



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

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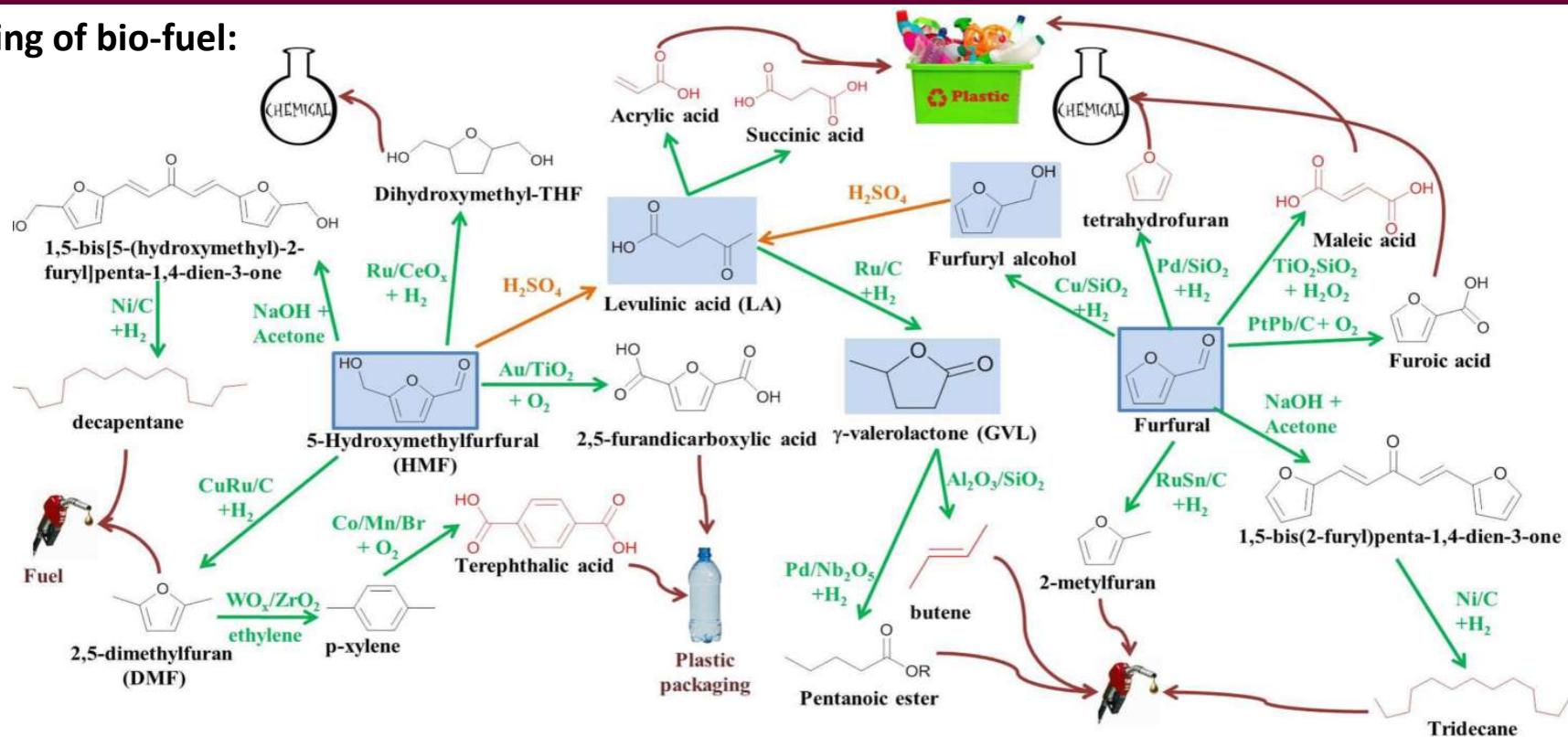
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Overview

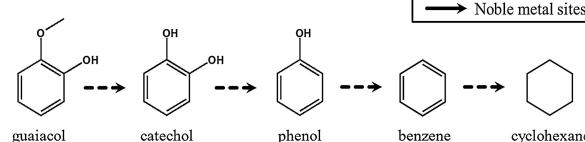
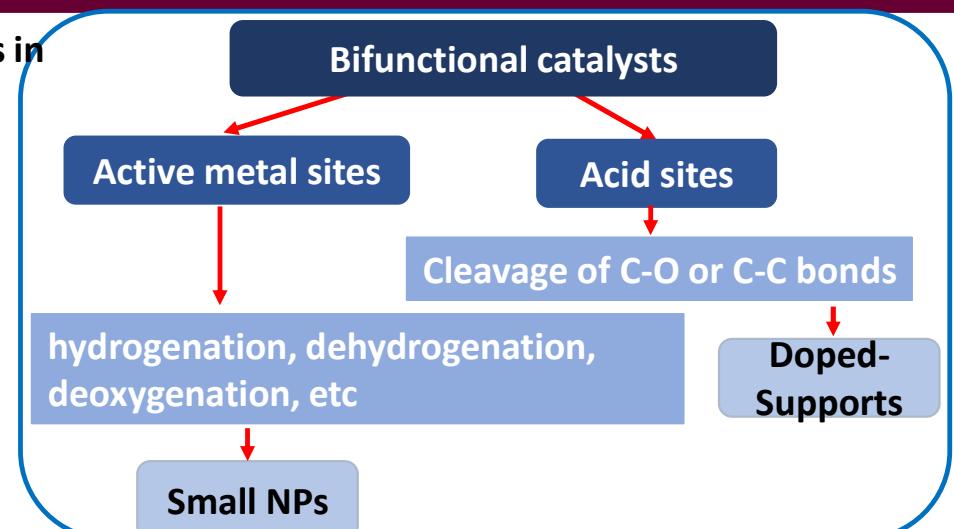
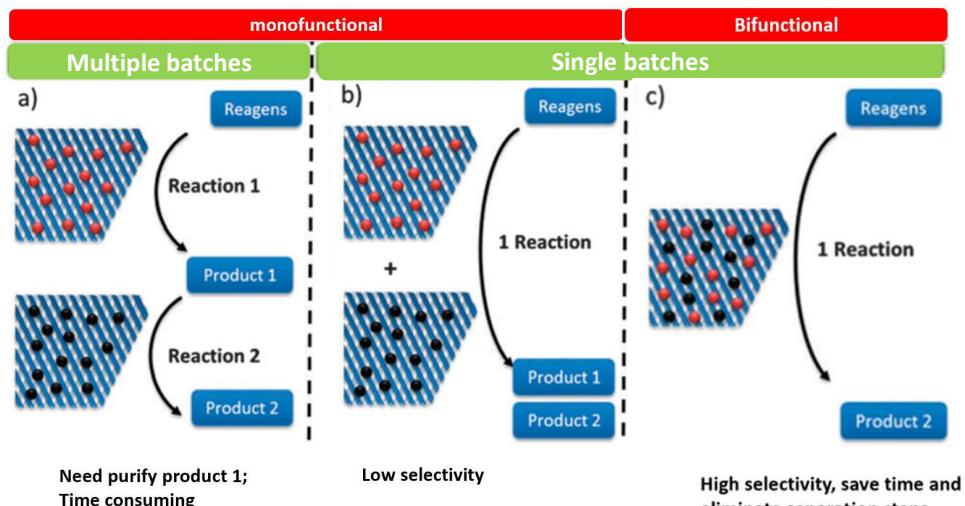
Upgrading of bio-fuel:



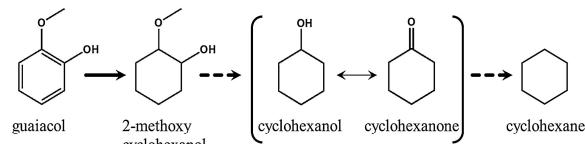
- ❖ Various sequential or cascade-reactions;
- ❖ Different active sites are required to get desired products.

Introduction

- Monofunctional catalysts **✗** cascade- or sequential reactions in one batch;
- Multiple use of monofunctional catalysts-low selectivity, more purification steps, time consuming;
- Bifunctional catalysts in one batch-high selectivity, less separation steps.



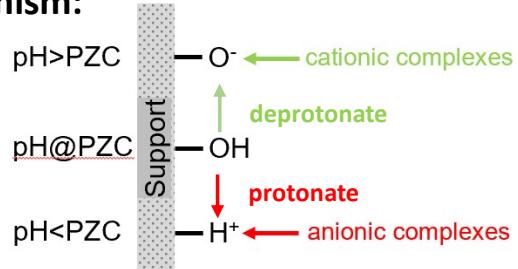
(a) HDO reaction pathway on the acid catalysts



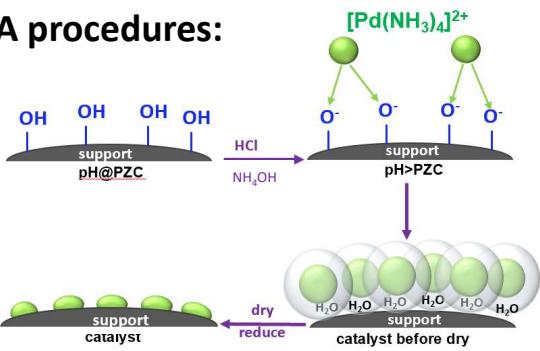
Scheme 1. Pathways for the HDO reaction of guaiacol using an acid catalyst and a bifunctional catalyst (noble metal and acid catalyst) [22].

Introduction

SEA (strong electrostatic adsorption) mechanism:



SEA procedures:



❖ Support surface charged by adjusting solution pH

❖ Adsorb appositively charged metal precursor

❖ Strong precursor-support interaction

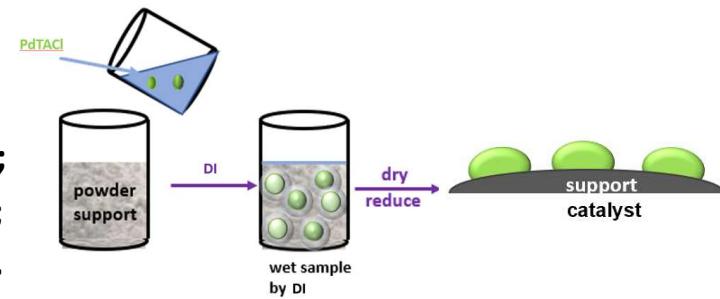
❖ Ultra-small particle size (<2nm)

DI: dry impregnation

❖ Poor precursor-support interaction;

❖ Metal complex migrate in drying or aggregate in reduction;

❖ Large particle and poor metal dispersion.



Objective

Project goal: Synthesize bifunctional catalysts with small Pd NPs and tuned acid sites with high catalytic performance for HDO of methyl-guaiacol.

It can be fulfilled by the following two points:

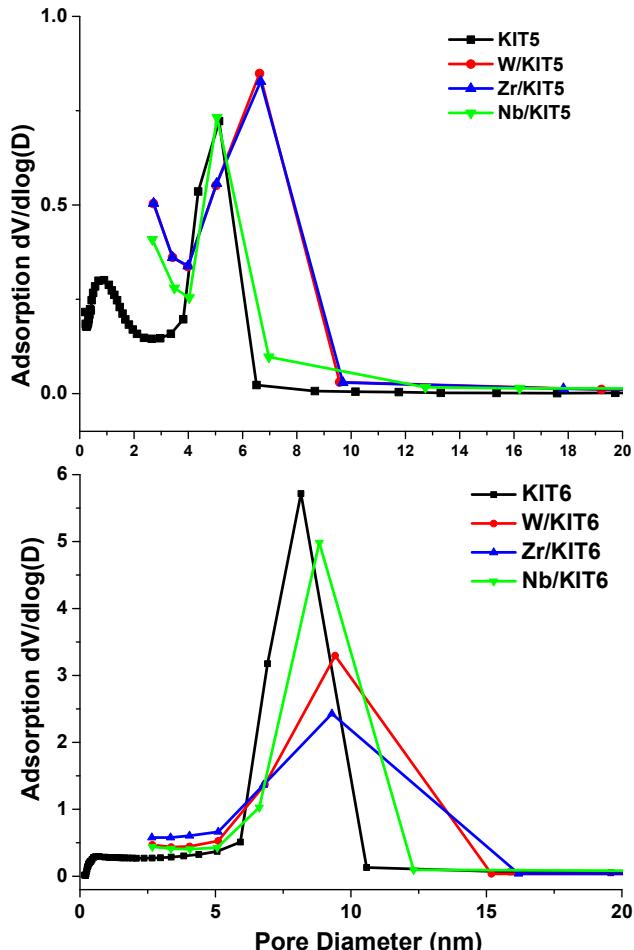
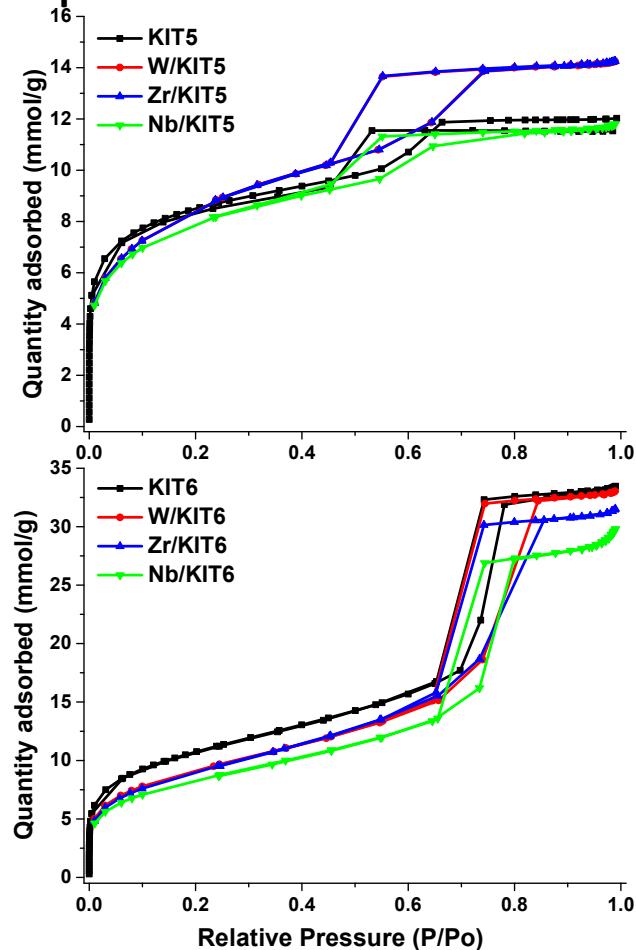
- ❖ **Metal dopants**--tunable acidity.
- ❖ **SEA**--small Pd NPs;

Part I - Metal-doped Silicas

-N_2 sorption for M-doped KIT5 & KIT6

- Isotherm curves:
 • type IV.

- Hysteresis loop:
 • M-KIT5-H2
pore neck,
network effects;
 • M-KIT6-H1
parallel curves,
ordered uniform
large mesopores.



- Pore size distribution:
 • M-KIT5
bimodal,
cage-type;
 • M-KIT6
Ultra-large pores

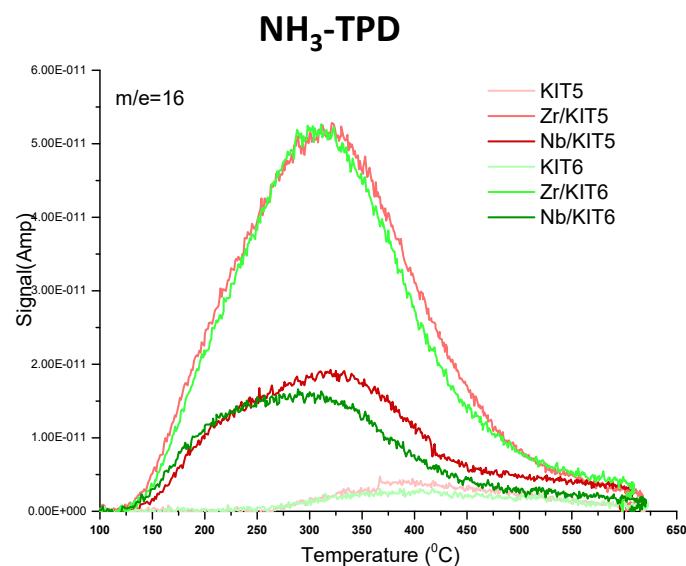
Part I - Metal-doped Silicas

--Surface area, textural structure and acidity

Sample	SA(m^2/g)	$V_{\text{pore}}(\text{cm}^3/\text{g})$	$D_{\text{ave}}(\text{nm})$	Acidity (mmol NH_3/g)
KIT-5	672	0.4	2.4	0.05
W-KIT-5	662	0.5	3.0	0.31*
Zr-KIT-5	661	0.5	3.0	0.63
Nb-KIT-5	635	0.4	2.6	0.25
KIT-6	858	1.2	5.4	0.04
W-KIT-6	713	1.1	6.4	0.48*
Zr-KIT-6	697	1.1	6.2	0.67
Nb-KIT-6	649	1.0	6.3	0.21

* from literature

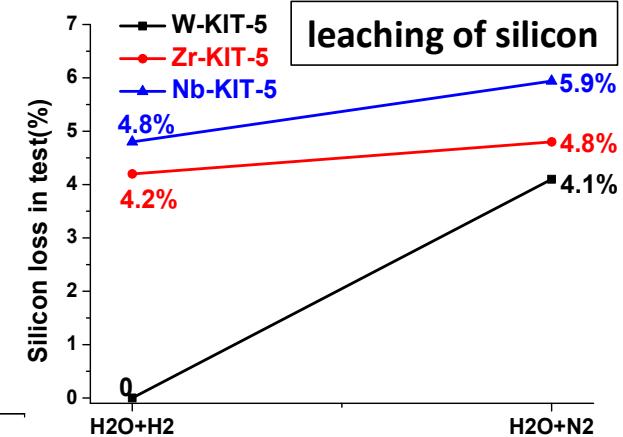
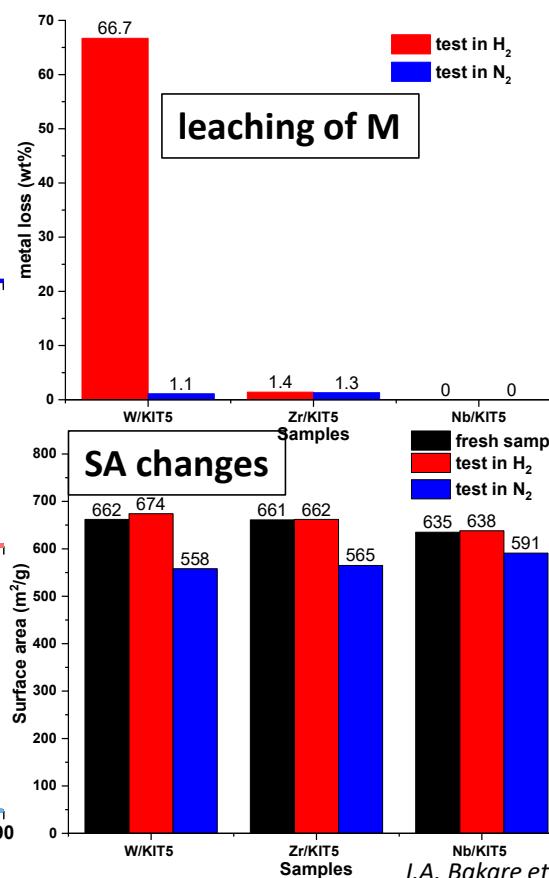
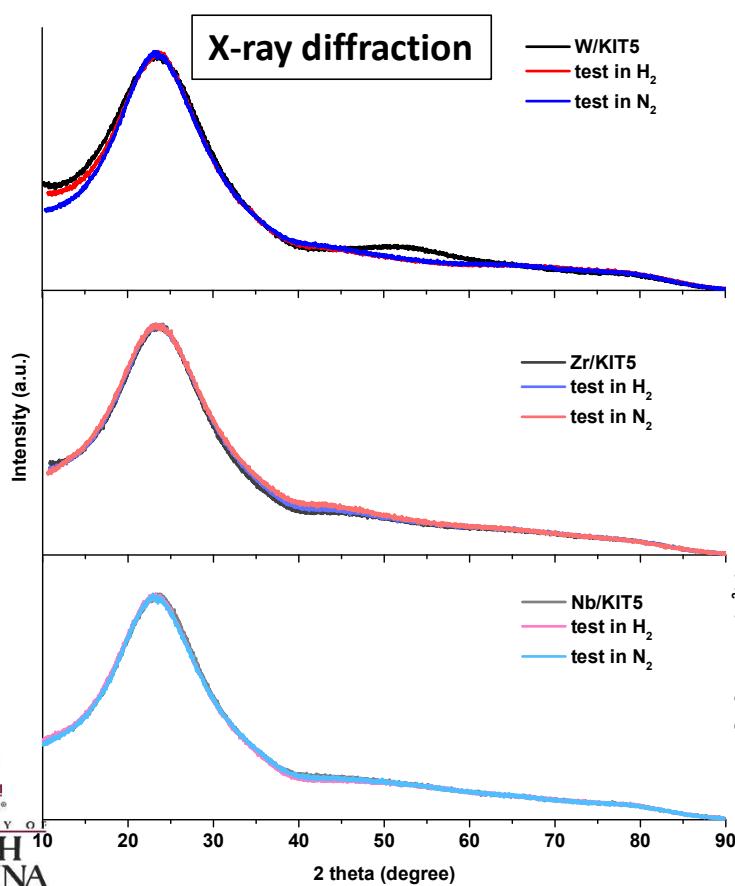
- M-doped KIT6 showed higher surface area and larger pores;
- Metal-dopants induced different amounts of acidity.



Part I - Metal-doped Silicas

--Hydrothermal stability test_XRD, SA loss and leaching

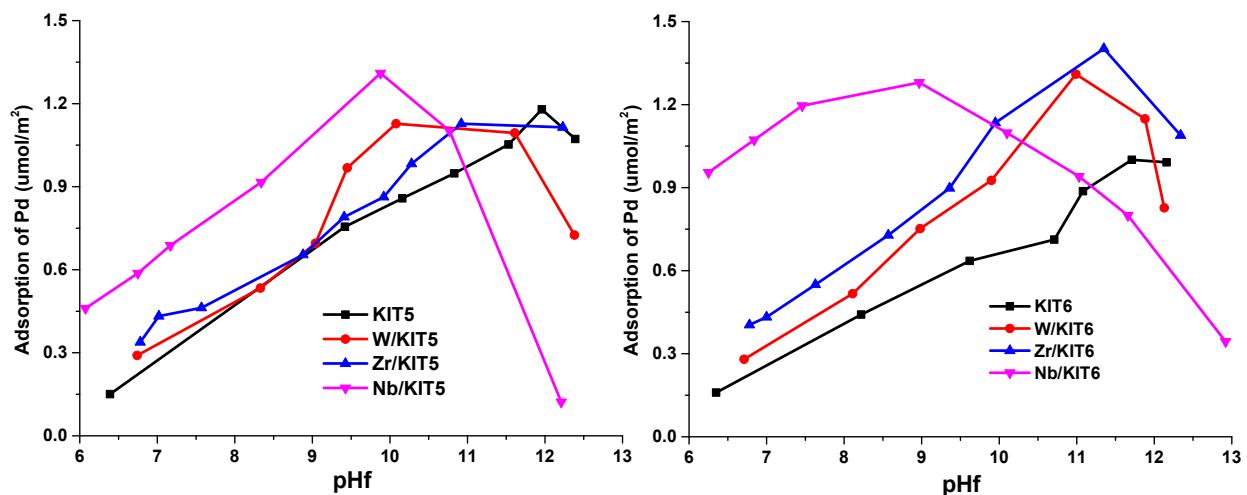
Condition--Temp.:115°C, initial pressure:12.5bar, solvent: DI H₂O, Gas: H₂ or N₂, 1 hr.



- Crystallinity structure of silica preserved;
- Significant leaching of tungsten;
- H₂ decreased the degradation of silica.

Part II- Catalysts Synthesis

Condition: $C_{PdTACl}=200\text{ppm}$, $SL=1000\text{m}^2/\text{L}$, 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.}	12.0	10.1	10.9	9.9	11.7	11.0	11.4	9.0
Γ _{max}	1.2	1.1	1.1	1.3	1.1	1.3	1.4	1.3

- Decreased PZCs and optimal pH over M-doped KIT5 & KIT6 due to the acidic property of metal dopants;
- Introduction of metal dopants hardly change the maximum adsorption of Pd.

Part II- Catalysts Synthesis

Synthesis condition:

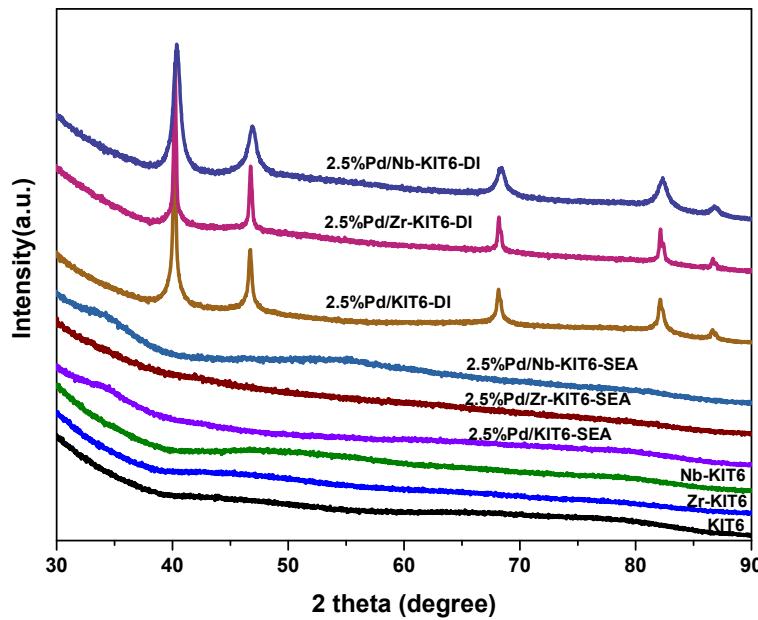
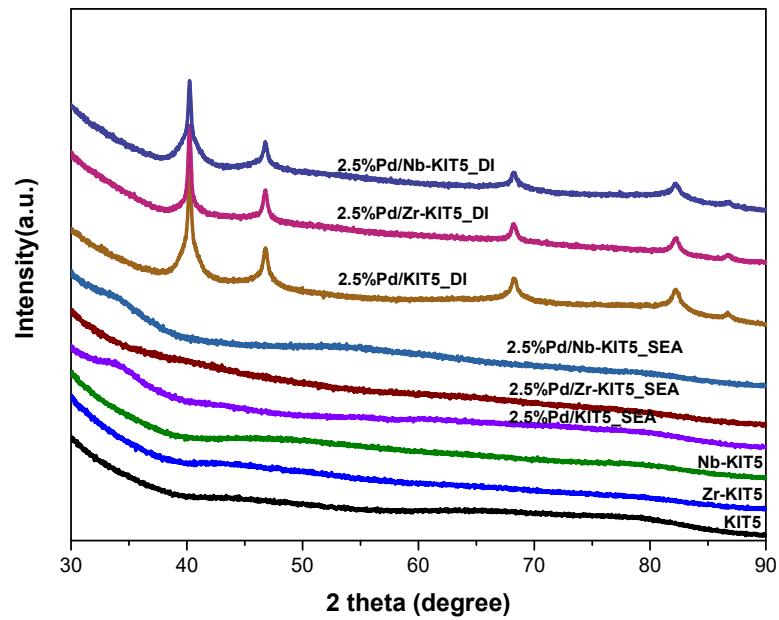
SEA: pH=pH_{opt.}, SA=1000m²/L, shake for 1A^h. catalysts were reduced at 200 °C in 20% H₂/N₂ for 1 hr.

sample	Mass loading of Pd	method
2.5%Pd/KIT5	2.5 wt%	SEA, DI
2.5%Pd/Zr-KIT5	2.5 wt%	SEA, DI
2.5%Pd/Nb-KIT5	2.5 wt%	SEA, DI
2.5%Pd/KIT6	2.5 wt%	SEA, DI
2.5%Pd/Zr-KIT6	2.5 wt%	SEA, DI
2.5%Pd/Nb-KIT6	2.5 wt%	SEA, DI
1.5%Pd/Zr-KIT5	1.5 wt%	SEA
0.75%Pd/Zr-KIT5	0.75 wt%	SEA
0.25%Pd/Zr-KIT5	0.25 wt%	SEA

- From the stability test, leaching of tungsten reached 66.7 wt%, no catalysts with W dopant.

Part III- Catalyst characterization

-X-ray diffraction patterns



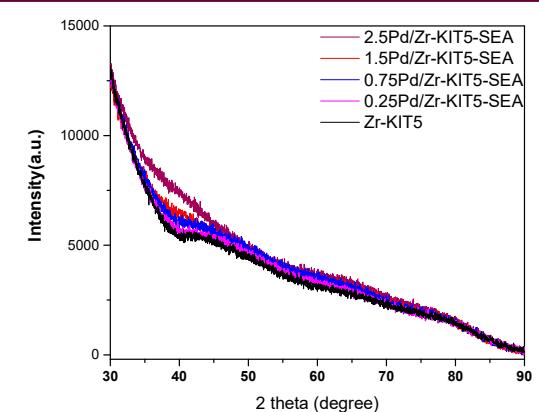
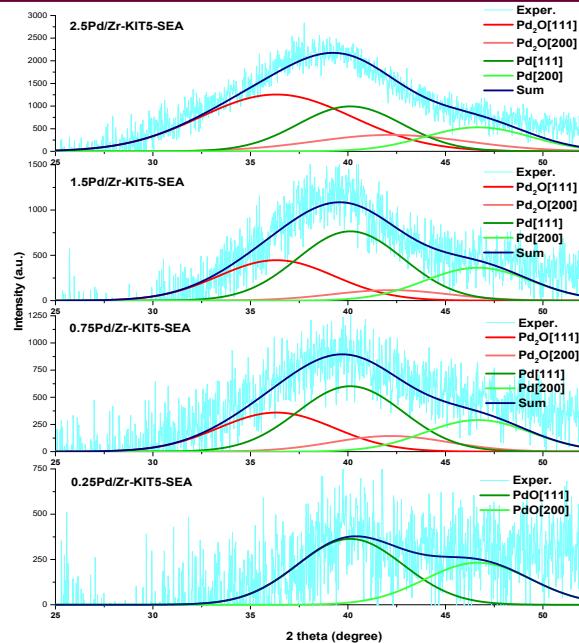
- SEA catalysts showed very broad peaks around 33.8° , which is Pd oxide;
- DI samples showed sharp peaks at positions of metallic Pd;
- SEA method---ultrasmall NPs.

Part III- Catalyst characterization

-Particle Size

Samples	Particle size (nm)	
	by XRD	O ₂ pre-covered H ₂ Chemisorption
2.5Pd/KIT5_SEA	1.5	1.2
2.5Pd/Zr-KIT5_SEA	1.1	1.5
2.5Pd/Nb-KIT5_SEA	1.1	1.5
2.5Pd/KIT5_DI	5.7	3.7
2.5Pd/Zr-KIT5_DI	10.7	14.3
2.5Pd/Nb-KIT5_DI	6.9	24.5
2.5Pd/KIT6_SEA	1.5	2.0
2.5Pd/Zr-KIT6_SEA	0.7	1.7
2.5Pd/Nb-KIT6_SEA	1.4	1.7
2.5Pd/KIT6_DI	12.8	13.7
2.5Pd/Zr-KIT6_DI	11.8	16.5
2.5Pd/Nb-KIT6_DI	6.8	29.0

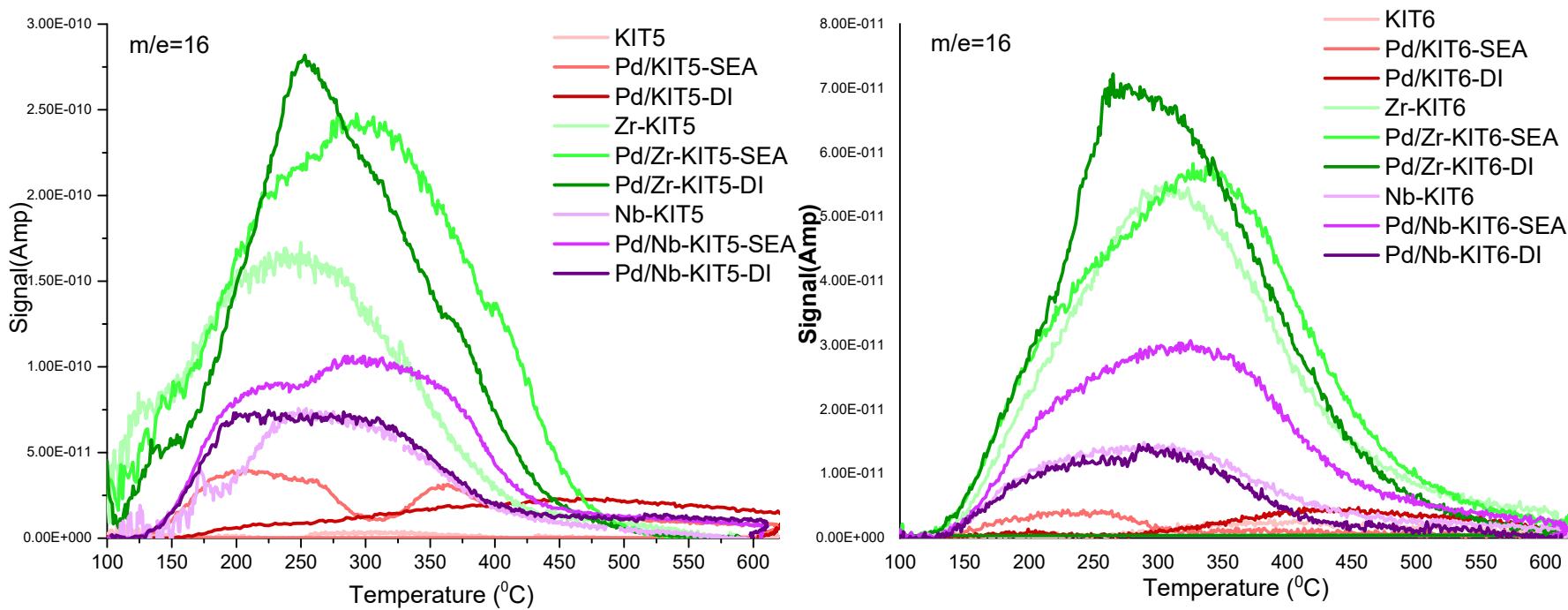
- ❖ Consistent particle size over all the SEA samples and DI sample w/o metal dopant.
- ❖ Larger particles by chemisorption for DI samples with metal-dopants;
- ❖ The particle size for 1.5, 0.75, 0.25 wt% Pd/Zr-KIT5_SEA are around 2.2 nm, larger than the particle size of 2.5wt%.
- ❖ The decoration of Zr and Nb on the surface of Pd NPs resulted in less palladium sites accessing to H₂ and the extent depends on the mobility of the decorated metal.



samples	Particle size(nm)	
	XRD	Chemisorption
2.5Pd/Zr-KIT5_SEA	1.1	1.5
1.5Pd/Zr-KIT5_SEA	1.3	2.2
0.75Pd/Zr-KIT5_SEA	1.3	2.2
0.25Pd/Zr-KIT5_SEA	1.4	2.2

Part III- Catalyst characterization

-NH₃-TPD spectra by mass spectra



- Zr, Nb introduced acidity into the nonacidic KIT5 and KIT6 silicas.

Part III- Catalyst characterization

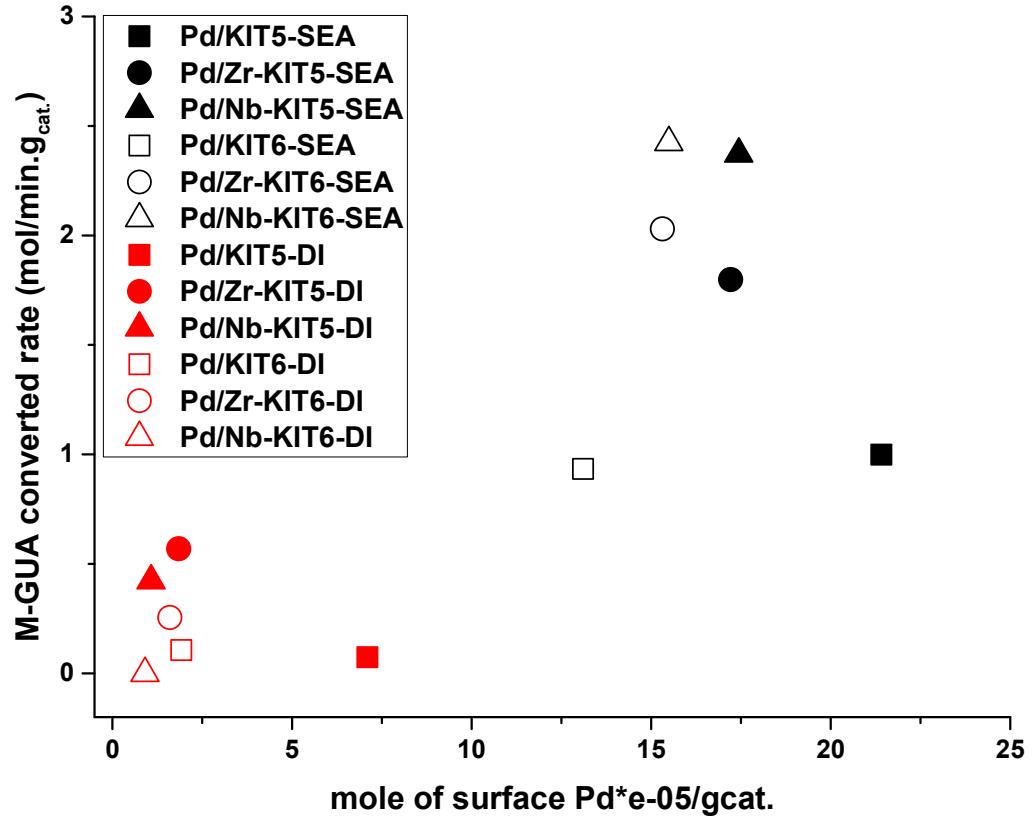
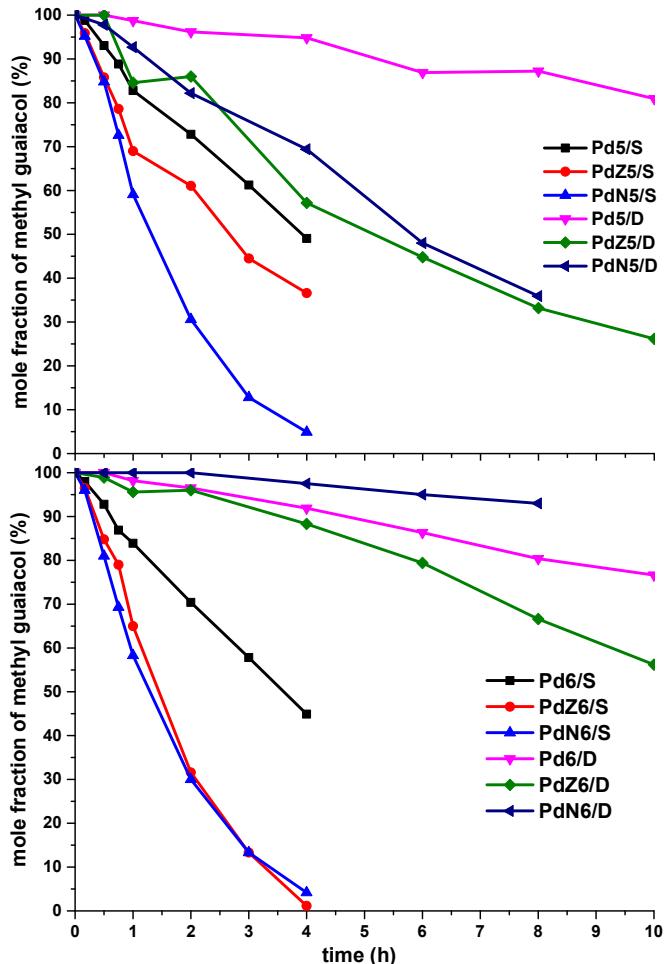
-Acidity from NH₃-TPD

Samples	Total Acidity (mmol NH ₃ /g)	Samples	Total Acidity (mmol NH ₃ /g)
KIT5	0.05	KIT6	0.04
Pd-KIT5-SEA	0.07	Pd/KIT6-SEA	0.03
Pd-KIT5-DI	0.04	Pd/KIT6-DI	0.05
Zr-KIT5	0.63	Zr-KIT6	0.67
Pd/Zr-KIT5-SEA	0.77	Pd/Zr-KIT6-SEA	0.69
Pd/Zr-KIT5-DI	0.67	Pd/Zr-KIT6-DI	0.71
Nb-KIT5	0.25	Nb-KIT6	0.21
Pd/Nb-KIT5-SEA	0.31	Pd/Nb-KIT6-SEA	0.37
Pd/Nb-KIT5-DI	0.23	Pd/Nb-KIT6-DI	0.20

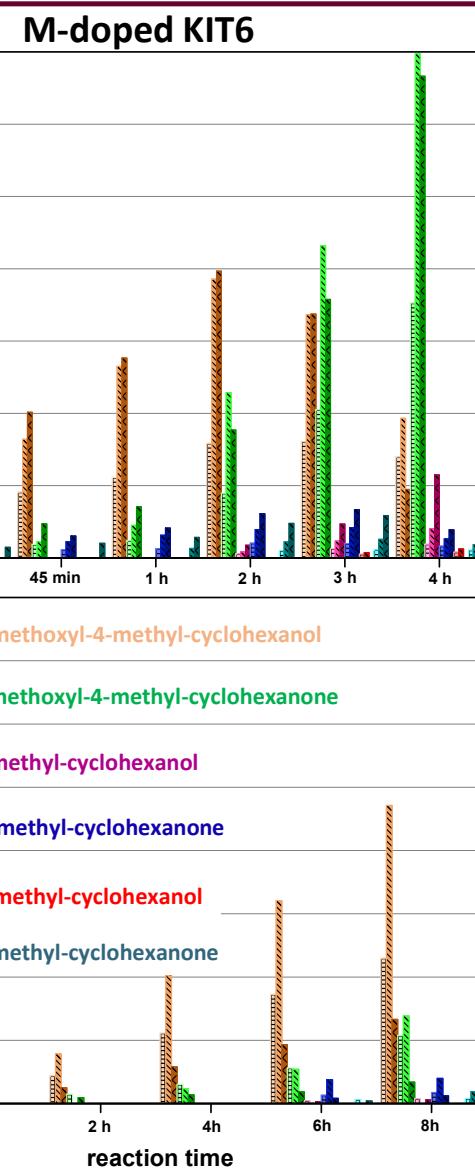
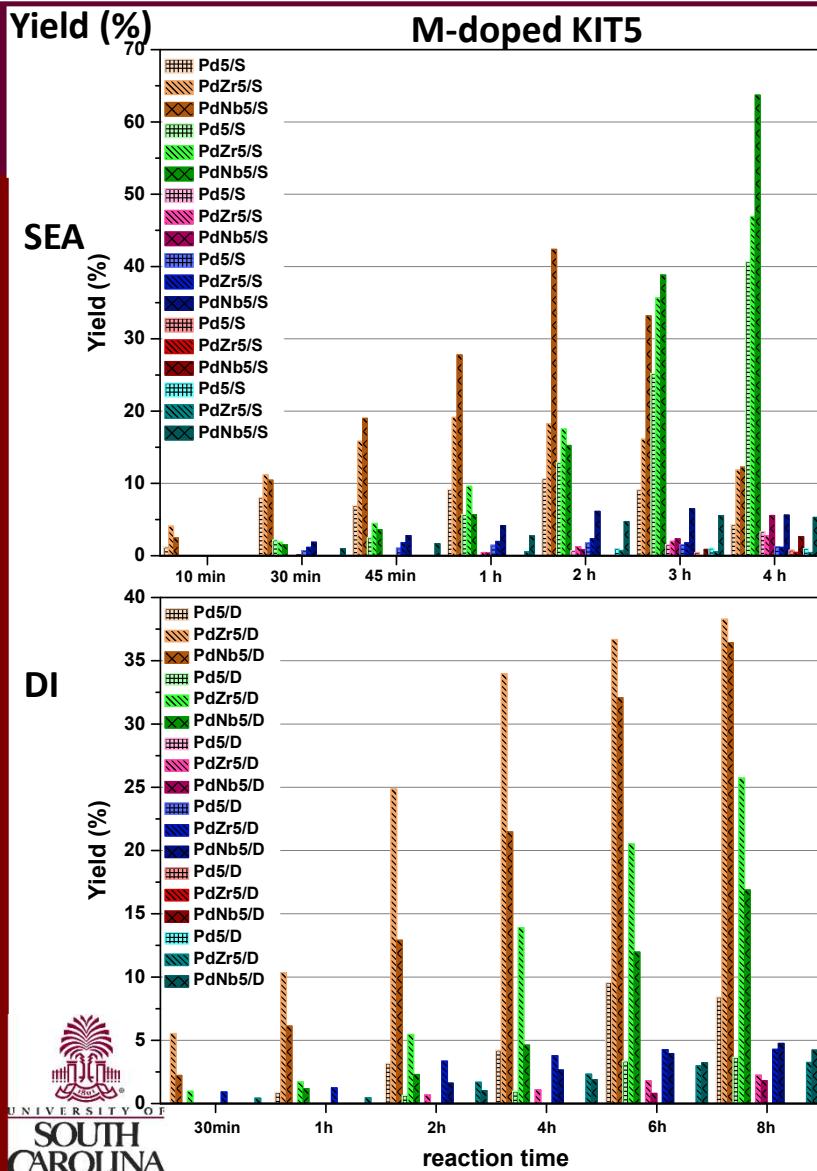
- Acidity of samples without metal-dopant is negligible.
- The acidity of catalysts and supports is similar;
- Zr introduced a larger amount of acidity than Nb.

Part IV- Catalyst evaluation

-HDO of methyl guaiacol Reaction condition: 115°C, 12.5bar, 900rpm, SEA run for 4 hrs, DI run for 10 hrs.



- **SEA samples:**
higher reaction rates;
smaller particles.
- **With M-dopants:**
higher reaction rates;
acidity.



Bifunctional catalysts by SEA:

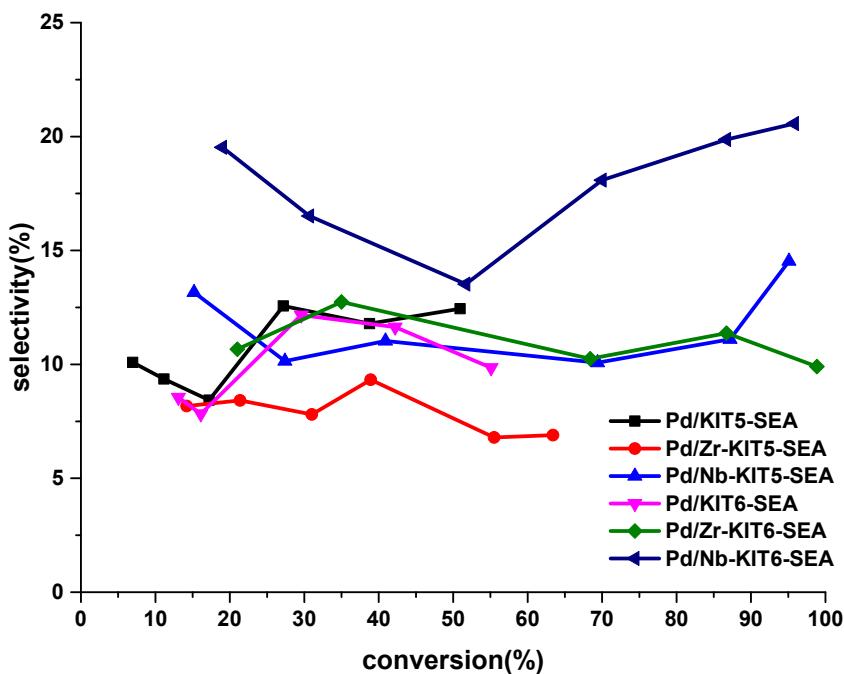
- 2-methoxyl-4-methyl-cyclohexanol increased then decreased;
- 2-methoxyl-4-methyl-cyclohexanone is the main product
- Bifunctional catalysts showed higher activity than the monofunctional ones.

Bifunctional catalysts by DI:

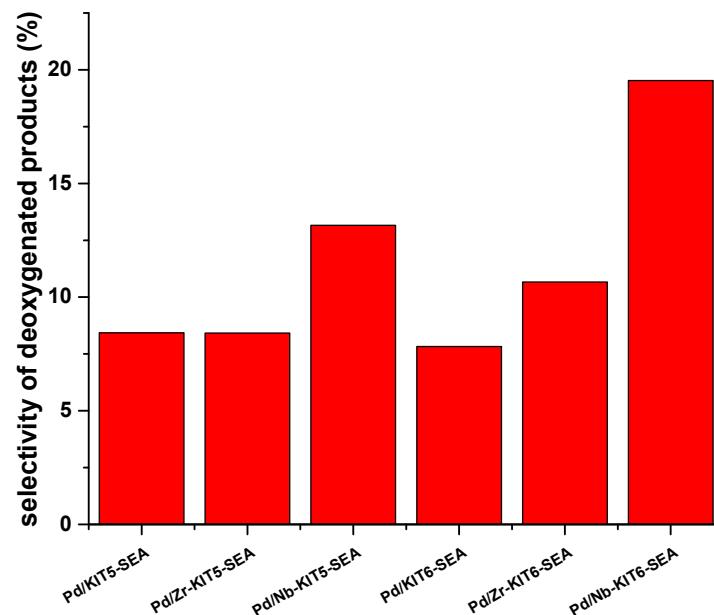
- The total yield of the products by DI is lower than SEA samples;
- 2-methoxyl-4-methyl-cyclohexanol is the main product.

Part IV- Catalyst evaluation

Selectivity vs conversion



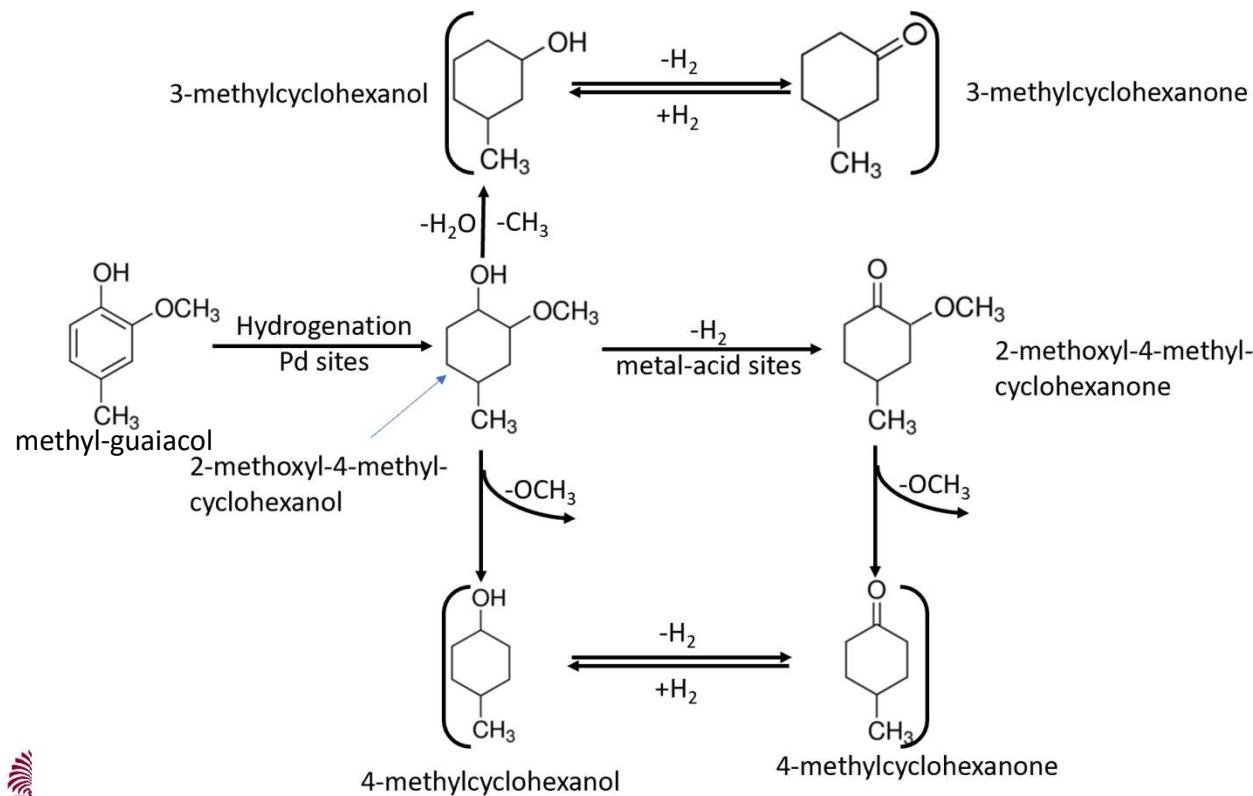
Selectivity of deoxygenated products



- Selectivity is independent with the conversion;
- Nb-doped bifunctional SEA samples higher selectivity may be due to an optimal ratio of acidic sites to Pd sites.

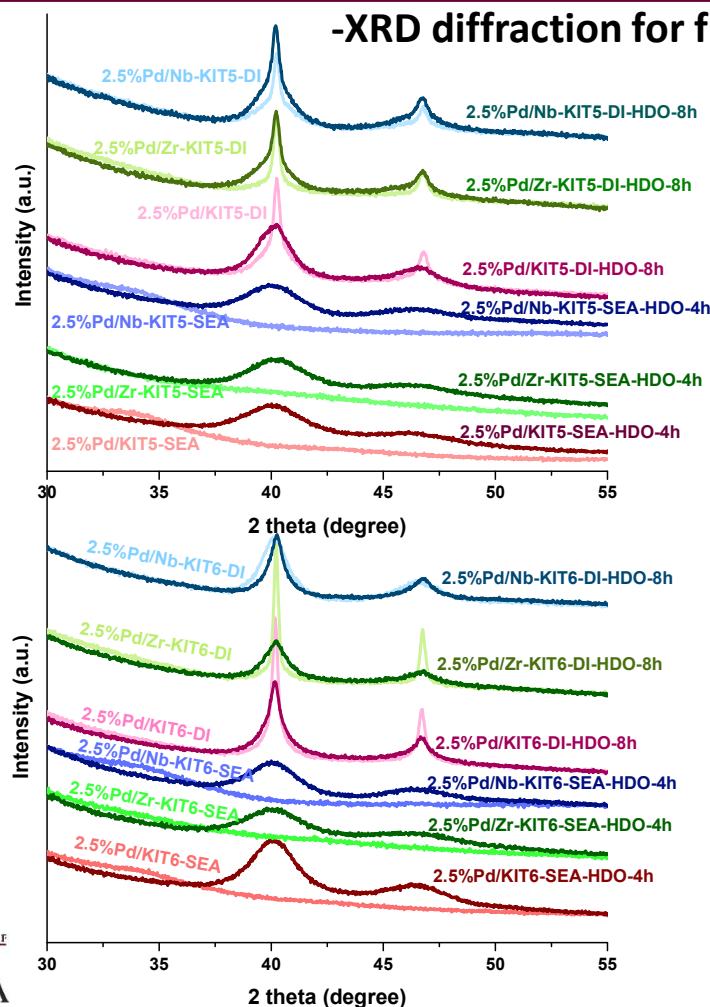
Part IV- Catalyst evaluation

-HDO reaction pathways



- **Hydrogenation**
benzene ring over Pd sites;
- **Dehydrogenation**
via hydroxyl over Pd-acid sites;
- **Demethoxylation**
via C_6-OCH_3 over metal-acid sites;
- **Demethylation**
via C_6O-CH_3 over metal-acid sites.

Part IV- Catalyst evaluation



Samples	Particle size(nm) by XRD		Pd leached (wt%)
	bf.reaction	HDO 4hrs	
2.5Pd/KIT5_SEA	1.5	2.2	0.130
2.5Pd/Zr-KIT5_SEA	1.3	2.3	0.133
2.5Pd/Nb-KIT5_SEA	1.1	2.4	0.145
2.5Pd/KIT6_SEA	1.5	2.6	0.125
2.5Pd/Zr-KIT6_SEA	0.7	1.8	0.125
2.5Pd/Nb-KIT6_SEA	1.4	3.0	0.125

Samples	Particle size(nm) by XRD		Pd leaching (%)
	bf.reaction	HDO 8hrs	
2.5Pd/KIT5_DI	5.7	3.4	0.143
2.5Pd/Zr-KIT5_DI	10.7	5.7	0.148
2.5Pd/Nb-KIT5_DI	6.9	6.5	0.140
2.5Pd/KIT6_DI	12.8	6.5	0.140
2.5Pd/Zr-KIT6_DI	11.8	4.3	0.130
2.5Pd/Nb-KIT6_DI	6.8	7.2	0.137

- Leaching of Pd in HDO is the same over SEA and DI catalysts;
- SEA catalysts: particle size increased due to metal sintering;
- DI catalysts: particle size decreased due to NPs restructuring.

Part V- 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;
- The catalytic performance of bifunctional catalysts strongly depends on the number of surface Pd sites and the acidity of the metal-dopants.



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Thanks!!!

Questions?

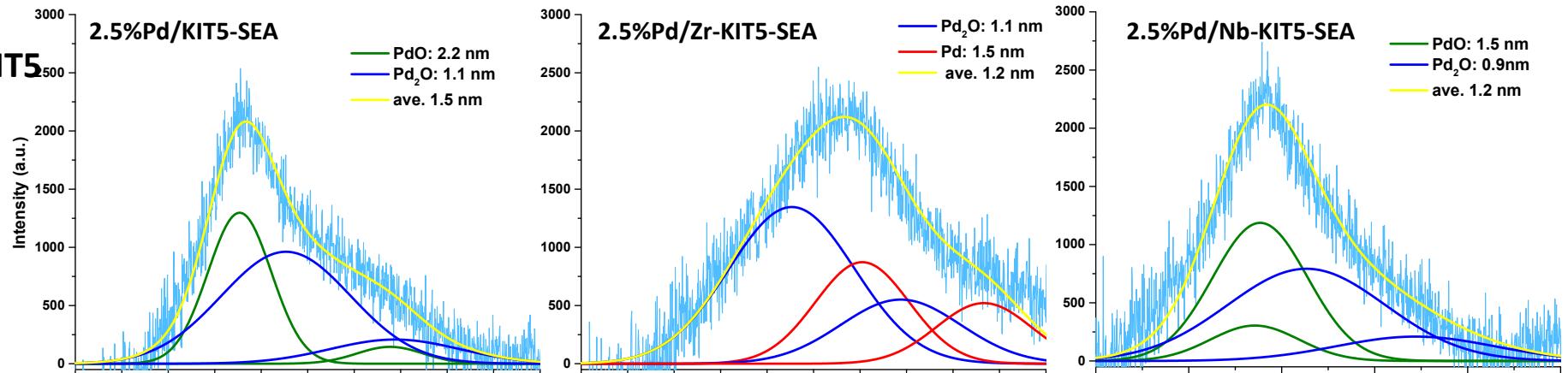


Part III- Catalyst characterization

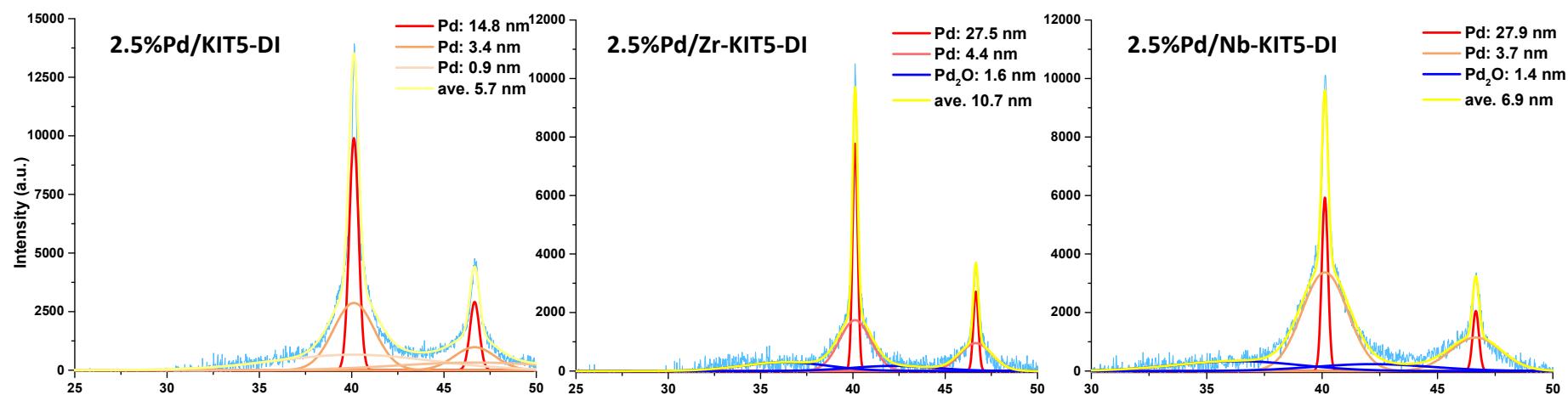
-XRD fitting

2.5%Pd/M-KIT5

SEA



DI

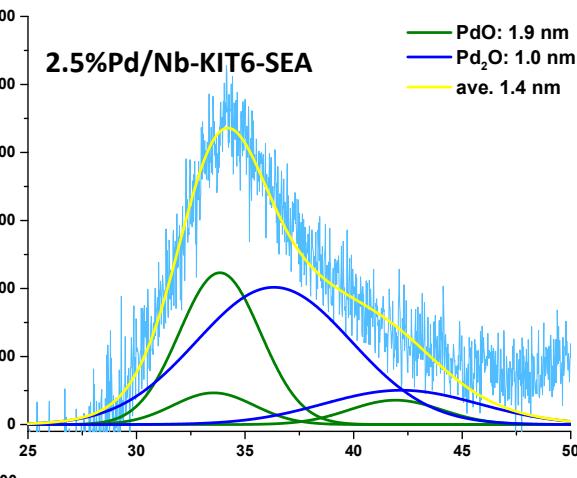
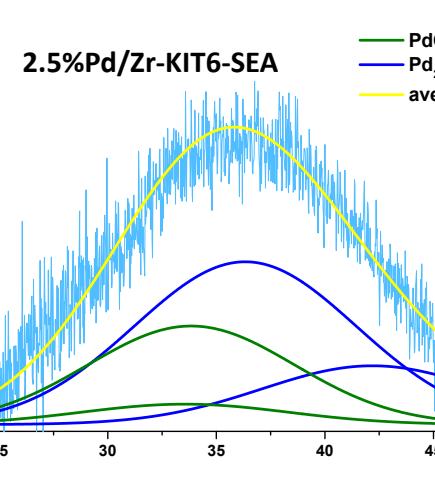
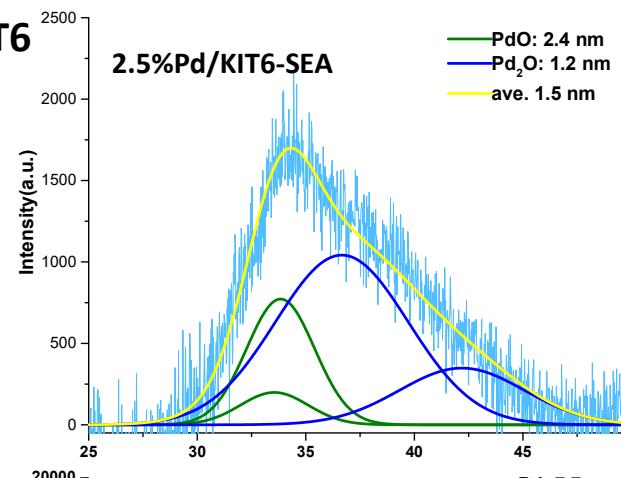


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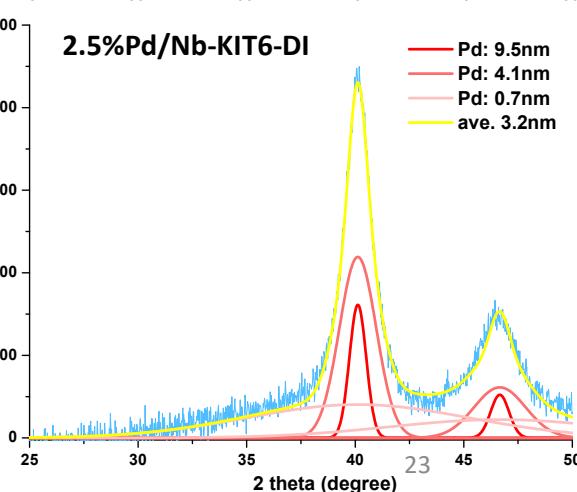
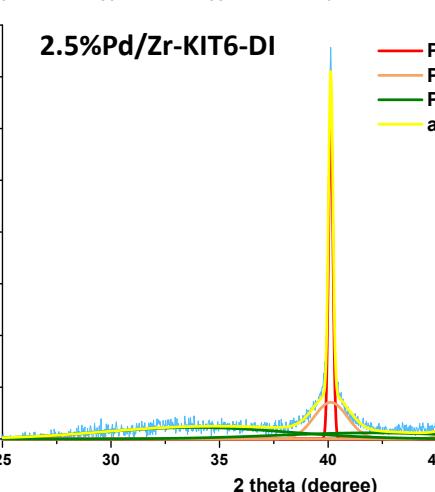
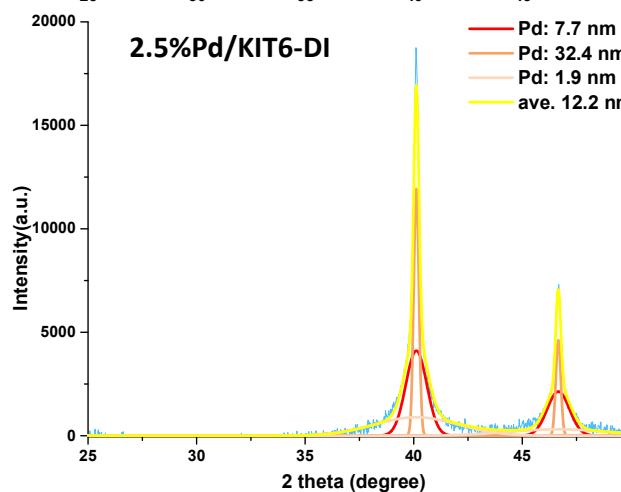
-XRD fitting

2.5%Pd/M-KIT6

SEA

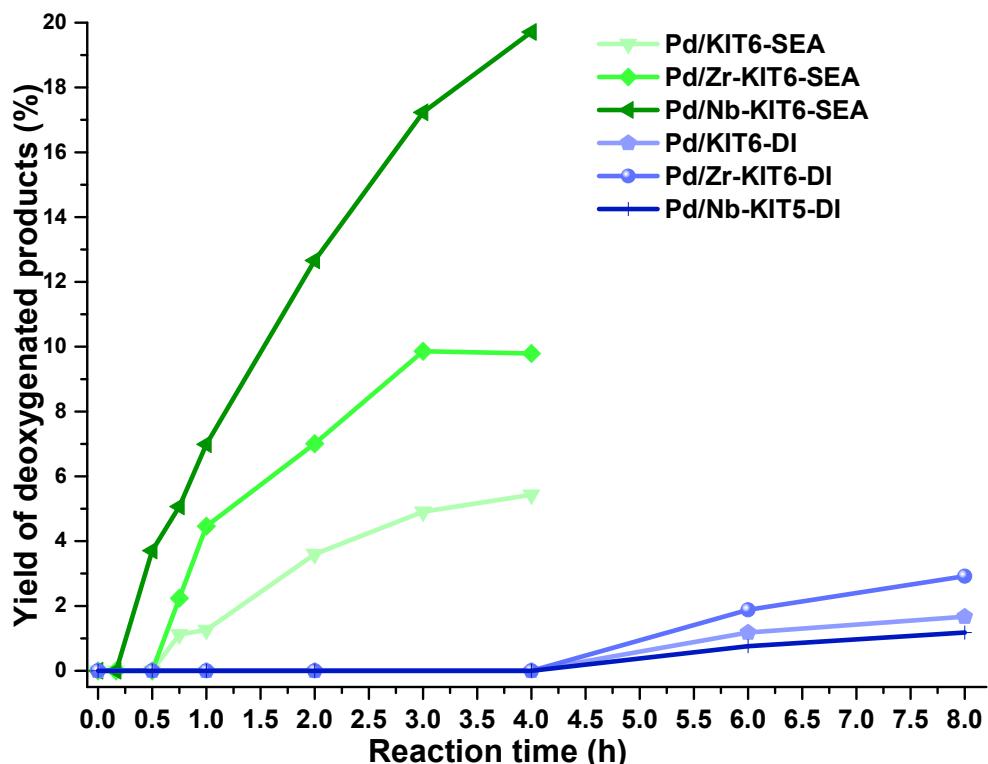
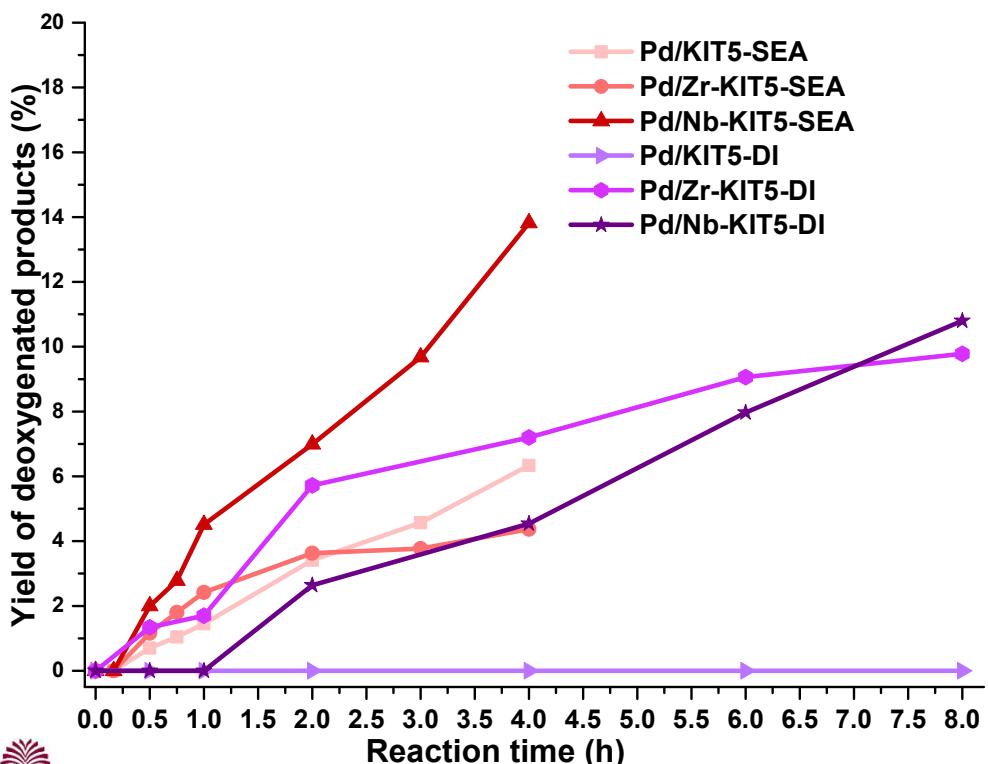


DI



Part IV- Catalyst evaluation

-Total yields of deoxygenated products



- Total yields of deoxygenated products over SEA catalysts are higher;
- Nb introduced the optimal balance of acid sites : Pd sites;

