CO Hydrogenation to Organic Compounds over Ni-Zn Nanoparticles in Liquid-Phase

Atsushi MURAMATSU, Katsutoshi YAMAMOTO, Hideyuki TAKAHASHI, Nobuaki SATO, and Shohei MAKIHARA

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Katahira, Aoba-ku, Sendai 980-8577, Japan

In our laboratory

Hybrid nanoparticles, nanocomposites

- Novel synthesis method.
  Liquid-phase reduction
  Selective reductive deposition in liquid phase
- Their characterization

CO hydrogenation is one of the characterization methods.
Activity and product distributions
→ characteristics of metal particles.

Background

Catalysts

- Novel catalyst preparation is always required.
  - Needs and seeds (break-through)
  - Utilization of resources
- Every-time demand to get best activities!

Nano-sized catalyst
Bimetallic or bimetal catalyst

↓

Activity promotion
Change of selectivity and so on

Objectives

1. Highly active Ni-Zn nanoparticles is prepared as a hydrogenation catalyst by Liquid Phase Reduction method.
2. Nanoparticle suspension is used as a CO hydrogenation catalyst. Their activities and selectivities are evaluated.
3. Laser Flash method is applied for new characterization technique for catalysts in the liquid-phase as a thermal diffusivity.

Liquid-Phase Reduction Method

0.01 mol/l $Ni(AA)_2$ in 2-propanol solution 50ml
0.002 mol/l $Zn(AA)_2$ in 2-propanol solution 10ml

↓

Heating(355K), 30min
N_2 flow(300ml/min)

← 0.1 mol/l $NaBH_4$ in 2-propanol 10ml

Reduction

↓

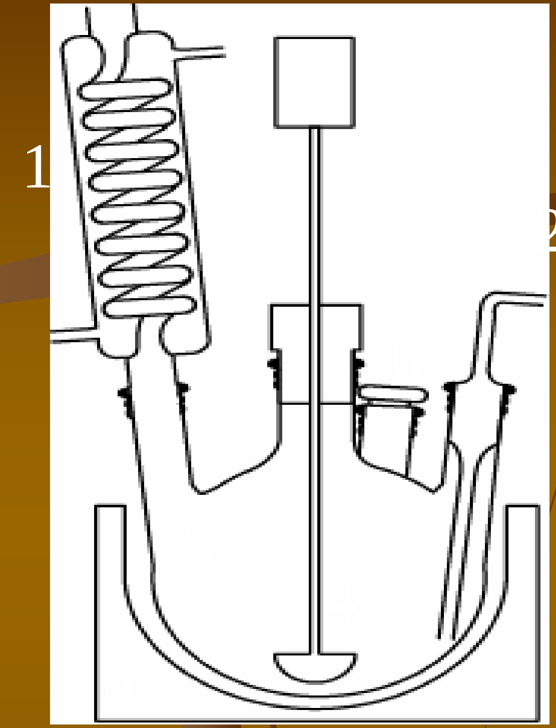
Heating(355K), 30min
N_2 flow(300ml/min)

← Hexadecane

Condensation

↓

Ni-Zn nanoparticles in hexadecane



1:Condenser
2:Gas inlet
3:4-neck flask
4:Stirrer
5:Heating mantle
6:Sample inlet

Catalyst Preparation

$Ni(AA)_2$=0.005mol•dm^{-3} const.
Zn/Ni = 0.2
2-propanol solution 40ml

↓

← N_2 gas flow (30min, 82℃)

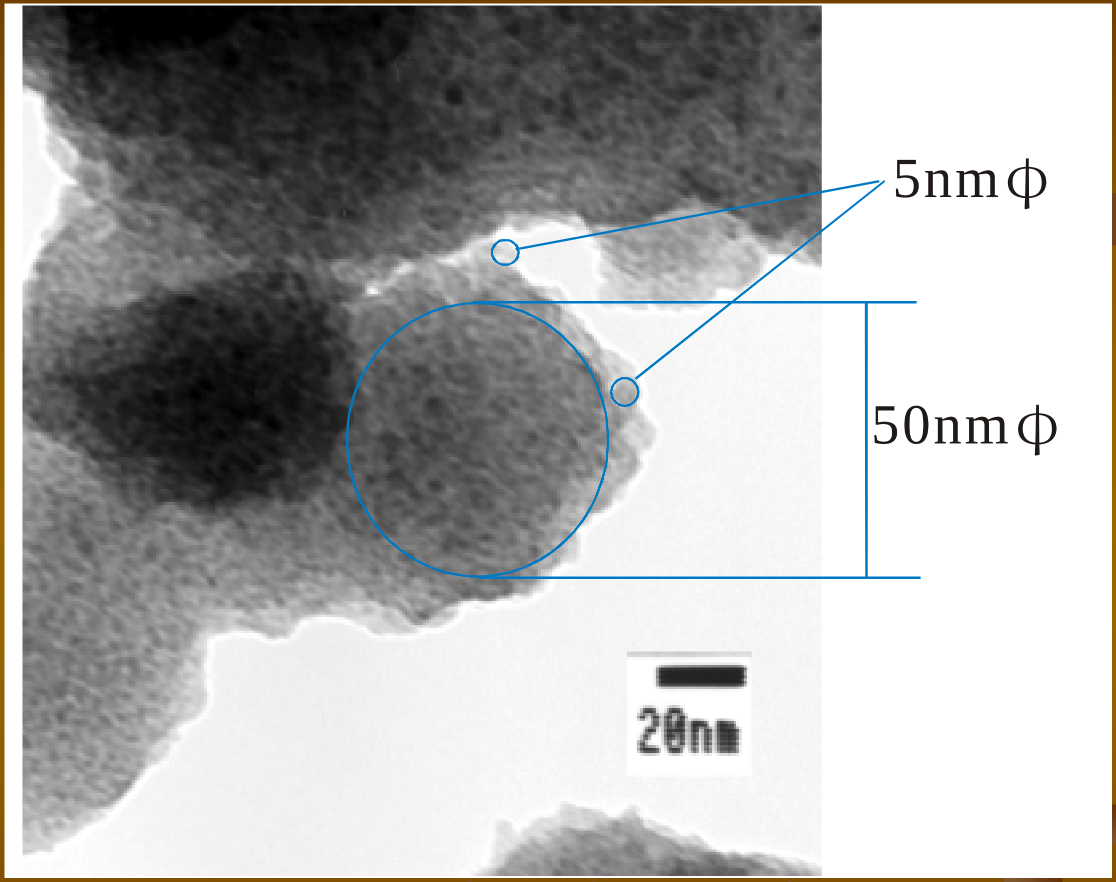
← 0.02mol•dm^{-3} $NaBH_4$ 10ml

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

↓

Ni-Zn nanoparticles

Ni-Zn nanoparticles



Primary particles = ca. 5nm
Aggregates = ca. 50 nm

CO hydrogenation

Reaction

$CO + H_2 \longrightarrow$ Hydrocarbons, Alcohols etc.

High pressure
Catalysts

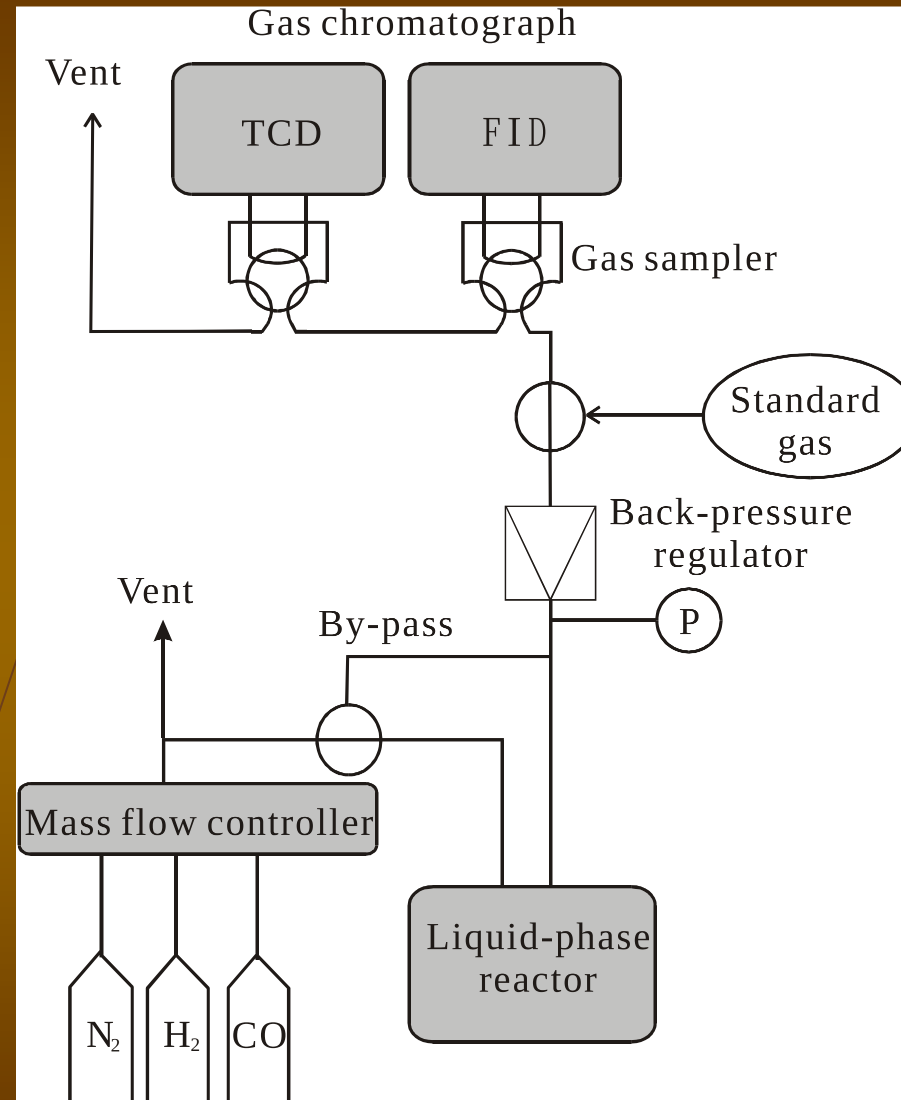
Ni-Zn nanoparticles in hexadecane 50ml

Temp.→573 K
Pressure→1.5 Mpa
Stir → 300 rpm

CO, H_2

Reaction 12 h

Analysis

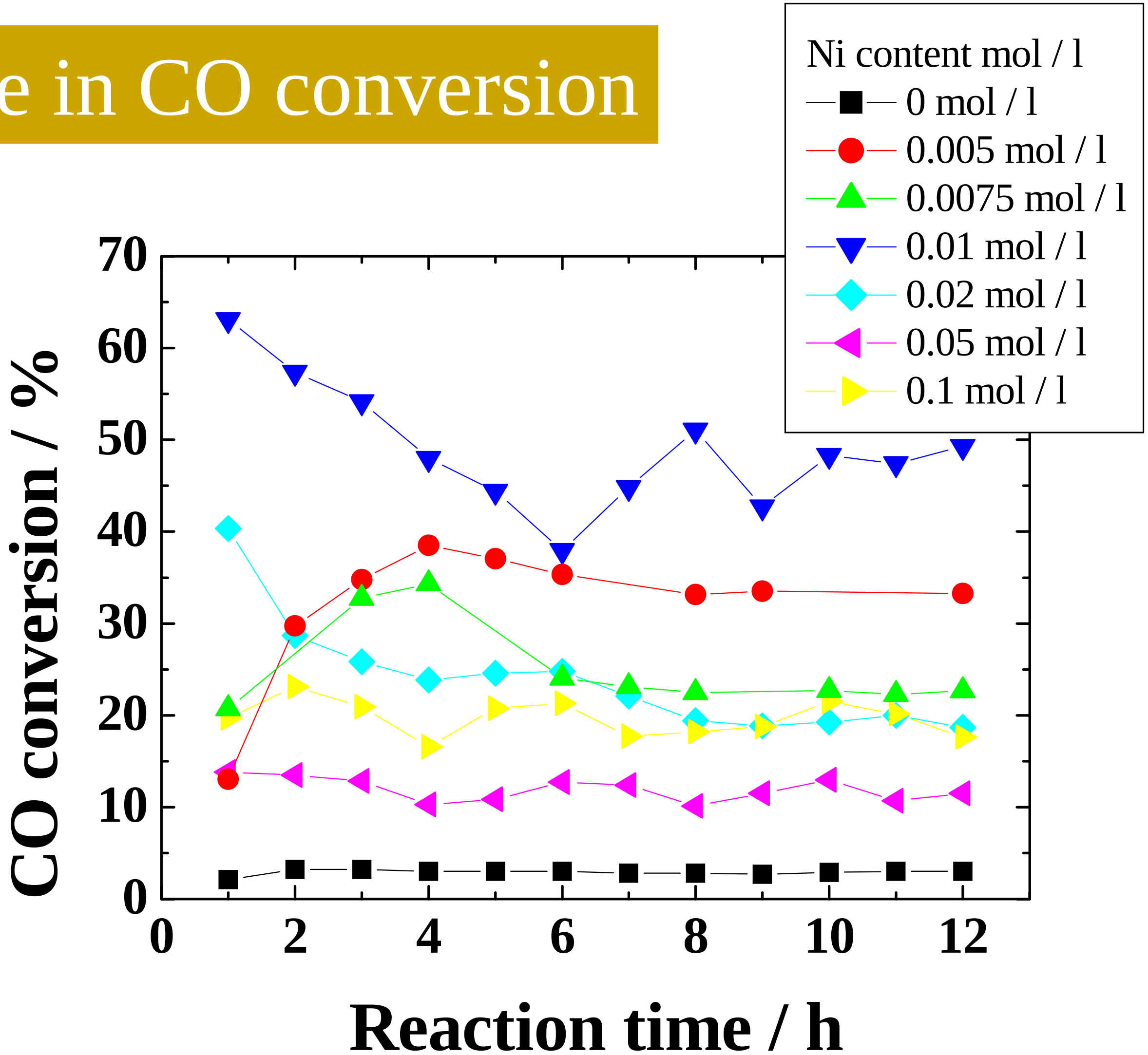


Reaction conditions

	Ni content/ mol / l	Flow rate /ml / min	
		H_2	CO
Case 1	0	7.5	7.5
Case 2	0.005	7.5	7.5
Case 3	0.0075	10.2	10.2
Case 4	0.01	15.0	15.0
Case 5	0.02	30.0	30.0
Case 6	0.05	75.0	75.0
Case 7	0.1	150.0	150.0

Reaction temperature : 573 K
Reaction pressure : 1.5 MPa
Revolving speed : 300 rpm
W/F(catalyst weight/flow rate) : 29.1 g-cat h / mol
Zn/Ni : 0.2

Change in CO conversion



0.005~0.01 mol/l -> active

Distribution

6 h

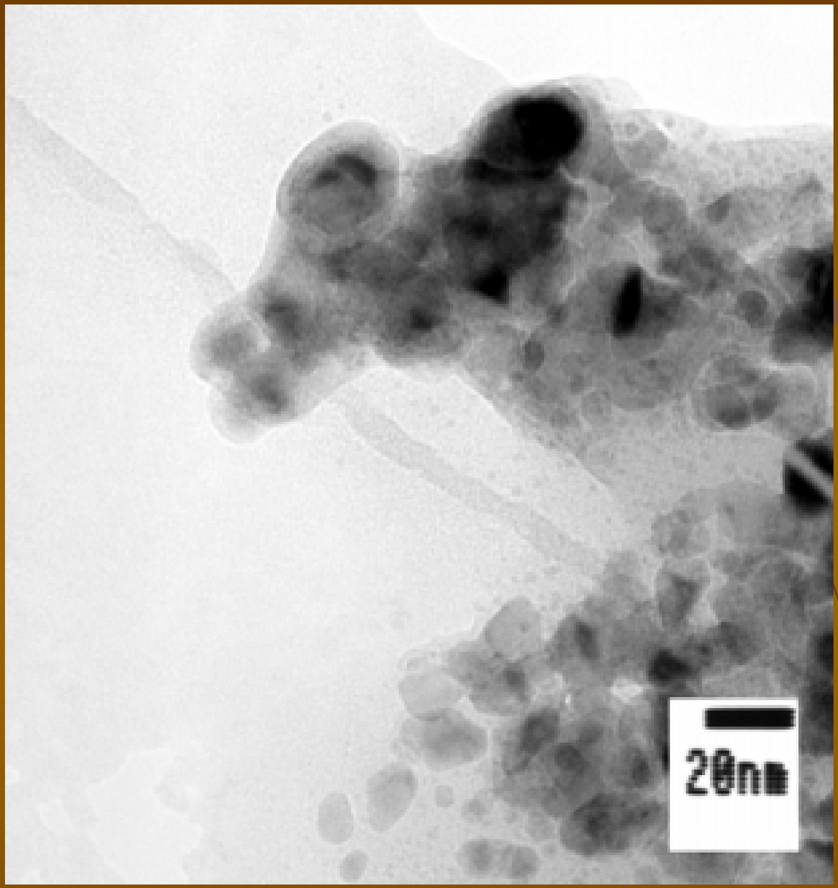
Ni content mol/l	Selectivity / %					
	methane	ethane	ethylene	propane	butane	CO_2
0.005	38.4	3.7	0.5	1.0	1.5	38.9
0.0075	38.3	2.5	0.2	0.7	2.1	38.9
0.01	41.8	2.8	0.1	0.3	0.5	42.2
0.02	34.9	3.2	0.8	1.0	0.5	37.0
0.05	42.5	0.9	0.1	0.1	0.4	50.2
0.1	50.5	1.0	0.0	0.0	0.2	44.0

Ni content mol/l	Selectivity / %				
	methanol	ethanol	acetone	1-propanol	2-propanol
0.005	12.2	1.4	0.7	1.3	0.4
0.0075	11.6	1.3	0.6	1.8	1.9
0.01	11.2	0.2	0.0	0.1	0.0
0.02	5.1	1.5	8.9	0.0	7.0
0.05	3.0	0.3	0.2	0.4	0.2
0.1	2.2	0.6	0.1	0.2	0.1

CH_4、CO_2、CH_3OH were formed.
0.005~0.01 mol/l -> high selectivity to methanol

Active in oxygenate production

Used Ni-Zn nanoparticles



Ni-Zn nanoparticles
- high activity
- life time

Methanol synthesis

Ni content : 0.01 mol/l (Zn/Ni=0.2)

5~20nm nanoparticles

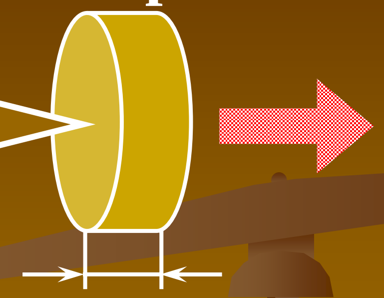
Laser Flash method

Short measurement time
No contact with specimen

Obtaining adiabatic state
Negligible for convection

Pulse laser

Sample

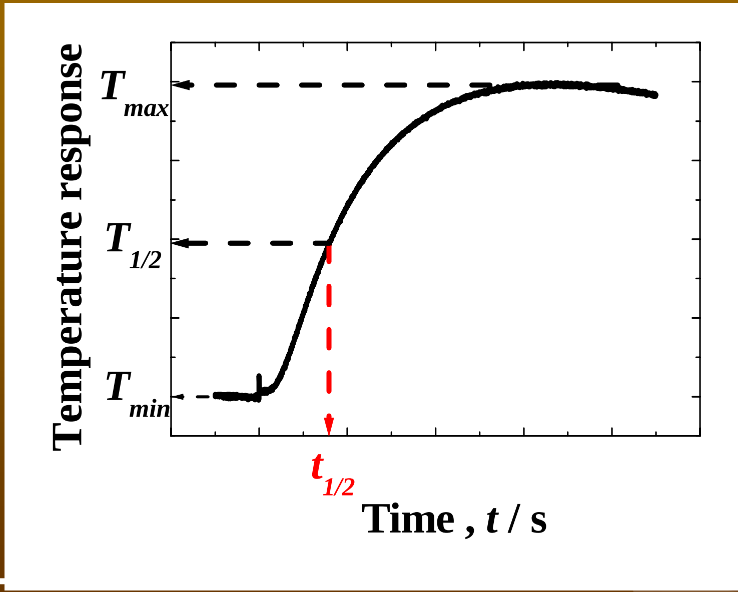


Detector

L

$t_{1/2}$ method

Temp. response of back side



$$\alpha = 0.1388 \times \frac{L^2}{t_{1/2}}$$

α : Thermal diffusivity [mm^2/s]

$(\alpha = \lambda / C_p \rho)$

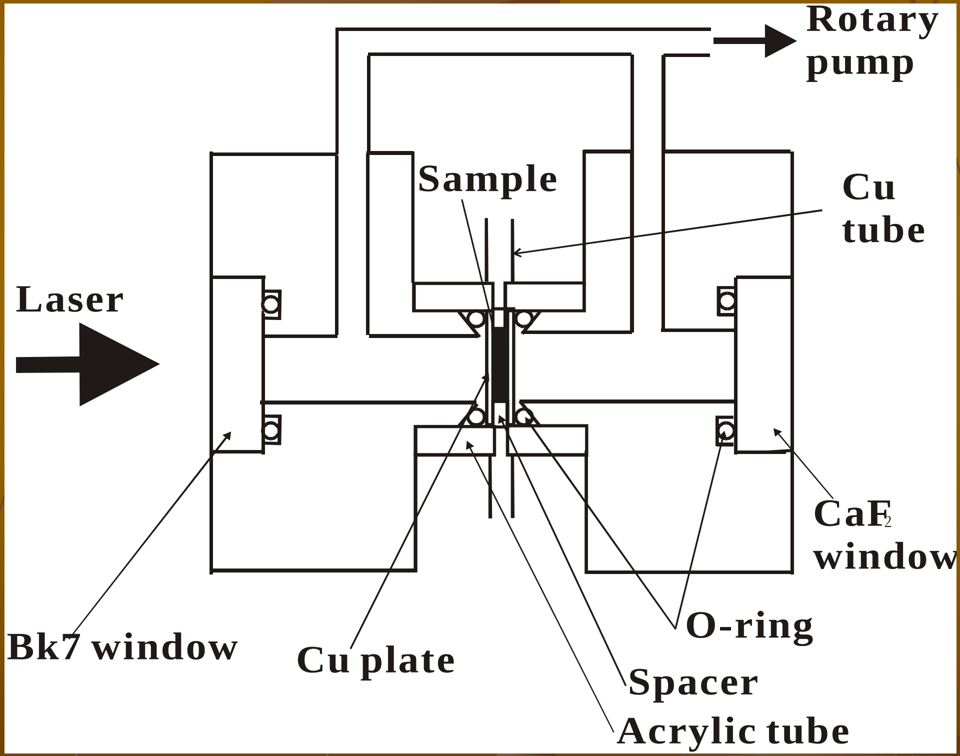
L : thickness [mm]

Cell design

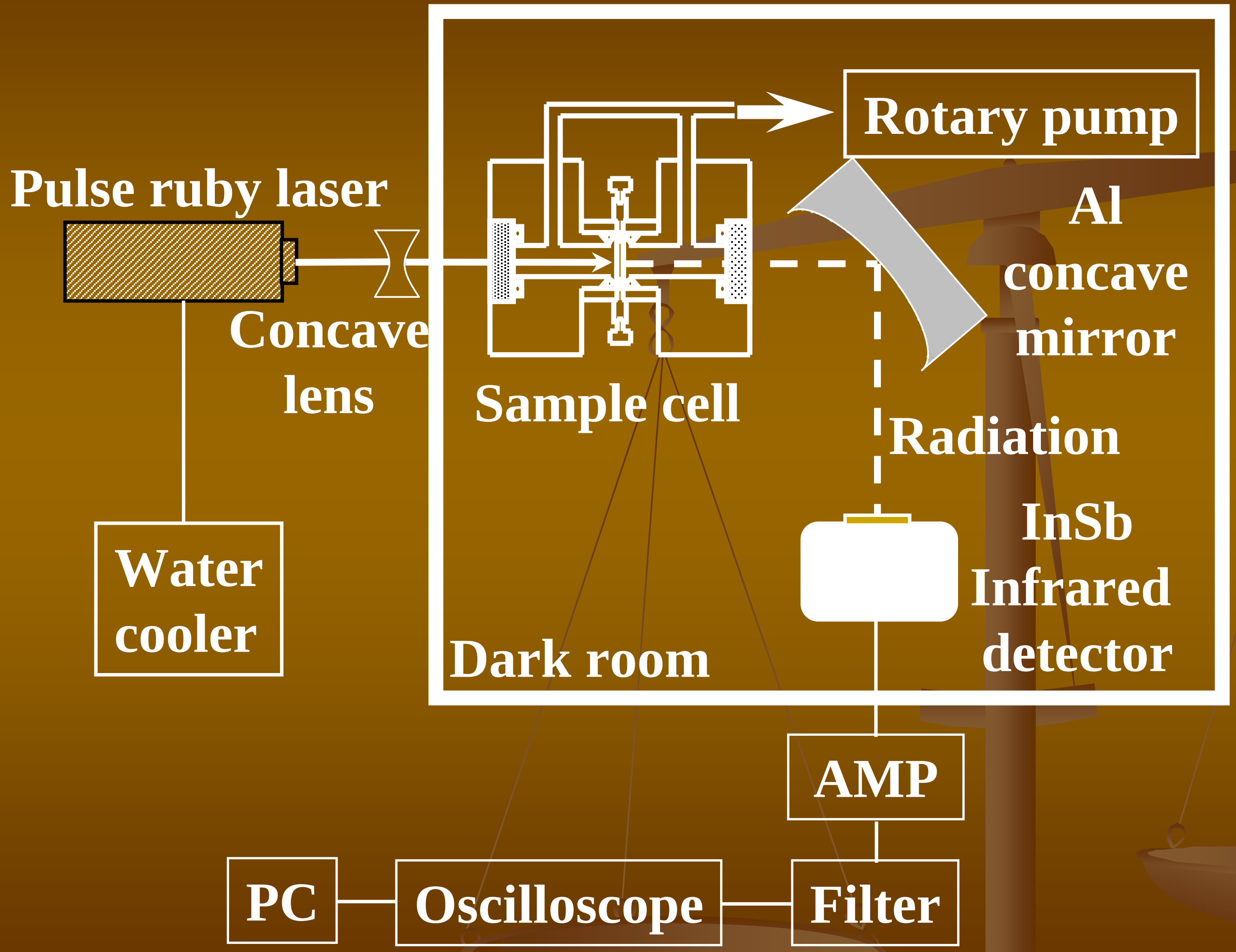
To measure thermal diffusivity of a liquid under atmospheric conditions

Features

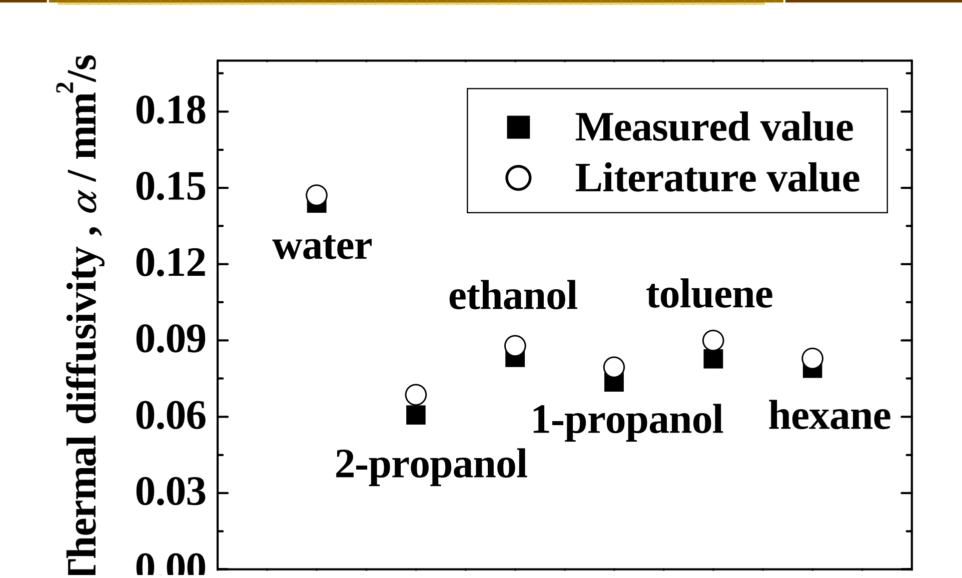
1. Materials are necessary to absorb laser beam and to emit infrared light.
2. Caloric leak is limited.
3. Light path is limited below 0.5mm.
4. Impurities should be avoided.
5. One-dimensional heat transmission is needed.



Outline of Laser Flash Apparatus

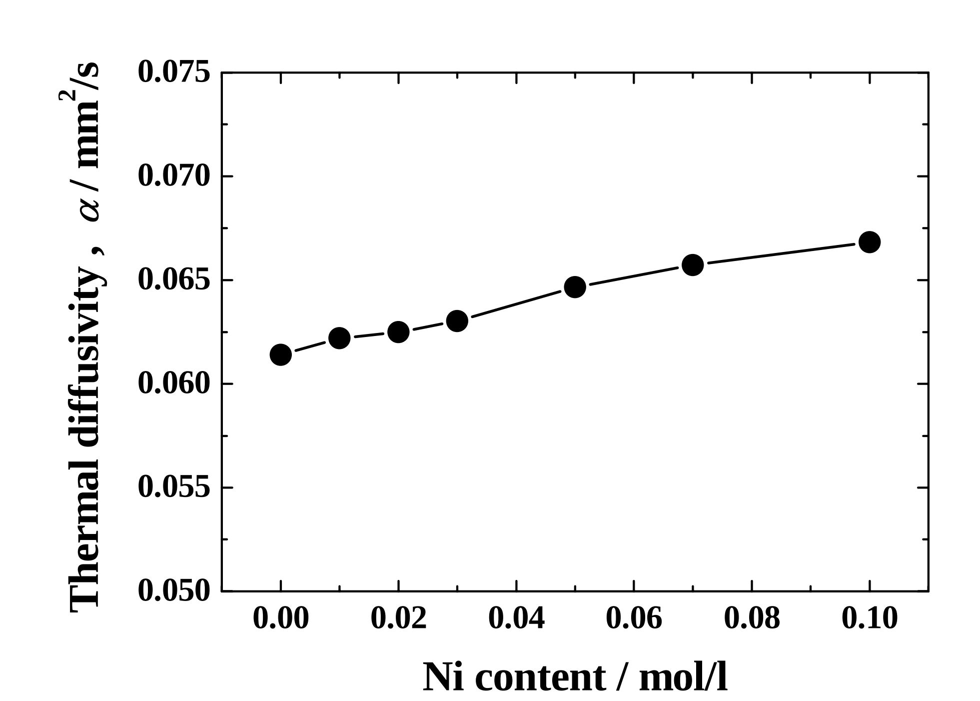


Results



Consistent with literature

Success in precise measurement of a liquid



- With increasing Ni-Zn particle amount, thermal diffusivity was increased linearly.
- 9 % increase was found for 0.1 mol/l particle suspension.

Summary

1. Ni-Zn bimetallic nanoparticles were prepared by liquid-phase reduction method.
2. They were found active for methanol synthesis in CO hydrogenation.
3. Even though the same contact time was chosen, the activity and selectivity of Ni-Zn nanoparticles was changed.
4. Thermal diffusivity of nanoparticle suspension was increased with increasing particle concentration.
5. Laser flash method to measure the thermal diffusivity was useful as a novel characterization technique for suspension catalysts.
6. Unfortunately the explanation of the solid concentration effect due to the thermal diffusivity was failed.

Next stage of this study

1. Try to explain the solid concentration effect by the stability of the suspension.
   - Dispersion and aggregation of particles
2. Promote the stability of Ni-Zn nanoparticles.
   - Selective deposition of Ni-Zn onto TiO_2 nanoparticles
3. Enhance the activity and selectivity to oxygenates.
   - Use of the adequate additives
4. Generalize the Laser Flash method.