JASTIP

# WP2: Innovations in Biomass Application for Catalytic Material Synthesis and Energy Devices

สวทช NSTDA

NANOTEC
a member of NSTDA

京都大学 Kyoto University

VISTEC
สถาบันวิทยสิริเมธี

# Kyoto University team

## Research themes for JASTIP

1. Synthesis and application of functional nanomaterials, such as carbon nanotube, carbon nanohorns, Pt nanoparticles, etc.

**This topic is focused to explain today,**
**especially on progress in development of $H_2$ absorption material.**

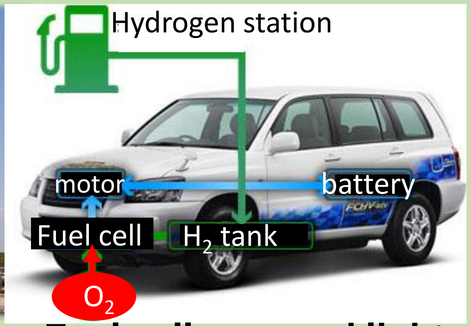
2. Research on application of algae for electric energy generation, catalyst nanoparticle formation, and water purification.

# Demand for advanced hydrogen storage media

## Current $H_2$ storage method

Compressed gas storage

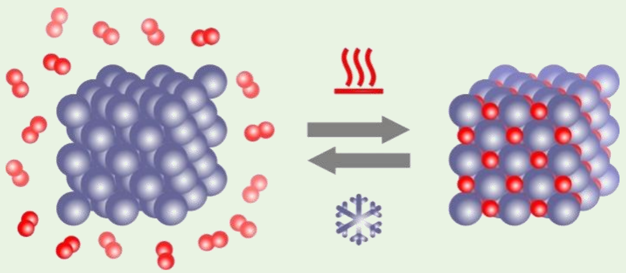

Liquid hydrogen storage(heavy)




Fuel cell car need light $H_2$ storage media

- ► High pressure => container cost
- ► Requires large space

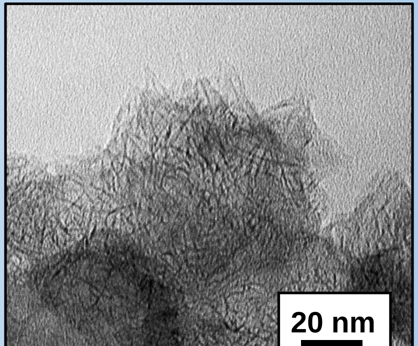
## Material-based $H_2$ storage

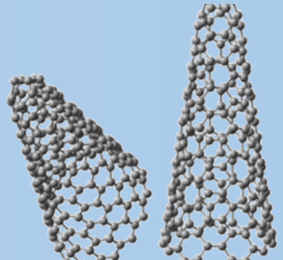


- ✓ lower volume requirement
- ✓ greater energy efficiency
- ✓ safety and ease of use

## Single-walled carbon nanohorns

Large surface area
Nano-scaled pores



### Gas-injected arc-in-water

- ✓ Cost-effective
- ✓ High purity
- ✓ Simplicity

# Study on metal/CNHs for application to hydrogen storage

## Thai team
## (NANOTEC center, Chulakongkorn Univ. )

**Experimental work:**

Natural Biomass (e.g. water hyacinth) can be used as raw material to prepare CNHs.

**Theoretical work:**

Molecular simulation has been conducted to elucidate reaction mechanism to store hydrogen by metal/CNHs.

## Japanese team (Kyoto Univ.)

**Experimental work:**

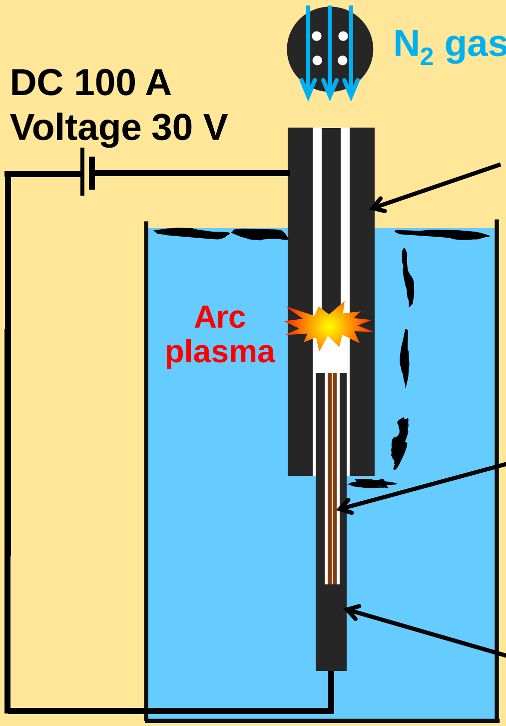
$H_2$ storage property is measured using Fe/CNHs produced by gas-injected arc-in-water method.

**Theoretical work:**

Molecular simulation has been conducted to elucidate reaction mechanism to store hydrogen by metal/CNHs from different view point from Thai team.

# Experimental
## (synthesis of Fe/CNHs and measurement of hydrogen storage property at high pressure)

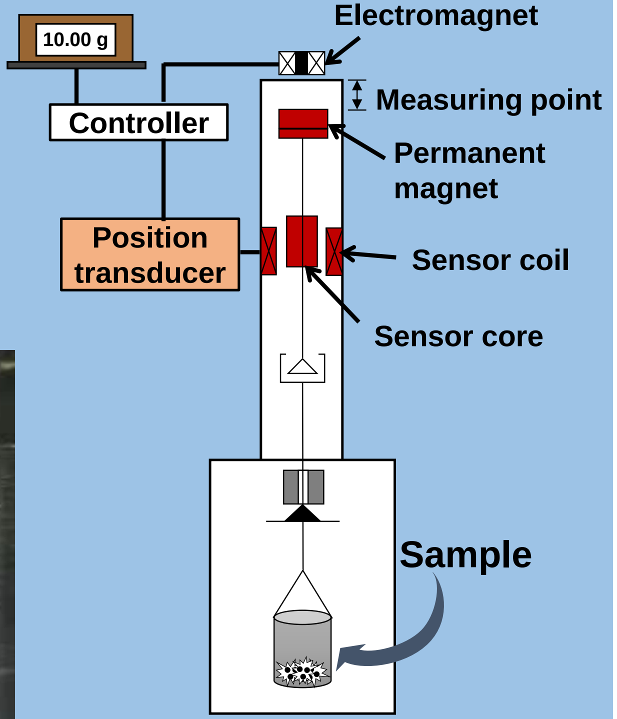
### Synthesis pure SWCNHs and SWCNHs/Fe




Schematic diagram of Arc discharge machine

### $H_2$ storage measurement

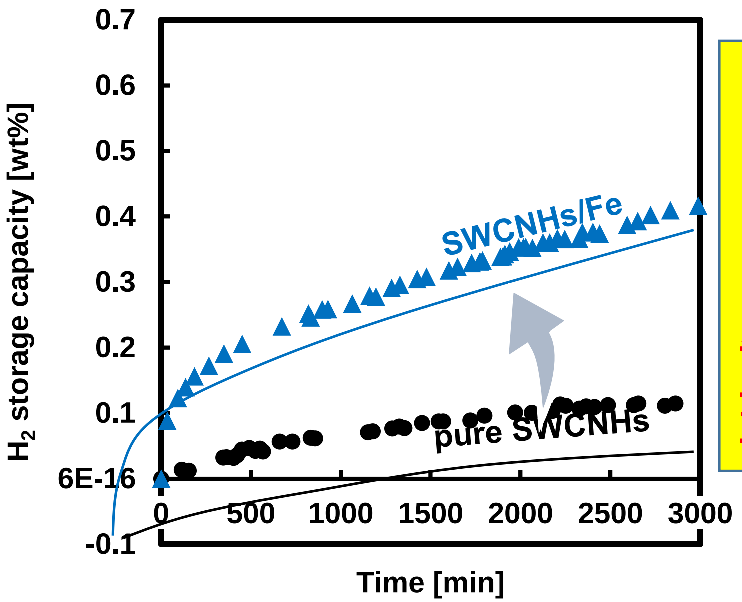
- High pressure $H_2$ gas
- vacuum condition




Magnetic suspension balance

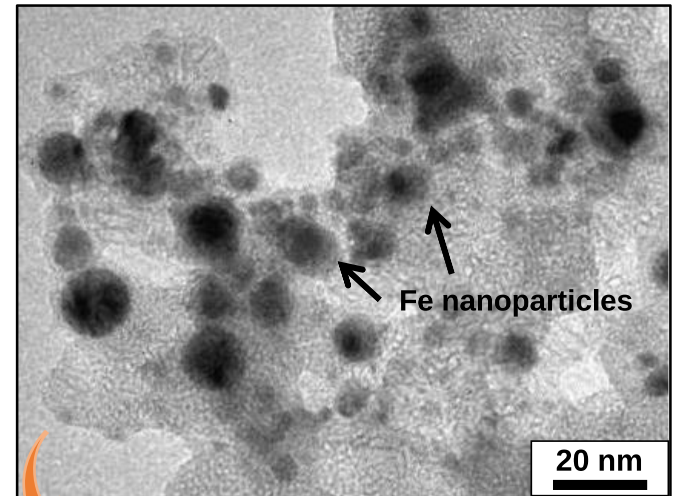
# Result (Storage of hydrogen)

## $H_2$ storage capacity at 2 MPa and 25 ºC




**$H_2$ storage is enhanced by dispersing Fe particle.**

**Adding Fe by 10.5wt% results in 4 times increase.**



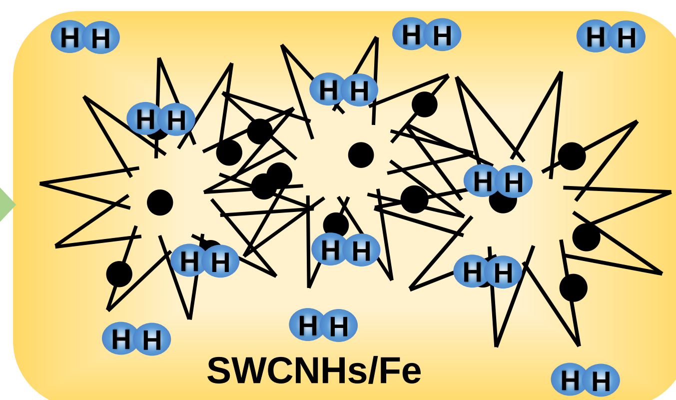

EDX analysis

▶ **Percent inclusion of Fe ~ 10 wt%**

**Fe is not $H_2$-absorbing metal.**

**+**

**pure SWCNHs**




**$H_2$ storage capacity improve by Fe nanoparticles**

**Dissociate to H atom**

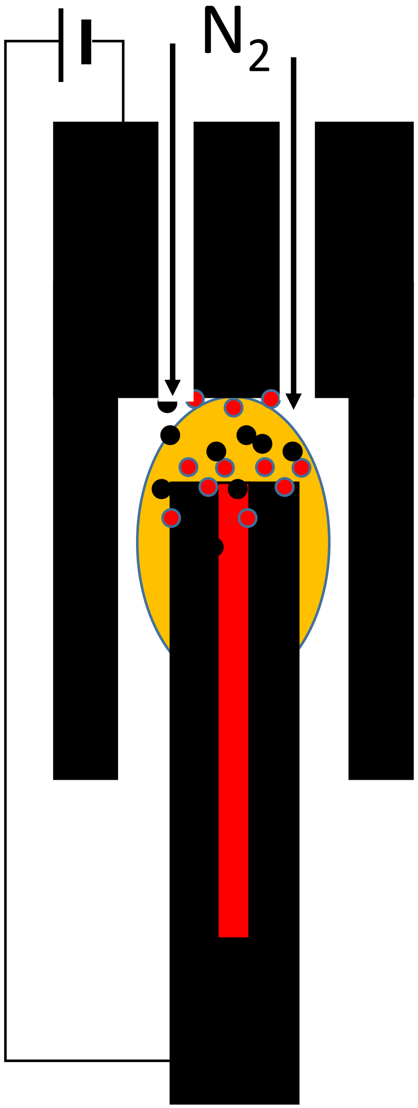
**Diffusion to carbon support**

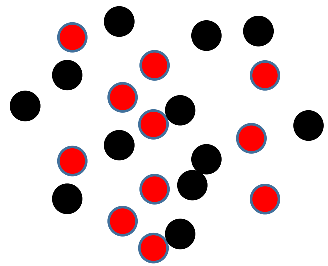
**$H_2$ spillover[2]**

CO adsorption experiment
=> Most metallic particles
are migrated in
SWCNHs

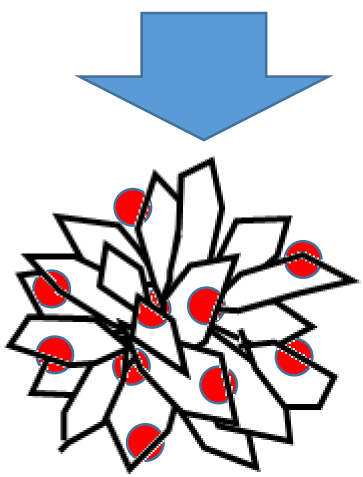
[2] Gardes *et al.*, *J. Catal.*, **35**, 145-148 (1974)

# Unique Fe-CNH hybrid structure realized by GI-AIW method

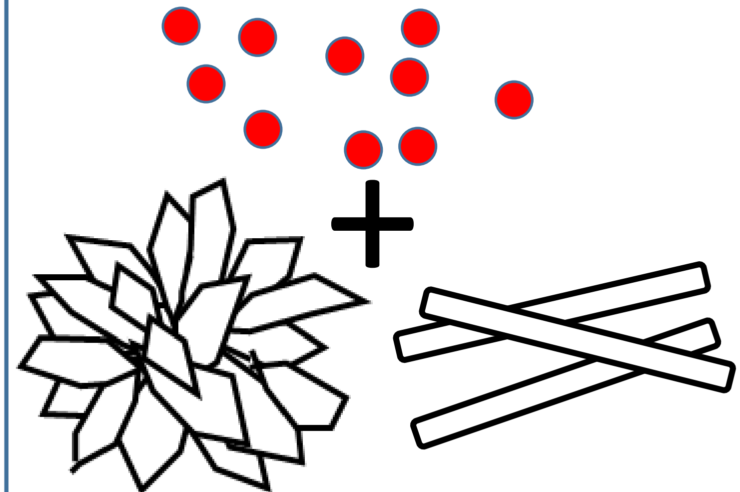


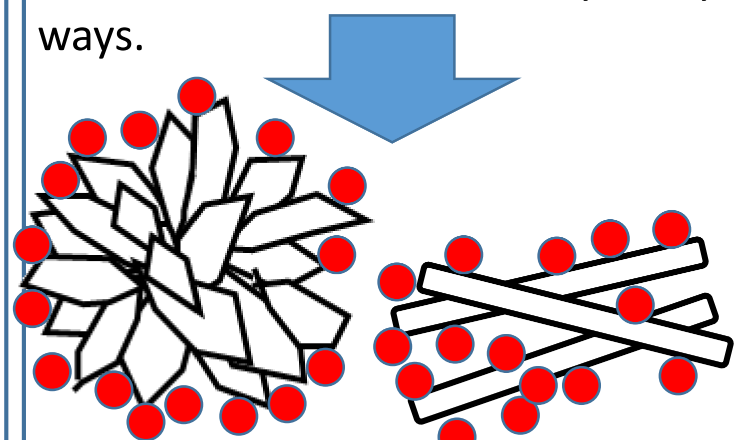
C and Fe evaporate and are solidified simultaneously.



Fe nanoparticles can exist in carbon wall.
('inwall' structure.)



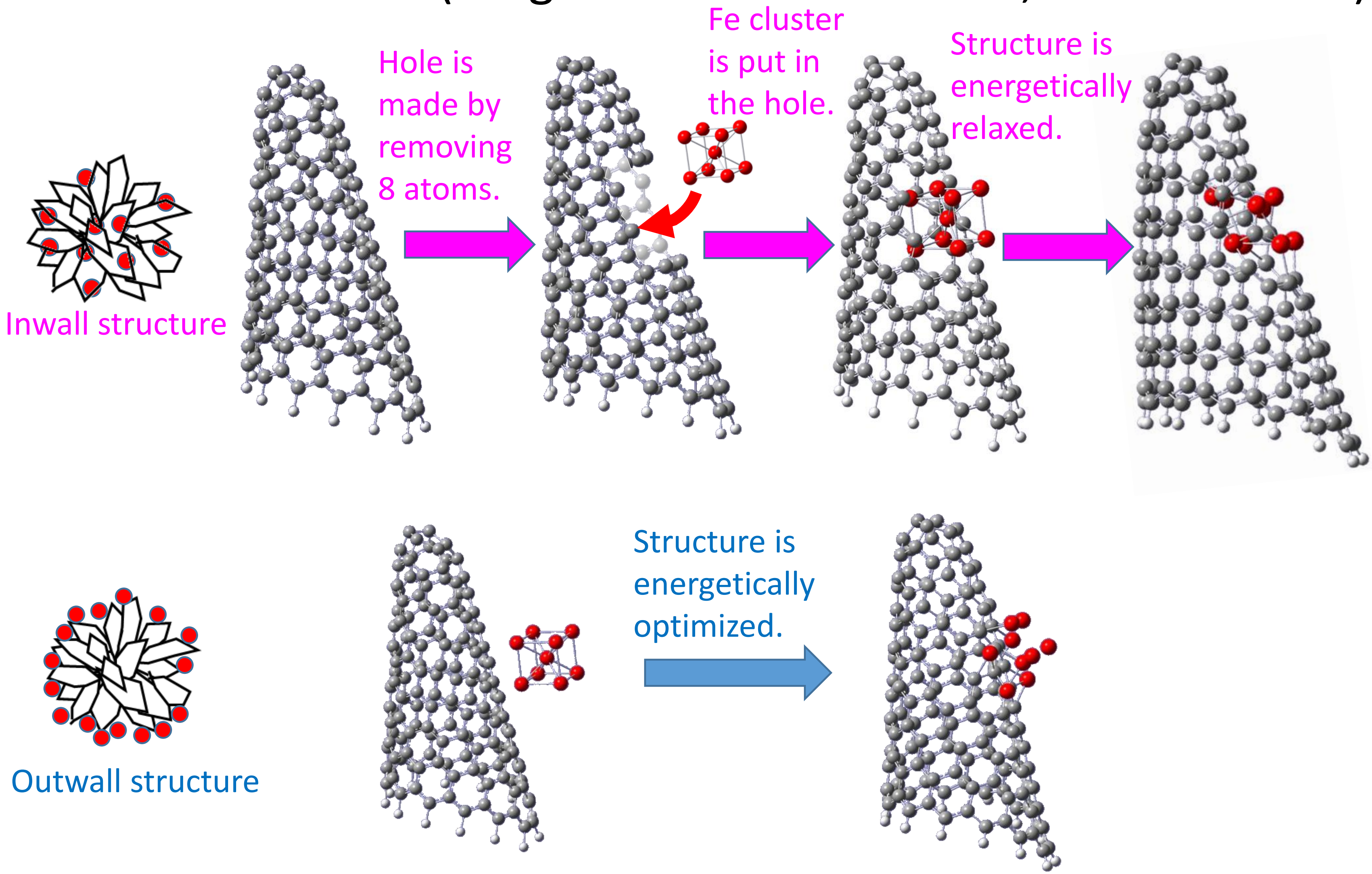
Fe are added on C surface by many ways.



C nano surface are decorated with Fe on outside surface.
('outwall'structure)

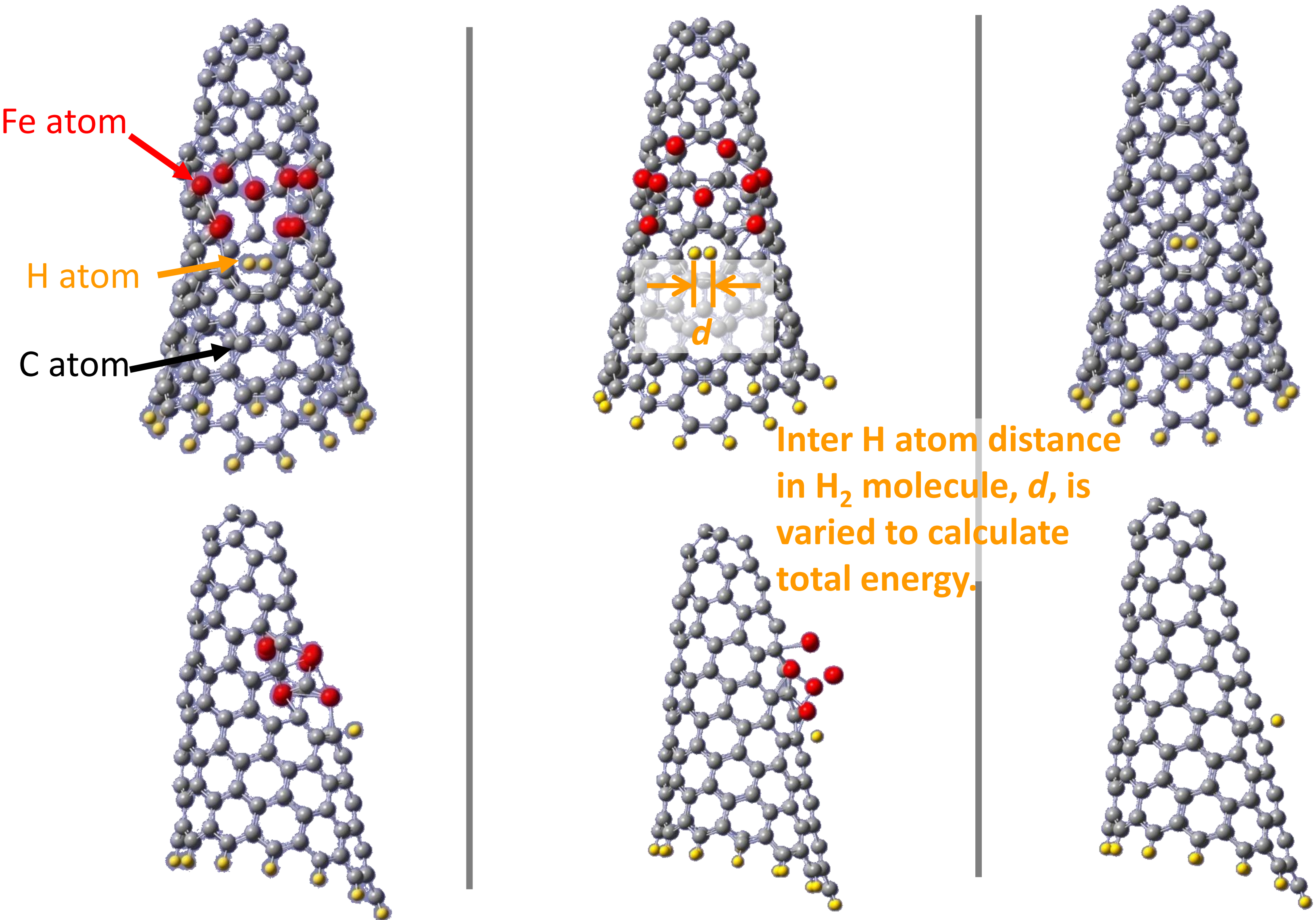
# Theoretical study on 'spill-over effect' on Fe-CNHs

## Modeling of Fe-CNHs structure for semiempirical molecular orbital calculation (Program: Gaussian R 09W, method: PM6)



# Theoretical study on 'spill-over effect' on Fe-CNHs

## Molecular models to calculate energy for dissociation of $H_2$ molecule



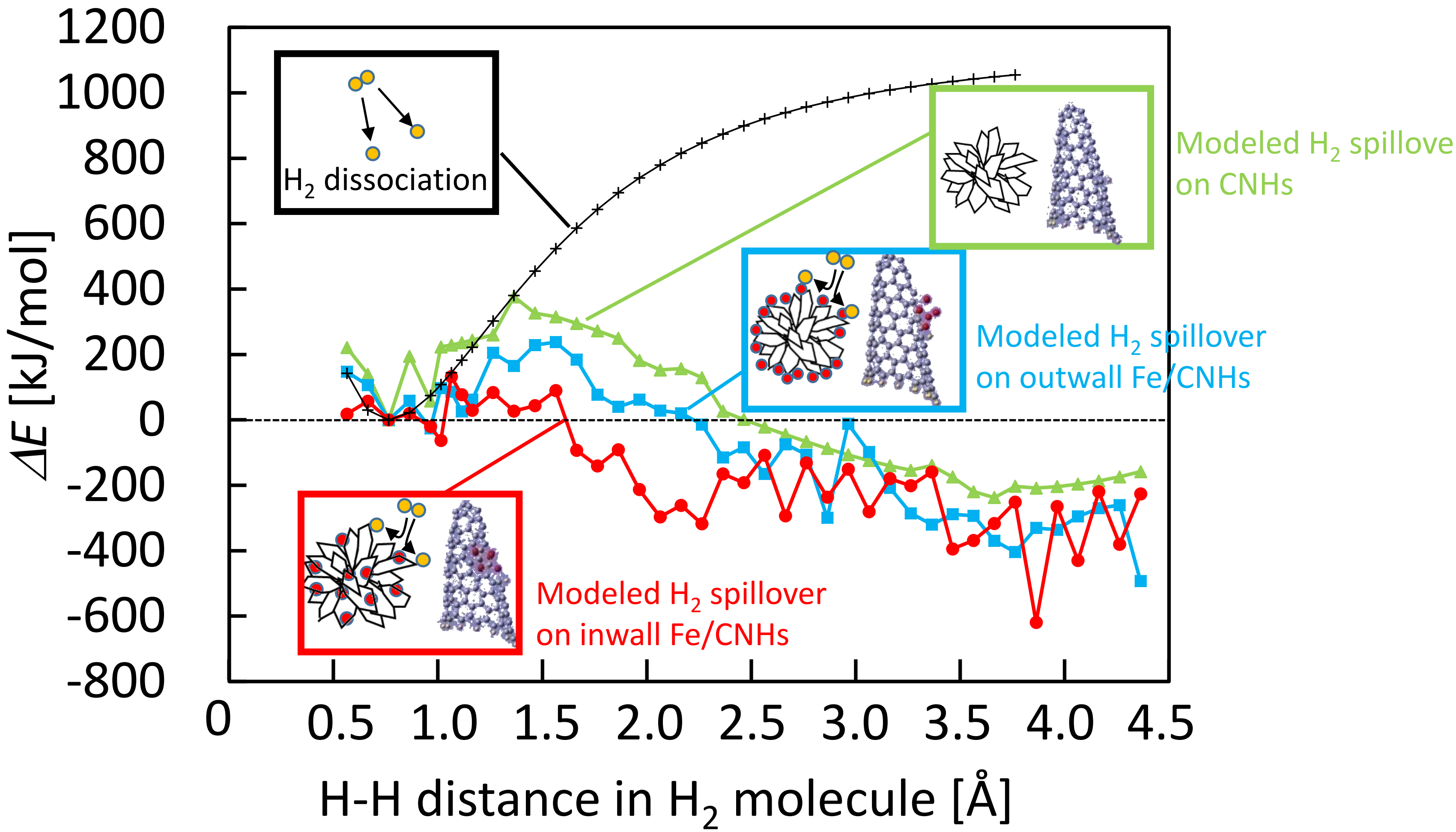

Inwall structure

outwall structure

CNH without Fe cluster

# Theoretical study on 'spill-over effect' on Fe-CNHs

$\Delta E$ = (total energy of $H_2$-Fe/CNHs)
− (total energy of $H_2$-Fe/CNHs at H-H distance in stable $H_2$ molecule)




Energy change by dissociating $H_2$ on two types of Fe/CNHs and CNHs and in vaccuum.

Activation energy for $H_2$ dissociation is very low on inwall Fe/CNHs.

$H_2$ storage by Fe-CNHs can be enhanced via spillover effect.

# Summary

$H_2$ storage by high pressure adsorption by CNHs can be highly enhanced by dispersing Fe nanoparticles.

Unique structure can be expected in Fe/CNHs produced by a gas-injected arc-in-water method, where Fe nanoparticles can exist in carbon wall of CNHs.

Semiempirical molecular orbital calculation exhibits low activation energy to dissociate $H_2$ around Fe nanoparticle at the inwall structure.

⇒ This result supports the hypothesis of the spillover effect to enhance H2 storage capacity of Fe/CNHs.

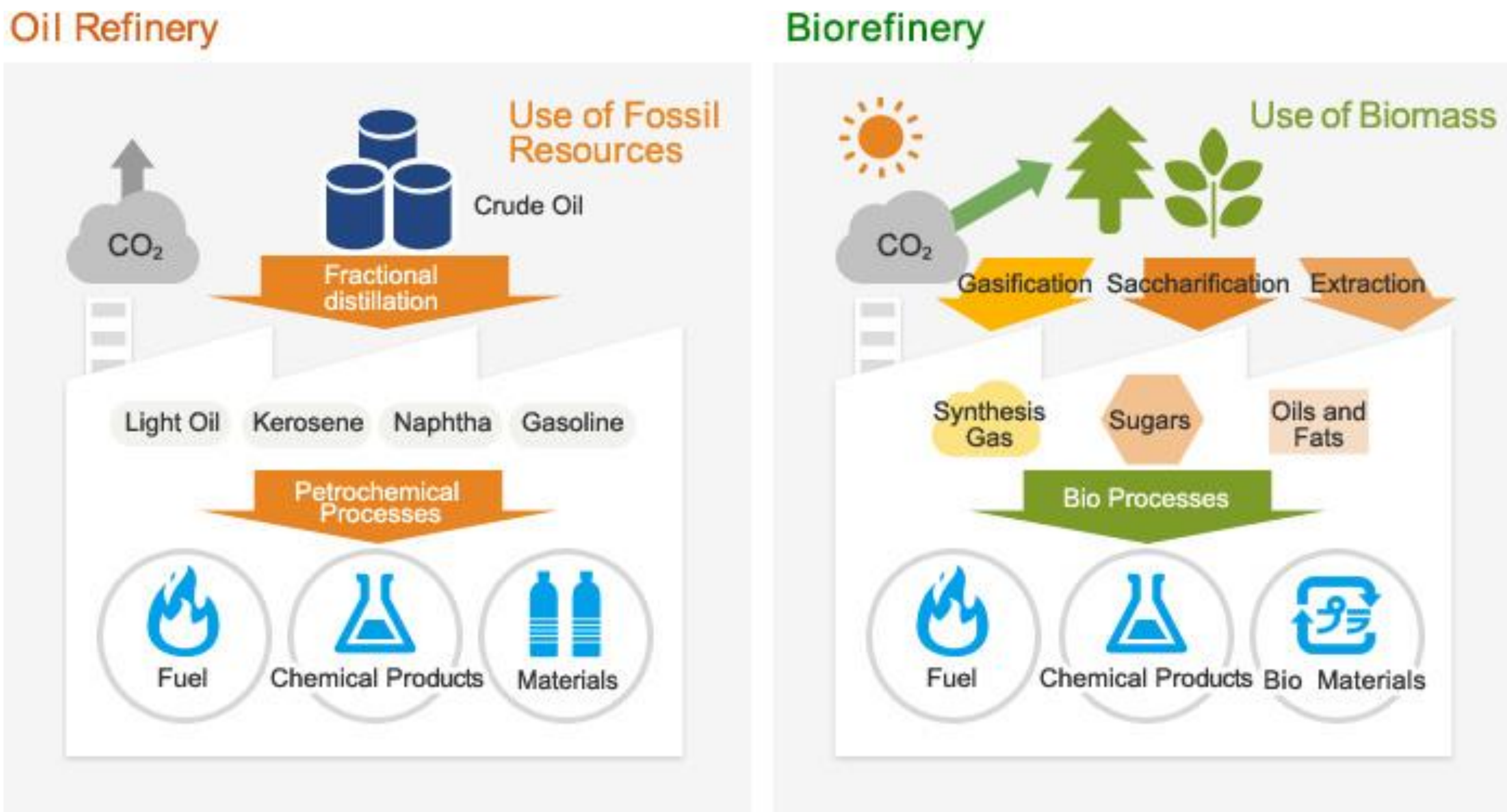
# NANOTEC/NSTDA and Thai team

## Research themes for JASTIP

1. Development of magnetic catalysts for biodiesel production – the Fe-based catalysts have been developed for biodiesel production using palm oil and methanol as feedstocks.
2. Development of carbon-based catalysts for biomass conversion – the carbon-supported catalysts have been developed for cellulosic sugar to furans.
3. Simulation study of hydrogen storage on carbon materials – various structures and orientation of H2 molecules on carbon surfaces have been theoretically studied.

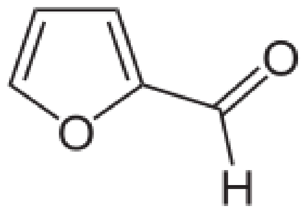
**These 2 topics are focused to explain today.**

# Catalysts for biorefinery applications




http://www.nipponpapergroup.com/english/research/organize/biomass.html

# Development of carbon-based catalysts for biomass conversion



$C_5H_4O_2$

<u>Furfural</u>

Beneficial usage

- Petroleum industrial solvent
- Chemical feedstock for bioenergy production

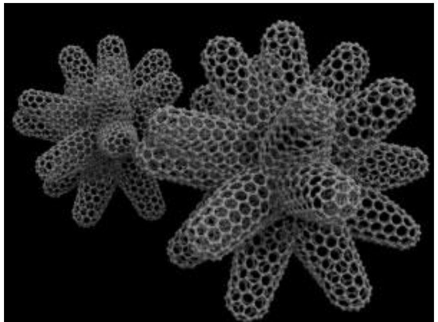
Commercial catalyst

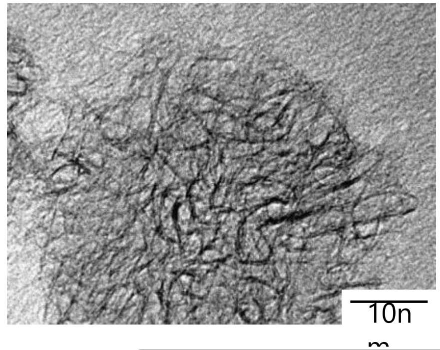
- Mineral acid ($H_2SO_4$ and HCl)

**Problem** : Severe corrosio
Excessive waste disposa
High investment in catalyst recovery pro

**Solid acid catalyst**

# Experimental






**Gas-inject arc-in-water (GI-AW)**

GI-AW method has some benefits, i.e., simplicity and capability for synthesizing various

Anode and metal wire preparation

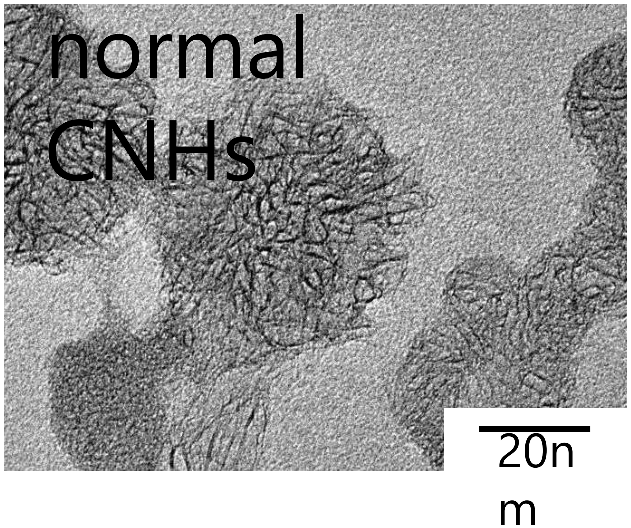
Arc discharge process

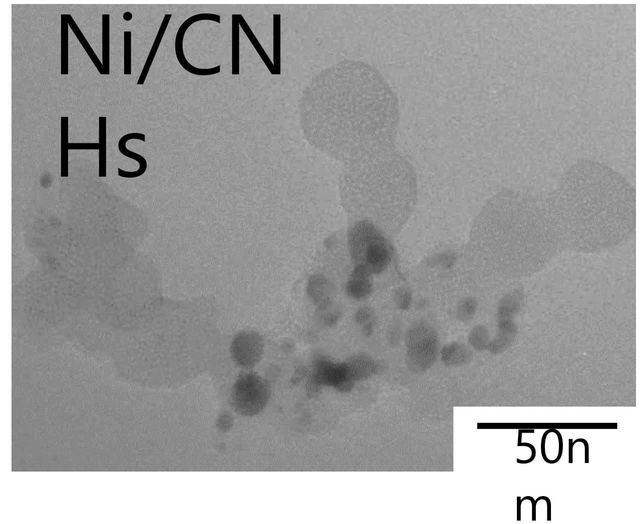
Product collection

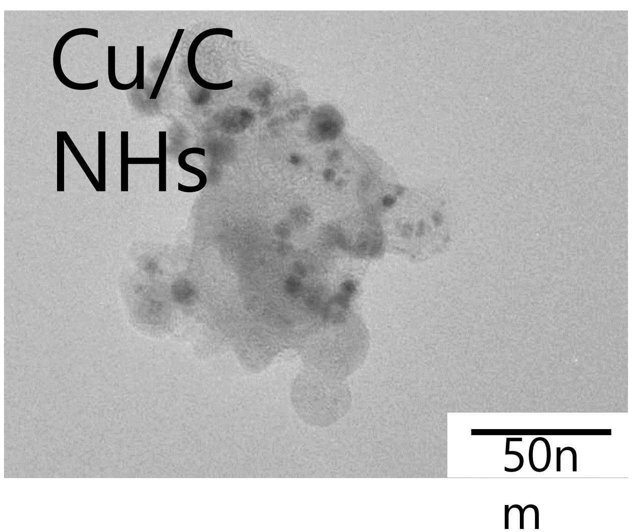
Analysis

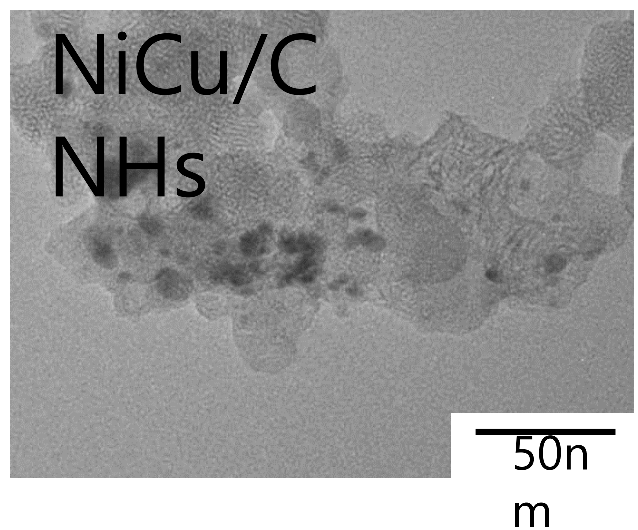
Reaction testing

# Results&Discussion
# TEM analyses

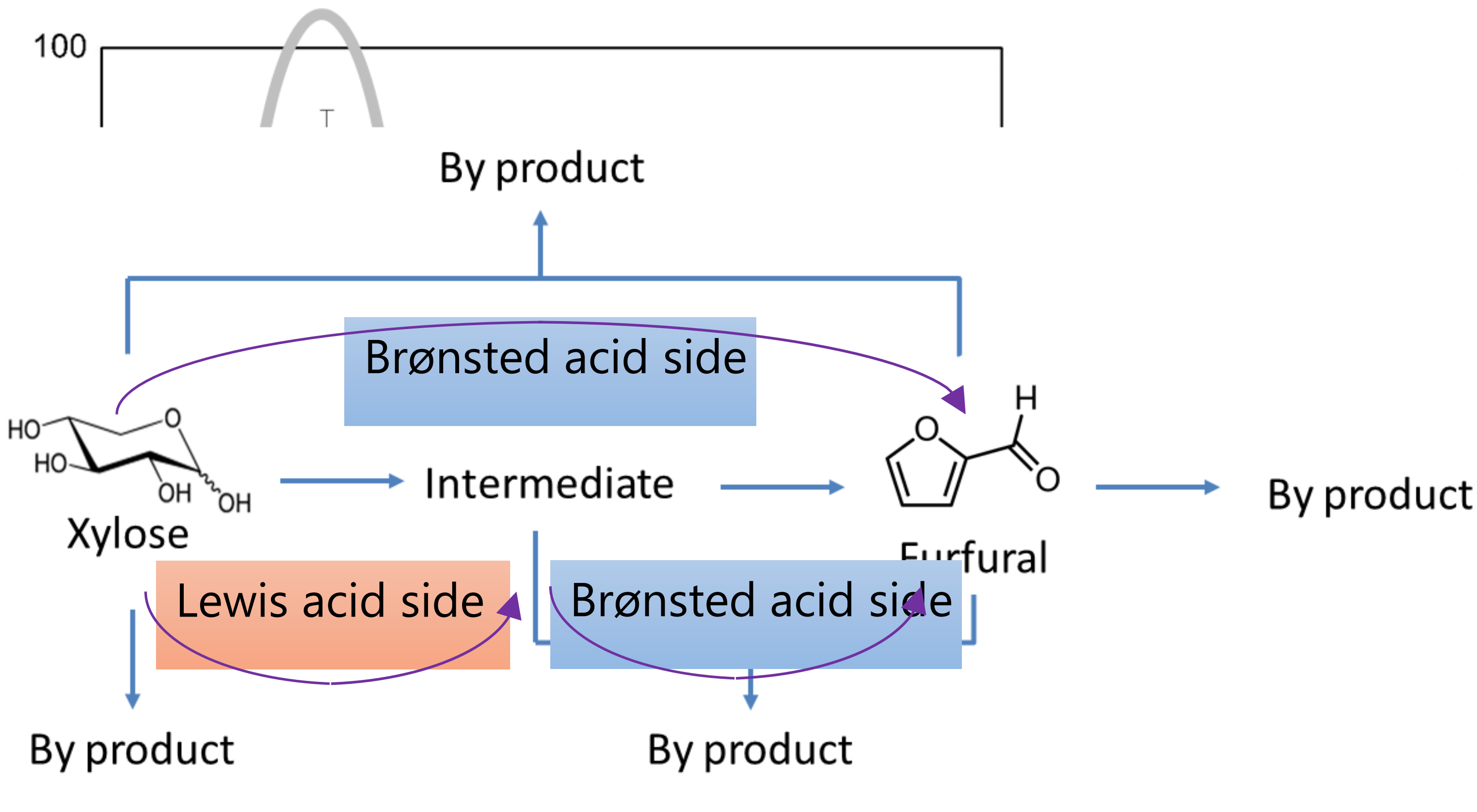


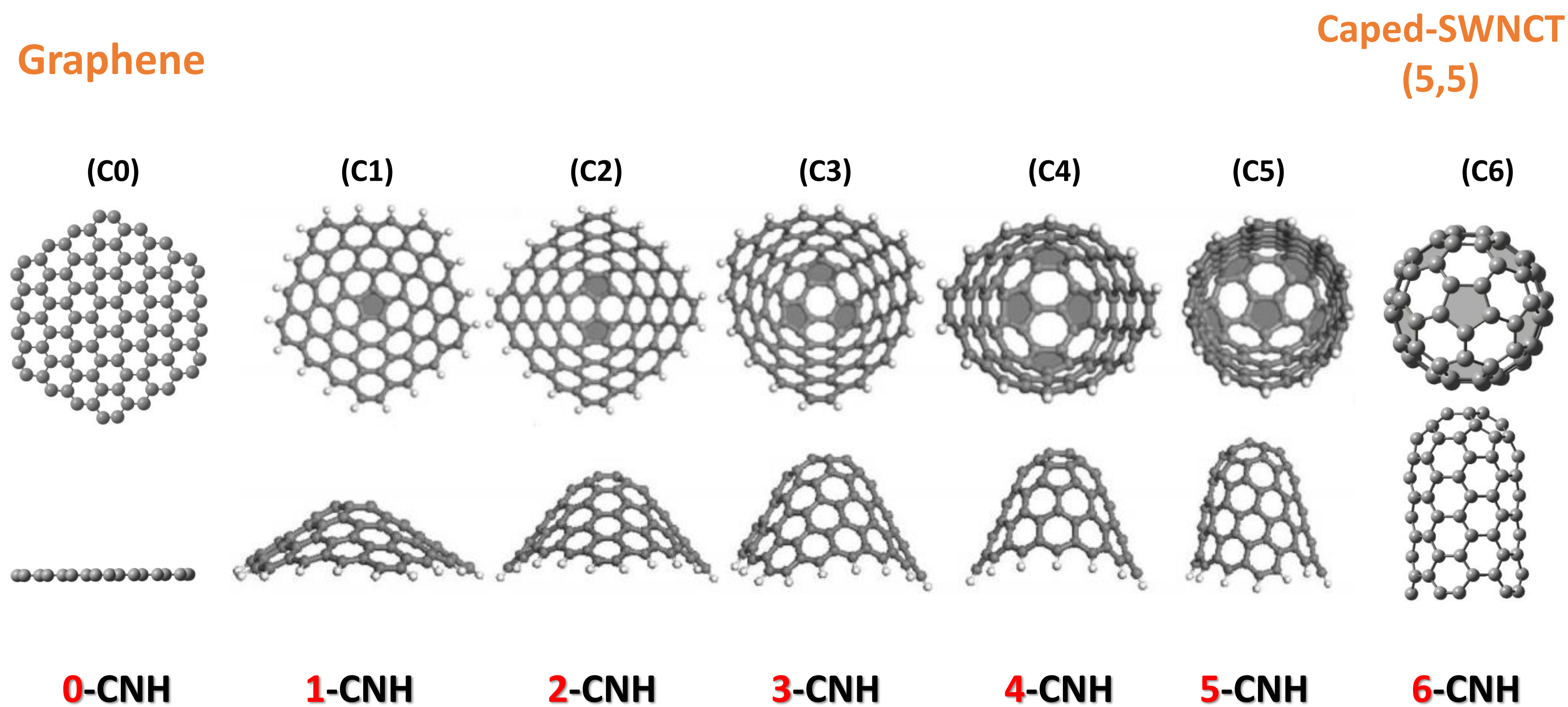



# Results&Discussion
## Furfural production



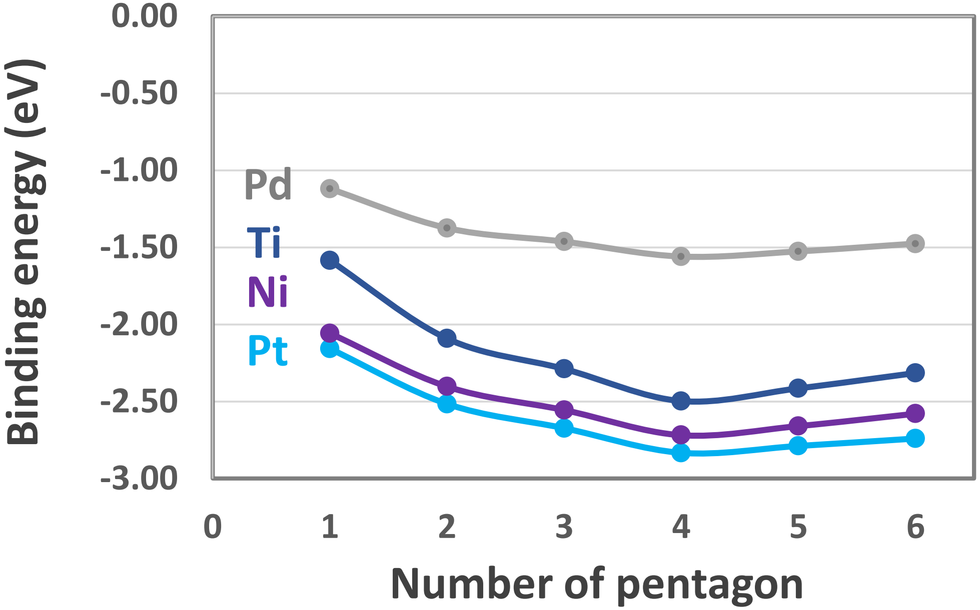

*By product: small organic acid, alcohol, humin etc.

# Representation of single CNH




**Shape of CNH depended on number of pentagon on the cone tip**

# Stability of metal-doped CNH

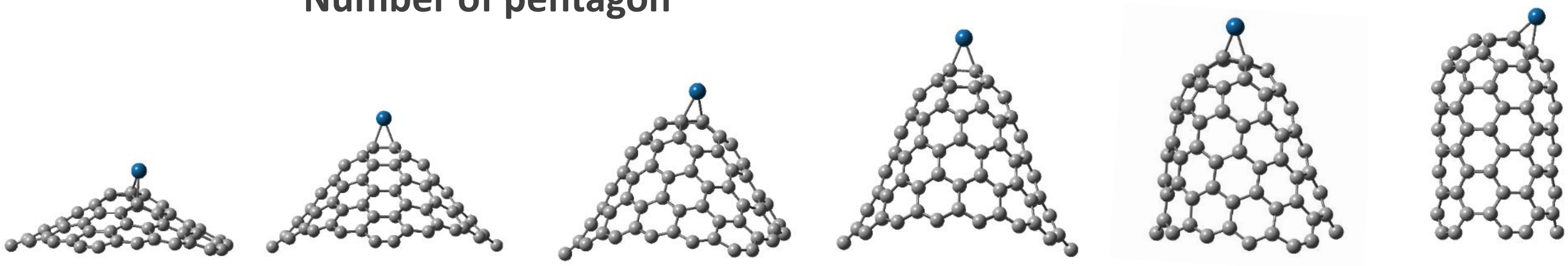



$$E_{bind} = E_{M/CNH} - E_M - E_{CNH}$$

The more negative $E_{bind}$,

the more stability of metal on CNH

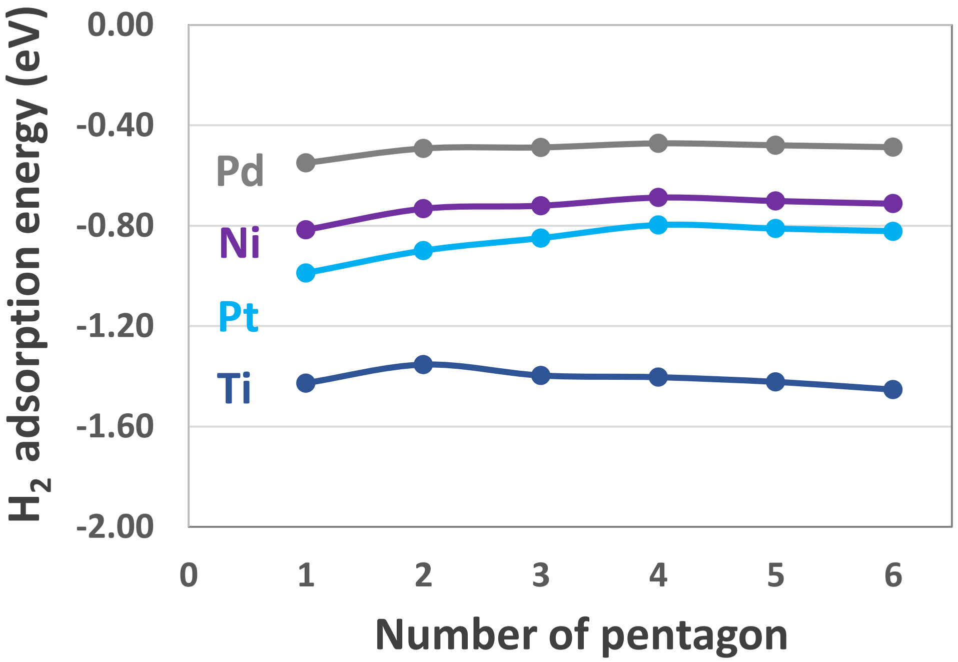
Pt-CNH > Ni-CNH > Ti-CNH > Pd-CNH



Pt/1-CNH Pt/2-CNH Pt/3-CNH Pt/4-CNH Pt/5-CNH Pt/6-CNH

**Metal binding stability depend on the metal type and shape of CNH**

# Hydrogen adsorption on metal-doped CNH




$$E_{H_2} = E_{H_2/M-CNH} - E_{M-CNH} - E_{H_2}$$

The more negative $E_{H2}$,

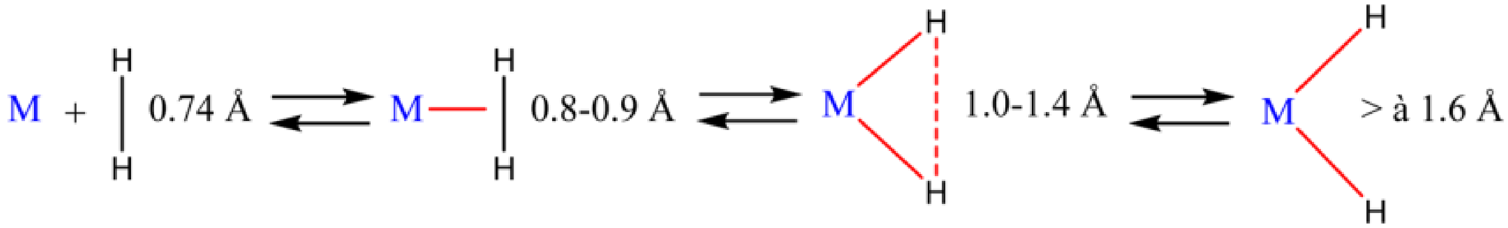
the more stability of $H_2$ adsorption

**$H_2$/Ti-CNH > $H_2$/Pt-CNH > $H_2$/Ni-CNH > $H_2$/Pt-CNH**

**Hydrogen adsorption strongly depend on the metal type rather than CNH shape**

H-H lengthening (stable $H_2$ complex)

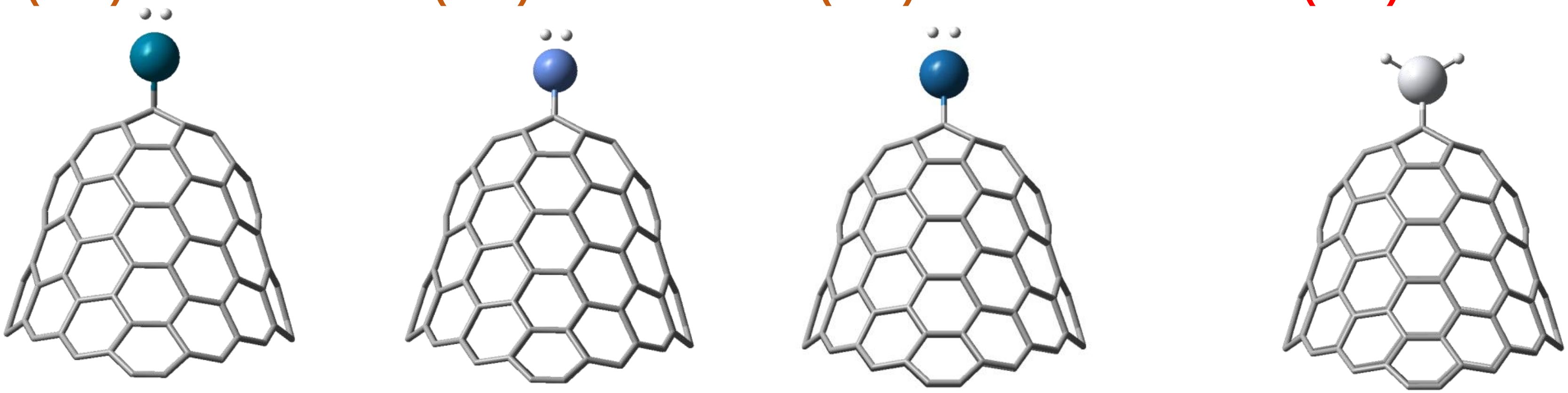
H-H separation (stable dihydride)




**Kubas-mode**

**Dissociation-mode**

d(H-H) = 0.79 Å | d(H-H) = 0.89 Å | d(H-H) = 0.86 Å | d(H-H) = 2.89 Å



**$H_2$/Pd-4CHN** (- 0.47 eV)

**$H_2$/Ni-4CHN** (- 0.69 eV)

**$H_2$/Pt-4CHN** (- 0.80 eV)

**$H_2$/Ti-4CHN** (- 1.40 eV)

**$H_2$ dissociation on Ti-CNH while adsorbed as $H_2$ molecules on Pt-CNH, Ni-CNH and Pt-CNH**

# Summary

- NiCu/CNHs has been successfully synthesized by one-step GI-AIW method.
- Ni/CNHs provide the good conversion and yield for dehydration of D-xylose to furfural.

- Metal binding stability depend on shape of CNH
- $H_2$ adsorption intensely depend on type of metal rather than the shape on CNH as the metal served as active site for hydrogen adsorption
- The adsorption modes of $H_2$ on Pt-CNH, Ni-CNH and Pd-CNH are Kubas-modes while the dissociative adsorption mode is found on Ti-CNH. Ti-CNH shows the highest potential for $H_2$ storage.

# Acknowledgement

Dr. Chompoonut Rungnim

Ms. Chuleeporn Luadthong

Ms. Chompoopitch Termvidchakorn

# Achievements

**Publication**

- T. Suntornlohanakul, N. Sano, H. Tamon, Self-ordered nanotube formation from nickel oxide via submerged arc in water, Applied Physics Express 9, 076001 (2016)
- C. Luadthong, P. Khemthong, W. Nualpaeng, K. Faungnawakij, Copper ferrite spinel oxide catalysts for palm oil methanolysis, Applied Catalysis A, 525 (2016) 68-75.

**Book**

- Vorranutch Itthibenchapong, Atthapon Srifa, Kajornsak Faungnawakij, "Ch.11 Heterogeneous Catalysts for Advanced Biofuel Production" in "Nanotechnology for Bioenergy and Biofuel Production" Editors Mahendra Rai and Silvio Silverio da Silva, Springer 2017.

**Award**

- Presentation Award: C. Termvidchakorn, N. Viriya-empikul, K. Faungnawakij, N. Sano, T. Charinpanitkul. Catalytic activity of sulfonated carbon nanotubes in dehydration of xylose, The 4th Joint Conference on Renewable Energy and Nanotechnology (JCREN2015）

-Kajornsak Faungnawakij, TRF-OHEC-SCOPUS Researcher Award 2017

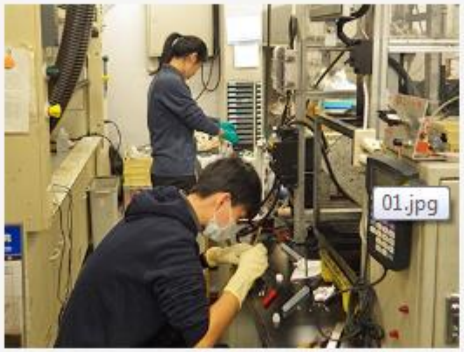
**Student exchange**

-Three students from chulalongkorn university visited Kyoto Univ. for research exchange program under JASTIP.

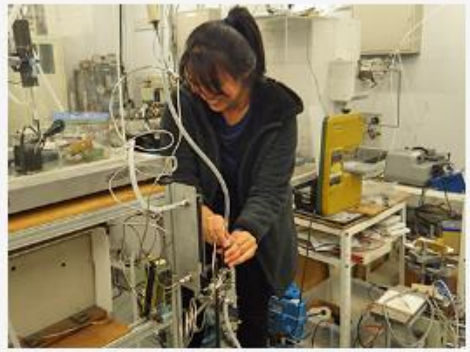
- Two JASTIP seminars were held in 2016 at Kyoto univ. (1$^{st}$) and NANOTEC (2$^{nd}$).

# JASTIP student exchange program

The program helped deepen the friendship between the Thai students and their Kyoto counterparts, while at the same time marking a new milestone in the research partnership among the participating institutions, including Chulalongkorn University as well as the National Nanotechnology Center (NANOTEC) of the Thailand National Science and Technology Development Agency (NSTDA).




Chulalongkorn University students conducting experiments in the separation engineering laboratory



Another intern at work

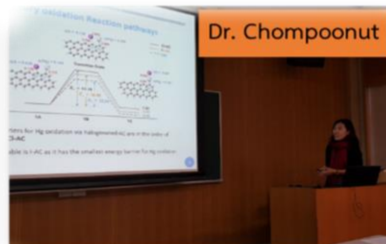
Enjoying fall foliage at Ohharano Shrine

The students from Sano's team joined the JASTIP seminar in NANOTEC and visited Chulalongkorn Univ. for lab tour and research discussion

# JASTIP seminars






at Kyoto Univ.
feb2016


at NANOTEC
sep2016

THANK YOU