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)

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

- Commercial catalysts

- Novel materials: Sulfides (RuS\textsubscript{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

\[
C_4H_4S(g) + 3H_2(g) \rightarrow C_4H_8(g) + H_2S(g)
\]

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.

\( \text{Ti}_8\text{C}_{12} \)

Courtesy of Ping Liu
High resolution X-ray photoelectron spectroscopy

Desulfurization

Destruction of SO₂ on Ru/TiO₂(110).
Photoemission data of S 2p after SO₂ being dosed on the Ru/TiO₂(110) surface, which was prepared by dosing ruthenium carbonyl on to TiO₂(110) for 80 min at RT and then heating to 700 K. It was found that SO₂ will dissociate on the Ru/TiO₂(110) surface to form atomic S adsorbates (binding energy ~ 161.6 eV) and molecular (SO₄) 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/TiO₂
SO₂ → S
Au nanoparticles in desulfurization

Sulfur dioxide destruction

Support effect

\[
\text{Au/TiO}_2
\]

\[
\text{SO}_2 \rightarrow S
\]
Magic Au nanoparticles

STM

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

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

<table>
<thead>
<tr>
<th>Mass 47 (arb. unit)</th>
<th>1.5 ML</th>
<th>1.0 ML</th>
<th>0.9 ML</th>
<th>0.3 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>4 K/s</td>
<td>160</td>
<td>140</td>
<td>120</td>
<td>100</td>
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</table>

TPD

Quadrupole Mass Spectrometer

Au deposition

CO$_a$ + O$_a$ $\rightarrow$ CO$_2$

$\theta_{\text{Au}}$

$\text{I}^2\text{R}$$\text{RuO}_x$/Ru(0001)

Au nanoparticles

CO$_2$
Ammonia synthesis

STM

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]

Fe based catalyst: 150 atm, 400 C

Ru/C catalyst: lower T, higher reactivity


200 nm x 200 nm

Ru/graphite
Synchrotron-based in situ XRD

TR-XRD at X7B of NSLS

To mass spectrometer

Products

Image Plate Detector

X-rays

Sample

Reactants

Diffraction Pattern

FIT2D

XAFS at U7A

sample

slit

Mono

NSLS

beam

detector

Photon Energy (eV)

395 400 405 410 415 420

Normalized Electron Yield (arb units)

N K-edge XANES

KNO_{2} standard

NO\textsubscript{3}

NO\textsubscript{2}

NO\textsubscript{x}

dehydrated BaY

hydrated BaY

Courtesy of Xianqin Wang