Enhancing Stability of Platinum on Silica by Surface Modification
- Application to CO Oxidation -

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1. The aim of this study
Preparation of highly dispersed platinum catalyst with sulfur tolerance and hydrothermal stability

2. Results
Characterization & catalytic performance
- Fresh catalysts
- Sulfated catalysts
- Hydrothermal aged catalysts

3. Conclusions
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Application possibility for automotive catalysts
1. The aim of this study: Preparation of highly dispersed platinum catalyst with sulfur tolerance and hydrothermal stability.
Designing active & stable Pt catalyst using silica

- **Alumina as a support for diesel oxidation catalyst**
  - **Advantage:** good interaction with platinum
  - **Disadvantage:** the formation of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) induces severe catalyst deactivation.

- **Silica as a support for platinum metal**
  - **Advantage:** chemical inertness (no S adsorption)
    - high surface area and thermal stability
    - processibility owing to surface hydroxyl group
  - **Disadvantage:** Pt can easily sinter on silica due to weak platinum interaction.

To have both good dispersion and sulfur tolerance

- **Two approach methods for the preparation of platinum catalysts**
  - Incorporation of metal oxide layer ($\text{TiO}_2$, $\text{ZrO}_2$) on silica
  - Treatment of impregnated platinum precursor with hydrogen peroxide
First method: incorporation of metal oxide layer on silica

- Reducibility introduction on silica
  - Reducible metal oxide: TiO$_2$, ZrO$_2$, CeO$_2$, V$_2$O$_5$
    cf. γ-Al$_2$O$_3$, SiO$_2$

- Acidity increase
  - γ-Al$_2$O$_3$ (SL/B), TiO$_2$-SiO$_2$ (SB), ZrO$_2$-SiO$_2$ (SB),
  - TiO$_2$ (ML) > ZrO$_2$ (MWL) ≈ SiO$_2$ (MWB)
  - S: Strong; M: Medium; W: Weak; B: Brönsted acid; L: Lewis acid

Acid strength and electronegativity of binary oxides

## Preparation methods of MO$_2$-SiO$_2$ (M = Ti or Zr)

<table>
<thead>
<tr>
<th>Type</th>
<th>Preparation method</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physically mixed</td>
<td>Solid state mixing</td>
<td>Weak Van der Waals forces Interaction</td>
</tr>
<tr>
<td>Chemically bonded</td>
<td>Impregnation</td>
<td>SiO$_2$ powder + M(NO$_3$)$_4$ aqueous solutions (M = Ti or Zr)</td>
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<tr>
<td></td>
<td>Co-precipitation</td>
<td>Si precursor + M precursor $\rightarrow$ pH adjustment</td>
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<tr>
<td></td>
<td>Sol-gel</td>
<td>Si precursor + M alkoxide $\rightarrow$ hydrolysis, condensation</td>
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<tr>
<td></td>
<td></td>
<td>SiO$_2$ powder + M alkoxide $\rightarrow$ reaction between alkoxide and OH group of silica</td>
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Among these methods, the sol-gel method is the most effective method for controlling textural and surface characteristics of mixed oxide.

Preparation method in this study
Second method: hydrogen peroxide treatment

Electron property change of support

- Ti
  - $\text{H}_2\text{O}_2$, $\text{H}_2\text{O}$
  - $\text{O} \rightarrow \text{Ti} \rightarrow \text{OO}^-$
- Zr
  - $\text{H}_2\text{O}_2$
  - Zr(IV) Superoxo-species


Oxygen linkage generation

- Pt
- TiO$_2$
- SiO$_2$

The oxo-species generated by hydrogen peroxide treatment change the electronic property of support and make oxygen linkage, result in further improvement of platinum dispersion on silica.
Our preparation procedure of highly dispersive platinum catalysts

**Sol-gel process**

\[
\text{Ti(OR)}_4 + \text{Si-OH} \rightarrow \text{RO}_4\text{Ti} \rightarrow \text{HO}_2\text{TiOH} \quad \text{or} \quad \text{RO}_4\text{Ti} \quad \Downarrow \quad \text{Ti(OR)}_4 + \text{Si-OH} \rightarrow \text{HO}_2\text{TiOH}
\]

**Incorporation of TiO}_2 or ZrO}_2**

**Impregnation of Pt precursor**

**Treatment of hydrogen peroxide**

\[
\text{H}_2\text{O}_2 \rightarrow \text{HO}_2\text{TiOH}
\]

**Treatment of H}_2\text{O}_2**

**Reduction**
Catalysts characterized after sulfation and hydrothermal aging

- Preparation of platinum catalysts (1wt%)
  - Pt/Ti-Si-H$_2$O$_2$, Pt/Zr-Si-H$_2$O$_2$, Pt/Si, Pt/Al

- Catalyst characterization
  - XRD, TEM, EXAFS, XANES, TPD, TPR

- Consecutive catalytic performances: CO oxidation
  - To verify the sulfur tolerance and hydrothermal stability of platinum catalysts

  Fresh catalysts

  Sulfated catalysts
  400 °C, 50 ppm SO$_2$, 3h

  Hydrothermal aged catalysts
  800 °C, w/ H2O, 2 h

Reaction condition:
- 200 ml/min (1% CO, 4% O$_2$, 5% H$_2$O, Ar)
- 0.1 g catalyst
- 60-300 °C, 2 °C/min
2. Results

Characterization & catalytic performance

- Fresh catalysts
- Sulfated catalysts
- Hydrothermal aged catalysts
Highly dispersed platinum on TiO$_2$-, ZrO$_2$- incorporated silica

- Pt peak on Pt/Si
  - Aggregation of platinum

- No Pt peak on Pt/Ti-Si-H$_2$O$_2$ and Pt/Zr-Si-H$_2$O$_2$
  - Improvement of platinum dispersion due to metal oxide incorporation
Dispersion improvement through incorporating TiO$_2$ and ZrO$_2$

- **Large Pt particles on Pt/Si**
  - Diameter of around 20 nm
- **Medium Pt particles on Pt/Al**
  - Diameter ranged in 5~7 nm
- **Small platinum particles on Pt/Ti-Si-H$_2$O$_2$ and Pt/Zr-Si-H$_2$O$_2$**
  - Diameter ranged in 1~4 nm

**Aggregated platinum particle**
Zr-Si-H$_2$O$_2$ support enhances adsorption of oxygen on Pt

- High whiteline intensity: high electron deficiency
- High electron deficiency: high oxygen adsorption property and high sulfur tolerance


- Pt/Al and Pt/Zr-Si-H$_2$O$_2$ had same XANES spectra in reductive condition, however Pt/Zr-Si-H$_2$O$_2$ had higher whiteline intensity than Pt/Al in oxidative condition.

- Higher whiteline intensity of Pt/Zr-Si-H$_2$O$_2$ means stronger adsorption property of oxygen and higher sulfur tolerance in oxidative condition.
Pt/Ti-Si-H$_2$O$_2$ showed high catalytic activity in fresh catalysts

1st CO oxidation over fresh catalysts

- Catalytic activity in CO oxidation ($T_{50\%}$, °C)
  - Pt/Ti-Si-H$_2$O$_2$ (148 °C)
  - > Pt/Zr-Si-H$_2$O$_2$ (165 °C)
  - > Pt/Al ≈ Pt/Si (218 °C)

- Higher catalytic activity over Pt/Ti-Si-H$_2$O$_2$ and Pt/Zr-Si-H$_2$O$_2$
  - Consistent w/ higher Pt dispersion
  - Apparently due to enhanced oxygen adsorption on Pt (see XANES result)
Impact of surface modification on surface acidobasicity

- **High acidity**: high platinum dispersion, **High basicity**: high sulfur adsorption
  - Pt/Al had strong acidic and basic sites, while Pt/Si had neither.
  - Pt/Zr-Si-H_2O_2 had more acidic and basic sites than Pt/Ti-Si-H_2O_2.
  - Thus, Pt/Ti-Si-H_2O_2 & Pt/Zr-Si-H_2O_2 show good Pt dispersion and better sulfur tolerance.
Pt/Ti-Si-H₂O₂ showed high catalytic activity after sulfation

- 2nd CO oxidation over sulfated catalysts

- Catalytic activity in CO oxidation ($T_{50\%}, ^\circC$)
  - Pt/Ti-Si-H₂O₂ (197 °C)
  - Pt/Zr-Si-H₂O₂ (204 °C)
  - Pt/Al (236 °C)
  - Pt/Si (256 °C)

- Decrease of catalytic activity over all catalysts
  - $T_{50\%}$ increases ~ 50 °C vs. fresh catalysts

- Relatively high catalytic activity over Pt/Ti-Si-H₂O₂ and Pt/Zr-Si-H₂O₂
  - Consistent w/ sulfur tolerance property due to low basicity and high electron deficiency in oxidative condition
Ti & Zr-incorporated catalysts exhibit better S tolerance than Pt/Al

- TPR (Temperature Programmed Reduction): Desulfation with 1% H₂

- Desorption peak area (μmol/g_cat·min)
  - Pt/Al (726) > Pt/Zr-Si-H₂O₂ (370)
    > Pt/Ti-Si-H₂O₂ (171) > Pt/Si (37)

- Pt/Al had most S species which are more stable.

- The relative low amount of sulfur desorbed and low temperature desorption peak on Pt/Ti-Si-H₂O₂ and Pt/Zr-Si-H₂O₂
  - Low basicity and high platinum dispersion, resulting in high catalytic activity after sulfation

- No sulfur desorption peak on Pt/Si
  - Although no sulfur adsorbed on Pt/Si (no basicity), its low platinum dispersion (no acidity) induces low catalytic activity after sulfation.
Pt/Zr-Si-H₂O₂ showed high catalytic activity after hydrothermal aging

3rd CO oxidation over hydrothermal aged catalysts

- Catalytic activity in CO oxidation ($T_{50\%}$, °C)
  - Pt/Zr-Si-H₂O₂ (218 °C) > Pt/Ti-Si-H₂O₂ (237 °C) > Pt/Al (241 °C) > Pt/Si (256 °C)

- Higher catalytic activity of Pt/Zr-Si-H₂O₂ after hydrothermal aging
  - Due to its hydrothermal stability (see next page XRD results)
Pt/Zr-Si-H$_2$O$_2$ maintains its platinum dispersion after hydrothermal aging

- **XRD results of hydrothermal aged catalysts**

  - Platinum peak increase of all catalysts means the platinum sintering of hydrothermal aged catalysts
    - However, Pt/Zr-Si-H$_2$O$_2$ had the smallest platinum peak.

  - Relatively high stability of Pt/Zr-Si-H$_2$O$_2$ after hydrothermal aging results in the best catalytic activity.
4. Conclusions

Results summary

Application possibility for automotive catalysts
## Various contributing factors to dispersion and S tolerance of Pt catalyst

<table>
<thead>
<tr>
<th></th>
<th>Dispersion (XRD, TEM, EXAFS)</th>
<th>Adsorption amount of sulfur (TPR)</th>
<th>Basicity (CO\textsubscript{2} TPD)</th>
<th>Acidity (NH\textsubscript{3} TPD)</th>
<th>Electron deficiency (XANES)</th>
<th>Catalytic activity (CO oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>Pt/Zr-Si-H\textsubscript{2}O\textsubscript{2}</td>
<td>high</td>
<td>medium</td>
<td>low</td>
<td>high</td>
<td>high even after aging</td>
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<tr>
<td></td>
<td>Pt/Ti-Si-H\textsubscript{2}O\textsubscript{2}</td>
<td>high</td>
<td>low</td>
<td>none</td>
<td>medium</td>
<td>high after sulfation</td>
</tr>
<tr>
<td></td>
<td>Pt/Si</td>
<td>low</td>
<td>very low</td>
<td>none</td>
<td>none</td>
<td>low</td>
</tr>
<tr>
<td></td>
<td>Pt/Al</td>
<td>medium</td>
<td>low</td>
<td>high</td>
<td>high</td>
<td>medium after aging</td>
</tr>
</tbody>
</table>

**Correlation**

- Catalytic activity
- Adsorption of acidic SO\textsubscript{2} on basic supports
- Dispersion, Oxygen Adsorption, S tolerance
- The highest catalytic activity of Pt/Zr-Si-H\textsubscript{2}O\textsubscript{2}

- **Merit**
- **Demerit**
Conclusions

1. Platinum catalysts on TiO$_2$-, ZrO$_2$-incorporated silica show higher catalytic activity than Pt/Al and Pt/Si in CO oxidation.

2. Pt/Ti-Si-H$_2$O$_2$ has the best sulfur tolerance property and Pt/Zr-Si-H$_2$O$_2$ shows the best hydrothermal stability.

3. Pt/Zr-Si-H$_2$O$_2$ has thermal stability, electron deficiency, high acidity and low basicity, resulting in high platinum dispersion even after hydrothermal aging and suppression of the adsorption of acidic SO$_2$.

Pt/Zr-Si-H$_2$O$_2$ represents its application possibility for the diesel oxidation catalysts
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Thank you!

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