Supported Metal-Acid Bifunctional Catalysts Synthesized by Electrostatic Adsorption of Pd onto Metal-Doped Silicas

Anhua Dong[1], John Meynard Tengco[1], Anand Ramanthan[2], John R. Regalbuto[1]*

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1 Department of Chemical Engineering
University of South Carolina, Columbia, SC, 29208
2 Department of Chemical & Petroleum Engineering
The University of Kansas, Lawrence, SK, 66044

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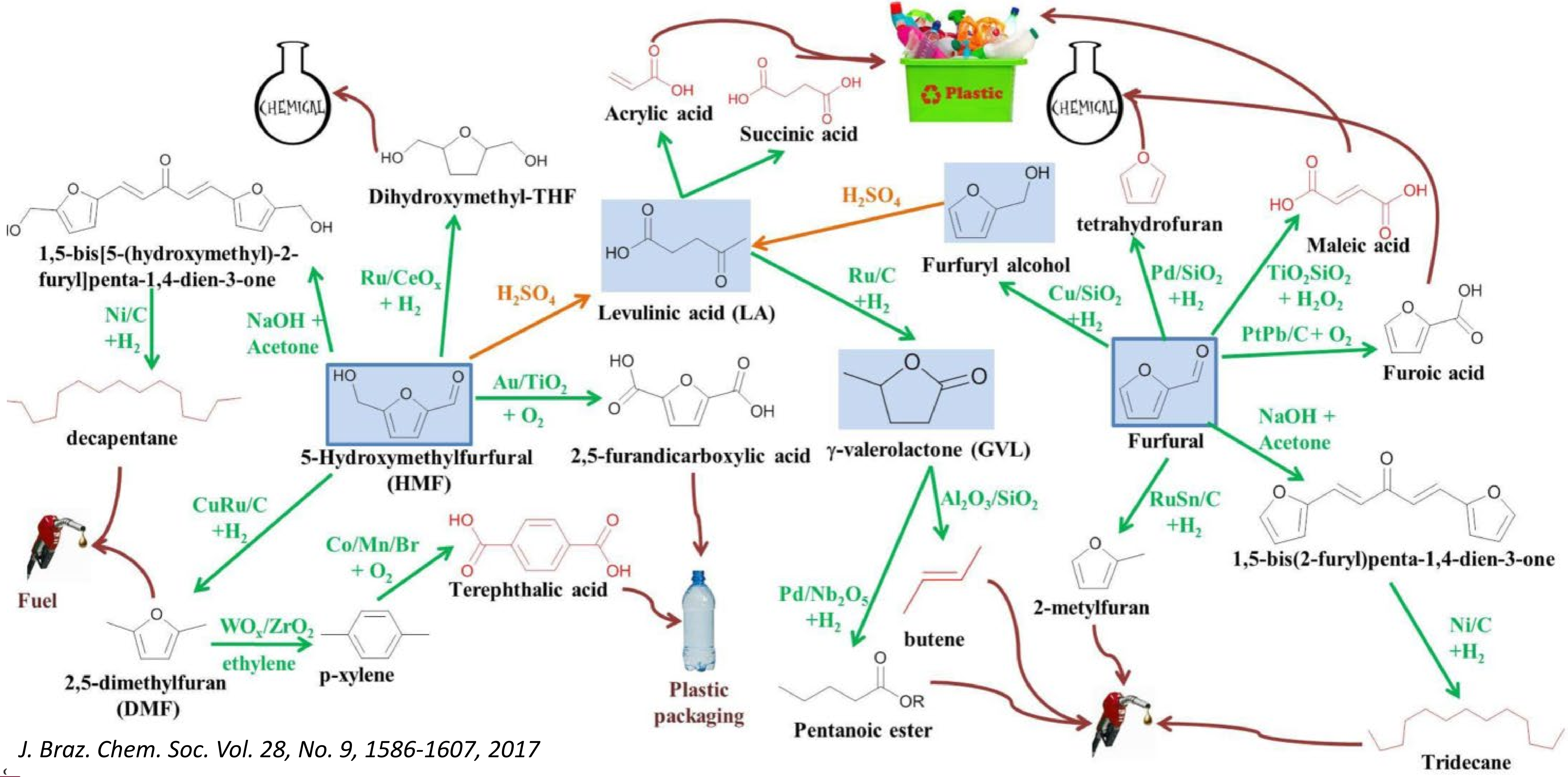
CERCAS

Overview

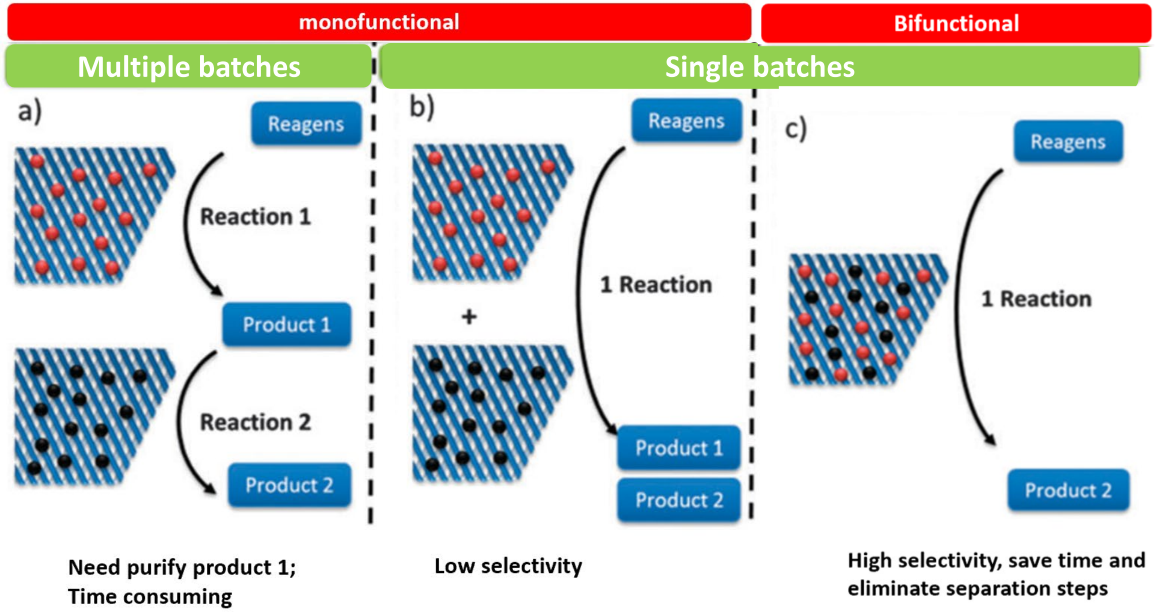


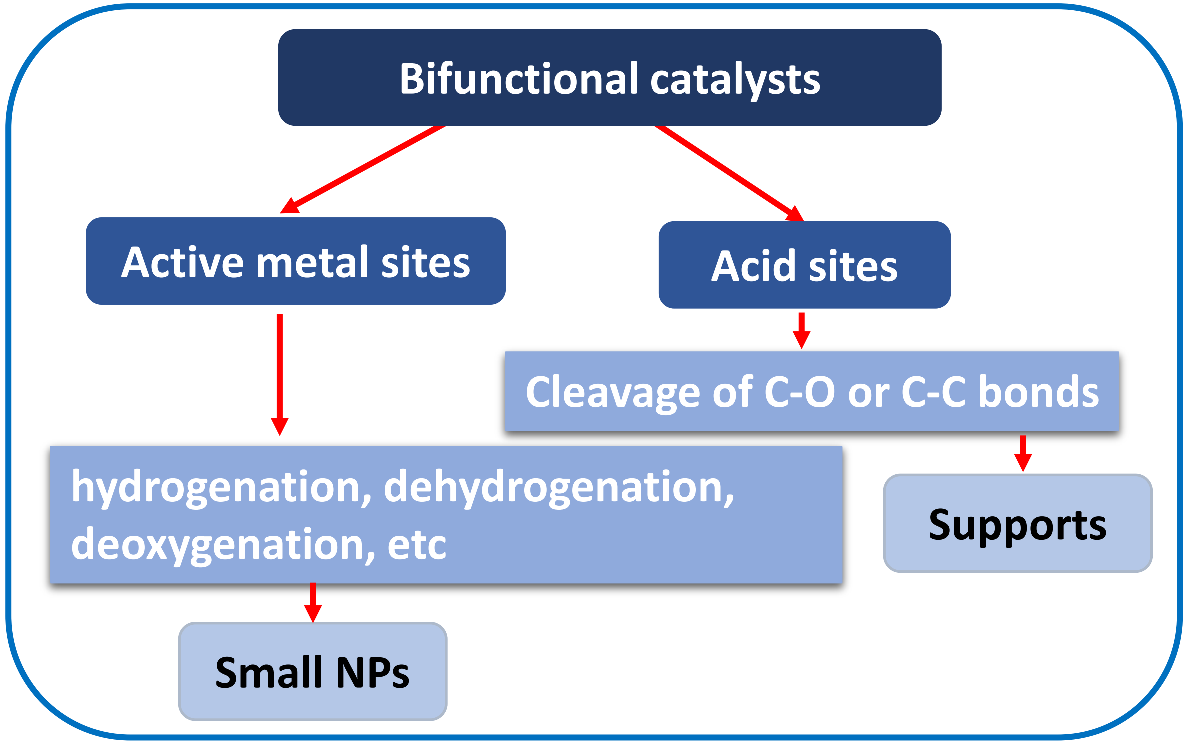
J. Braz. Chem. Soc. Vol. 28, No. 9, 1586-1607, 2017

❖ To get desired products, different kinds of sequential or cascade-reactions are involved.

Introduction

- Monofunctional catalysts can hardly be capable of catalyzing the cascade- or sequential reactions in one batch;
- The mixture or the sequential use of different monofunctional catalysts- low selectivity, more purification steps, time consuming;
- Bifunctional catalysts with different active sites open a door for sequential or cascade- reactions .





e.g. Pd/Nb_2O_5 for direct conversion of GVL into pentanoic acid.

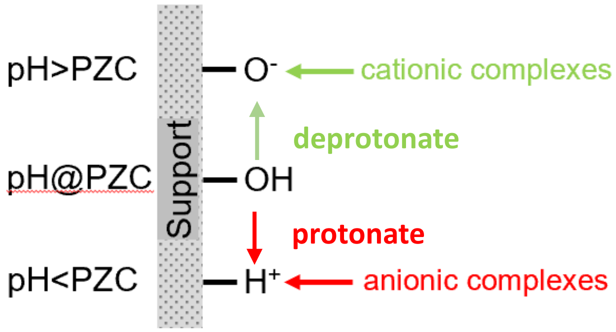
$$\text{GVL} \xrightarrow{\text{Acidic } Nb_2O_5} \text{ring-opening} \xrightarrow[\text{hydrogenation}]{\text{Pd NPs}} \text{Pentanoic acid}$$

GVL--γ-Valerolactone

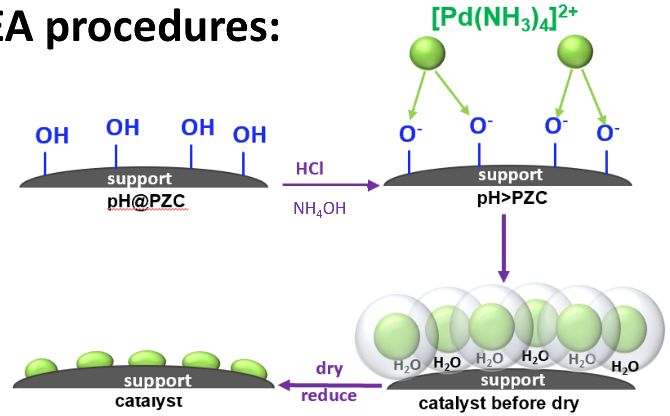
H.N. Pham et al./ Applied Catalysis A: General 397 (2011) 153-162

Introduction

SEA mechanism:



SEA procedures:



❖ Support surface charged by changing solution pH

❖ Adsorb appositively charged metal precursor(s)

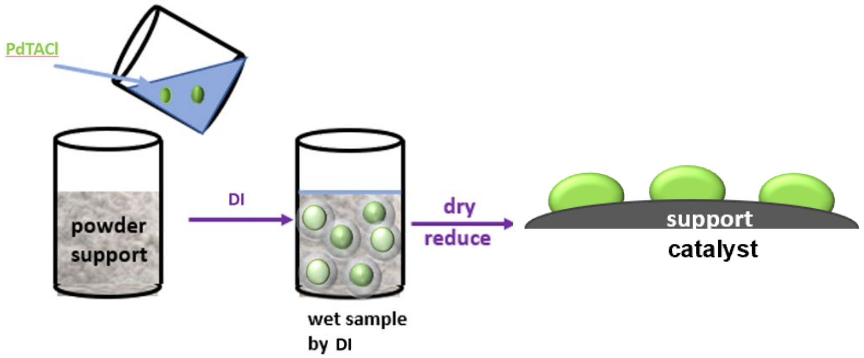
❖ Strong metal-support interaction

❖ Ultra-small particle size(<1.5nm)

❖ Poor precursor-support interaction;

❖ Metal complex migrate in drying or aggregate in reduction;

❖ Large particle size and poor metal dispersion.



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Introduction

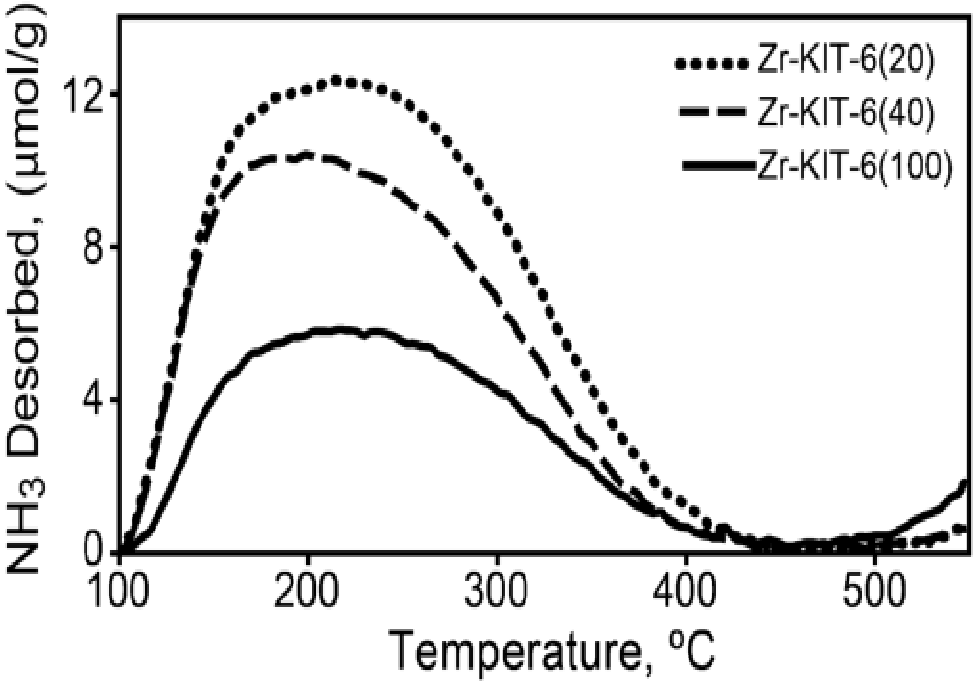

Figure 7. Temperature-programmed desorption of ammonia (NH_3-TPD) from Zr-KIT-6(x) materials.

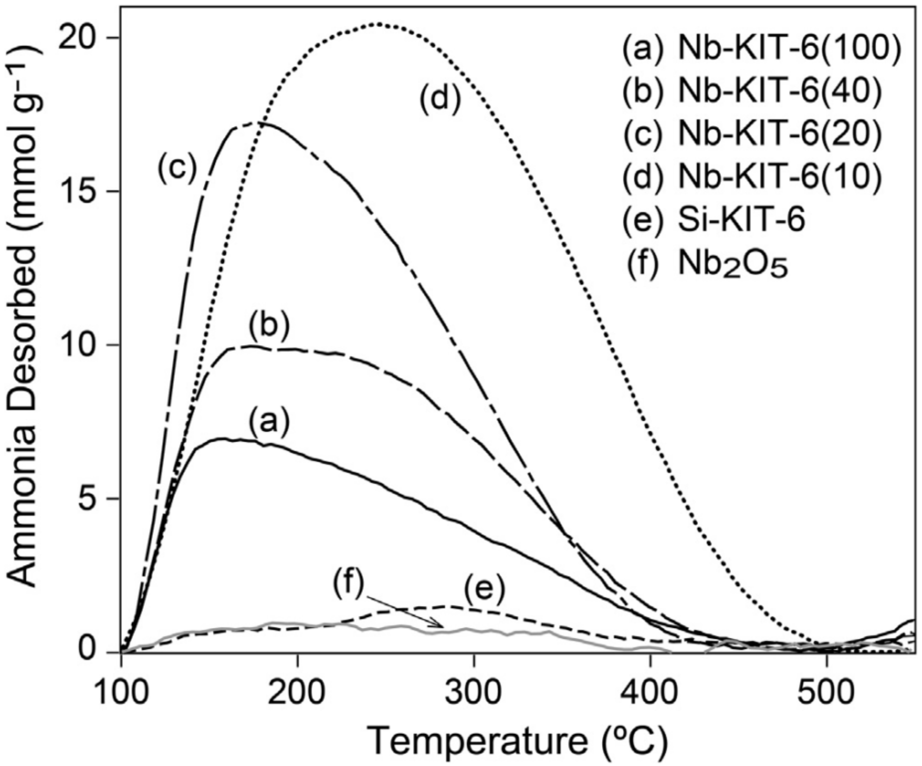

Fig. 9. Temperature programmed desorption of ammonia (NH_3-TPD) from Nb-KIT-6 samples compared with Si-KIT-6 and bulk Nb_2O_5.

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Ind. Eng. Chem. Res. 2013, 52, 15481-15487;
J Porous Mater (2012) 19: 961-968

Objective

The **goal** of this work is to synthesize bifunctional catalysts with small particles and tuned acid sites for γ-valerolactone conversion. It can be fulfilled by the following two points:

- Using different metals to adjust the acidity of silicas;
- Prepare small palladium NPs on silicas with tuned acidity sites by SEA method.

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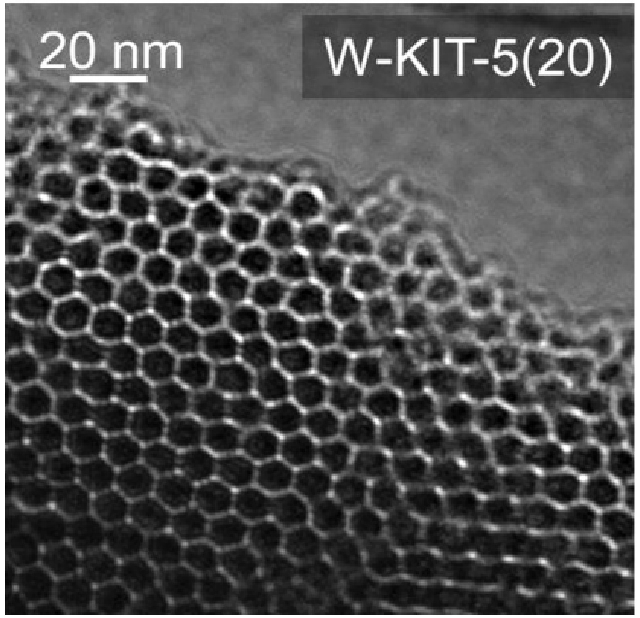
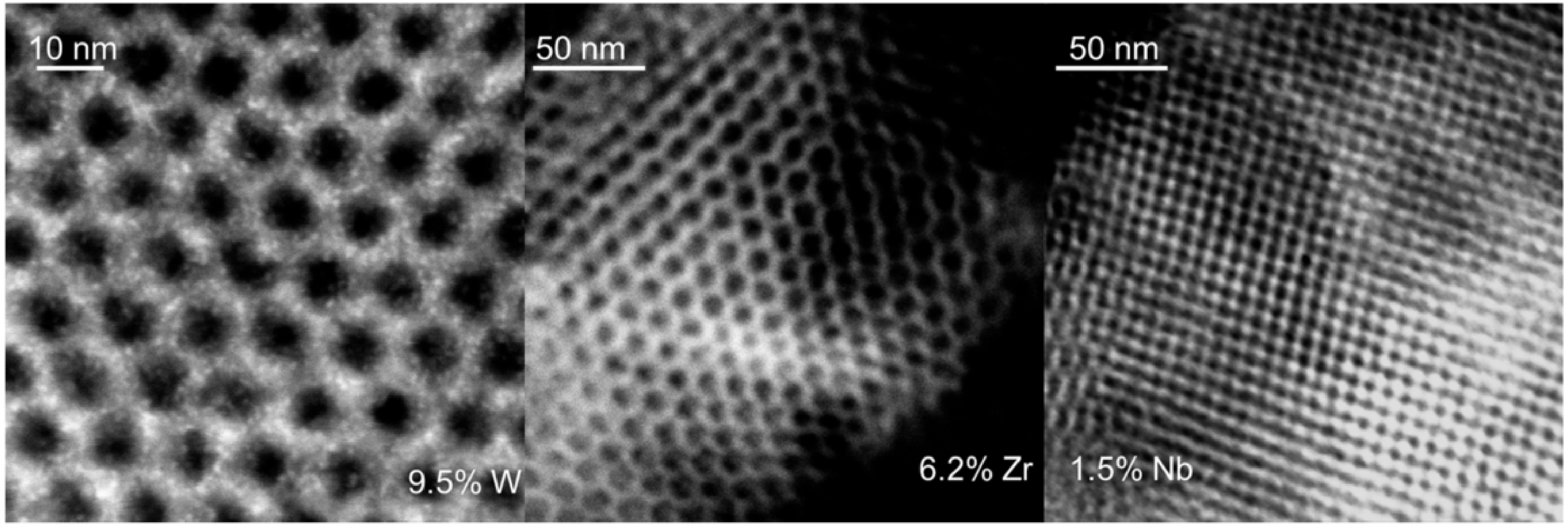
Part Ⅰ - Metal-doped Silicas

-Structure of metal (W, Zr, Nb)-doped KIT5 and KIT6

KIT5- cage type mesoporous silica



KIT6- 3D ultra large mesoporous silica



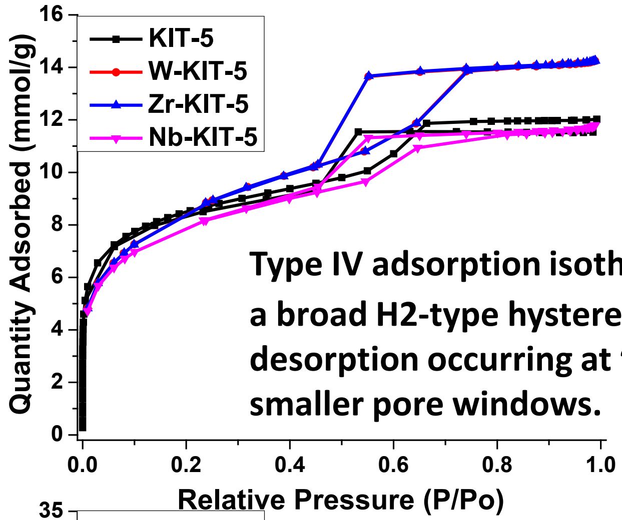
❖ Metal-dopants can be highly dispersed in the ordered structures of KIT5 and KIT6 silicas by hydrothermal synthesis method.

J. Porous Mater (2012) 19: 961-968;
Molecules 2018, 23, 263.

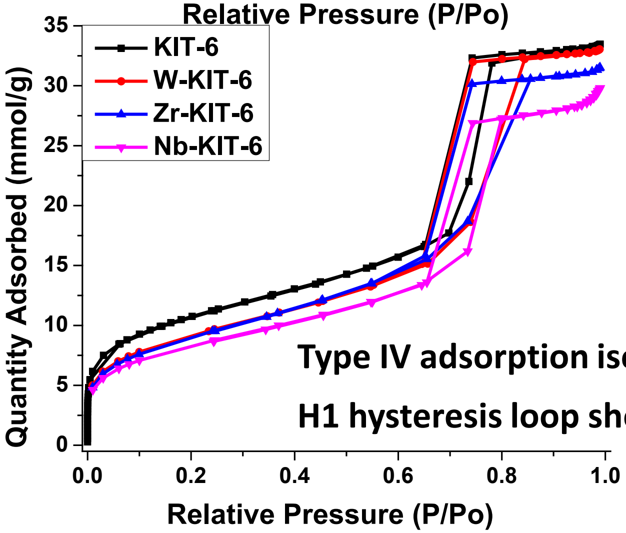
Part Ⅰ - Metal-doped Silicas

-N_2 physisorption characterization

--Isotherm Curves

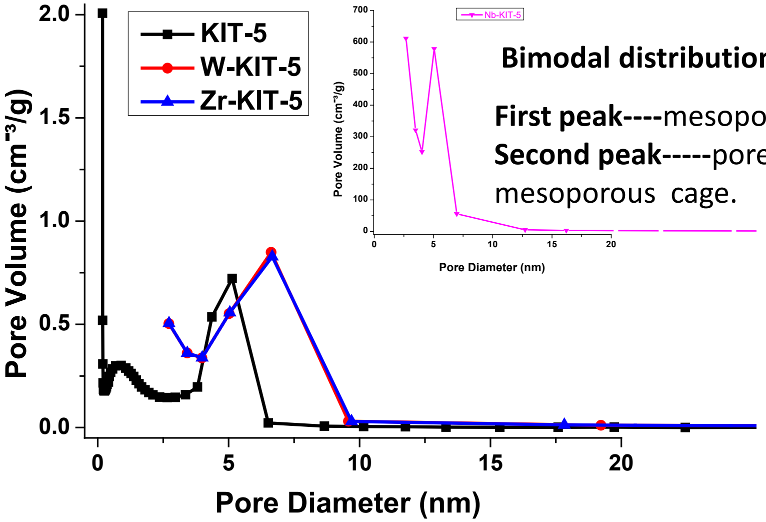


Type IV adsorption isotherm-mesopores;
a broad H2-type hysteresis loop with desorption occurring at ~0.42p/p_0 due to the smaller pore windows.



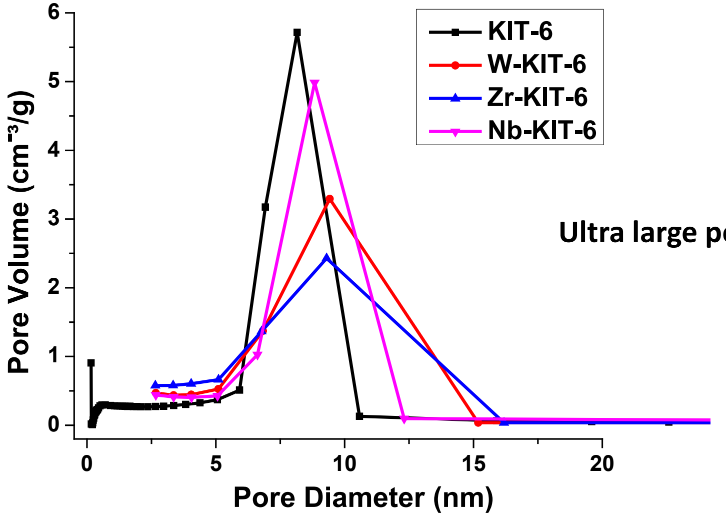
Type IV adsorption isotherm-mesopores;
H1 hysteresis loop shows uniformity of pores.

--Pore Size Distribution



Bimodal distribution:

First peak----mesopore entrance size;
Second peak-----pore diameter of the primary mesoporous cage.



Ultra large pores

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Part Ⅰ - Metal-doped Silicas

--Surface area, pore volume and average pore diameter

Sample	SA(m^2/g)	V_{pore}(cm^3/g)	D_{ave}(nm)	Total acidity mmol NH_3/g *
KIT-5	672	0.4	2.4	0.02
W-KIT-5	662	0.5	3.0	0.31
Zr-KIT-5	661	0.5	3.0	<0.59
Nb-KIT-5	635	0.4	2.6	
KIT-6	858	1.2	5.4	0.05
W-KIT-6	713	1.1	6.4	0.48
Zr-KIT-6	697	1.1	6.2	0.89
Nb-KIT-6	649	1.0	6.3	0.23

Atomic ratio of Si/M=20
M=W, Zr, Nb

- ➢ **KIT-6 and metal-doped KIT-6 materials have higher surface area and larger pores;**
- ➢ **Metal-dopants could alter the acidity of the silicas.**

*** From literatures:**
J. Porous Mater (2012) 19: 961-968; Microporous and Mesoporous Materials 175 (2013) 43-49; Microporous and Mesoporous Materials 190 (2014) 240-247; Microporous and Mesoporous Materials 167 (2013) 207-212; Chemical Engineering Journal 278 (2015) 113-121.

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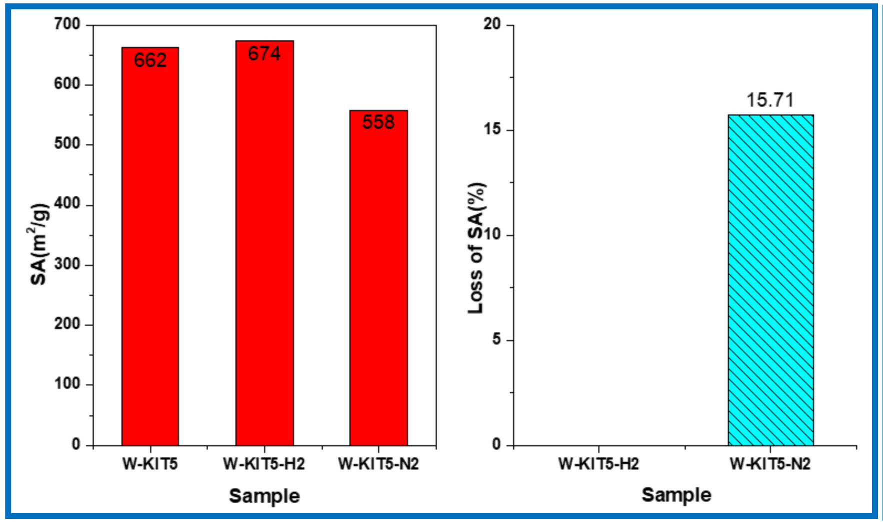
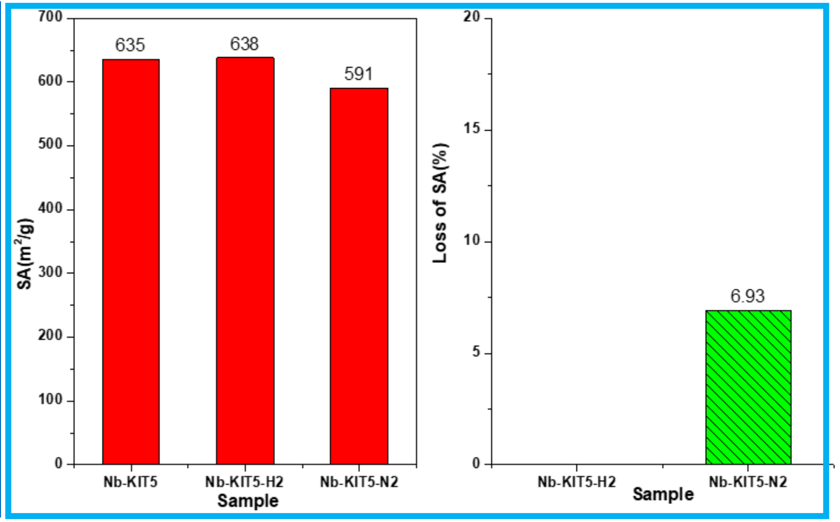
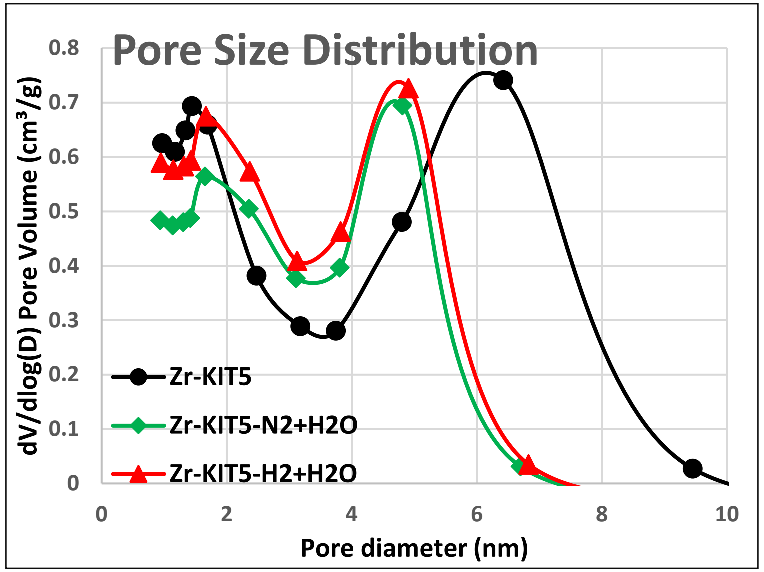
Part Ⅰ - Metal-doped Silicas

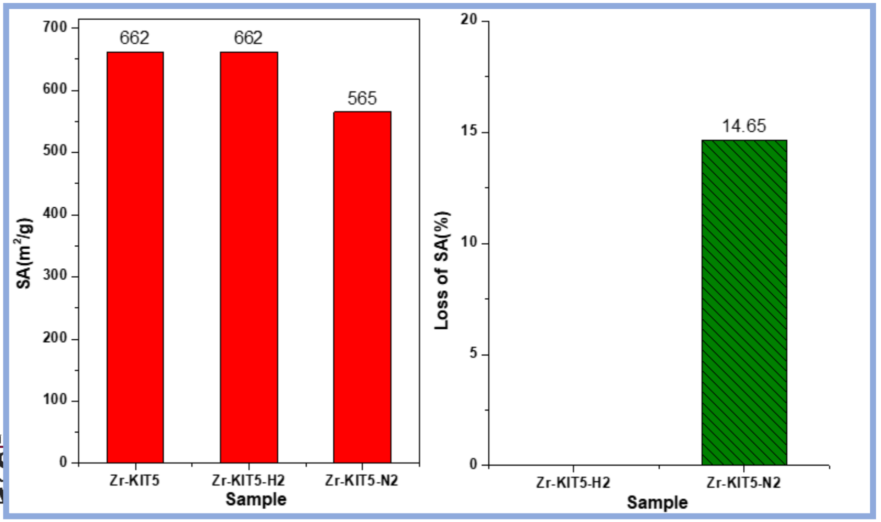
--Thermal stability test_SA loss

Condition--Temp.:110^{o}C, intial pressure:180psi, solvent: DI H_2O, Gas: H_2 or N_2,1 hr, calc. 500 ^{o}C for 3 hrs.









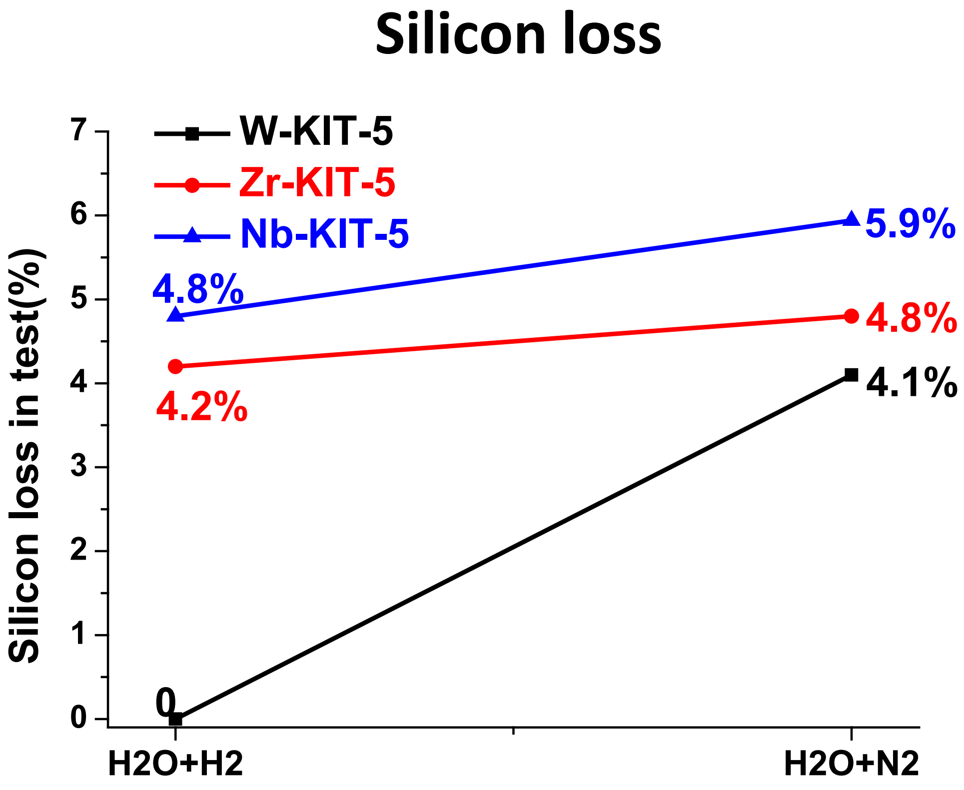
❖ **H_2 atmosphere can better stabilize the surface area.**

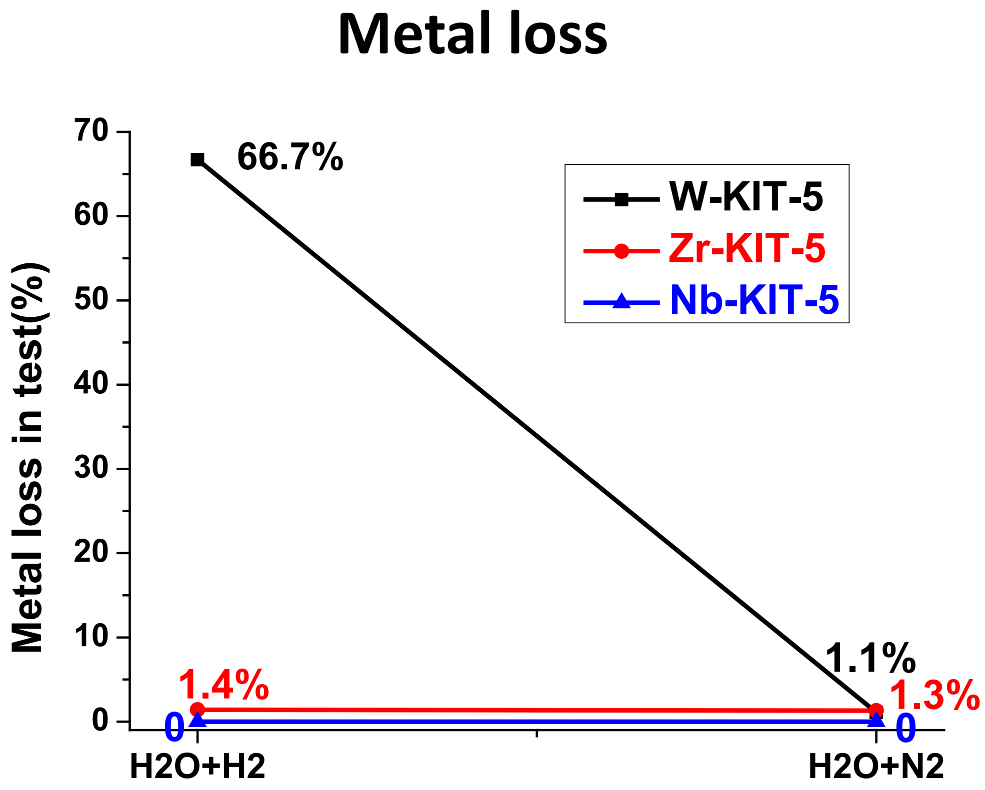
Solubility of N_2 or H_2 in DI water

Gas	Purge at 1atm (saturated) at 25 ^{o}C	T=110 ^{o}C, P=180 psi
N_2	0.61mmol/L	0.3mmol/L (0.084 g/L)
H_2	0.78mmol/L	0.7mmol/L (0.014g/L)

Part Ⅰ - Metal-doped Silicas

--Thermal stability test_silicon and metal loss



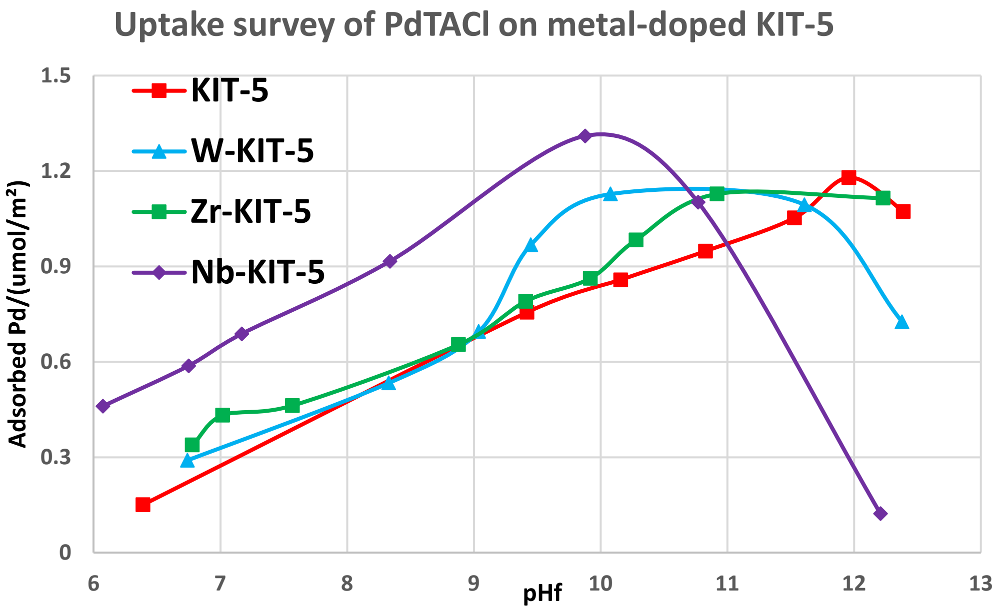


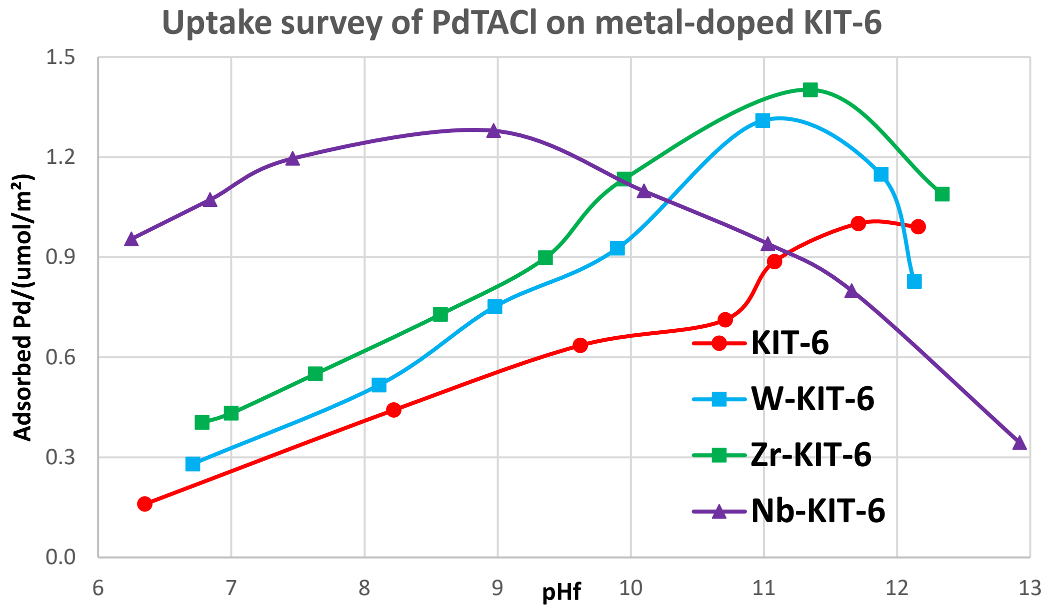
❖ **Loss of W in H_2 atmosphere reached 66.7%, while loss of silicon and other metals was negligible.**

Part Ⅱ - Bifunctional Catalysts Synthesis

--Uptake survey

Condition: C_{PdTACl}=200ppm, SL=1000m^2/L, pH adjusted by HCl and NH_4OH, shaking for 1 hr.





	KIT5	W-KIT5	Zr-KIT5	Nb-KIT5	KIT6	W-KIT6	Zr-KIT6	Nb-KIT6
PZC	3.4	1.2	2.4	2.1	3.6	1.3	2.4	2.2
$pH_{opt.}$	11.96	10.08	10.92	9.88	11.71	10.99	11.35	8.97
Γ_{max}	1.18	1.13	1.13	1.31	1.00	1.31	1.40	1.28

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Part Ⅱ - Bifunctional Catalysts Synthesis

--Deposition of Pd NPs

sample	Mass loading of Pd	method	condition
Pd/M*-doped KIT5	2.5 wt%	SEA, DI	$pH_{opt.}$ 1000m^2/L, 180^{o}C reduction (SEA); V_{pore}~0.9ml/g (DI)
Pd/M-doped KIT6	2.5 wt%	SEA	$pH_{opt.}$ 1000m^2/L, 180^{o}C reduction (SEA)

Will deposit Pd on metal-doped KIT6 by DI.

***M-W, Zr, Nb**

--Characterization

- X-ray diffraction
- H_2-chemisorption

→ Check particle size and metal dispersion

- NH_3-TPD → Verify the acidity of the supported-NPs

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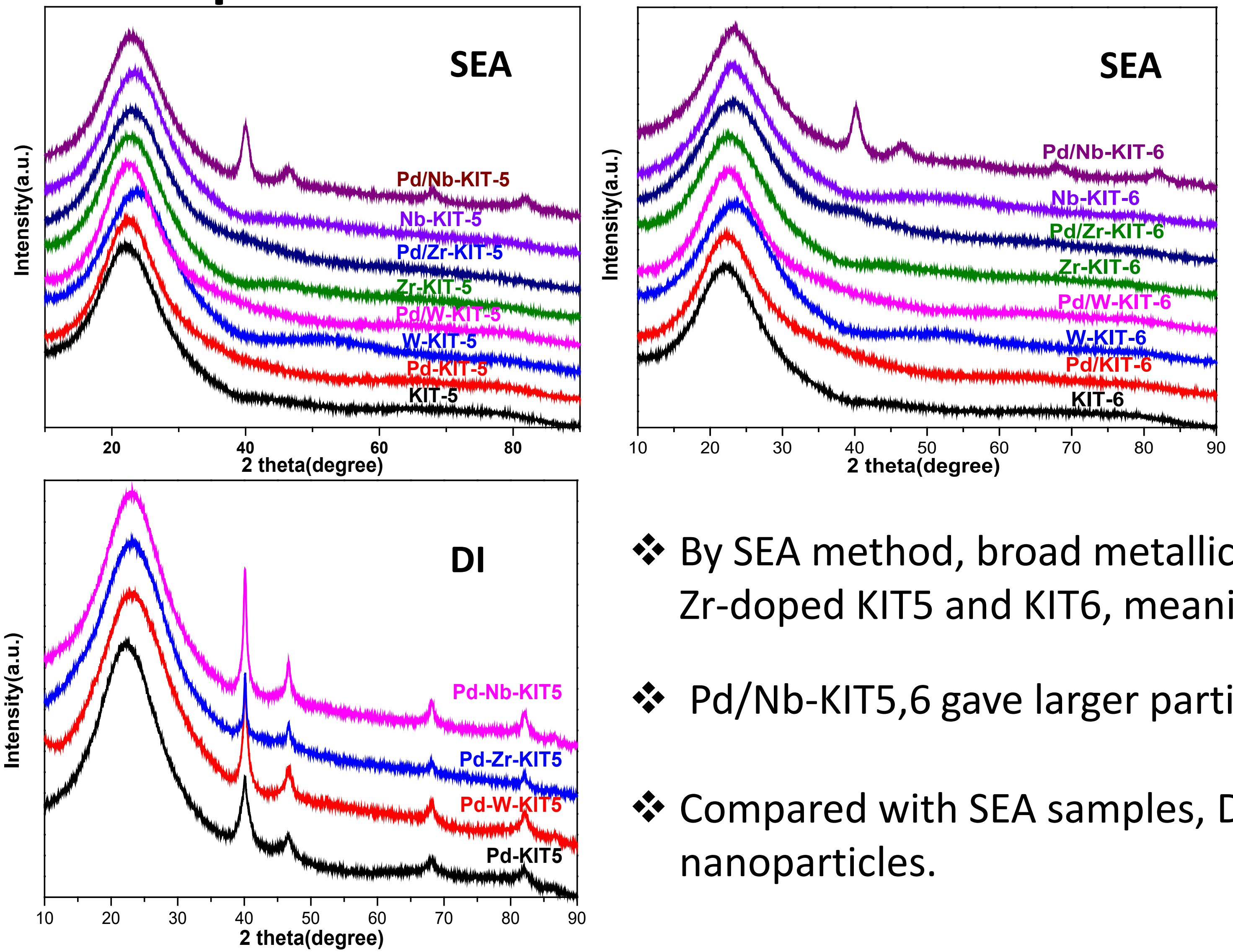
Part Ⅱ - Bifunctional Catalysts Synthesis

--Normalized XRD patterns



- ❖ By SEA method, broad metallic peaks appeared on pure, W, Zr-doped KIT5 and KIT6, meaning smaller particle size;
- ❖ Pd/Nb-KIT5,6 gave larger particle size. Still try to find out why;
- ❖ Compared with SEA samples, DI method showed much larger nanoparticles.

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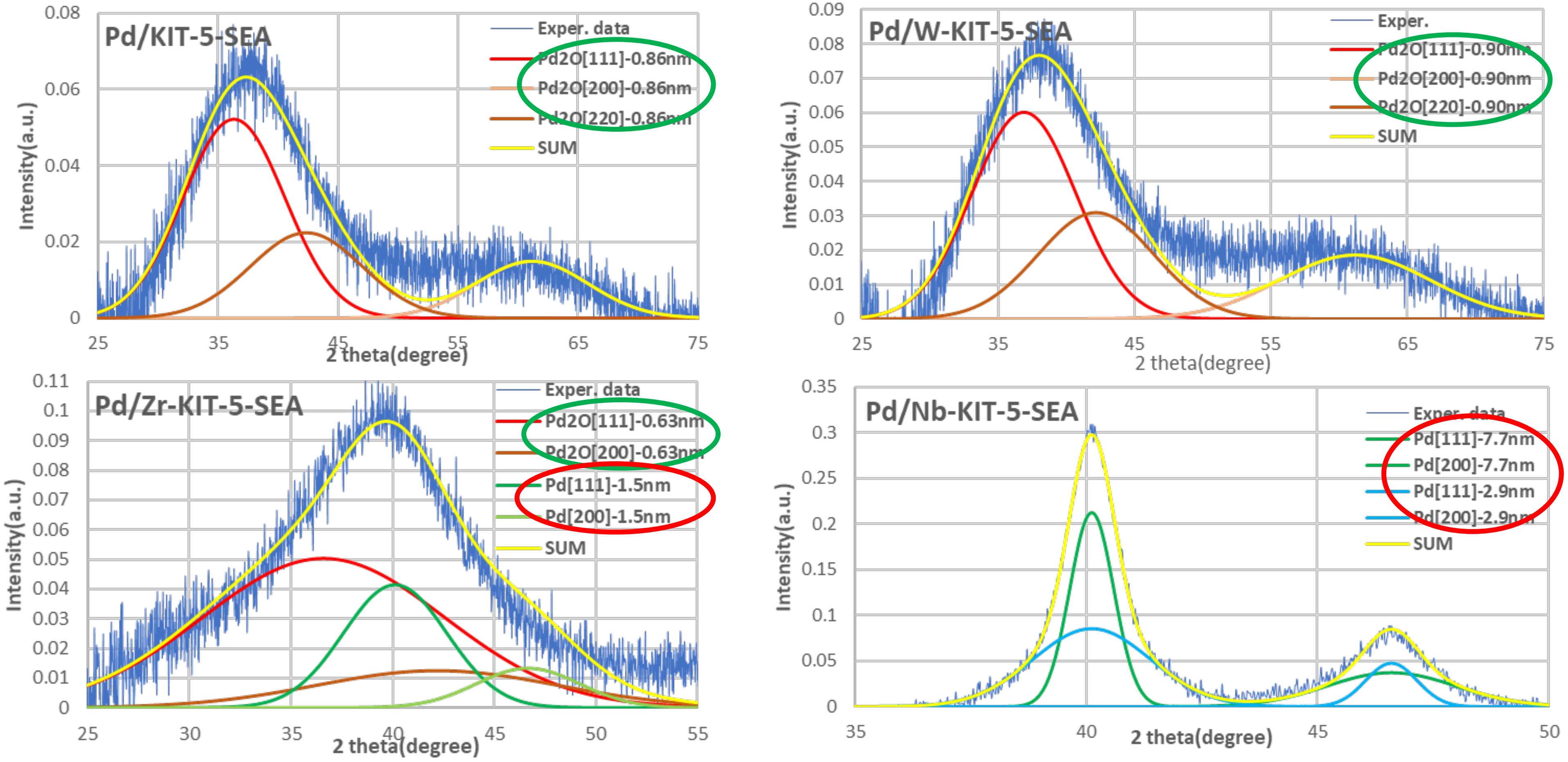
Part Ⅱ - Bifunctional Catalysts Synthesis

--Deconvoluted XRD patterns



- ❖ Small Pd nanoparticles were oxidized (pure, W, Zr-doped KIT5);
- ❖ Large Pd particles kept in the metal phase (Zr, Nb-doped KIT5);
- ❖ SEA sample with Zr and Nb dopants showed bimodal particle size.

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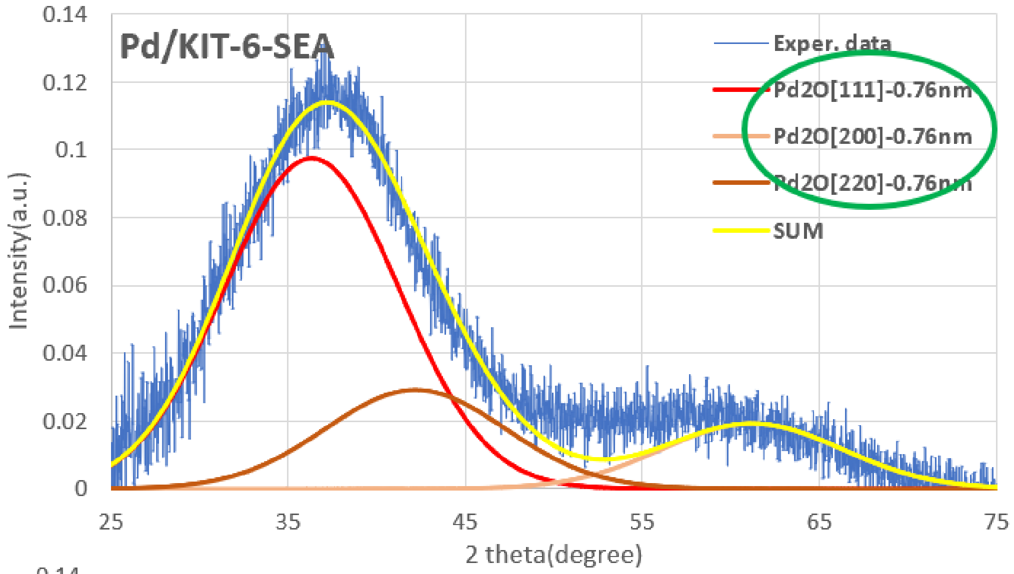
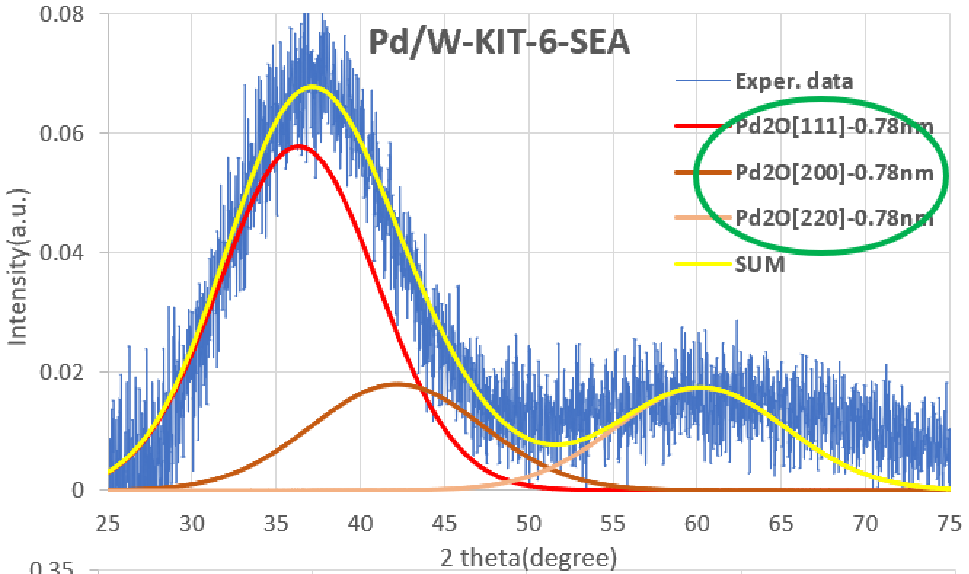
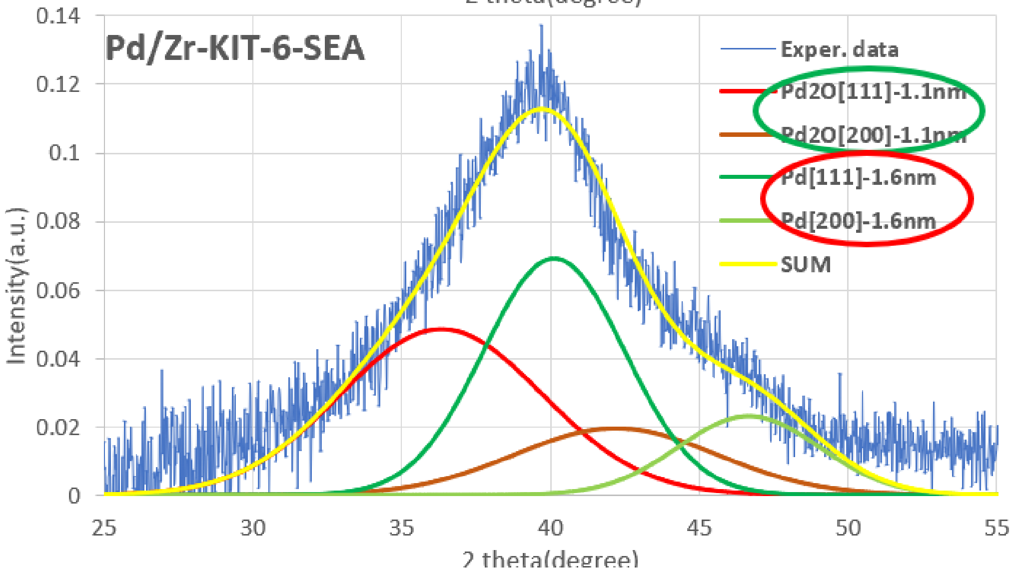
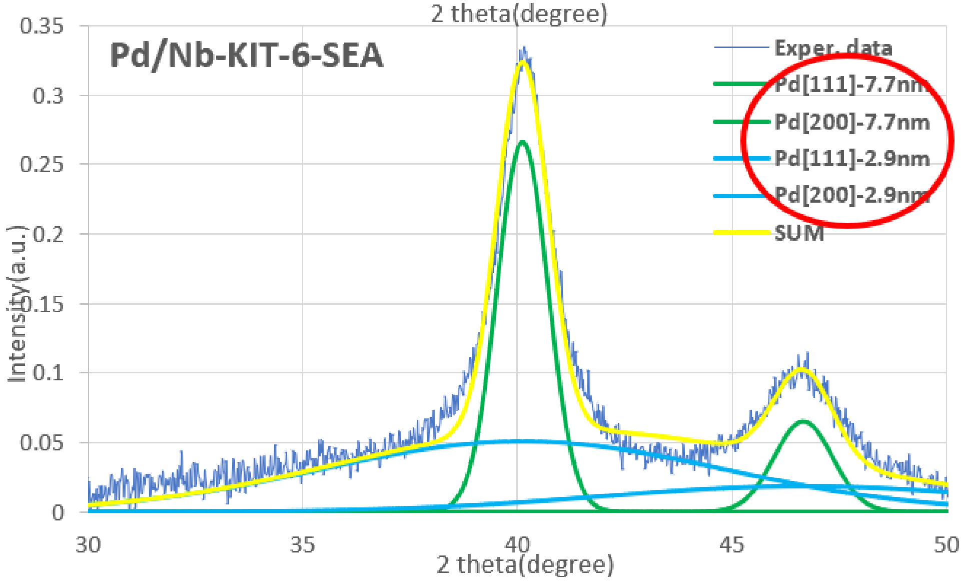
Part Ⅱ - Bifunctional Catalysts Synthesis

--Deconvoluted XRD patterns









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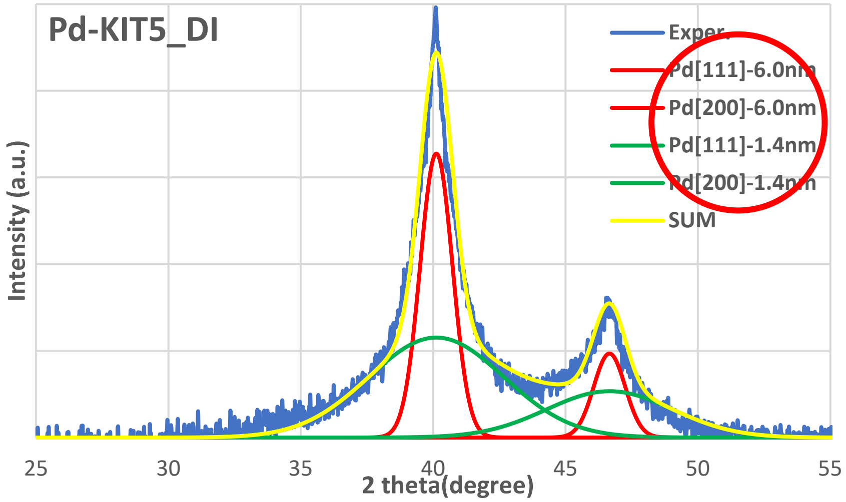
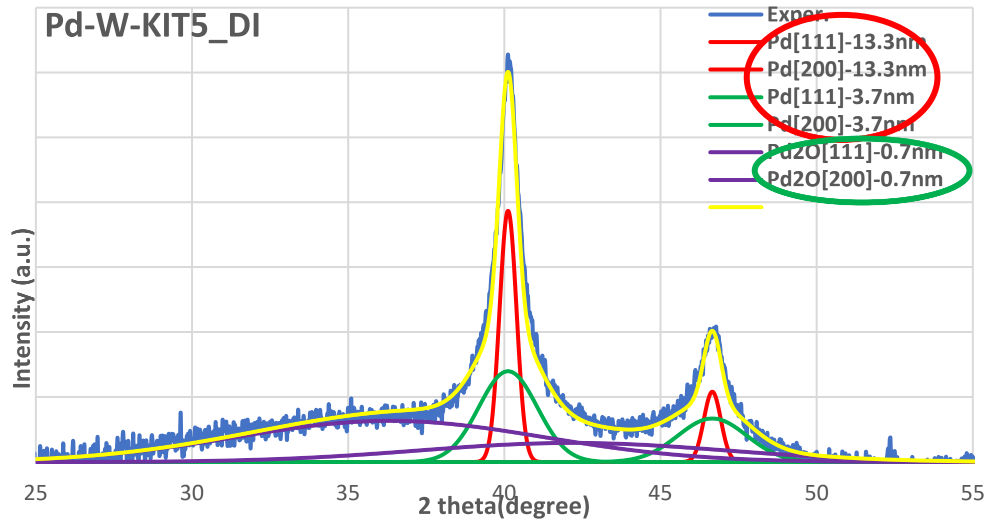
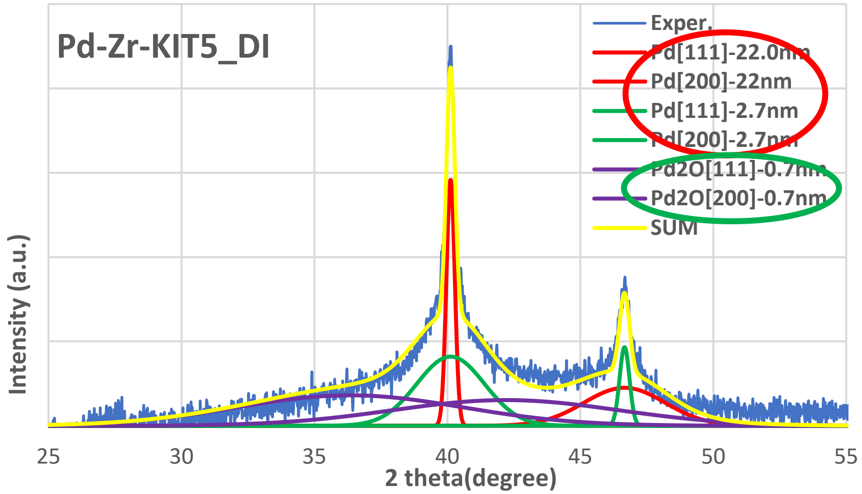
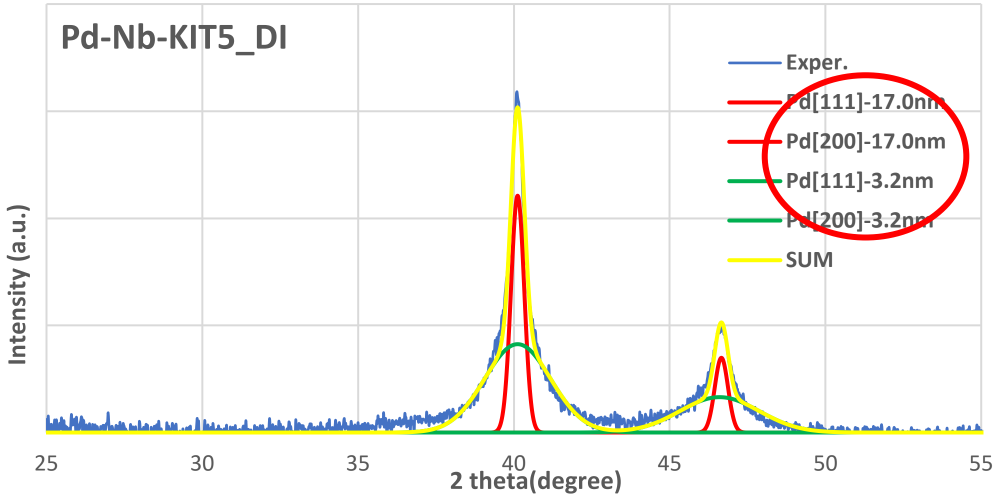
Part Ⅱ - Bifunctional Catalysts Synthesis

--Deconvoluted XRD patterns









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- Bimodal or three different particle sizes can be observed on DI samples, meaning palladium NPs were poorly dispersed.

Part Ⅱ - Bifunctional Catalysts Synthesis

-- Particle size comparison btw. XRD and Chemisorption

Sample-SEA	Pd/KIT5-SEA	Pd/W-KIT5-SEA	Pd/Zr-KIT5-SEA	Pd/Nb-KIT5-SEA	Pd/KIT6-SEA	Pd/W-KIT6-SEA	Pd/Zr-KIT6-SEA	Pd/Nb-KIT6-SEA
d_{XRD}	0.82 nm	0.90 nm	0.86 nm	5.0 nm	0.76 nm	0.78 nm	1.3 nm	5.0 nm
$d_{Chem.}$	1.5 nm	1.4 nm	1.7 nm	5.4 nm	2.0 nm	1.6 nm	1.8 nm	3.4 nm
Metal dispersion	73%	81%	66%	17%	55%	69%	63%	29%
Sample-DI	**Pd/KIT5-DI**	**Pd/W-KIT5-DI**	**Pd/Zr-KIT5-DI**	**Pd/Nb-KIT5-DI**				
d_{XRD}	3.6 nm	3.6 nm	4.0 nm	3.7 nm				
$d_{Chem.}$	3.7 nm	20.4 nm	13.3 nm	36.5 nm				
Metal dispersion	30.2%	4.6%	8.4%	3.1%				

- By SEA method, the particle sizes from XRD and H_2-chemisorption are consistent;
- In the case of DI method, with exception of Pd-KIT5, chemisorption gave larger metallic particles due to the decoration of W, Zr and Nb on the surface of Pd NPs which can inhibit the hydrogen chemisorption and the extent depends on the mobility of the decorated metal; **Will do TPR to verify it.**

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Part Ⅲ-Conclusion and Future work

-- Conclusion

- Acidity of KIT5 and KIT6 can be adjusted by doping different metals(W, Zr, Nb);
- SEA is an effective method to synthesize Pd NPs with ultra-small size.

-- Future work

- ICP - metal (W, Zr, Nb) loss during SEA preparation;
- Ammonia-TPD - acidity of the catalysts;
- γ-valerolactone conversion - catalytic performance.

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Thanks!!!

Questions?

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