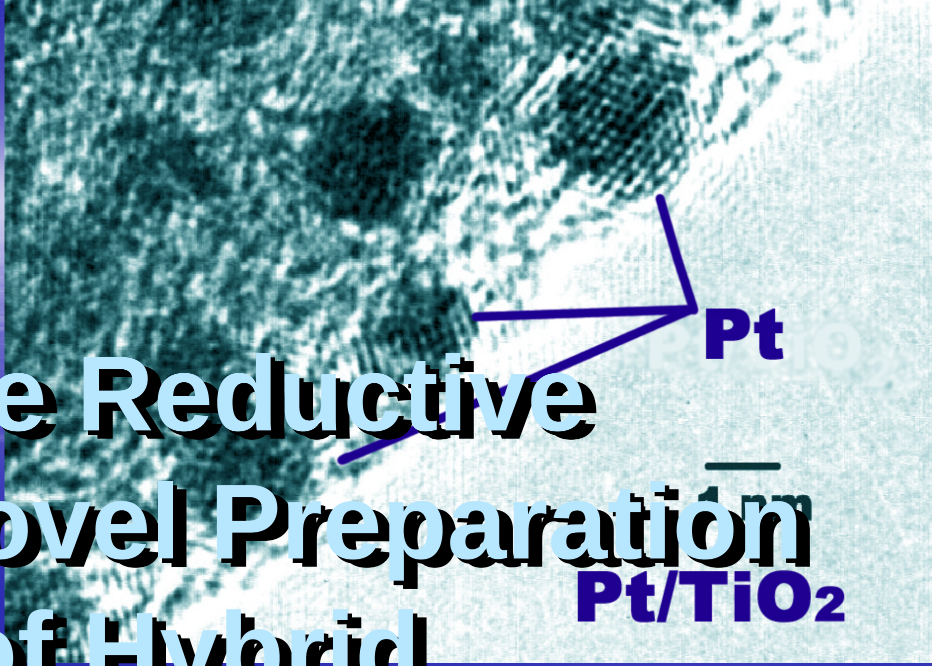
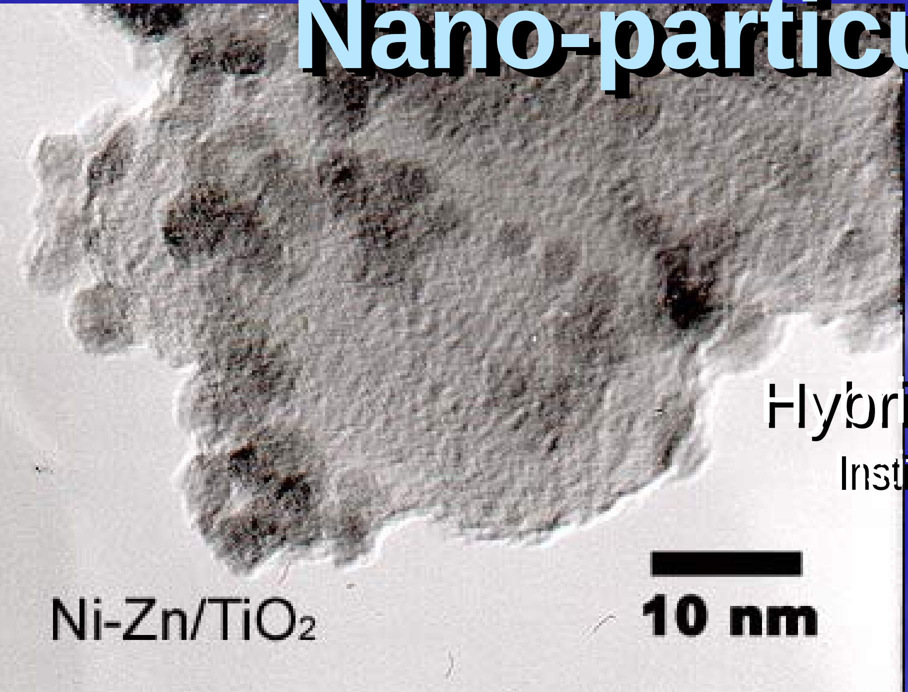



# Liquid-Phase Reductive Deposition as Novel Preparation Method of Hybrid Nano-particulate Catalysts

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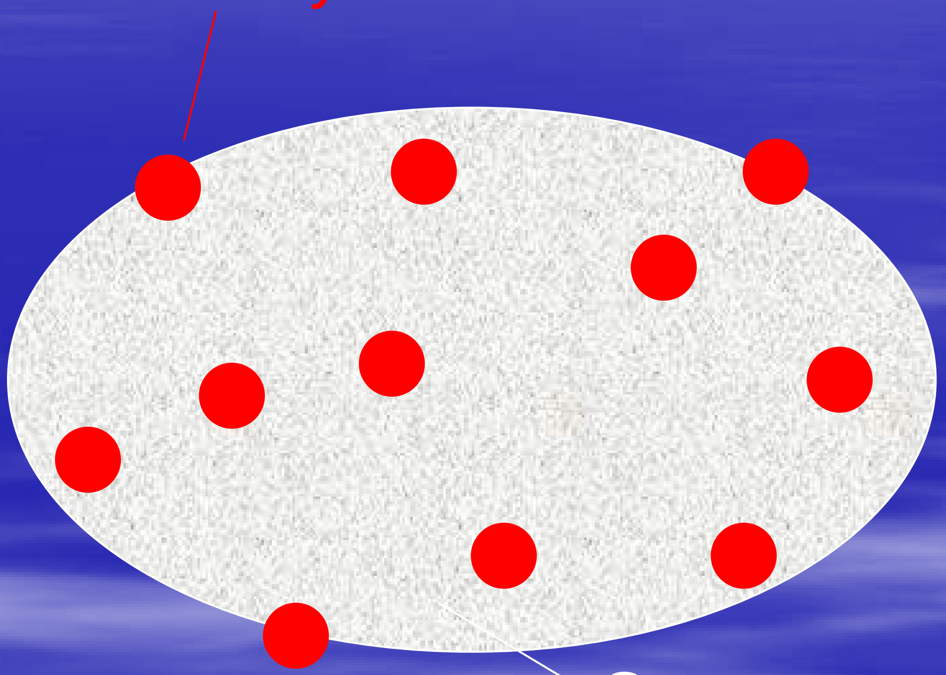
# BACKGROUND

# Supported catalysts

- Metal particles are supported on a carrier.
- The carrier is a porous material.

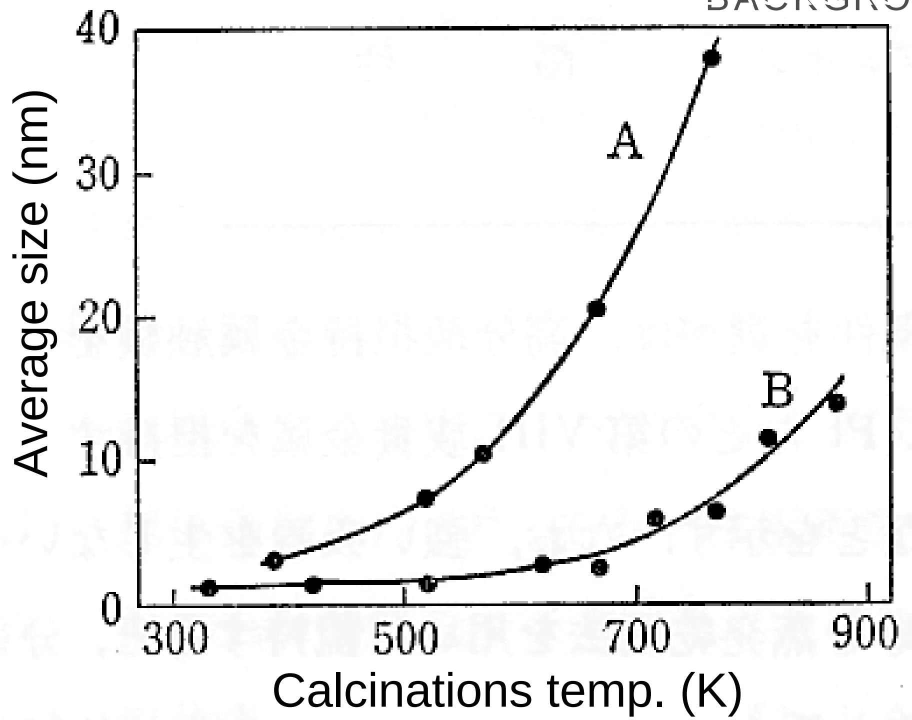


# Problem

## Relationship between preparation method and dispersity of metal

Dispersity = surface metal / bulk metal

It depends on metal size in general.




Effect of preparation method on average size of metals and their thermal stability.

A: impregnation method with $H_2PtCl_6$
B: ion exchange method with $[Pt(NH_3)_4]Cl_2$

Ref. H. Arai, Surface 17, 680 (1979).

# Relationship between preparation method and dispersity of metal

Adsorption uptake of H and CO is in proportional to surface metal amounts.

Uptake : large

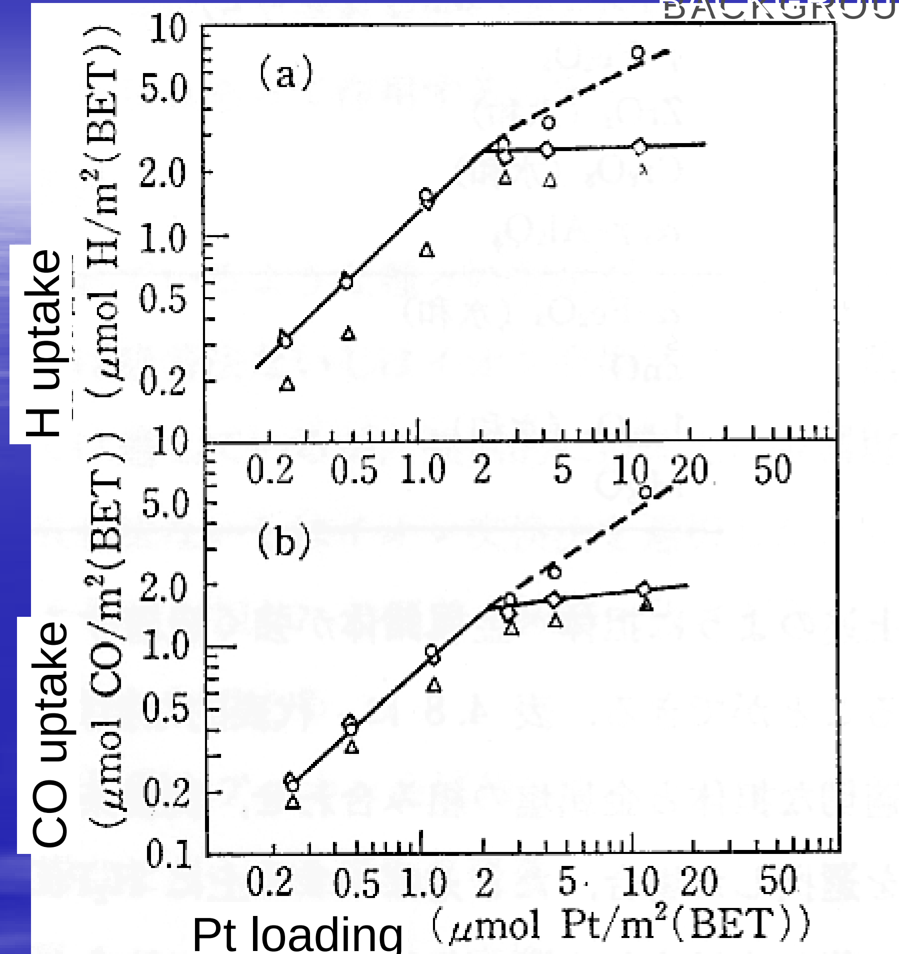
↓

Active surface area: large

Surface area became unchanged over a certain loading of Pt.

→

With increasing Pt, its size was increased.




Adsorption uptakes of H and CO on Pt/γ-$Al_2O_3$ as a function of Pt loading.

○: reduced by $H_2$ at 300℃ for 2h

△: $H_2$ at 500℃ for 2h

▲: $H_2$ at 750℃ for 2h

◇: calcined by $O_2$ at 500℃ for 5h.

H. C. Yao, M. Sieg, H. K. Plummer, Jr., *J. Catal.*, 59, 367 (1979)

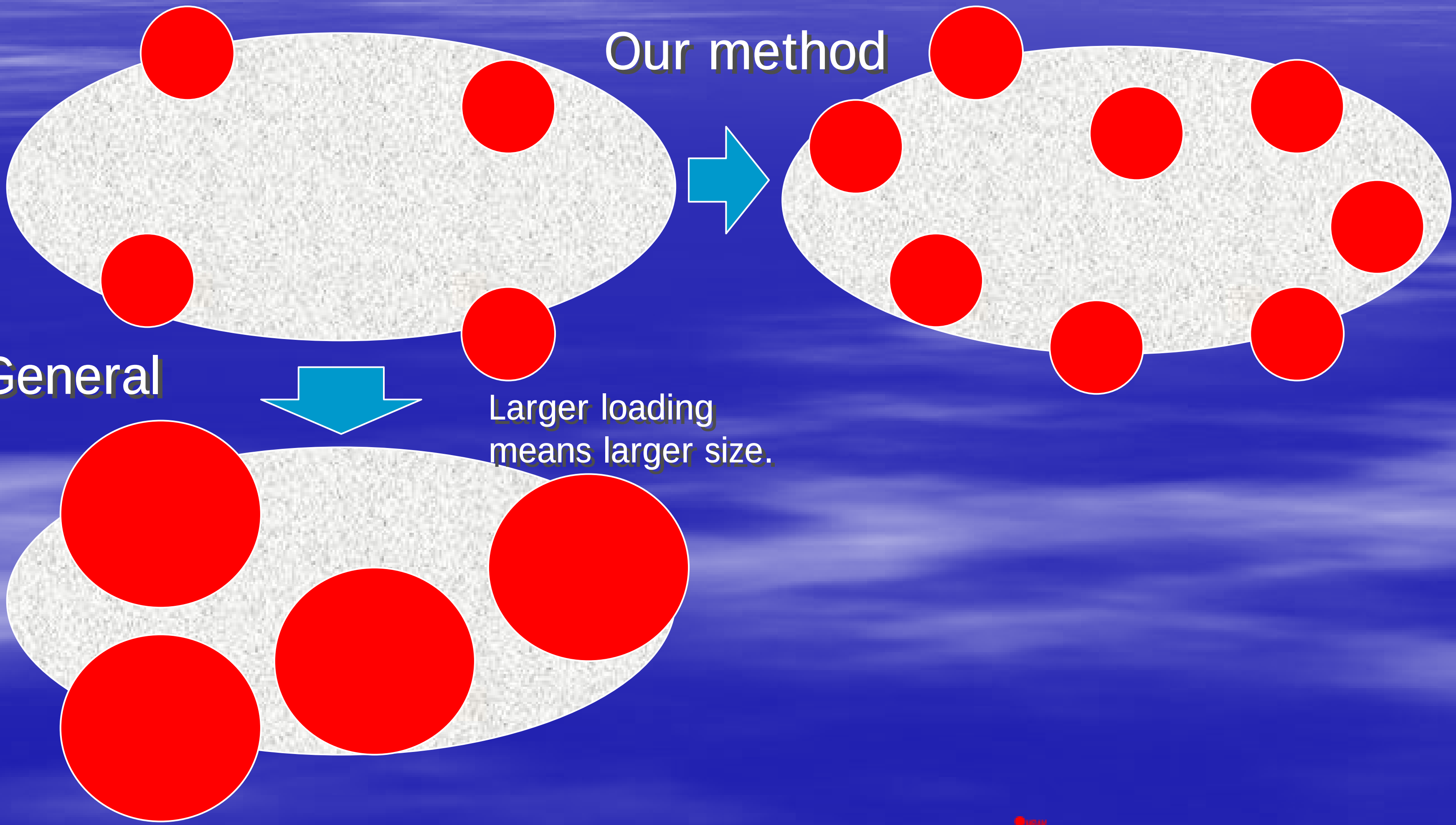
# Catalyst preparation methods

- Impregnation
    - Including incipient wetness method, etc.
  - Immerse support materials in metal salt solution.
  - Drying it up and calcining it well.
- Ion exchange
- Coprecipitation

# Disadvantages

- Impregnation
  - – Easy control for loading.
  - – Very difficult to decrease catalyst metal size.
- Ion exchange
  - – Easy control for metal size.
  - – Very difficult to increase loading.

## Loading is increased but size should be the same.

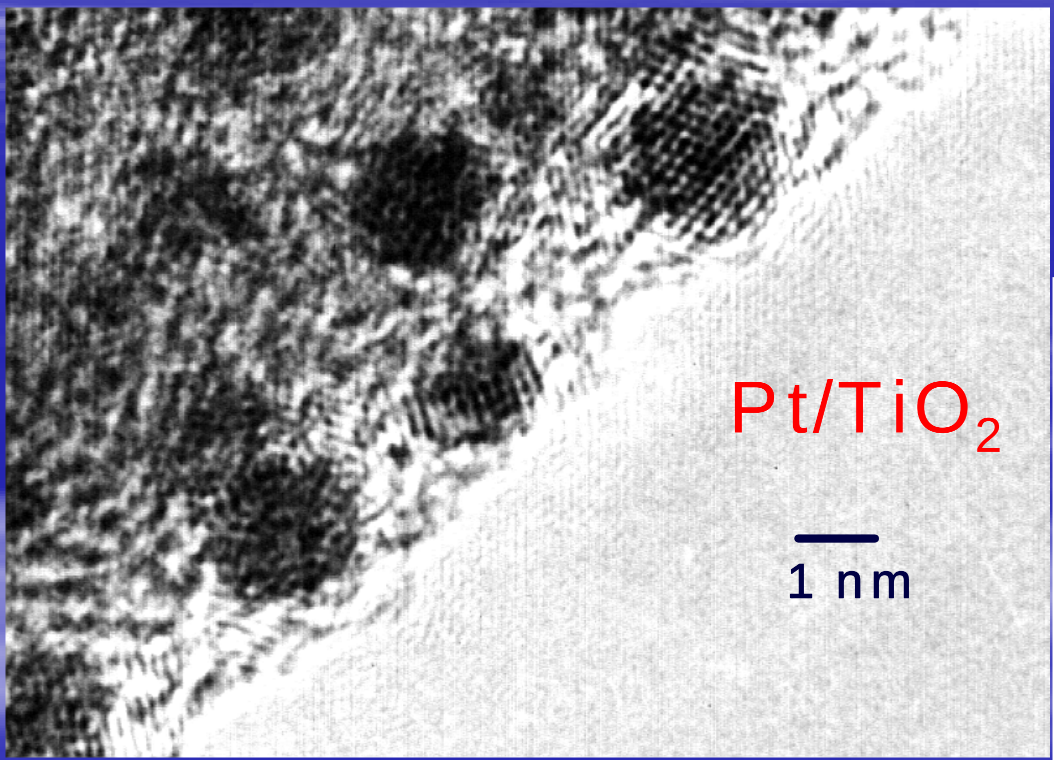


# Selective Deposition Method

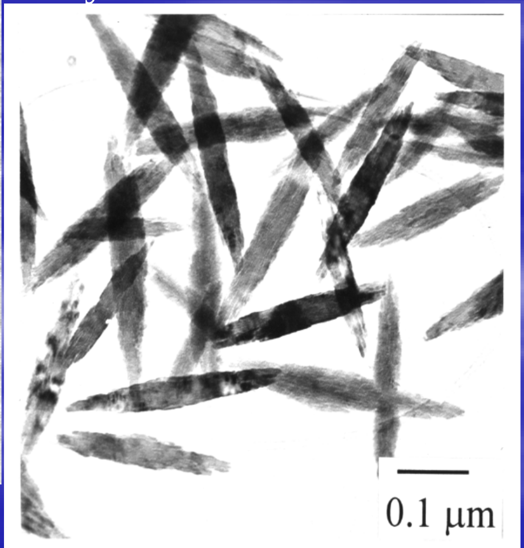
# Selective Deposition

- Control of complex form of noble metal solution
  - Adjust pH to form hydroxide complexes
  - ca. $Pt(OH)_4$ complex
- Aging them at 100℃ 2days
  - Formation of precursory complex
- Formation of noble nanoparticles by reduction
- Loading = 20 wt%, but ~1nm in size.

# Selective Deposition of Noble Metal Nanoparticles on Well-Defined Oxide Particle and their Application to Hydrogenation Catalyst




Support:
Single-crystalline anatase-type $TiO_2$
Monodispersed particles prepared by the Gel-Sol method.



[Noble metal salt] = 2.0 × $10^{-4}$ mol $dm^{-3}$
($HAuCl_4$; $RuCl_3$, $RhCl_3$, $PdCl_2$, $H_2IrCl_6$, $H_2PtCl_6$)

NaOH

Formation of precursor complex

Storing at room temp. for 24 h pH ~7

Support particles = 1.6 g $dm^{-3}$

Ultrasonic dispersion (30 min)

Selective deposition

Aging (100℃, 48 h)

Reduction by $H_2$ if necessary

Metal nanoparticles of Au, Ru, Rh, Pd, Ir, and Pt

Table Catalytic properties of supported Pt nanoparticles.

| Support | Specific surface area ($m^2$ $g^{-1}$) | Method | Pt loading (wt%) | Particle size (nm) | Dispersity (H/M) | 1-octene conversion (%) |
|---|---|---|---|---|---|---|
| $TiO_2$, ellipsoid (anatase) | 37.5 | ***This study*** | 3.0 | 1.1 | 0.99 | 11.9 |
| | | ***This study*** | 18.9 | 1.3 | 0.86 | 35.7 |
| | | Ion-exchange method | 3.6 | 1.4 | 0.98 | 3.7 |
| | | Impregnation method | 20.0 | 6.3 | 0.40 | 9.7 |
| $\alpha$-$Fe_2O_3$, ellipsoid (A)* | 136 | ***This study*** | 22.0 | 2.0 | 0.09 | 4.6 |
| $SiO_2$ (prepare by Stober method) | 4.20 | ***This study*** | 13.6 | 10 - 50 | 0.31 | 5.0 |
| $ZrO_2$ (B)** | 118 | ***This study*** | 18.0 | 2.4 | 0.86 | 19.4 |
| $Al_2O_3$ CSJ-ref. cat ALO6 | 156 | ***This study*** | 18.0 | 1.6 | 0.85 | 52.1 |
| | | Ion-exchange method | 3.0 | 1.2 | 1.00 | 10.6 |
| | | Impregnation method | 18.0 | 4.8 | 0.28 | 21.2 |

Selective Deposition method → Highly dispersed catalysts with high loading

# Challenging to prepare Ni nanoparticles

- Nanoparticles of noble metals can be obtained by Selective Deposition Method.
- But, Ni is well known as very difficult to make it nanometer size.
- Ni particles are easily aggregated each other.
- Conventional methods of catalyst preparation cannot give nanoparticles of Ni.

# Difficulty to obtain Ni nanoparticles

**Ni-Zn nanoparticles synthesized by Liquid Phase Reduction method**

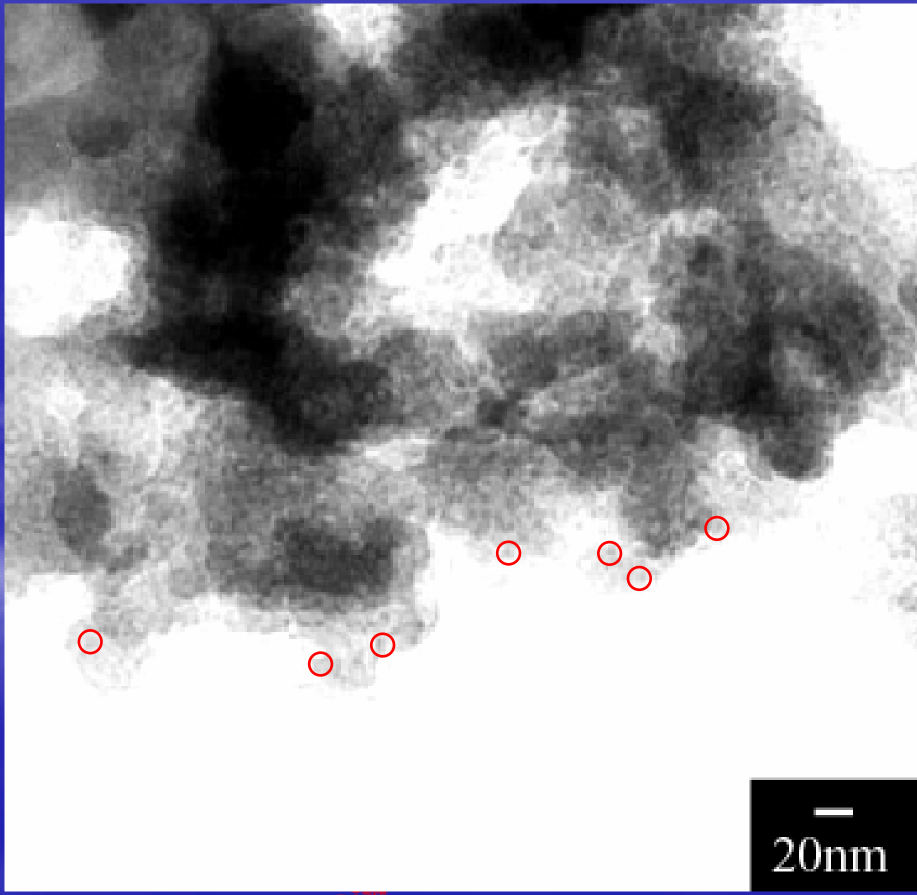
- **Amorphous (contain :B)**
- **c.a. 5～10 nm**
- **High Surface Activity**

  **⇒High catalytic activity**

  **⇒Aggregation**

**As-prepared particles are rather unstable, since tremendous aggregation sometimes occurs in the solution.**

**Ni-Zn nanoparticles**



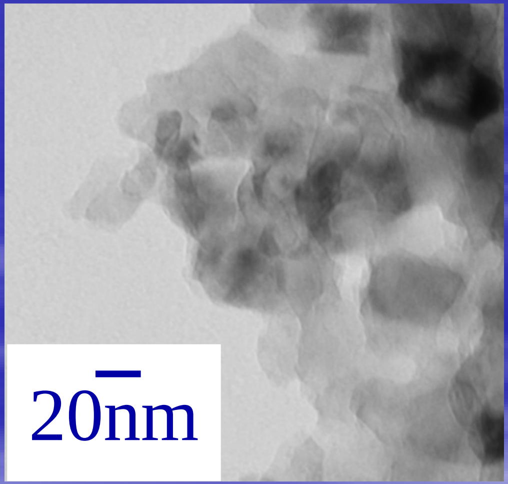
# Objective of this study

# Objective

**Reductive Selective Deposition of Ni-Zn Nanoparticles onto $TiO_2$ Fine Particles (ST01) in the Liquid Phase (Ni-Zn/$TiO_2$)**

↓

**Catalytic activity measurements and characterizations of Ni-Zn/$TiO_2$ nanocomposite synthesized.**




**$TiO_2$, ST01**

# Experimental

## Liquid Phase Reduction method

**Dissolution of metal complex**

⇩

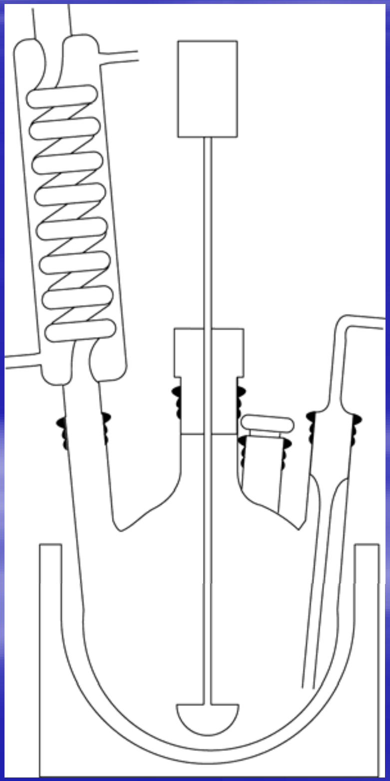
**Synthesis of metal nanoparticles by using the reduction agent**

High recovery rate by easy method
Nanoparticles can be directly obtained from any precursor compounds soluble in a specific solvent.

**Ni source：Ni(AA)$_2$ (AA=$CH_3COCHCOCH_3$)**
**Zn source ： Zn(AA)$_2$**
**Reducing agent：$NaBH_4$**

# Experimental procedure

$Ni(AA)_2$=0.005mol·dm$^{-3}$ const.
Zn/Ni=0.0 to 1.0
2-propanol solution 40ml



← $TiO_2$=0.125g

← $N_2$ gas flow (30min, 82℃)

← 0.02mol·dm$^{-3}$ $NaBH_4$ 10ml

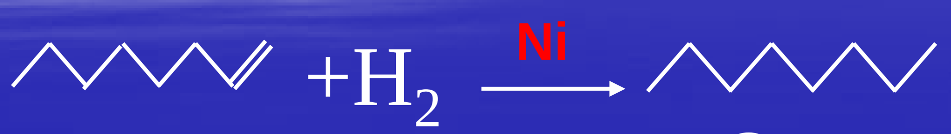
$$2Ni^{2+} + BH_4^- \rightarrow 2Ni + B^{3+} + 2H_2$$

← Catalytic activity measurement

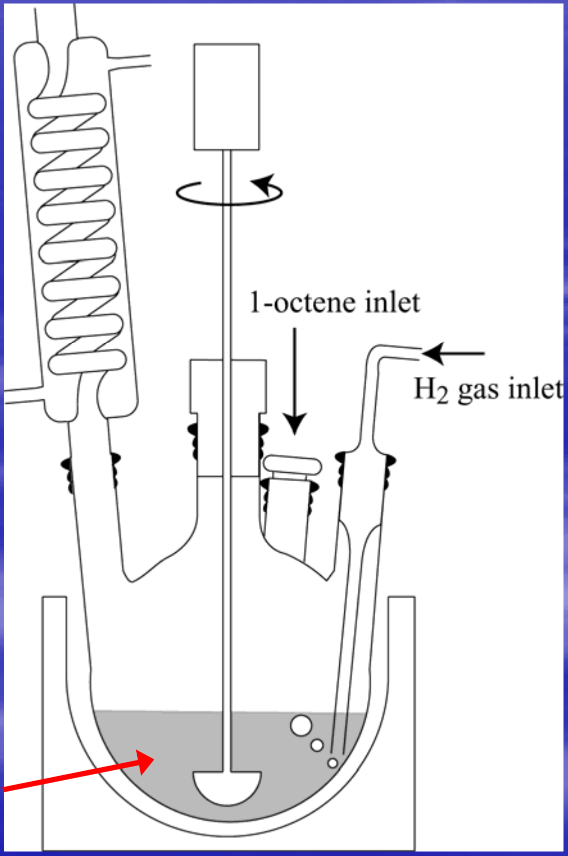
↓

**$Ni\text{-}Zn/TiO_2$ nanocomposite**

# Catalytic activity measurement

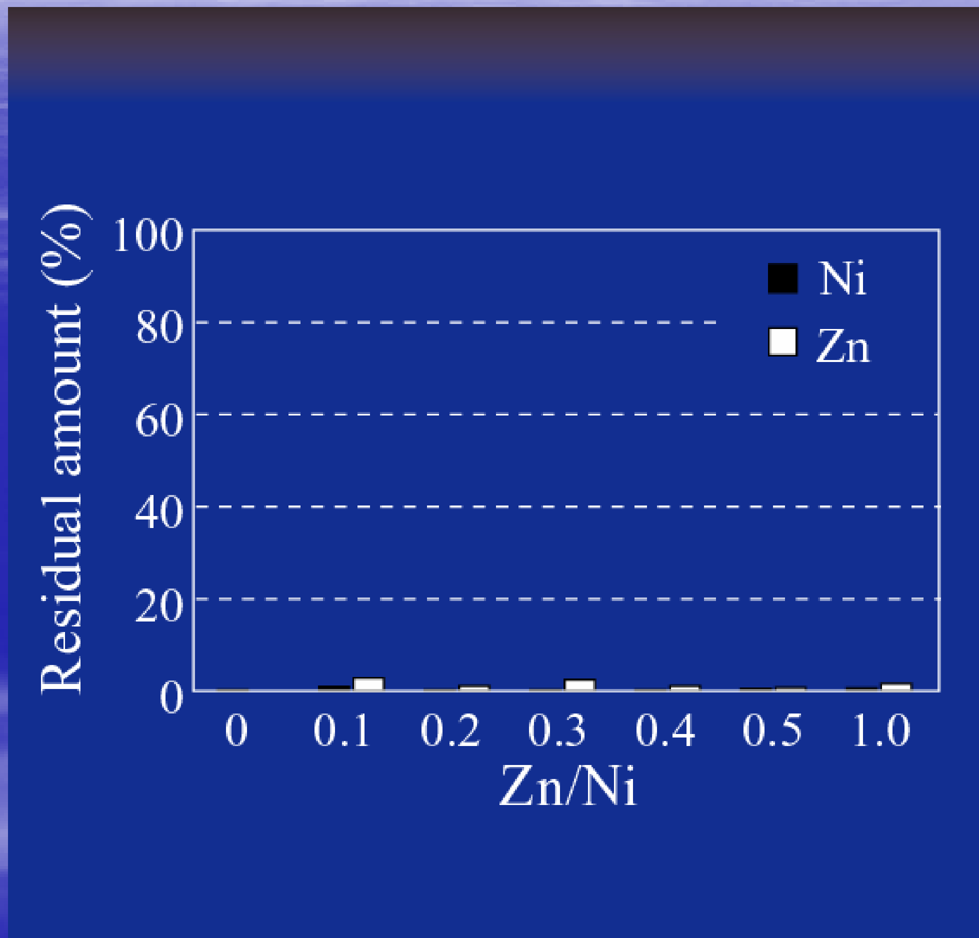



1-Octene n-Octane




Simple method to characterize the condition of Ni.

# Residual amount of Ni and Zn in the solution after synthesized the nanoparticles

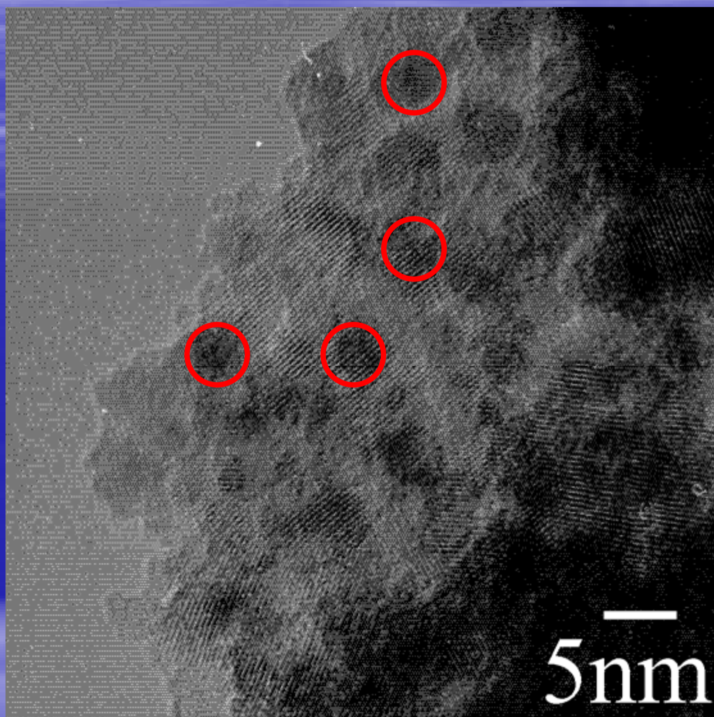



Almost all metal was deposited on the $TiO_2$ supports.

# Results and Discussion

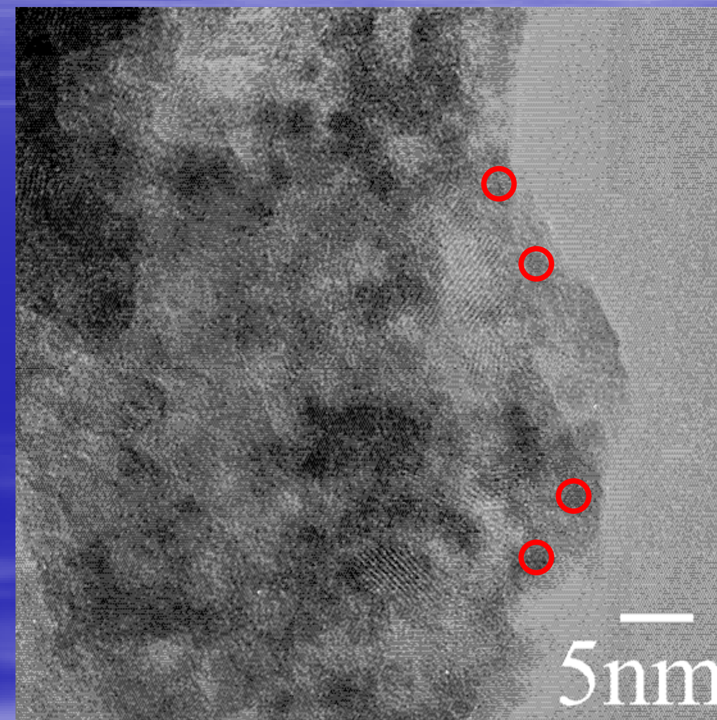
# HR-TEM images of Zn-Ni/$TiO_2$ nanocomposite

**Average size: c.a.5-6nm**




**(a) Zn/Ni=0.2**

**Average size: c.a.1-2nm**



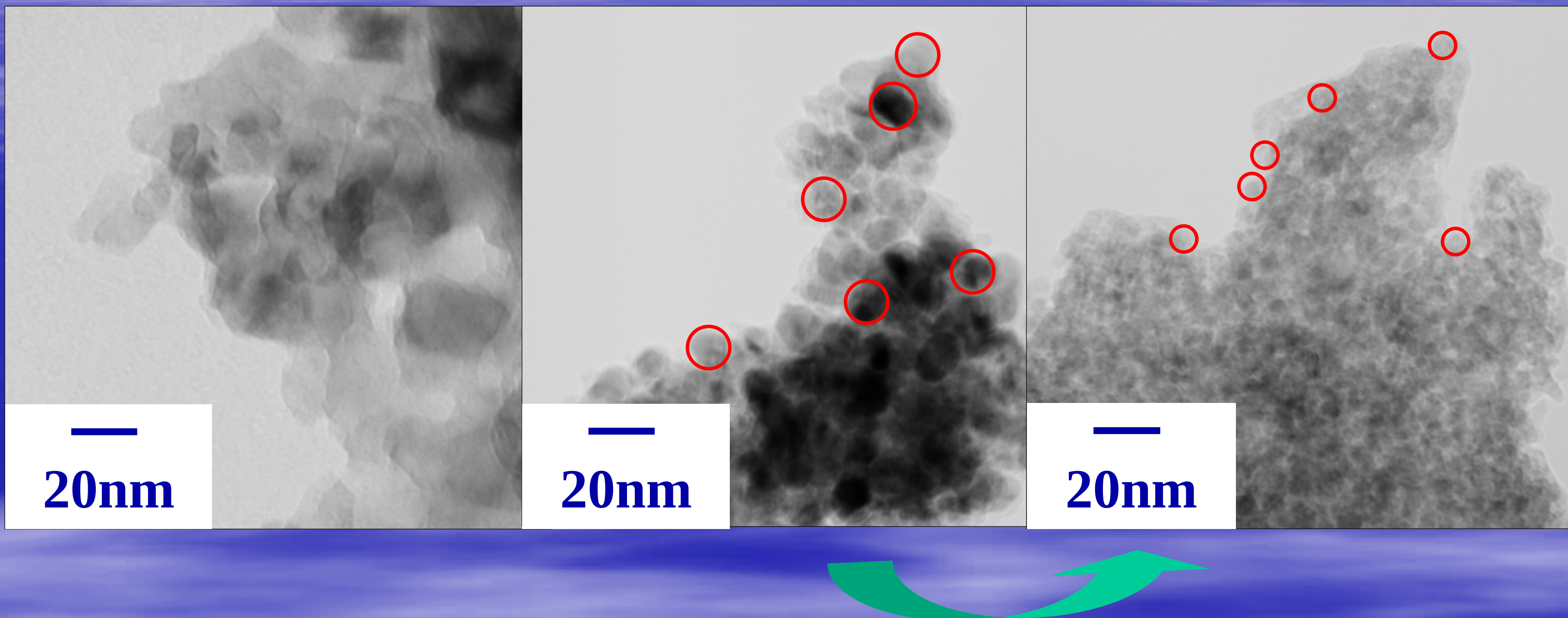

**(b) Zn/Ni=1.0**

The particle size appears to decrease with increasing amounts of Zn added.

(a) ST01

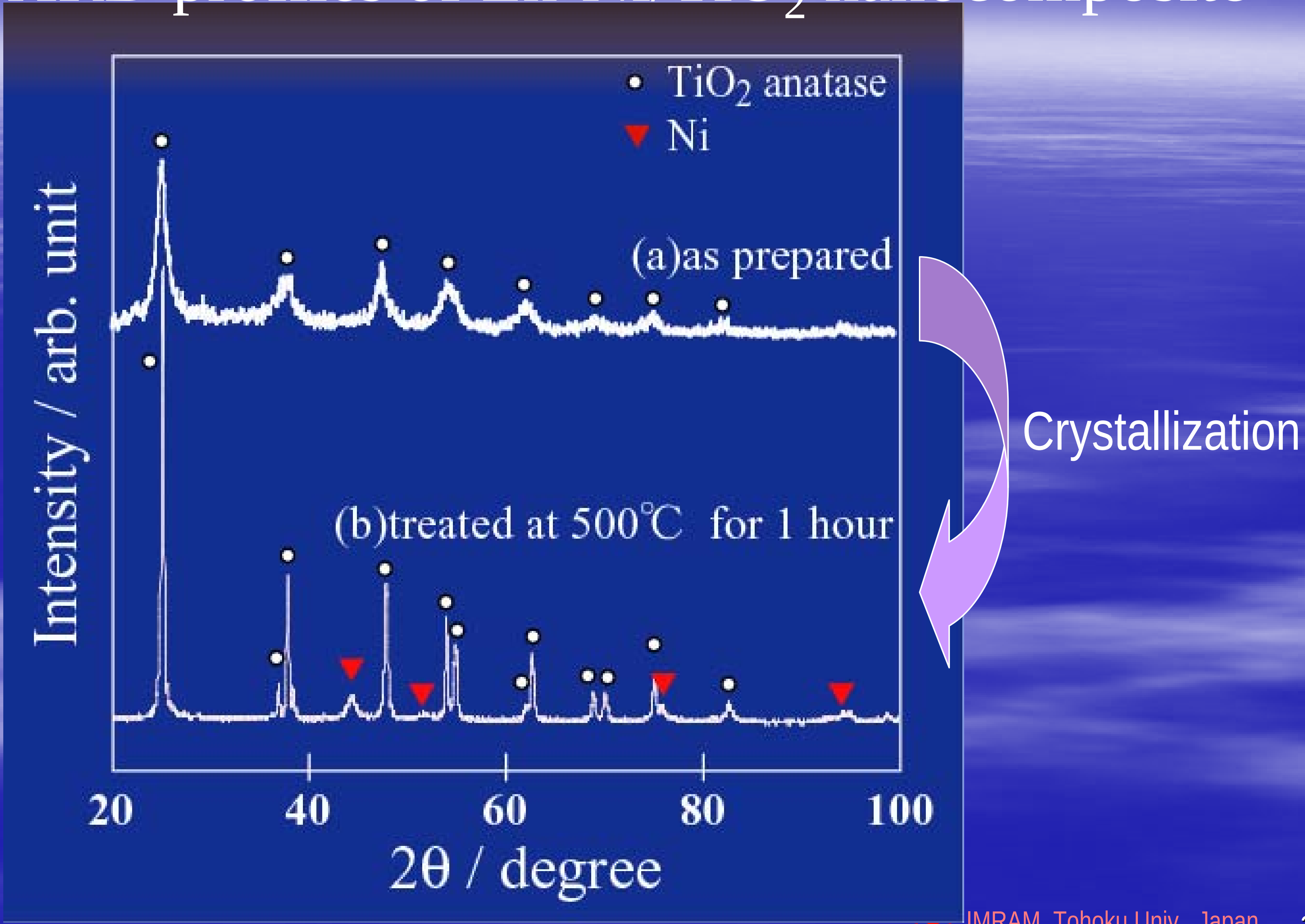
(b) Ni-Zn/ST01 Zn/Ni=0.1

(c) Ni-Zn/ST01 Zn/Ni=1.0

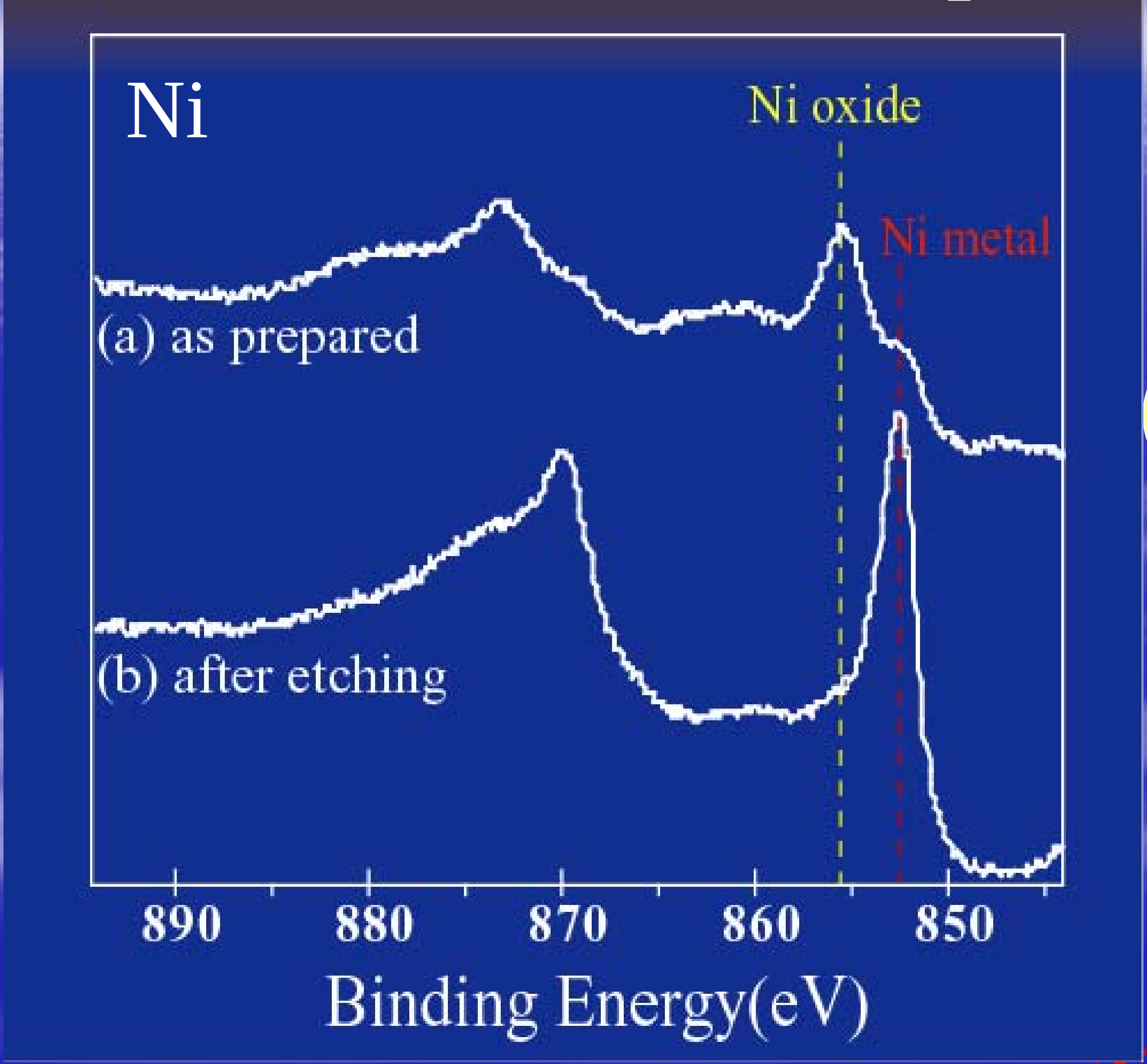


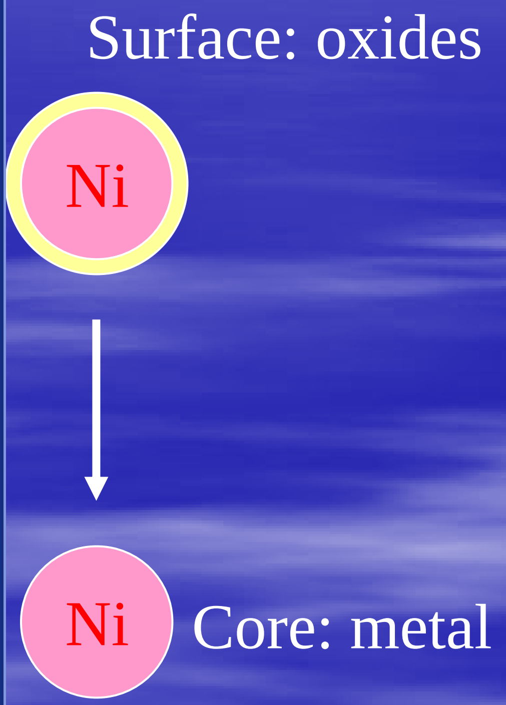

With increasing Zn, the size was decreased.

# XRD profiles of Zn-Ni/$TiO_2$ nanocomposite

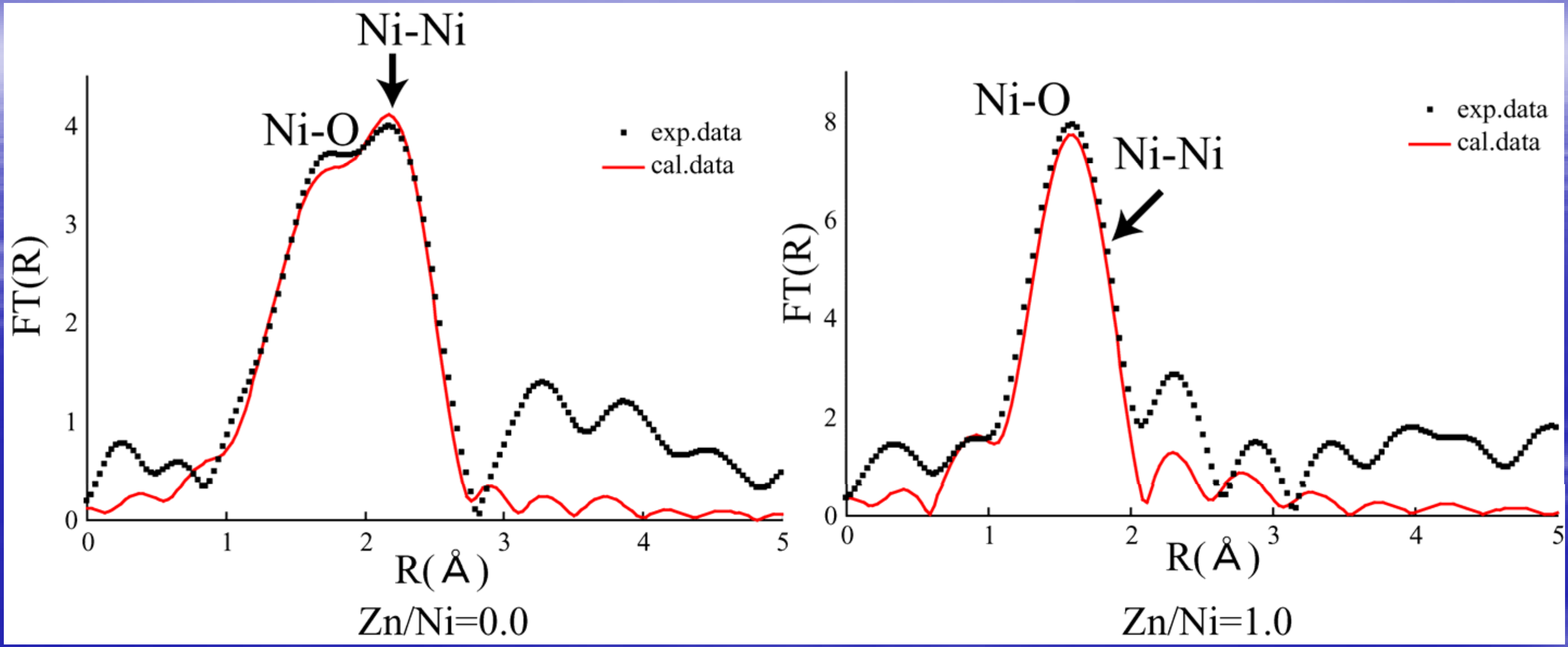


# XPS profiles of Zn-Ni/$TiO_2$ nanocomposite



# Results of EXAFS (Ni-Kedge)

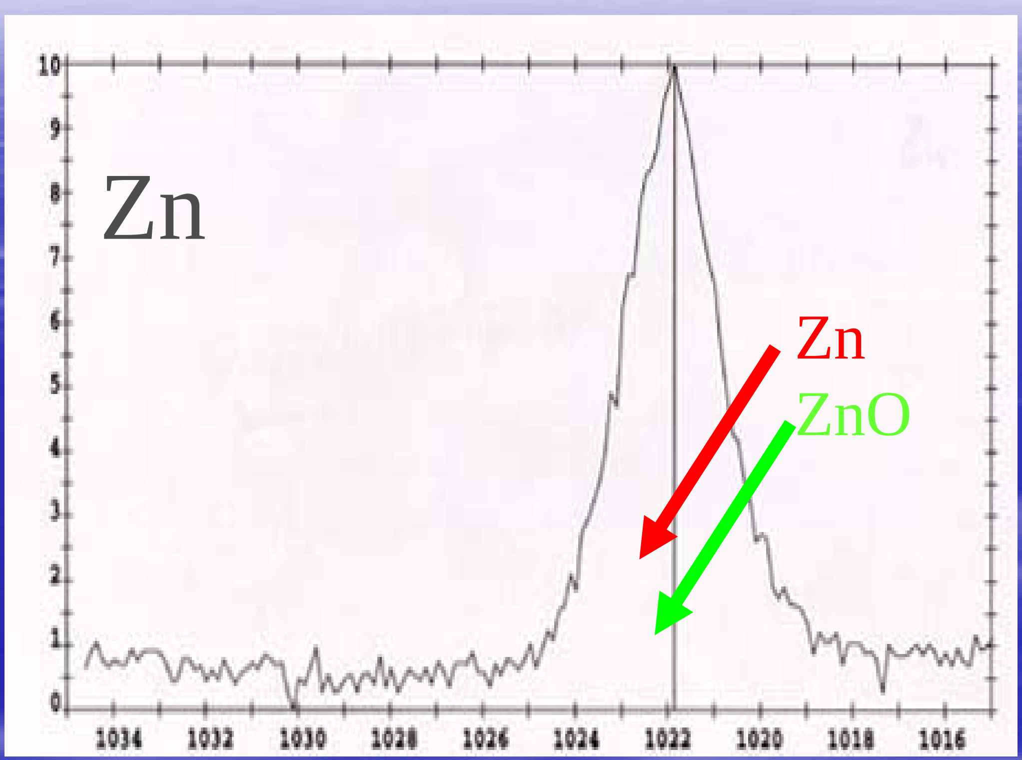



Large particle size small

26.7% Amount of Boron 39.4%

Large amount of B contained in the particles ⇒ Intermetallic compound ⇒ amorphous

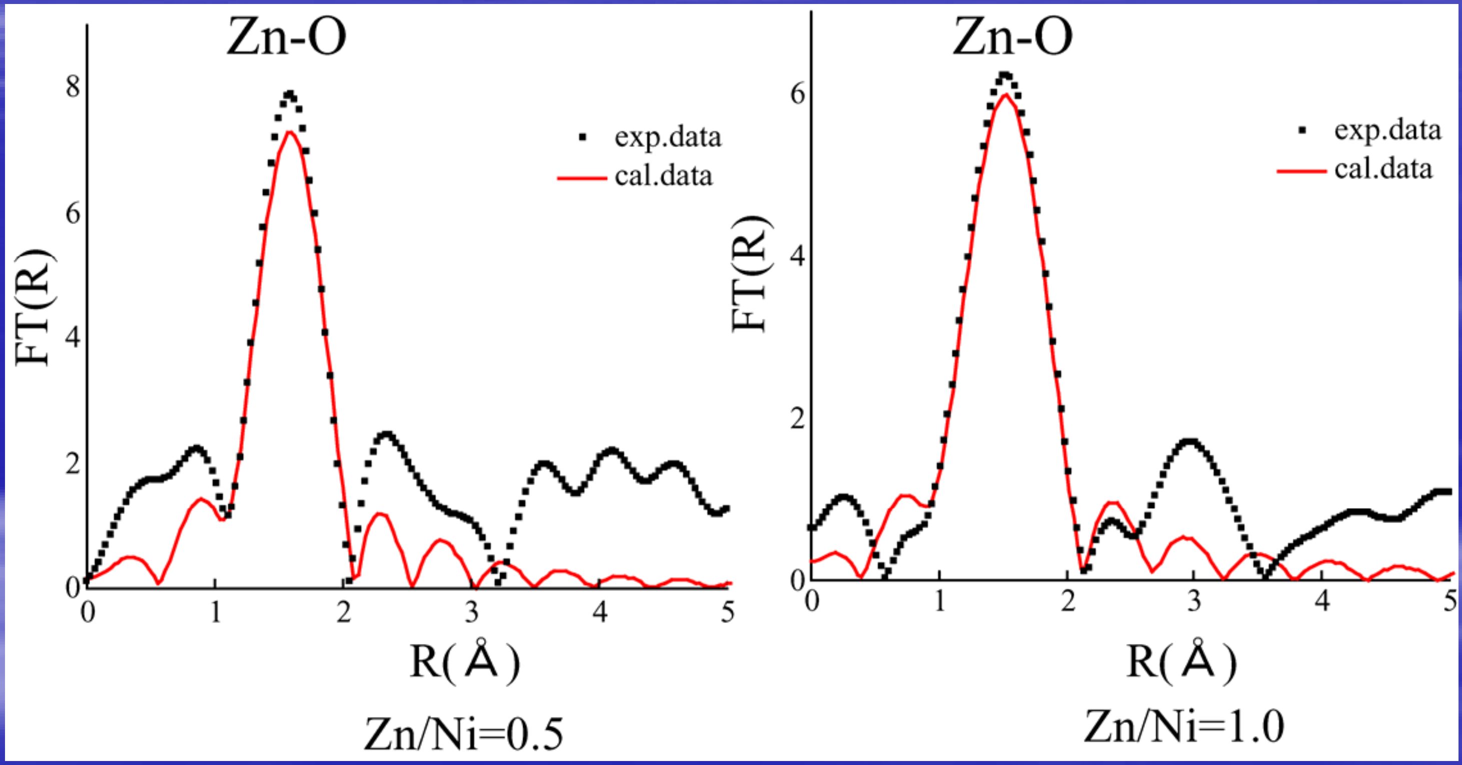
# XPS profiles of Zn-Ni/$TiO_2$ nanocomposite



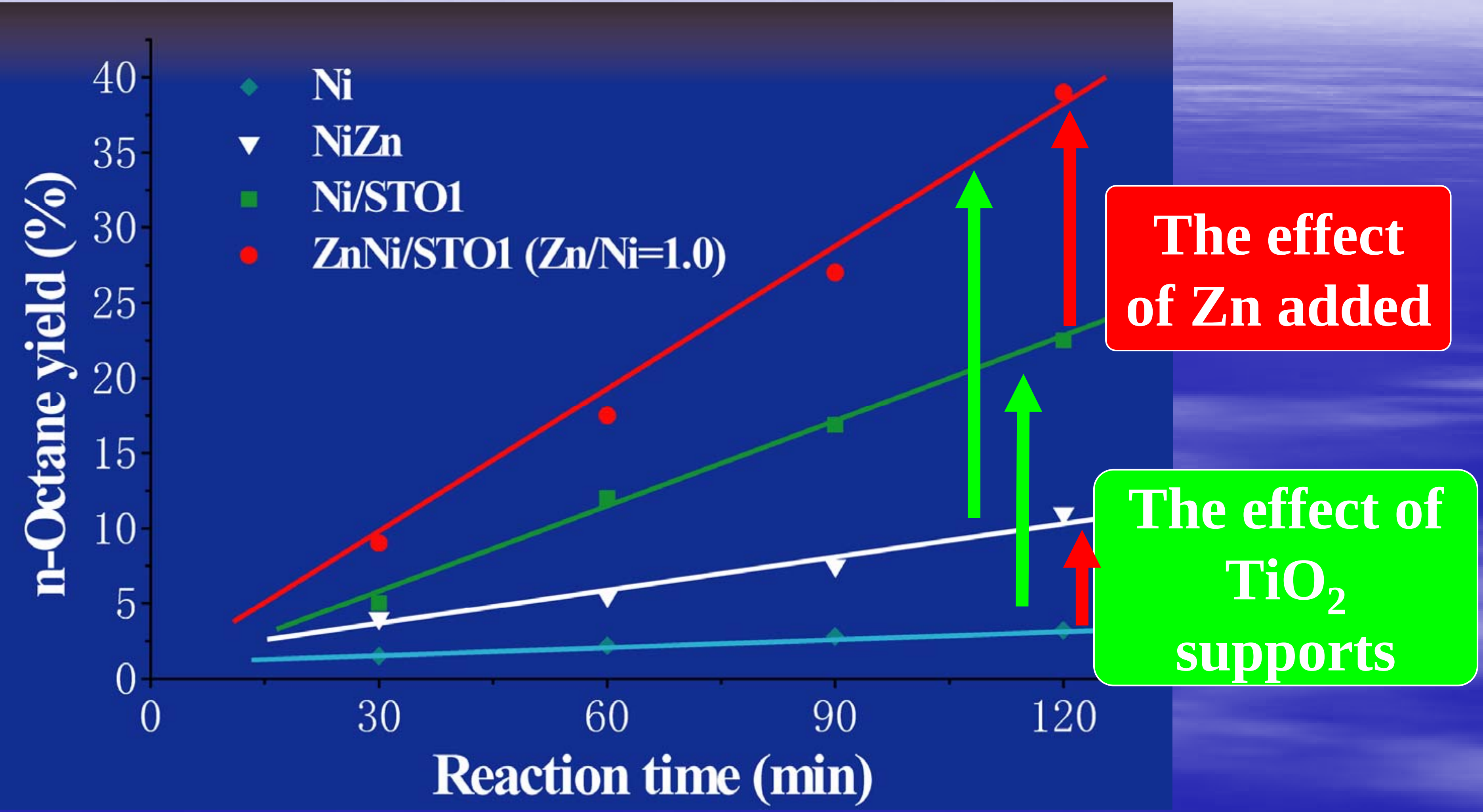

The identification of Zn state is difficult in this experiment because the peak positions of Zn and ZnO in ESCA spectra are very close.

⇒EXAFS

# Results of EXAFS (Zn-K edge)

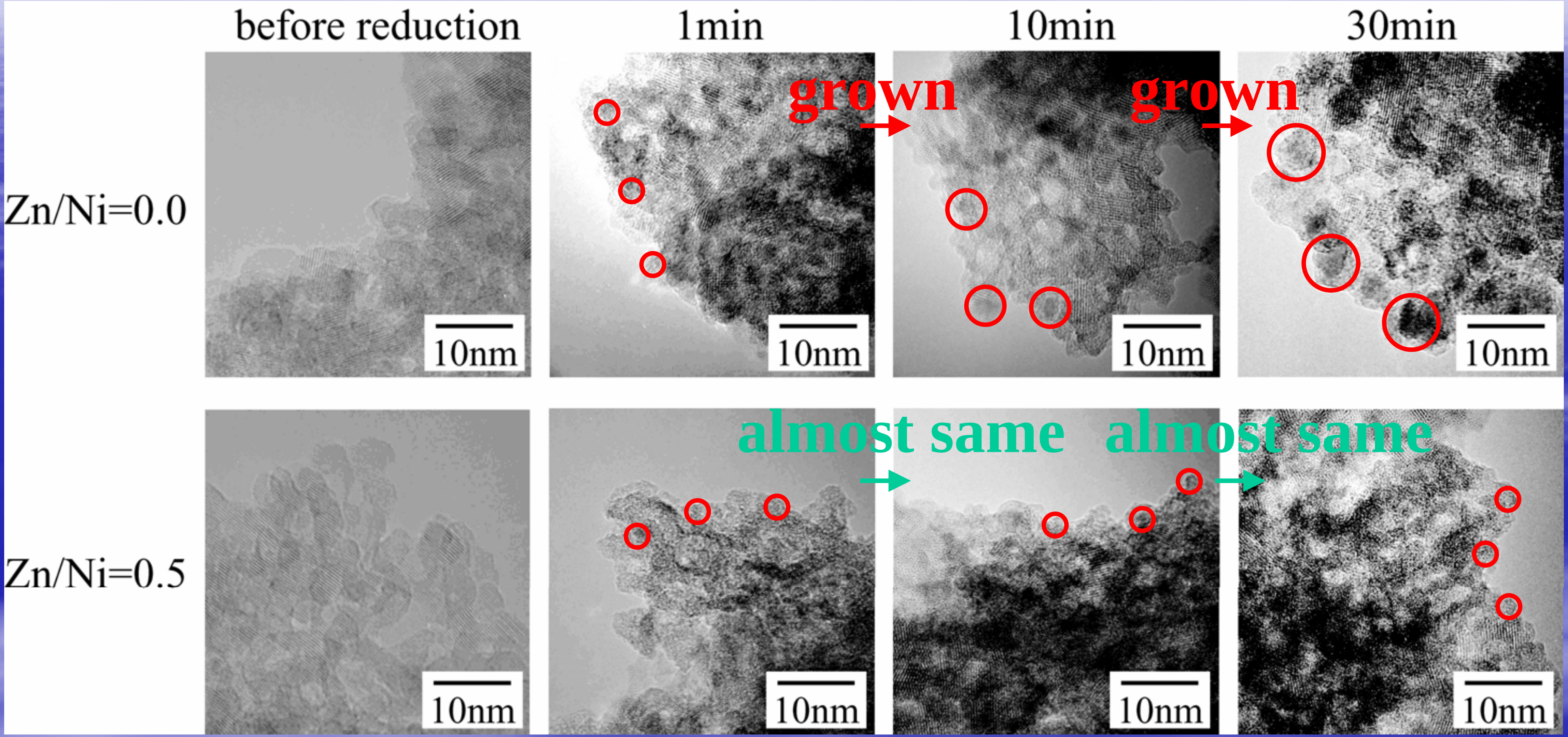


# Hydrogenation catalytic activity measurement




Ni < Ni-Zn < Ni/$TiO_2$ < Ni-Zn/$TiO_2$

# HR-TEM images of Ni-Zn/$TiO_2$ nanocomposite




Particle size: 5-6nm (Ni), 1-2nm (Ni-Zn)
Heterogeneous nucleation
Zn addition suppressed the growth.

# saturated adsorption amount

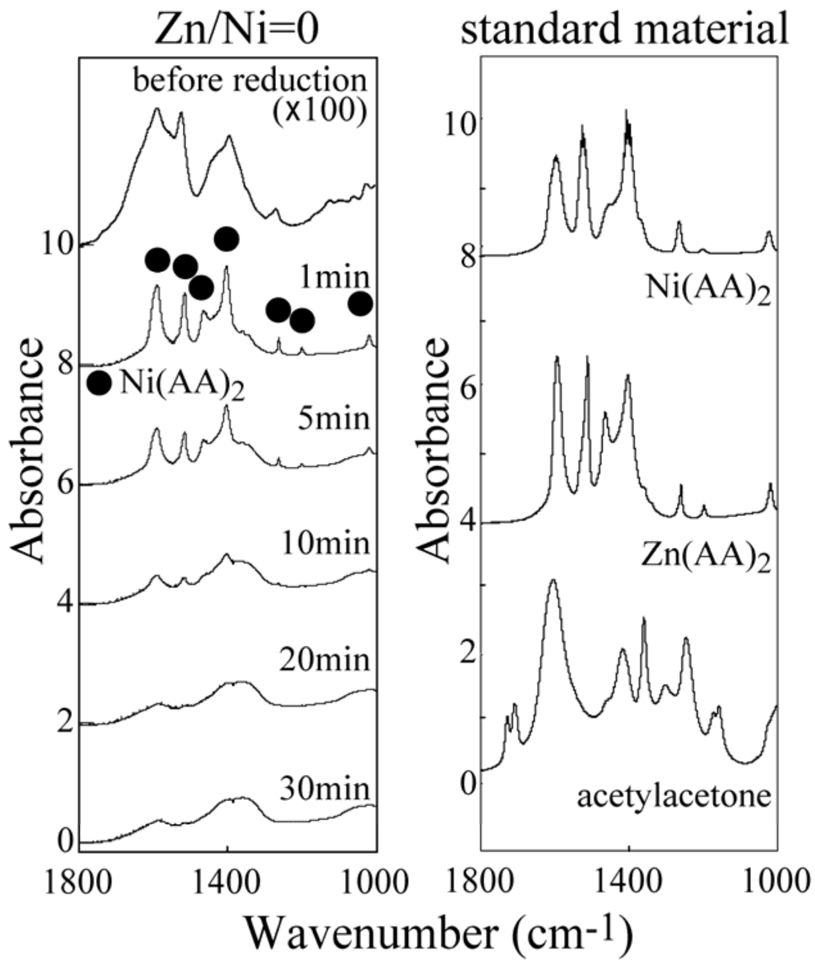
| | saturated adsorption amount of $Ni(AA)_2$ | saturated adsorption amount of $Zn(AA)_2$ |
|---|---|---|
| Ni only | 1.3mmol/g | |
| Zn only | | 2.8mmol/g |
| Zn/Ni=1.0 | 2.0mmol/g | 2.8mmol/g |

Zn addition→$Ni(AA)_2$ adsorption increased.

**Increase in nucleation site**

**→ decrease in size.**

# FT-IR measurement of Ni-Zn/$TiO_2$ nanocomposite




| Zn/Ni | | 0 | 0.3 | 0.5 |
|---|---|---|---|---|
| starting amount of $Ni(AA)_2$ and $Zn(AA)_2$ (x $10^{-4}$mol) | | 2.5 | 3.25 | 3.75 |
| amount of $Ni(AA)_2$ and $Zn(AA)_2$ in the sample powder after reduction (x $10^{-4}$mol) | 1min | 2.30 | 3.03 | 3.61 |
| | 5min | 1.61 | 2.14 | 3.26 |
| | 10min | 0.94 | 1.29 | 2.78 |

# Summary

- Ni-Zn nanoparticles was successfully deposited on the $TiO_2$ nanoparticles.
- Ni nanoparticles were found amorphous.
- The state of Nickel was metallic.
- The addition of Zinc

  The particle size is decreased with increasing the Zn added.

  The catalytic activity of Ni-Zn/$TiO_2$ was 3 times higher than unsupported Ni nanoparticles.

  The amount of organic compound adsorbed was increased.
- Zn addition plays an outstanding effect and stabilization of Ni nanoparticles by deposition onto $TiO_2$.

# Our Papers

- Reduction Deposition of Ni-Zn Nanoparticles Selectively on $TiO_2$ Fine Particles in the Liquid Phase
  - Hideyuki Takahashi,Yoji Sunagawa,Saratuya Myagmarjav,Katsutoshi Yamamoto,Nobuaki Sato,Atsushi Muramatsu
  - Materials Transactions,44(11),2414-2416(2003)
- Characterization of the Ni-Zn/$TiO_2$ Nanocomposite Synthesized by the Liquid-Phase Selective-Deposition Method
  - Sarantuya Myagmarjav, Hideyuki Takahashi, Yoji Sunagawa, Katsutoshi Yamamoto, Nobuaki Sato, Eiichiro Matsubara, Atsushi Muramatsu
  - Materials Transactions,45(7),2035-2038(2004)