Int'l H_2 Storage Technologies Conference

Organic Hydrides for Carrying Hydrogen

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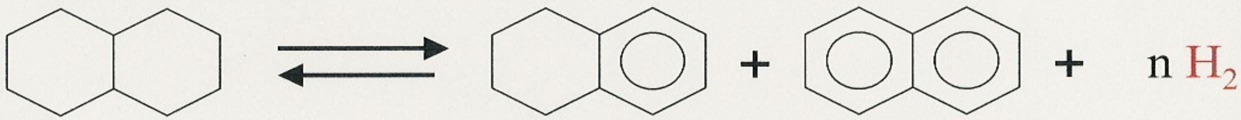
Hydrogen supply from Decalin

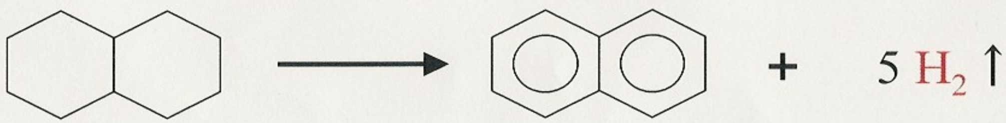
Conventional gas-solid heterogeneous catalysis

From thermodynamic requirements (> 500℃)

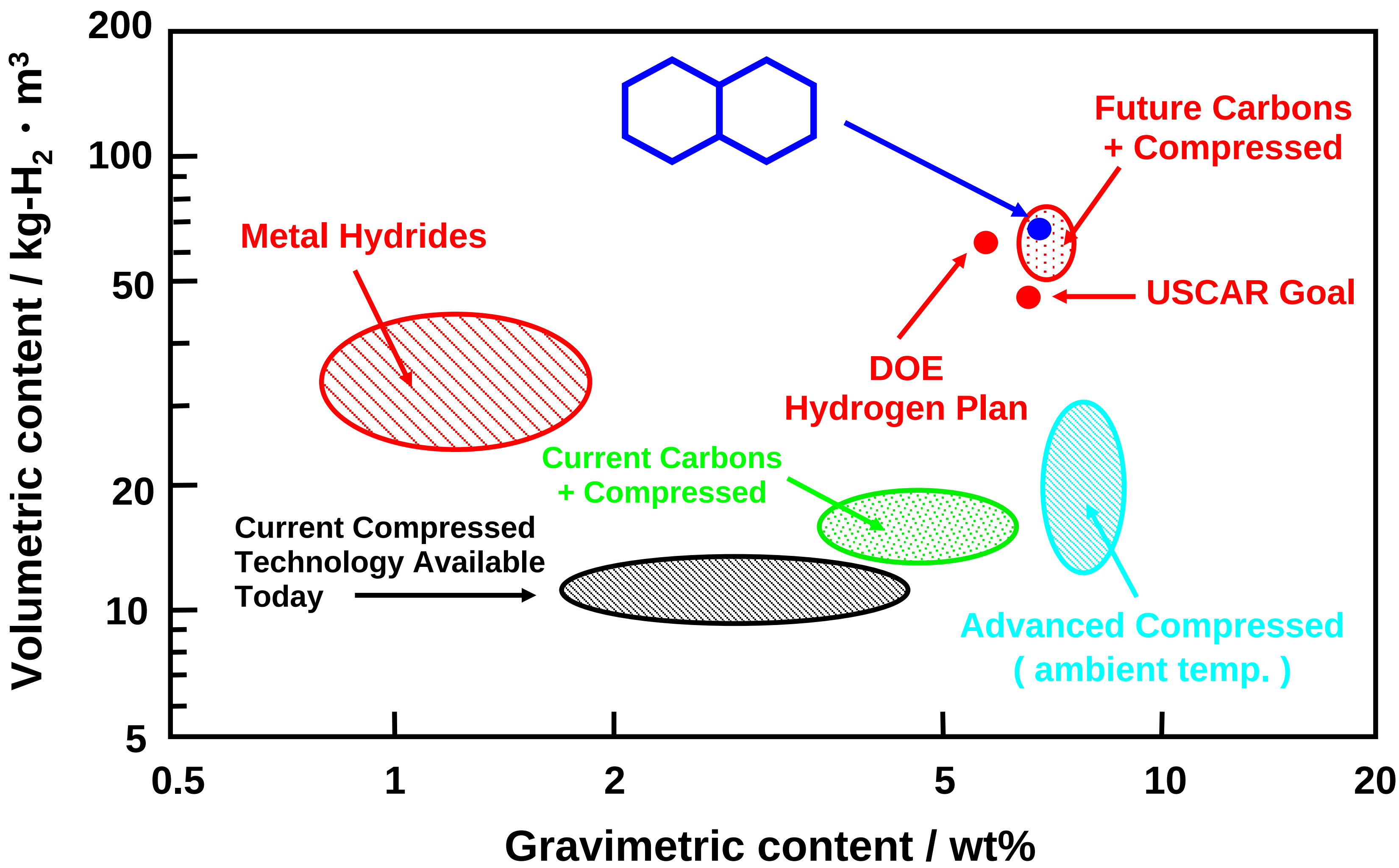


Present liquid-solid heterogeneous catalysis

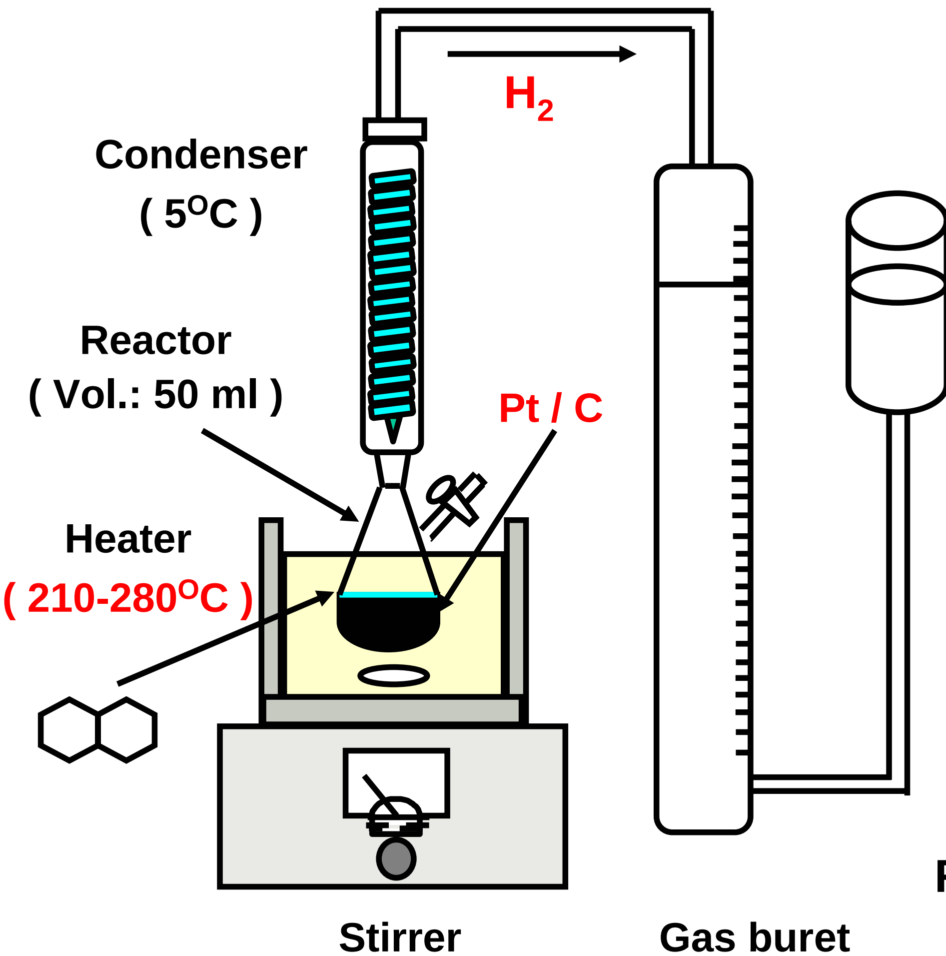
Under boiling and refluxing conditions (< 280℃)



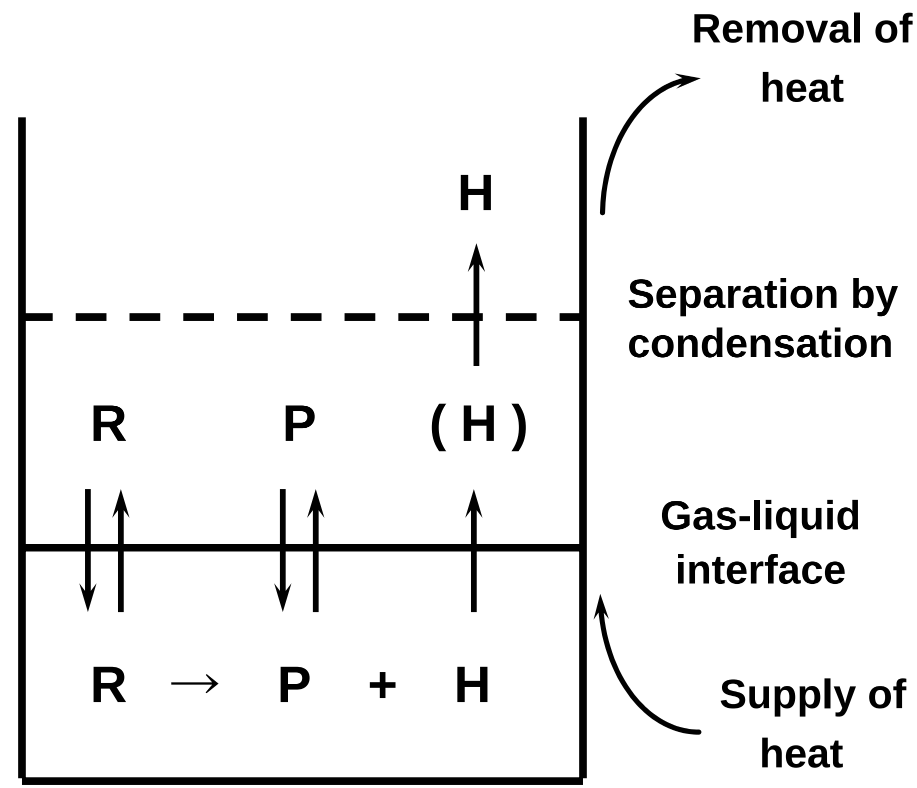
Comparison of Capacities of Hydrogen Storage Medium



Catalytic Dehydrogenation under Reactive Distillation Conditions in Batch-wise Operation



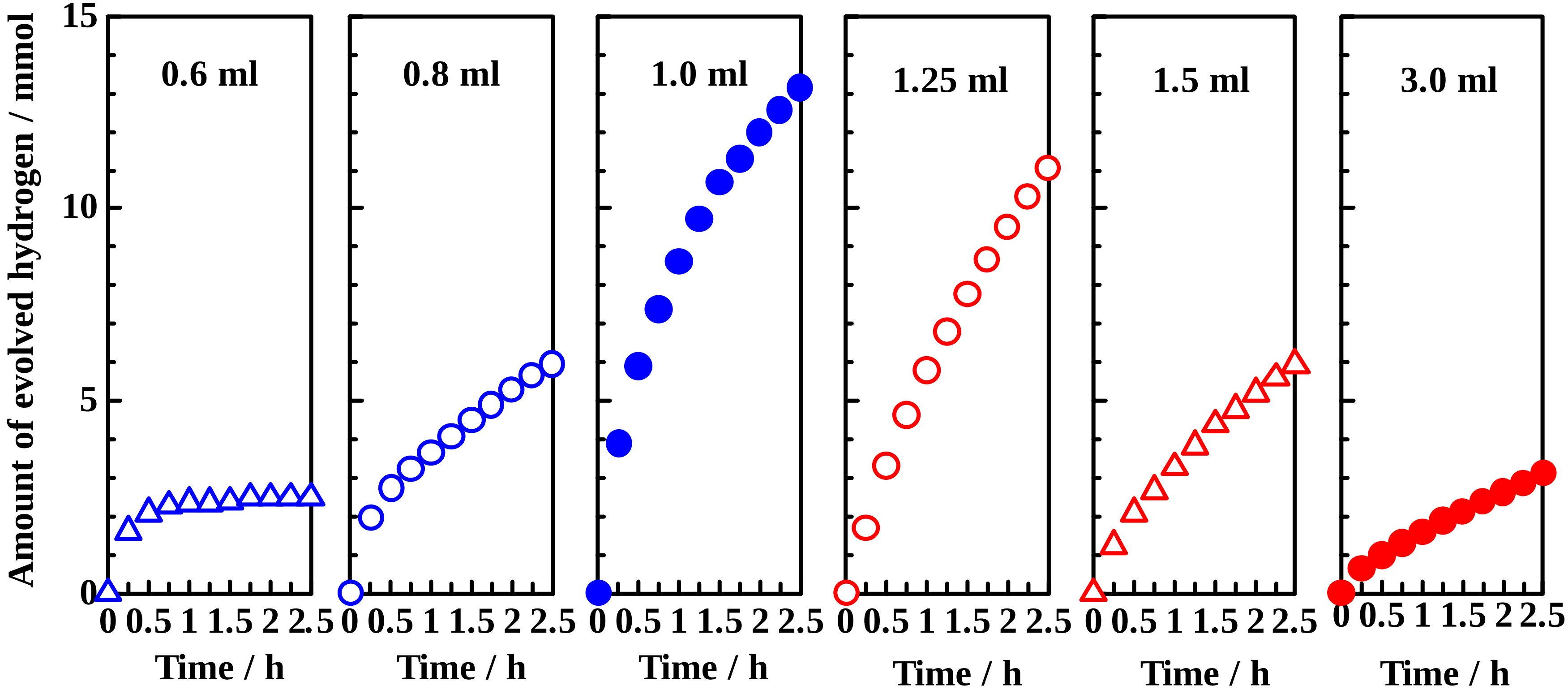
Batch-wise apparatus



R: Reactant, P: Liquid product, H: Hydrogen

Liquid-phase dehydrogenation under reactive distillation conditions

Time Courses of Hydrogen Evolved from Decalin with Pt / C Catalyst at Various Charged Amounts of Decalin

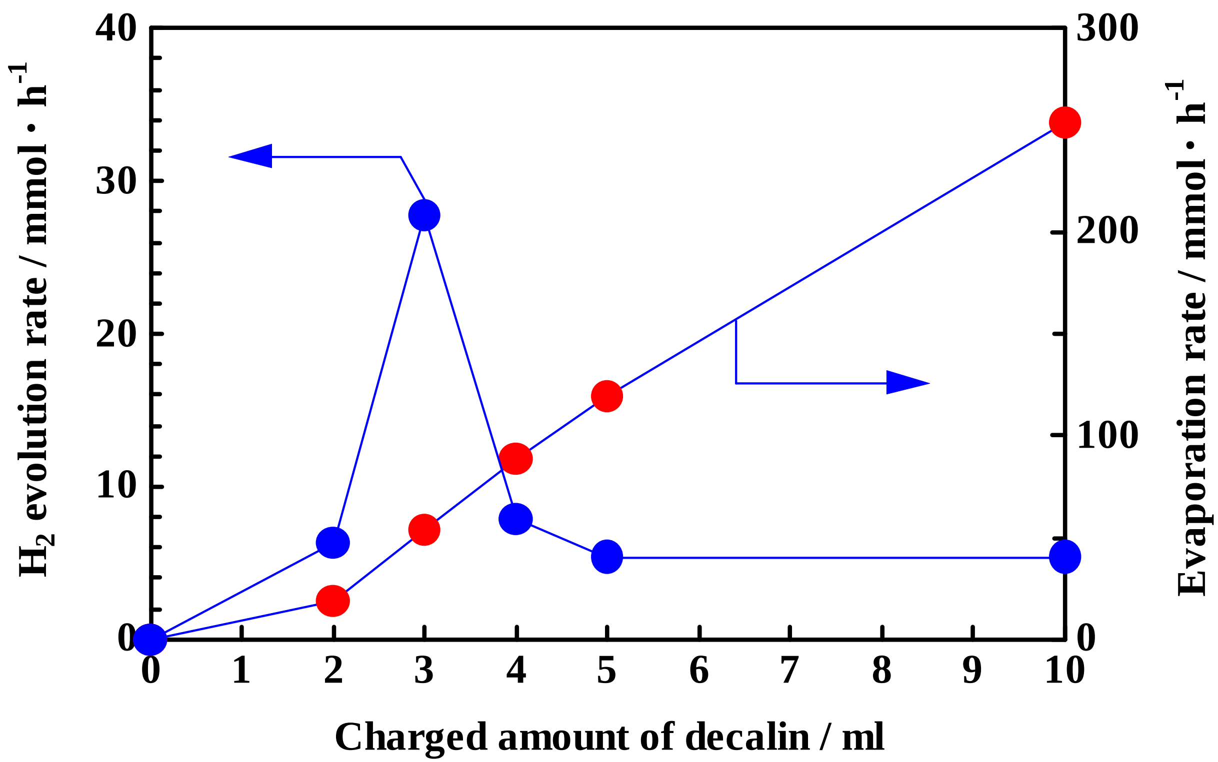


Charged amount of decalin: 0.6 (△), 0.8 (○), 1.0 (●), 1.25 (○), 1.5 (△), 3.0 ml (●)

Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 0.30 g

Reaction conditions: Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

Hydrogen Evolution and Evaporation Rates as a Function of Decalin Amount in Batch-wise Operation

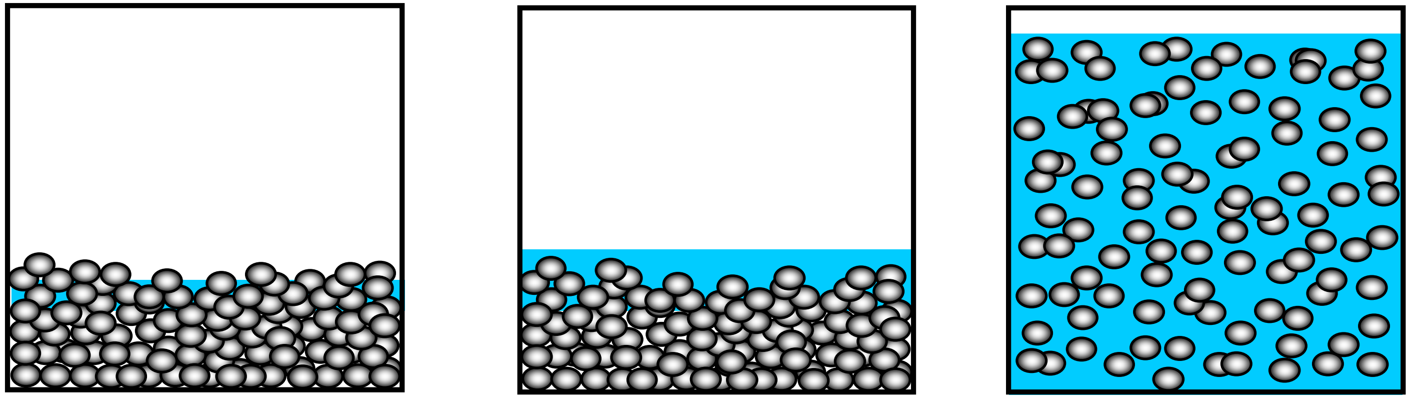


Catalyst : Carbon-supported platinum particles (5 wt-metal%) 0.75 g

Reaction conditions : Boiling and refluxing by heating at 210℃ and cooling at 5℃

Evaporation rate : Measured from condensates for carbon support at the same conditions

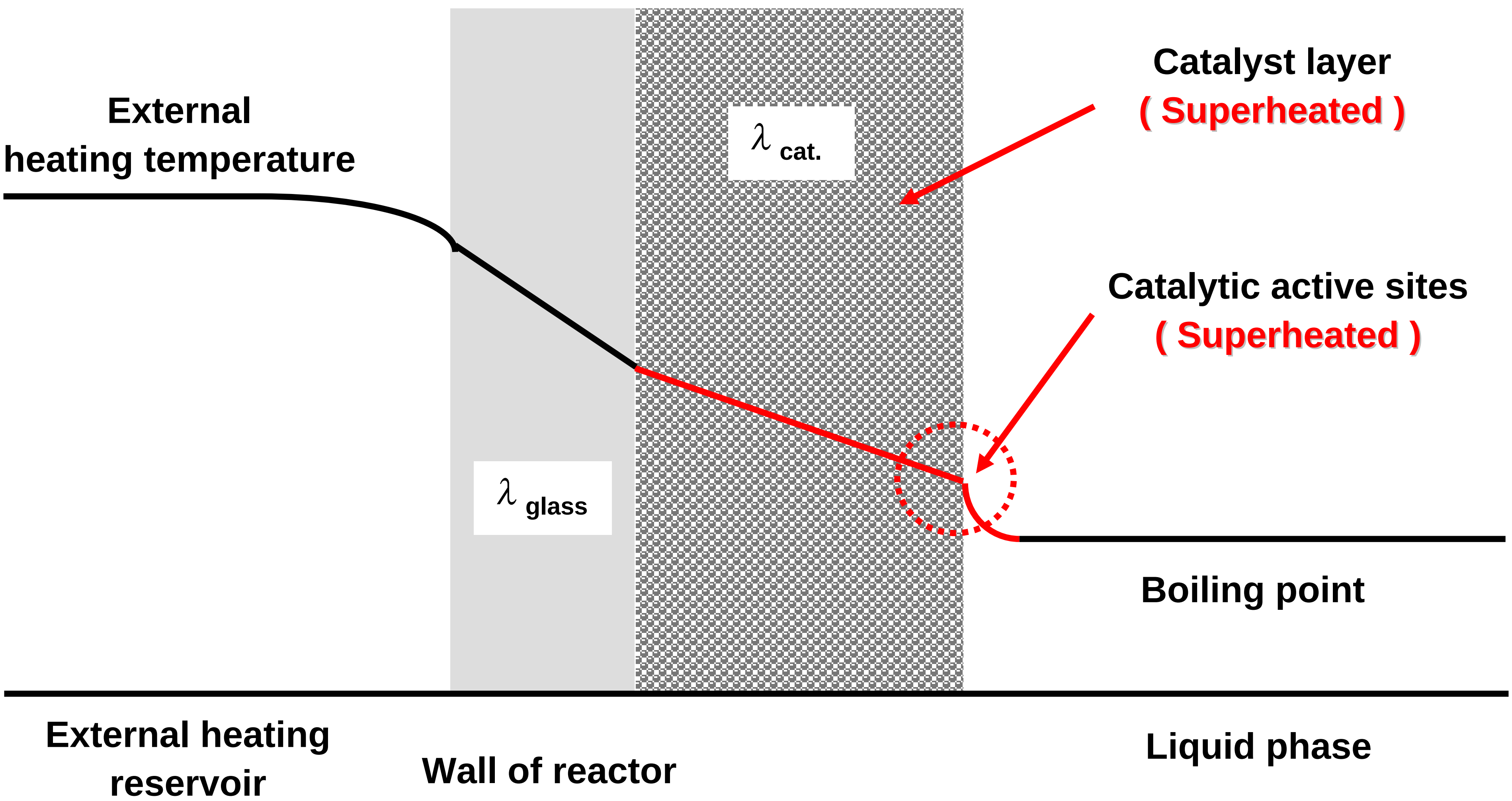
Characteristics of Dehydrogenation Catalyst Immersed with Liquid Substrate under Boiling Conditions



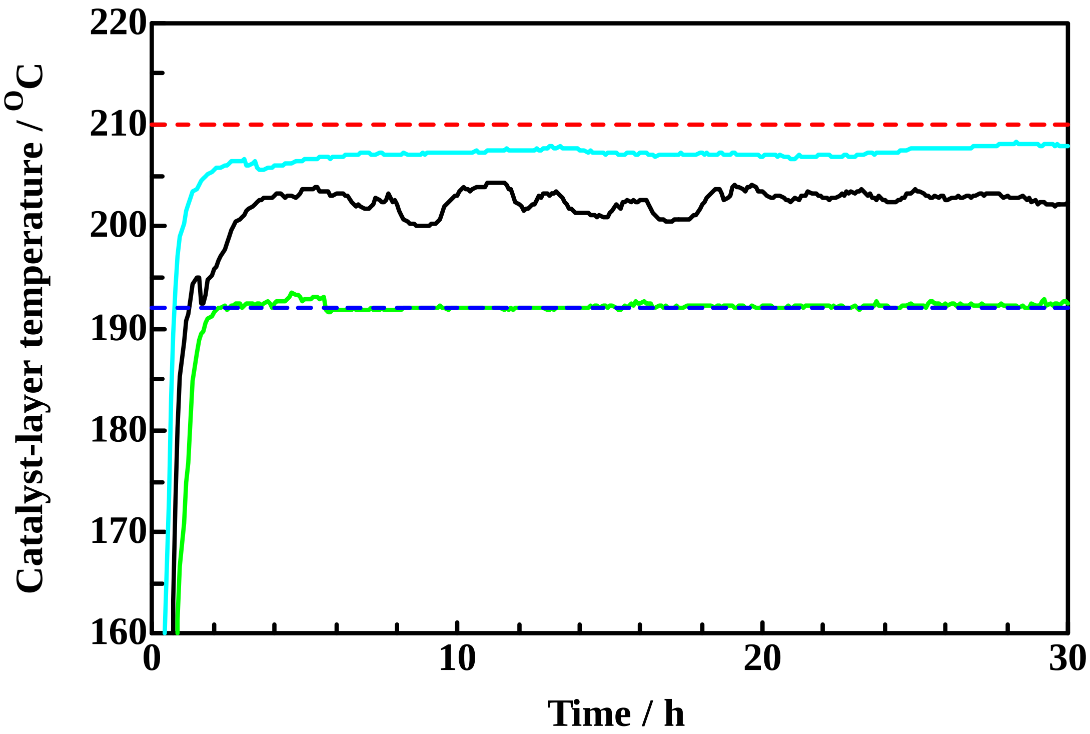
	Sand-bath state	*Superheated liquid-film state*	Suspended state
Amount ratio of catalyst to solution	Large	Medium	Small
Temperature gradient	$T_{ext} > T_{cat} > T_{liq}$	$T_{ext} > T_{cat} > T_{liq}$	$T_{ext} > T_{cat} = T_{liq}$
Reaction rate	Medium	Large	Small
Conversion	Medium	Large	Small

T_{ext}: External heating temp. T_{cat}: Catalyst-layer temp. T_{liq}: Boiling point

Temperature Gradient among Glass-wall, Catalyst-layer and Solution under Superheated Liquid-film Conditions



Relationship of Charged Amount of Decalin with Catalyst-layer Temperature

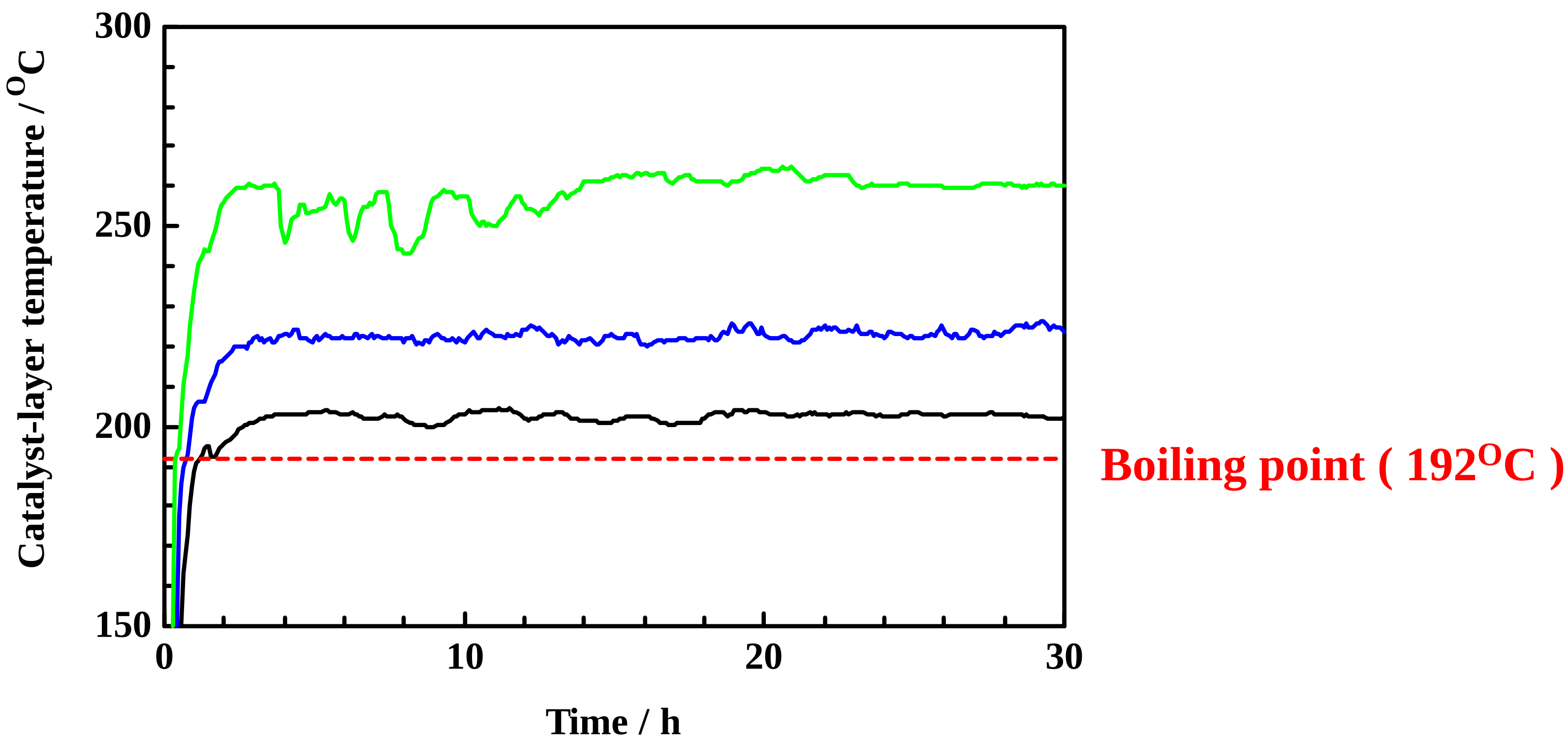


Charged amount of decalin : 0 ml (——), 1.0 ml (——) and 3.0 ml (——)

External heating temp. : $210^{O}C$ (- - -) Boiling point of decalin : $192^{O}C$ (- - -)

Boiling and refluxing by heating at $210^{O}C$ and cooling at $5^{O}C$, Activated carbon: 285 mg

Relationship of External Heating Temperature with Catalyst-layer Temperature

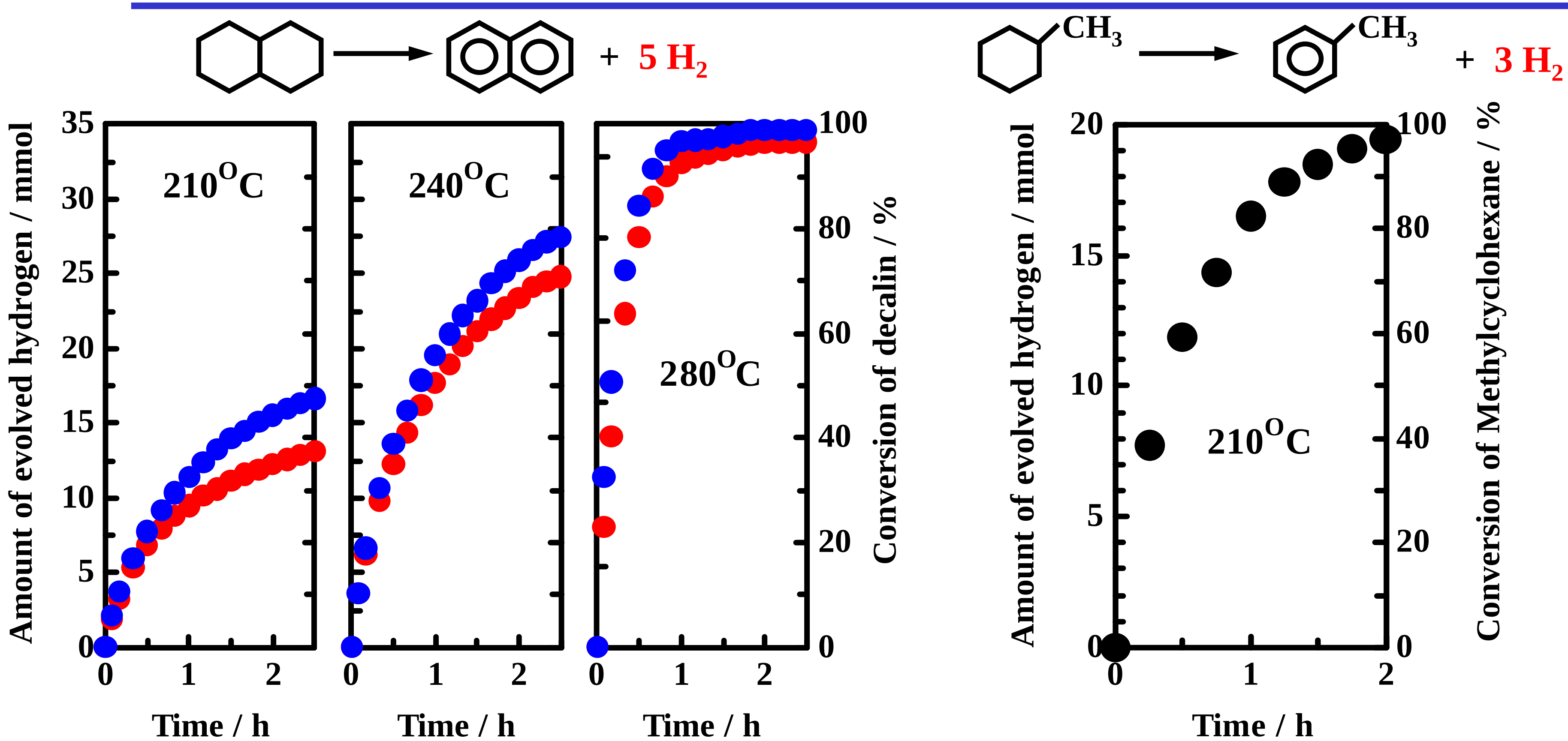


Charged amount of decalin : 1.0 ml, Amount of activated carbon : 285 mg

External heating temp. : $210^{O}C$ (——), $240^{O}C$ (——) and $280^{O}C$ (——)

Boiling and refluxing conditions (Cooling at $5^{O}C$), Boiling point : $192^{O}C$ (- - -)

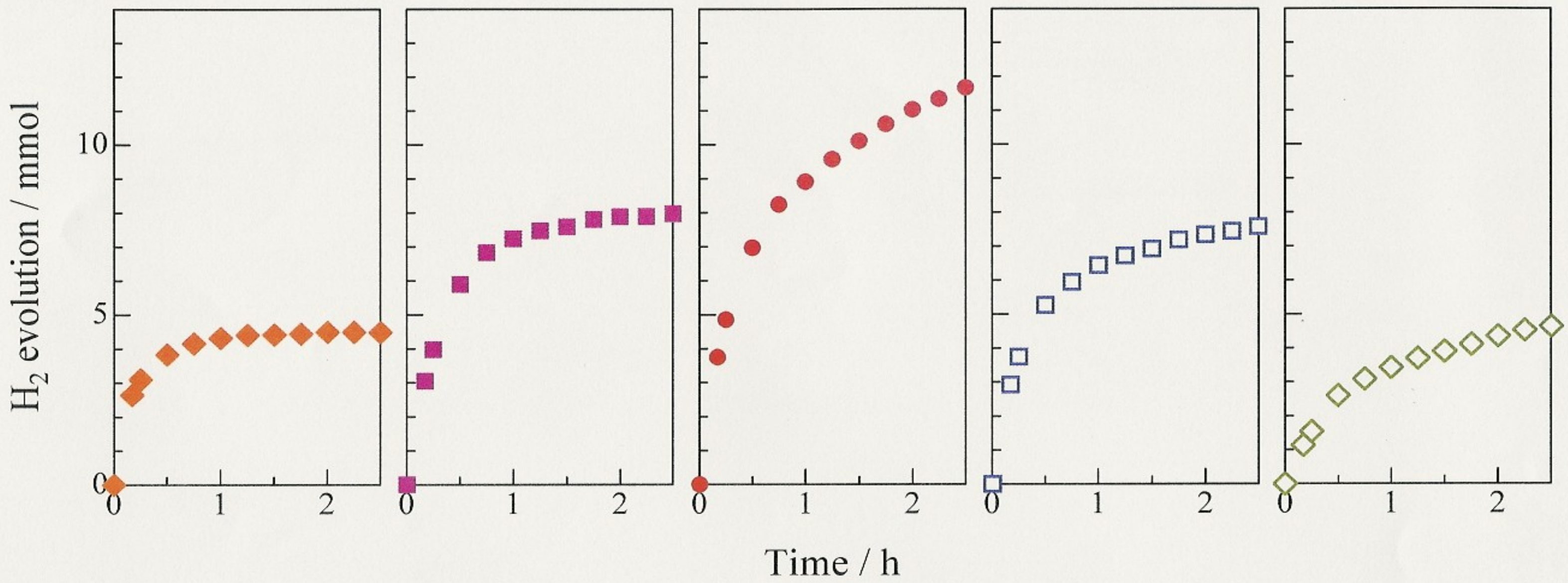
Dehydrogenation Activities for Decalin and MCH with Pt-based Catalysts at Various Heating Temperatures under Superheated Liquid-film Conditions



● : Pt / C (5 wt%), ● : Pt-Re / C (5 wt-Pt%, Pt / Re = 4), ● : Pt-Ir (5 wt%, Pt / Ir = 4)

Catalyst / solution ratio : 0.3 g / 1.0 ml (superheated liquid-film state)

Reaction conditions : Boiling and refluxing by heating at 210, 240, $280^{O}C$ and cooling at $5^{O}C$

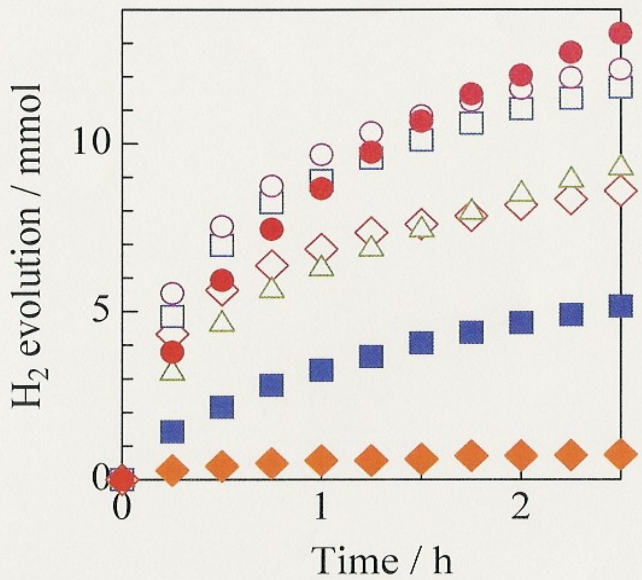


Amount of decalin (◆ : 0.25 ml, ■ : 0.50 m, ● : 0.75 ml, □ : 1.00 ml, ◇ : 1.25 ml)

Catalyst : Carbon-supported Ni-Ru bimetallic catalyst (10 wt-metal%, Ni/Ru=4) 317 mg

Reaction conditions : Boiling and refluxing conditions (heating at 280℃, cooling at 5℃)

Relationship of decalin / catalyst amount ratio with the activities of hydrogen evolution



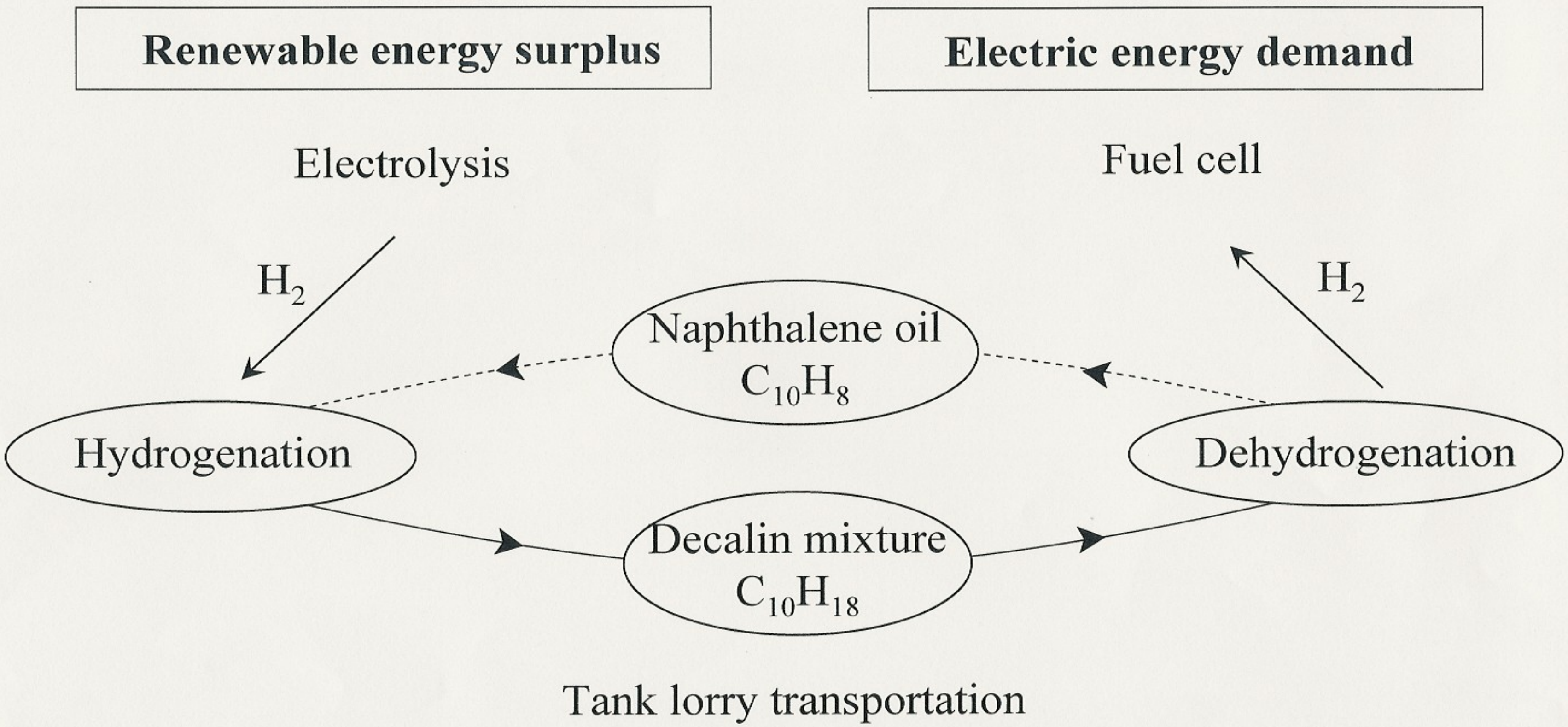
Pt / C ●, Ru / C ■, Ni / C ◆ (support carbon 285 mg)

Ru/Ni ratio = 1 : 8 ◇, 1 : 4 □, 1 : 1 ○, 4 : 1 △

Decalin heated at 280℃(Pt/C only 210℃) & chilled at 5℃

Pt/C (5 wt%) / 1.0 ml, Others (10 wt-metal%) / 0.75 ml

Comparison of decalin dehydrogenation activities between Ni-Ru bimetallic and platinum catalyst



Transportation of hydrogen energy with catalyst-assisted decalin dehydrogenation / naphthalene hydrogenation pair

Roles of Organic Chemical Hydride in Hydrogen Internal Combustion Engine

Heat flow from Hydrogen ICE to Superheated Reactor for Dehydrogenation

[Waste heat at a high temperature] Q

= [Dehydrogenation heat of organic hydride] ΔH_r

+ [Evaporation heat accompanying the reaction] ΔH_v

[Waste heat generated in ICE and finally accepted in radiator]

= [Enthalpy enrichment of fuel through hydrogen evolution]

+ [Efficient transfer of exhaust heats through boiling & cooling]

Ongoing & Expected Collaborations

Ongoing Collaborations

The present study has been financially supported by New Energy and Industrial Technology Development Organization (NEDO) since 2000.

Collaborations Expected in Near Future

1. Collaborations with petroleum companies are expected regarding storage, transportation & distribution of hydrogen by using organic hydrides and existing gas stations / tank lorries.

2. Collaborations with automobile companies are expected regarding practical design of on-board reactor for hydrogen supply from organic hydrides needed to operate ICE-vehicles driven by H_2 or FC-vehicles.

International Partnership for the Hydrogen Economy

Int'l H_2 Storage Technologies Conference

Background

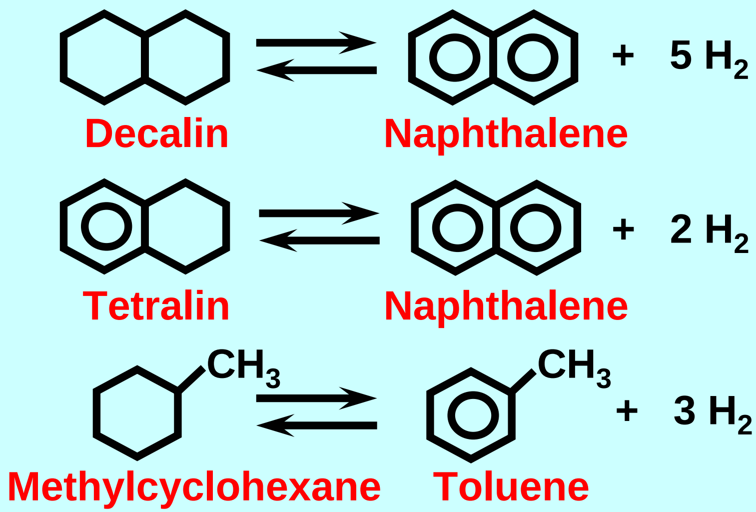
Hydrogen for ICE-vehicles driven by hydrogen & Stationary Fuel Cells

Key Technologies: *Storage, Transportation and Supply*

Suitable Medium for Hydrogen Storage

- (1) High Storage Capacity
- (2) Safe & Economical
- (3) Facile Reversibility

Organic chemical hydride

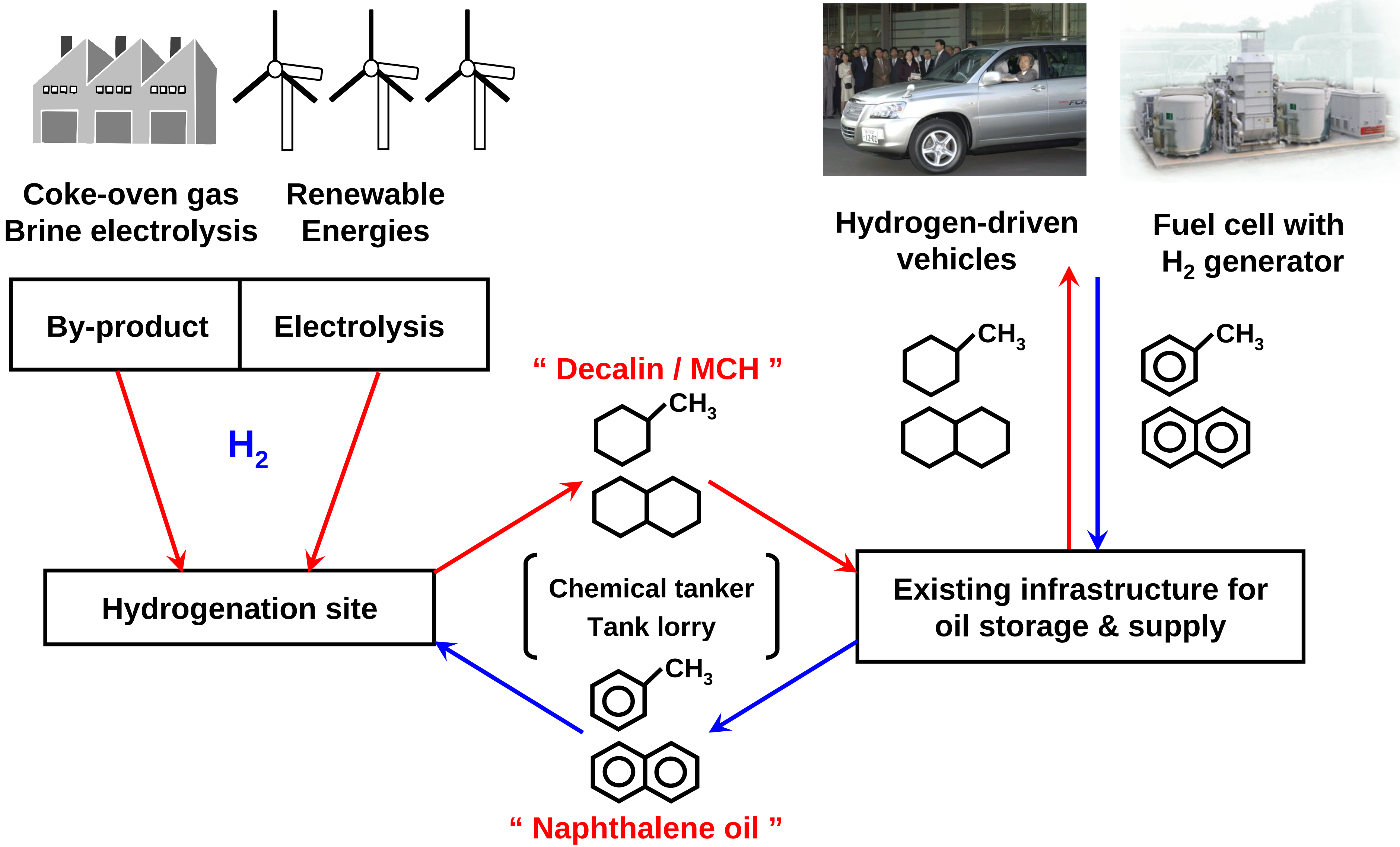


Rapid Hydrogen Supply to Fuel Cells under Mild Conditions

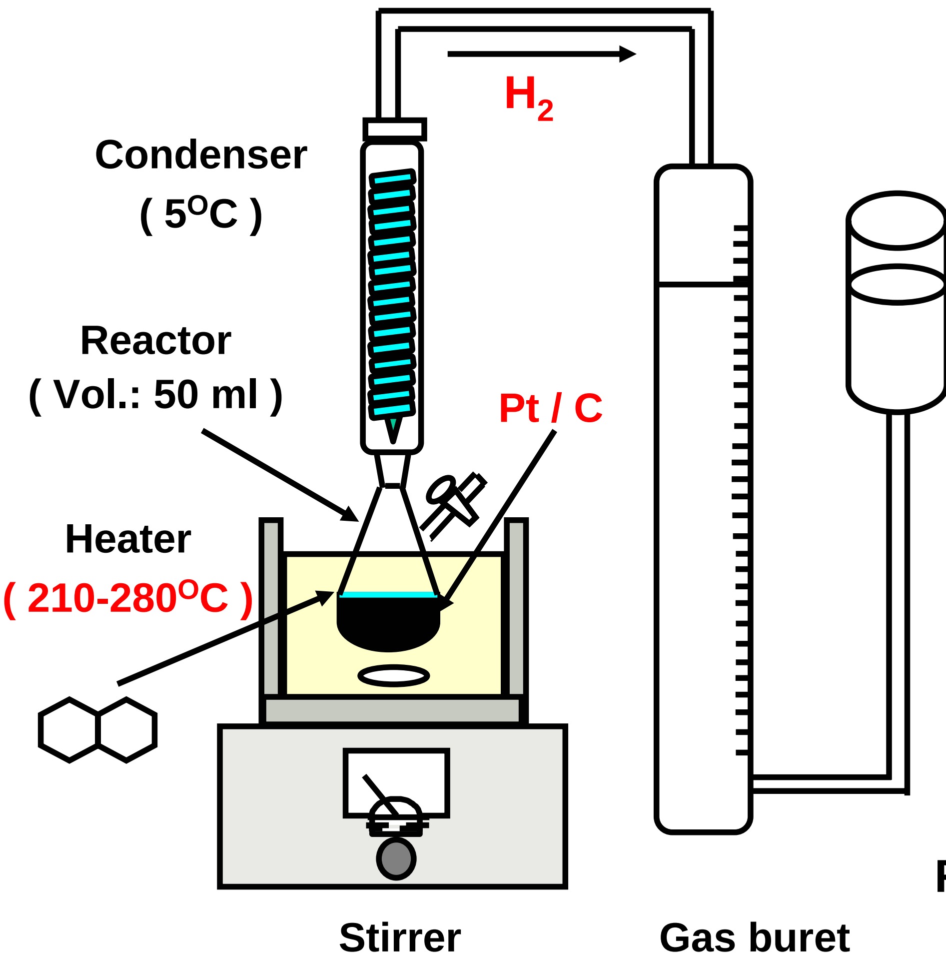
- (1) Small exergy consumption
- (2) No coke formation

Superheated liquid-film-type catalysis under reactive distillation conditions

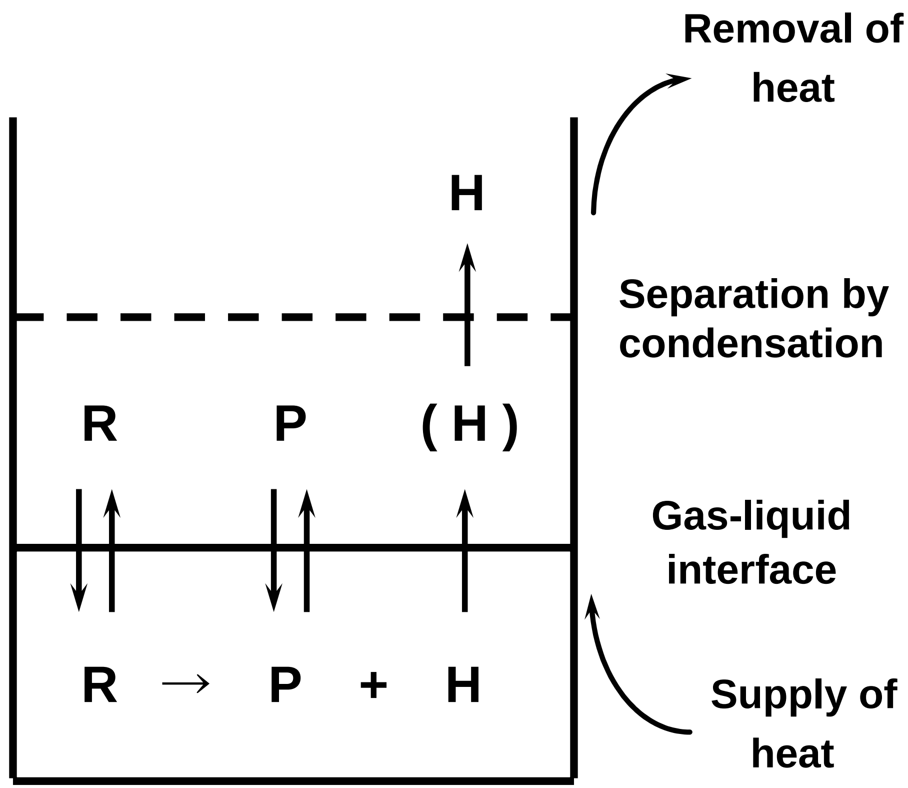
Hydrogen Energy Systems by Using Chemical Organic Hydrides



Catalytic Dehydrogenation under Reactive Distillation Conditions in Batch-wise Operation



Batch-wise apparatus



R: Reactant, P: Liquid product, H: Hydrogen

Liquid-phase dehydrogenation under reactive distillation conditions

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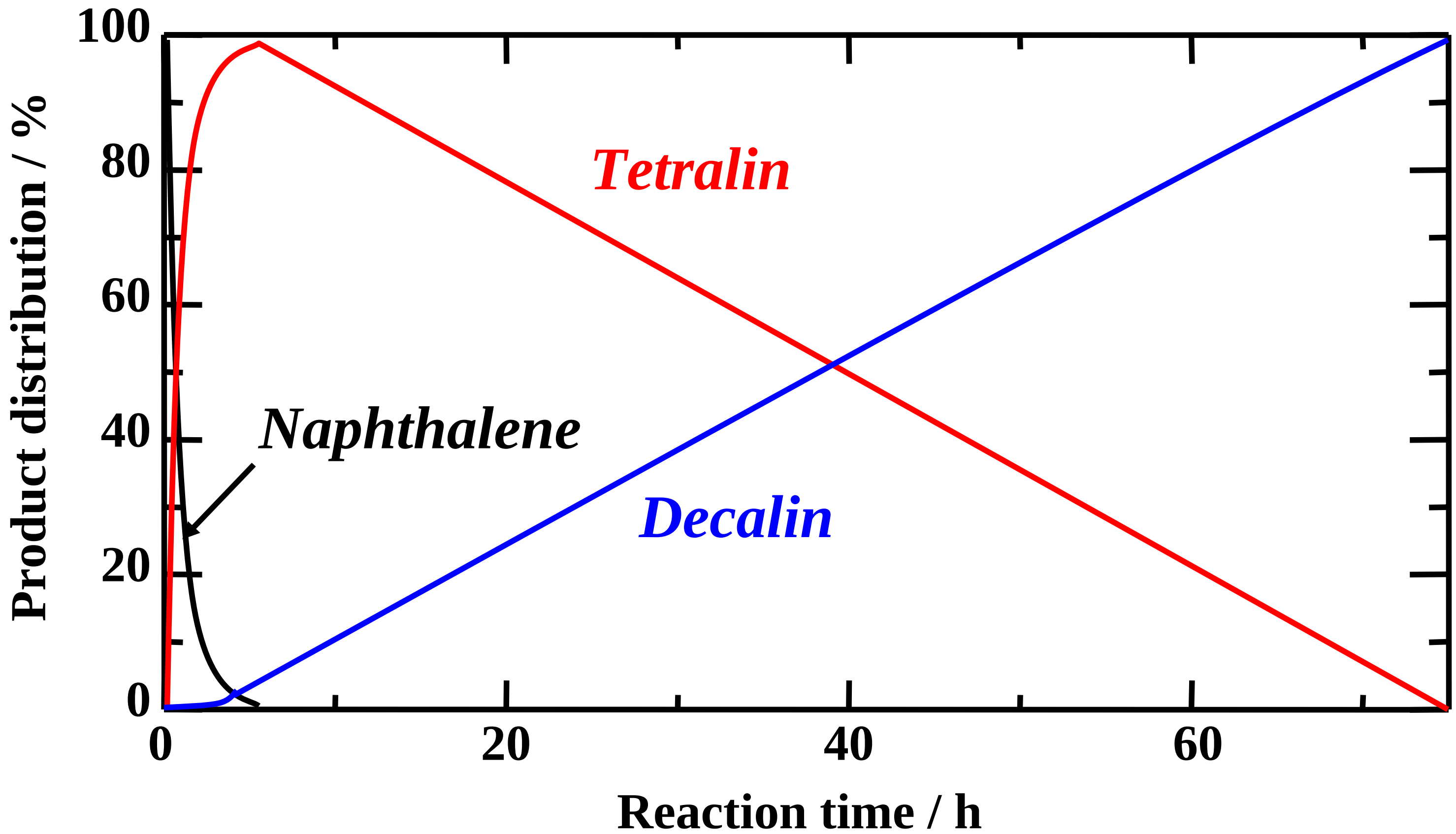
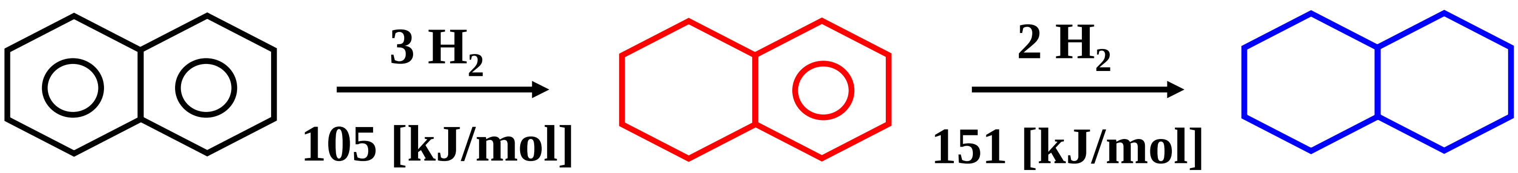
Components Candidates of "Naphthalene Oil"

Candidate compound	Melting point [°C]	Boiling point [°C]	Storage capacity of hydrogen [wt%]	[L / 5 kg-H_2]
Toluene	-94.5	110.6	6.2	104.1
o-Xylene	-25.2	144.4	5.4	116.3
m-Xylene	-47.4	139.3	5.4	121.4
Naphthalene	80.2	217.0	7.3	76.5-78.9
1-Methylnaphthalene	-30.6	244.8	6.6	84.9-87.2

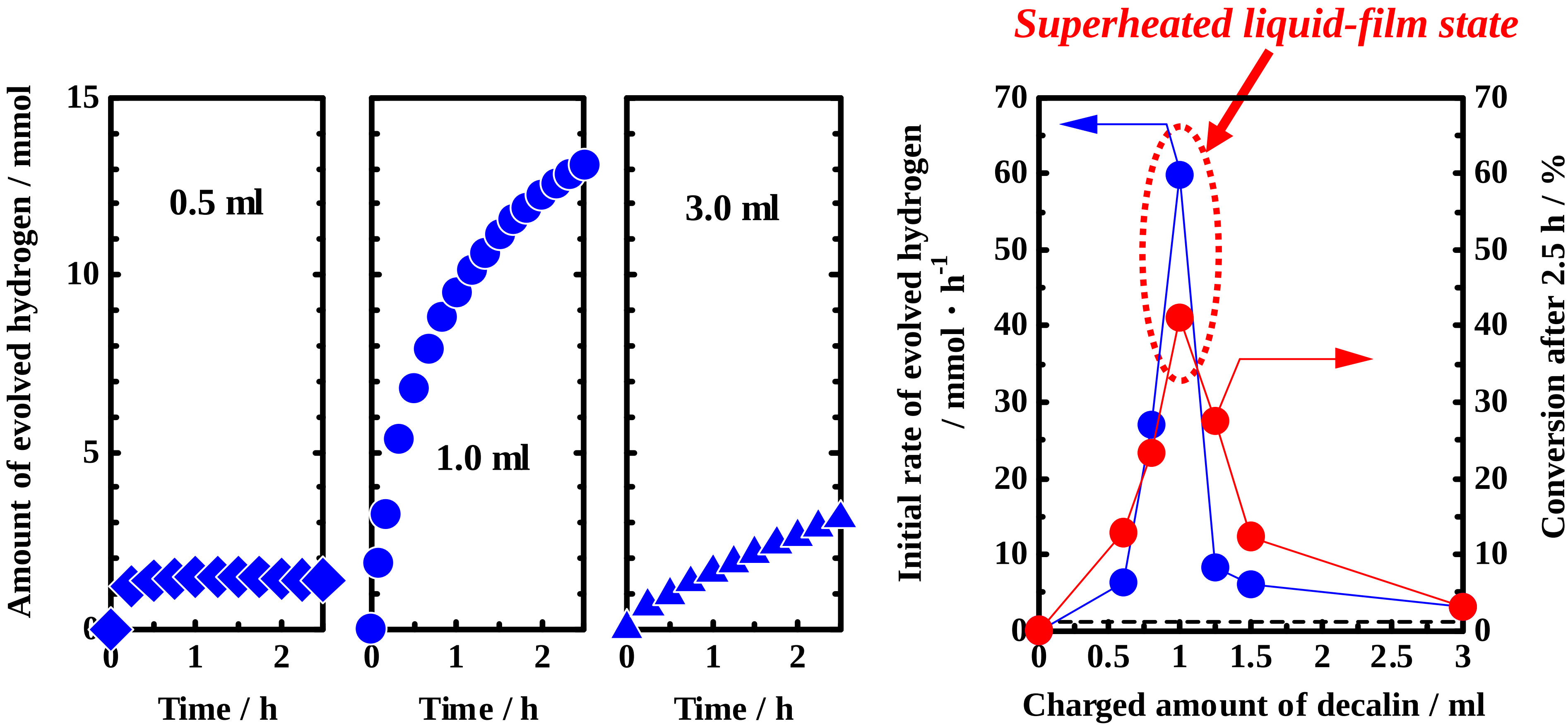
Reaction Sequence of Naphthalene Hydrogenation



Catalyst : Pd / C (5 wt%), Initial pressure : 68 atm, A. W. Weitkamp, Adv. Catal., 18, 21 (1968).



Relationship of Catalytic Dehydrogenation Activities with Charged Amount of Decalin in Batch-wise Operation

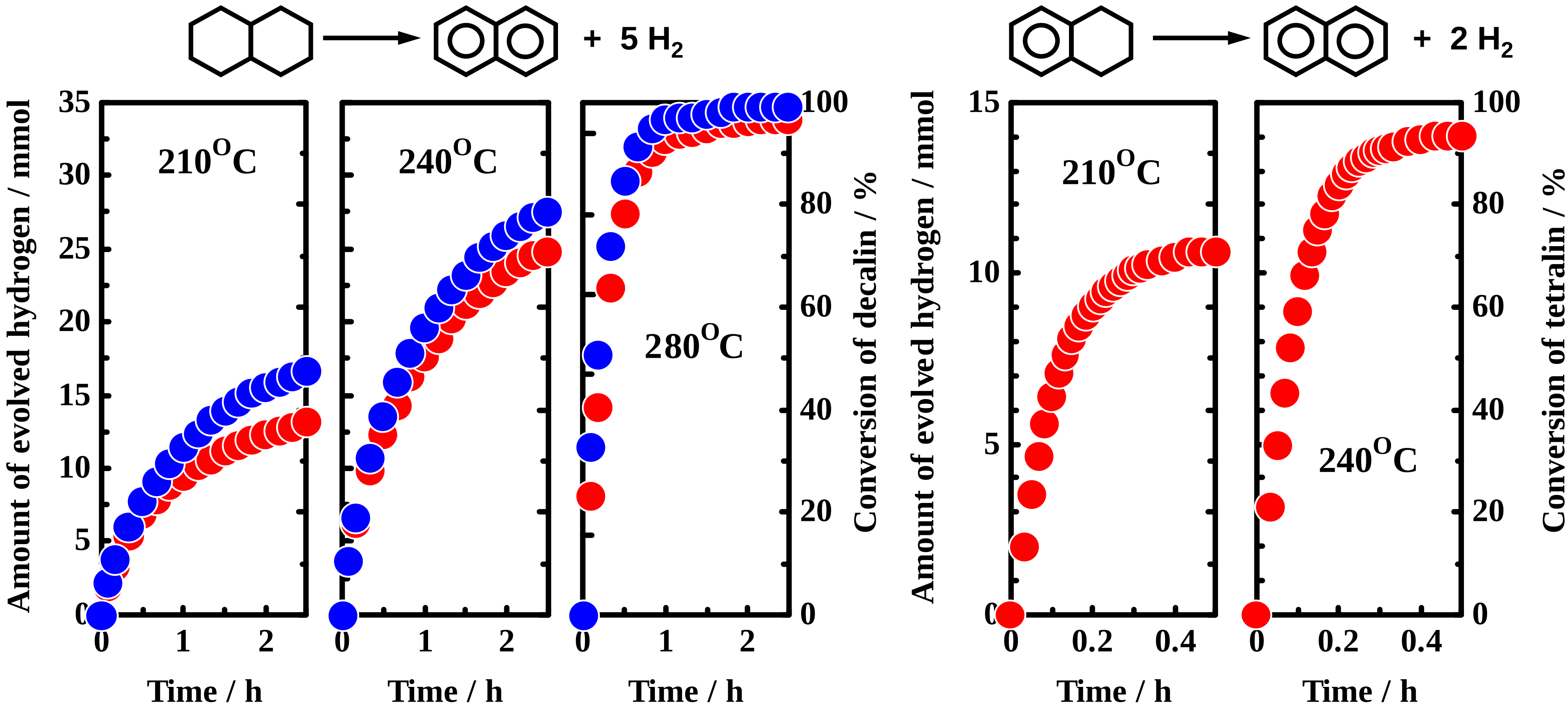


-------: Equilibrium conversion of decalin dehydrogenation at 210^{O}C, 1 atm

Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 0.30 g

Reaction conditions: Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

Hydrogen Evolution from Organic Hydrides with Pt-based Cats. at Various Heating Temps. under Superheated Liquid-film Conditions

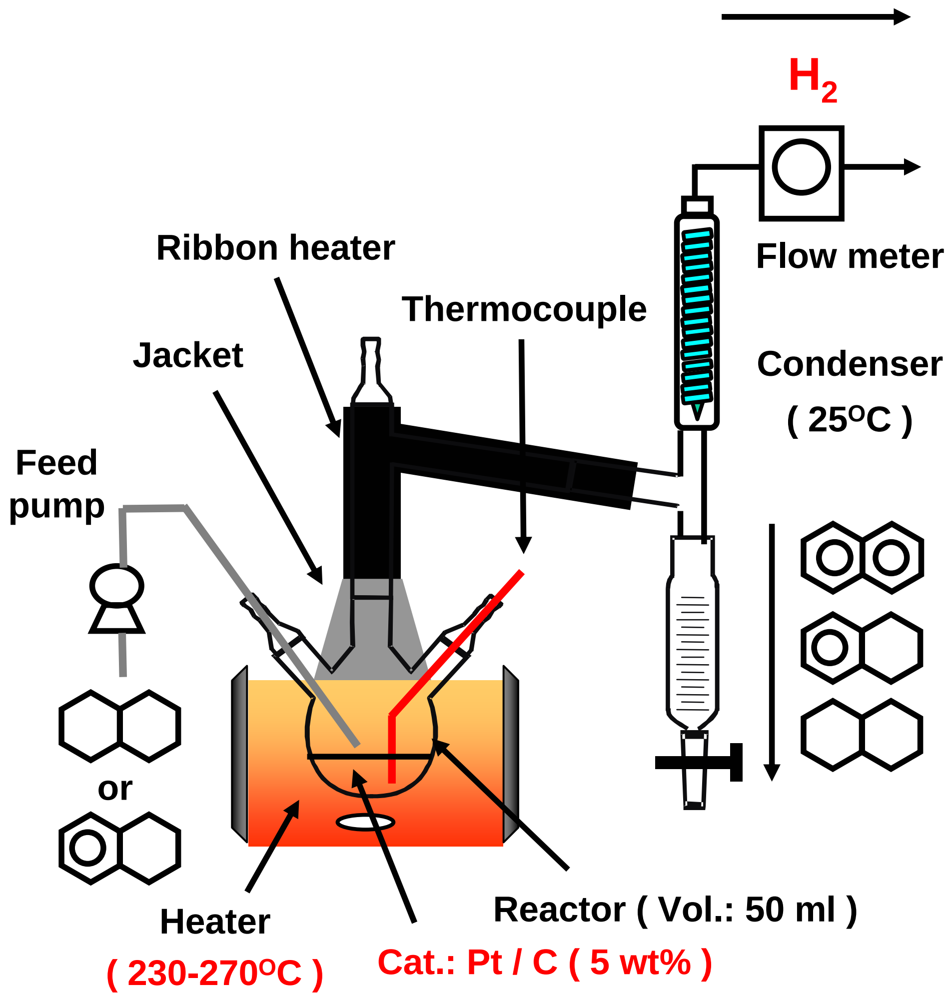


●: Pt / C (5 wt-metal%), ●: Pt-Re / C (5 wt-Pt%, Pt / Re = 4)

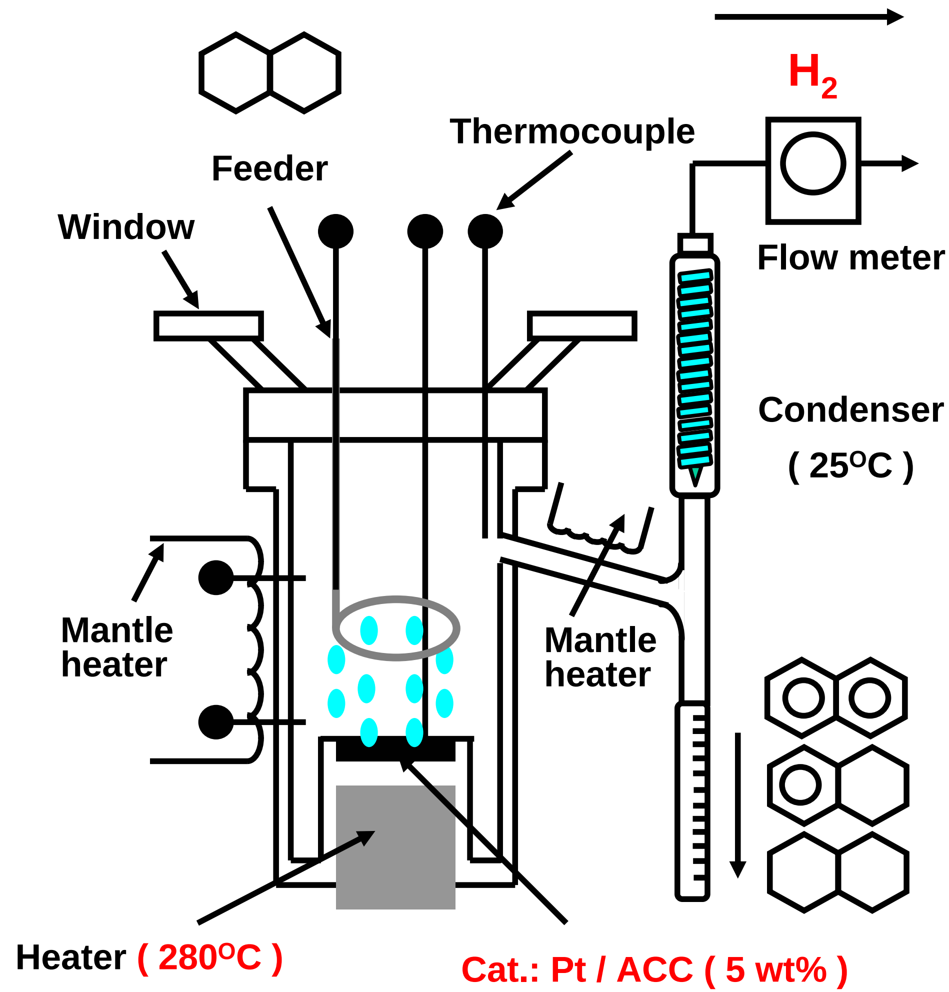
Catalyst / solution ratio: 300 mg / 1.0 ml (superheated liquid-film state)

Reaction conditions: Boiling and refluxing by heating at 210-280°C and cooling at 5°C

Experimental Apparatus for Catalytic Dehydrogenation under Reactive Distillation Conditions in Continuous Operation

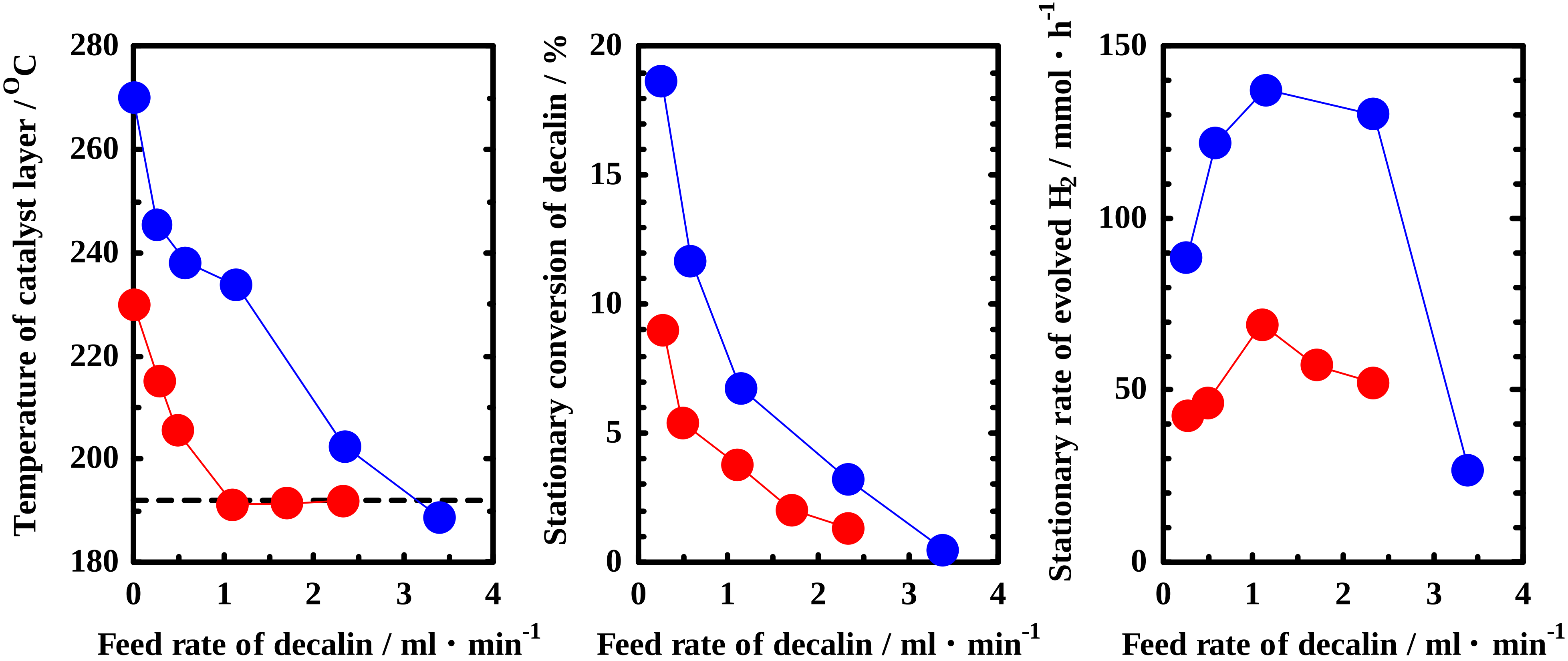


Continuous operation at laboratory scale



Continuous operation at bench scale

Relationship of Cat.-layer Temp. and Dehydrogenation Activities with Feed Rate of Decalin in Continuous Operation

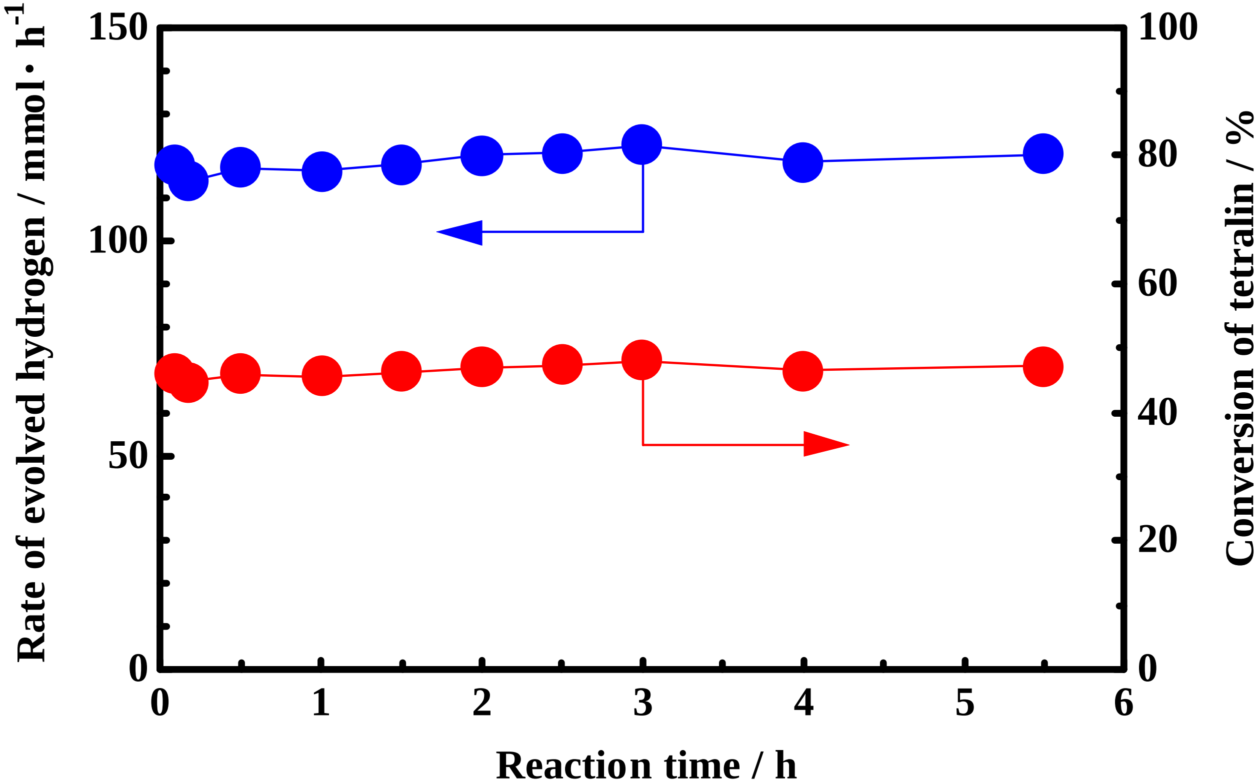


-------: Boiling point of decalin (192^{O}C)

Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 1.1 g

Reaction conditions: Boiling and refluxing by heating at 230^{O}C (●), 270^{O}C (●) and cooling at 25^{O}C

Long-term Test for Continuous Hydrogen Supply from Tetralin with Pt / C Catalyst in Liquid-film State

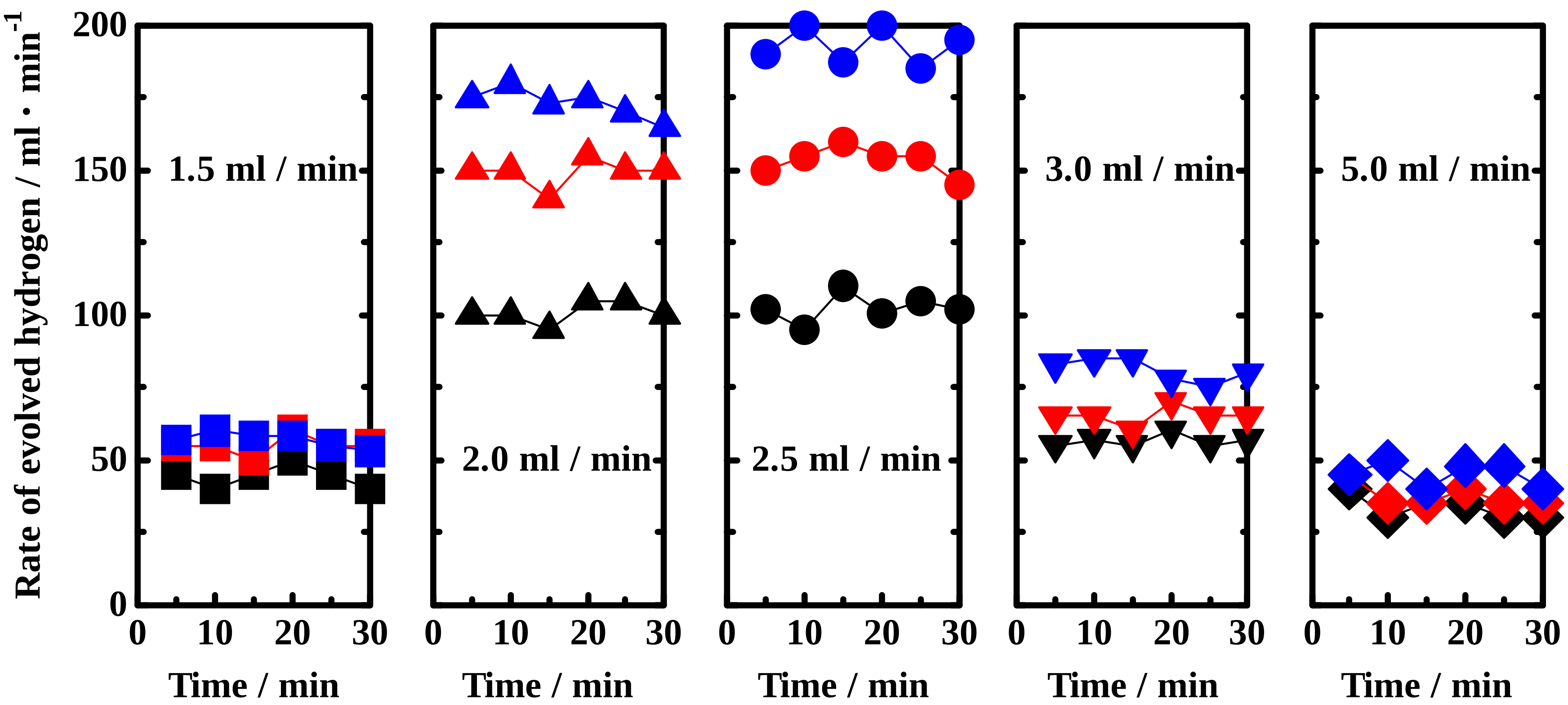


Catalyst: Carbon-supported platinum particles (5 wt-metal%) 1.1 g

Feed rate of tetralin: 0.5 ml / min (superheated liquid-film conditions)

Reaction conditions: Boiling and refluxing by heating at 240^{O}C and cooling at 25^{O}C

Time Courses of Evolution Rates of Hydrogen from Decalin at Various Feed Rates in Continuous Operation



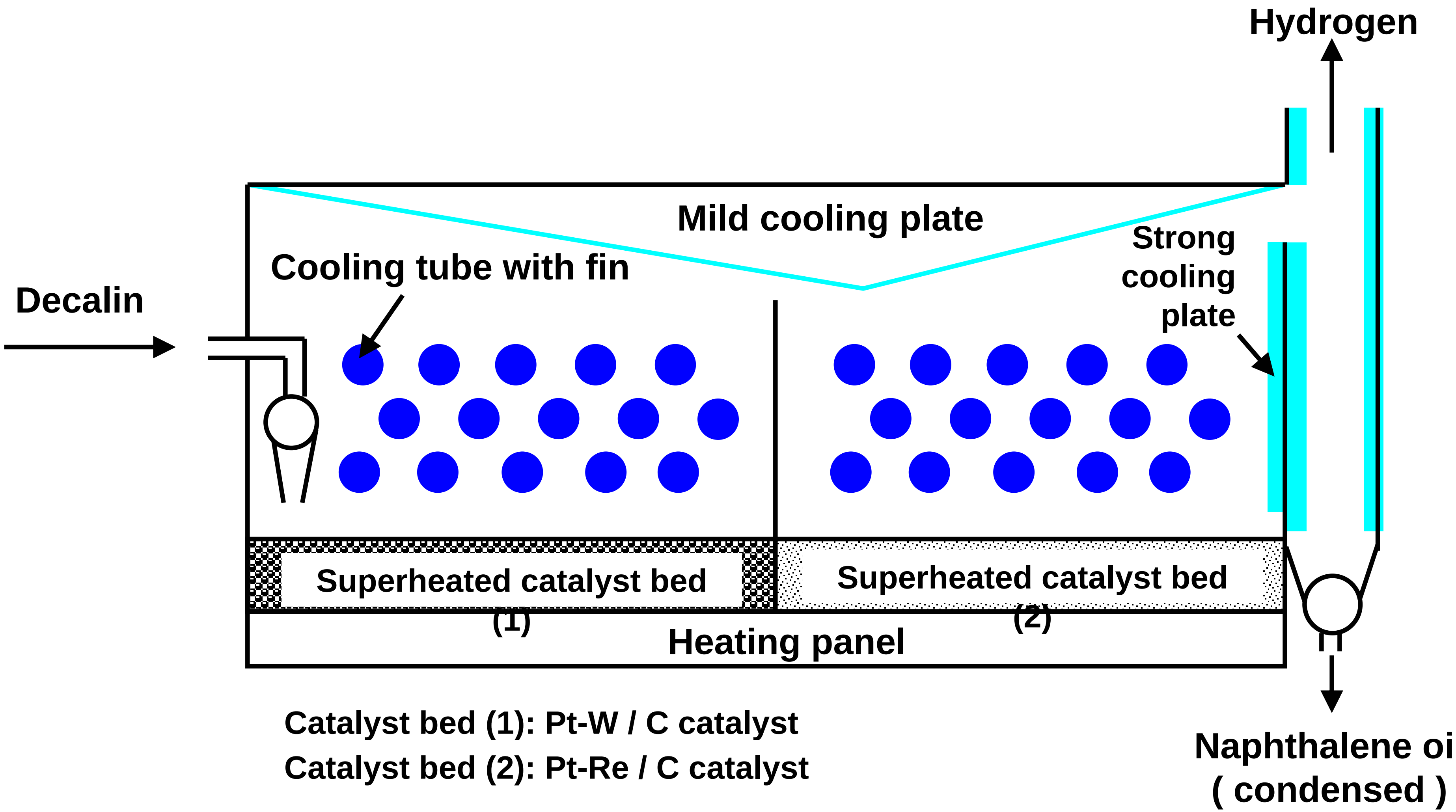
Feed rate of decalin: 1.5, 2.0, 2.5, 3.0 and 5.0 ml / min

Catalyst: Platinum nano-particles supported on activated carbon cloth (5 wt-metal%)

0.29 g (one layer, black), 0.58 g (two layers, red) and 0.87 g (three layers, blue)

Reaction conditions: Boiling and refluxing by heating at 280^{O}C and cooling at 25^{O}C

A Basic Design of Piston-flow Type Reactor for Dehydrogenation under Superheated Liquid-film Conditions



Catalyst bed (1): Pt-W / C catalyst

Catalyst bed (2): Pt-Re / C catalyst

Conclusions & Ongoing / Expected Collaborations

Conclusions

1. Catalytic hydrogen supply from organic chemical hydrides with carbon-supported metallic particles in "superheated liquid-film states" under reactive distillation conditions was efficiently attained in batch-wise operation at moderate temperatures of 210-280^{O}C.

2. Rapid hydrogen generation from organic chemical hydrides under superheated liquid-film conditions in continuous mode was well demonstrated at both laboratory and bench scale.

Ongoing Collaborations

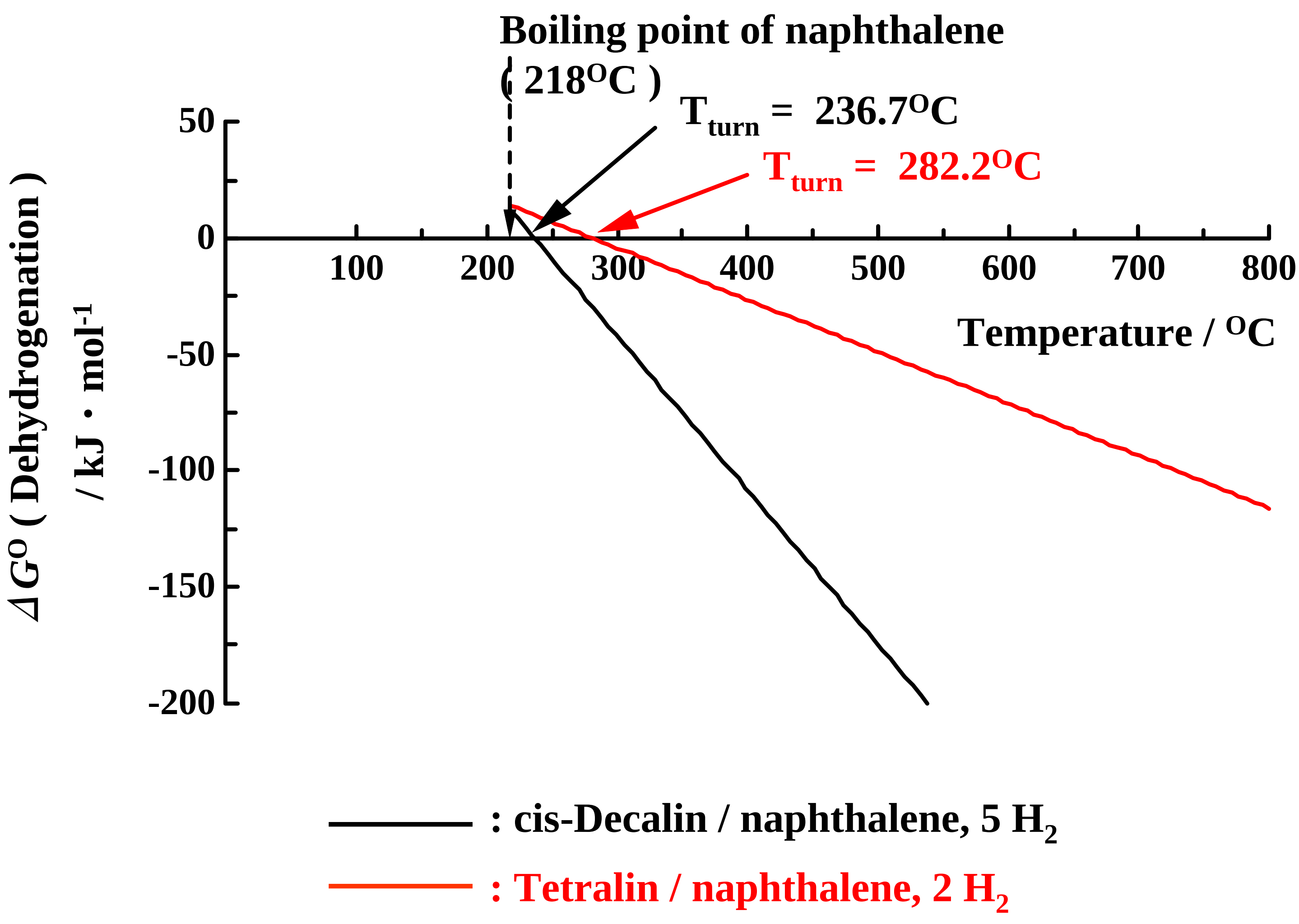
The present study has been financially supported by New Energy and Industrial Technology Development Organization (NEDO) since 2000.

Collaborations Expected in Near Future

1. Collaborations with petroleum companies are expected regarding storage, transportation & distribution of hydrogen by using organic hydrides and existing gas stations / tank lorries.

2. Collaborations with automobile companies are expected regarding practical design of on-board reactor for hydrogen supply from organic hydrides needed for operating vehicles powered by hydrogen-fueled internal combustion engines or fuel-cell vehicles.

Gibbs Energy Change of Reaction Pairs of Dehydrogenation / Hydrogenation as a Function of Temp.



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Preparation Scheme of Carbon-supported Platinum-based Catalysts

Activated carbon pretreated by NaOH aq. (pH 14)

(BET surface area: 3100 m^2/g, pore size: 2.0 nm)

1. Adsorption of K_2PtCl_4 aq. at 25^{O}C for 48 h
2. Reduction by $NaBH_4$ aq. at 90^{O}C for 30 min
3. Washing by water of 1 L
4. Evacuation at 70^{O}C for 10 h

Pt / C catalyst (5 wt-metal%)

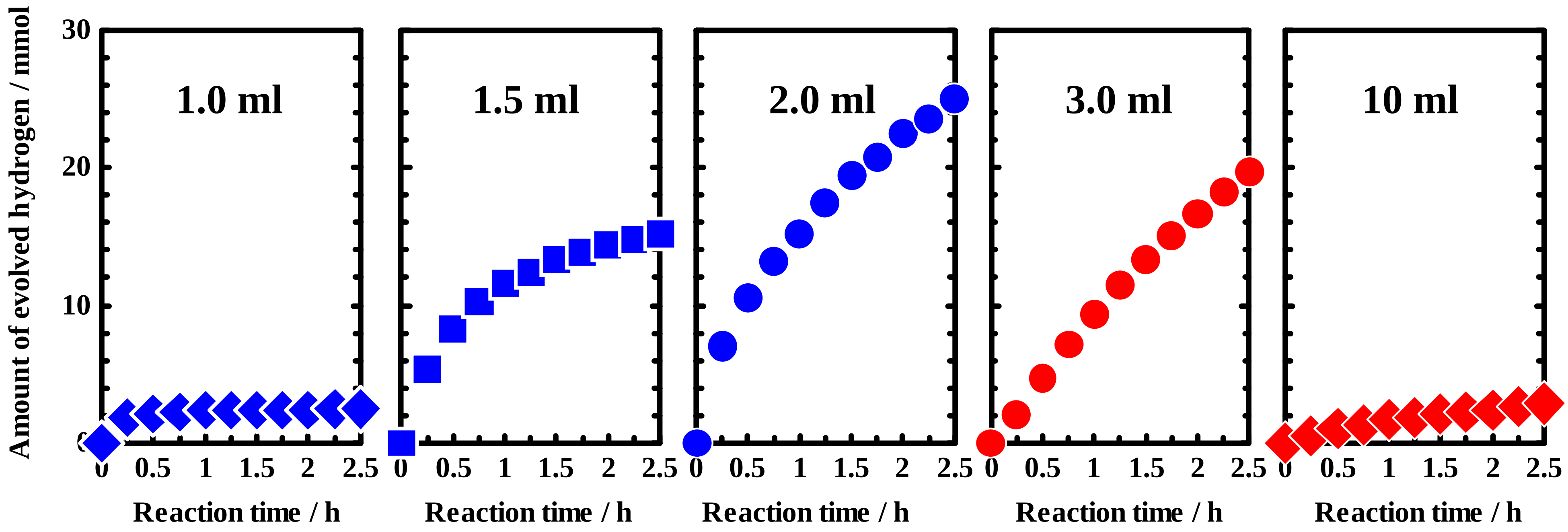
1. Evacuation at 160^{O}C for 1 h
2. Addition of $W(CO)_6$
3. Stirring under N_2 atmosphere at 25^{O}C for 1 h
4. Stirring under N_2 atmosphere at 240^{O}C for 3 h
5. Evacuation at 160^{O}C for 1 h

Pt-W / C cat. (5 wt-Pt%, Pt / W = 5)

1. Evacuation at 180^{O}C for 1 h
2. Addition of $Re(cp)(CO)_3$
3. Stirring under N_2 atmosphere at 25^{O}C for 1 h
4. Stirring under N_2 atmosphere at 100^{O}C for 1 h
5. Stirring under H_2 atmosphere at 240^{O}C for 3 h
6. Evacuation at 180^{O}C for 1 h

Pt-Re / C cat. (5 wt-Pt%, Pt / Re = 4)

Time Courses of Hydrogen Evolved from Decalin with Pt / C Catalyst at Various Charged Amounts of Decalin

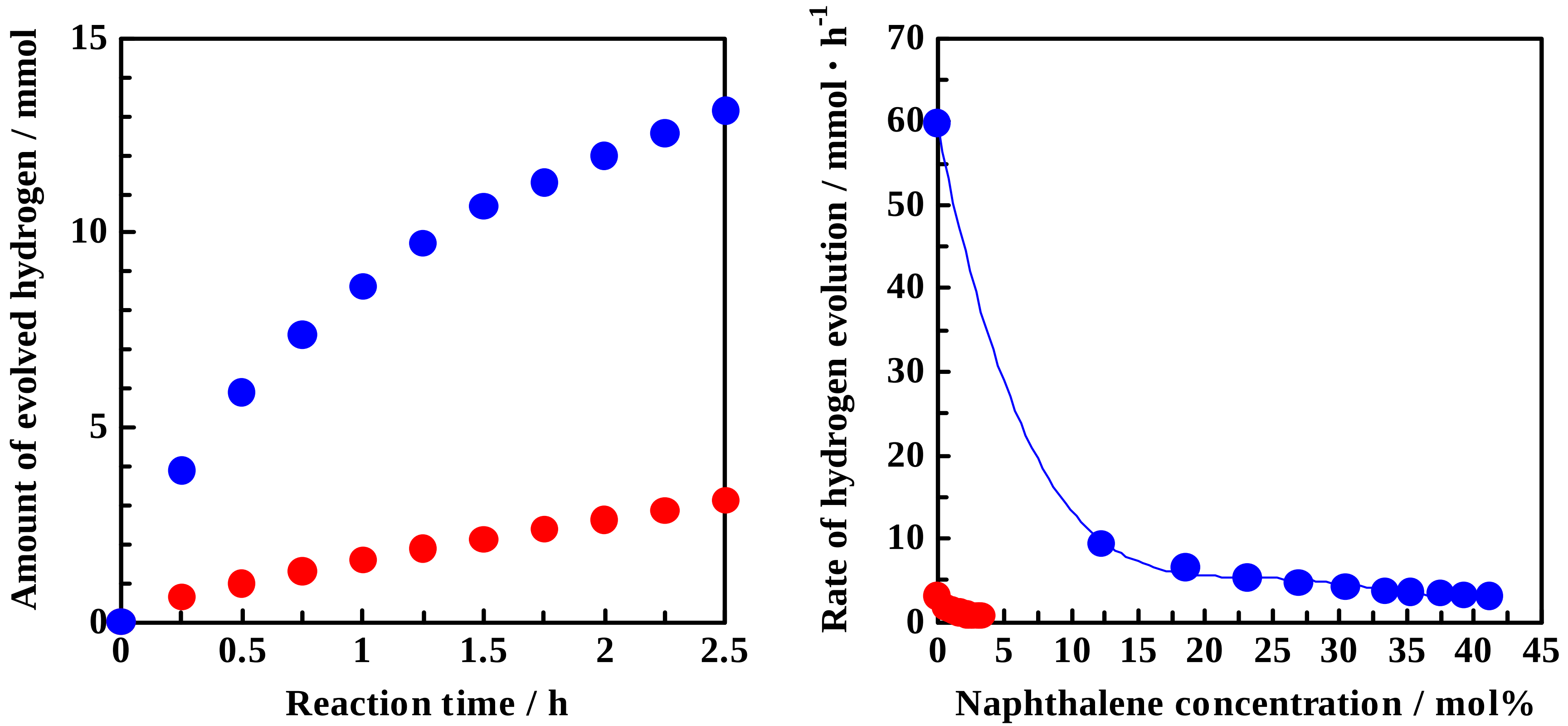


Charged amount of decalin: 1.0 (◆), 1.5 (■), 2.0 (●), 3.0 (●), 10 ml (◆)

Catalyst: Carbon-supported platinum nano-particles (Pt / C, 5 wt-metal%) 0.75 g

Reaction conditions: Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

Time Courses of Evolved Hydrogen with Pt / C Cat. and Reaction Rate as a Function of Naphthalene Concentration



Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 0.30 g

Decalin solution: 1.0 ml (●) (liquid-film state), 3.0 ml (●) (suspended state)

Reaction conditions: Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

Contrast between Superheated Liquid-film and Suspended States in Catalytic Decalin Dehydrogenation

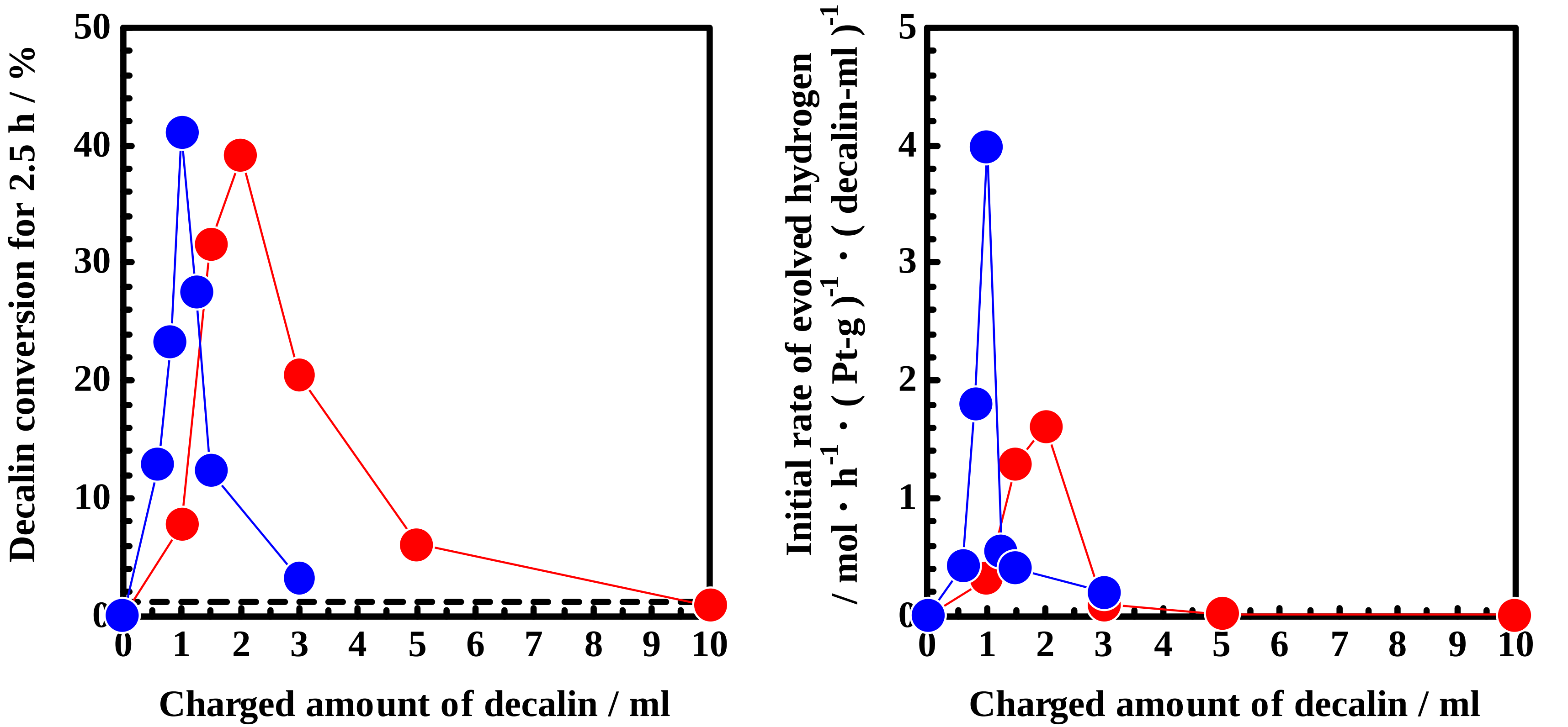
	Superheated liquid-film state	Suspended state
Catalyst / solution ratio (g / ml)	0.30 / 1.0	0.30 / 3.0
Rate constant: *k* (mol / h・Pt-g)	3.3	0.21
Retardation constant: *K* (ml / mmol)	5.2	16.4

Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 0.30 g

Reaction conditions: Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

k and *K* calculated from the equation: $v = k / (1 + K [\text{naphthalene}])$

Relationship of catalytic dehydrogenation activities with charged amounts of decalin



-------: Equilibrium conversion (1.2%) for decalin dehydrogenation at 210^{O}C and 1 atm

Catalyst: Carbon-supported platinum nano-particles (Pt / C, 5 wt-metal%) 0.30 g (●) and 0.75 g (●)

Reaction conditions : Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

Comparison of Kinetic Parameters in Superheated Liquid-film States at different amount ratios

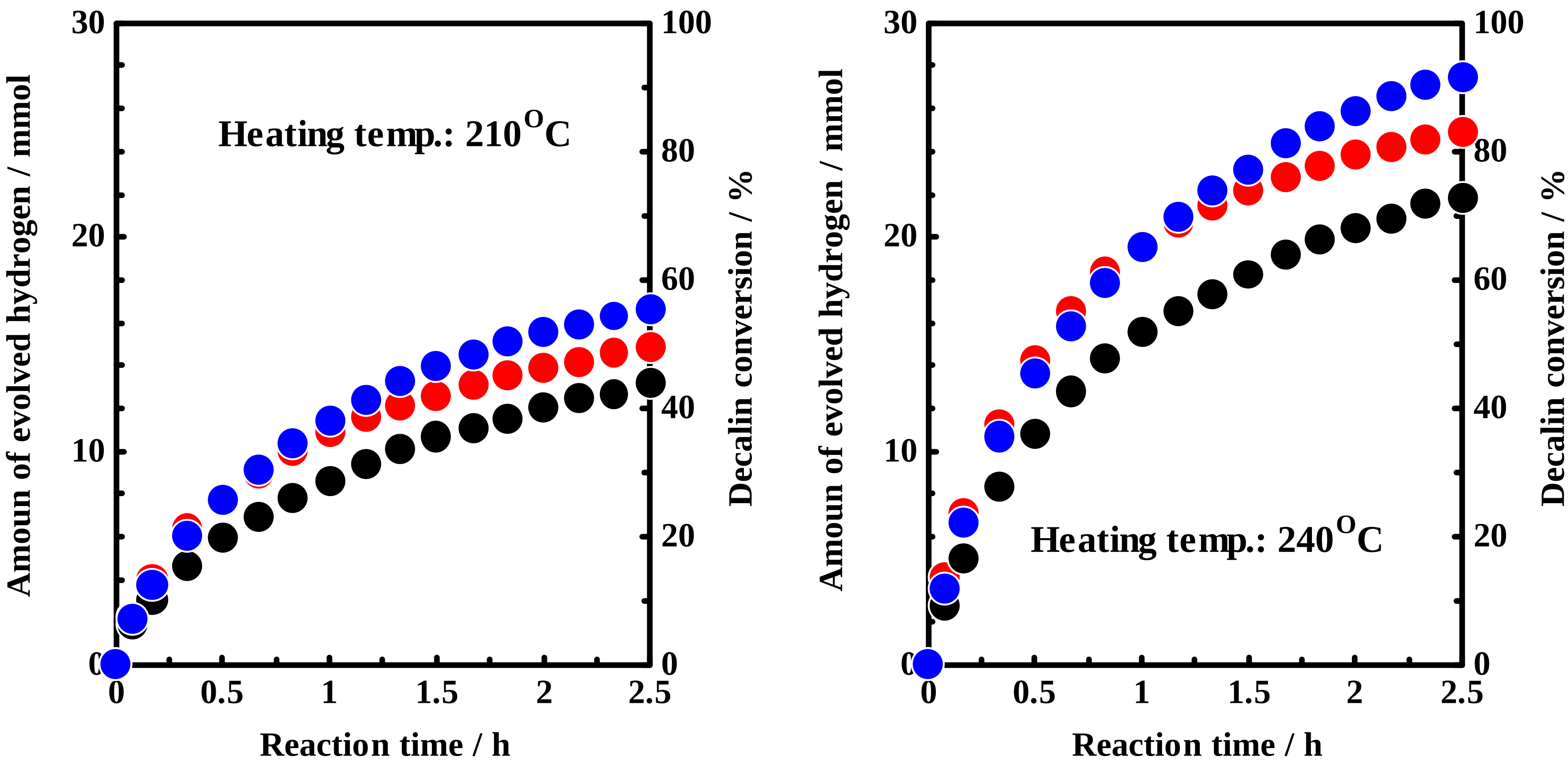
	Superheated liquid-film state	
Catalyst / solution ratio (g / ml)	0.30 / 1.0	0.75 / 2.0
Rate constant: *k* (mol / h · Pt-g)	3.3	2.9
Retardation constant: *K* (ml / mmol)	5.2	7.6

Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 0.30 g

Reaction conditions: Boiling and refluxing by heating at 210^{O}C and cooling at 5^{O}C

***k* and *K* calculated from the equation: $v = k / (1 + K [\text{ naphthalene }])$**

Time Courses of Dehydrogenation Activities with Pt-based Catalysts under Superheated Liquid-film Conditions

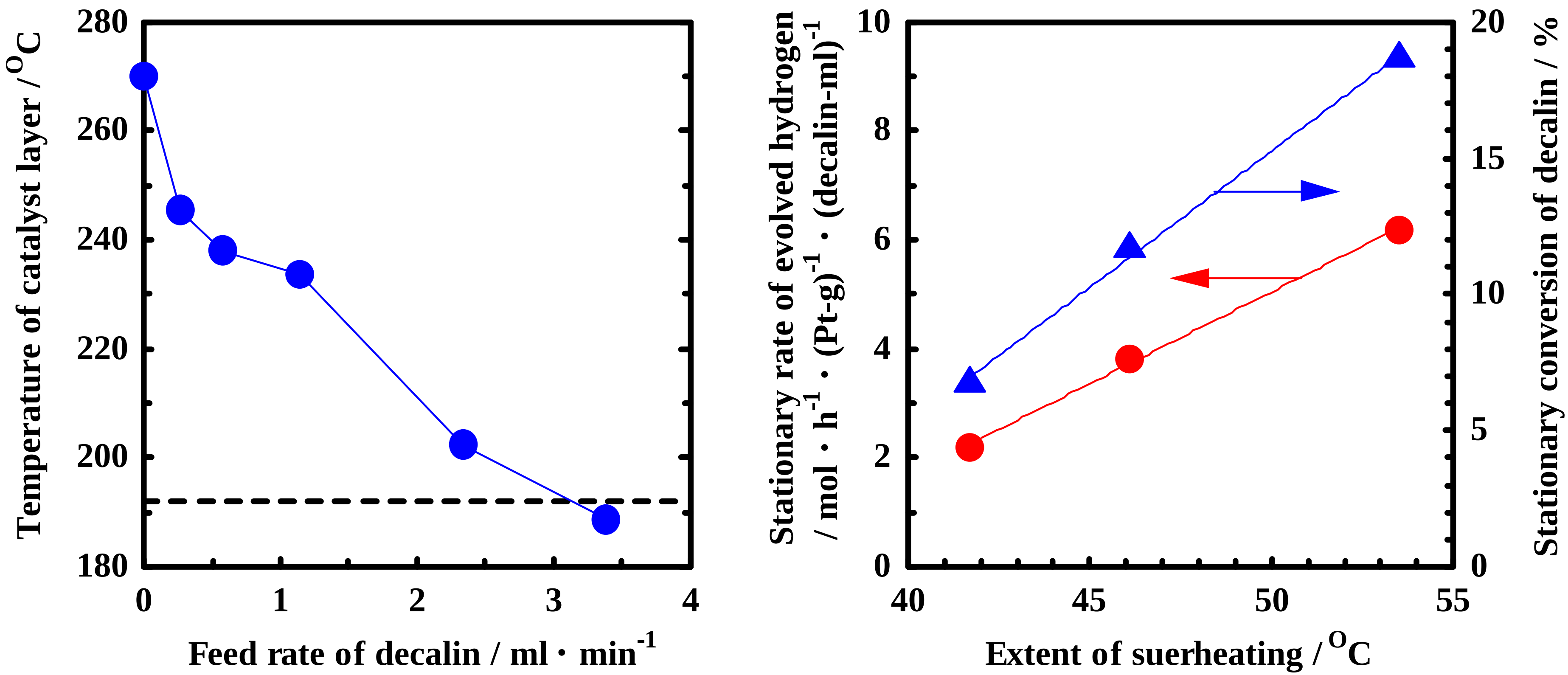


Catalyst: Pt / C (5 wt%, ●), Pt-W / C (5 wt-Pt%, Pt / W = 5, ●) and Pt-Re / C (5 wt-Pt%, Pt / Re = 4, ●) 0.30 g

Charged amount of decalin solution: 1.0 ml (superheated liquid-film conditions)

Reaction conditions: Boiling and refluxing by heating at 210 and 240^{O}C and cooling at 5^{O}C

Relationship of Catalyst-layer Temperature with Feed Rate and Dehydrogenation Activities as a Function of Extent of Superheating



-------: Boiling point of decalin (192°C)

Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 1.1 g

Reaction conditions: Boiling and refluxing by heating at 270°C and cooling at 25°C

Comparison of Dehydrogenation Activities for Decalin and Tetralin in Continuous Operation

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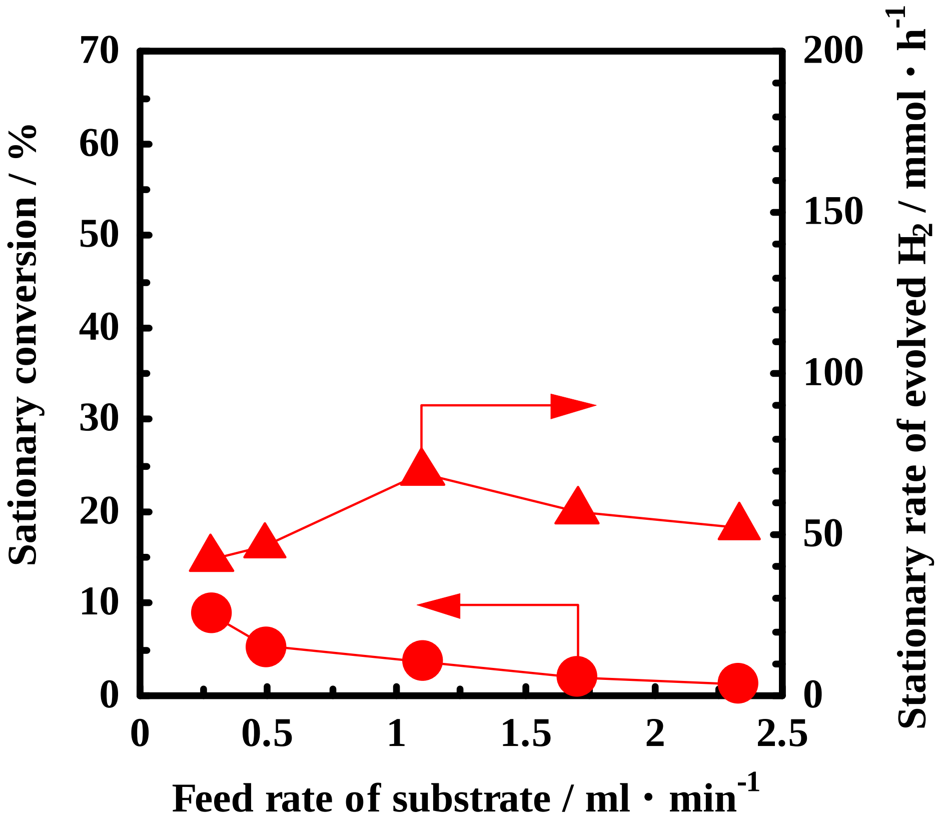
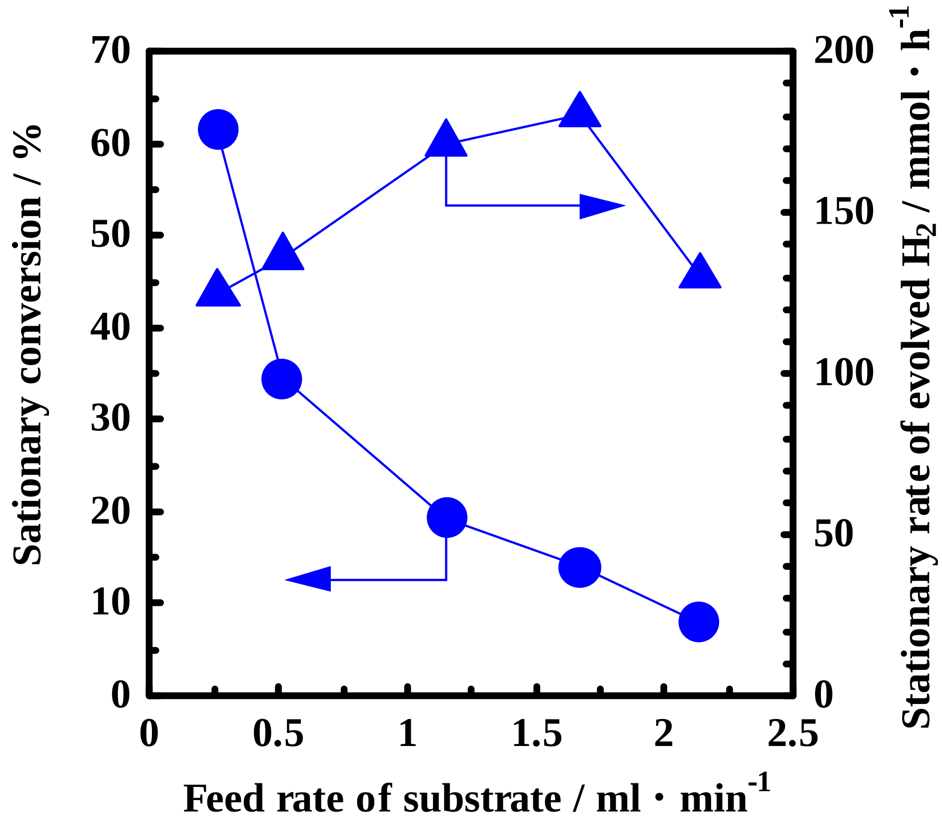
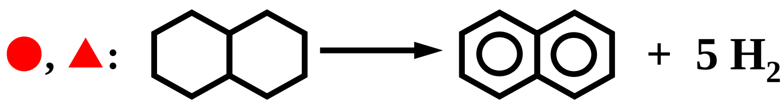
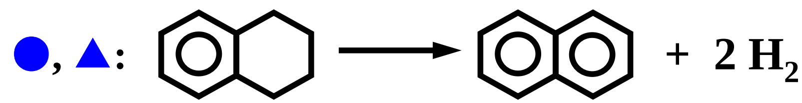




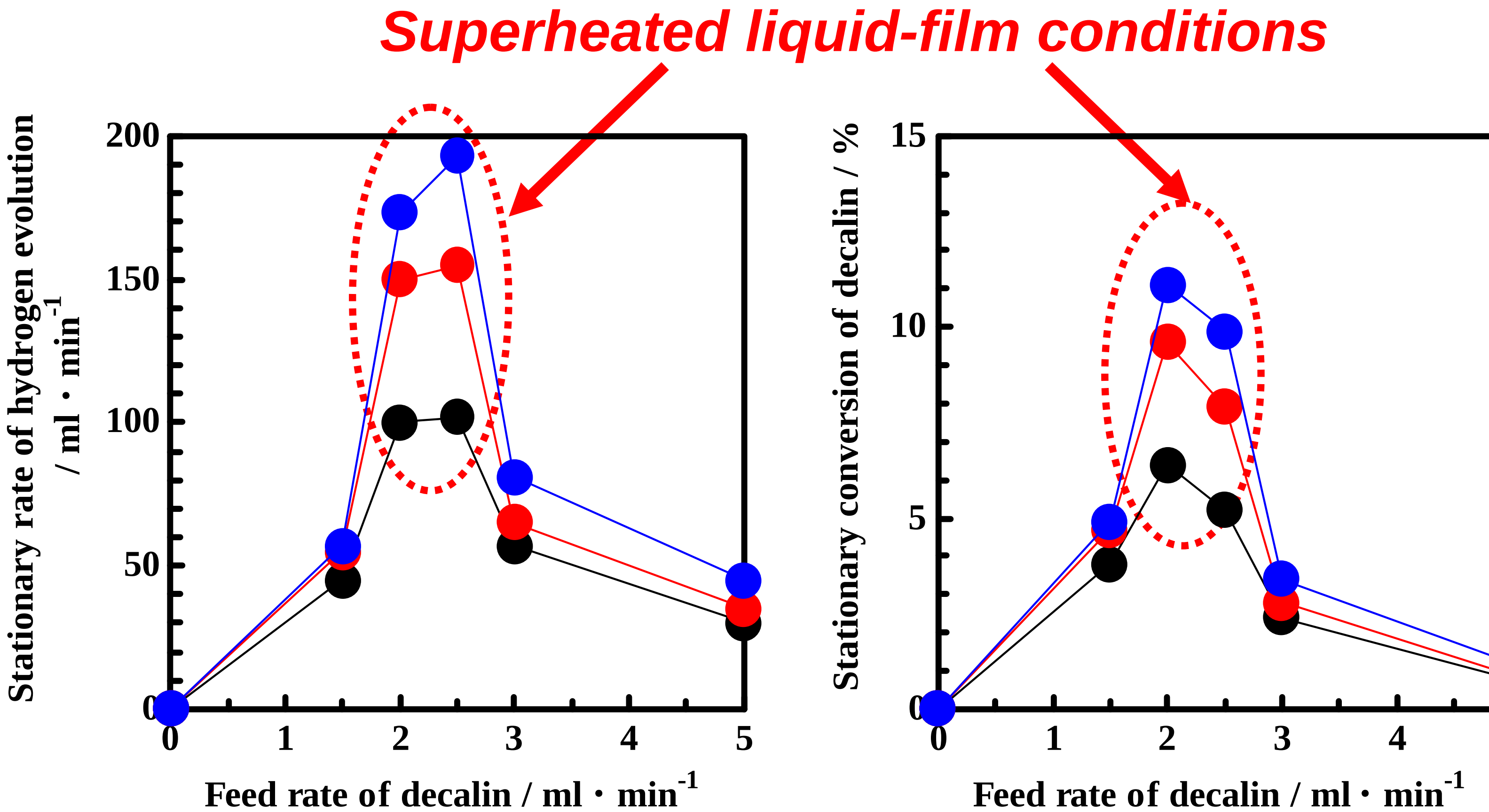




Catalyst: Carbon-supported platinum nano-particles (5 wt-metal%) 1.1 g

Reaction conditions: Boiling and refluxing by heating at 230^{O}C and cooling at 25^{O}C

Relationship between Dehydrogenation Activities and Feed Rates of Decalin in Continuous Operation



Catalyst: Platinum nano-particles supported on activated carbon cloth (5 wt-metal%)

0.29 g (one layer, black), 0.58 g (two layers, red), 0.87 g (three layers, blue)

Reaction conditions: Boiling and refluxing by heating at 280^{O}C and cooling at 25^{O}C

Catalyst-Heating Area for Dehydrogenation Needed to a 50 kW Power of Fuel Cell

☆ From experimental results in a continuous-type reactor, stationary rates of hydrogen evolution per area of catalyst layer (V_H [mol / m^2 · h]) are given as

$$V_H = 5 \times (A / 100) \times D$$

where A [%] is the stationary one-pass conversion of decalin and D [mol / m^2 · h] the feed rate of decalin per area of the catalyst layer (5 cm ϕ disk-shaped ACC).

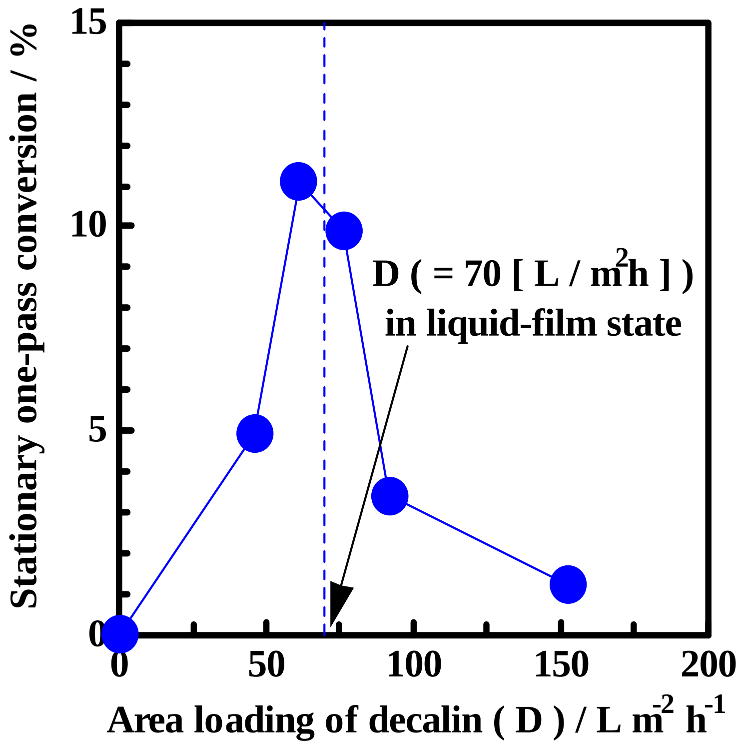
☆ Catalyst-layer area (S [m^2]), needed for any desired stationary rate of hydrogen evolution (L_H [mol / h]), is given as

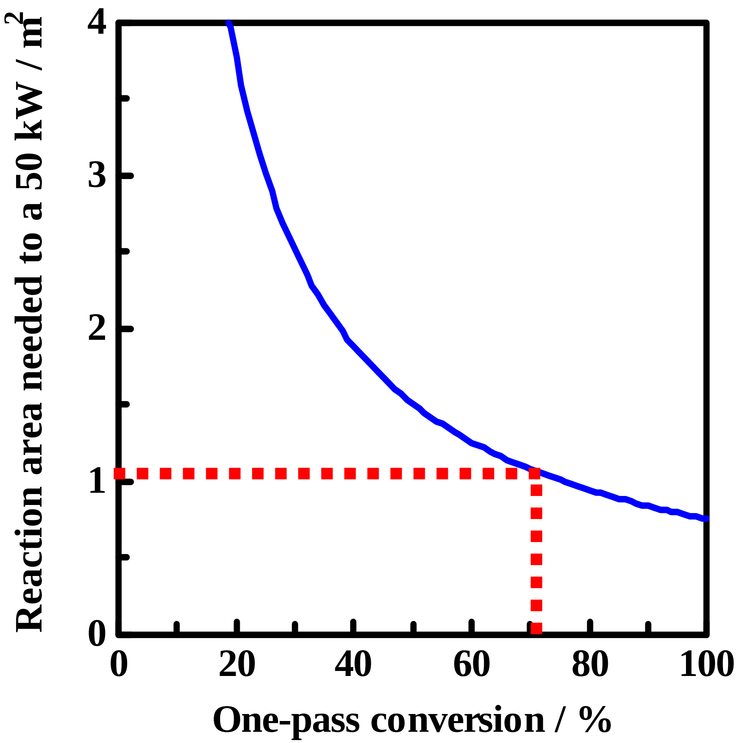
$$S = L_H / V_H = L_H / [5 \times (A / 100) \times D]$$

☆ Since the needed hydrogen rate (L_H) is ca. 1.7 x 10^3 [mol / h] for 50 kW power at the energy conversion efficiency of 45%, the catalyst-layer area (S) is deduced to

$$S = 3.4 \times 10^4 / (A \cdot D)$$

Relationship of Stationary Conversion with Area Loading of Decalin and with Reaction Area Needed to a 50 kW Power





Catalyst: Pt nano-particles supported on activated carbon cloth (5 wt-metal%) three layers (0.87 g)

Reaction conditions: Boiling and refluxing by heating at 280^{O}C and cooling at 25^{O}C

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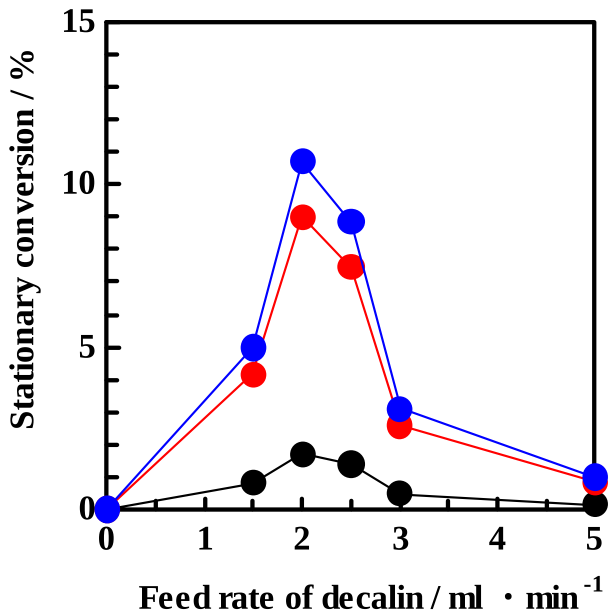
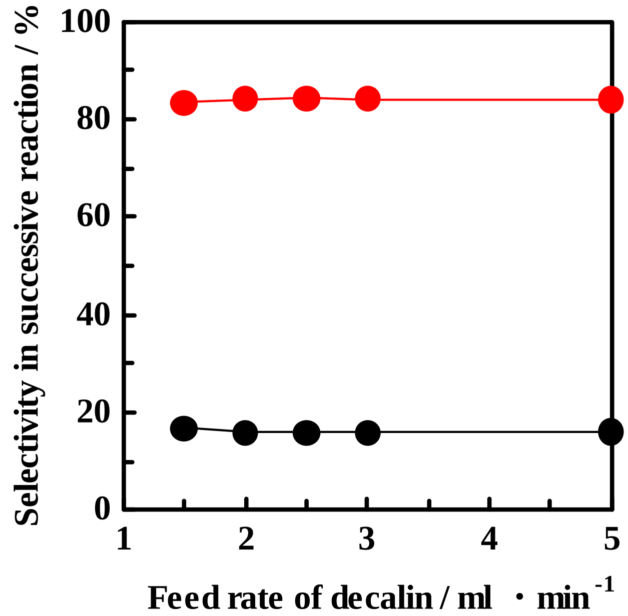
Relationship of Conversion & Product Distribution with Feed Rate of Decalin in Continuous Operation





● : Decalin → Tetralin
● : Decalin → Naphthalene
● : Converted decalin (● = ● + ●)

● : Naphthalene
● : Tetralin

Catalyst: Pt particles supported on activated carbon cloth (5 wt%, D = 5 cm) 0.58 g

Reaction conditions: Boiling and refluxing by heating at 280^{O}C and cooling at 25^{O}C

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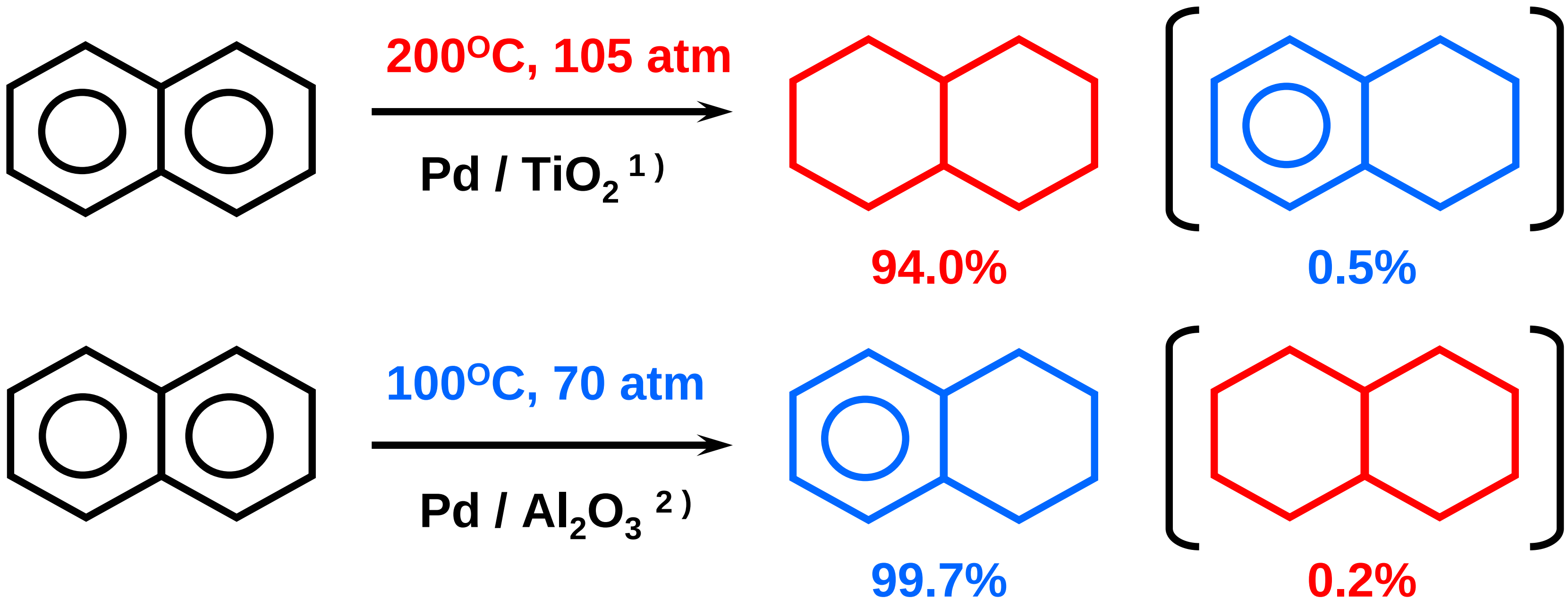
Catalytic Naphthalene Hydrogenation



1) S.D. Lin et al., Catal. Today, 31, 93-104 (1996) 2) A.W. Weitkamp, Adv. Catal., 18, 1-110 (1968)

Hydrogenation to tetralin proceeds much faster than hydrogenation to decalin under mild conditions (low temp. & pressure)