Overview of surface science and catalysis

by Qifei Wu

- Correlations between reactivity and structure
- Heterogeneous catalysis: e.g. hydrodesulfurization, CO oxidation, Ammonia synthesis
- Catalytic surfaces: single crystal transition metals, metal nanoparticles (Au), metal oxides, sulfides, carbides
- Methods and techniques: UHV-STM, XPS, TPD; XRD; DFT

Abbreviations

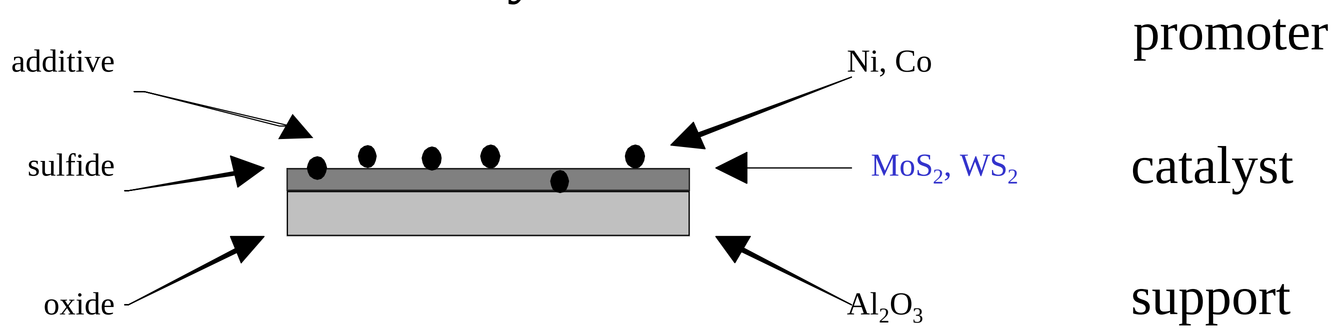
- STM: scanning tunneling microscopy
- TPD: temperature programmed desorption
- XPS: X-ray photoelectron spectroscopy
- XRD: X-ray diffraction
- DFT: density functional theory
- XAFS: X-ray absorption fine structure

Background of hydrodesulfurization catalysis

- Crude oil contains S-impurity (R-S; environmental hazard)

$$H_2 + R\text{-}S \xrightarrow[P,\ T]{\text{catalyst}} RH + H_2S$$

- Commercial catalysts



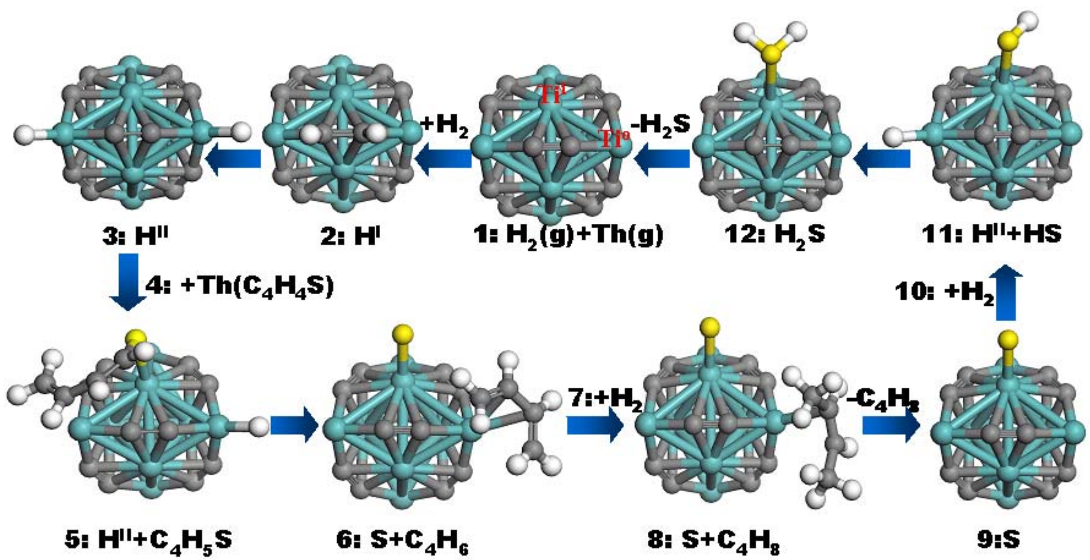
- Novel materials: Sulfides (RuS_2), carbides (MoC, TiC)

Density Functional Theory in Catalysis

Employ DFT to understand the underlying mechanism of a catalytic reaction, and therefore achieve the rational design for catalysis.

Hydrodesulfurization (HDS) on metcar nanoparticles

$$C_4H_4S(g) + 3H_2(g) \rightarrow C_4H_8(g) + H_2S(g)$$



Ti_8C_{12}

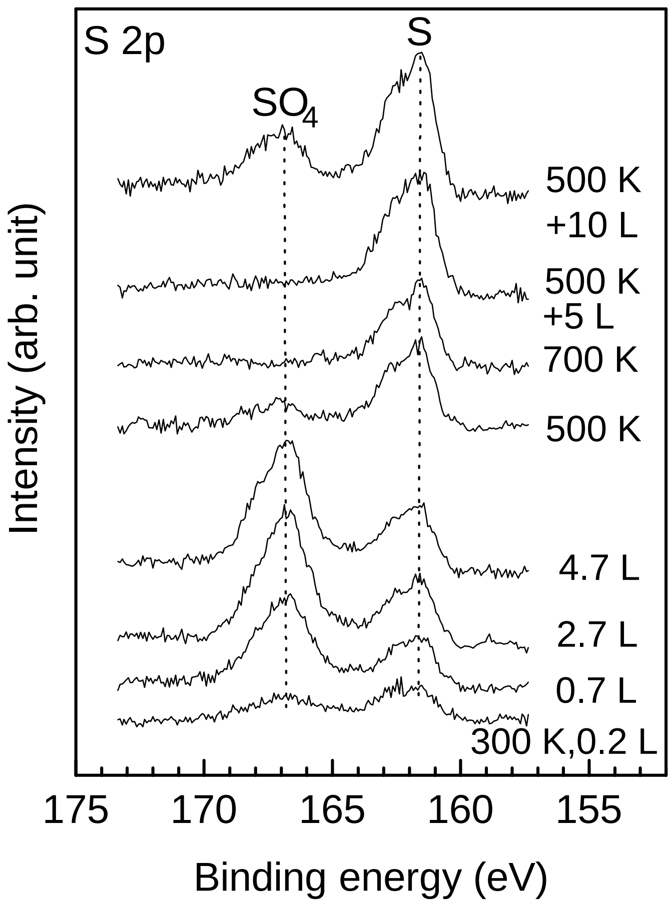
Courtesy of Ping Liu

According to our DFT calculations:

- Metcars are the better catalysts for HDS than the other metal carbide materials.
- Metcars have better properties than the commercial catalyst for HDS.

High resolution X-ray photoelectron spectroscopy

U7a

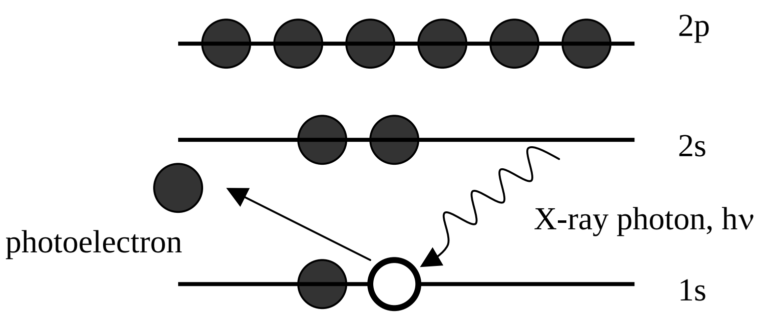


Desulfurization

Destruction of SO_2 on Ru/TiO_2(110). Photoemission data of S 2p after SO_2 being dosed on the Ru/TiO_2(110) surface, which was prepared by dosing ruthenium carbonyl on to TiO_2(110) for 80 min at RT and then heating to 700 K. It was found that SO_2 will dissociate on the Ru/TiO_2(110) surface to form atomic S adsorbates (binding energy ~ 161.6 eV) and molecular (SO_4) adsorbates (binding energy ~ 166.6 eV). The spectra were taken at a photon energy hν = 380 eV. This work was done by **Xueying Zhao**, et al.

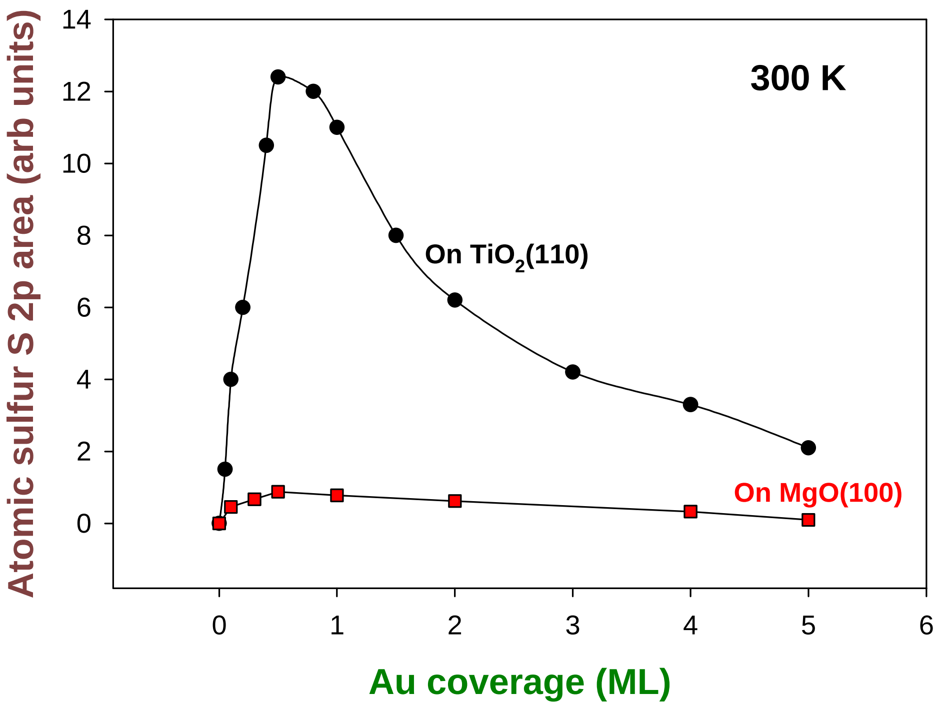
Ru/TiO_2

$SO_2 \rightarrow S$



Au nanoparticles in desulfurization

Sulfur dioxide destruction



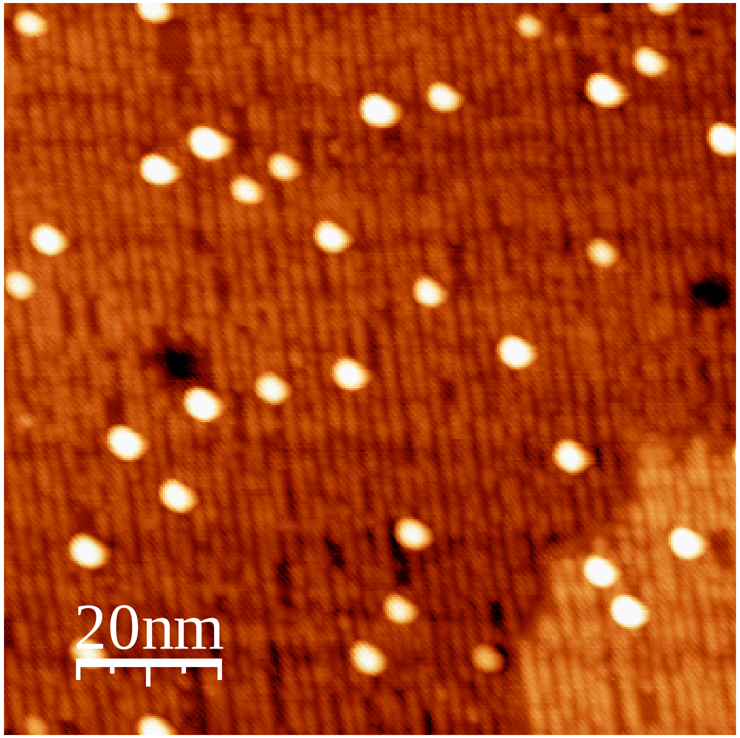
Support effect

Au/TiO_2

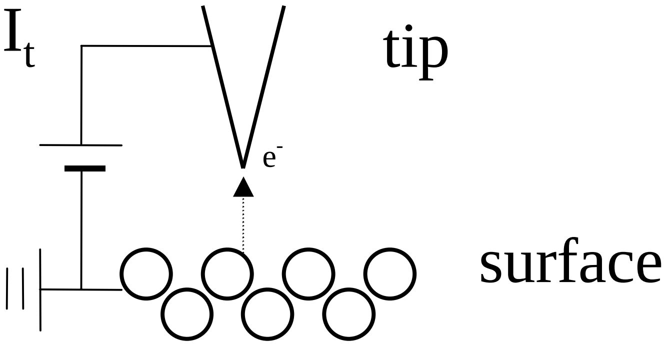
$SO_2 \rightarrow S$

Magic Au nanoparticles

STM



Au/TiO_2(110)

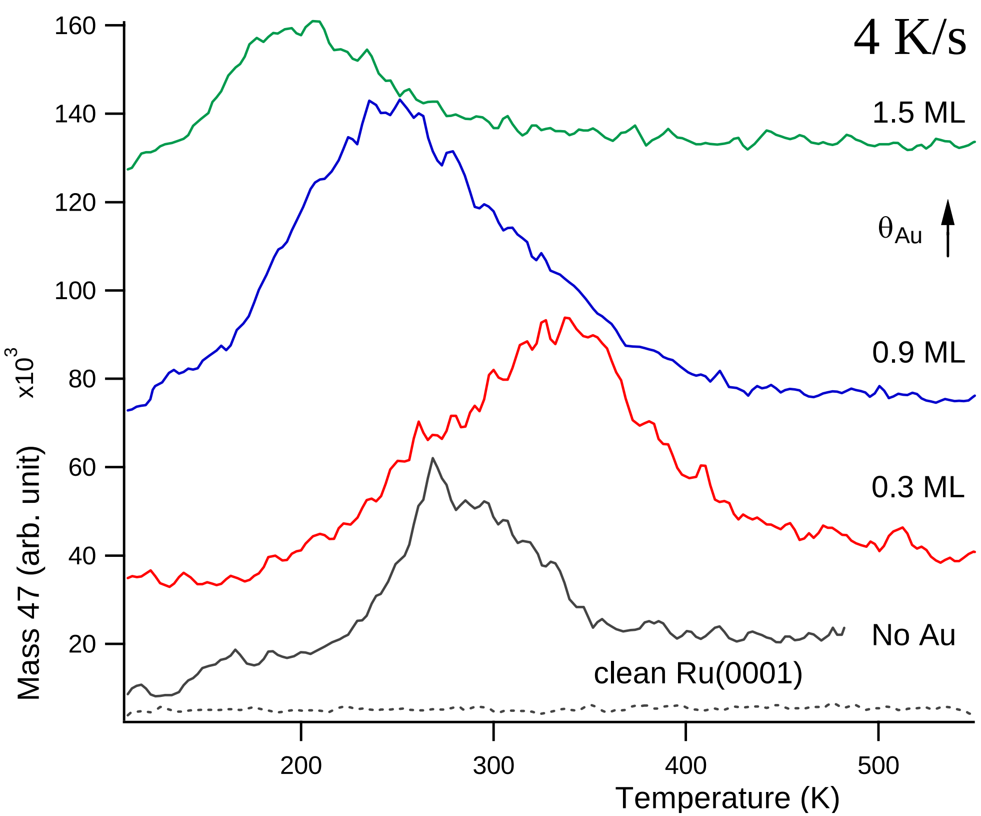


Bulk gold: unreactive
Nano gold: striking reactivity

Gold **nanoparticles** (~ 3 nm) on titania: much more active than commercial catalysts

Au nanoparticles in LT CO oxidation

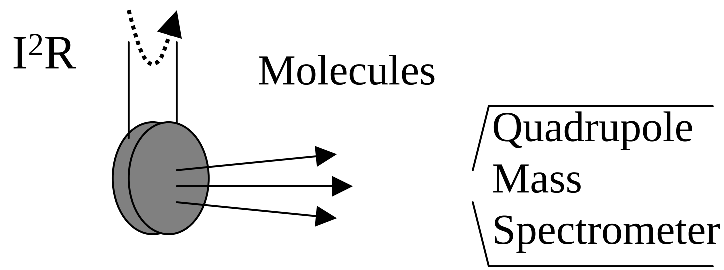
$^{13}C^{16}O^{18}O$ yield

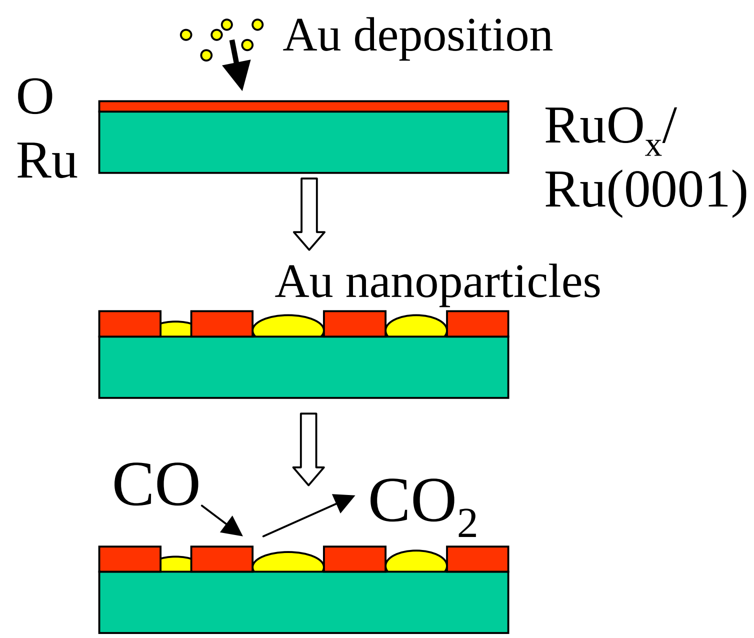


Au/RuO_x

$$CO_a + O_a \rightarrow CO_2$$

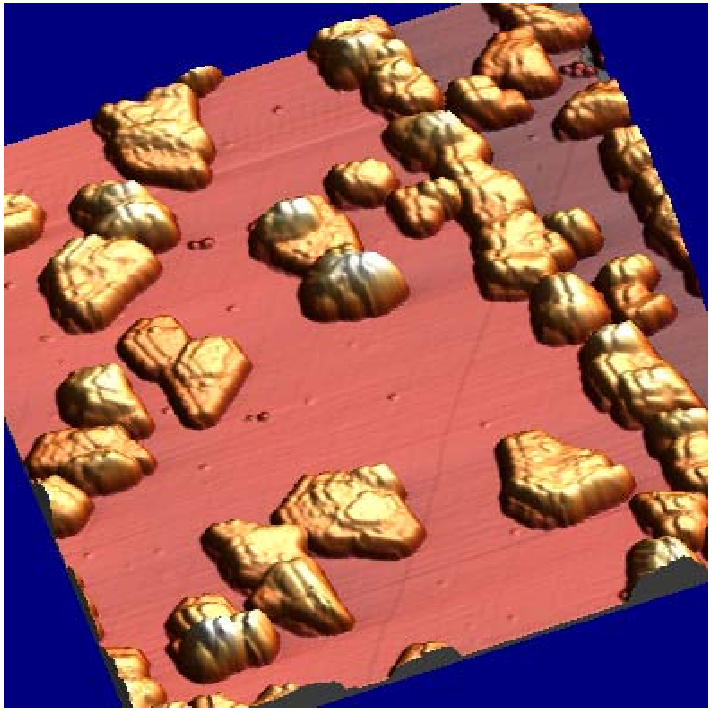
TPD





Ammonia synthesis

STM



200 nm x 200 nm

Ru/graphite

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

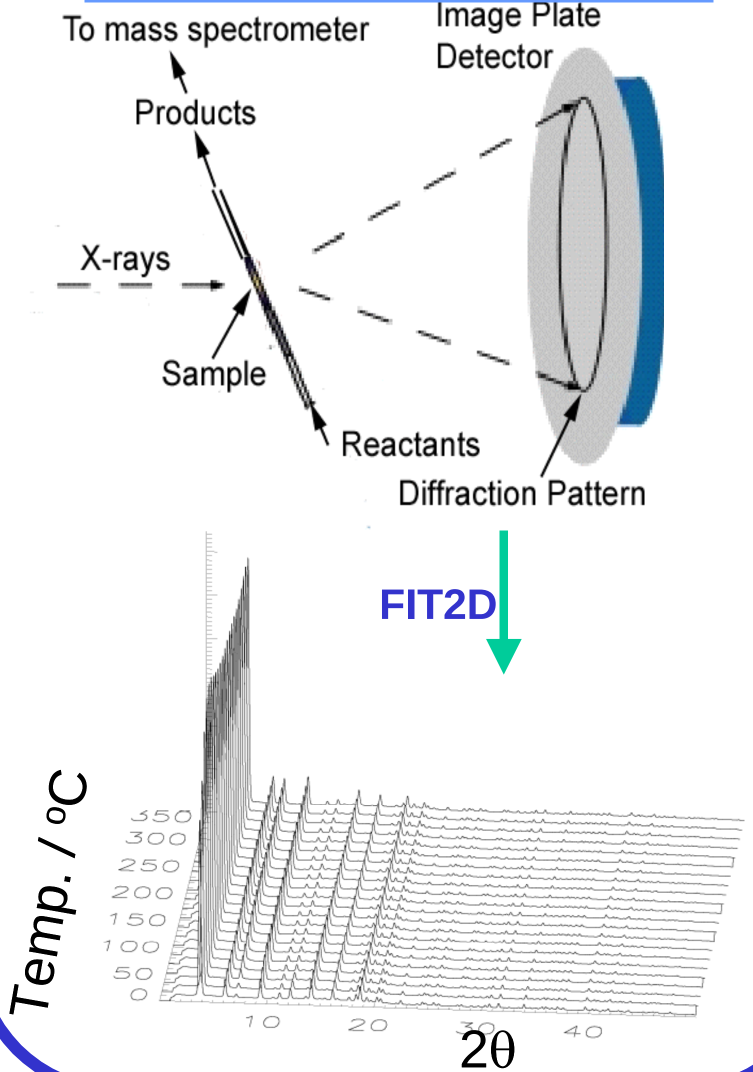
Fe based catalyst: 150 atm, 400 C

Ru/C catalyst: lower T, higher reactivity

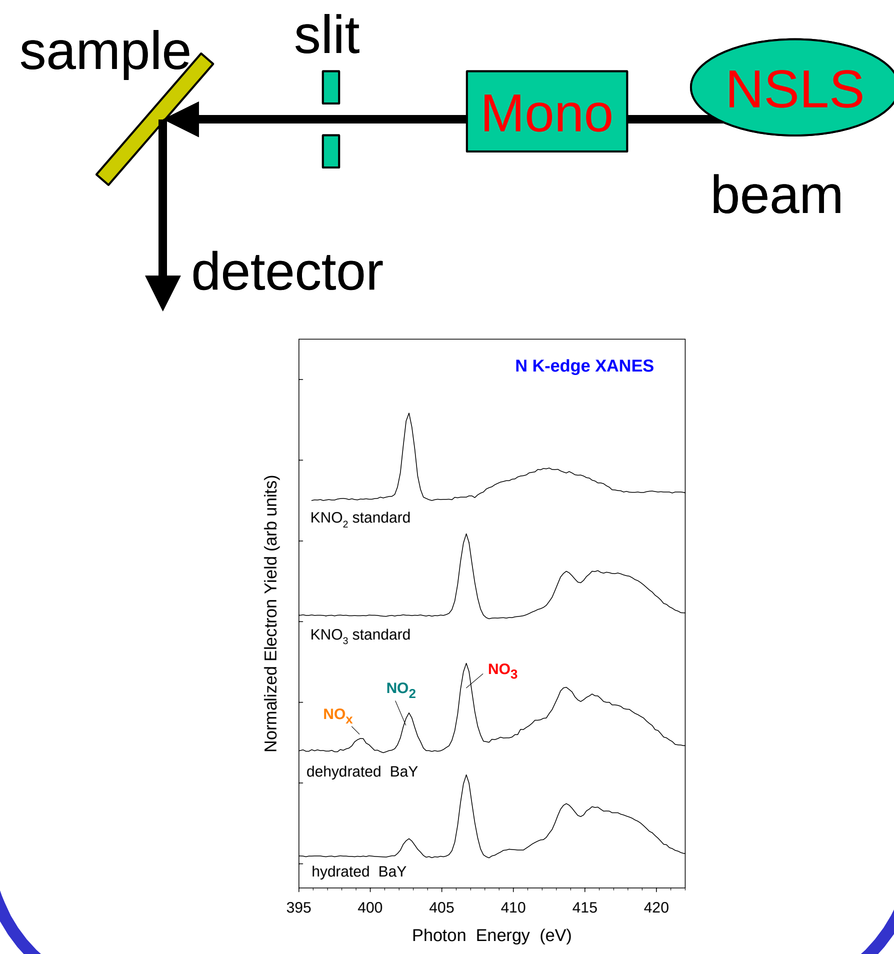
Z. Song et. al, *J. Am. Chem. Soc.*, 126 (2004) 8576-8584

Synchrotron-based *in situ XRD*

TR-XRD at X7B of NSLS



XAFS at U7A



CHEMISTRY

Courtesy of Xianqin Wang

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