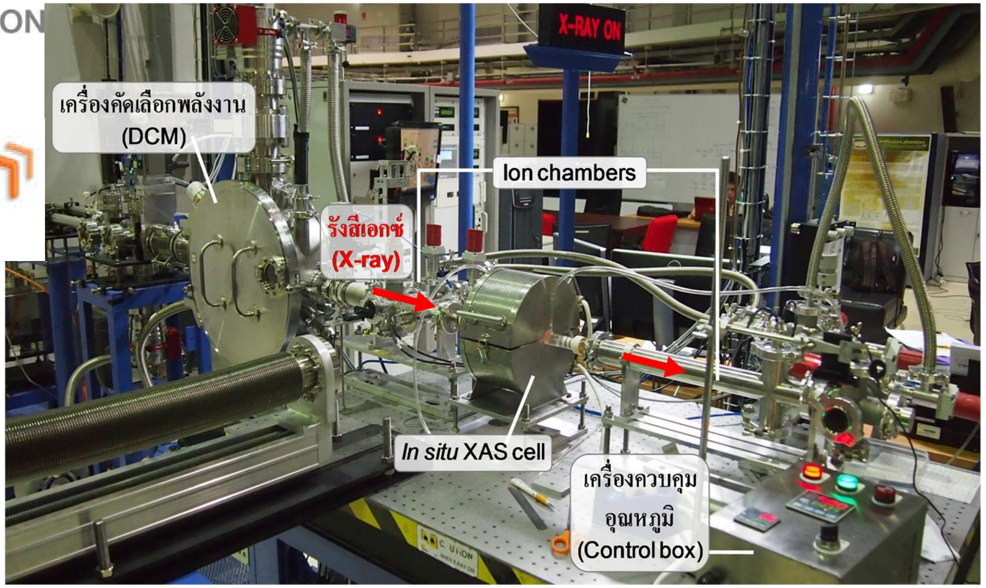
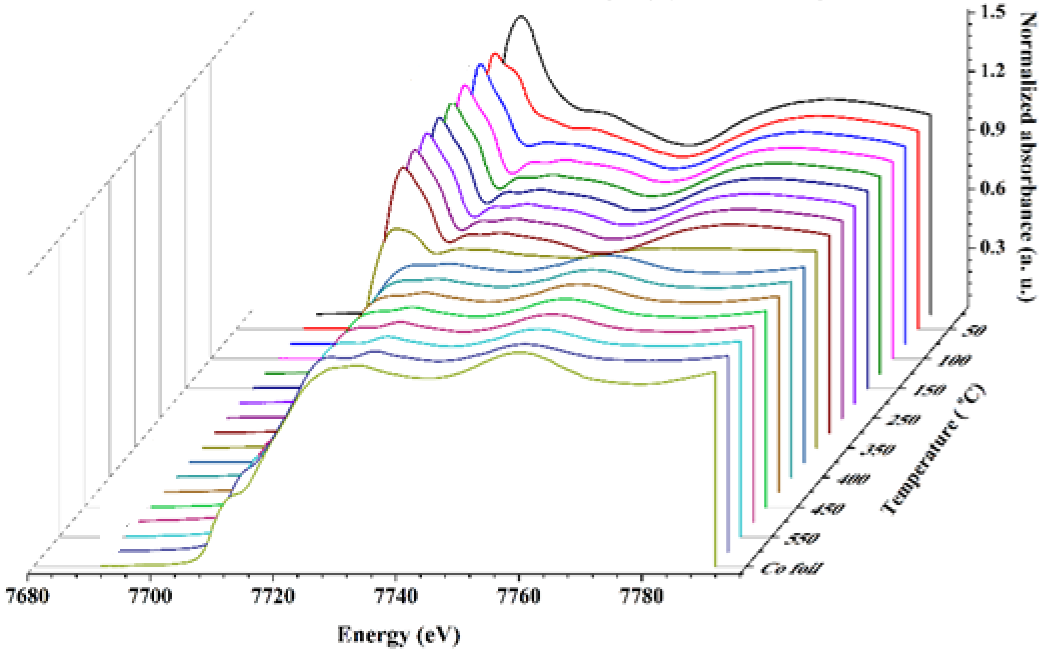
In situ X-ray absorption spectroscopy (XAS) for investigation and characterization of nanomaterials



Beamline 5.2

In situ XAS

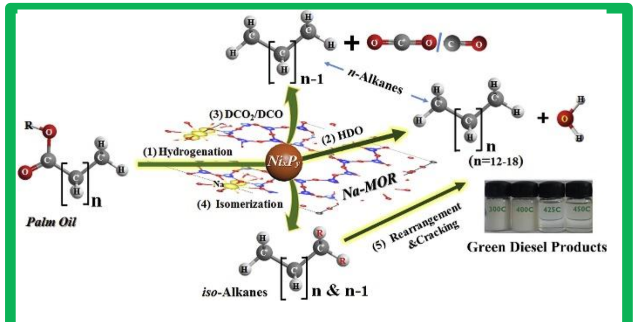


Dr. Nattawut Osakoo

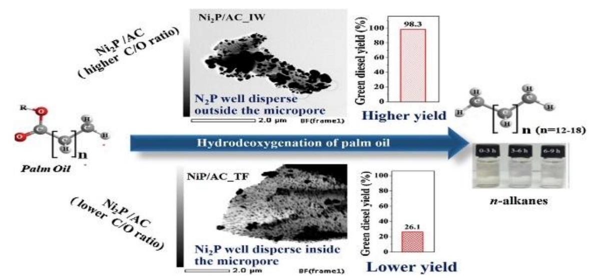
Full-time Researcher at Materials Research Center for Sustainability in Energy and Environment, School of Chemistry, Institute of Science & Institute of Research and Development, Suranaree University of Technology.

Selected publication

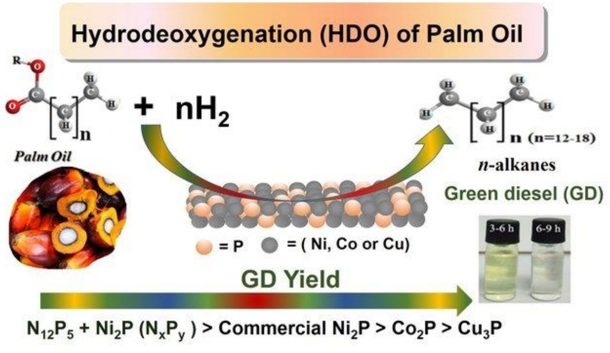
❖ Biodiesel and Bio-hydrogenated diesel production



Fuel Processing Technology, **2020**, *198*, *106236*

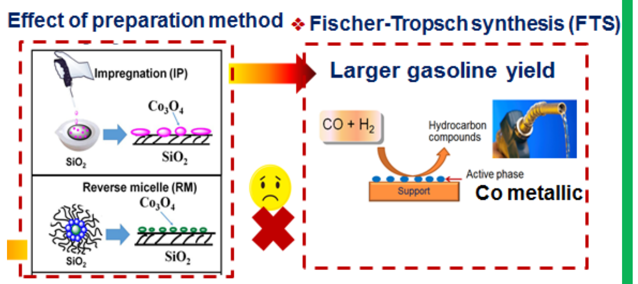


Catalysis Today, **2020,** In Press, Corrected Proof



Molecular Catalysis 2021, 111422
In Press, Corrected Proof

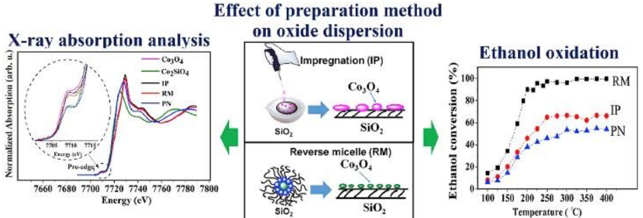
❖ Fischer-Tropsch synthesis



Applied Catalysis A: General, **2013,** 464– 465, 269– 280

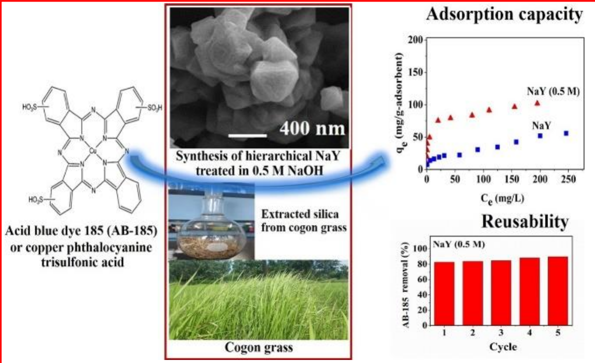
Dr. Nattawut Osakoo

❖ Remove of air pollutant by catalytic oxidation and aquatic system by adsorption process



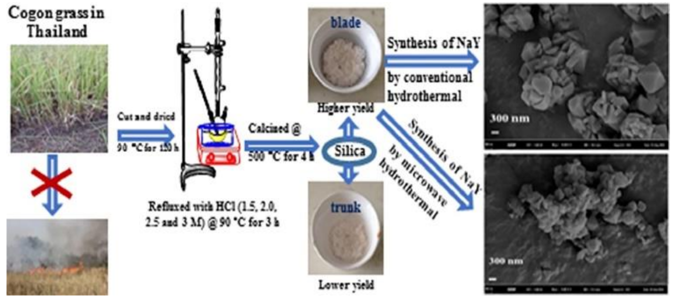
Sample	Linear Combination Analysis (%)		
	Co_3O_4	CoO	Co_2SiO_4
IP	100	0	0
RM	92	0	8
PN	43	15	42

Radiation Physics and Chemistry, **2020**, 171, 108718



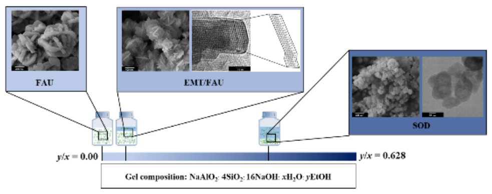
Journal of Environmental Chemical Engineering, **2020**, 8, 104114

❖ Zeolite synthesis and mesoporous modification from renewable silica sources

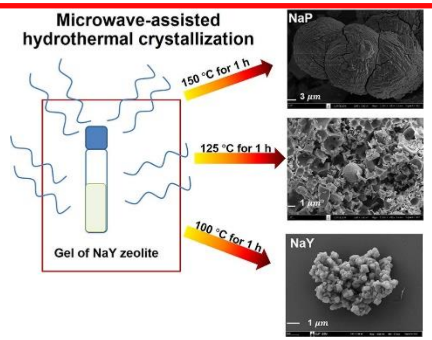


Journal of the Taiwan Institute of Chemical Engineers, **2018**, *83*, *152-158*

EMT/FAU intergrowth



Materials Research Express, **2020**, 7, 075011

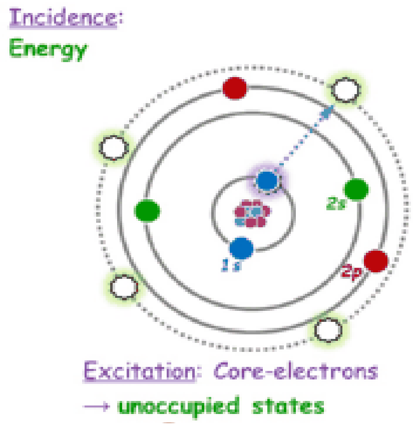


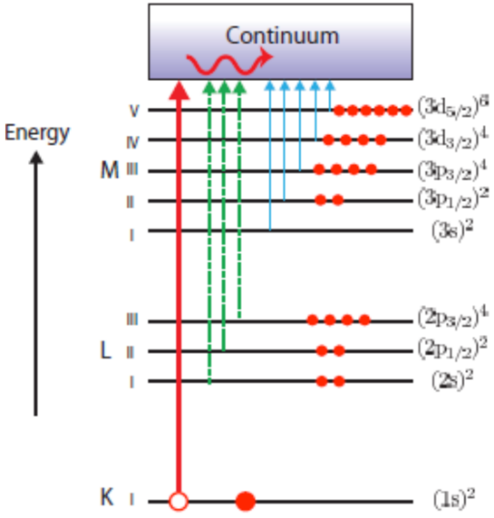
Materials Letters, **2020**, *272*, *127845*

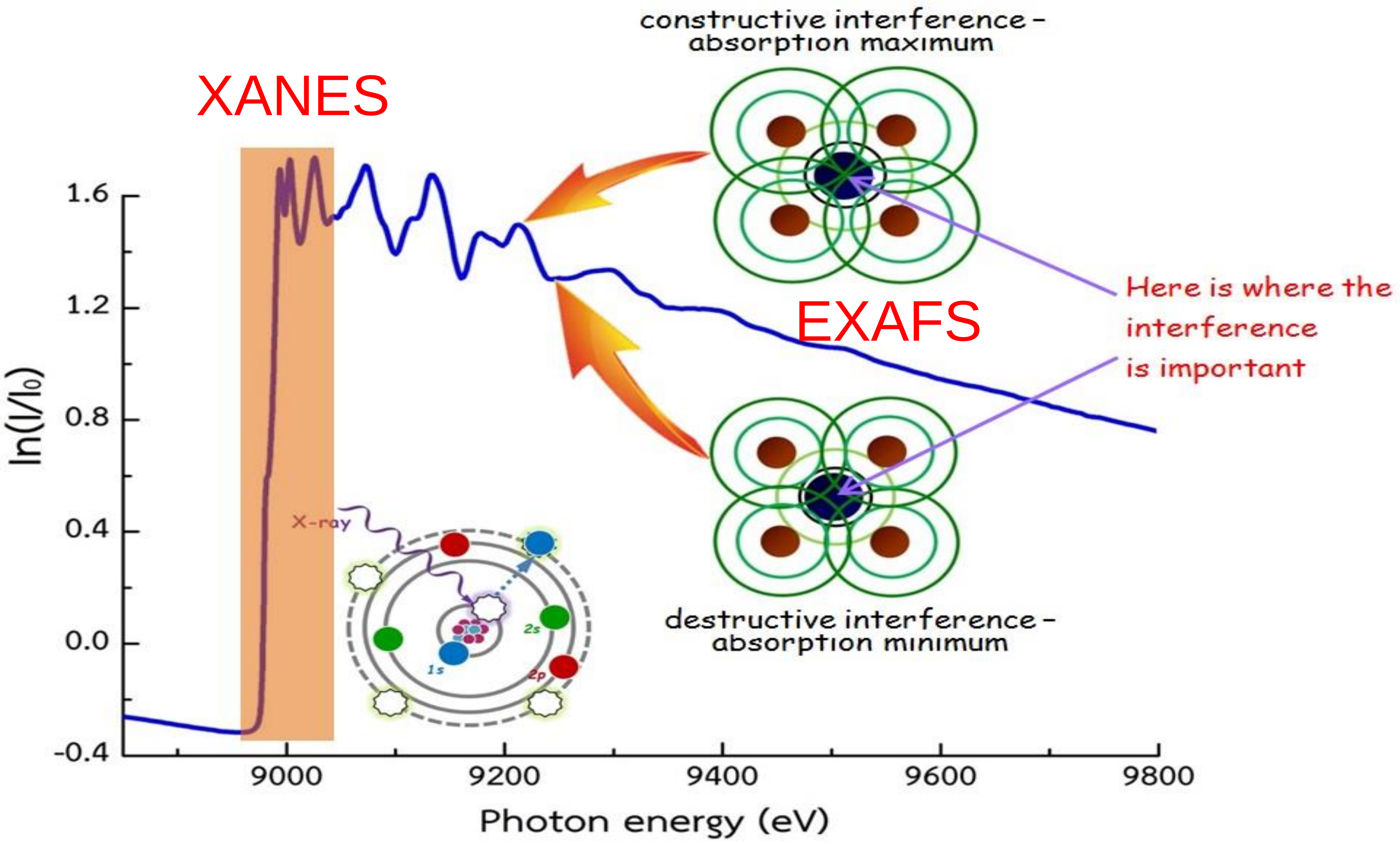
Outline

- Principle of XAS
- Advantages of XAS for nanomaterials
- Case study of XAS as an outstanding tool for nanomaterials
- Why *in situ* XAS is a crucial tool
- Case study of *in situ* XAS as an outstanding tool for nanomaterials

Principle of XAS

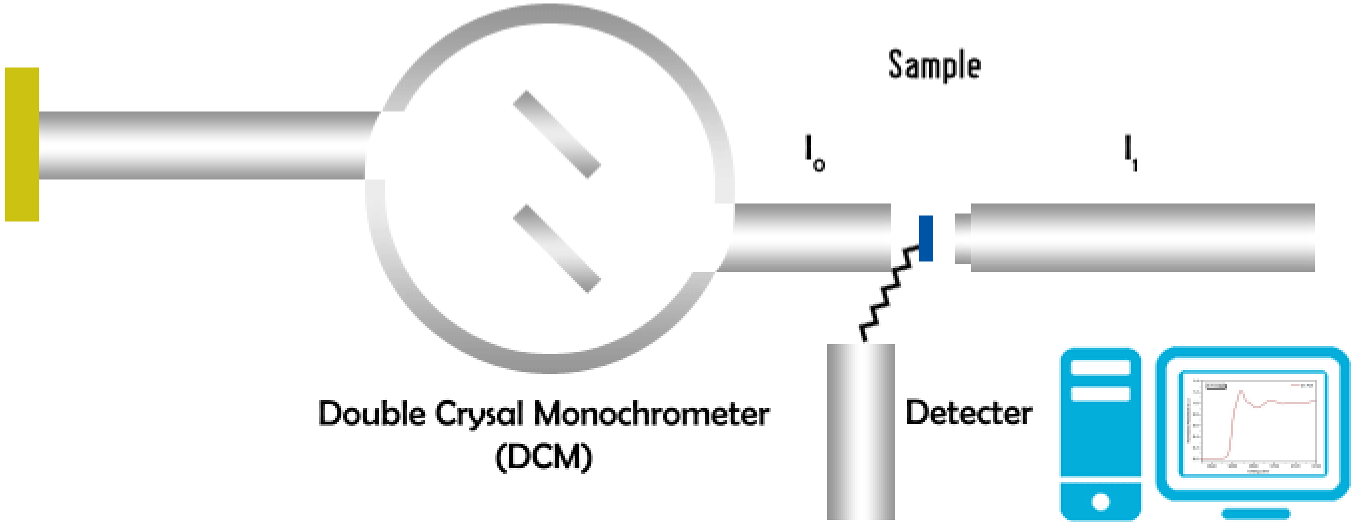


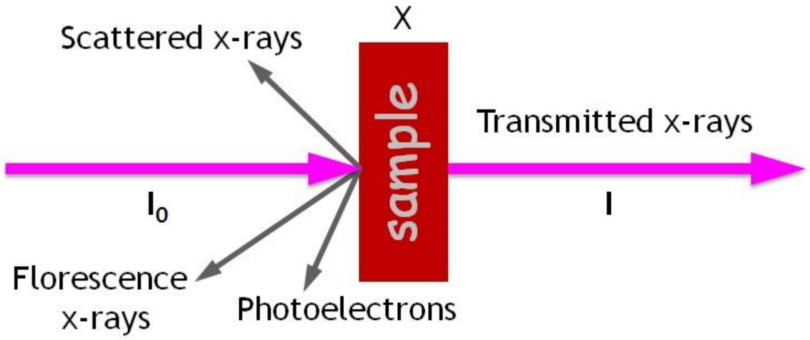




https://www.slri.or.th/th/beamline/sut-nanotec-slri.html?view=article&id=4590:data-and-spectrum-xas&catid=282:sut-nanotec-slri

Beamline 5.2: XAS station (beam size 13 mm)



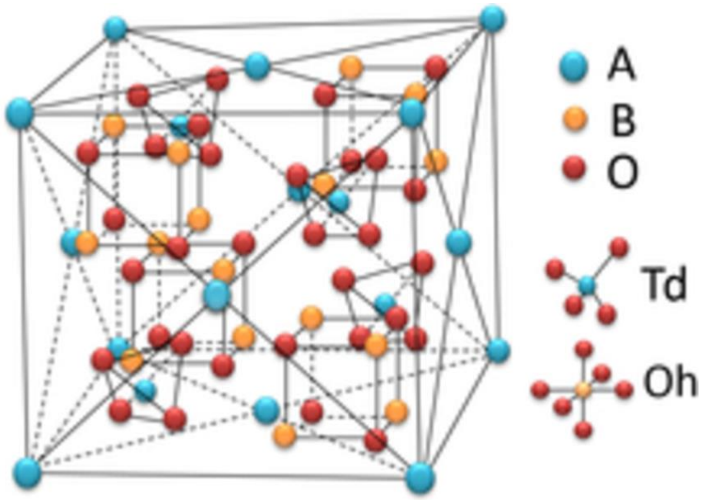


https://www.slri.or.th/th/beamline/sut-nanotec-slri.html?view=article&id=4590:data-and-spectrum-xas&catid=282:sut-nanotec-slri

XAS data

X-ray Absorption Spectroscopy (XAS)

1. X-ray Absorption Near Edge Spectroscopy (XANES)
   - ❖ Provides information on chemical states
     - ➢ Oxidation state
     - ➢ Local coordination environment
     - ➢ Electronic structure
2. Extended X-ray Absorption Fine Structure (EXAFS)
   - ❖ Provides local (~10 Å) structural parameters
     - ➢ Nearest Neighbors (coordination numbers)
     - ➢ Bond distances
     - ➢ Disorder



Advantages

-XAS is a direct measure of valence state. Since each element has its own edge energy, an element’s valence can be measured even in a heterogeneous sample.

-Since x-rays are deeply penetrating into matter, samples often require only preparation.

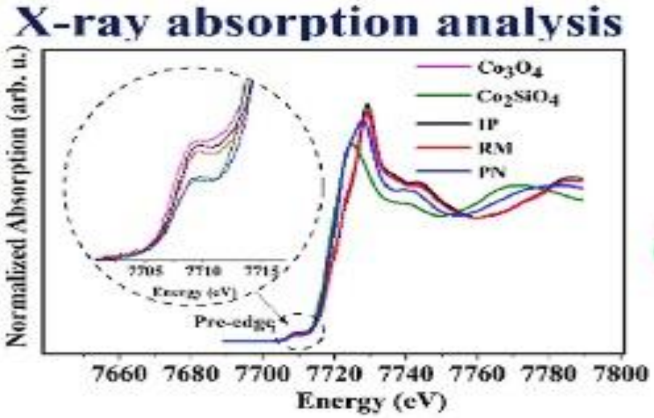
-The samples crystalline, amorphous, thin film, in solution, surface adsorbed are detected by XAS.

*** X-ray diffraction (XRD) is suitable for crystalline sample with the crystalline size larger than 5 nm.***

Osakoo et al., *Radiation Physics and Chemistry*, **2020**, 171, 108718

Case study of XAS as an outstanding tool

Development and characterization of silica supported cobalt oxides for ethanol oxidation using different preparation methods



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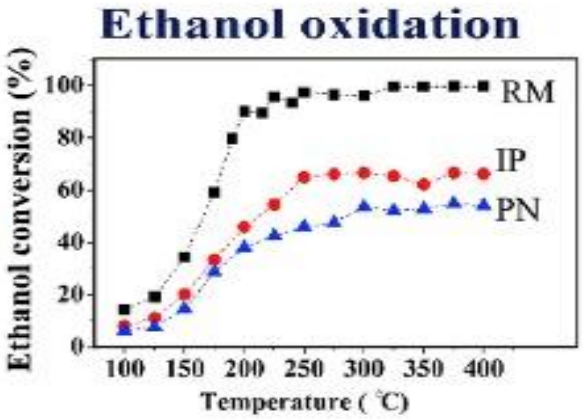


Ethanol oxidation activity:
RM > IP> PN

Osakoo et al., *Radiation Physics and Chemistry*, **2020**, 171, 108718

Why ethanol oxidation is necessary to study ?

Gasohol

Gasoline + ethanol
(95, 91, E10, E20)

Incomplete combustion →

CO, VOCs
acetaldehyde

Vehicle exhaust pipe

Pollutants that damage brain neurons and bind with hemoglobin in blood

$$\text{Ethanol} + O_2 \xrightarrow[\text{Catalyst}]{\text{Oxidation}} CO_2$$

Less toxic than CO and acetaldehyde

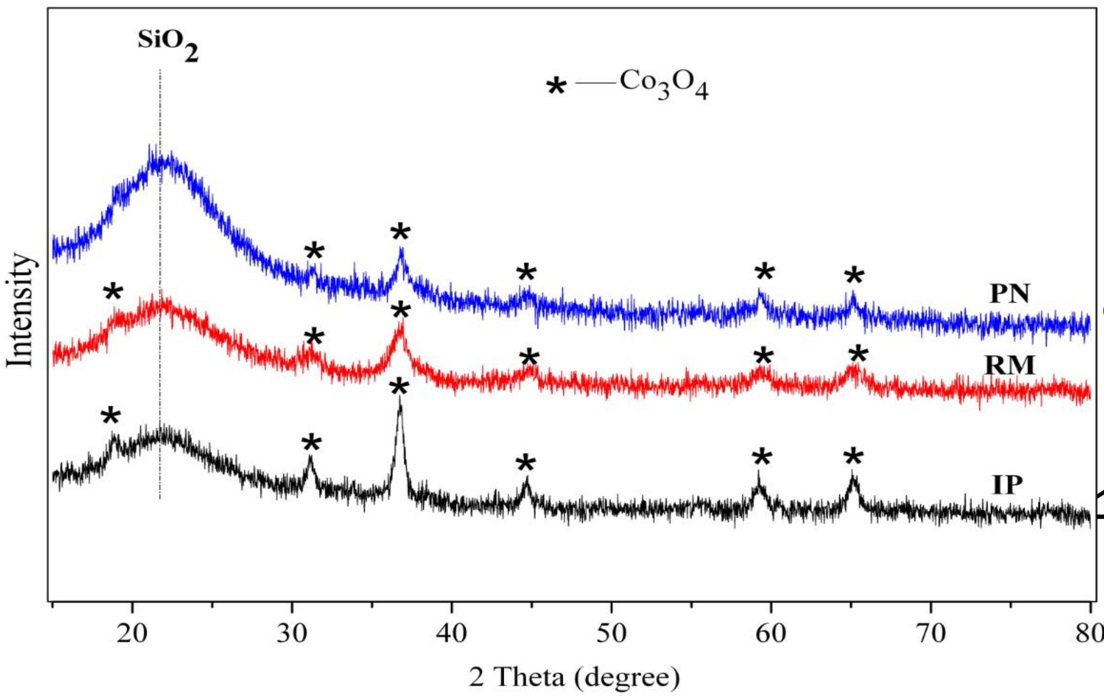
Requirements for a complete ethanol oxidation

1. **Sufficient oxygen**
2. **Effective catalyst for ethanol oxidation**
   - active at low temperature

Osakoo et al., Radiation Physics and Chemistry, **2020**, 171, 108718

Case study of XAS as an outstanding tool

Scherrer equation: crystal size of Co_3O_4 $= \frac{0.89\lambda}{B \cos \theta}$



9.2 nm

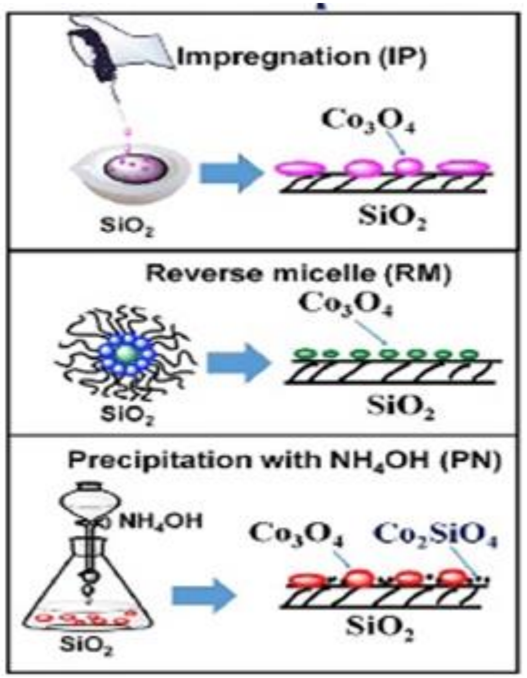
7.1 nm

15.2 nm

Calcined in air @ 300 °C for 3 h

Prepared catalyst from Cobalt nitrate precursor

Co_3O_4 is desired



All catalyst show the characteristic peaks of Co_3O_4 spinel structure.

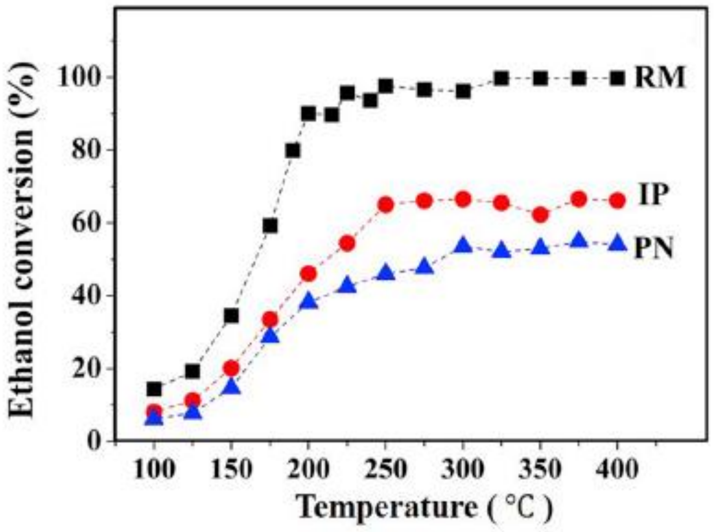
Crystal size of Co_3O_4 : IP > PN > RM

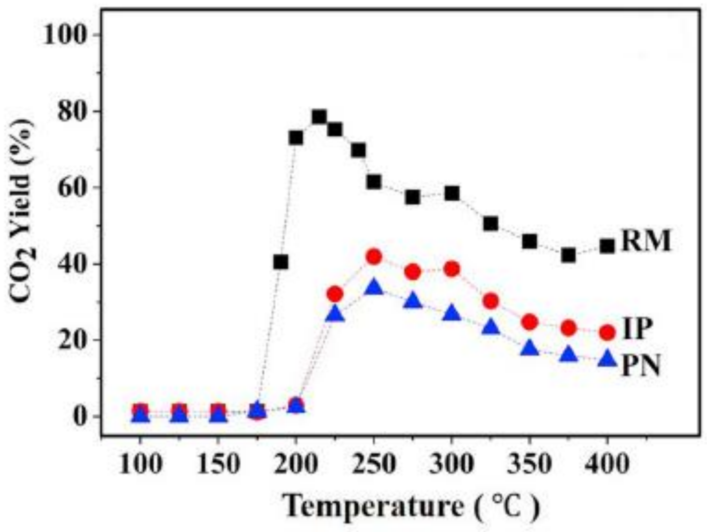
The smallest crystal size in RM could implies the highest Co_3O_4 dispersion.

Osakoo et al., Radiation Physics and Chemistry, **2020**, 171, 108718

Metal content, crystal size and dispersion of Co_3O_4 and surface chemical states

Catalysts	XRF	XRD	H_2-TPR
	Metal content (Co wt. %)	Crystal size of Co_3O_4 (nm)	(Co^{3+} / Co^{3+} + Co^{2+})
PN	9.92±0.14	9.2	0.20
RM	**10.82±0.50**	**7.1**	**0.28**
IP	10.29±0.23	15.2	0.23

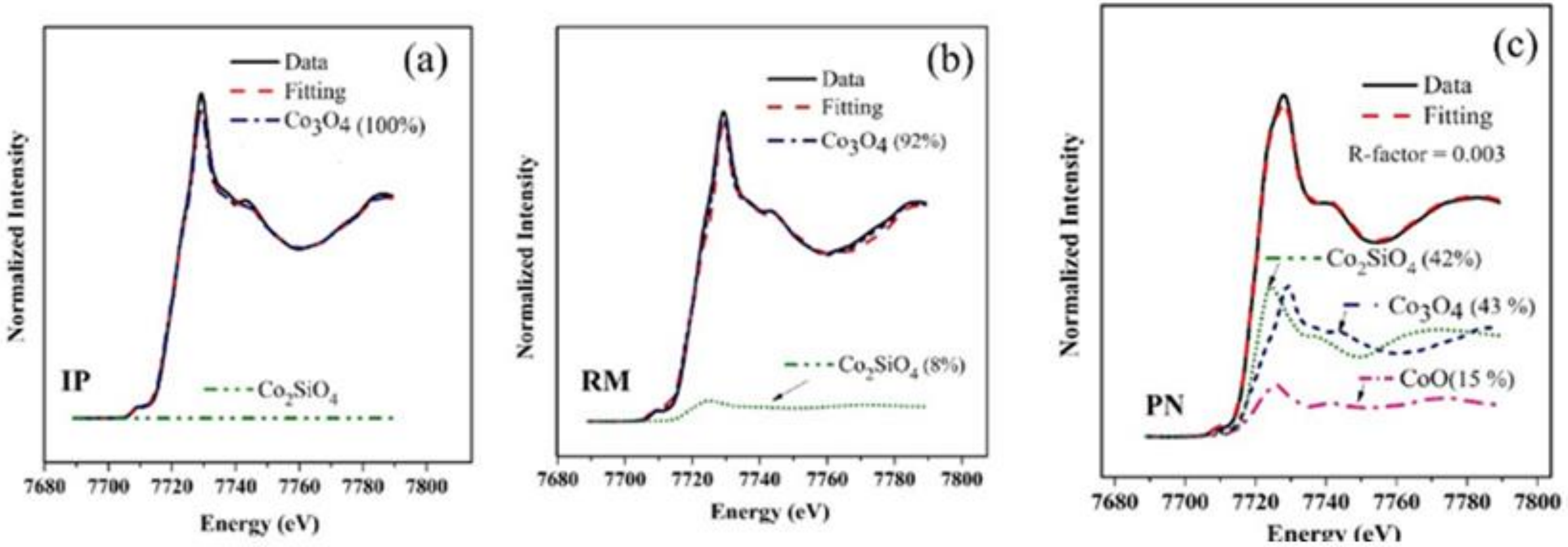




Why conversion and yield in IP are larger than that in PN ?

The RM method provides a better dispersion of Co_3O_4 on SiO_2 and richer surface Co^{3+} than PN and IP methods.

Form and oxidation state of catalysts characterized by XANES



All measurements are done in ex situ XAS

***** Co_2SiO_4 and CoO, amorphous phases are not detected by XRD*****

- **IP and RM methods give mainly Co_3O_4.**
- PN method provides mixed phases of Co_3O_4 (~ 43%), Co_2SiO_4 (~ 42%) and CoO (15%).

What is the step that causes the formation of Co_2SiO_4 and CoO in PN?

***In situ* XAS measurement of PN catalyst during calcination in air could help us to understand and minimize the formation of undesired phases.**

Why *in situ* XAS is a crucial tool?

Ex situ XAS

Nanomaterial preparation → **Thermal treatment process** → **Desired phase**

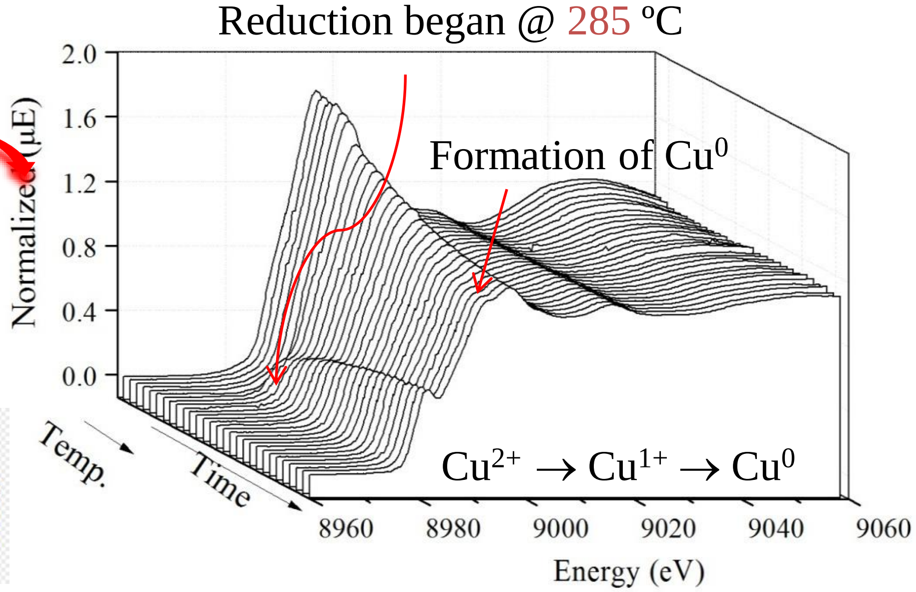
Measurement is done at room temp.

Restructured nanomaterials are hard to probe

In situ XAS

Beamline 5.2

Nanomaterial preparation → **Thermal treatment in various atmospheric gases such as H_2, O_2, N_2, He and Ar** → Desired phase



***In situ* XAS can probe and follow the change of nanostructure throughout the process.**

In situ XAS cell set up at BL 5.2

Temperature range:

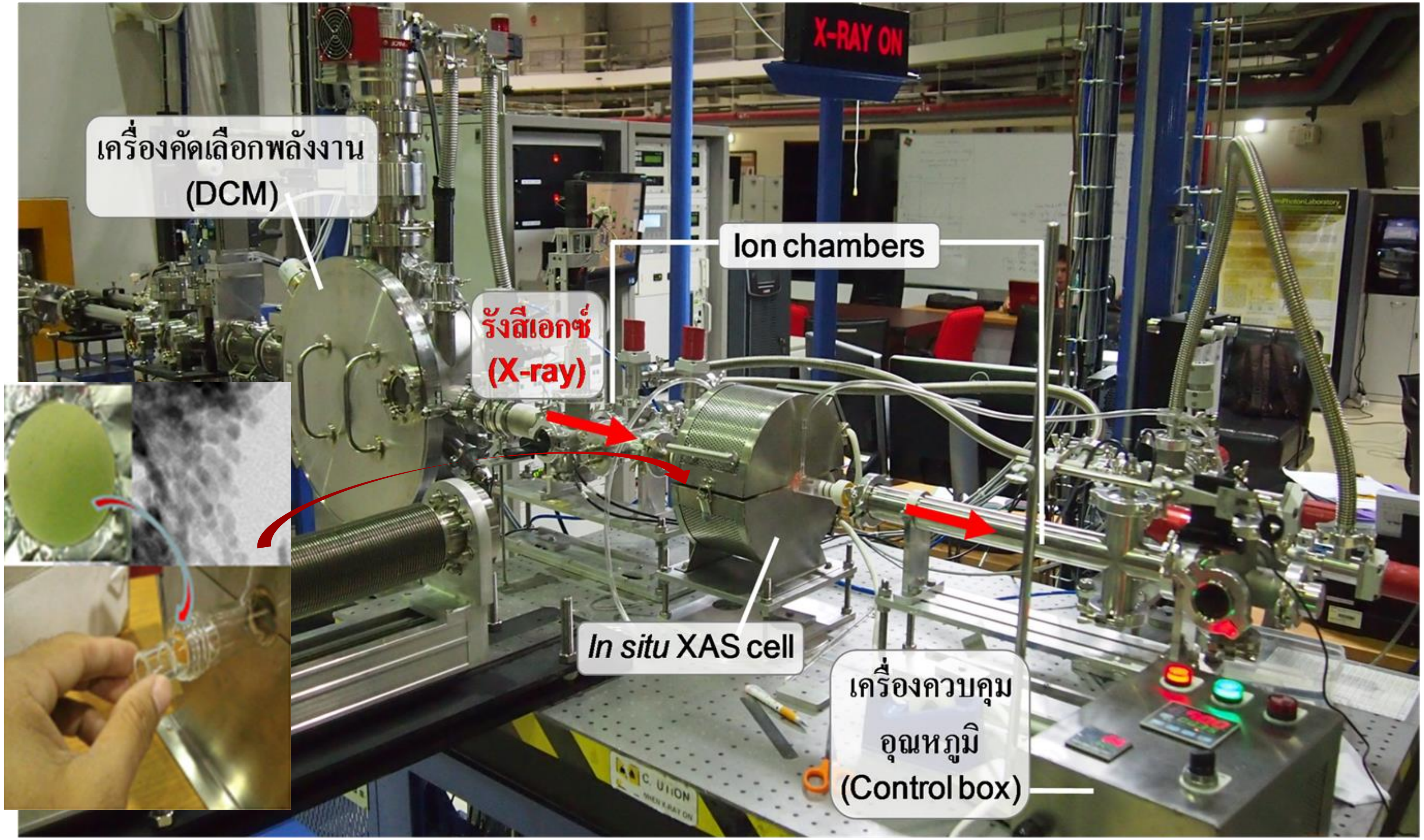
25 °C - 1000 °C

Gas:

H_2, O_2, N_2, He and Ar

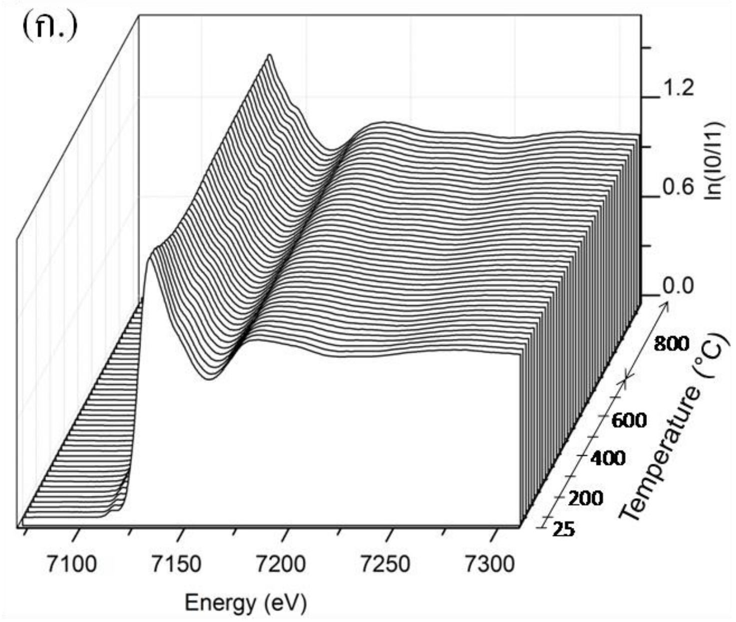
Flow rate:

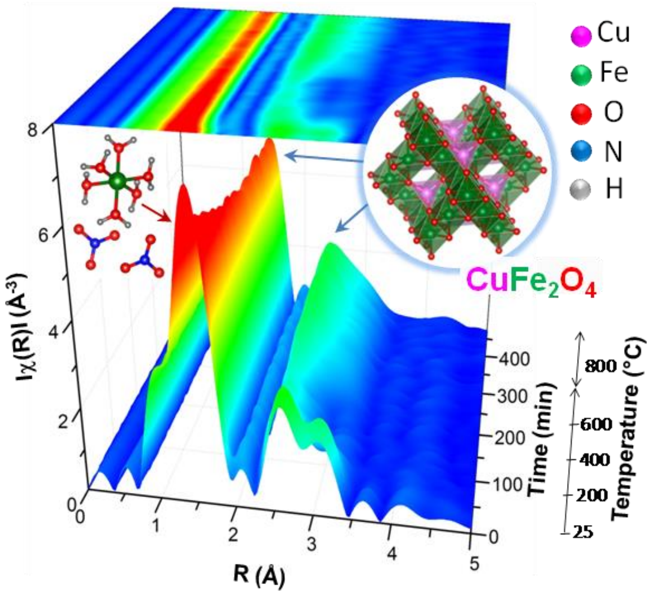
1 – 100 mL/min

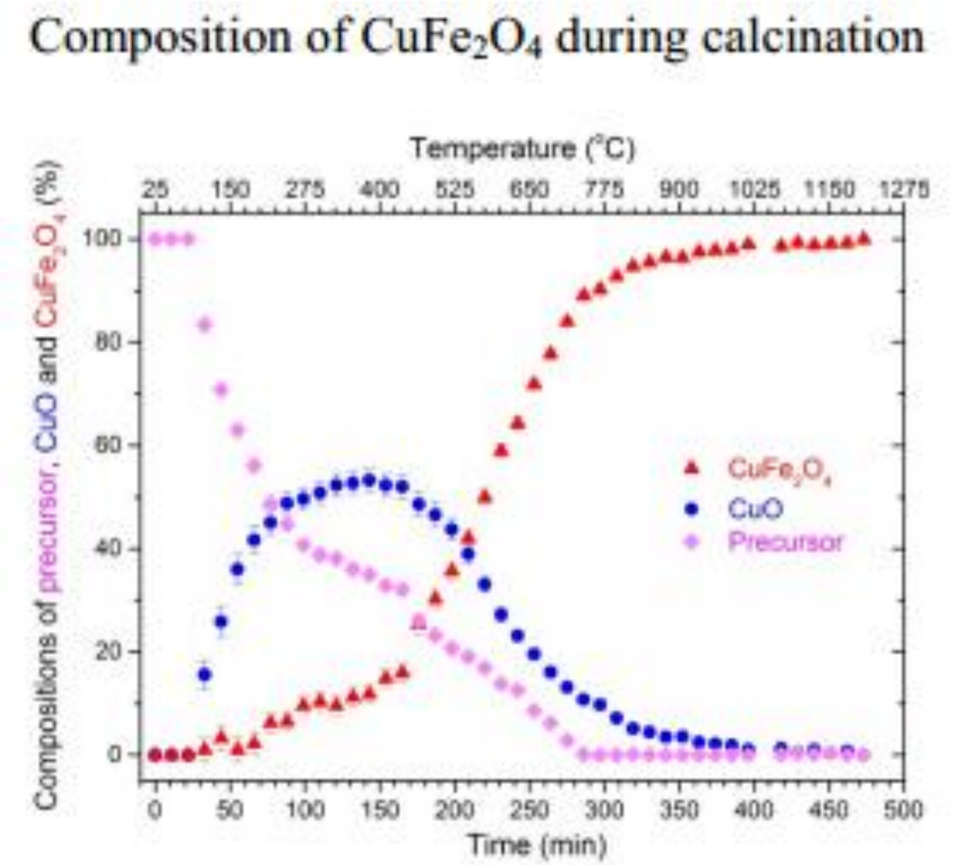


Oxidation process under O_2 atmosphere investigated by *in situ* XAS

The formation of $CuFe_2O_4$ prepared from copper and iron nitrate precursors by co-impregnation on SBA-15

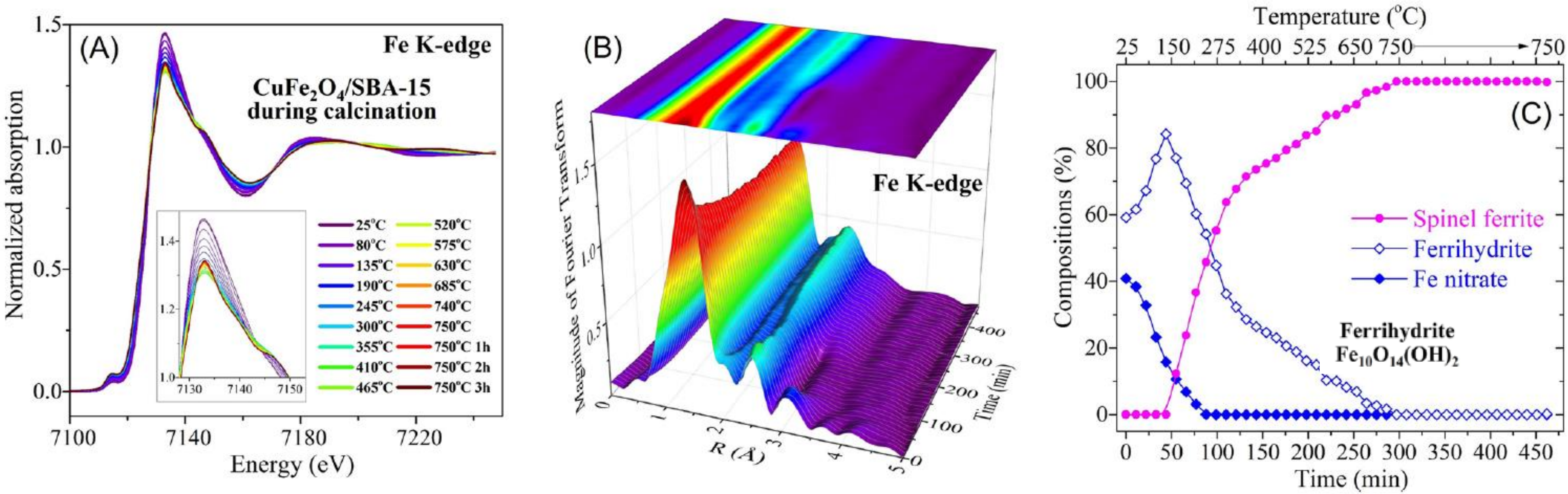






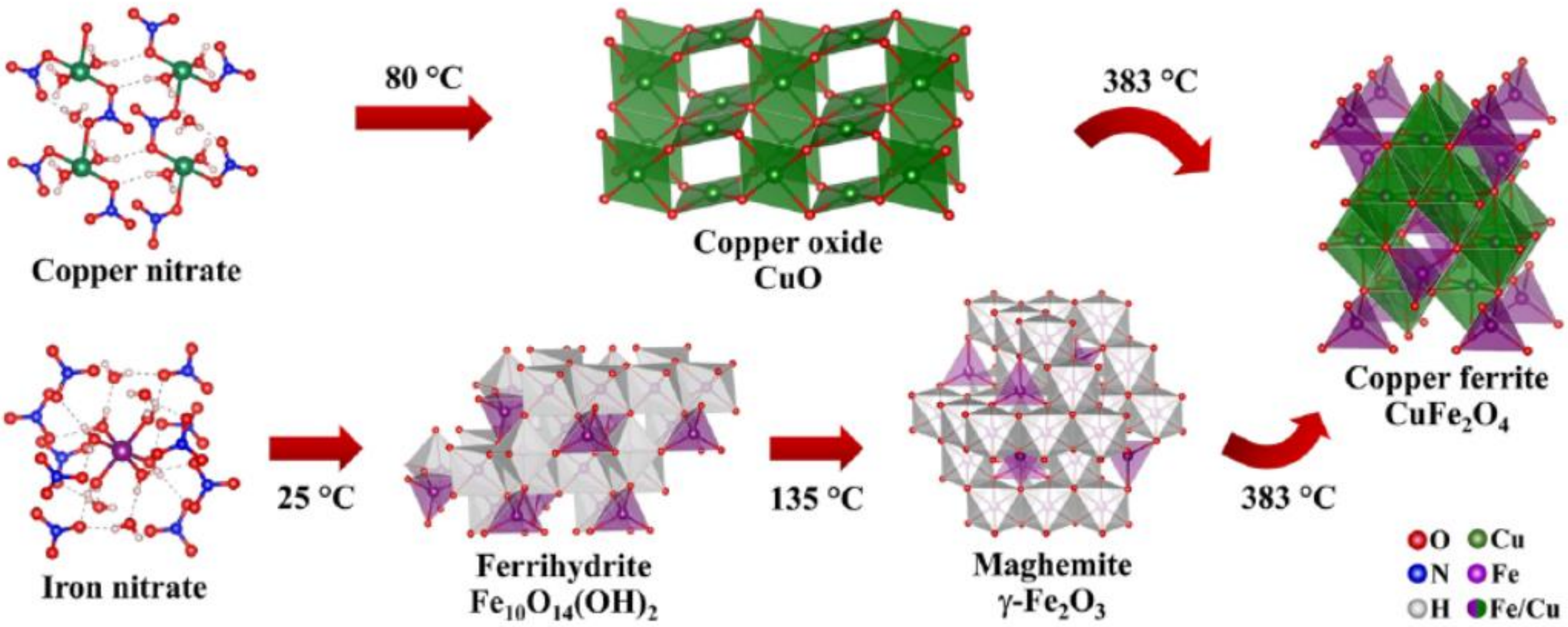
The formation of $CuFe_2O_4$, amorphous phase is observed at low temperature but not detected by *in situ* XRD.

Oxidation process under O_2 atmosphere investigated by *in situ* XAS



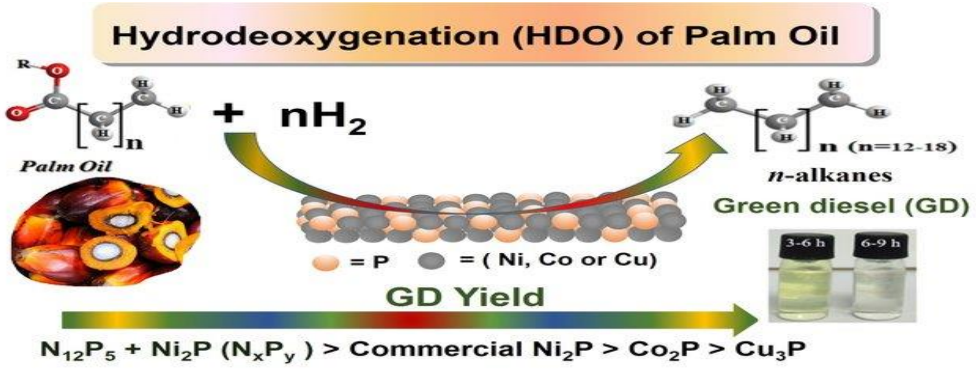
Khemthong et al., *Inorganic Chemistry*. 2019, 58, 6584−6587

Formation mechanism of $CuFe_2O_4$ spinel on SBA-15

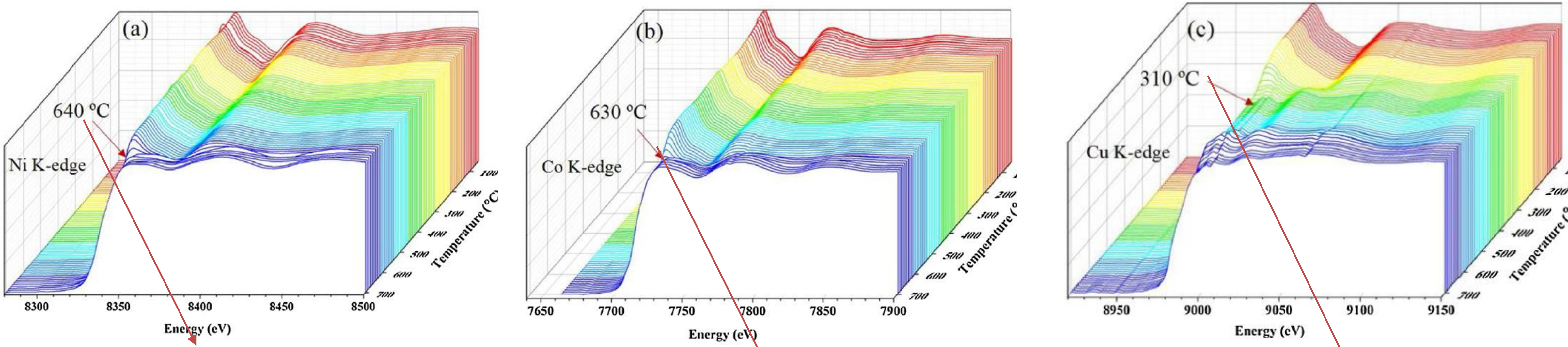


Khemthong et al., *Inorganic Chemistry*. 2019, 58, 6584−6587

Reduction process under H_2 atmosphere investigated by *in situ* TR-XAS



Spectra of *in situ* time-resolved X-ray absorption spectroscopy (TR-XAS) of calcined Ni-based (a), Co-based (b), and Cu-based (c) catalysts **@ Beamline 2.2**



α-$Ni_2P_2O_7 \rightarrow Ni_2P + Ni_{12}P_5$

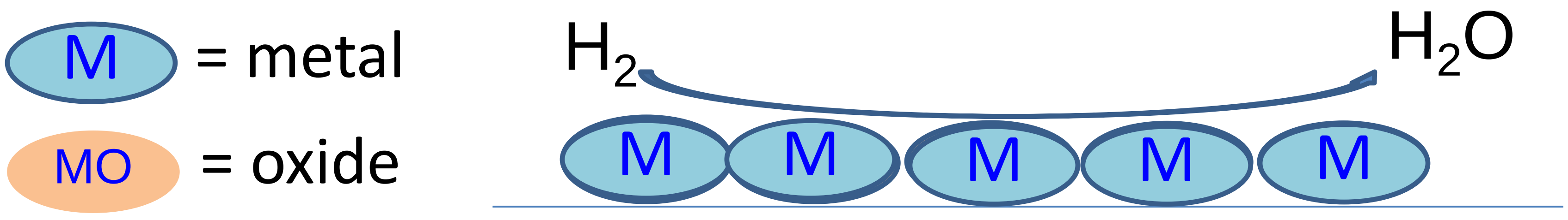
α-$Co_2P_2O_7 \rightarrow Co_2P$

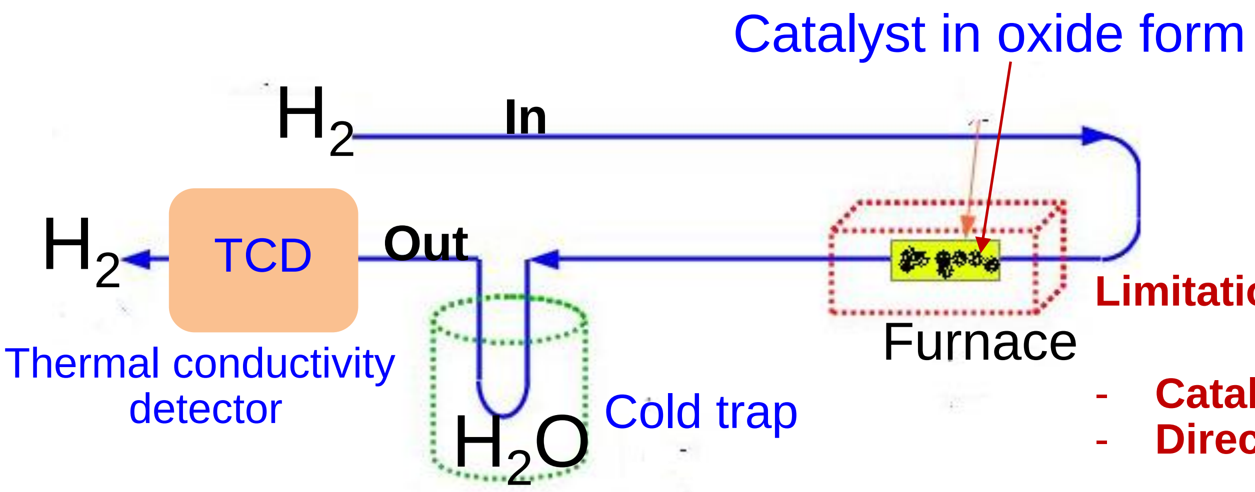
α-$Cu_2P_2O_7 \rightarrow Cu_3P$

Ruangudomsakul et al., *Molecular Catalysis* 2021, 111422 In Press, Corrected Proof

General process for reduction behavior investigation of catalyst by H_2-temperature programmed reduction (H_2-TPR)

- To study the reduction behavior of catalyst
  - Metal oxide to metal
  - 5 % Hydrogen reactive gas in Ar or N_2
  - Heating in a flowing of 5 % H_2 in Ar or N_2





- Three steps of reduction

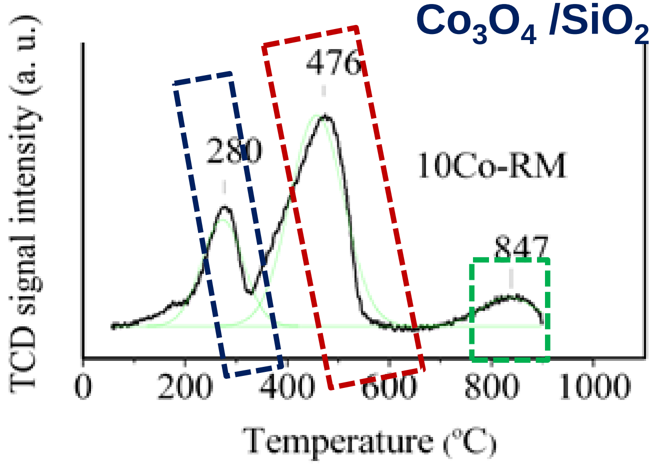
$Co_3O_4 \rightarrow CoO$

$CoO \rightarrow Co^0$

Co- with strong interaction on support $\rightarrow Co^0$

or cobalt silicate $\rightarrow Co^0$

Co_3O_4 /SiO_2



Limitation

- **Catalyst must be transformed in metal oxide before measurement**
- **Direct reduction of metal precursor is hard to probe by TCD**

Why the investigation of reduction behavior in catalyst is a crucial step?

Research into **cobalt catalysts** is crucial area to industry due to their extensive applications in a range of industrial processes:

-Fischer-Tropsch synthesis
- Hydrogenolysis
- Hydrocracking
- Hydrogenation

However, active form of catalyst is metal leading to several steps in catalyst preparation

Statement of problems

The preparation of cobalt catalysts typically involves many steps:

-Impregnation of cobalt salt solution throughout the supports

-Drying the catalyst to remove adsorbed water

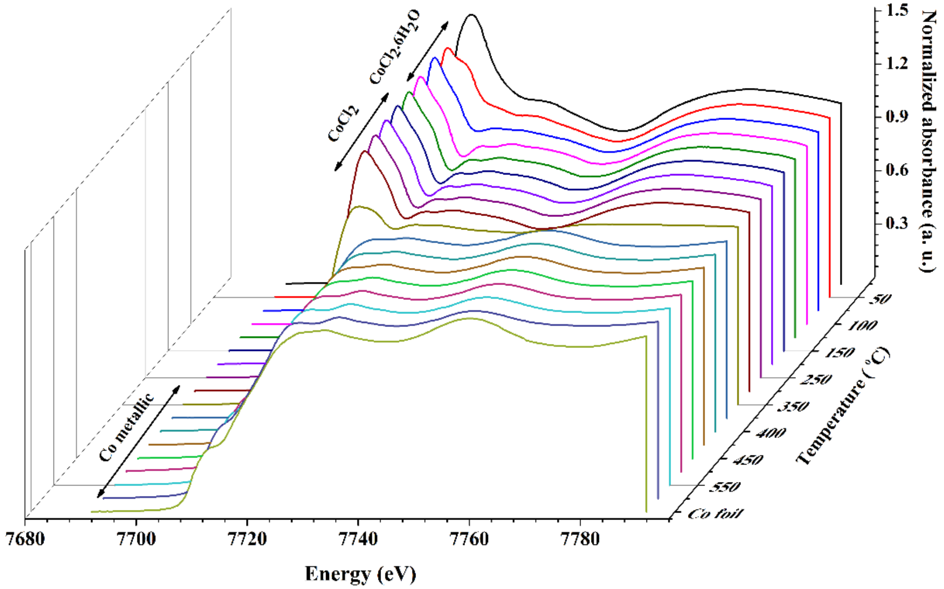
-Calcination in air to give oxide forms

-Reduction in H_2 to obtain metallic form

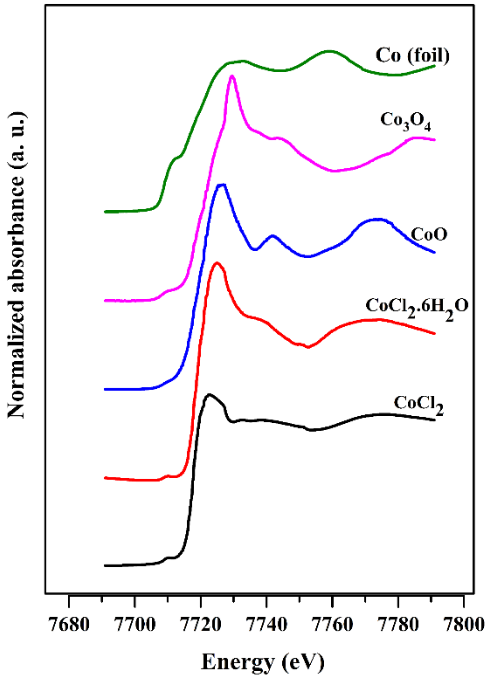
****All process are time-consuming and high cost.

The attempt to minimize the step in catalyst preparation is desired such as direct reduction of cobalt precursor in H_2 atmosphere.

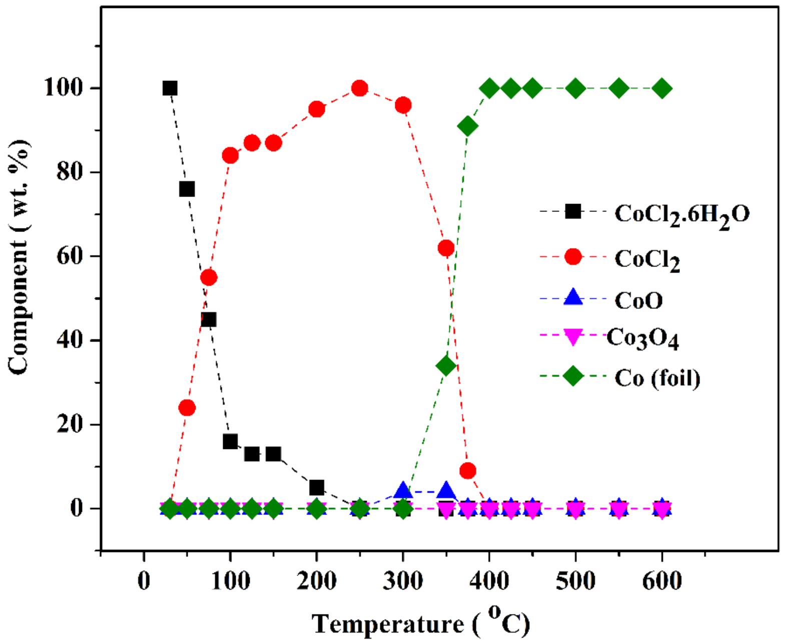
Investigation of direct reduction of metal precursor is achieved by *in situ* XAS



Standards



Linear combination analysis (LCA) result



Cobalt chloride is almost completely reduced at the temperature of 400 °C , similar to **Co_3O_4.**

Conclusions

■ XAS technique can detect several forms of samples including crystalline, amorphous, thin film, in solution and surface adsorbed.

.

■ *In situ* XAS can probe and follow the change of nanostructure throughout the process.

■ Investigation of direct reduction of metal precursor is achieved by *In situ* XAS.

Operando XAS can prob the change of nanostructure during reaction testing

Acknowledgements

Full-time Doctoral Researcher Grant, SUT

Catalysis & Chemical Analysis Labs

Materials Research Center for Sustainability in Energy and Environment

Prof. Dr. Jatuporn Wittayakun

SYNCHROTRON THAILAND CENTRAL LAB

NANOTEC a member of NSTDA

Prof. Dr. Jatuporn Wittayakun

Catalysis group @ SUT
- Ethanol oxidation
- Phenol hydroxylation
- Tranesterification (biodiesel)
- Synthesis of butanol from ethanol
- Bio-hydrogenated diesel production
- Zeolite synthesis and applications

Assoc. Dr. Dr.Sanchai Prayoonpokarach

-Paraquat adsorption

-Tranesterification (biodiesel)

มหาวิทยาลัยขอนแก่น Khon Kaen University

Assist. Dr. Sirinuch Loiha

- Zeolite synthesis and applications
- XANES and EXAFS interpretation

CARL VON OSSIETZKY universität OLDENBURG

Prof. Dr. Dr. h.c. Frank Rößner

- Fischer-Tropsch synthesis
- Tranesterification (biodiesel)
- Zeolite synthesis and applications

NANOTEC a member of NSTDA

Dr. Pongtanawat Khemthong

- Bio-hydrogenated diesel production

-XANES and EXAFS interpretation

Thank you

SYNCHROTRON THAILAND CENTRAL LAB

Dr. Yingyot Poo-arporn

Time-resolved X-ray absorption spectroscopy (TR-XAS)

Dr. Pinit Kidkhunthod

X-ray absorption spectroscopy (XAS, including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)

Dr. Narong Chanlek

X-ray photoelectron spectroscopy (XPS)

Thank You

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16th NSTDA Annual Conference

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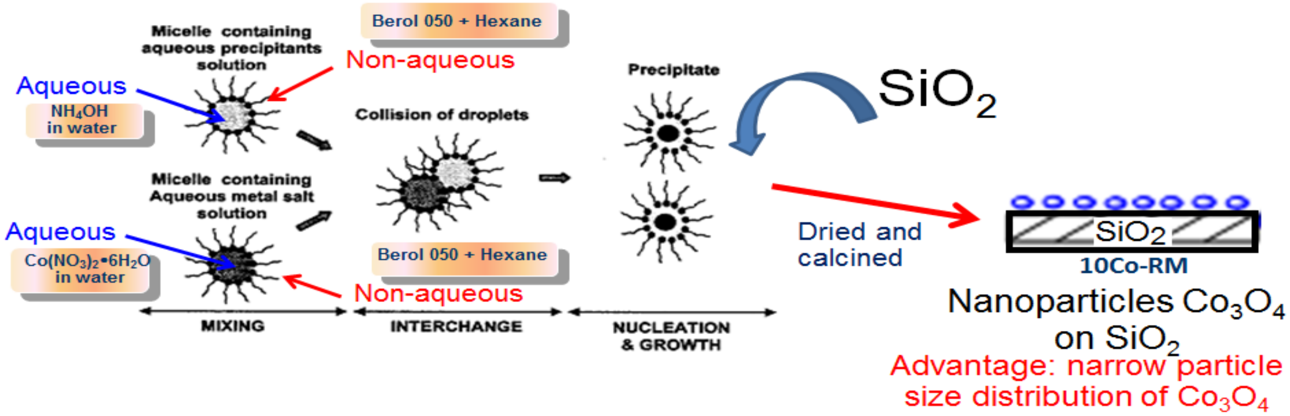
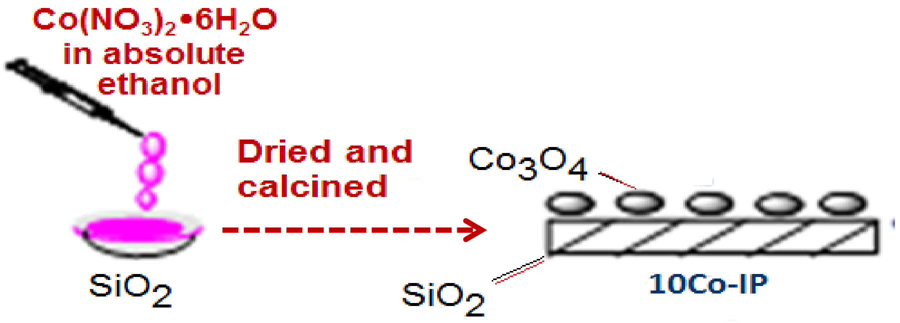
Catalysis & Chemical Analysis Labs

Catalyst preparation

1) Precipitation with reverse micelle technique (water-in-oil) (RM)

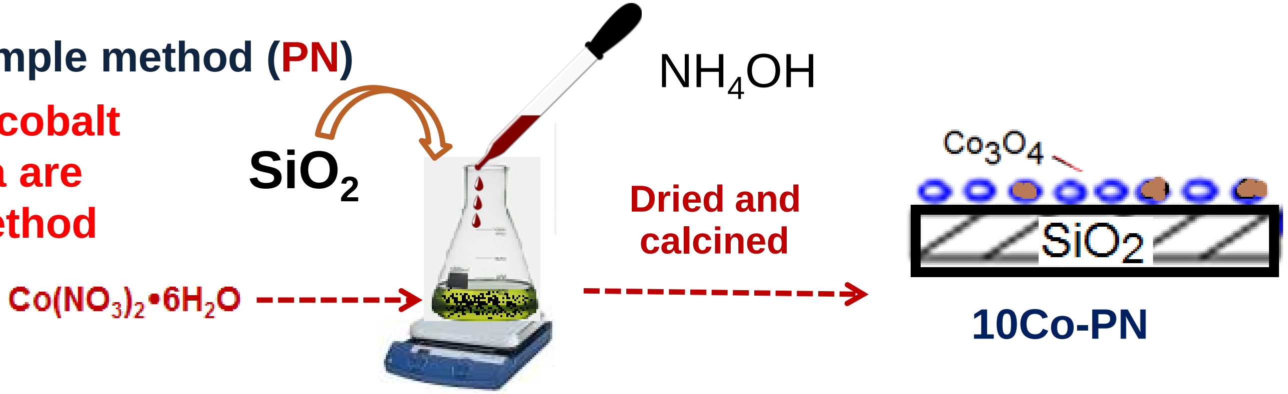


2) Impregnation (IP)

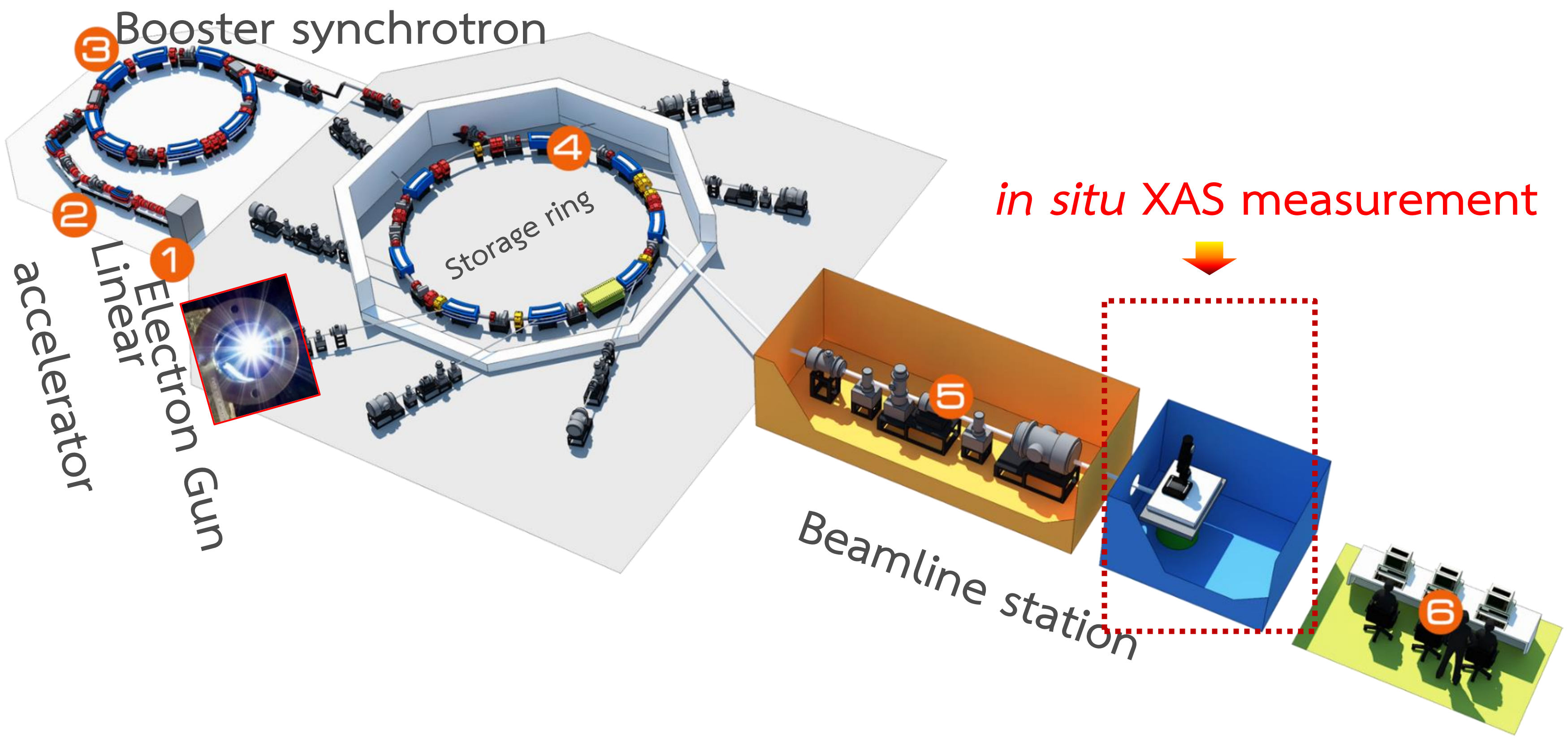


3) Precipitation with simple method (PN)

*The concentrations of cobalt precursor and ammonia are similar to that of RM method



Synchrotron radiation



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