Heterogeneous catalysis over first-row transition metal nanoparticles

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• Metallic nanoparticles show many interesting types of catalytic behavior.
• Sintering is inevitable under severe reaction conditions.

► By Mobil researchers in 1992
   MCM-41, MCM-48, and MCM-50
   \[ V_p > 1 \text{ cc/g}; \quad D_p = 20 \sim 100\text{Å}; \quad S_{\text{BET}} > 1000 \text{ m}^2/\text{g} \]

► Low diffusion resistance
   Large molecule reaction

► Ion exchangeable

► Alteration of pore size

► Flexible framework structure
   Isomorphous substitution of Si with a broad range of metal ions

Self assembly of surfactant

condensation of silica source

removal of surfactant


Synthesis of metal substituted MCM-41

**Synthesis**

- Cab-O-Sil
- TMASi (10 wt% SiO₂)
- Water
- Metal precursor
- Silica solution
- Silica-Metal solution
- Anti-foaming agent
- Surfactant
- pH adjustment
- Gel
- Autoclaving for 6 days at 100°C

**Post synthesis treatment**

- Final M-MCM-41
  - M: Co or Ni
- Calcining at 540°C for 5 hrs under air
- Calcining at 540°C for 1 hr under He
- Calcining from room temperature to 540°C for 17 hrs under He
- Filtering, washing, and drying
Rapid synthesis

Scheme 3.1

CTAB → P123 → SiO2

Self-assembly of CTAB
Self-assembly of P123
Condensation of silica
Removal of surfactant

Column pressure (Kpsi)
Flow rate (ml/min)

Scheme of the proposed synthetic procedure for chiral mesoporous silica

Nanotechnology, 2010, 21, 165103/1; Journal of physical chemistry C 2010, 114, 14353
Stabilize noble metal nanoparticles

Ship-in-a-bottle confinement

Catalyst synthesis method:
- Direct incorporation vs. impregnation method
- Anchoring effect
- Post-synthesis grafting method

Chemically probed reactions:
- CO2 dry reforming of methane
- SWCNT synthesis
- CO/CO2 methanation
Reducing environment

Direct synthesis of Co-MCM-41
Temperature programmed CO methanation on Co-MCM-41

Co impregnated Si-MCM-41 reduced at 500°C for 30 min

Co-MCM-41 reduced at 700°C for 30 min

Catalysis Today, 2007, 123, 122-132
CO Methanation on Ni-MCM-41

Ni-MCM-41 reduced at 700°C for 30 min

Ni impregnated Si-MCM-41 reduced at 500°C for 30 min

Catalysis Today, 2007, 123, 122-132
Hydrogen production

Steam reforming of methane (SRM)
\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2, \quad \Delta H^0_{298} = 209 \text{ kJ mol}^{-1} \]

Partial oxidation of methane (POM)
\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2, \quad \Delta H^0_{298} = -36 \text{ kJ mol}^{-1} \]

Carbon dioxide reforming of methane (CDRM)
\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2, \quad \Delta H^0_{298} = 247\text{kJ mol}^{-1} \]

Autothermal reforming of methane (ATRM)
\[ \text{CH}_4 + \frac{x}{2}\text{O}_2 + (1-x)\text{H}_2\text{O} \rightarrow \text{CO} + (3-x)\text{H}_2 \]
\[ \text{CH}_4 + x\text{O}_2 + (1-2x)\text{CO}_2 \rightarrow (2-2x)\text{CO} + 2\text{H}_2 \]
CO\textsubscript{2} dry reforming of methane

\[ \text{CH}_4 + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO} \]

Mesoporous material matrix
### Ni-MCM-41

#### Table of Properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel Si/Ni ratio</th>
<th>Ni content (%)</th>
<th>Surface area (m²g⁻¹)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(a)</td>
<td>100</td>
<td>0.3</td>
<td>875</td>
<td>2.8</td>
</tr>
<tr>
<td>Ni(b)</td>
<td>50</td>
<td>0.6</td>
<td>834</td>
<td>2.8</td>
</tr>
<tr>
<td>Ni(c)</td>
<td>25</td>
<td>1.2</td>
<td>635</td>
<td>2.7</td>
</tr>
<tr>
<td>Ni(d)</td>
<td>12.5</td>
<td>3.9</td>
<td>489</td>
<td>2.5</td>
</tr>
<tr>
<td>Ni(e)</td>
<td>8</td>
<td>-</td>
<td>385</td>
<td>-</td>
</tr>
</tbody>
</table>
CO2 dry reforming of methane over Ni-MCM-41

Under H₂ pretreatment
- Ni(b)
- Ni(c)
- Ni(d)

Without H₂ pretreatment
- Ni(d1)
- Ni/MCM-41
- Ni/SiO2

CH₄ conversion, %

Time on stream, h

Applied Catalysis A-General, 2009, 358, 110
Characterization

Ni/SiO$_2$ -------- 21.8
Ni/MCM-41 --- 19.3
Ni-MCM-41 ---------- 6.3

Coke deposition
Ni/SiO$_2$ -------- 10.1
Ni/MCM-41 ----- 8.1
Ni-MCM-41 --------- 5.7
Challenges

- Large scale production of SWCNT with controlled structure and properties.
  - solution - catalytic process
- Controlling the metallic cluster size, which nucleates the growth of SWNT.
  - too small: carbon solubility is zero
  - too big: unwanted carbon species
- Stable metallic clusters at high reaction temperature

Co-MCM-41

TEM data showing particle-tube relation
Narrow diameter distribution of SWCNT (0.8 ±0.05 nm)

Journal of Physical Chemistry B 2004, 108(40), 15565-15571

Co-MCM-41
Reduction temperature of Co $\propto$ pore diameter
<table>
<thead>
<tr>
<th>Pore diameter (nm)</th>
<th>First shell average coordination number</th>
<th>After reduction at 700°C by H₂ for 30 minutes</th>
<th>After CO disproportionation at 800°C for 1 hour</th>
<th>After TPR from room temperature to 900°C and soaked for 1 hr at 900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co-Co</td>
<td>Co-O</td>
<td>Co-Co</td>
<td>Co-O</td>
</tr>
<tr>
<td>1.90 (C10)*</td>
<td>1.15</td>
<td>3.35</td>
<td>6.13</td>
<td>2.03</td>
</tr>
<tr>
<td>2.24 (C12)*</td>
<td>2.97</td>
<td>2.76</td>
<td>6.56</td>
<td>2.01</td>
</tr>
<tr>
<td>2.57 (C14)*</td>
<td>4.65</td>
<td>1.81</td>
<td>6.98</td>
<td>1.54</td>
</tr>
<tr>
<td>2.85 (C16)*</td>
<td>4.86</td>
<td>1.73</td>
<td>7.17</td>
<td>1.36</td>
</tr>
<tr>
<td>3.10 (C18)*</td>
<td>6.31</td>
<td>1.24</td>
<td>7.43</td>
<td>0.70</td>
</tr>
</tbody>
</table>

( )* : carbon number of surfactant

Co metallic cluster size control

pH effect

The graphs illustrate the TCD signal at different pH levels: pH=11, pH=11.5, and pH=12. Each graph shows the temperature in °C on the x-axis and the TCD signal on the y-axis. The data points are represented by different colored lines, with experimental data marked by dots and fitting results by solid lines.

- **pH=11**: Shows a peak at around 750 °C with a TCD signal value of approximately 55.
- **pH=11.5**: Displays a similar peak at 750 °C with a slightly lower TCD signal value of about 50.
- **pH=12**: Exhibits a peak at 700 °C with a TCD signal value of approximately 40.

Additional labels in the graph include:
- **Surface Co oxide**
- **Surface compounds** on the surface, 1, and subsurface, 2
- **Bulk compound** in the pore wall, 3
- **Amorphous silica wall**

**Topics in Catalysis, 2005, 34(1-4), 31-40**
TEOS + CoSO$_4$·7H$_2$O + TEA + H$_2$O

Stirred for 0.5 hrs

Add TEAOH

Aged for 24 hrs

Dred for 24 hr

Hydrothermal Treatment

180°C, 8 hrs

Calcine
tetrahedrally coordinated Co\(^{2+}\) in the framework

typical cobalt mixed oxide peaks

charge transfer between metal and surrounding oxygen

Partial substitution?
Metal anchoring effect (<400°C)

Ni/SiO₂  
RhCr/NaY Zeolite

Tzou et al., Langmuir 1986, 2, 773.

Co-MCM-41 (>700°C)
Impregnation of 1wt% Co on the different supports → reduction at 500°C for 2 hr

1wt% Co impregnated Si-MCM-41

1wt% Co impregnated 1wt% Co-MCM-41
(partially reduced at 500°C for 30 min)

1wt% Co impregnated 1wt% Co-MCM-41

Anchoring effect
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Metal particle size (nm)</th>
<th></th>
<th></th>
<th>Normalized ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reduced at 400°C for 30 min</td>
<td>Reduced at 500°C for 30 min</td>
<td>Reduced at 500°C for 2 hr</td>
<td></td>
</tr>
<tr>
<td>1wt% Co impregnated Si-MCM-41</td>
<td>5.9</td>
<td>8.2</td>
<td>35.9</td>
<td>1</td>
</tr>
<tr>
<td>1wt% Co impregnated pre-reduced 1wt% Co-MCM-41</td>
<td>5.4</td>
<td>5.5</td>
<td>10.7</td>
<td>3.4</td>
</tr>
<tr>
<td>1wt% Co impregnated 1wt% Co-MCM-41</td>
<td>-</td>
<td>-</td>
<td>12.0</td>
<td>3.0</td>
</tr>
<tr>
<td>1wt% Co impregnated 1wt% Ti-MCM-41</td>
<td>-</td>
<td>-</td>
<td>11.4</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Anchoring effect

Co cluster size (nm) vs. Reduction time at 700°C (min)

- 1wt% Co-MCM-41
- 1wt% Co-MCM41
- 1wt% Co-Zr-MCM41
- 1wt% Co-Ti-MCM41

Catalysis Today, 2007, 123, 122-132
All the metals were introduced during MCM-41 hydrothermal synthesis.

For all the samples, $S_g > 900 \text{m}^2\text{g}^{-1}$, pore size: 2.5-2.7 nm.
a. Most of Ni species in MCM-41 catalysts exist in the distorted tetrahedral environment.

b. The local symmetry of Ni varies with the content of Zr, especially over 2Ni-2Zr.

c. Ti species observed, distorted tetrahedral (m), penta-/octahedral (s).

d. Mn species observed, tetrahedral & octahedral.
CO2 dry reforming of methane over Ni-M-MCM-41

(A) CH₄ initial conversion, %

(B) CH₄ conversion, %

Journal of Catalysis, 2009, 266, 380
Various crystalline phases

(1): □, quartz
(2): ○, tridymite
(3): *, graphite carbon
(4): ▼, metallic Ni

a. Stable phase SiO$_2$ formed over 2Ni-1Ti, 2Ni-1Mn and Ni-MCM-41.

b. No crystalline SiO$_2$ found on Ni-Zr system.

c. All Ni-Zr possess good thermal stability, while Ni-Ti and Ni-Mn are reverse.
A: Ni-MCM-41; B: 2Ni-1Zr; C: 2Ni-1Ti; D: 2Ni-1Mn; (E) 2Ni-1Zr illustrating carbon
Total carbon deposition (%): Ni-MCM-41 (4.1) < 2Ni-0.5Zr (5.0) < 2Ni-1.5Zr (5.3) < 2Ni-1Zr (6.0) < 2Ni-2Zr (7.7)
The role of Zr incorporation

- Promote the thermal stability of catalyst.
- Leading to the formation of Ni-ZrO$_2$ boundary sites.
- Facilitate well-dispersion of Ni active sites.
- Increase the reactivity of carbonaceous species.
CO Methanation on Ni-MCM-41 at 400°C

- Ni impregnated Si-MCM-41 reduced at 500°C for 30 min
- Ni-MCM-41 reduced at 700°C for 30 min

Catalysis Today, 2007, 123, 122-132
Occlusion by silica matrix

- CO incorporated & reduced at 700°C for 30 min
- CO impregnated & reduced at 500°C for 30 min
- CO incorporated & reduced at 800°C for 30 min

Graph showing absorbance vs. wavenumber (cm$^{-1}$) with peaks at different temperatures:
- CO in the impregnated & reduced sample at 500°C
- CO in the incorporated & reduced sample at 700°C
- CO in the incorporated & reduced sample at 800°C

Legend:
- CO
- Co$^{2+}$
- Co$^{3+}$

And CO molecules
Co impregnated Si-MCM-41 reduced at 500°C for 30 min

Co-MCM-41 reduced at 900°C for 30 min (complete reduction)

Conversion of CO

Temperature (°C)

Impregnated sample

Incorporated sample

Oclusion by silica matrix
Occlusion by silica matrix

a) Complete coverage

b) Partial coverage

c) Complete exposure
Hydrogen bonding

Refluxing in anhydrous toluene under N2 atmosphere

Ligand Exchange

Post-synthesis grafting method

Grafting

Calcination

nickel (II) acetylacetonate
Ni grafted MCM-41/SBA-15

The reduction peaks shift towards high temperature with Ni loading, suggesting hydrosilicate are easily produced at high Ni content.

Higher reduction peak over Ni-grafted catalysts indicates a strong interaction of metal and support.
Activity sequence at 750°C & 72 h: 5Ni-SBA-15 > 5Ni/MCM-41 > 5Ni/SBA-15 > 5Ni-MCM-41.

The lower H₂/CO ratio over 5Ni/SBA-15 & 5Ni-MCM-41 is related to RWGS due to the presence of high concentration of unreactive CO₂.
The grafted catalysts have lower carbon formation compared to the impregnated counterpart.

The grafted catalysts have more active carbon than the impregnated catalysts.
Ni particle size (nm)

5Ni-SBA-15: 9.2
5Ni/SBA-15: 31.2
5Ni-MCM-41: 7.6
5Ni/MCM-41: 12.1

Deactivation analysis
5Ni-SBA-15: Improved metal dispersion and carbon resistance.
5Ni/SBA-15: metal sintering
5Ni-MCM-41: carbon formation
5Ni/MCM-41: metal sintering + carbon formation
CO2 dry reforming of methane over Ni grafted TUD-1

- Stable activity sequence:
  Ni-GRF > Ni-DHT > Ni-IMP.

- The better anchoring effect of Ni in Ni-grafted TUD-1 is the basis to its improved activity and stability.

- In view of Ni-IMP’s very low and unsustainable activity, Ni sintering is the major reason for its deactivation.

*Applied Catalysis B-Environmental, 2010, 95, 374*
The carbon formed on Ni-DHT and Ni-GRF are mainly relatively inert carbon species.
From BET test, some losses in surface area, pore volume and pore size were seen. However, the meso-porous features still remain.

Peaks assignment in TPH:

For Ni-DHT,
- $506^\circ C$, $\alpha$-carbon,
- $573^\circ C$, $\beta$-carbon,
- $842^\circ C$, $\gamma$-carbon.

For Ni-GRF,
- $576^\circ C$, $\beta$-carbon.
The exposure of well-dispersed smaller Ni particles and good reactivity of carbon species are the two reasons responsible for the improved catalytic activity over Ni-GRF.
Mesoporous materials are good candidates to stabilize first-row transition metal nanoclusters.

Direct synthesis method is simple, better than impregnation, but lack of sophisticated control, not applicable to certain mesoporous materials.

Non-reduced metal oxide can further stabilize the metal nanoparticles by anchoring effort.

Post-synthesis grafting is a promising method, but a bit complicated.

These first-row transition metallic catalysts are active in reactions, e.g., SWCNT production, methanation, dry reforming.
Concluding remarks

- Significant catalytic activity can be obtained at temperatures as low as 500°C over highly ordered Ni-incorporated MCM-41.

- The structural stability and strong anchoring of Zr towards active sites and partial activation of CO2 by Zr are the main influential factors. The decoration of Ni with TiOx and MnOx hindered the accessibility of Ni active sites.

- By post-synthesis grafting Ni onto SBA-15 and MCM-41, a high activity and long-term stability catalyst was found. The superior catalytic behavior was closely related with the strong resistance toward carbon formation and active metal sintering.

- On testing TUD-1 supported Ni catalysts with different preparation method, Ni-grafted TUD-1 also exhibited the highest catalytic activity and catalytic stability. Strong anchoring effect via grafting method is the underlying reason for the small Ni particle size and improved catalytic performance despite a high carbon formation.