Enhancing Stability of Platinum on Silica by Surface Modification

- Application to CO Oxidation -

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Outline

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

- Results summary
- 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 ($Al_2(SO_4)_3$) 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 (TiO_2, 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_2O_5

  cf. γ-Al_2O_3, SiO_2

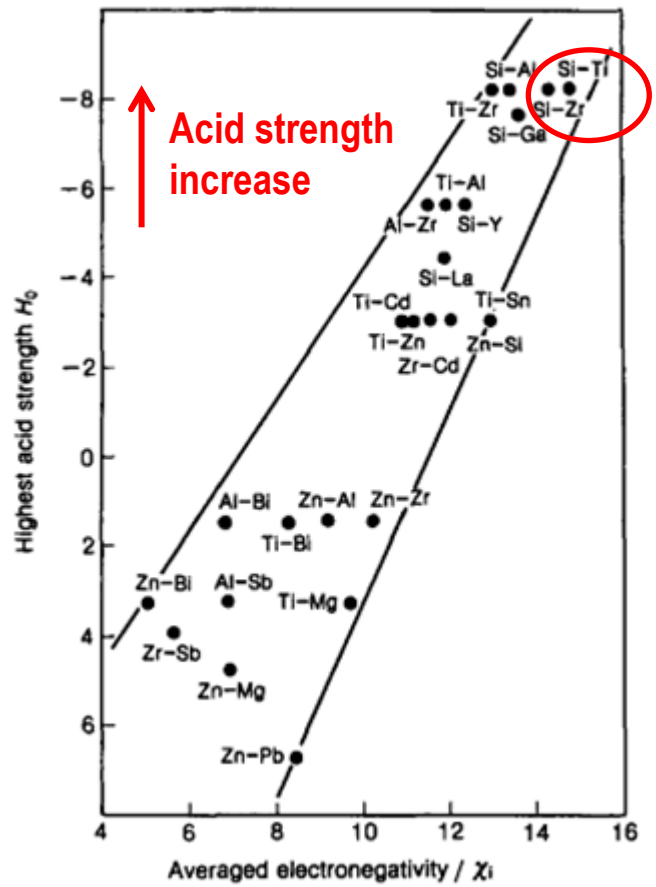
❑ **Acidity increase** *Metal oxide: Chemistry and applications, 2006, CRC, 273 p.*

γ-Al_2O_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

Reducibility and acidity of support induce strong platinum-support interaction.



Acid strength and electronegativity of binary oxides

New Solid Acid and Bases, 1989, Elsevier, 113 p.

Preparation methods of MO_2-SiO_2 (M = Ti or Zr)

Type	Preparation method	Remark
Physically mixed	Solid state mixing	Weak Van der Waals forces Interaction
Chemically bonded	Impregnation	SiO_2 powder + $M(NO_3)_4$ aqueous solutions (M = Ti or Zr)
	Co-precipitation	Si precursor + M precursor → pH adjustment
	Sol-gel	Si precursor + M alkoxide → hydrolysis, condensation
		SiO_2 powder + M alkoxide → reaction between alkoxide and OH group of silica

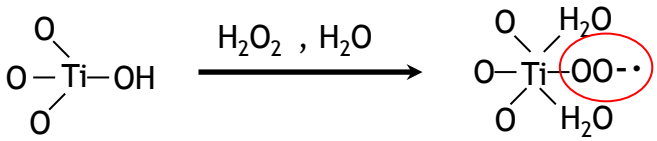
Among these methods, the sol-gel method is the most effective method for controlling textural and surface characteristics of mixed oxide.

Preparation method in this study

Second method: hydrogen peroxide treatment

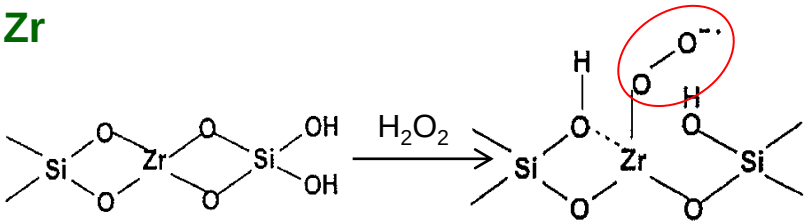
❑ Electron property change of support

Ti



Catal. Lett., 16 (1992) 109

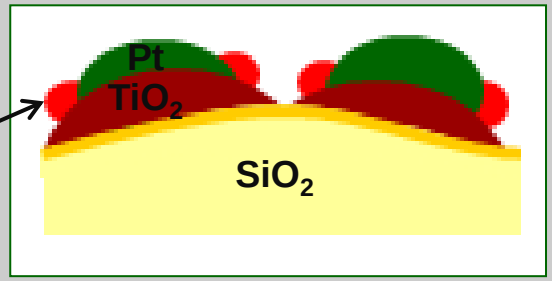
Zr



Appl. Catal. A, 369 (2009) 27

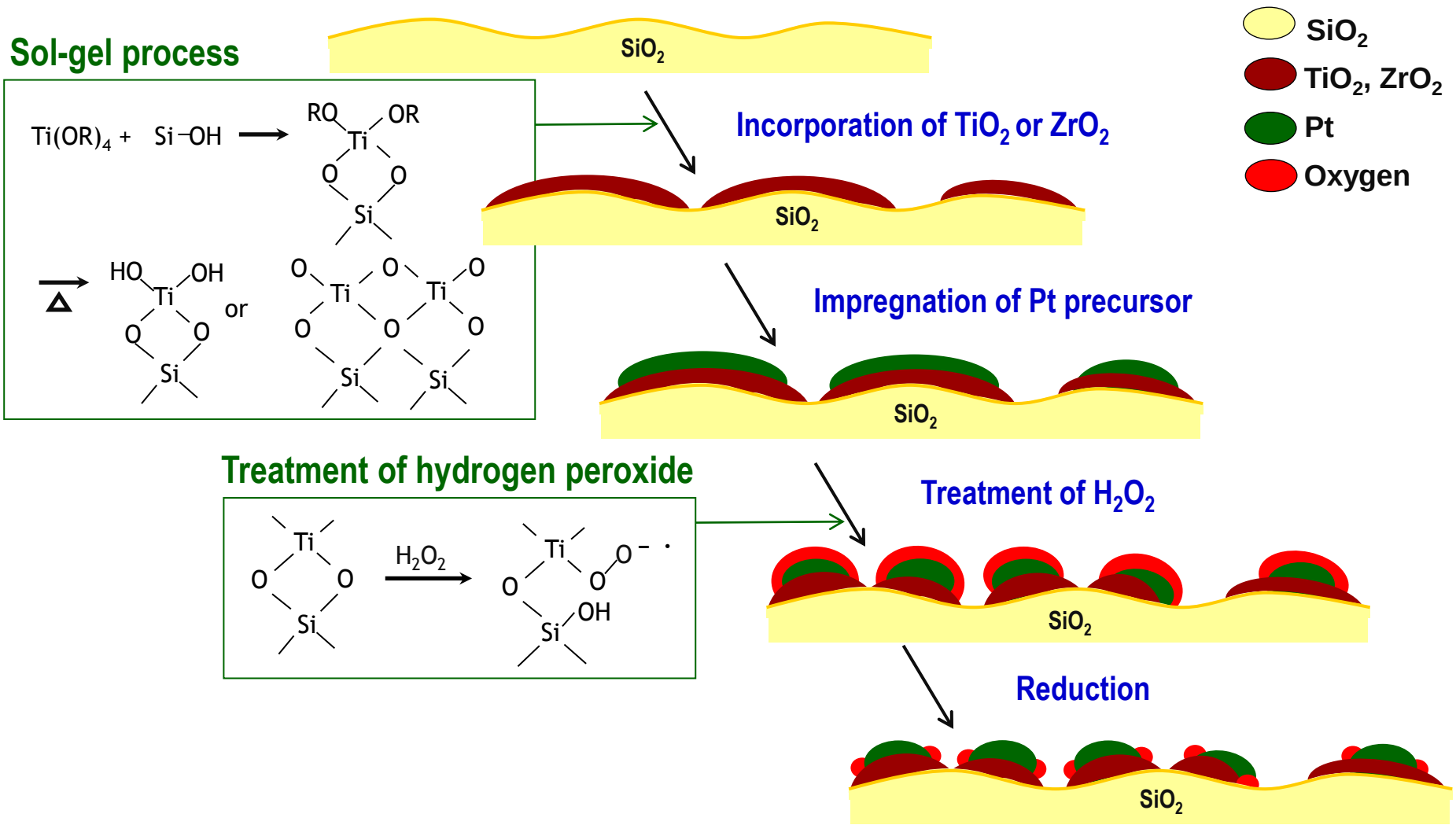
Zr(IV) Superoxo-species

❑ Oxygen linkage generation



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



Catalysts characterized after sulfation and hydrothermal aging

- **Preparation of platinum catalysts (1wt%)**
  - Pt/Ti-Si-H_2O_2, Pt/Zr-Si-H_2O_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 ^{o}C, 50 ppm SO_2, 3h

↓

Hydrothermal aged catalysts

800 ^{o}C, w/ H2O, 2 h

Reaction condition:

- 200 ml/min (1% CO, 4% O_2, 5% H_2O, Ar)
- 0.1 g catalyst
- 60-300 ^{o}C, 2 ^{o}C/min

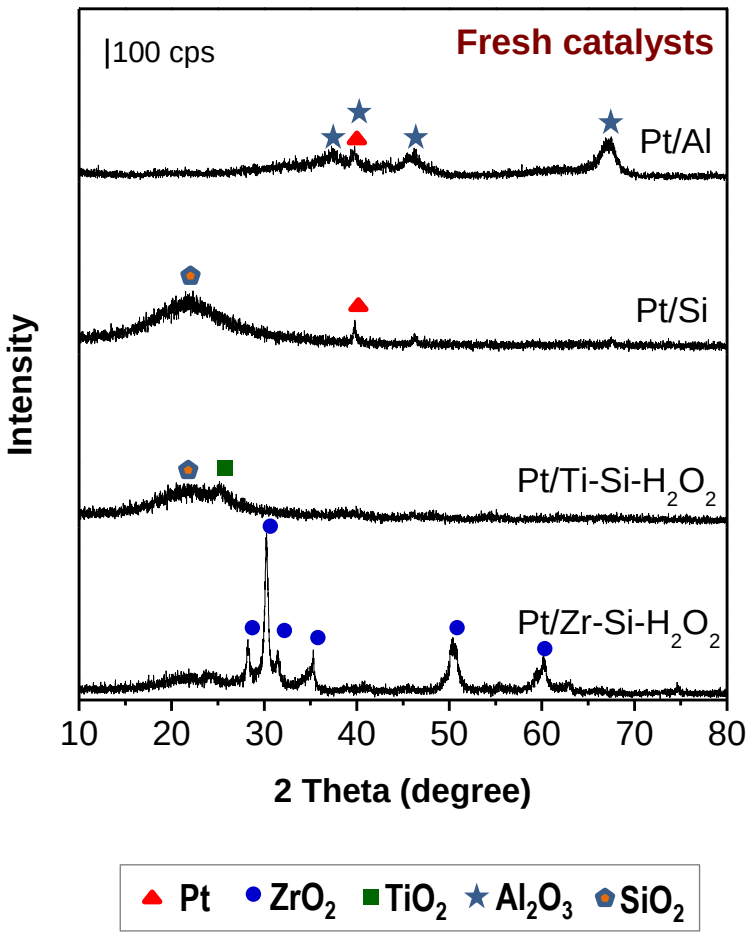
2. Results

Characterization & catalytic performance

- Fresh catalysts
- Sulfated catalysts
- Hydrothermal aged catalysts

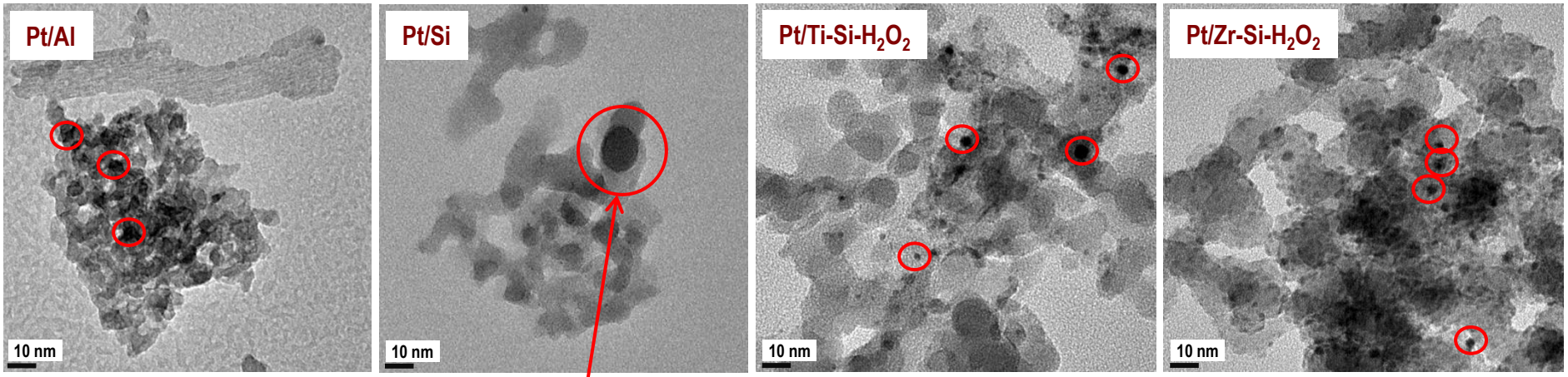
Highly dispersed platinum on TiO_2-, ZrO_2- incorporated silica

❑ XRD results of fresh catalysts

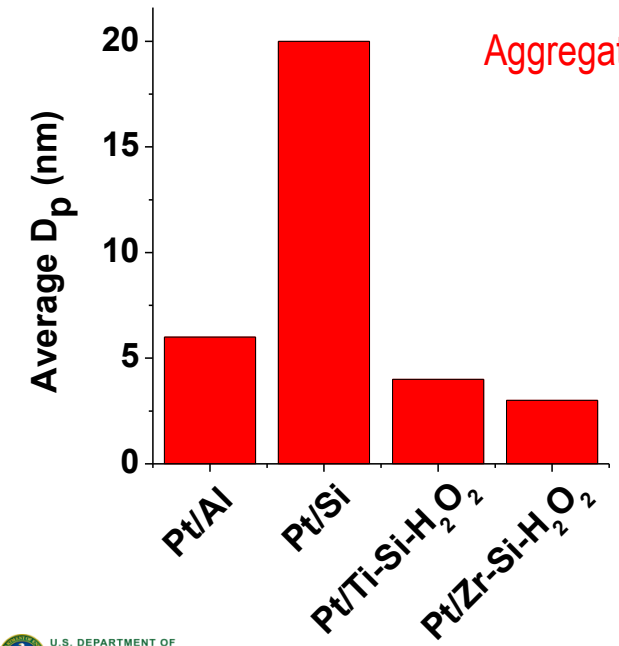


- **Pt peak on Pt/Si**
  - Aggregation of platinum
- **No Pt peak on Pt/Ti-Si-H_2O_2 and Pt/Zr-Si-H_2O_2**
  - Improvement of platinum dispersion due to metal oxide incorporation

Dispersion improvement through incorporating TiO_2 and ZrO_2



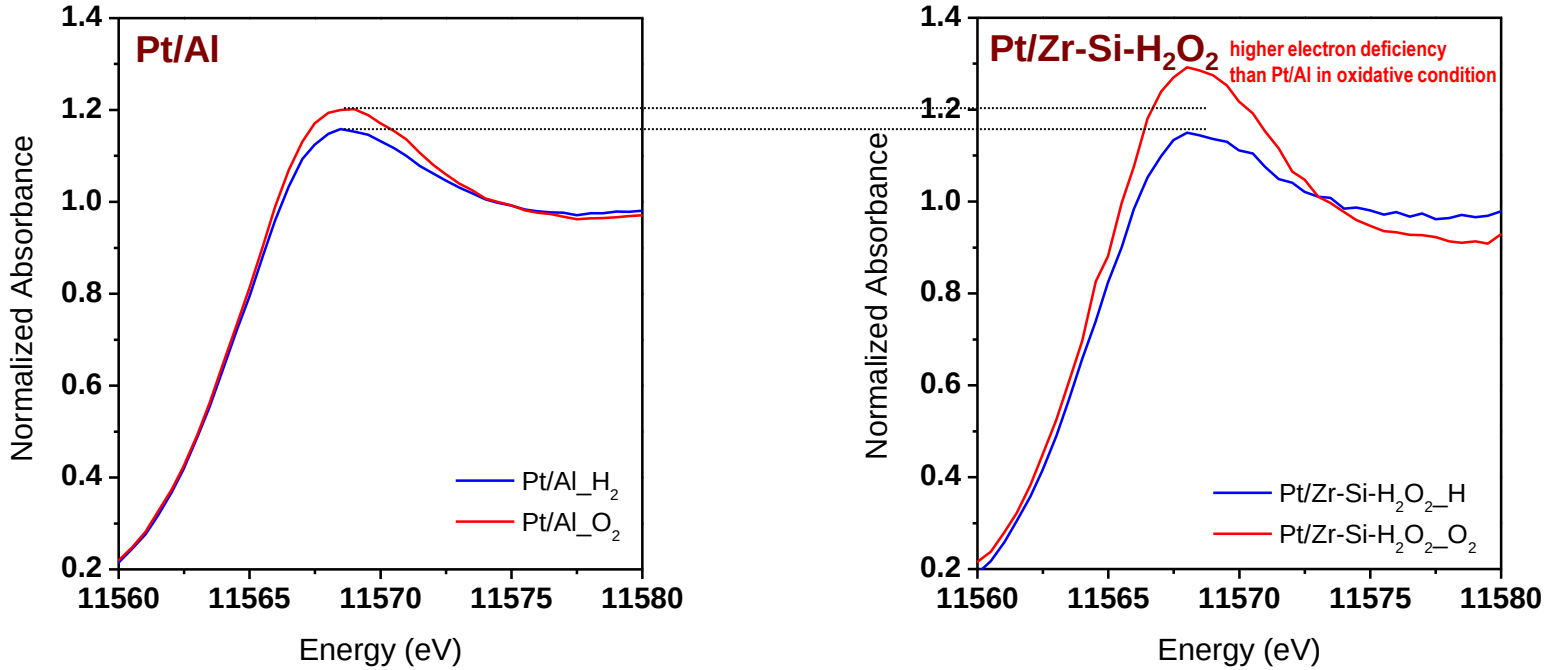
Aggregated platinum particle



- **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_2O_2 and Pt/Zr-Si-H_2O_2**
  - Diameter ranged in 1~4 nm

Zr-Si-H_2O_2 support enhances adsorption of oxygen on Pt

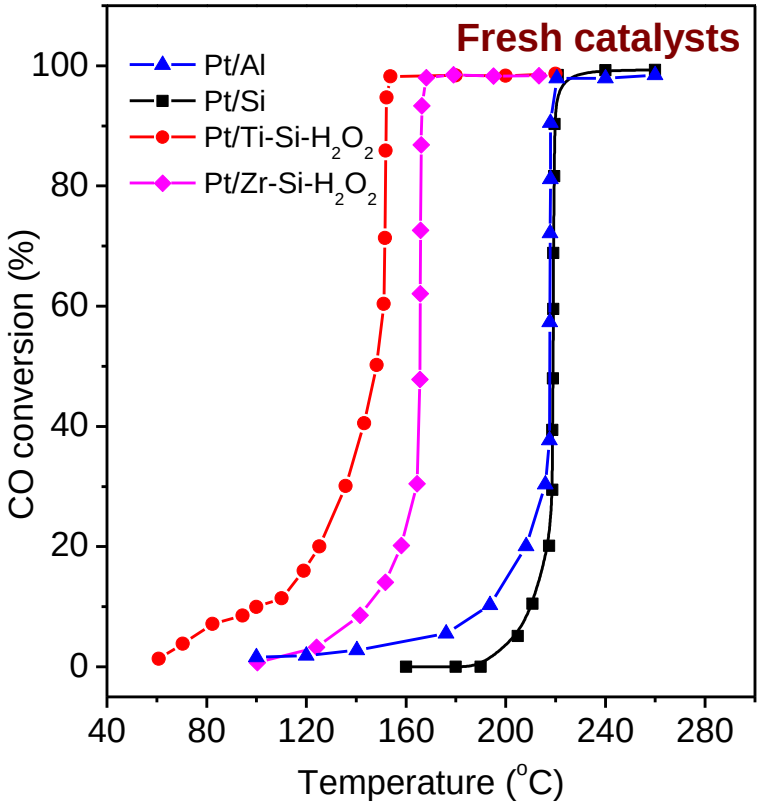
❑ Pt L_{III}-edge XANES spectra from Advanced Photon Source at ANL

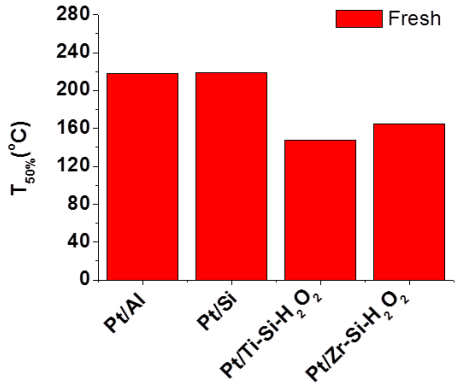


- **High whiteline intensity: high electron deficiency**
  High electron deficiency: high oxygen adsorption property and high sulfur tolerance
  [X-ray Absorption Fine Structure for Catalysts and Surface, World Scientific, 1996; Oxygen Complexes and Oxygen Activation by Transition Metals, Plenum Press, 1988; Catalyst Deactivation, Vol. 6, Elsevier, 1980.]
- **Pt/Al and Pt/Zr-Si-H_2O_2 had same XANES spectra in reductive condition, however Pt/Zr-Si-H_2O_2 had higher whiteline intensity than Pt/Al in oxidative condition.**
- **Higher whiteline intensity of Pt/Zr-Si-H_2O_2 means stronger adsorption property of oxygen and higher sulfur tolerance in oxidative condition.**

Pt/Ti-Si-H_2O_2 showed high catalytic activity in fresh catalysts

❑ 1st CO oxidation over fresh catalysts



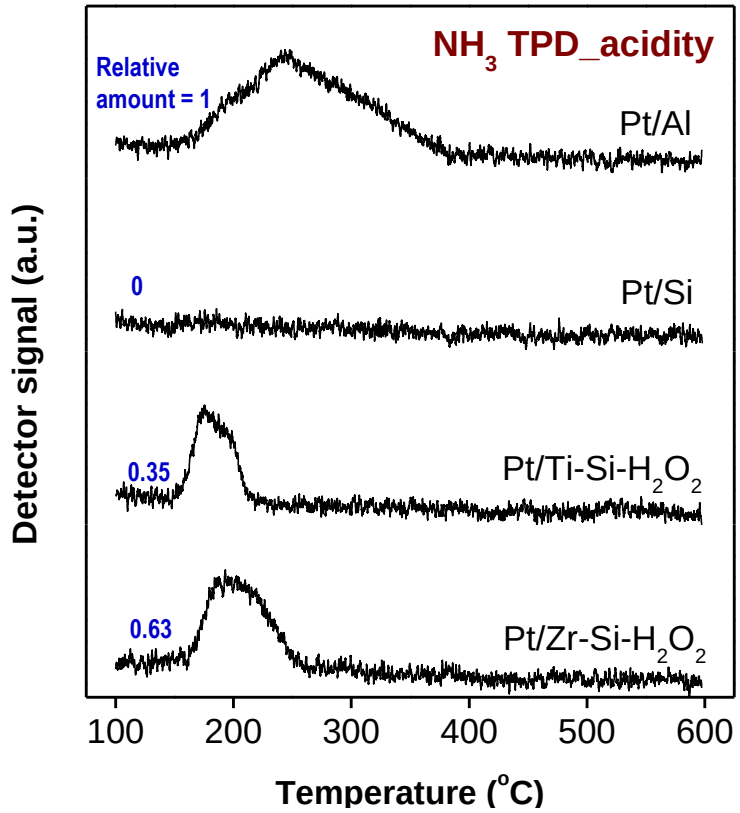


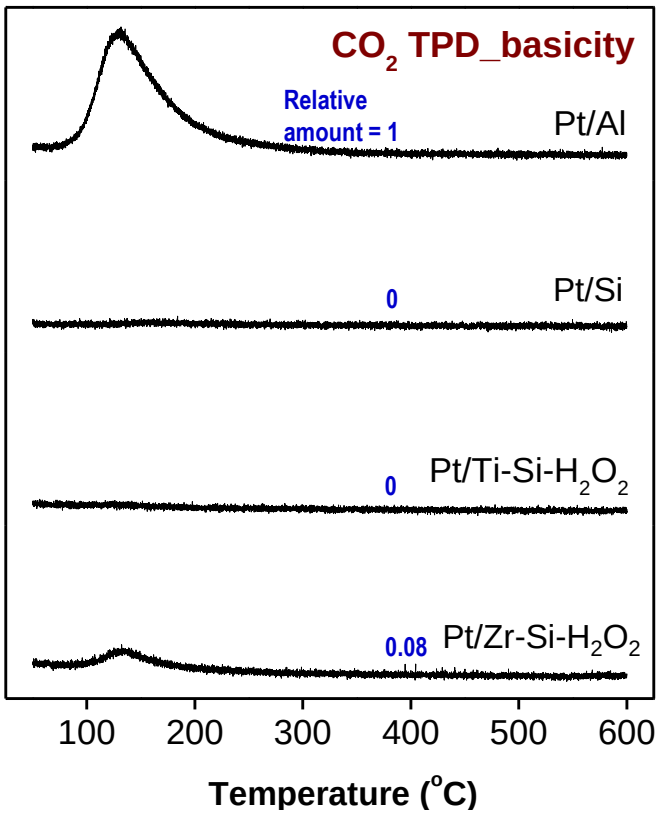
- **Catalytic activity in CO oxidation ($T_{50\%}$, °C)**
  - Pt/Ti-Si-H_2O_2 (148 °C)
    > Pt/Zr-Si-H_2O_2 (165 °C)
    > Pt/Al ≈ Pt/Si (218 °C)

- **Higher catalytic activity over Pt/Ti-Si-H_2O_2 and Pt/Zr-Si-H_2O_2**
  - Consistent w/ higher Pt dispersion
  - Apparently due to enhanced oxygen adsorption on Pt (see XANES result)

Impact of surface modification on surface acidobasicity

❑ TPD (Temperature Programmed Desorption)





- **High acidity: high platinum dispersion, High basicity: high sulfur adsorption**

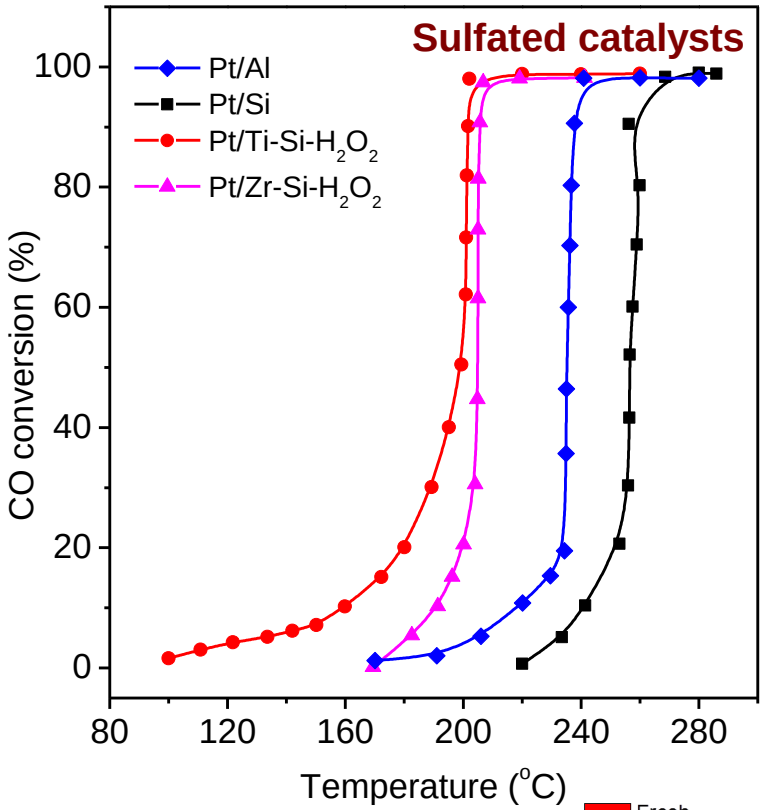
- Pt/Al had strong acidic and basic sites, while Pt/Si had neither.

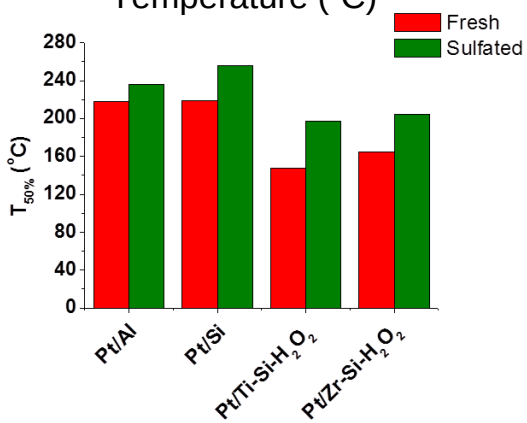
- Pt/Zr-Si-H_2O_2 had more acidic and basic sites than Pt/Ti-Si-H_2O_2.

- Thus, Pt/Ti-Si-H_2O_2 & Pt/Zr-Si-H_2O_2 show good Pt dispersion and better sulfur tolerance.

Pt/Ti-Si-H_2O_2 showed high catalytic activity after sulfation

❑ 2nd CO oxidation over sulfated catalysts

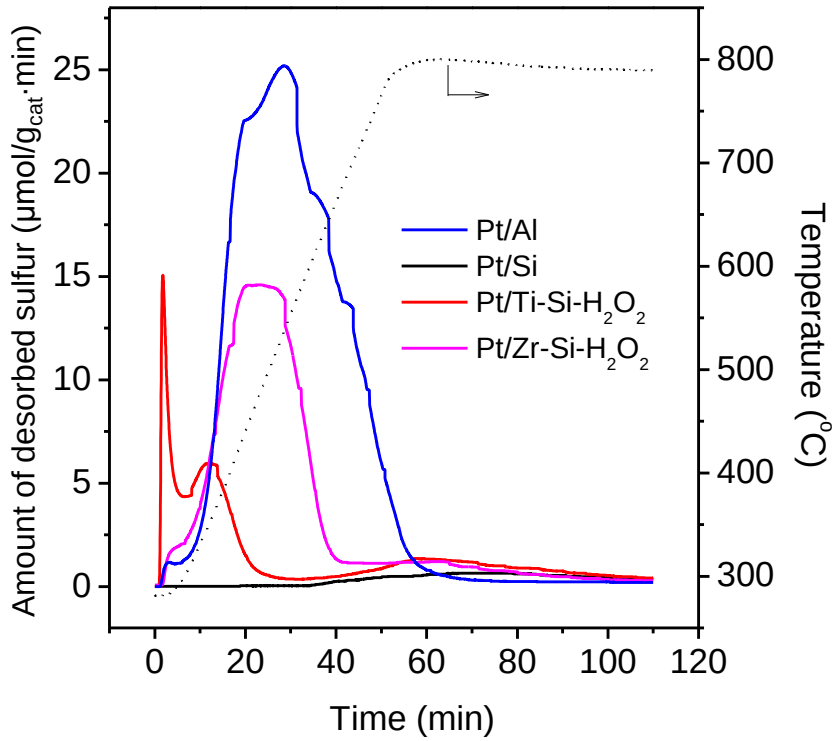




- **Catalytic activity in CO oxidation ($T_{50\%}$, °C)**
  - Pt/Ti-Si-H_2O_2 (197 °C)
    > Pt/Zr-Si-H_2O_2 (204 °C)
    > Pt/Al (236 °C)
    > Pt/Si (256 °C)
- **Decrease of catalytic activity over all catalysts**
  - $T_{50\%}$ increases ~ 50 °C vs. fresh catalysts
- **Relatively high catalytic activity over Pt/Ti-Si-H_2O_2 and Pt/Zr-Si-H_2O_2**
  - 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

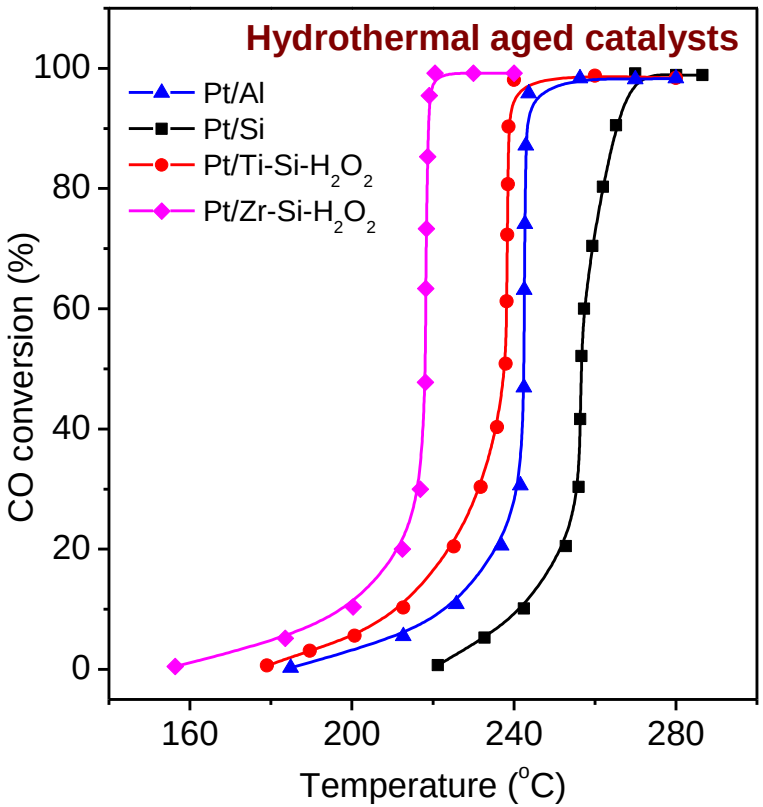
❑ TPR (Temperature Programmed Reduction): Desulfation with 1% H_2

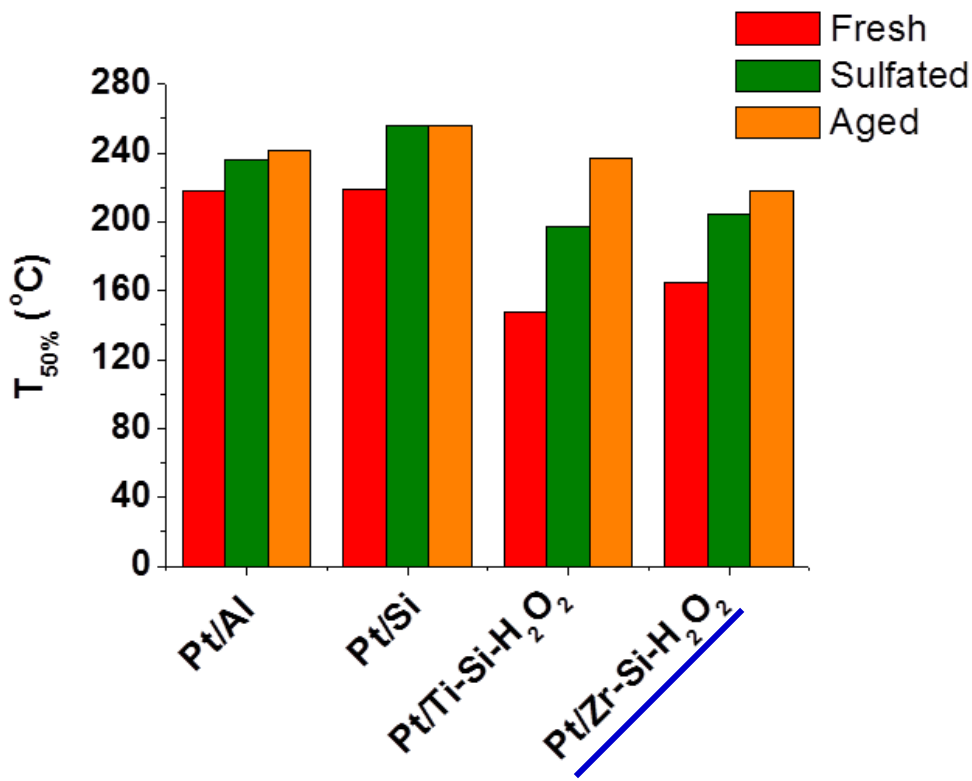


- **Desorption peak area** (μmol/g_{cat}·min)
  - Pt/Al (726) > Pt/Zr-Si-H_2O_2 (370) > Pt/Ti-Si-H_2O_2 (171) > Pt/Si (37)
- **Pt/Al had most S species which are more stable.**
- **The relative low amount of sulfur desorbed and low temperature desorption peak on Pt/Ti-Si-H_2O_2 and Pt/Zr-Si-H_2O_2**
  - 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-H_2O_2 showed high catalytic activity after hydrothermal aging

❑ 3rd CO oxidation over hydrothermal aged catalysts





- **Catalytic activity in CO oxidation ($T_{50\%}$, °C)**

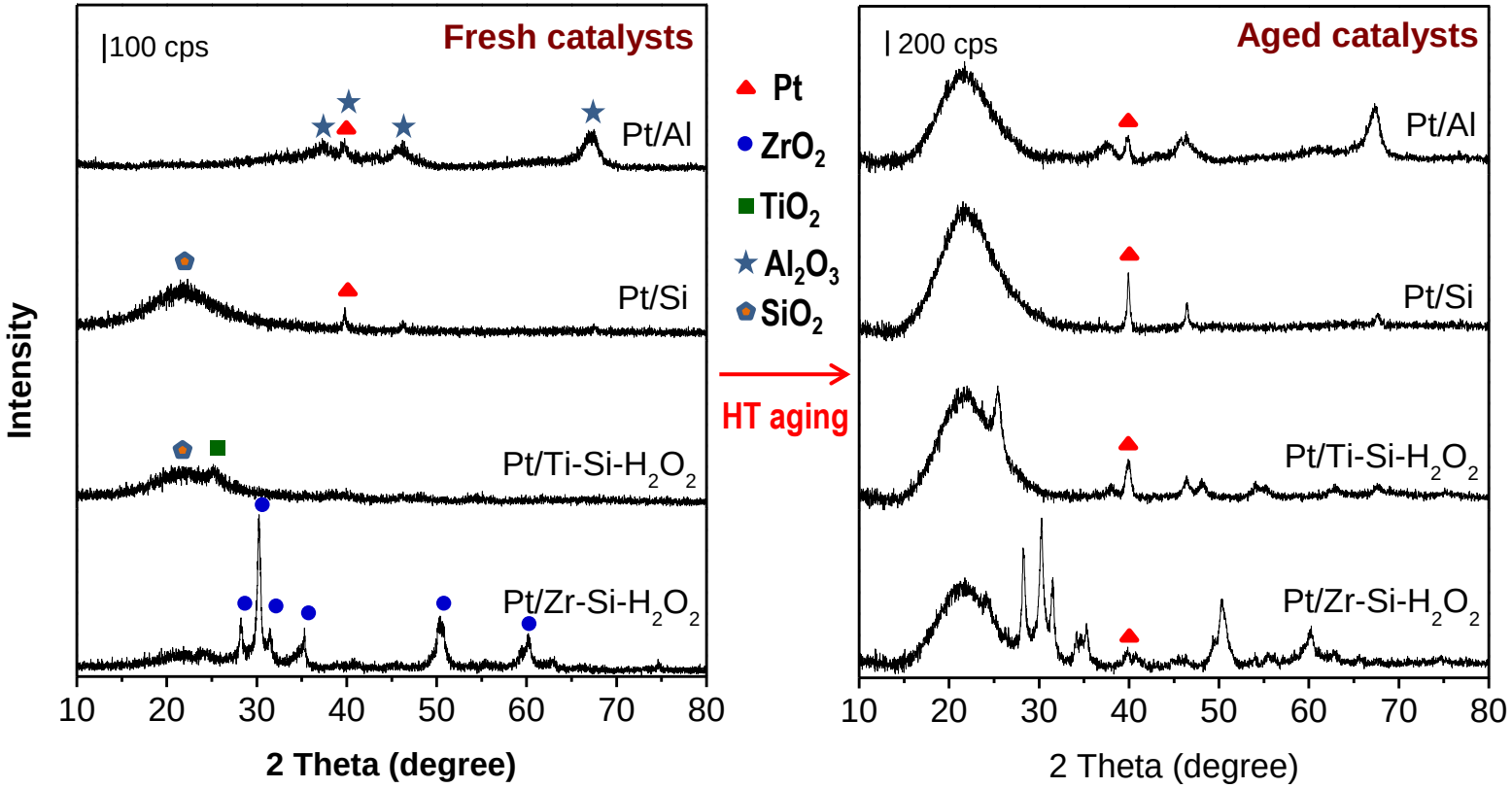
  - Pt/Zr-Si-H_2O_2 (218 °C) > Pt/Ti-Si-H_2O_2 (237 °C) > Pt/Al (241 °C) > Pt/Si (256 °C)

- **Higher catalytic activity of Pt/Zr-Si-H_2O_2 after hydrothermal aging**

  - Due to its hydrothermal stability (see next page XRD results)

Pt/Zr-Si-H_2O_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_2O_2 had the smallest platinum peak.
- **Relatively high stability of Pt/Zr-Si-H_2O_2 after hydrothermal aging results in the best catalytic activity.**

4. Conclusions

- Results summary
- Application possibility for automotive catalysts

Results summary

- **Various contributing factors to dispersion and S tolerance of Pt catalyst**

	Dispersion (XRD, TEM, EXAFS)		Adsorption amount of sulfur (TPR)	Basicity (CO_2 TPD)	Acidity (NH_3 TPD)	Electron deficiency (XANES)	Catalytic activity (CO oxidation)
	Fresh	Aged					
Pt/Zr-Si-H_2O_2	high	high	medium	low	high	high	high even after aging
Pt/Ti-Si-H_2O_2	high	low	low	none	medium	medium	high after sulfation
Pt/Si	low	very low	very low	none	none	very low	low
Pt/Al	medium	low	high	high	very high	very low	medium after aging
Correlation	*Catalytic activity*		*Adsorption of acidic SO_2 on basic supports*		*Dispersion, Oxygen Adsorption, S tolerance*		*The highest catalytic activity of Pt/Zr-Si-H_2O_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_2O_2 has the best sulfur tolerance property and Pt/Zr-Si-H_2O_2 shows the best hydrothermal stability.

3. Pt/Zr-Si-H_2O_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_2O_2 represents its application possibility for the diesel oxidation catalysts

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