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.

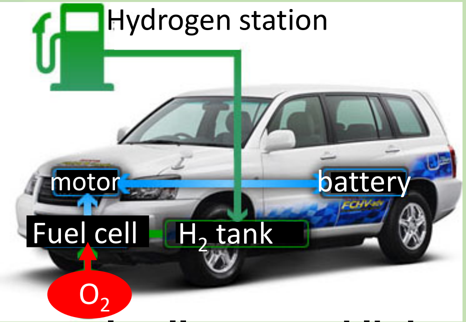
2. Research on application of algae for electric energy generation, catalyst nanoparticle formation, and water purification.

Demand for advanced hydrogen storage media

Current H_2 storage method

Compressed gas storage

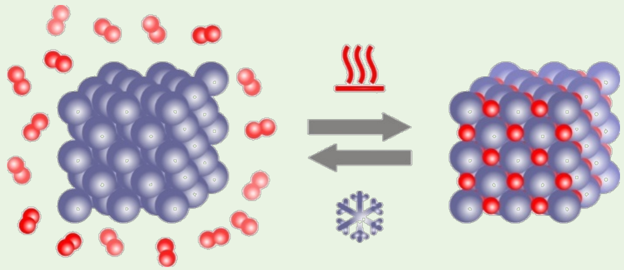
Liquid hydrogen storage(heavy)



Fuel cell car need light H_2 storage media

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

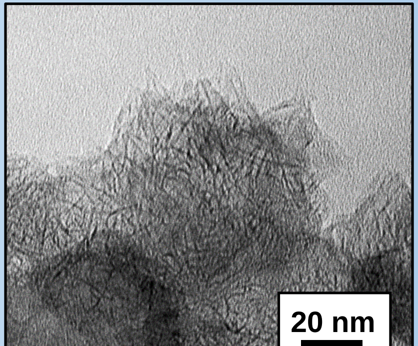
Material-based H_2 storage

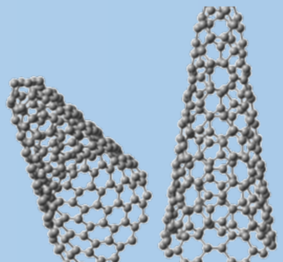


✓ lower volume requirement
✓ greater energy efficiency
✓ safety and ease of use

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:

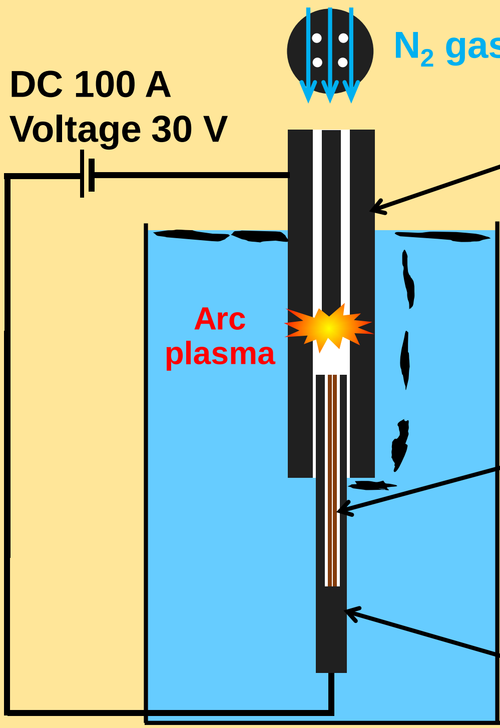
H_2 storage property is measured using Fe/CNHs produced by gas-injected arc-in-water method.

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



Cathode (ϕ 20 mm, length 50 mm)
top holes: ϕ 2 mm, length 25 mm
bottom hole: ϕ 12 mm, length 25 mm

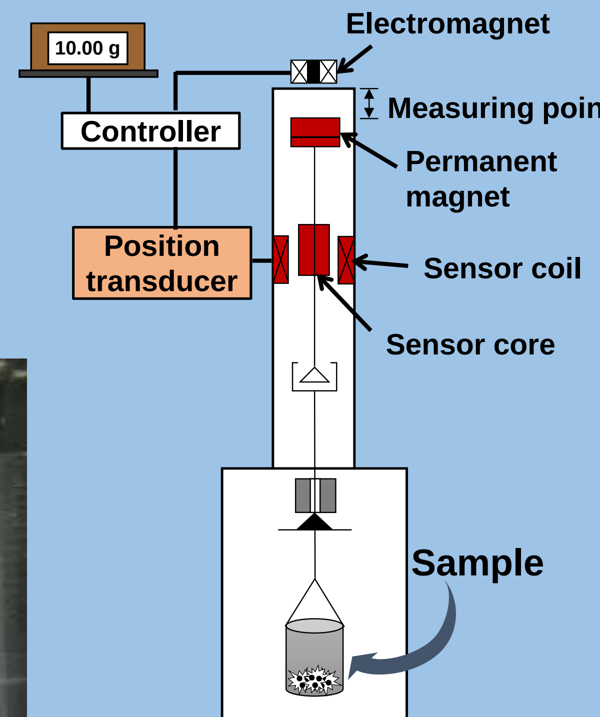
Fe wires/no wire for p-SWCNHs
(ϕ 0.3 mm x 5 wires, length 60 mm)

Anode (ϕ 6 mm, length 75 mm)
middle hole: ϕ 1.5 mm, length 60 mm

Schematic diagram of Arc discharge machine

H_2 storage measurement

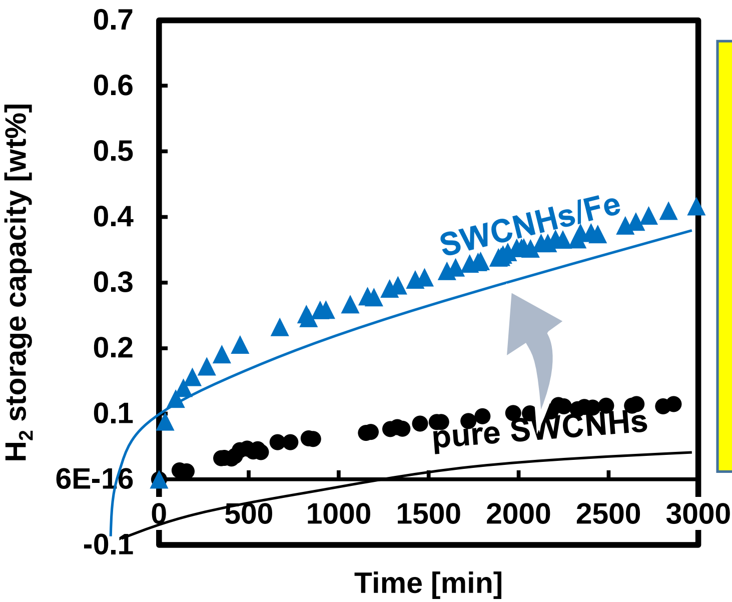
- High pressure H_2 gas
- vacuum condition



Magnetic suspension balance

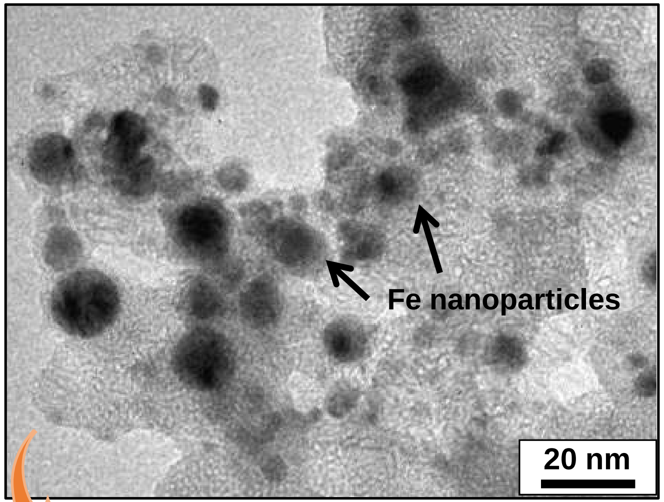
Result (Storage of hydrogen)

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.



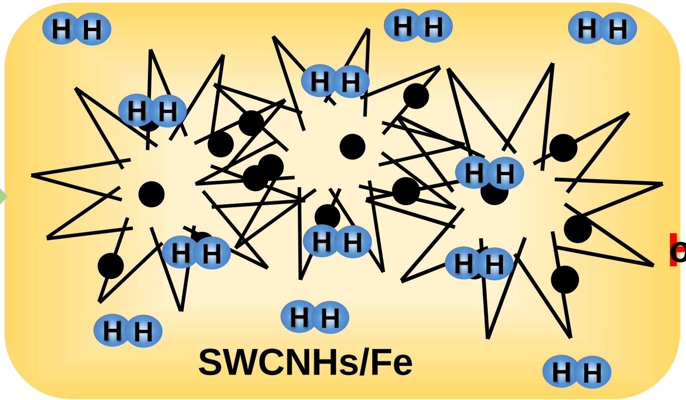
EDX analysis

▶ Percent inclusion of Fe ~ 10 wt%

Fe is not H_2-absorbing metal.

+

pure SWCNHs



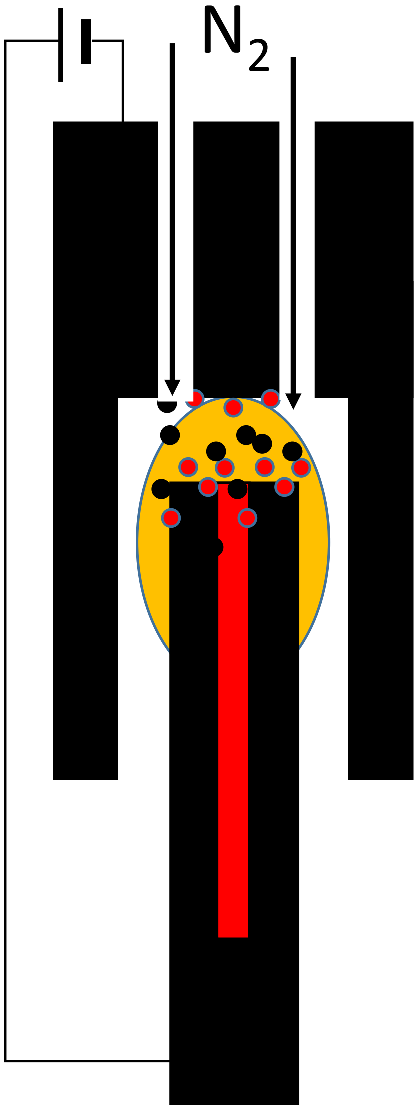
H_2 storage capacity improve by

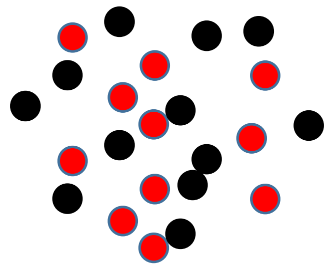
H_2 spillover[2]

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

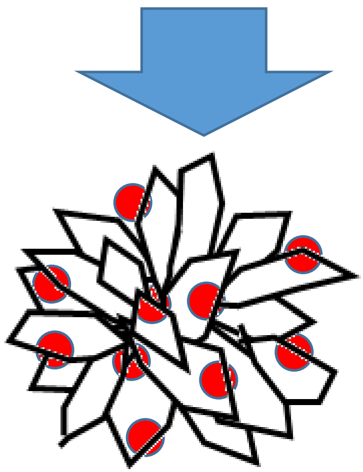
[2] Gardes *et al.*, *J. Catal.*, **35**, 145-148 (1974)

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

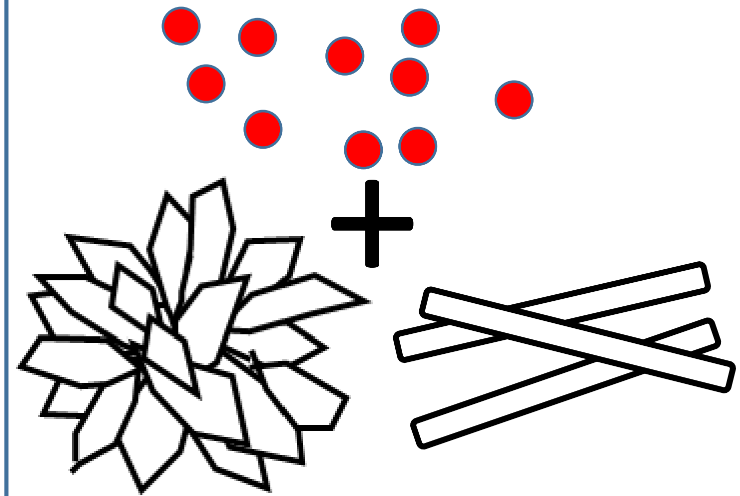




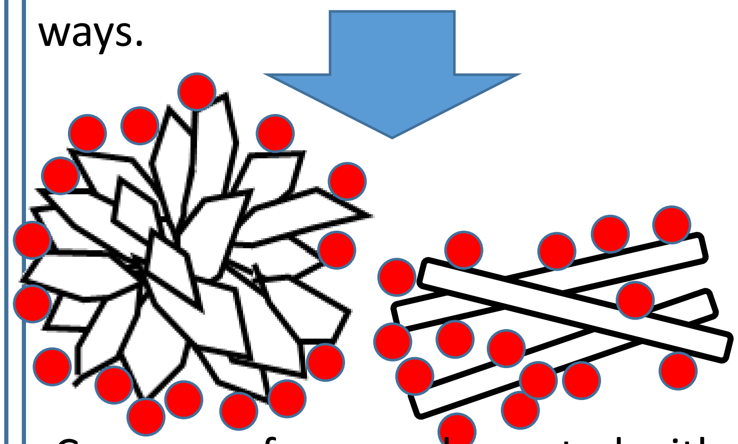
C and Fe evaporate and are solidified simultaneously.



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



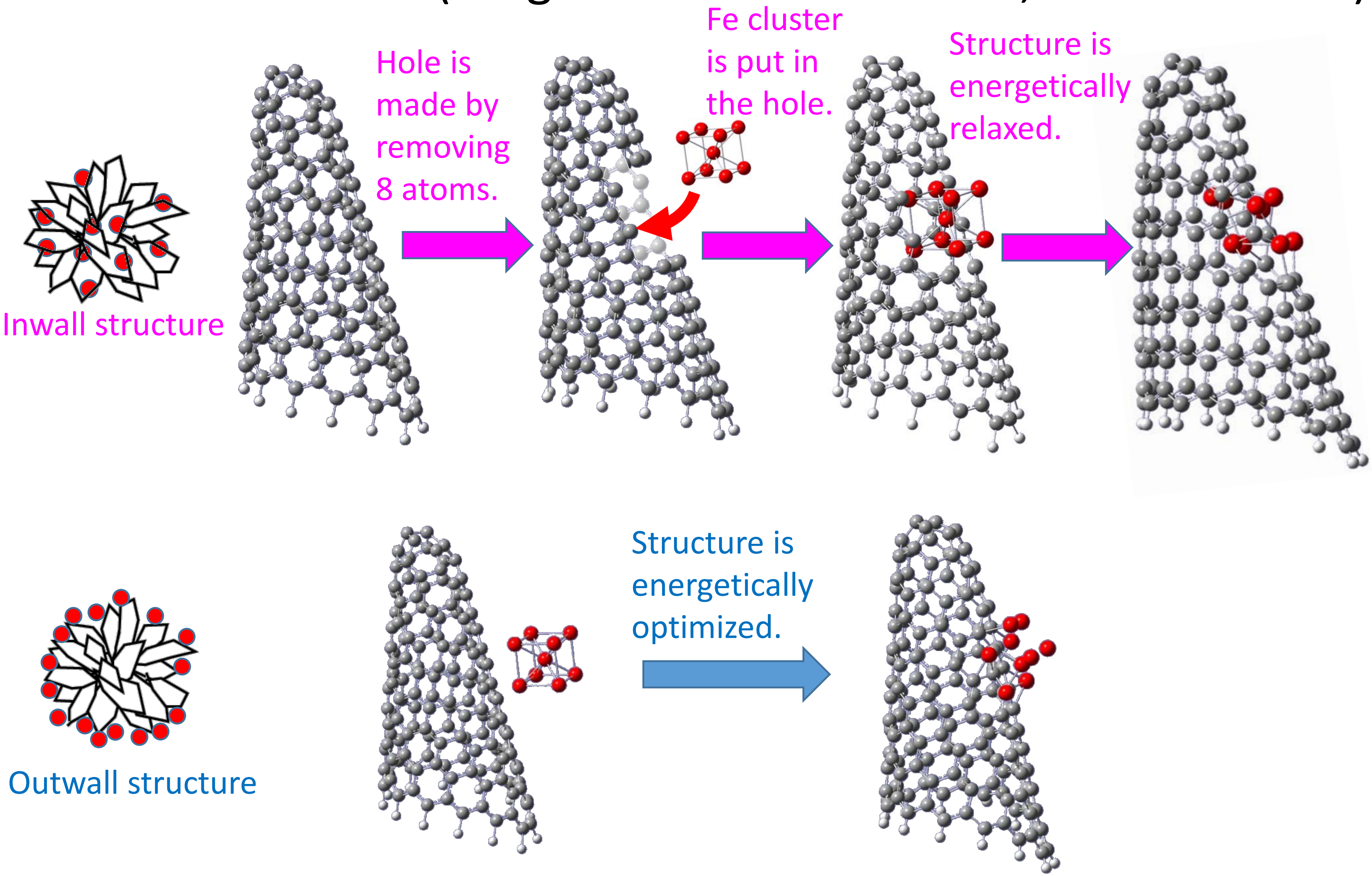
Fe are added on C surface by many ways.



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

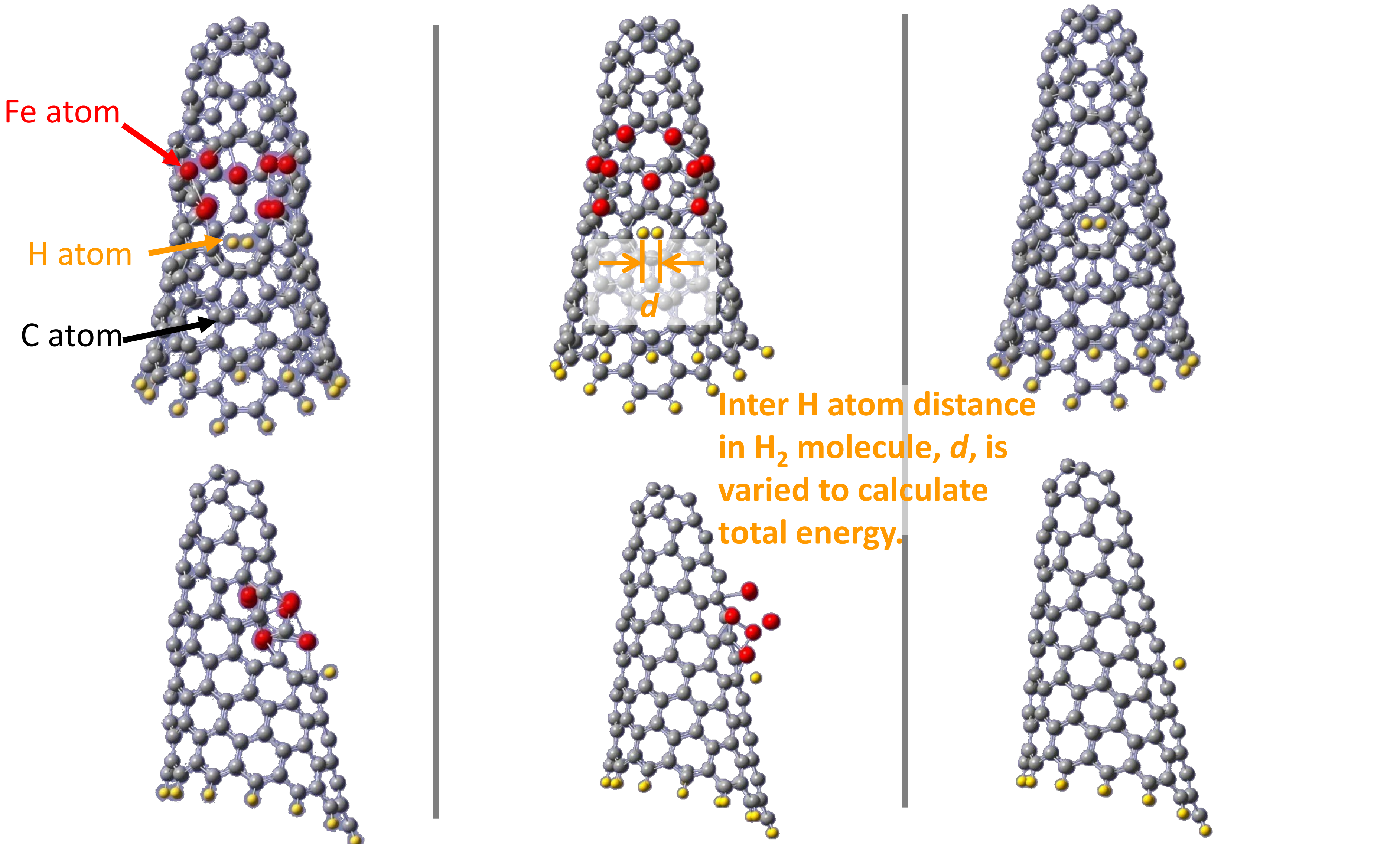
Theoretical study on 'spill-over effect' on Fe-CNHs

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

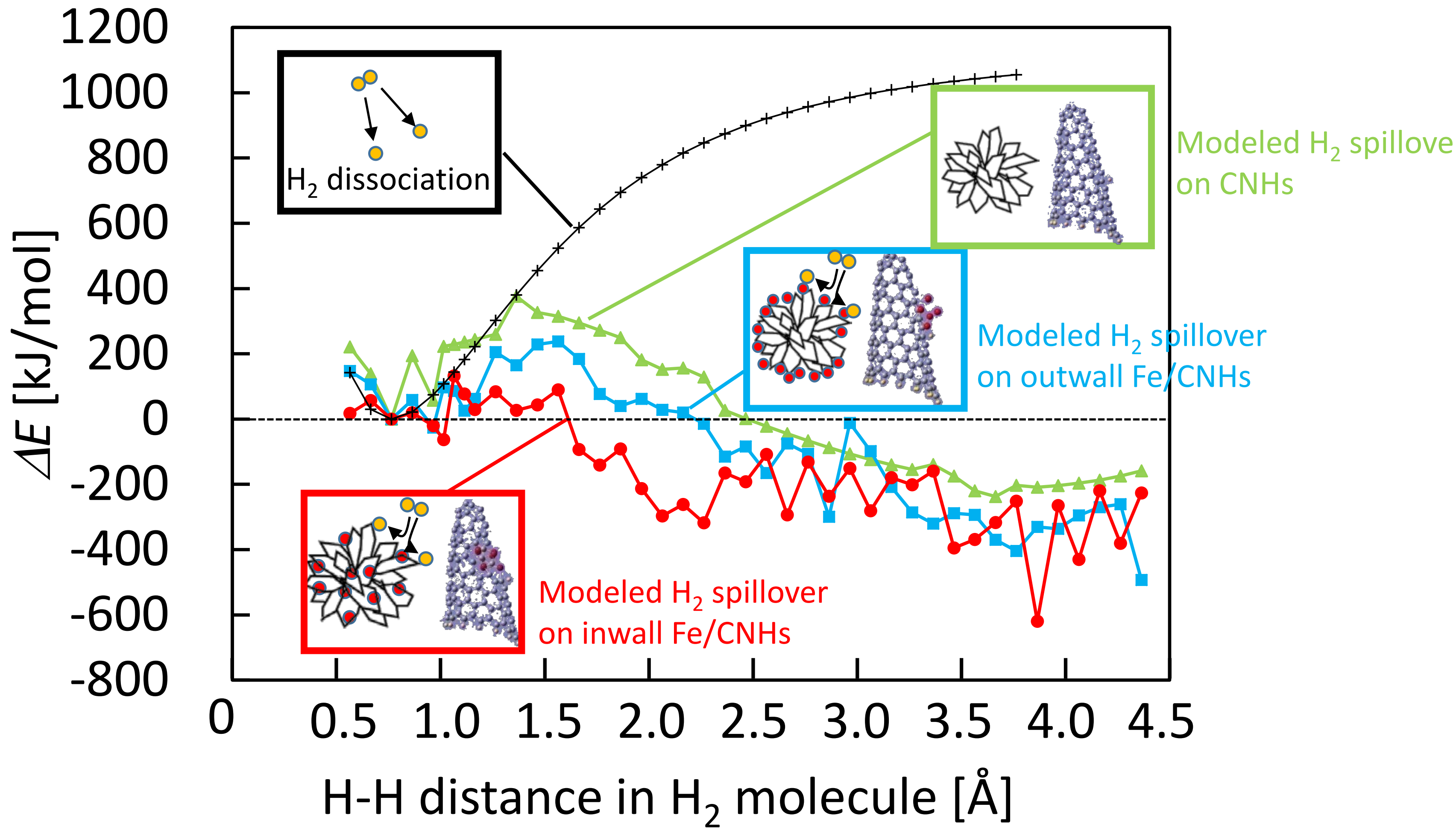
Molecular models to calculate energy for dissociation of H_2 molecule



Inwall structure　　outwall structure　　CNH without Fe cluster

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

ΔE = (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.

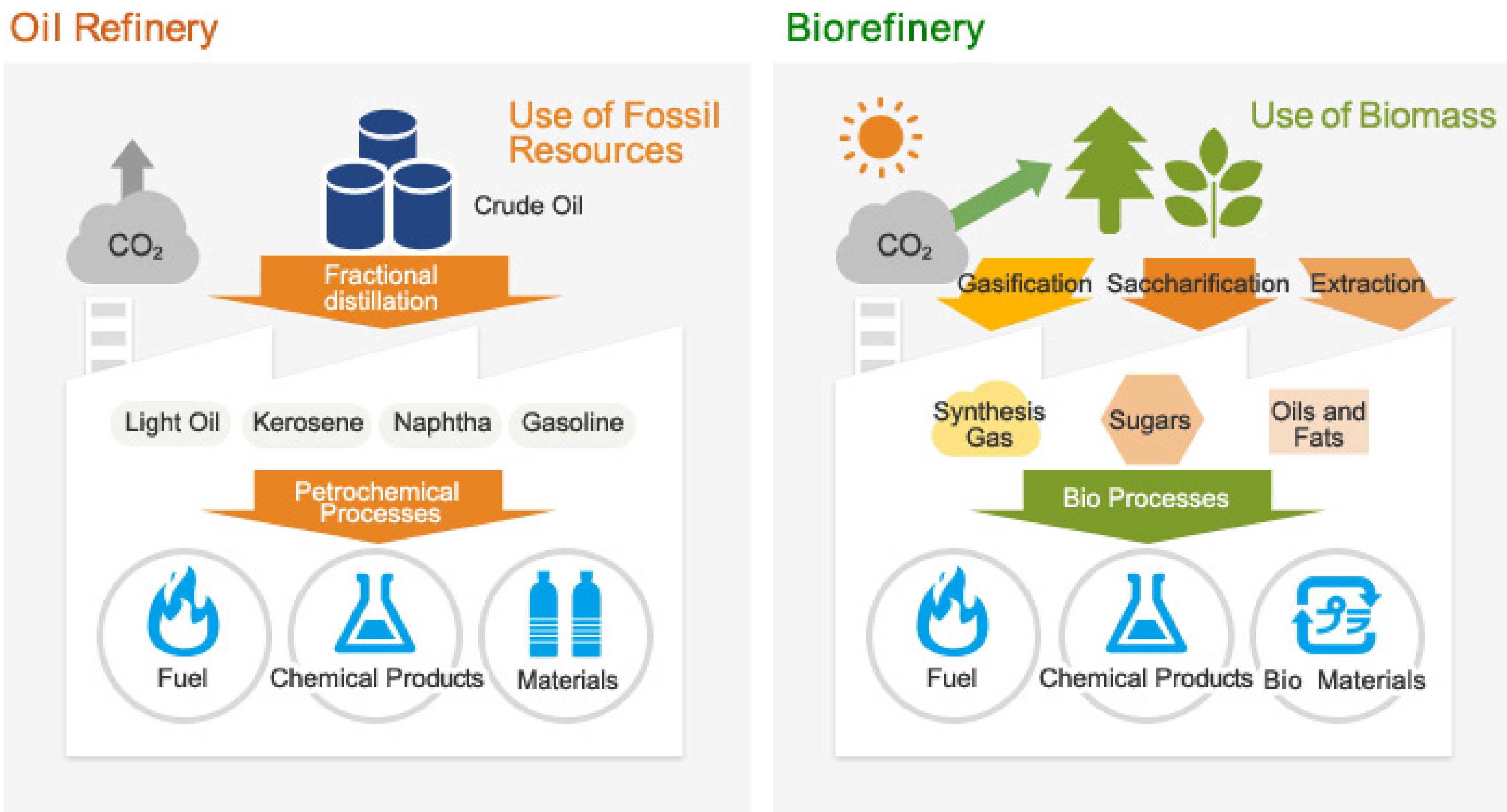
NANOTEC/NSTDA and Thai team

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.

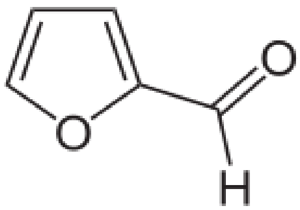
These 2 topics are focused to explain today.

Catalysts for biorefinery applications



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

Development of carbon-based catalysts for biomass conversion



$C_5H_4O_2$

Furfural

Beneficial usage

- Petroleum industrial solvent
- Chemical feedstock for bioenergy production

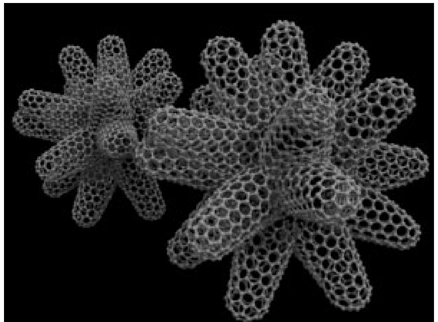
Commercial catalyst

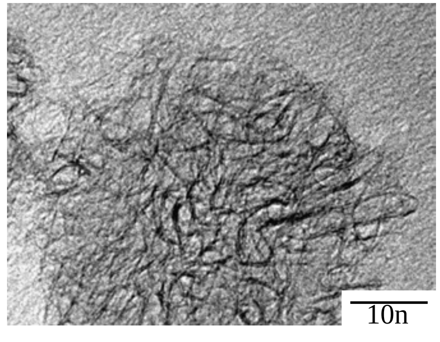
- Mineral acid (H_2SO_4 and HCl)

Solid acid catalyst

Problem : Severe corrosion
Excessive waste disposal
High investment in catalyst recovery process

Experimental



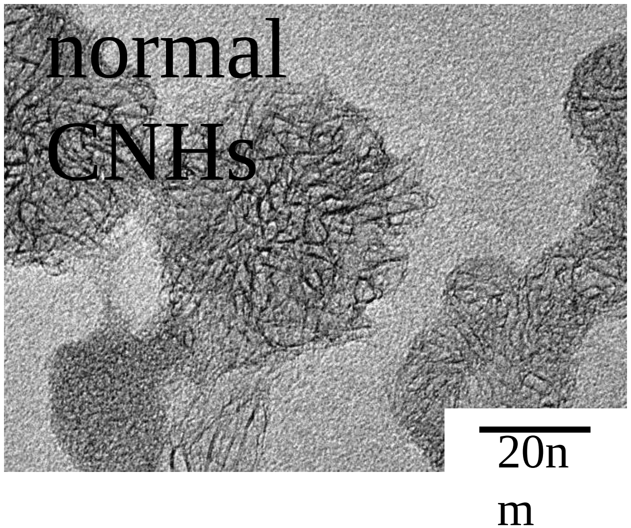


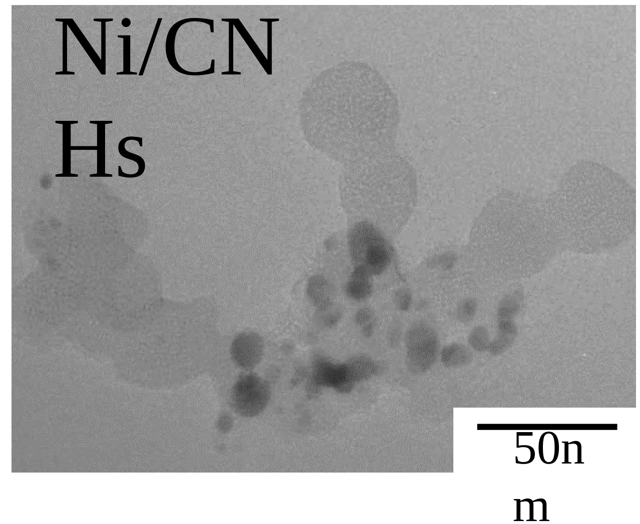
Gas-inject arc-in-water (GI-AW)

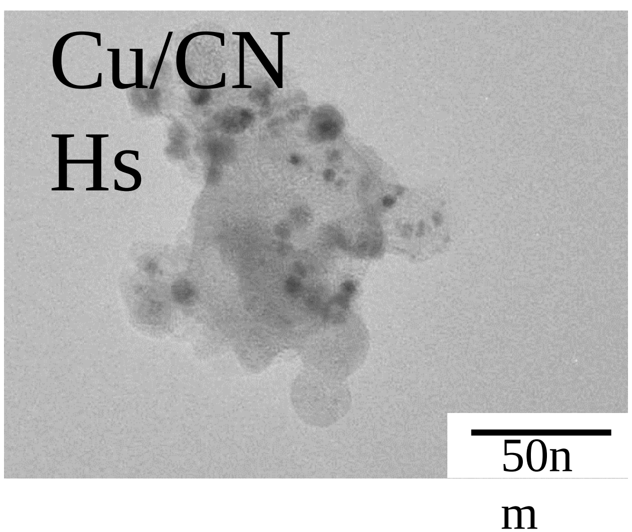
GI-AW method has some benefits, i.e., simplicity and capability for synthesizing various nanomaterials

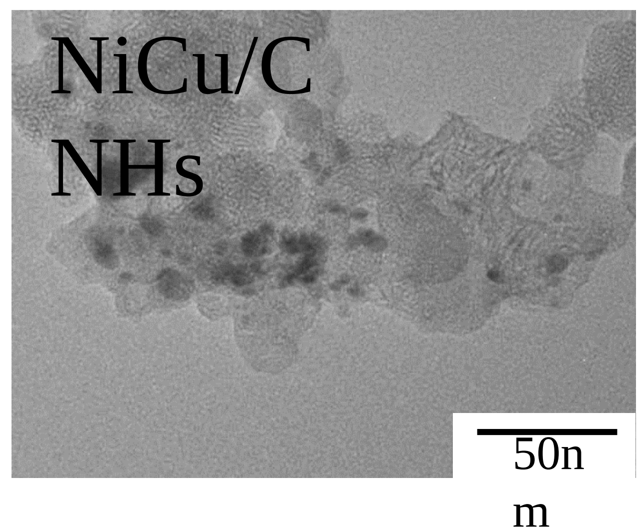
- Anode and metal wire preparation
- Arc discharge process
- Product collection
- Analysis
- Reaction testing

Results&Discussion
TEM analyses

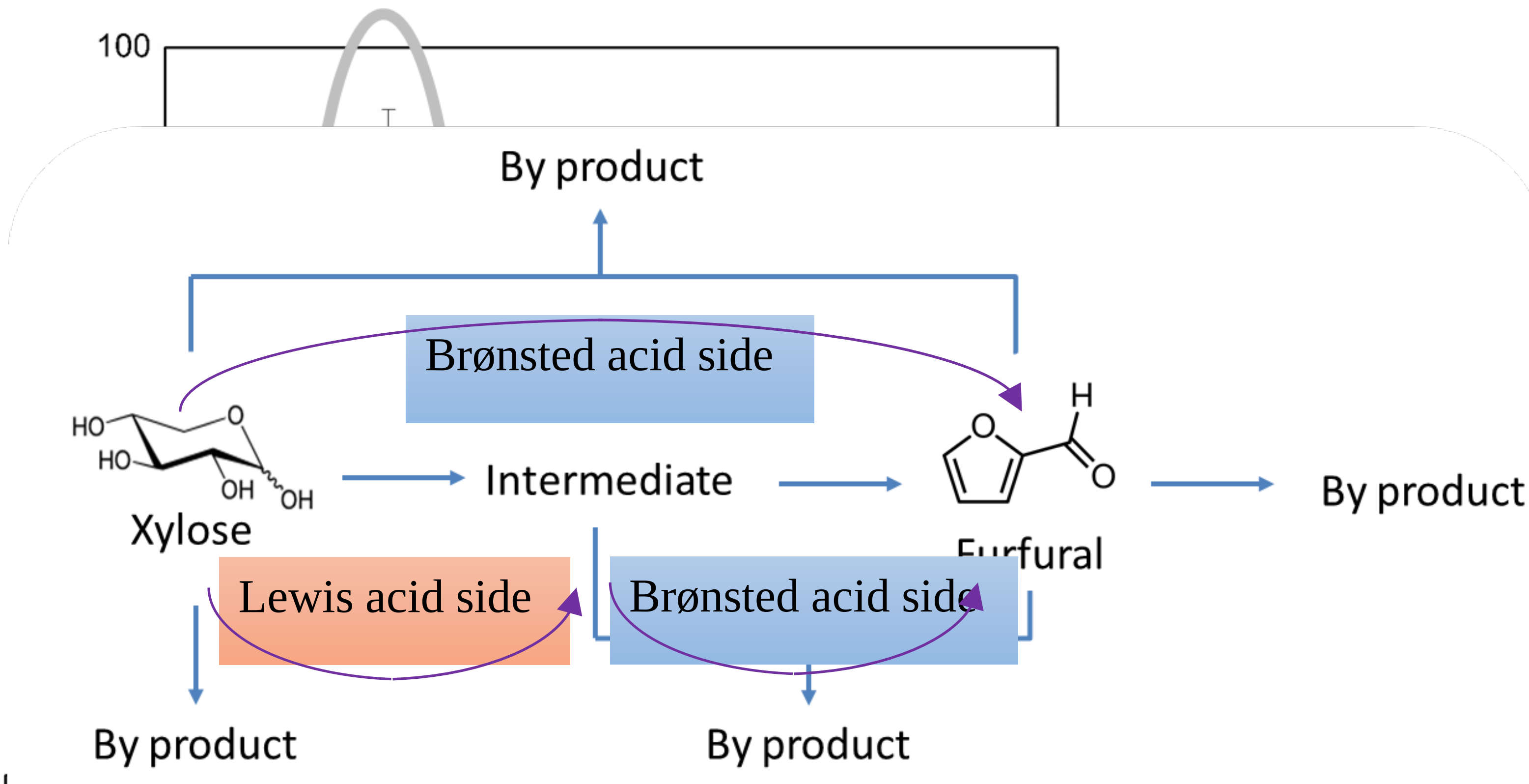






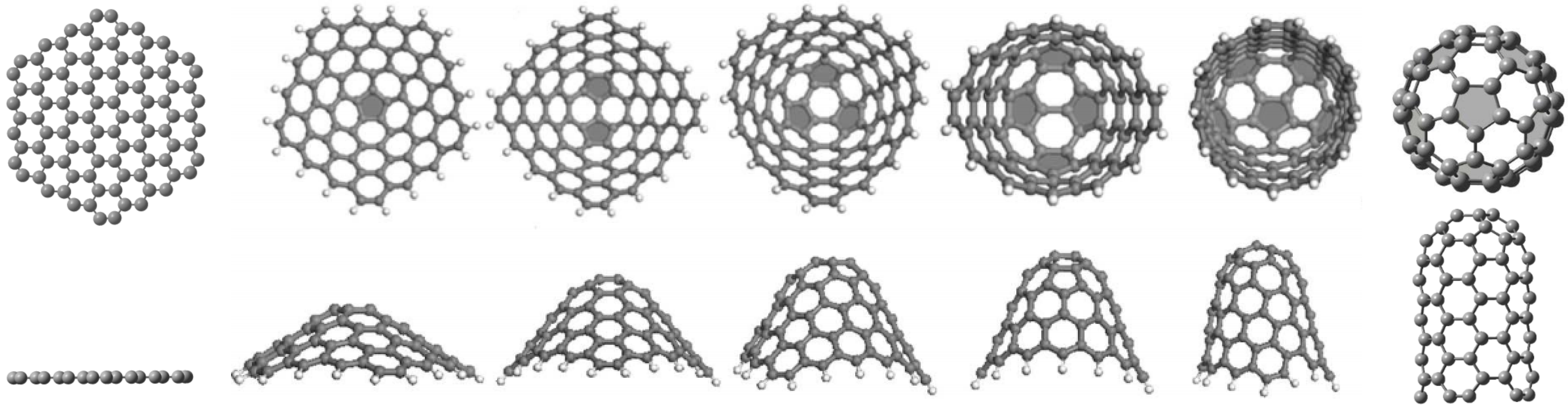


Results&Discussion
Furfural production



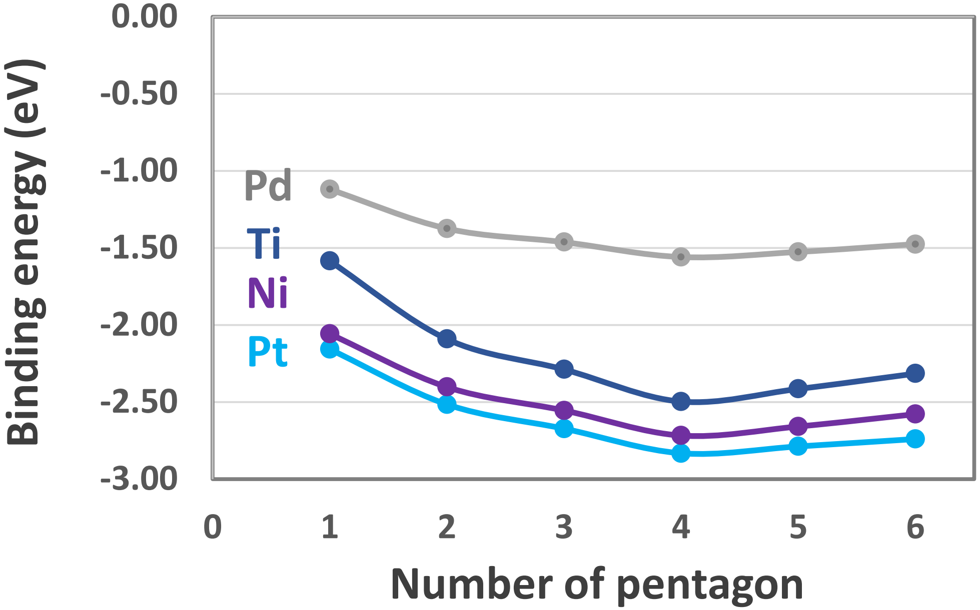
*By product: small organic acid, alcohol, humin etc.

Representation of single CNH



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

Stability of metal-doped CNH

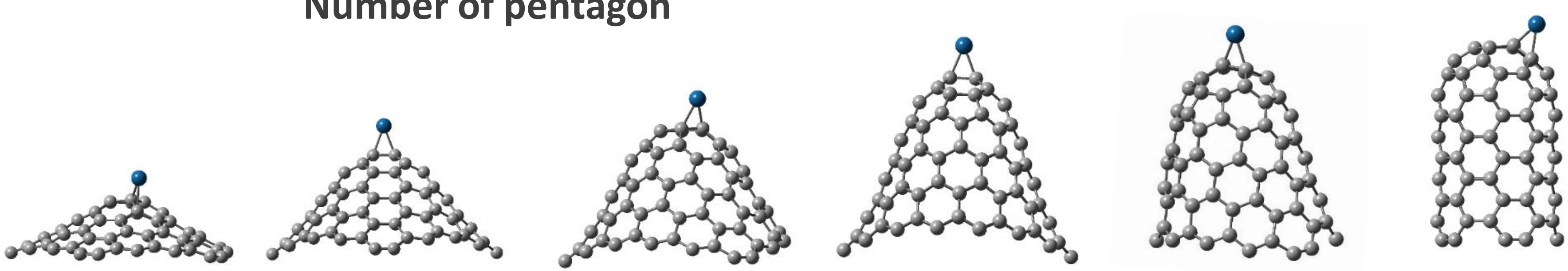


$$E_{bind} = E_{M/CNH} - E_{M} - E_{CNH}$$

The more negative E_{bind},

the more stability of metal on CNH

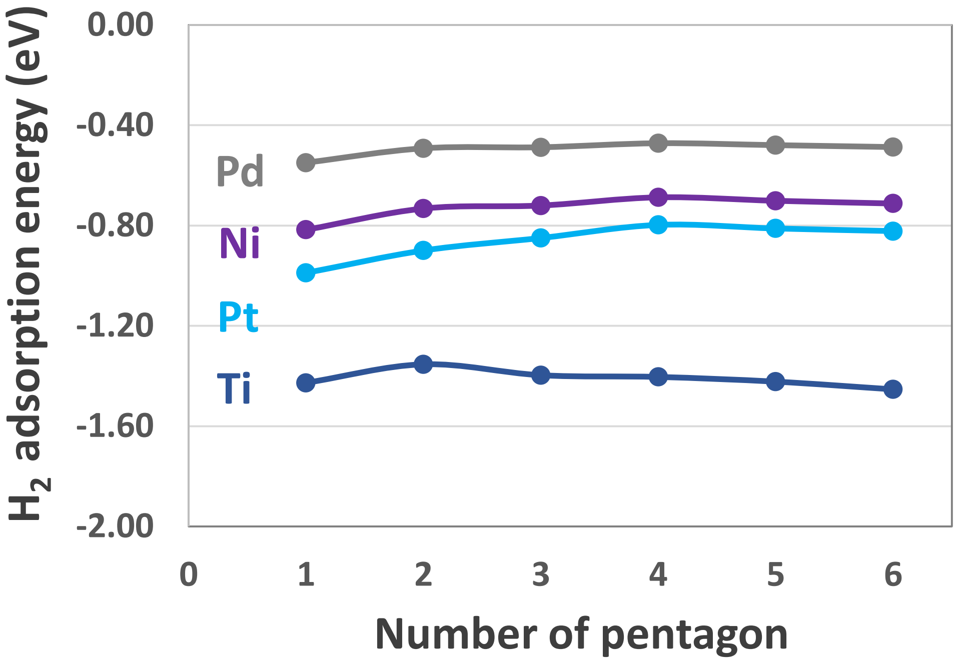
Pt-CNH > Ni-CNH > Ti-CNH > Pd-CNH



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},

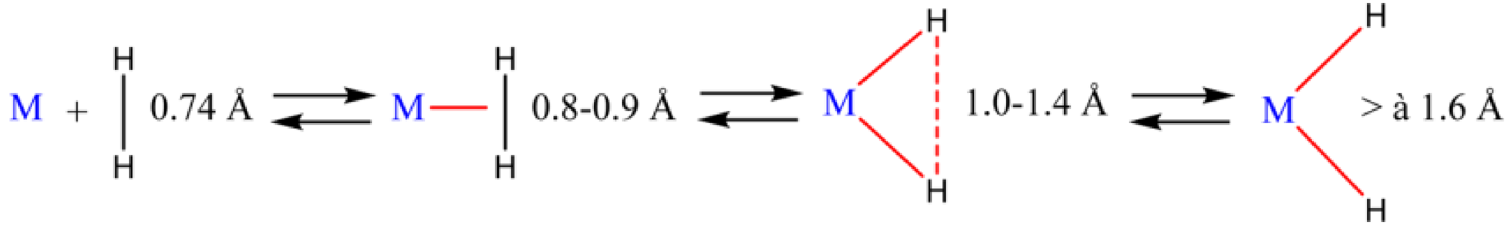
the more stability of H_2 adsorption

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)

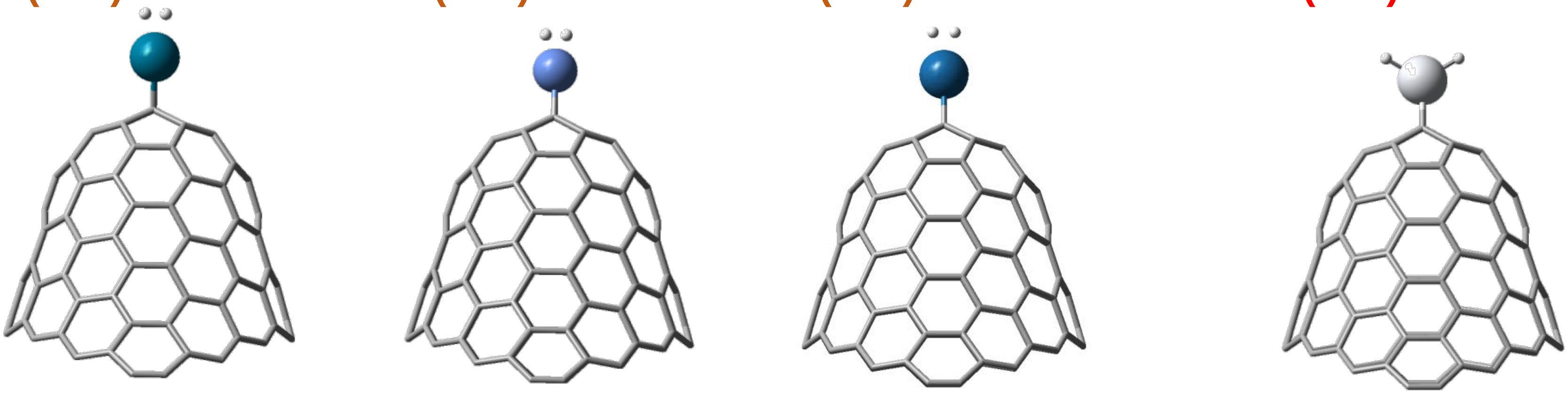
H-H separation
(stable dihydride)



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

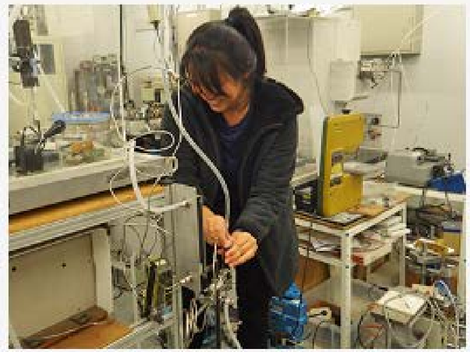
Student exchange

-Three students from chulalongkorn university visited Kyoto Univ. for research exchange program under JASTIP.
- Two JASTIP seminars were held in 2016 at Kyoto univ. (1st) and NANOTEC (2nd).

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

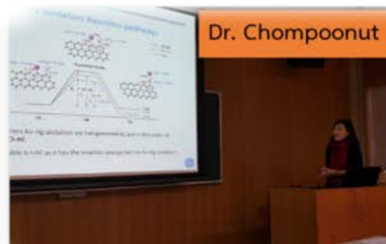


Another intern at work

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