Characterization of Ni-Zn/TiO_2 nanoparticles synthesized by *liquid phase selective-deposition method*

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Introduction

Typical preparation method of the supported metal catalyst

Impregnation

- The simple method of the supported catalyst synthesis.
- The unsuitableness for preparing the supported catalysts of nanometer size with good dispersiveness.

Ion-exchange

- The obtainable method of the supported nanocatalysts with high dispersibility.
- The suitableness for the precious metal catalysts.
- The low support quantity (i.e. ~5 wt%).
- About Ni, etc.., which is easy to grow, the difficulty of getting the catalysts of several nm.

Hydrogen reduction at several hundred ºC

Liquid phase reduction method

The metal complex dissolved in the solvent is reduced to the metal by reducing agent.

- The simplicity and high yield
- The possibility of the combination of various metals, if the starting materials are soluble.
- Metal nanoparticles of 10 nm diameter or less.
- Amorphous particles.
- The decrease of the particle size by adding Zn.

✓Ni source: Nickel acetylacetonate complex /$Ni(acac)_2{\cdot}2H_2O$

✓Zn source: Zinc acetylacetonate complex /$Zn(acac)_2{\cdot}2H_2O$ (acac=$CH_3COCHCOCH_3$)

✓Reductant: Sodium borohydride /$NaBH_4$

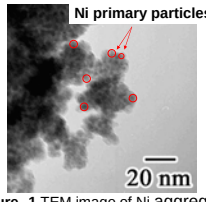


Figure 1 TEM image of Ni aggregate by "liquid phase reduction method"

Aggregation and deactivation

Liquid phase selective-deposition method

- Development and characterization of "*liquid phase selective-deposition method*" which prevents the aggregation of nanoparticles by expanding the liquid phase reduction method.
- Combination between high-loading and dispersibility with "*liquid phase selective-deposition method*".

Results and discussion

The schematic synthesis procedure

$Ni(acac)_2{\cdot}2H_2O$

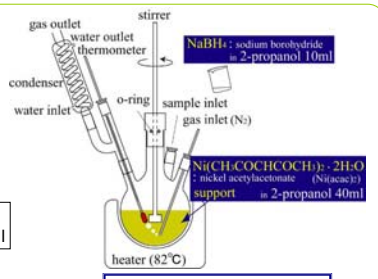
Dissolution — 2-propanol 40 ml

Dispersion for 30 min. — Support (TiO_2)

agitation at 82 ºC for 30 min.

Reduction — $NaBH_4$ /2-propanol solution 10 ml

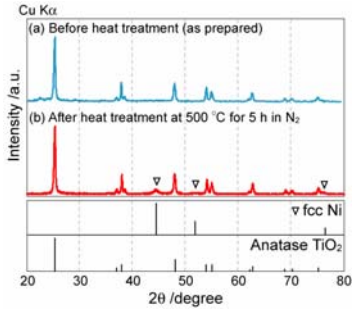
Ni/TiO_2



10 wt%Ni/TiO_2
[$Ni(acac)_2$]: 2.5×10^{-3} mol/l
[$NaBH_4$]: 1.0×10^{-2} mol/l
[TiO_2]: 2.5 g/l

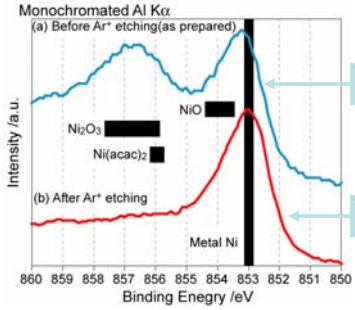
Figure 2 Scheme of Ni/TiO_2 composite synthesis

The X-ray analysis



Ni particles have the amorphous like structure

Figure 4 X-ray diffraction patterns of 10wt%Ni/TiO_2: (a) before, and (b) after heat treatment at 500 ºC for 5 h in N_2



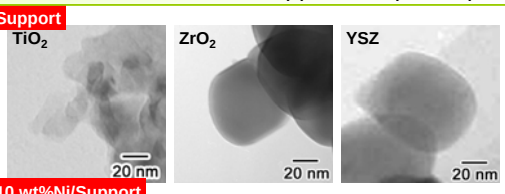
The Ni surface was oxidized in the handling under the atmospheric condition

The initial state of Ni in the nanoparticles must be metallic

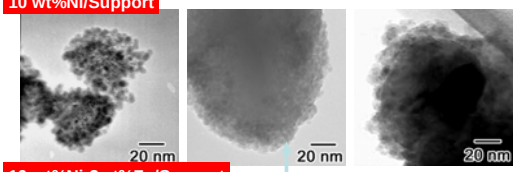
Figure 5 XPS spectra for the Ni $2p_{3/2}$ region of 10wt%Ni/TiO_2: (a) before, and (b) after Ar^+ etching

The TEM observation of Ni/support composite particles

Support

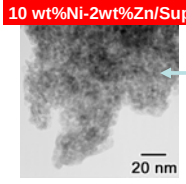


10 wt%Ni/Support



The selection deposition of Ni is possible on various supports

10 wt%Ni-2wt%Zn/Support



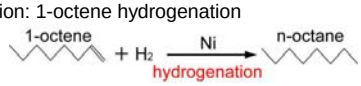
Supported Ni particles were about 5 nm

By the Zn addition, Ni particles became smaller as 2 nm

Figure 3 TEM Images of Ni or Ni-Zn synthesized onto TiO_2, ZrO_2, and YSZ
(YSZ: Yttria Stabilized Zirconia)

The catalytic activity test

Model reaction: 1-octene hydrogenation

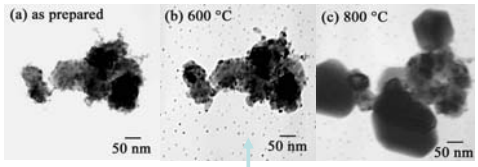


Reaction conditions
1-octene : 5.0 ml
H_2 flow rate : 0.1 mol/h
reaction temperature: 82 ºC
reaction time : 120 min

Figure 7 Scheme of 1-octene hydrogenation reaction with Ni catalyst

The verification of thermal stabilization

10wt%Ni/YSZ



10wt%Ni-2wt%Zn/YSZ

Nanoparticles were stable to 600 ºC

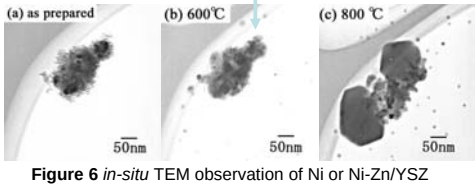


Figure 6 *in-situ* TEM observation of Ni or Ni-Zn/YSZ
(YSZ: Yttria Stabilized Zirconia)

The effect of the effective surface area from the Ni size

The deactivation was prevented by the immobilization of Ni nanoparticles

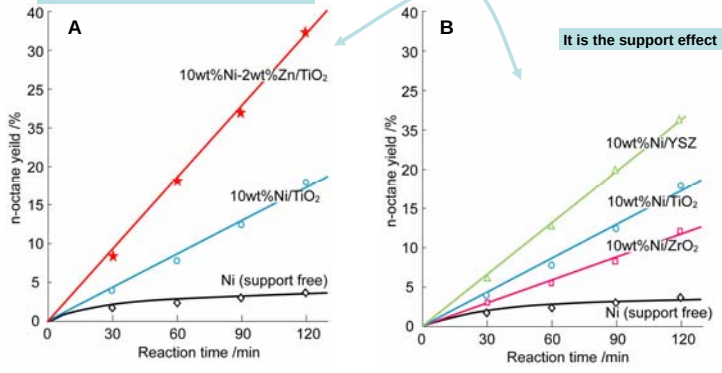


Figure 8 n-octane yield of the 1-octene hydrogenation reaction with Ni catalysts: (A) with various Ni, and (B) with various supports

Conclusion

- We succeeded in the development of *liquid phase selective-deposition method*.
- We realized the high loading of nanometer-size Ni with high dispersibility.
- That Ni was the metallic state, and showed the high hydrogenation catalytic activity without agglutinating.