Molecular Simulation for Catalysis

Wei-Xue Li

University of Science and Technology of China
Hefei National Laboratory for Physical Sciences at the Microscale
Catalysis, Surface Science, Theory

1918 Nobel Prize
Fritz Haber
Ammonia Synthesis

1918 Nobel Prize
Fritz Haber
Ammonia Synthesis

Ammonia synthesis

Nobel Prize (2007)
G. Ertl (Fritz-Haber Institute MPG)
Chemical Process of Solid Surface

Nobel Prize (1998)
W. Kohn
Density Functional Theory
Sabatier Principle (1912):
The interaction between the catalysts and the substrate should be just right: neither too strong nor too weak.
Active Sites: Structure Sensitivity

**Morphology**

Ammonia synthesis:
Fe (111) = 400 Fe (110)
Fe (111) = 15 Fe (100)


**Size**


**Boundary**

Fu, Li, Ma, Bao, Science 328 (2010) 1141

**Crystal Phase Effect**

JACS 135 (2013) 16284

JACS 139 (2017) 2267

Face Centered Cubic Cobalt

Hexagonal Close Packed Cobalt

H-assisted Route

Activity

Low

High

Direct Route
Stability of NanoCatalysts

High Surface Area

Quantum Size Effect


Syngas Conversion

Morphology / Crystallography, Strain, Interface

CO Activation

\[
\begin{align*}
\text{CO} + \text{H} & \rightarrow \text{C} + \text{O} + \text{H} \rightarrow \text{CH} + \text{O} \\
\text{CO} + \text{H} & \rightarrow \text{CHO} \quad \rightarrow \text{CH} + \text{O}
\end{align*}
\]

Carbon Chain Growth (Co, Fe, Ru)

\[
\begin{align*}
\text{CH}_x + \text{CH}_y & \rightarrow \text{CH}_x \text{CH}_y \\
\text{CH}_x \text{CHO} & \rightarrow \text{CH}_x \text{CH} + \text{O}
\end{align*}
\]

Oxygenates (Rh)

\[
\begin{align*}
\text{CH}_x + \text{CO} & \rightarrow \text{CH}_x \text{CO} \\
\text{CH}_x + \text{CHO} & \rightarrow \text{CH}_x \text{CHO}
\end{align*}
\]

Size Effect of Co Catalysts for FTS

Low activity at small size (origin remains in debates)
- Blocking of edge/corner by CO
- Absence of B5 site
- Oxidization
HCP Co was more active than FCC Co! Why?

Cobalt carbide not active for FTS
Equilibrium Morphology

\[ \Delta G = \min \left\{ \sum_{i} f_i \times \gamma_i \right\} \]

\( \gamma_i \): surface energy
\( f_i \): ratio of facet exposed

**Gibbs-Wulff Theorem:**

\[ \frac{\gamma_1}{d_1} = \frac{\gamma_2}{d_2} = \ldots = \frac{\gamma_n}{d_n} \]

\( d \): length from wulff point to the surface
Equilibrium Morphology of FCC Cobalt

Calculated surface energy of Fcc Co (J/m²)

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>γ</th>
<th>(hkl)</th>
<th>γ</th>
<th>(hkl)</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>2.04</td>
<td>(221)</td>
<td>2.32</td>
<td>(110)</td>
<td>2.41</td>
</tr>
<tr>
<td>(211)</td>
<td>2.42</td>
<td>(100)</td>
<td>2.47</td>
<td>(311)</td>
<td>2.49</td>
</tr>
<tr>
<td>(321)</td>
<td>2.49</td>
<td>(320)</td>
<td>2.55</td>
<td>(210)</td>
<td>2.60</td>
</tr>
<tr>
<td>(310)</td>
<td>2.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Gibbs-Wulff Theorem:

\[ \frac{\gamma_1}{d_1} = \frac{\gamma_2}{d_2} = \ldots = \frac{\gamma_n}{d_n} \]

d: length from Wulff point to the surface

Liu, Su, Li, JACS (2013) 135 (2013) 16284-16287
CO Adsorption and Dissociation on FCC Co

CO (gas) + * → CO* → C* + O*

<table>
<thead>
<tr>
<th>facet</th>
<th>$E_{ads}$</th>
<th>$E_{act}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>$-1.61$</td>
<td>2.48</td>
</tr>
<tr>
<td>(100)</td>
<td>$-1.71$</td>
<td>1.49</td>
</tr>
<tr>
<td>(311)</td>
<td>$-1.71$</td>
<td>1.56</td>
</tr>
<tr>
<td>(110)</td>
<td>$-1.61$</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Adsorption structural less sensitive
Dissociation highly sensitive

Co (111)

Co (311) 1.78 Å
Morphology of HCP and FCC Cobalt

- **Point Group: D_{3h}**
- (10-12) + (10-11)+(10-10) facets covers 75 % of surface area

- **Point Group: O_{h}**
- (111) facets covers 70 % of surface area

---

Liu, Su, Li, JACS (2013) 135 (2013) 16284-16287
**CO Adsorption & Dissociation**

CO (gas) + * → CO* → C* +O*

## HCP Cobalt

<table>
<thead>
<tr>
<th>facet</th>
<th>$E_{ads}$</th>
<th>$E_{act}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10–11)</td>
<td>−1.85</td>
<td>1.21</td>
</tr>
<tr>
<td>(10–10)</td>
<td>−1.70</td>
<td>1.79</td>
</tr>
<tr>
<td>(0001)</td>
<td>−1.64</td>
<td>2.46</td>
</tr>
<tr>
<td>(10–12)</td>
<td>−1.77</td>
<td>1.34</td>
</tr>
<tr>
<td>(11–20)</td>
<td>−1.65</td>
<td>1.39</td>
</tr>
<tr>
<td>(11–21)</td>
<td>−1.82</td>
<td>1.07</td>
</tr>
</tbody>
</table>

## FCC Cobalt

<table>
<thead>
<tr>
<th>facet</th>
<th>$E_{ads}$</th>
<th>$E_{act}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>−1.61</td>
<td>2.48</td>
</tr>
<tr>
<td>(100)</td>
<td>−1.71</td>
<td>1.49</td>
</tr>
<tr>
<td>(311)</td>
<td>−1.71</td>
<td>1.56</td>
</tr>
<tr>
<td>(110)</td>
<td>−1.61</td>
<td>1.47</td>
</tr>
</tbody>
</table>

**Adsorption structural insensitive**

**Dissociation sensitive; More active facets on HCP Co**

*Liu, Su, Li, JACS (2013) 135 (2013) 16284-16287*
Why HCP Co is more active to dissociate CO?

Flexibility of formation of the favorable active sites:
4-fold site for C and 3-fold site for O

Liu, Su, Li, JACS (2013) 135 (2013) 16284-16287
CO Dissociation Rate

\[ r = k\theta^*_\text{CO}\theta^* = kP_{\text{CO}}/(1 + KP_{\text{CO}})^2 \]

- Strong morphology effect for HCP Co
- Hcp Co (10-11) is abundant and highly active

Liu, Su, Li, JACS (2013) 135 (2013) 16284-16287
CO Dissociation under H₂

CHO* \rightarrow CH* + O*

Potential Energy (eV)

(A) HCP Co

(B) FCC Co

Direct Route

H-assisted Route
HCP versus FCC for Cobalt catalysts

Face Centered Cubic Cobalt

Hexagonal Close Packed Cobalt

H-assisted Route  Activity  Direct Route
Low  High

Liu, Su, Li, JACS (2013) 135 (2013) 16284-16287
Why Crystal Phases Matter?

Different crystal phases have structures with distinct intrinsic activity and site density!
How Different Crystal Phases Formed

Supported nanocatalysts could transit to different crystal phase under working conditions.

Different phases (even in metastable) could be synthesized.
How Different Crystal Phases Formed

Under working conditions, metal phase could transit to oxide and carbide phase

- Active Phases
- Active Sites
- Mechanism
- Stability

Oxide and carbide have completely different coordination, electronic properties
Cobalt Carbide

*Inactive Phase: deactivation for FTS

*Noble-metal like may be used to replace the precious metals.

ACS Catal. 2015, 5, 3620-3624
CO Activation on Co and Co$_2$C

- Co$_2$C: molecular adsorption, thermal neutral
- Co: dissociative adsorption, exothermic

ACS Catal. 2015, 5, 3620-3624
Alcohol Synthesis at Co/Co$_2$C interface

- Co$_2$C site for CO molecular adsorption
- Co site for CO dissociation and CHx formation

CO + CH$_2$ $\rightarrow$ CH$_2$CO

<table>
<thead>
<tr>
<th>Transition state for CO insertion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@Co$_2$C interface</td>
</tr>
<tr>
<td>Co$_2$C(111) surface</td>
</tr>
</tbody>
</table>

ACS Catal. 2015, 5, 3620-3624
# High alcohol Synthesis at Co/Co$_2$C Interface

Free from precious metal catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO Con%</th>
<th>Selectivity (C %)</th>
<th>Alcohol distribution (C %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$C_1$-$C_4$</td>
<td>$CO_2$</td>
</tr>
<tr>
<td>Co@Co$_2$C/AC1</td>
<td>71.4</td>
<td>20.8</td>
<td>5.1</td>
</tr>
<tr>
<td>Co/AC2</td>
<td>55.5</td>
<td>31.5</td>
<td>7.6</td>
</tr>
</tbody>
</table>

493 K, 3.0 MPa, $H_2/CO=2:1$, 33.6 mL min$^{-1}$

*ACS Catal. 2015, 5, 3620-3624*
**Co$_2$C Nanoprisms for Direct Production of Lower Olefins**

**Table 1 | Catalytic performance of the CoMn catalyst at different H$_2$/CO ratios and reaction pressures**

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>H$_2$/CO ratio</th>
<th>CO conversion (C%)</th>
<th>CO$_2$ selectivity (C%)</th>
<th>Product selectivity (C%, CO$_2$-free)</th>
<th>Olefin/paraffin ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH$_4$</td>
<td>C$_{2-4}$</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>31.8</td>
<td>47.3</td>
<td>5.0</td>
<td>60.8</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>11.5</td>
<td>48.0</td>
<td>3.7</td>
<td>50.0</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>6.3</td>
<td>48.3</td>
<td>2.4</td>
<td>45.1</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>14.3</td>
<td>48.4</td>
<td>4.2</td>
<td>44.3</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>23.6</td>
<td>48.0</td>
<td>3.7</td>
<td>41.2</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>28.6</td>
<td>46.6</td>
<td>4.6</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Reaction conditions: 250°C, 2,000 ml h$^{-1}$ g$_{cat}$$^{-1}$ (where g$_{cat}$ denotes grams of catalyst). Oxy., oxygenates.

Active Sites: Basis for design of better catalysts

- Intrinsic activity (TOF)

- Site Distribution

Size, Morphology and Phase
Ruthenium Catalysts

Morphology from Wulff Construction based on DFT

Li, Zhang and Ma, JACS 139 (2017) 2267
(0001) step-B has the lowest barrier (0.93 eV) but the density is low
(10-11) facet is the most abundant but the barrier is high (>1.35 eV)
→ low specific activity

Li, Zhang and Ma, JACS 139 (2017) 2267
FCC Ruthenium for CO Activation

- (100), (211), (110) open facets as well as (111) step B fall in the modest barrier of [1.12-1.20 eV]

- Denser sites with modest barriers → higher specific activity

Li, Zhang and Ma, JACS 139 (2017) 2267
Synthesis of FCC Ru Catalysts

Li, Zhang and Ma, JACS 139 (2017) 2267

- Using FCC Pt as core, Fcc Ru was synthesized
- More open facets exposed as verified below
Ru Catalysts for aqueous Fischer-Tropsch Synthesis

Specific activity of FCC Ru is six times larger than HC Ru
Apparent Barrier of Ru Catalysts for FTS

- FTS barrier of FCC Ru (1.21 eV) is higher than HCP Ru (1.05 eV)
- Density of the active sites ~ 100 times higher
More open facets of FCC Ru Exposed

Exp

Simulation

(110), (112) and (311) facets cover ~ 60% surface exposed

Excellent agreement with theoretical prediction

Li, Zhang and Ma, JACS 139 (2017) 2267
Catalysis based on Crystal Phases of Catalysts

**Metal Crystal Phases**
- Different Symmetry
- Different Morphology

**Metal Compounds**
- Different Chemical State
- Different Coordination
  - Alloys, Oxide
  - Carbide, Sulfides

<table>
<thead>
<tr>
<th>Metal Crystal Phases</th>
<th>Metal Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc, Ti, V, Gr, Mn, Fe, Co, Ni, Cu, Zn</td>
<td>Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd</td>
</tr>
<tr>
<td>La, Hf, Ta, W</td>
<td>Ir, Pt, Au, Hg</td>
</tr>
<tr>
<td>hcp</td>
<td>hcp</td>
</tr>
</tbody>
</table>

---

University of Science and Technology of China

Hefei National Laboratory for Physical Sciences at the Microscale
Thank you

Wan Qixin
Shasha Wang
Chuanqi Huang
Bingyan Zhang
Peipei Chen
Hao Lin
Minzhen Jian
Chuwei Zhu
Shiyan Cao

NSFC, USTC, CAS, MOST

Dr Jinxun Liu (刘进勋)
Dr. Runhai Ouyang (欧阳润海)
Sulei Hu (胡素磊)

Prof. Ding Ma (Peking U)
Prof. Yunjie Ding (DICP)
Prof. Weixin Huang (USTC)
Prof. Junling Lu (USTC)
Prof. Xinhe Bao (DICP/Fudan)