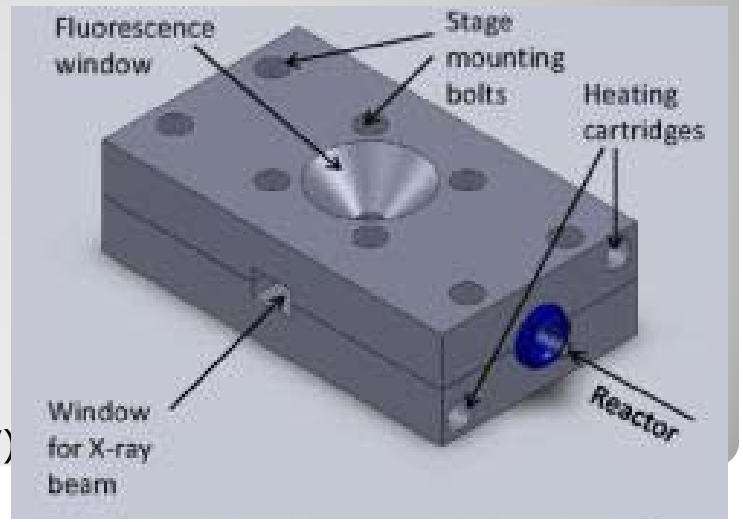
HT multi-sample XAS tube reactor

- In-situ XAS transmission
- Simultaneous gas treatment of up to 6 samples
- Temperature range: RT- 950 ^{o}C
- Pellet sample
- Product analysis (RGA)

Small-volume Reactor Cells







Claussen flow cell

- In-situ XAS, XRD, Raman
- Powder sample
- P < 120 atm.
- Temp. range: -190 - 975°C.
- Product Analysis (RGA)

Modifications

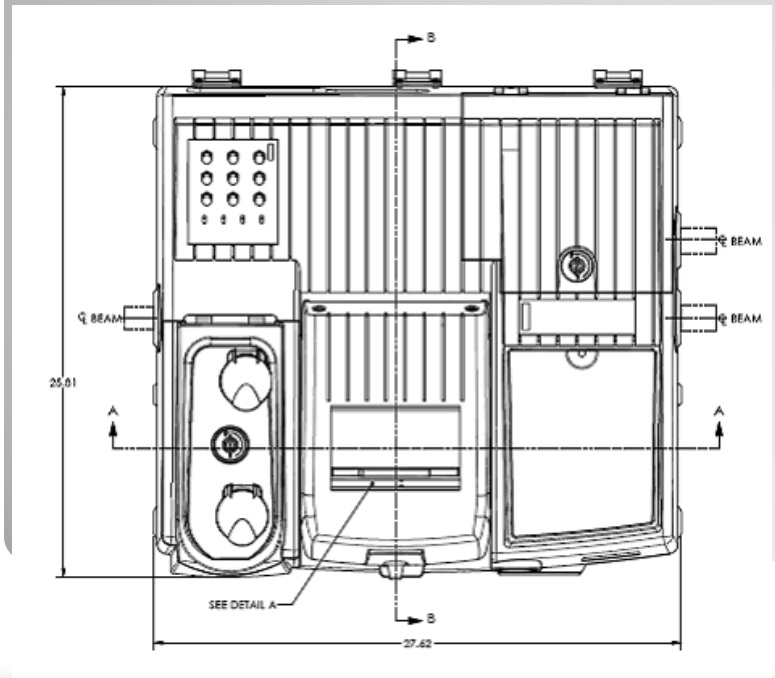
- Uniform temperature

Tubings

- Kapton / polyimide (< 400 ºC, >4 keV)
- quartz (< 1000 ºC, > 10 keV)
- glassy carbon (<600 ºC, > 6 keV)

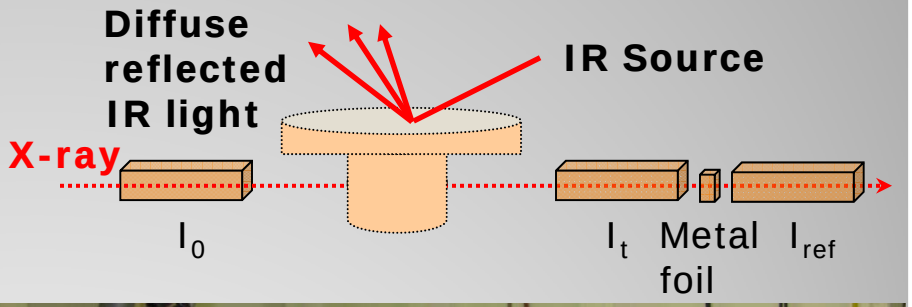
Nicolet 6700 FTIR Spectrometer

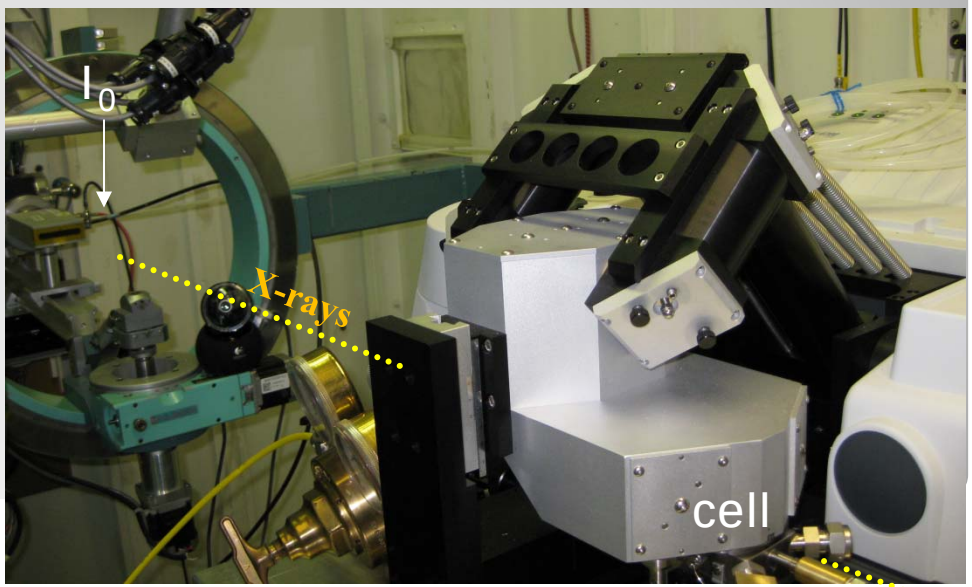
- Compact design;
- Two independent detectors can be placed in the system;
- X-ray penetrates < 0.4 mm below the catalyst surface.
- IR spectrum is a consequence of the molecular change in permanent <u>dipole moment</u>

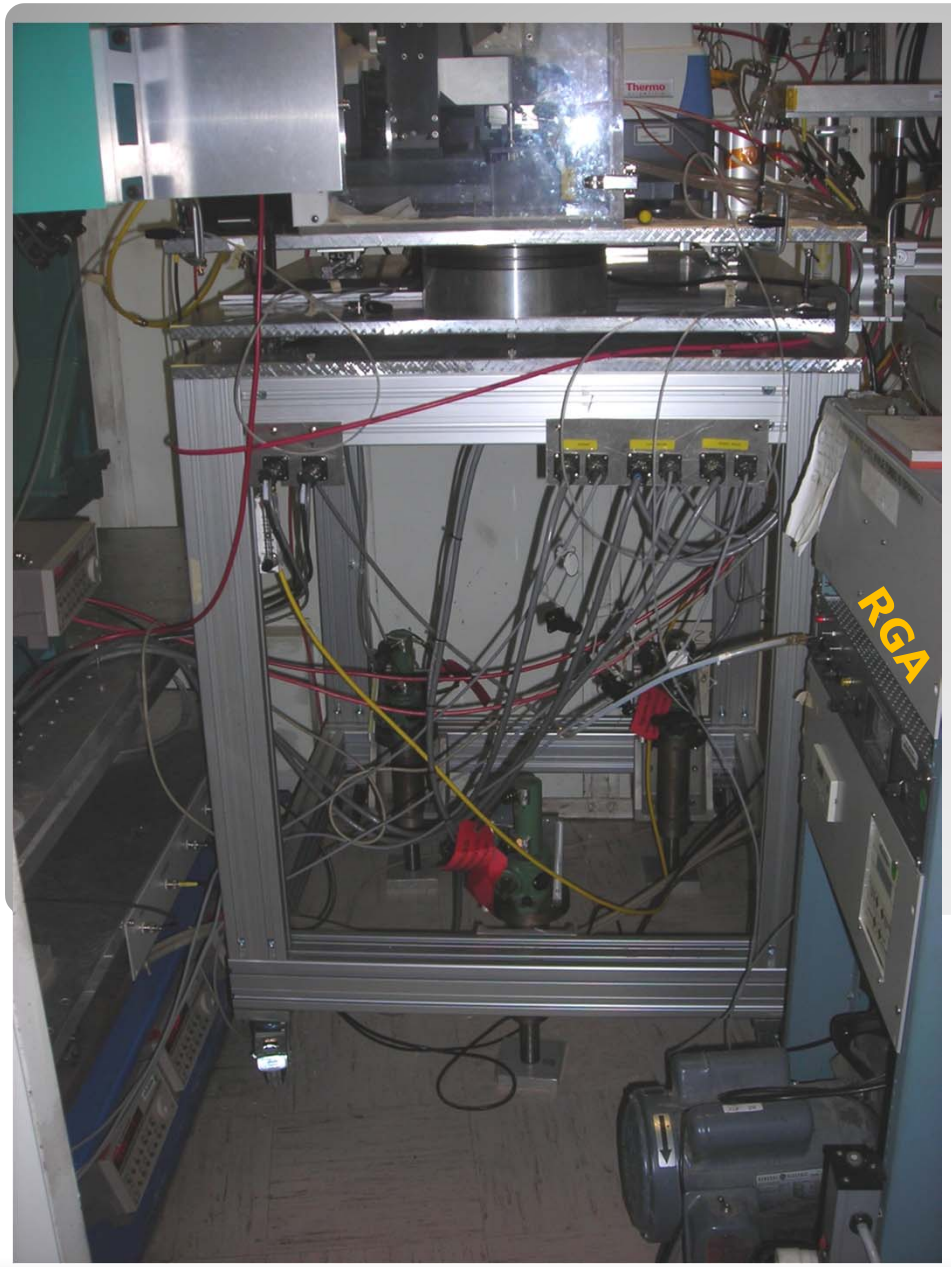


XAS / DRIFTS Setup

Simultaneous detection of XAS and DRIFTS:
Top of sample surface in sample cup irradiated by IR (Harrick Scientific)
DRIFTS penetration depth reaches 3 mm
X-ray passes ~1 mm below the top of cup



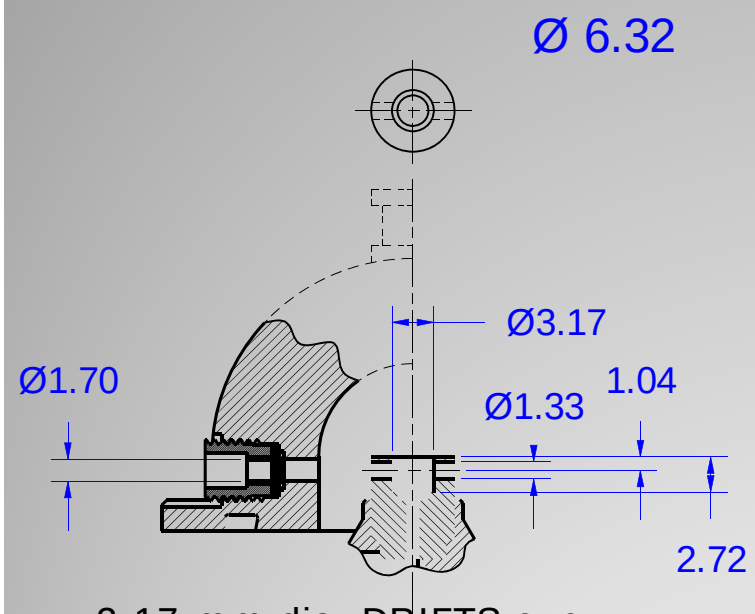


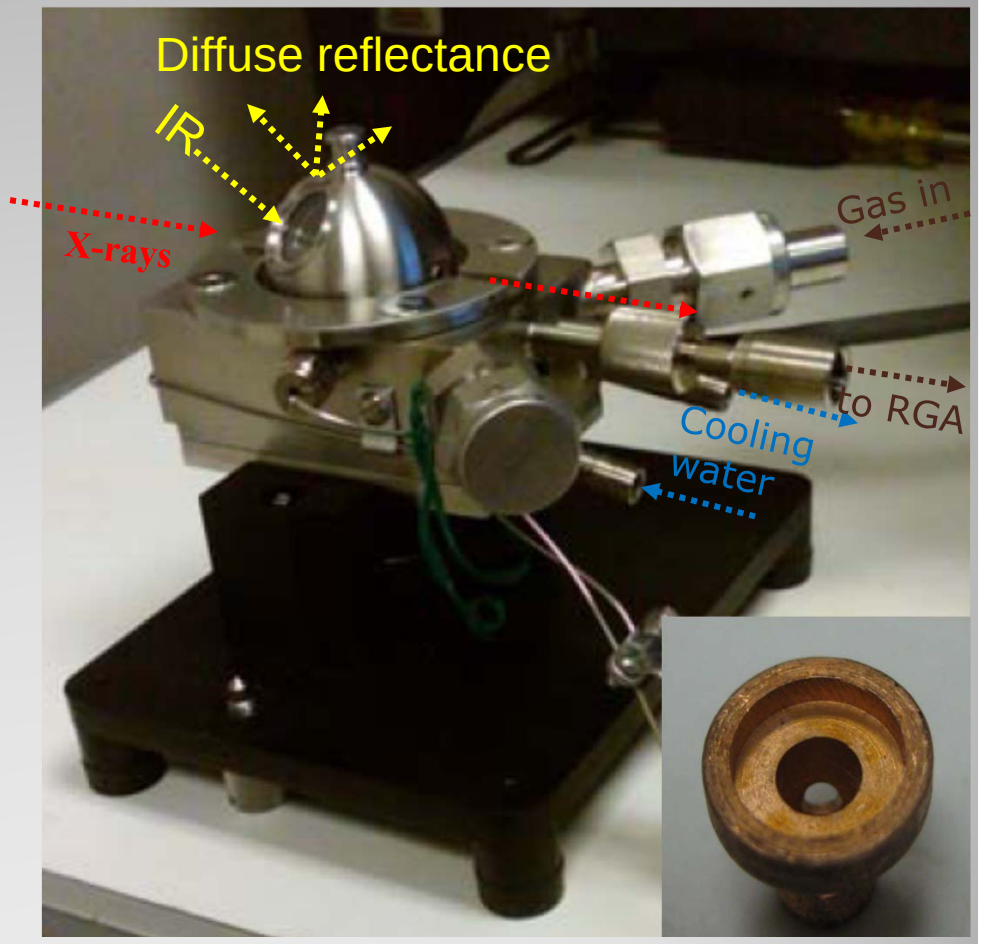


XAS / DRIFTS: Sample alignment

- Wheels to roll into the hutch;
- Motorized stages for precise alignment of the beam to the sample:
  - 3 independent motors for lift & tilt of the table
  - Perpendicular motion to the beam
  - Rotation (pivot) around the z-axis through the sample

XAS / DRIFTS Cell and schematics





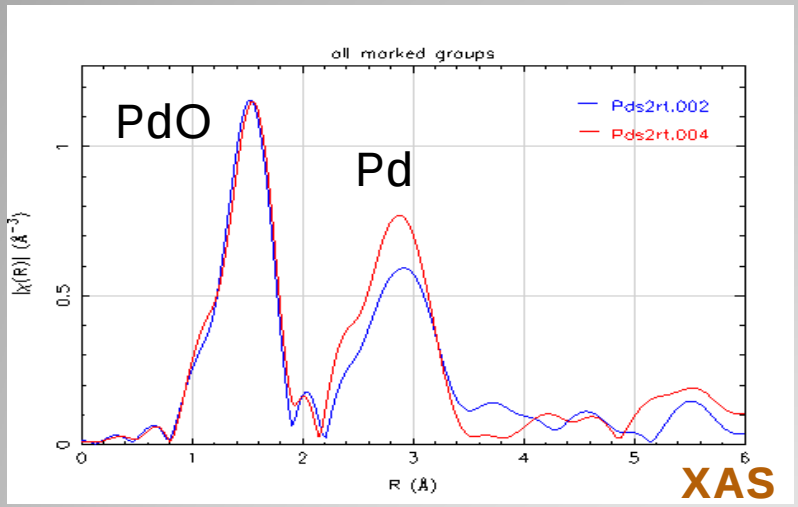
- 3.17 mm dia. DRIFTS cup;
- Glassy carbon windows;
- X-ray beam penetrates <0.4 mm below the catalyst surface;
- Large penetration depth with low IR-absorbing substrates.

- Powder sample;
- Purged / vacuumed cell;
- Temp. range: RT – 450 ºC (purged);
- Cell inserts for correct XAS absorption;

- Tilted focusing and collimating mirrors
- minimize specular reflectance;
- Spectra converted into Kubelka-Munk units to correct for scattering efficiency.

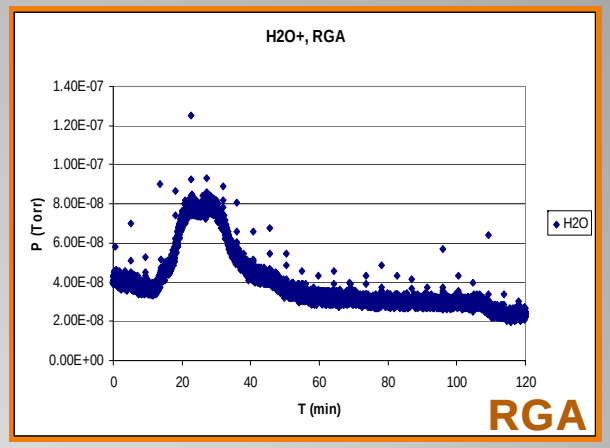
N.S. Marinkovic et al., *Nucl.Instrum.Methods* A **649** (2011) 204.

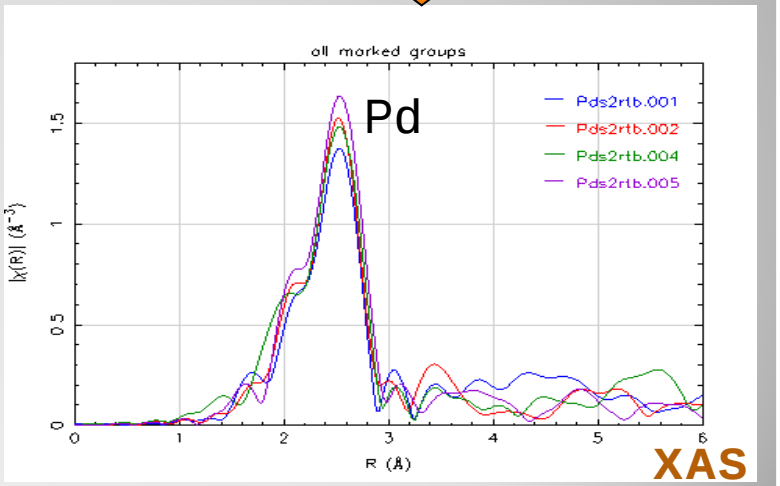
EXAFS / RGA example: PdO catalyst reduction by H_2



400 °C

H_2 stream





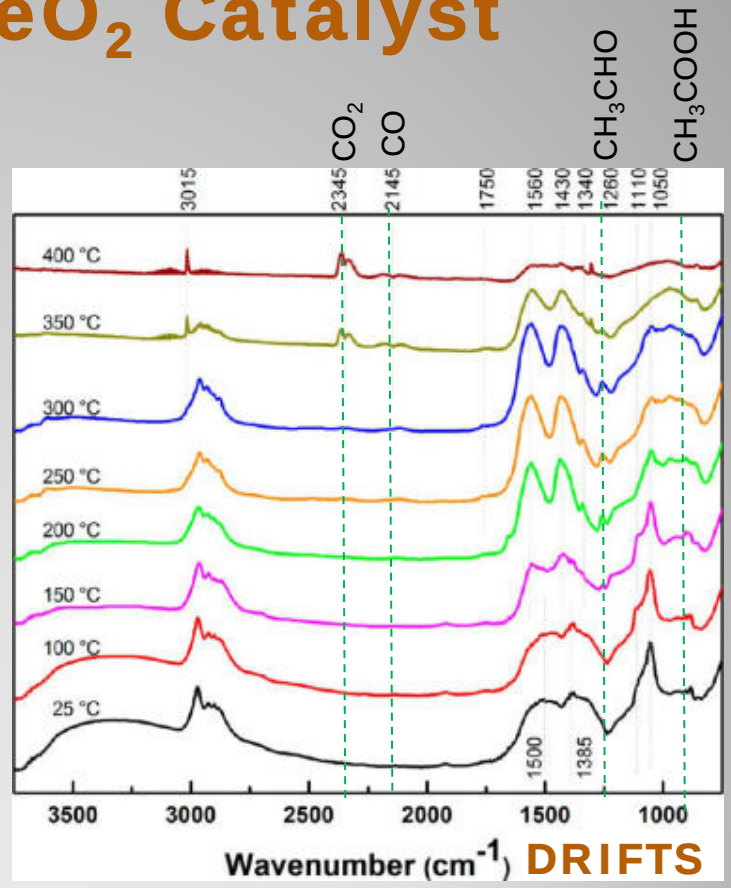
- Oxidized Pd-based catalyst show Pd-O.
- Reduction in H_2 stream at 400 °C produces water peak (m/e= 18) is observed.
- Pd-O contribution disappears after reduction in H_2 and Pd peak intensifies.

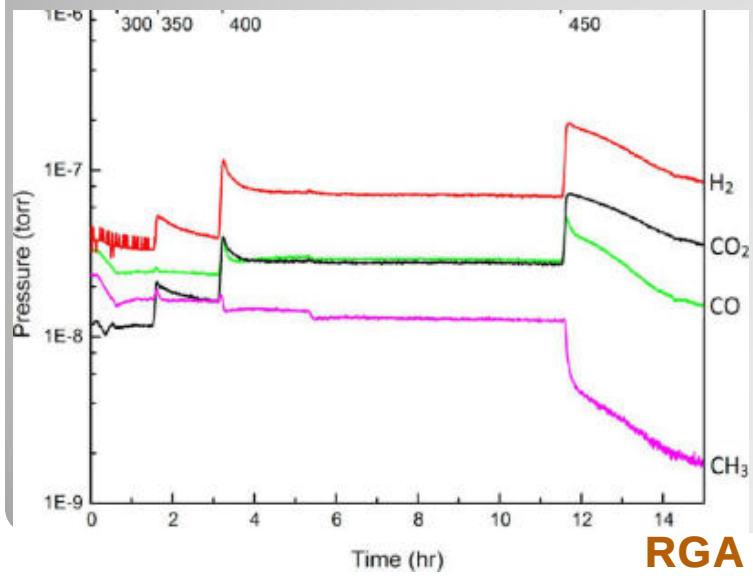
W.Lonergan et al., *J.Catal.* **271** (2010) 239.

DRIFTS/RGA example: Ethanol Steam reforming on Ni/CeO_2 Catalyst

Ni/CeO_2 is an active catalyst for ethanol reforming due to a synergic effect of metallic Ni and Ce^{3+}. Ni adsorbs EtOH and cleavages C-C bond, and Ce^{3+} decomposes water to provide OH groups which facilitate oxidation of EtOH fractions to H_2 and CO_2.

DRIFTS identified CO_2 as a major constituent, while acetaldehyde and acetic acid were not observed.





RGA identified H_2, CO, CO_2 and ethanol (by CH_3 fraction). $CO:CO_2$ ratio was found to be 1:6, production of H_2 is intensified and ethanol decreases due to consumption of EtOH.

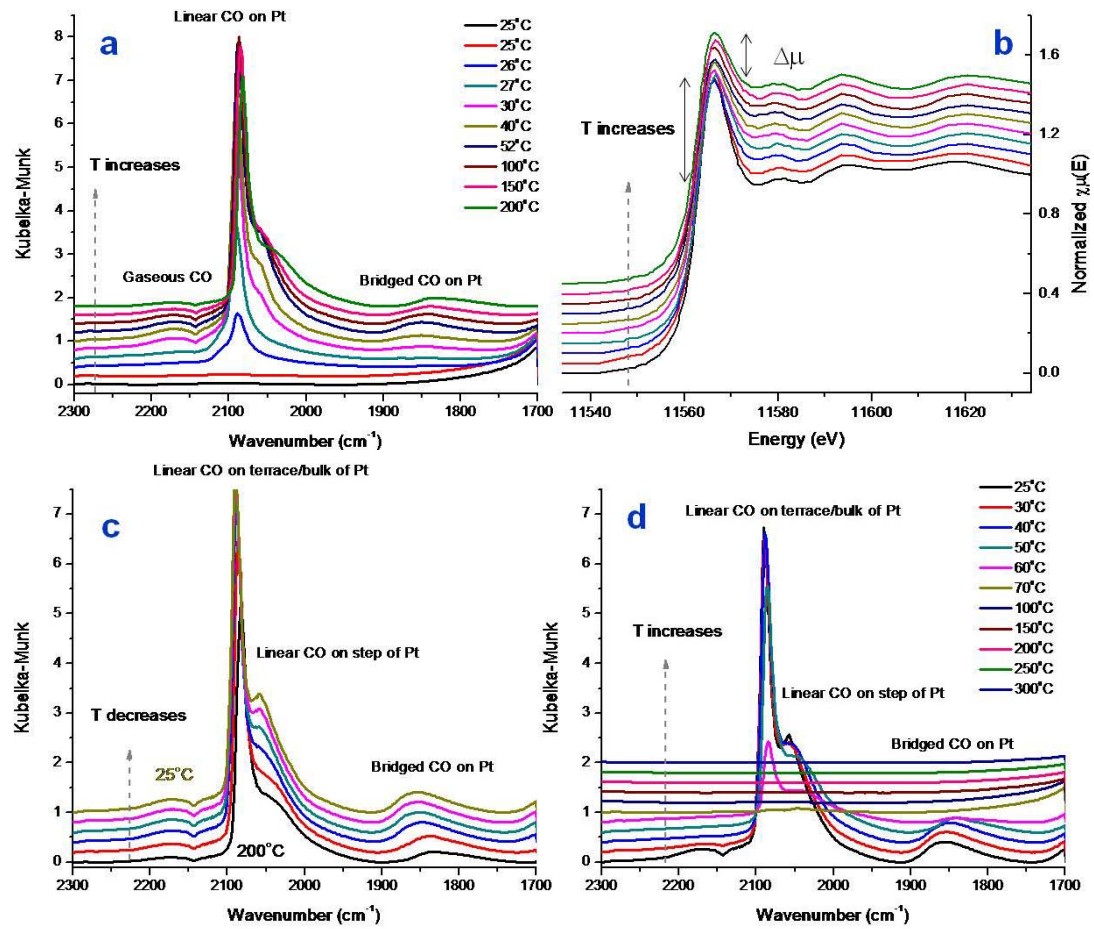
W. Xu et al., *ACS Catalysis* **3** (2013) 975.

XAS / DRIFTS examples: CO adsorption on γ-alumina-supported Pt nanocatalysts

(a) CO adsorbed on Pt shows CO_L and CO_B. The CO adsorption is affected by its coverage, nature and oxidation state of the metal and the pretreatment process.

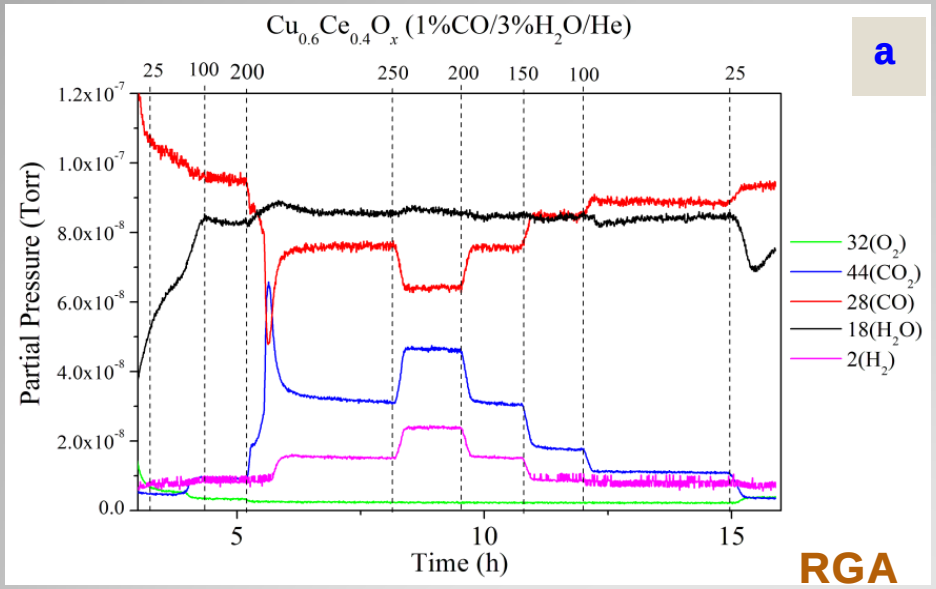
(b) Complementary XAFS allows to follow the electronic and geometrical structure evolution of metal species during *in-situ* pretreatment.

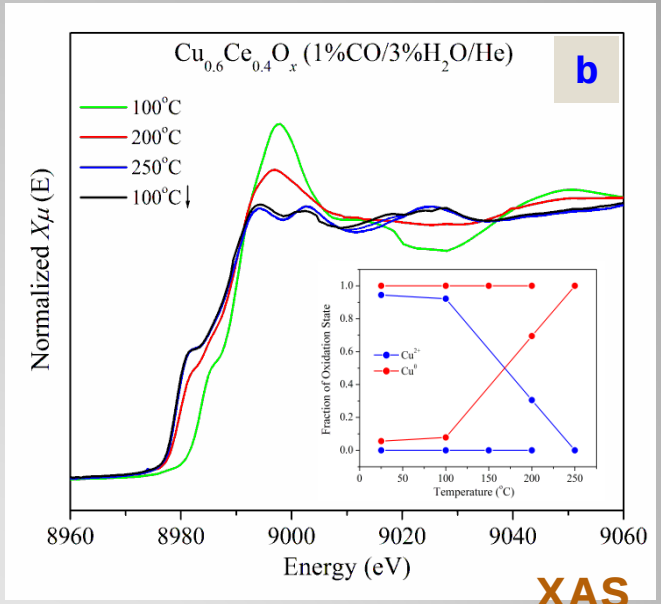
(c), (d) The effects of temperature and coverage on the CO adsorption were followed by DRIFTS in both adsorption (c), and desorption process (d).



N.S. Marinkovic et al., *J.Synchrotron Rad*. **18** (2011) 447.

XAS/DRIFTS examples: WGS on CeO_2/CuO_x Inverse Catalyst

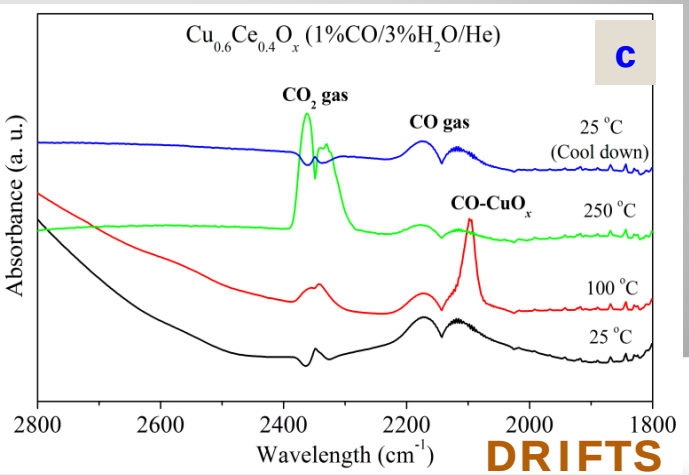




(a) Inverse CeO_2/CuO ($Cu_{0.6}Ce_{0.4}O_x$) catalyst was prepared by reverse micro-emulsion method shows high activity for the low-temperature (WGS) reaction.

(b) Transmission XAFS shows reduction of Cu; Linear combination (insert) determines Cu oxidation states during the reaction at different temperatures.

(c) DRIFTS identifies species on CeO_2/CuO_x surface: adsorbed CO on CuO_x and carbonate-like species, as well as gaseous CO and CO_2.



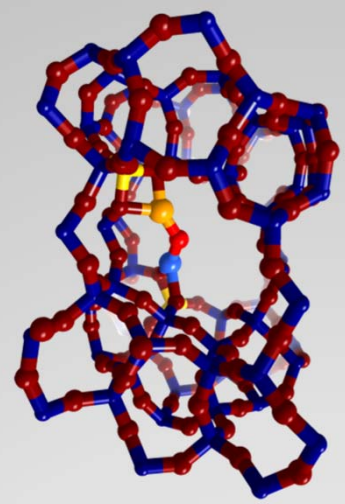
XAS/DRIFTS examples: zeolite-supported Cu nanocluseters

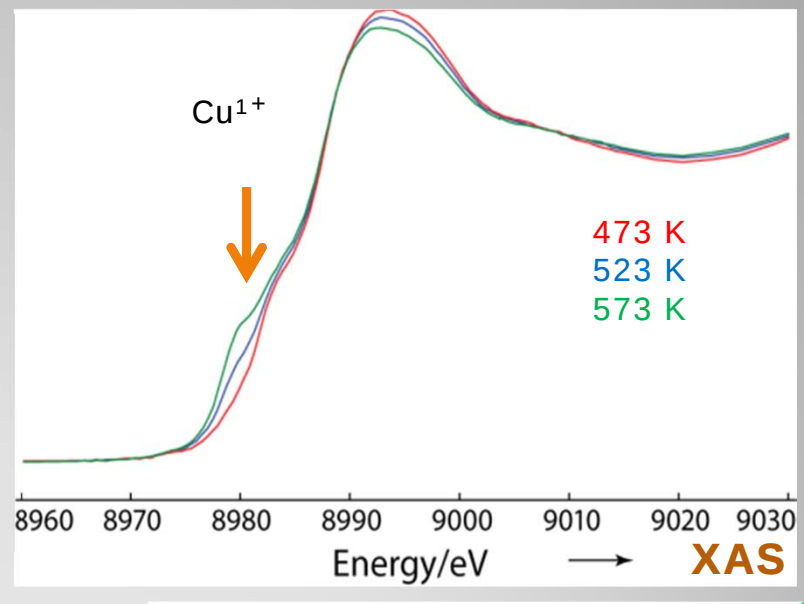
Direct conversion of methane to methanol is difficult reaction, conducted through a multi-step process. A direct route may be done on copper-containing ZSM-5 zeolite.

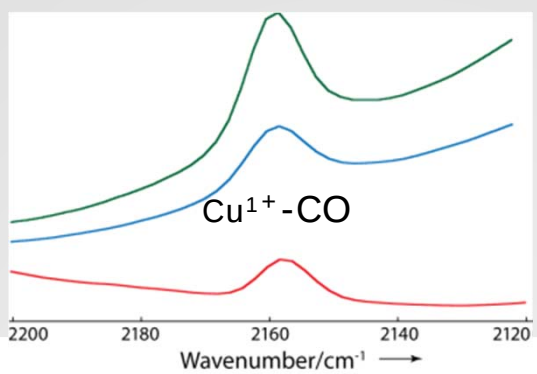
XAFS shows methane-induced reduction of Cu^{2+} to Cu^{1+}.

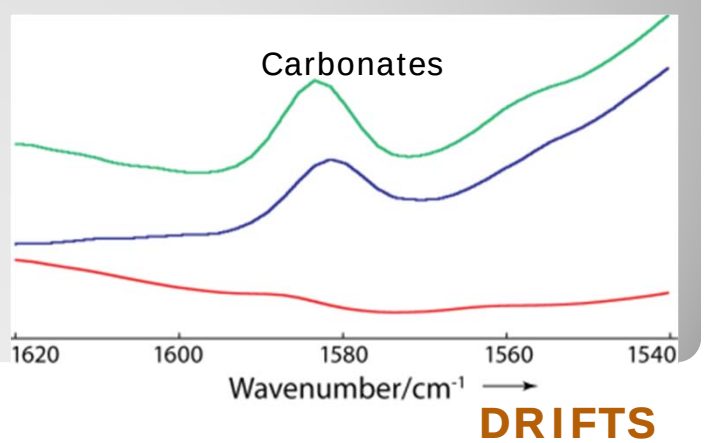
DRIFTS identifies surface species (Cu^{1+}-CO complex, carbonates).

Zn accelerates Cu reduction: greater fraction of Cu sites are involved in the reaction in the case of CuZnZSM-5.

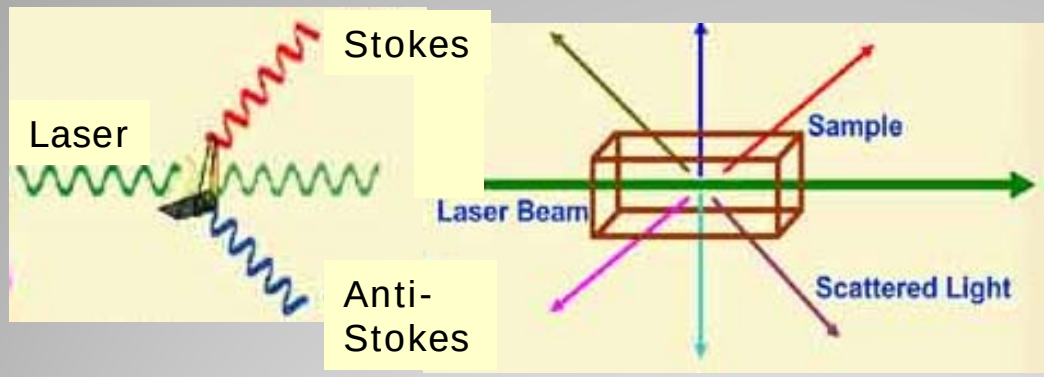


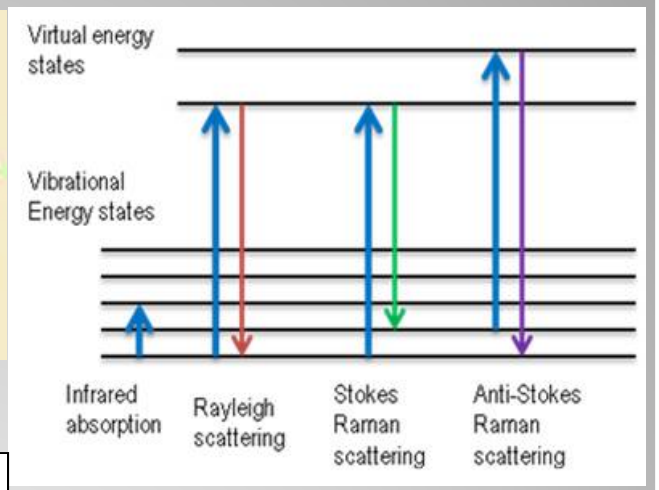


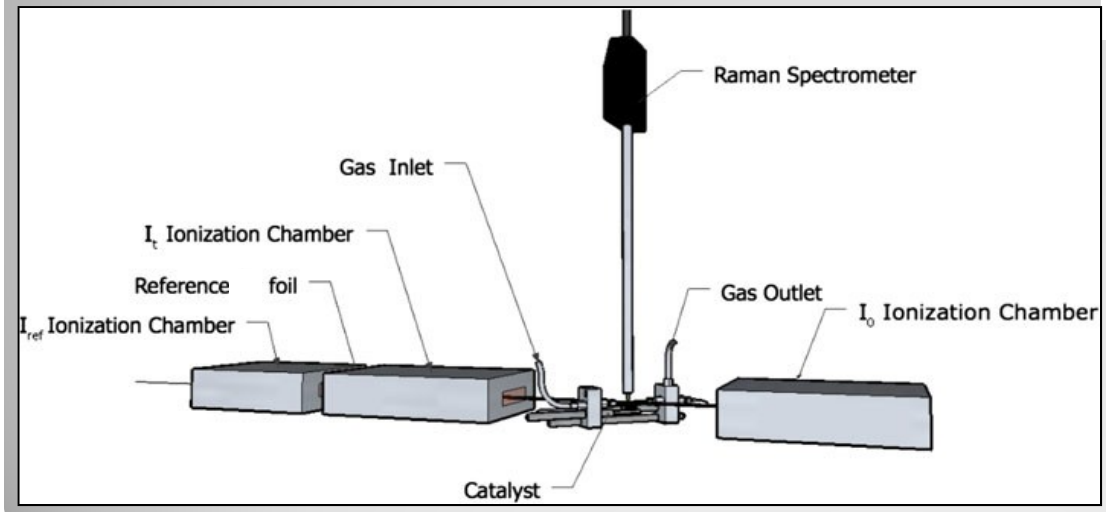




Raman Principle, XAS/Raman Schematics





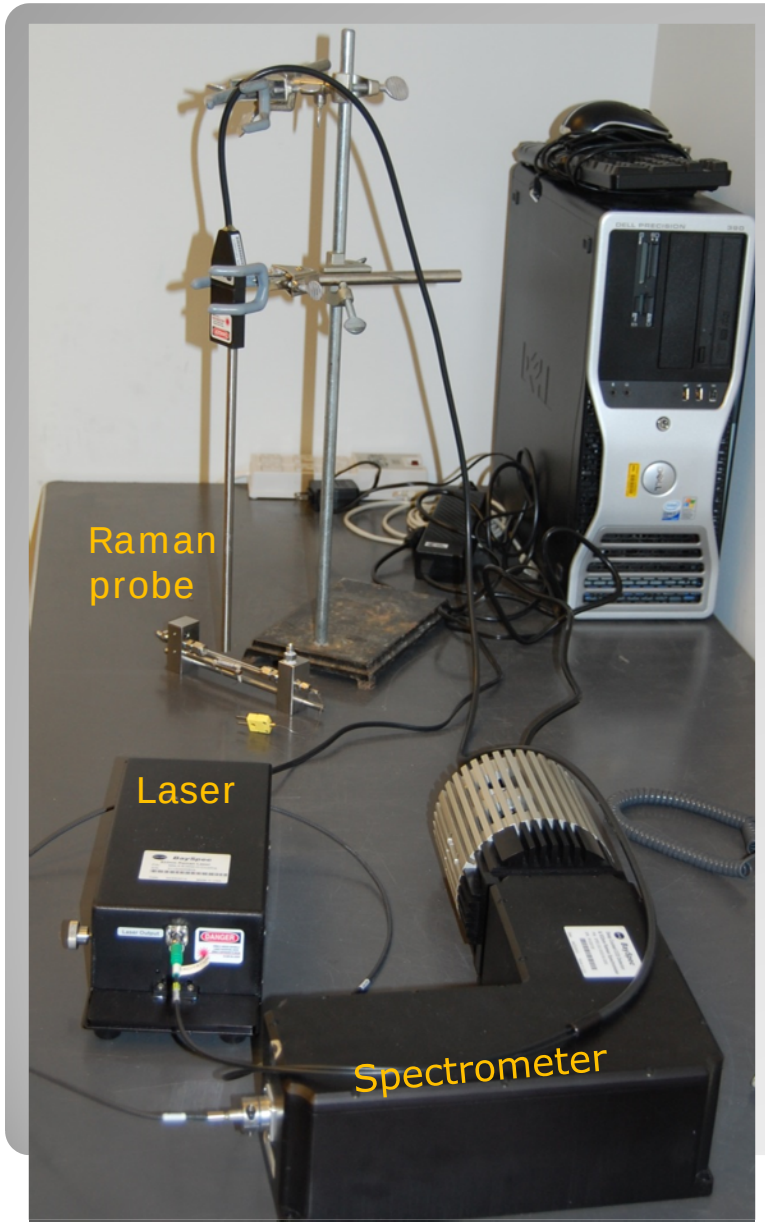


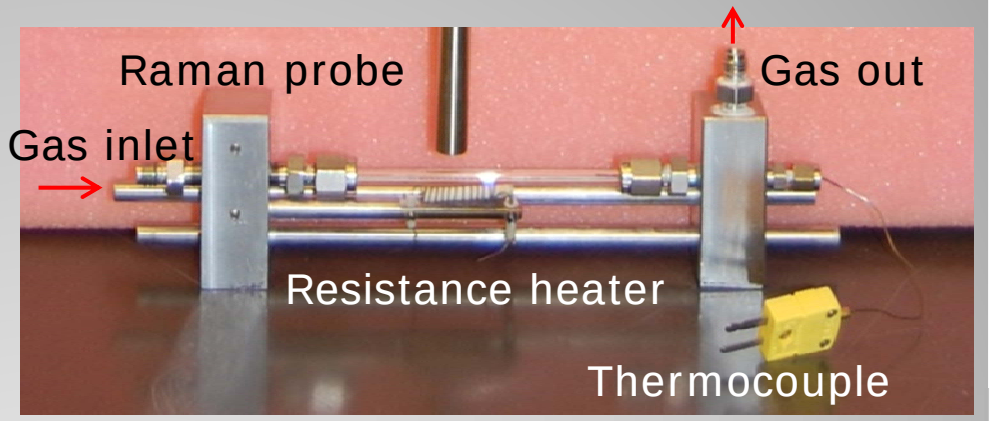
Spectrum arises as a consequence of the change in the <u>polarizability</u> of the molecule.

Raman active vibrations are often silent in IR, and *vice versa*. Thus, IR and Raman are complementary techniques.

- 23 mW, 532 nm Laser excitation
- Non-contact Raman probe provides both excitation and signal through fiber optics

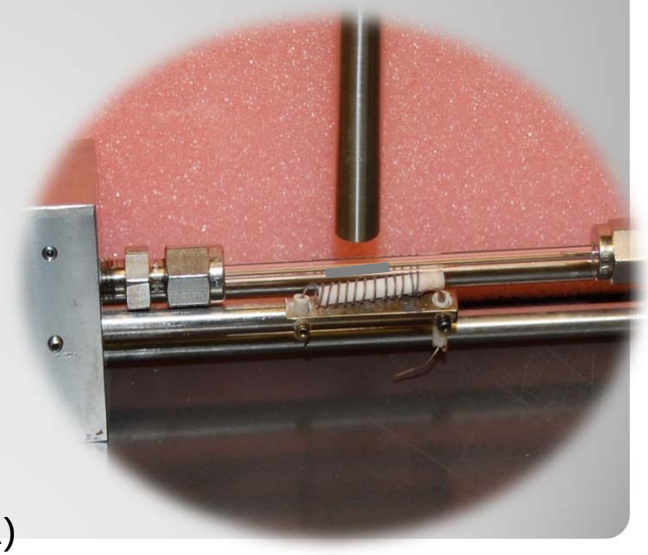
XAS/Raman Setup



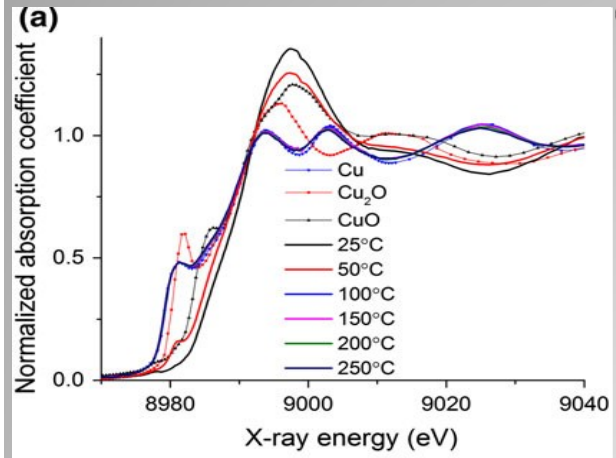


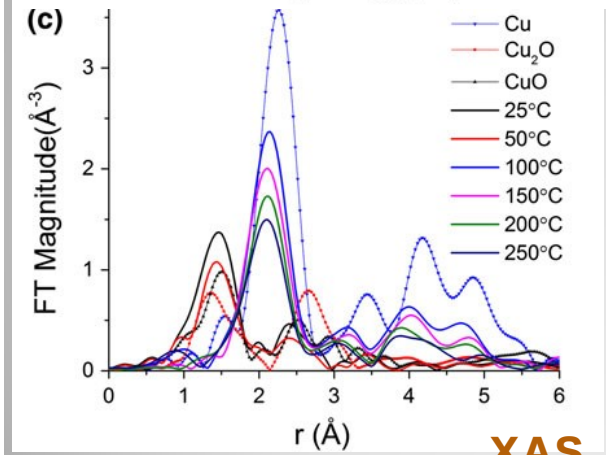
Claussen flow cell tubing:

- 1 mm OD, 0.9 mm ID quartz tube, XAS > 7 keV
- 3.2 mm OD, 3 mm ID quartz tube, XAS / 10 keV
- Product Analysis Techniques (RGA)

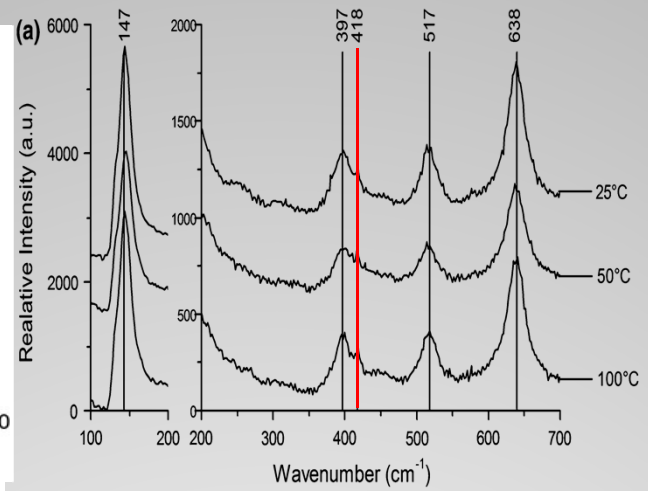


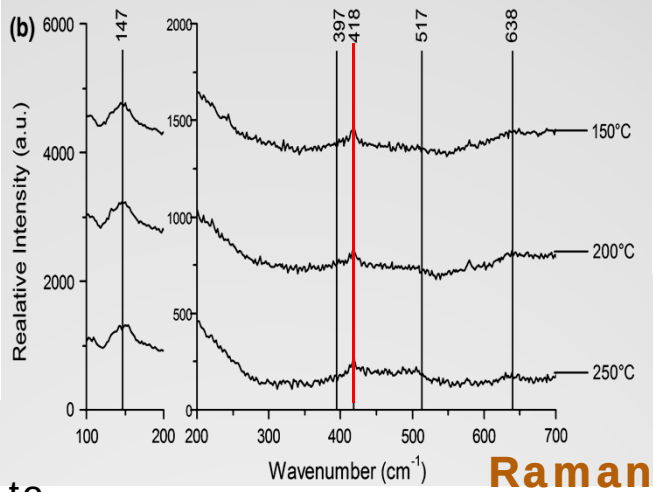
XAS / Raman / RGA examples: CO→ CO_2 conversion on CuO_x / TiO_2



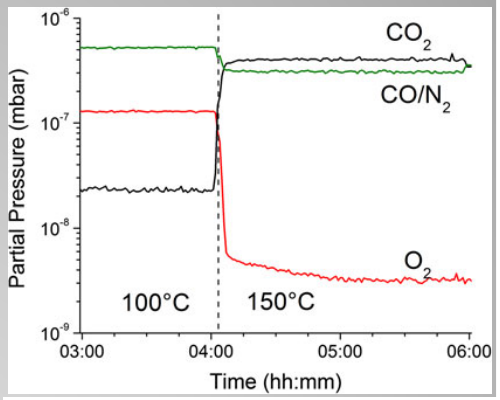


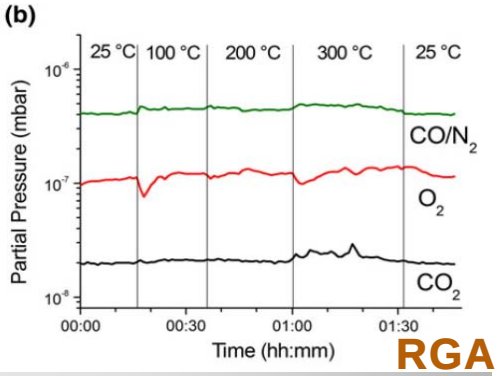
XAS





Raman





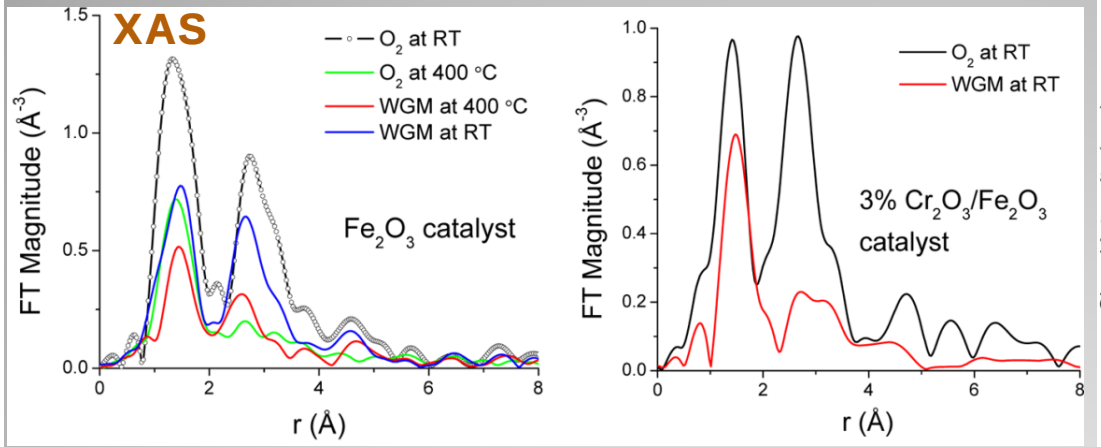
RGA

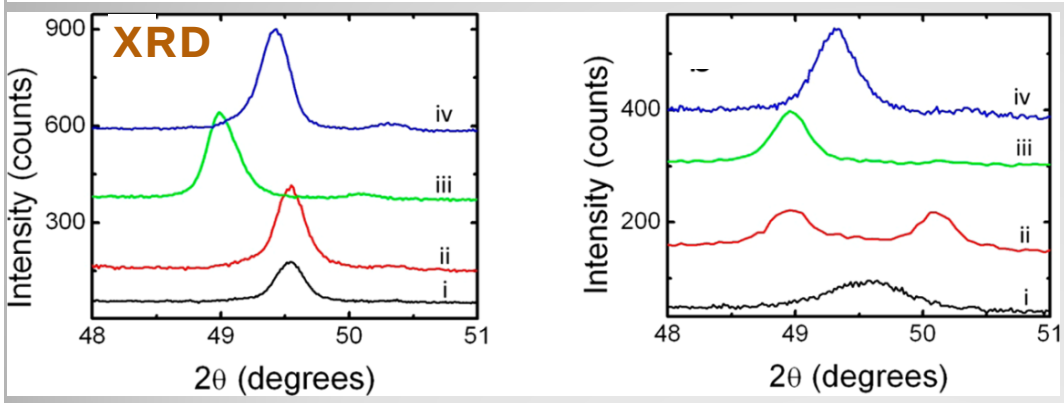
CuO_x / TiO_2 (anatase) is active for CO → CO_2 conversion, whereas pure TiO_2 is not.

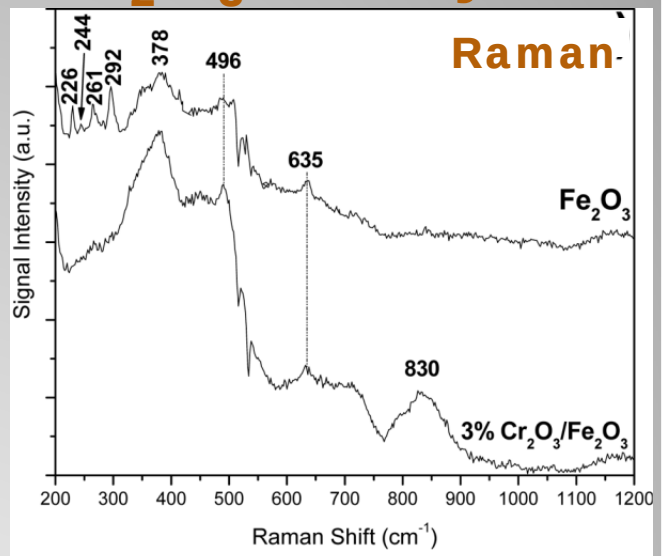
Only with the combination of Raman and XAS it was possible to detect both Cu metallic phase and Cu_2O: Metallic Cu insensitive in Raman, detectable by XAS; Cu_2O identified with Raman, XAS may overlook it due to the dominating Cu metal lines.

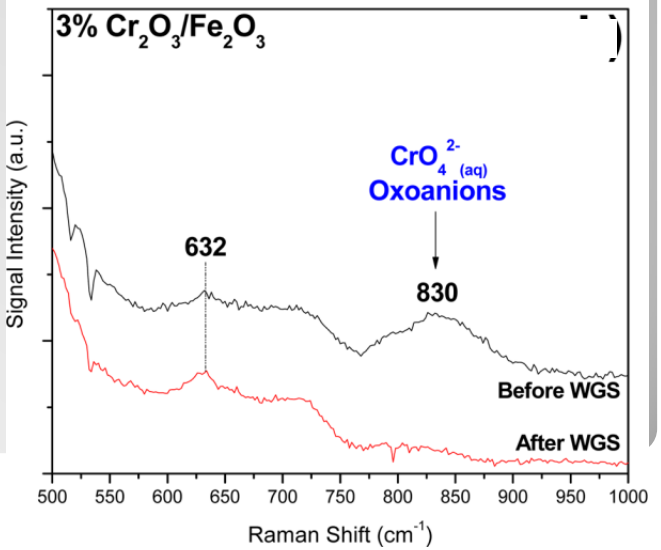
A. Patlolla et al., *Topics Catal.* **56** (2013) 896.

Combined XAS / XRD / Raman study of WGS on pure and Cr_2O_3-stabilized Fe_2O_3 catalysts









- Activation of catalyst for WGS follows the partial CO-reduction of oxide phases at elevated temperatures.
- Combination of XAS and XRD show short- and long-ordered or disordered phases in the catalysts.
- Raman provides insight in role of the catalytic components in WGS reaction.

A.Patlolla et al., *ACS Catal.*, **2** (2012) 2216.

Acknowledgements:

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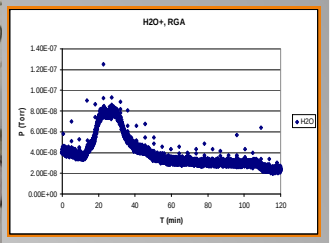
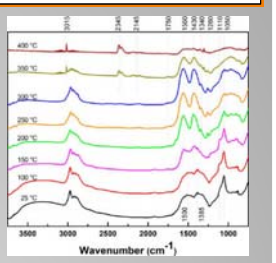
Qi Wang, Steve Ehrlich,
Anatoly Frenkel

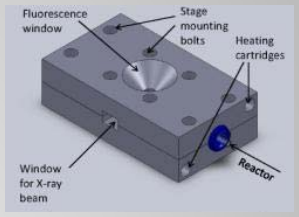
Claussen cell modifications:
Ayman Karim, Marc Porosoff

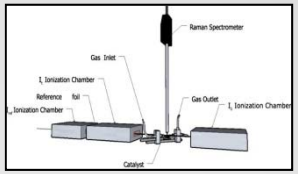
XAS/Raman:
Anitha Patlolla, Yuanyuan Li,
Philipp Baumann, Anatoly Frenkel

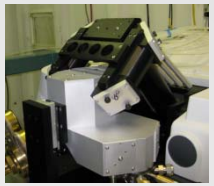
Instrumentation: Thermo Nicolet,
Harrick Scientific, BaySpec, Inc.

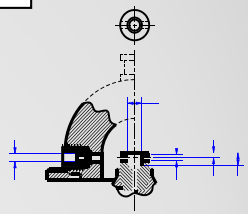












Thank you!