

# A Stability Analysis of Electroless Deposition Derived Ni-Pt Catalysts for the Dry Reforming of Methane

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# Introduction

## Dry Reforming of Methane



## Side Reactions

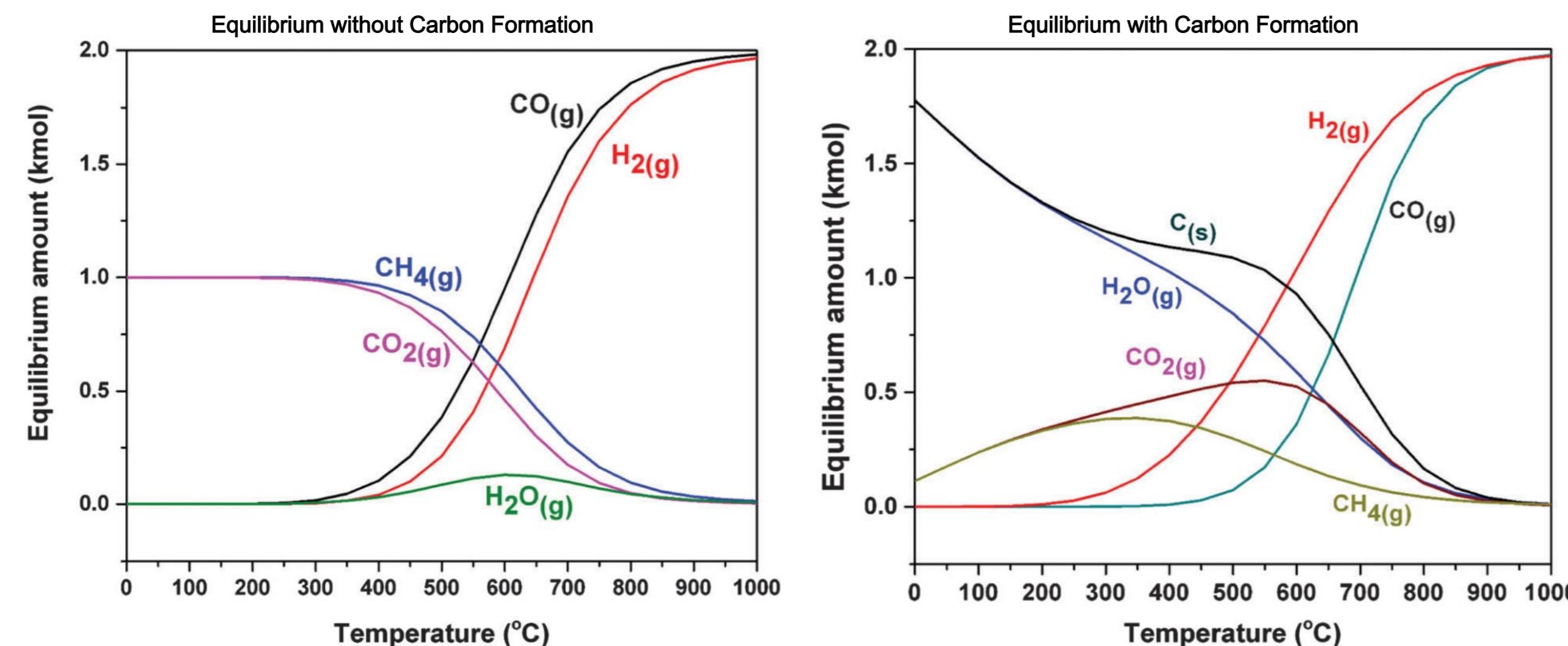
Reverse water -gas shift



Methane decomposition



Boudouard reaction

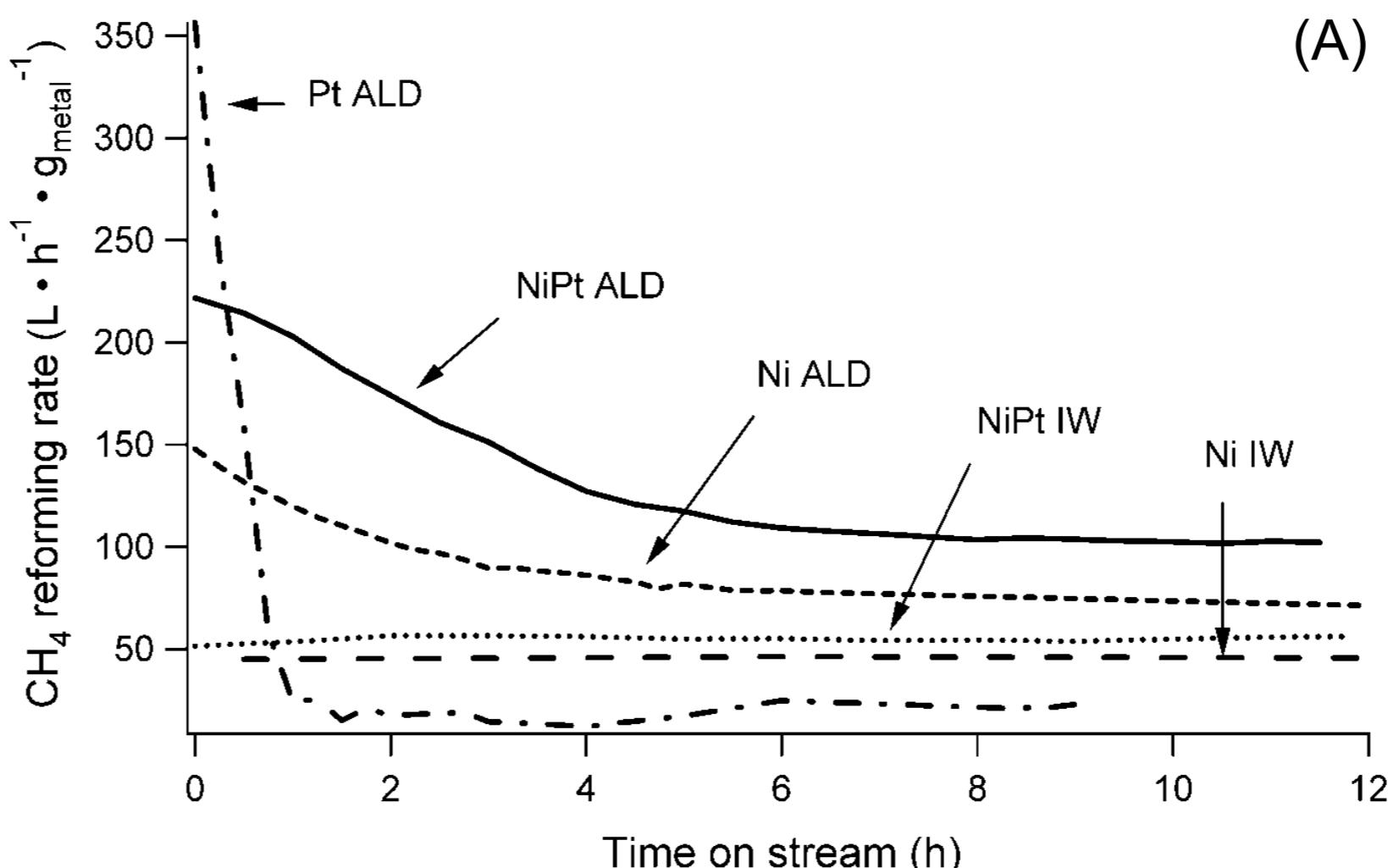


# Why Ni -Pt?

01

## Ni -Pt: Atomic Layer Deposition

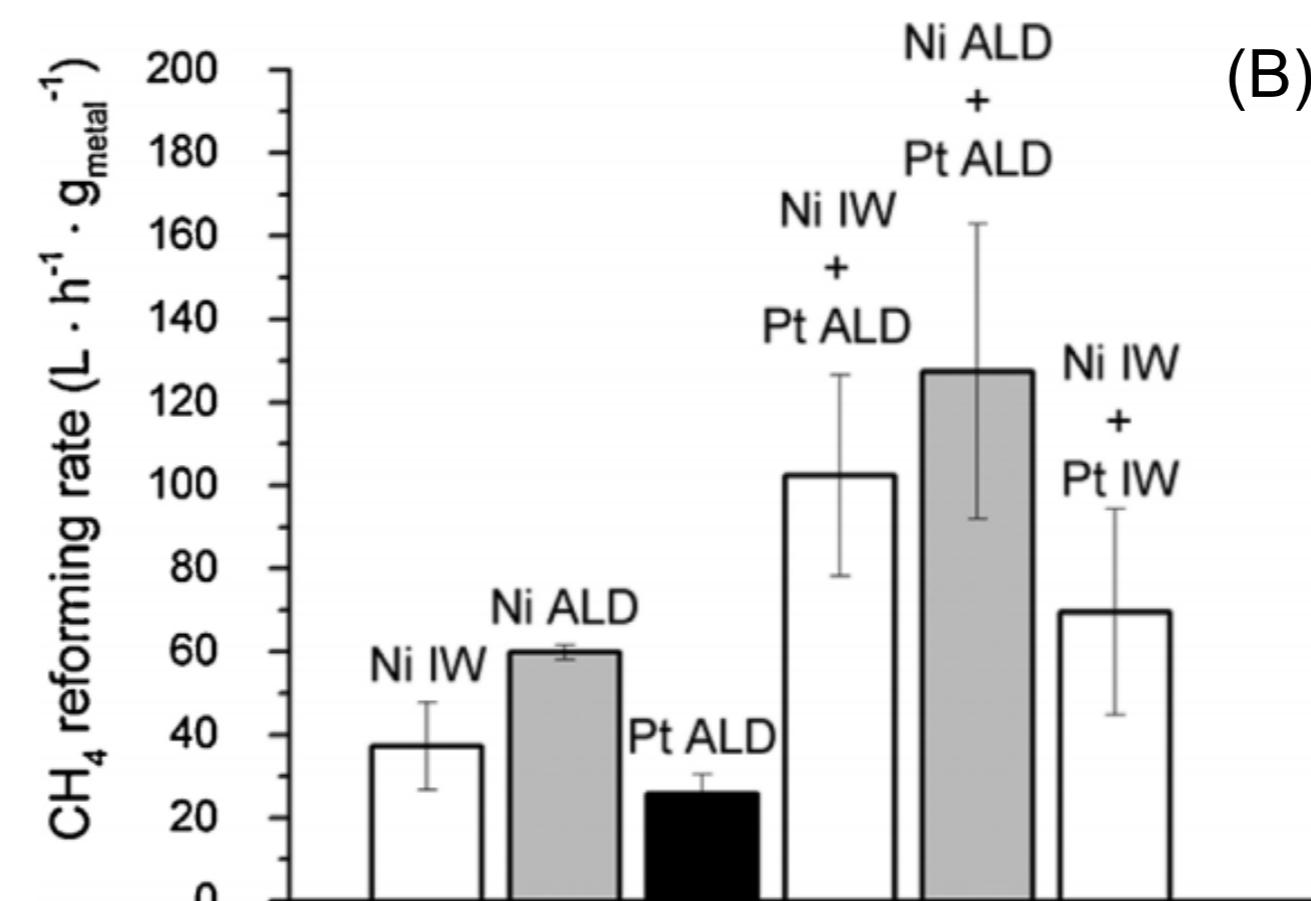
- Previous studies have shown Pt can improve both stability (Figure A) and activity (Figure B).
- Greater stability is attributed to a reduction of the Nickel (Ni) ensemble which reduces the rate of complete CH decomposition to Carbon.
- Improved activity is thought to be the result of Pt assisted NiO reduction which enhances surface hydroxyl formation.



02

## Ni -Pt: Electroless Deposition

- Compared with ALD, ED can produce highly structured surfaces with greater potential for industrial scalability.
- Platinum (Pt) is place directly on the Nickel (Ni) maximizing bimetallic interaction.
- Final particle size and composition can be controlled to a target specification.

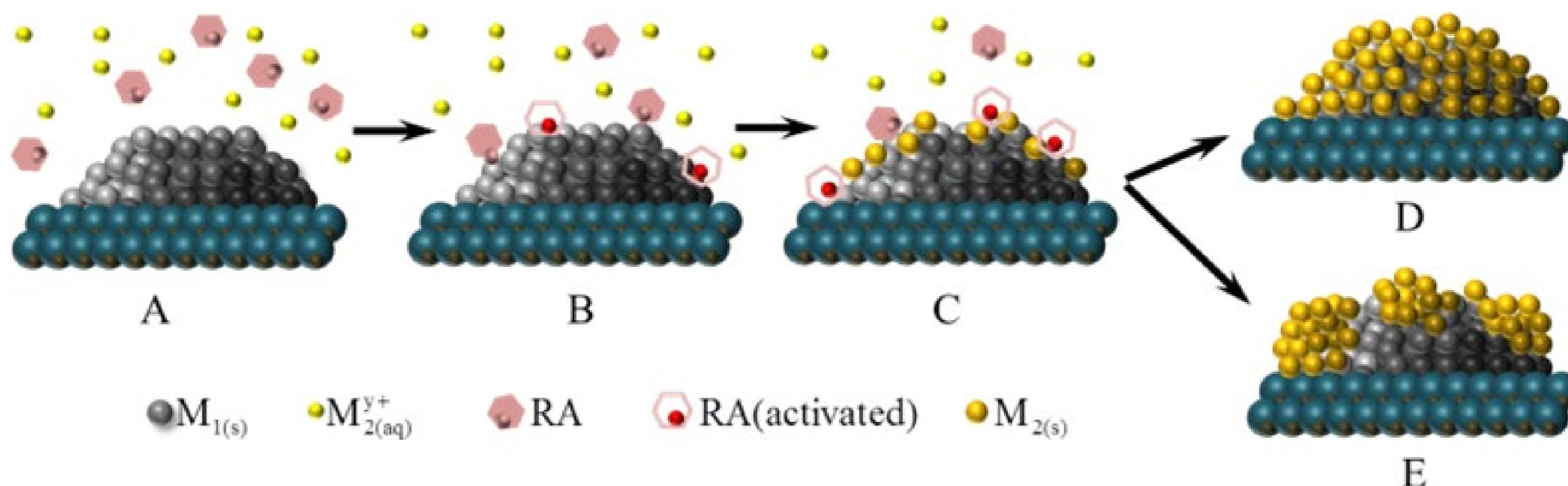


# Electroless Deposition (ED)

$$(1) \ Rate_{ThermalRxn} = (k'_o)(e^{-E'_a/RT})(C_{RA})^\alpha(C_{Msalt})^\beta$$

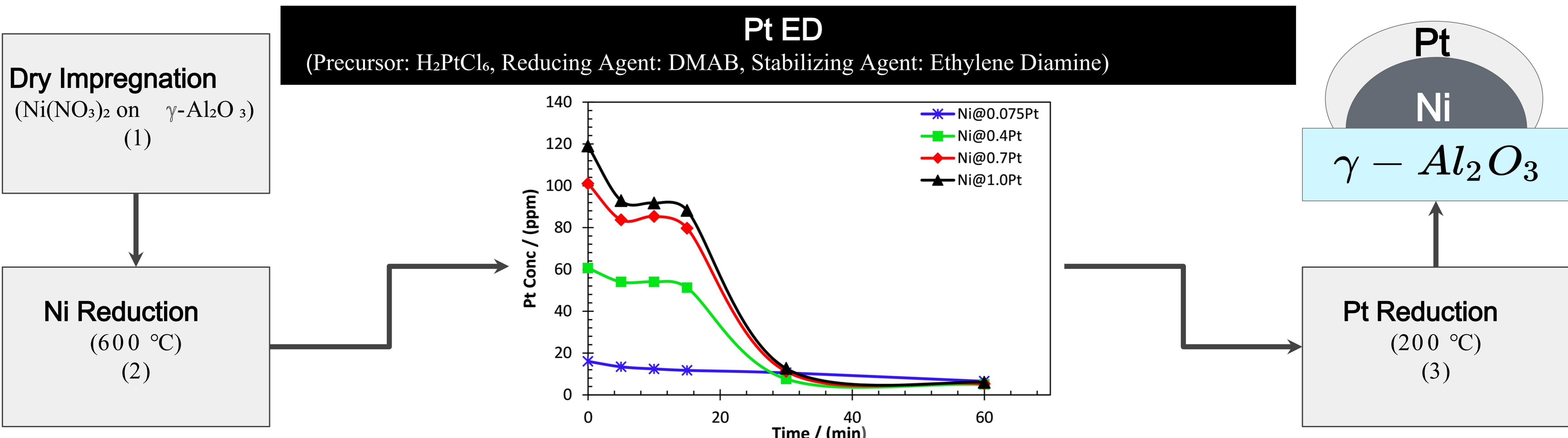
$$(2) \ Rate_{depMonA} = (k''_o)(e^{-E''_a/RT})(C_{RA})^\alpha(C_{Msalt})^\beta(C_{Asites})^\gamma$$

$$(3) \ Rate_{depMonM} = (k'''_o)(e^{-E'''_a/RT})(C_{RA})^\alpha(C_{Msalt})^\beta(C_{Msites})^\gamma$$

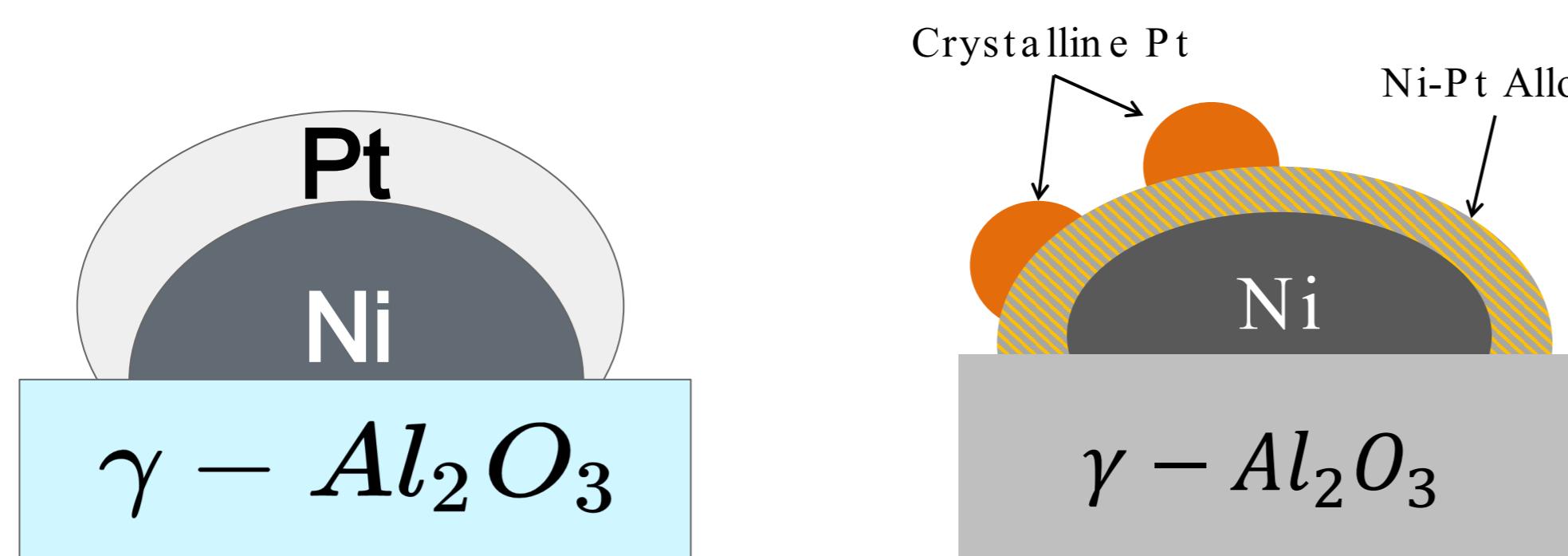
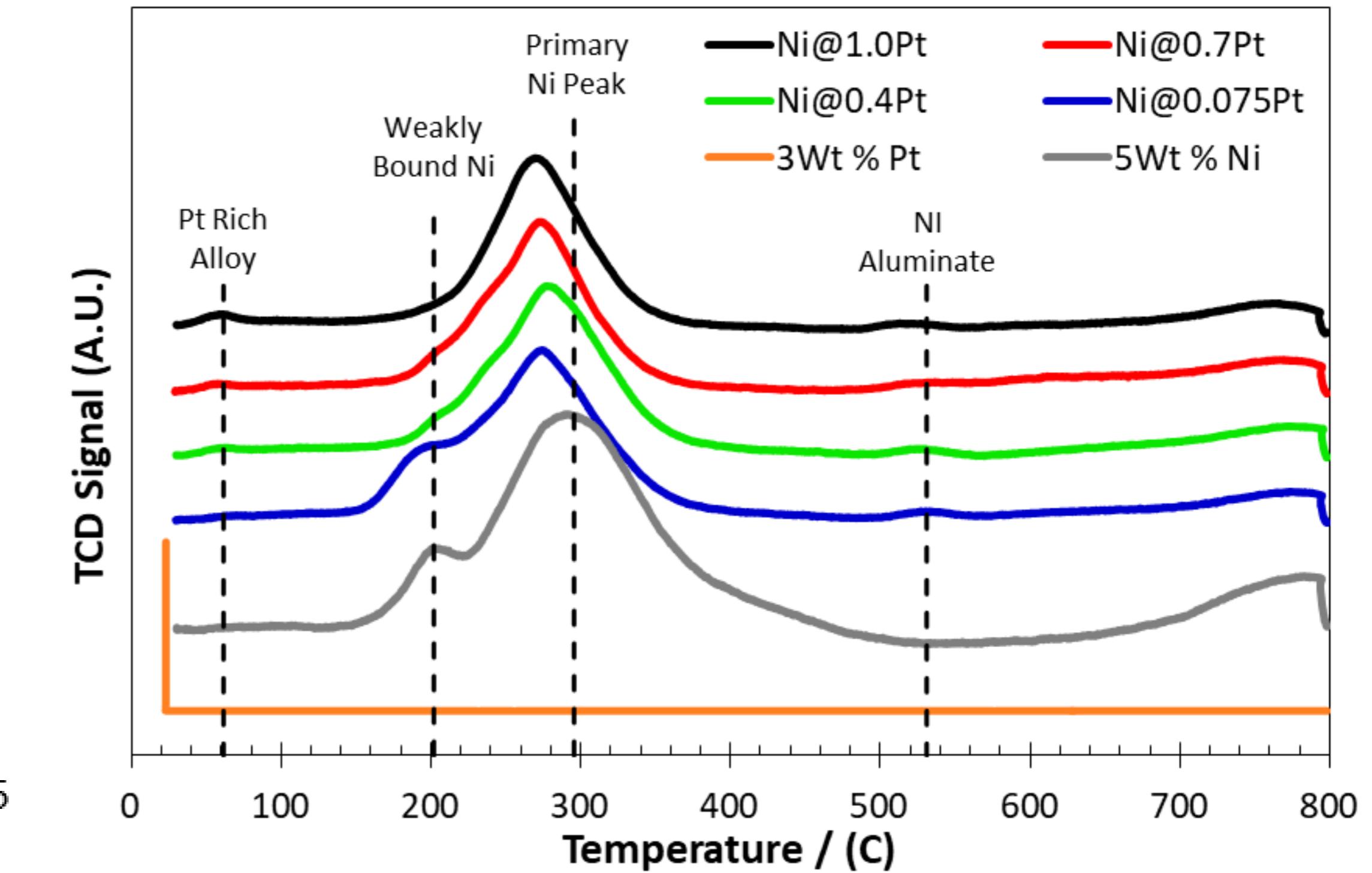
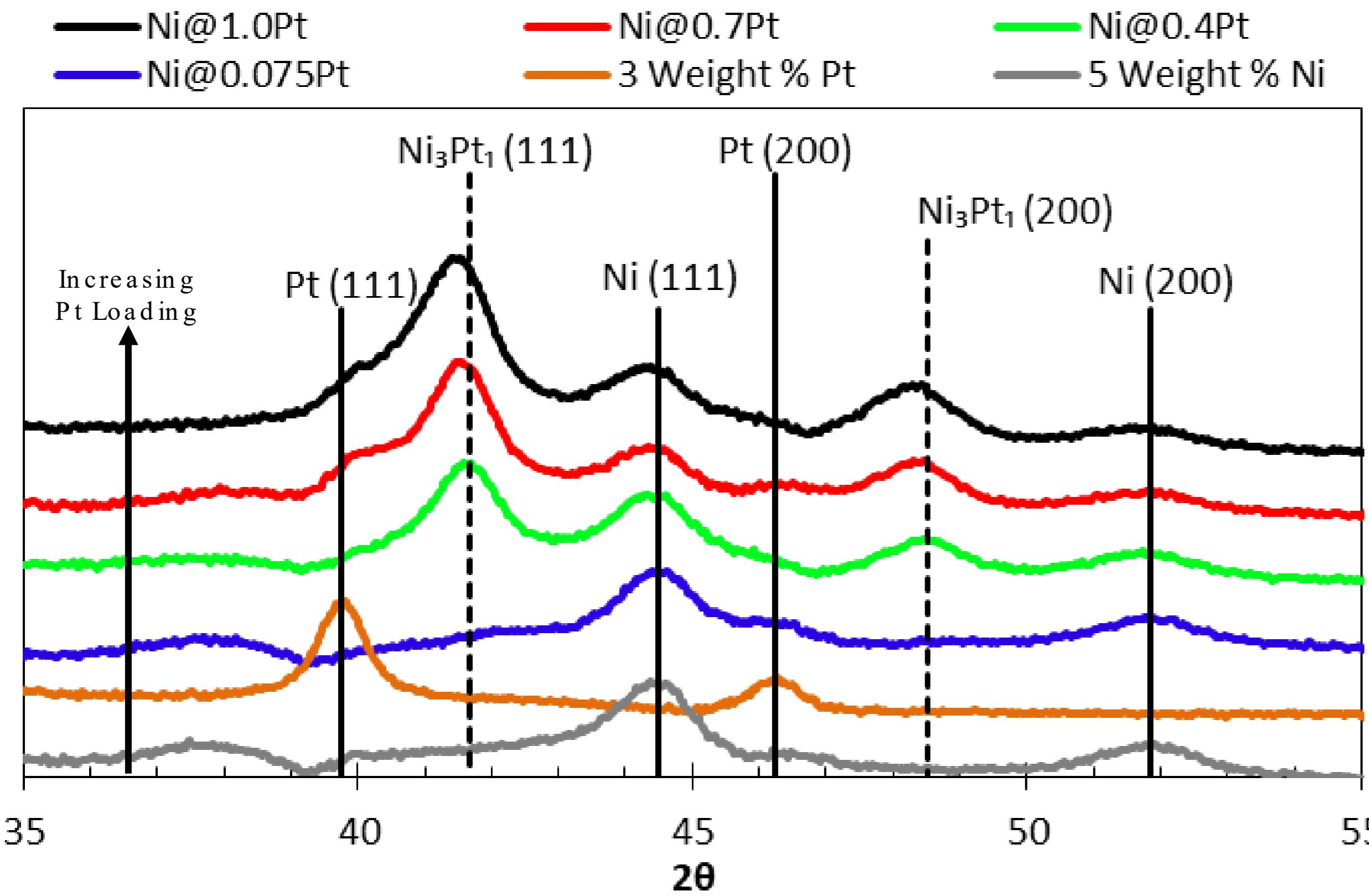


# Synthesis

Catalyst ID	Weight % Ni	Weight % Pt	Atomic % Ni	Atomic % Pt	Ni/Pt Atomic Ratio
<b>Ni / <math>\gamma\text{-Al}_2\text{O}_3</math></b>	5.0	0	100	0	-
<b>Ni@0.075Pt</b>	5.0	0.2	98.8	1.2	82.3
<b>Ni@0.4Pt</b>	5.0	1.1	93.8	6.2	15.3
<b>Ni@0.7Pt</b>	5.0	1.9	89.8	10.2	8.8
<b>Ni@1.0Pt</b>	5.0	2.75	85.8	14.2	6.0
<b>Pt / <math>\gamma\text{-Al}_2\text{O}_3</math></b>	0	3	0	100	0

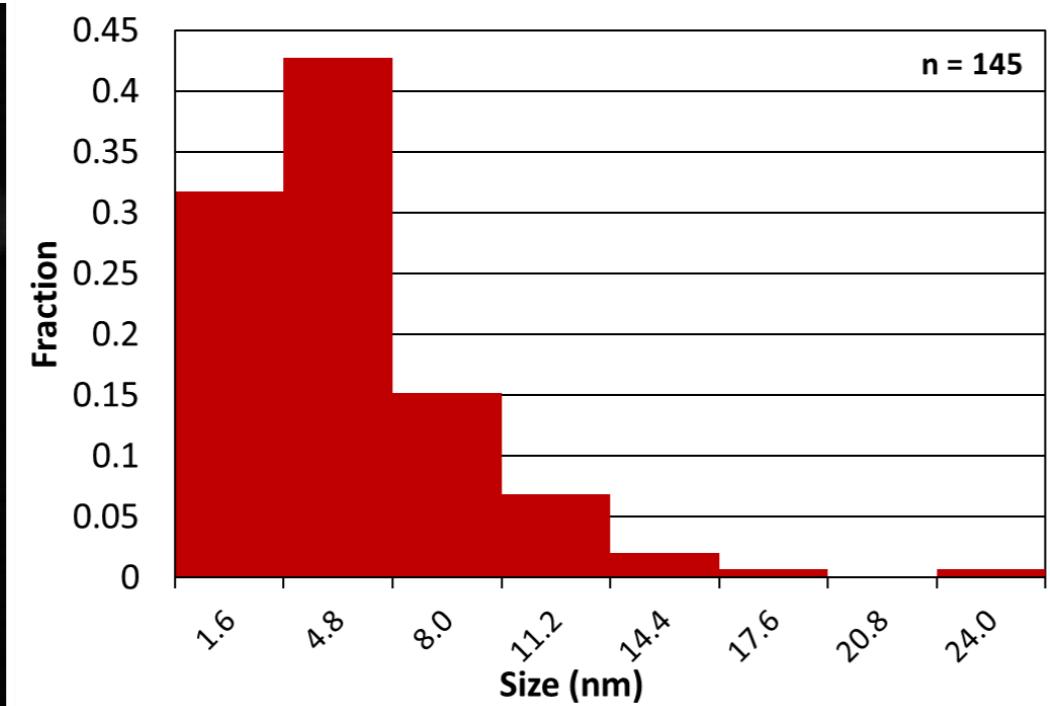
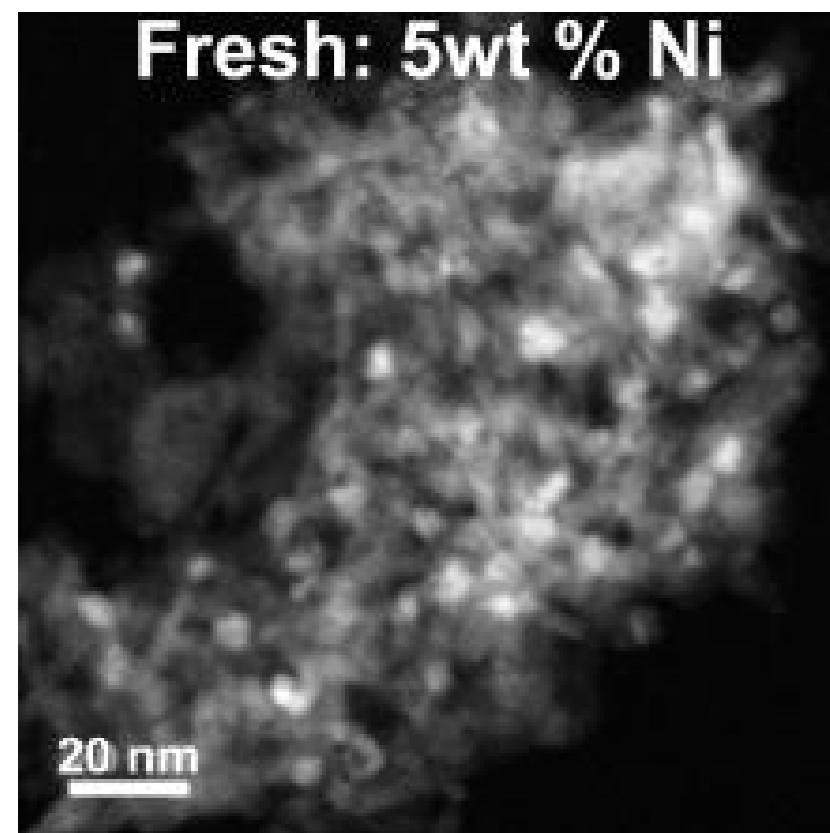


# Fresh Reduction Characterization



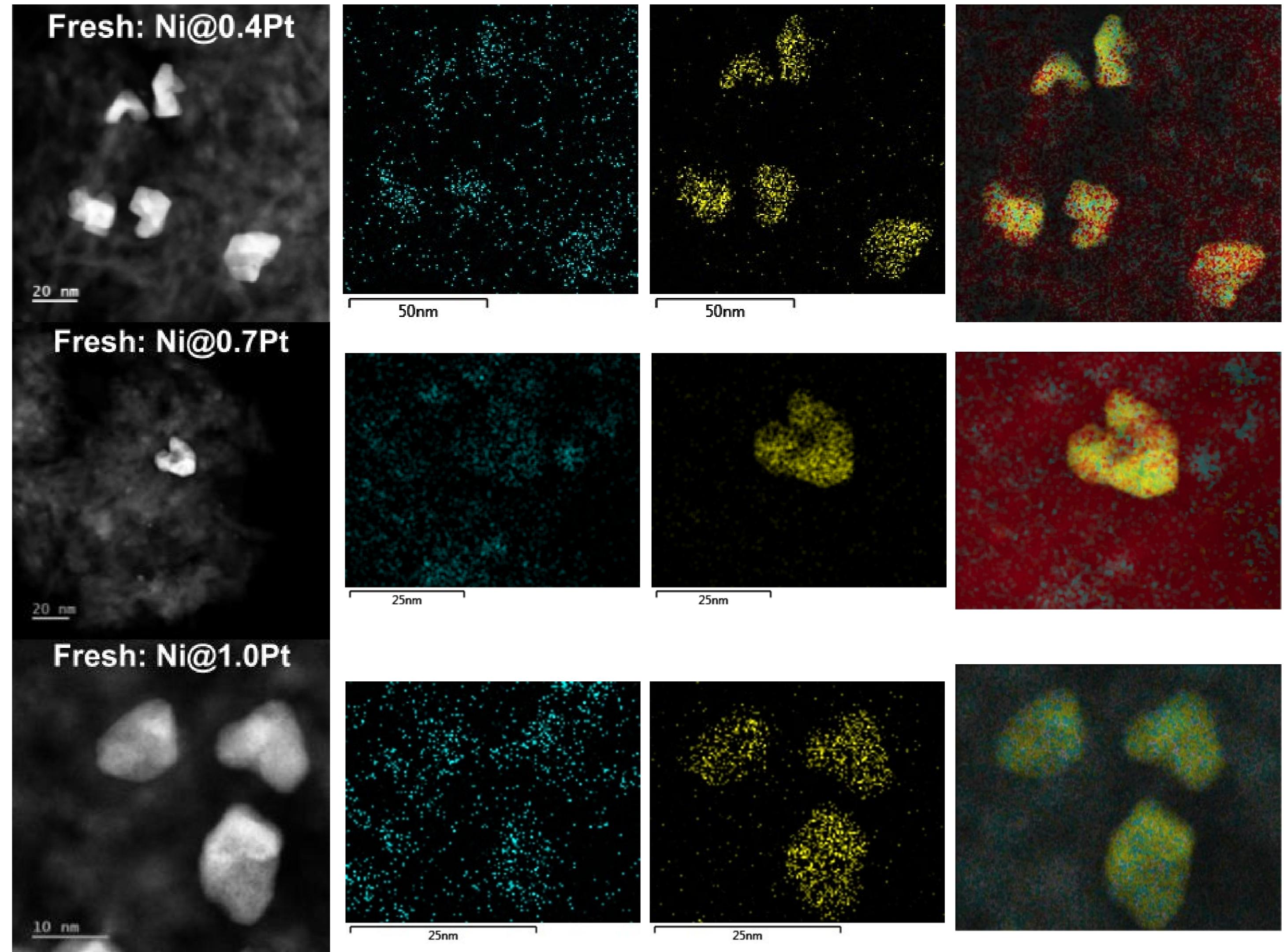
- XRD patterns indicate the formation of a Ni-Pt alloy with evidence of crystalline Pt sites.
- TPR results suggest that Pt assists the reduction of Ni compounds with a maximum difference of  $30^{\circ}\text{C}$  at 1 monolayer Pt.

# Fresh Reduction Characterization



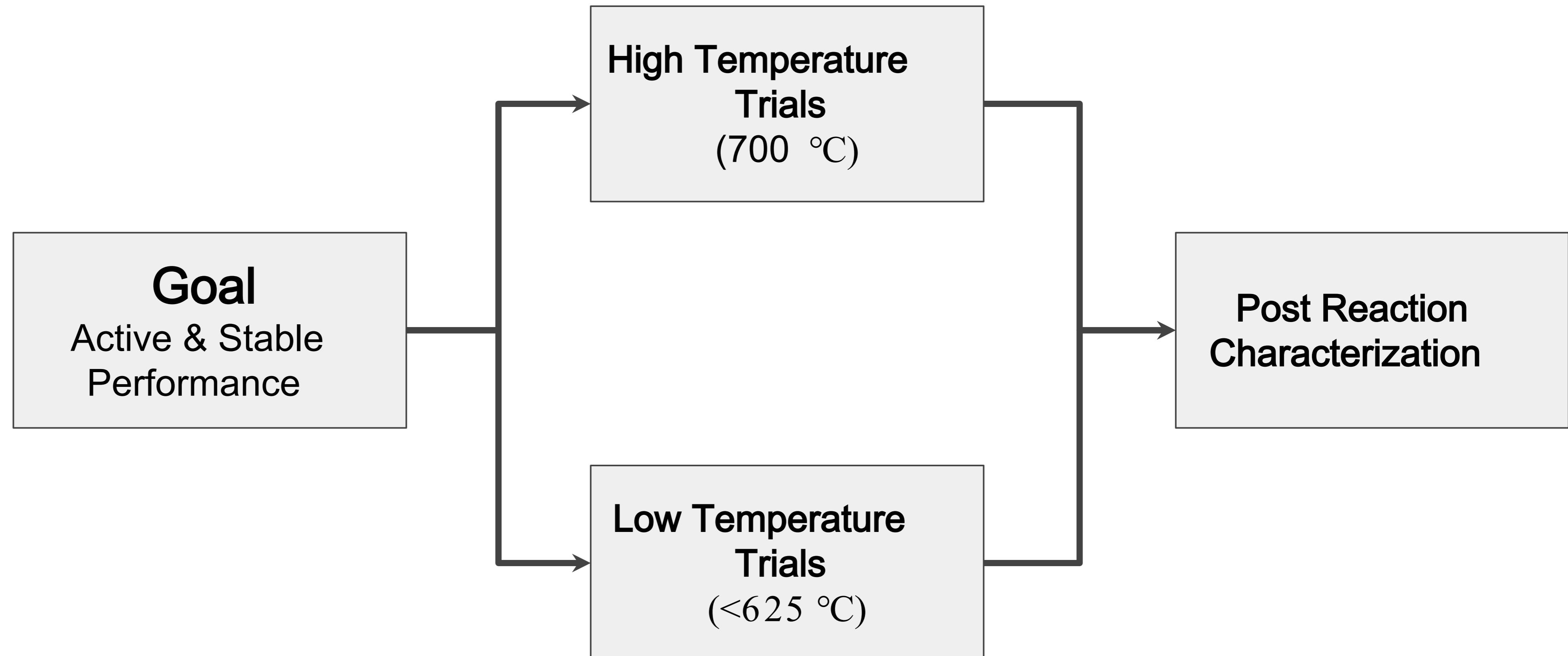
	MEAN	SD
D <sub>n</sub>	6.0	3.6
D <sub>s</sub>	10.7	6.0
D <sub>v</sub>	13.7	8.6

- **Red:** Alum in u m , **Blue:** Nickle, **Yellow:** Platinum
- A review of all captured images shows no evidence of metallic Pt on the  $\gamma\text{-}Al_2O_3$  support.
- EDX suggests autocatalytic deposition of Pt forming crystalline sites on Ni seeds.

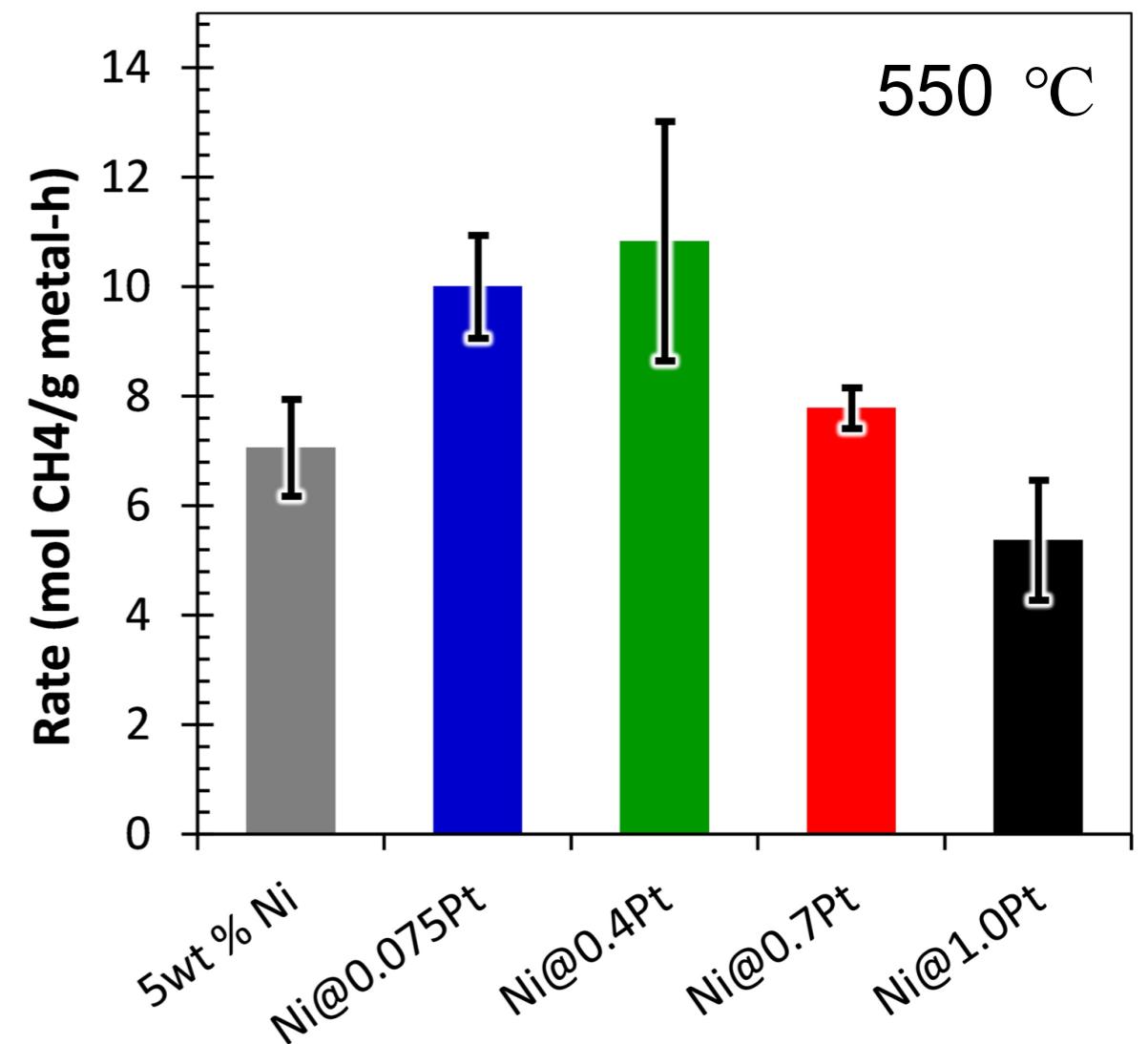
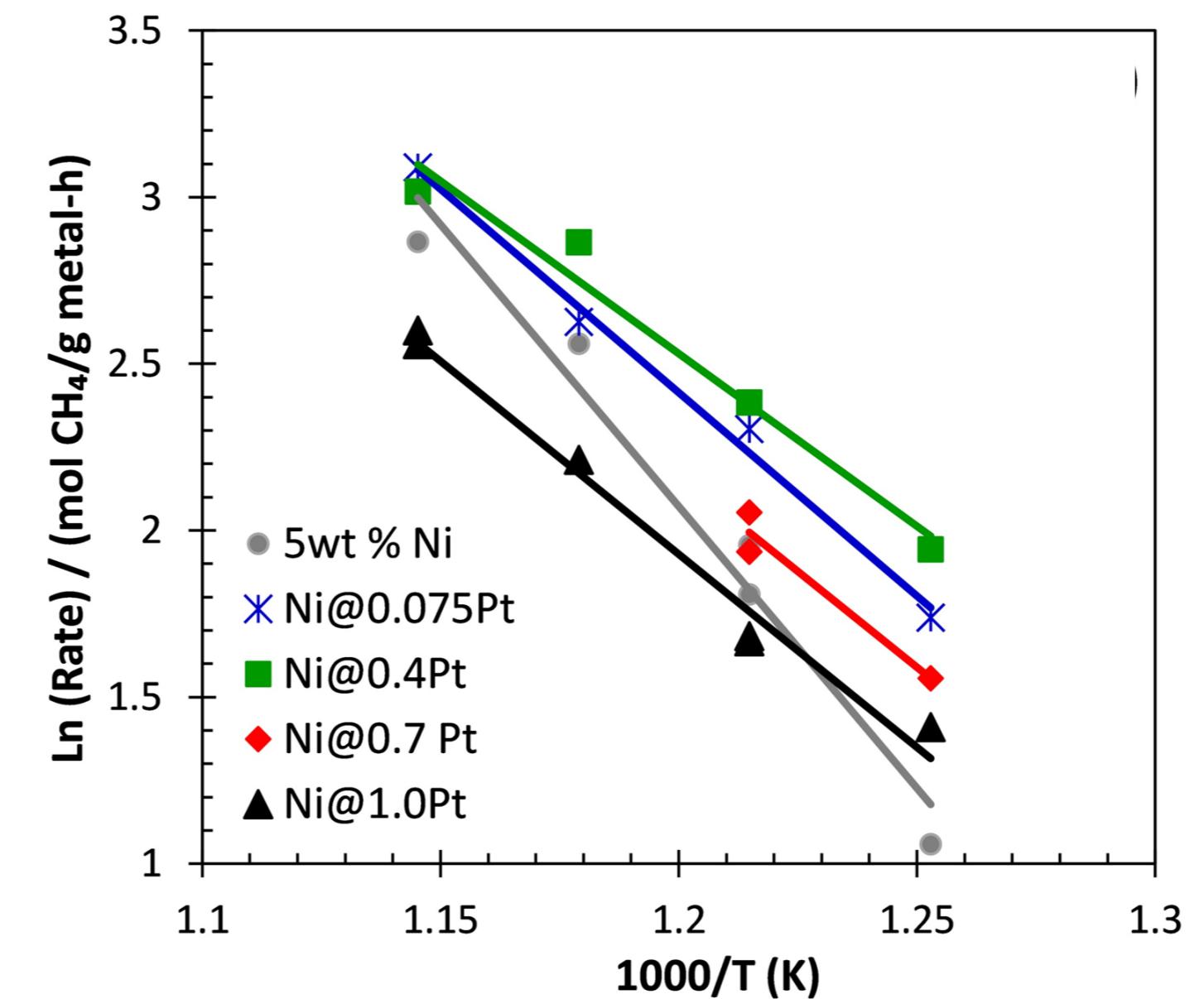
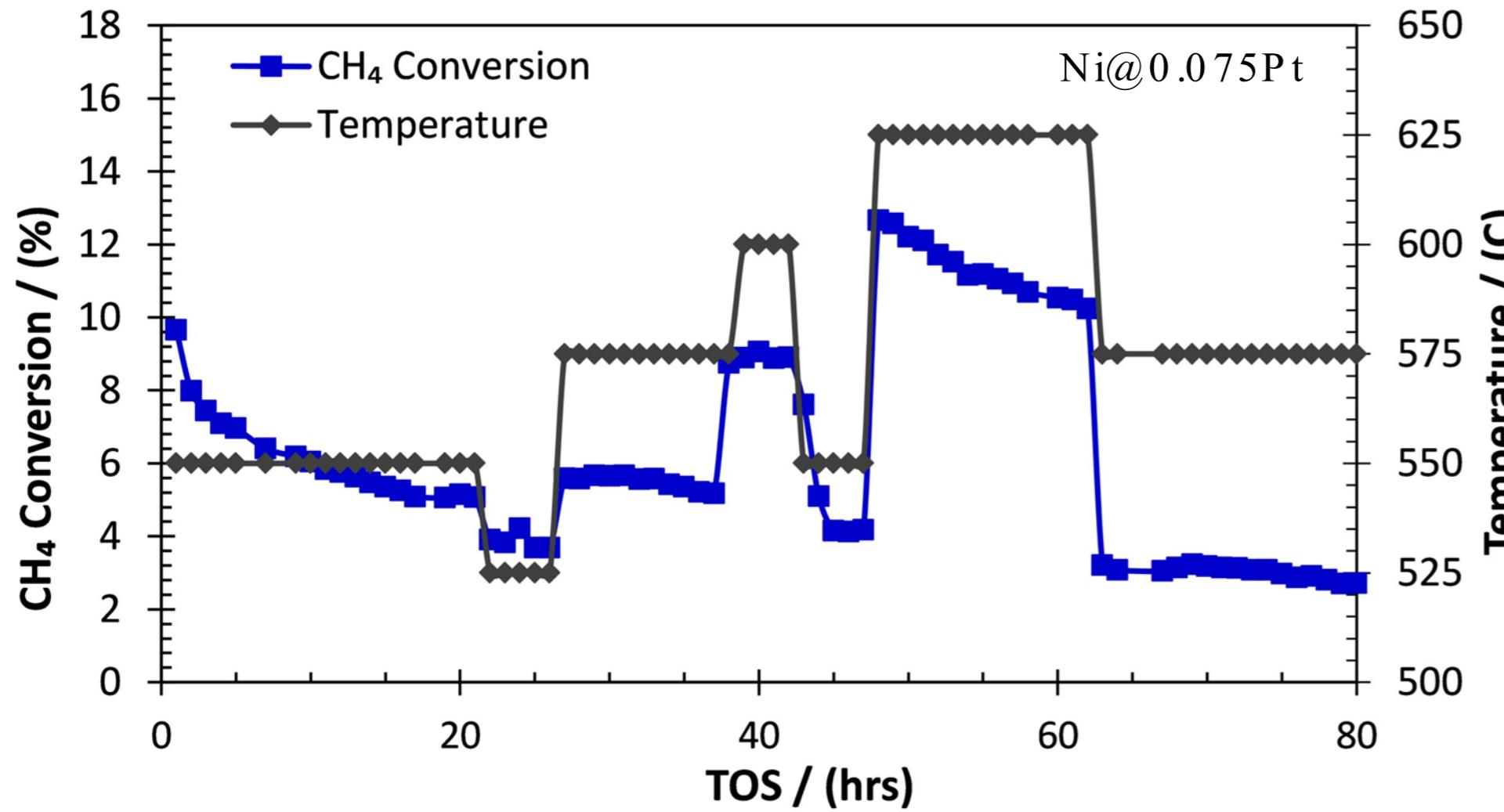


NOTE: "Fresh" notation indicates samples were reduced in H<sub>2</sub> at 600 °C (Ni) and 300 °C (Pt).

# Evaluation



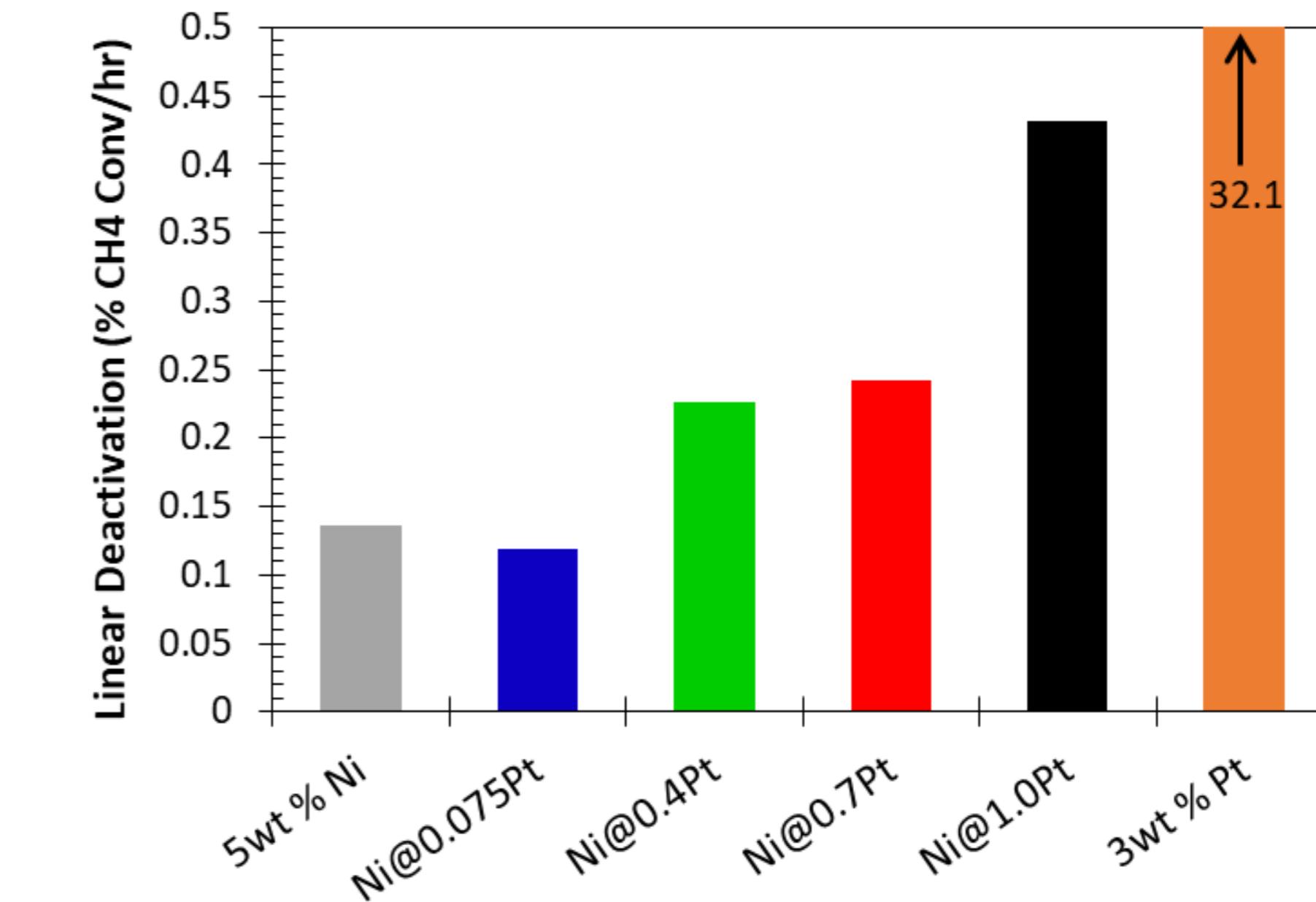
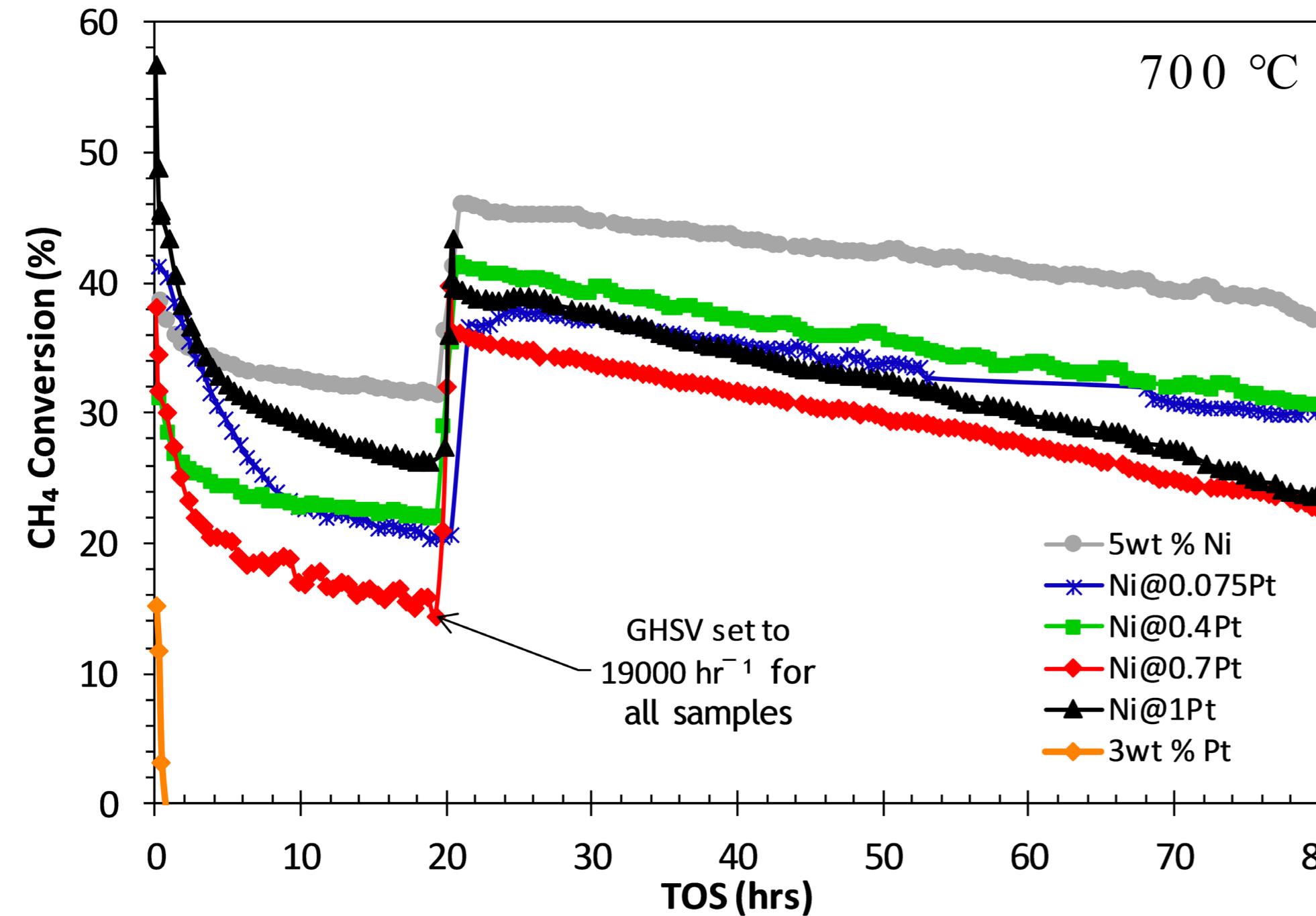
# Low Temperature Results ( $T < 600$ °C)



- Time on stream plots (TOS) show stability at temperatures below 600 °C.
- Activity loss is permanent after returning to low temperature conditions (25-35 vs 60+ hrs TOS).
- At low Pt loadings CH<sub>4</sub> conversion rates are increased with an optimum between 0.075 and 0.4 monolayers.

Catalyst	Ni/Pt Atomic Ratio	E <sub>a'</sub> (kJ/mol)	ln(A')
5wt% Ni	-	122.2	19.7
Ni@0.075Pt	83.3	101.5	16.6
Ni@0.4Pt	14.3	86.2	15.0
Ni@0.7Pt	8.8	95.8	16.0
Ni@1.0Pt	5.9	96.4	15.8
3wt% Pt	-	-	-

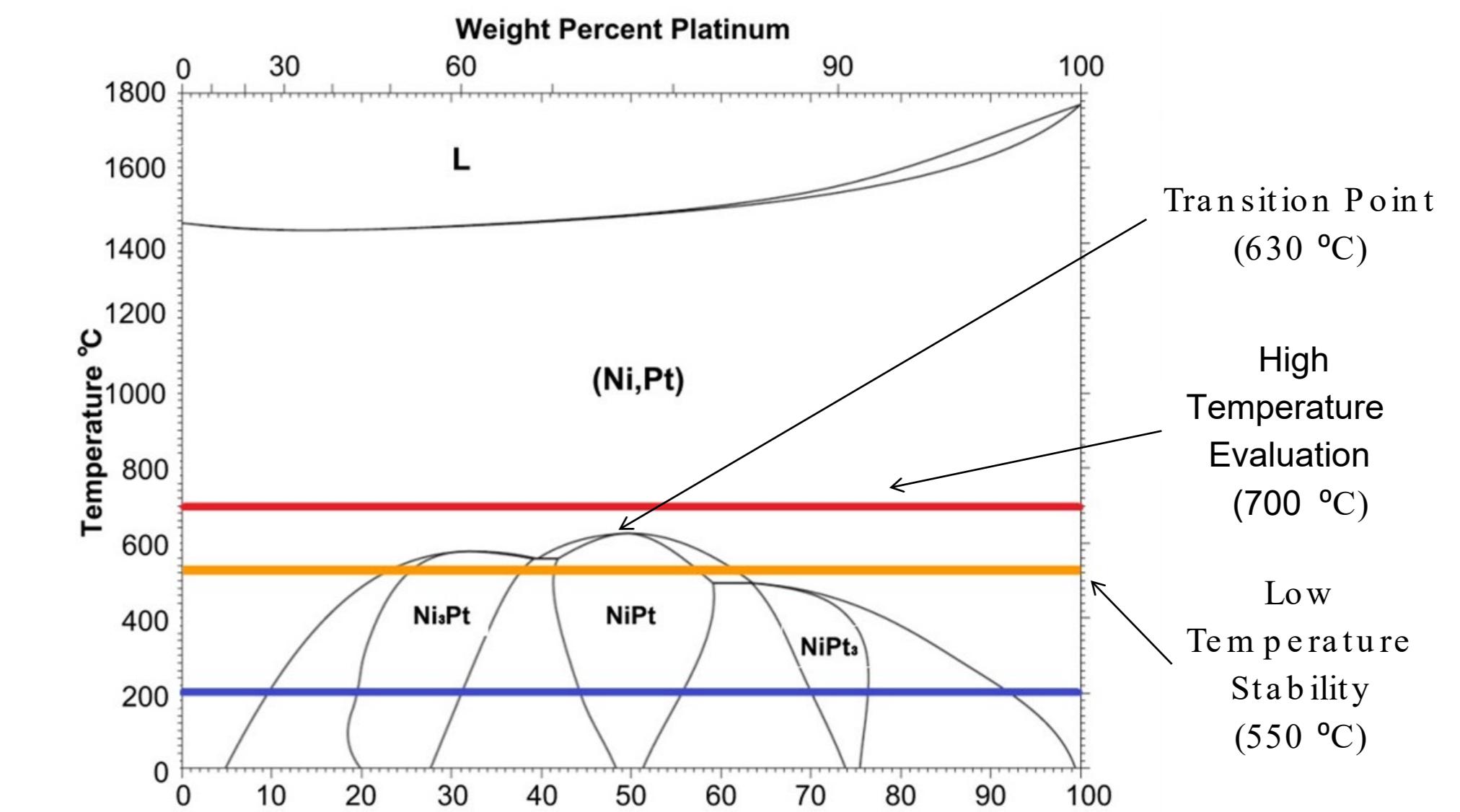
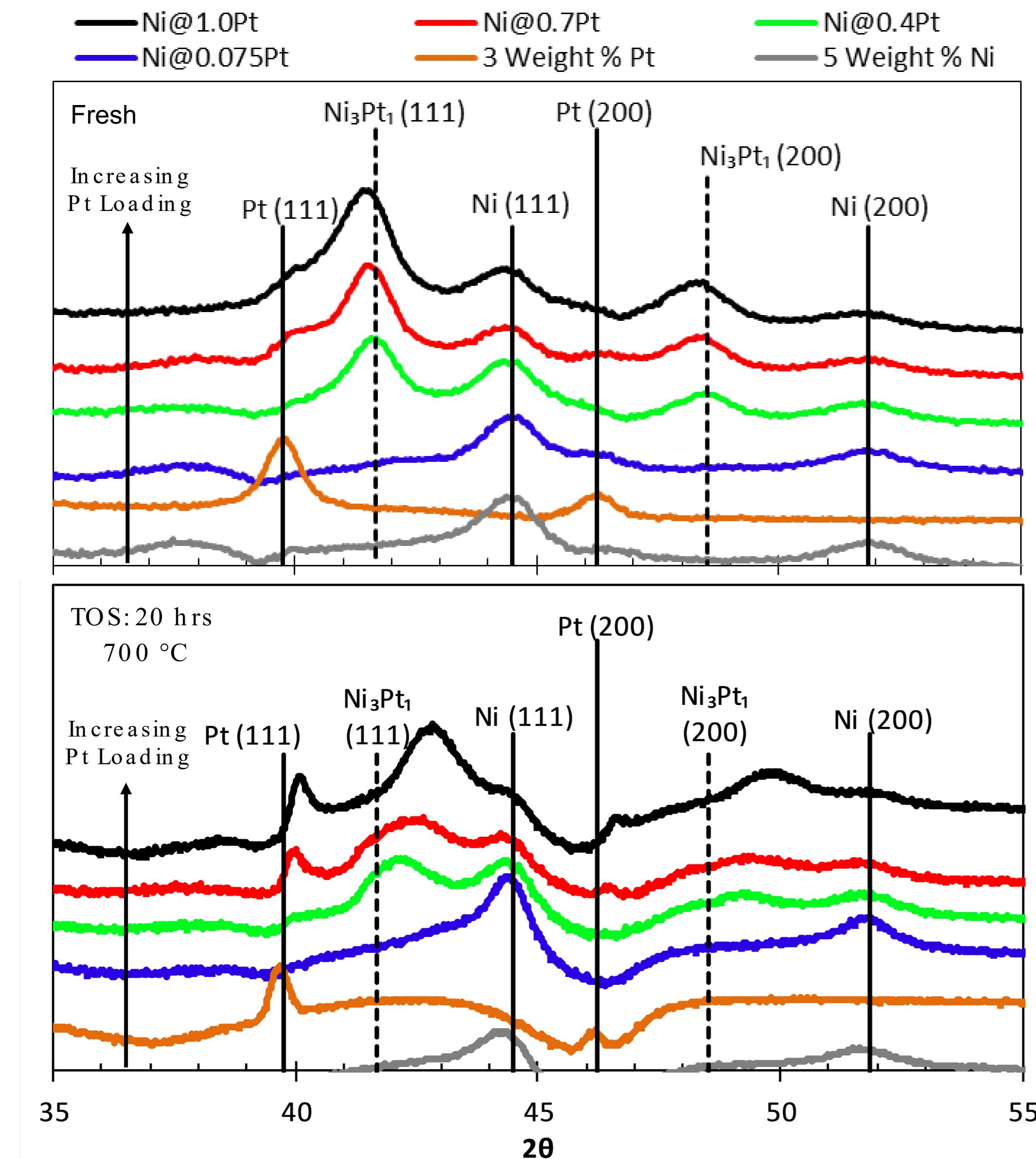
# High Temperature Results ( $T=700$ °C)



Catalyst	Ni/Pt Atomic Ratio	Deactivation rate (mmol CH <sub>4</sub> h <sup>-2</sup> g <sub>metal</sub> <sup>-1</sup> ) <sup>b</sup>
5wt% Ni	-	121.2
Ni@0.075Pt	83.3	145.8
Ni@0.4Pt	14.3	205.2
Ni@0.7Pt	8.8	242.1
Ni@1.0Pt	5.9	262.8
3wt% Pt	-	6774

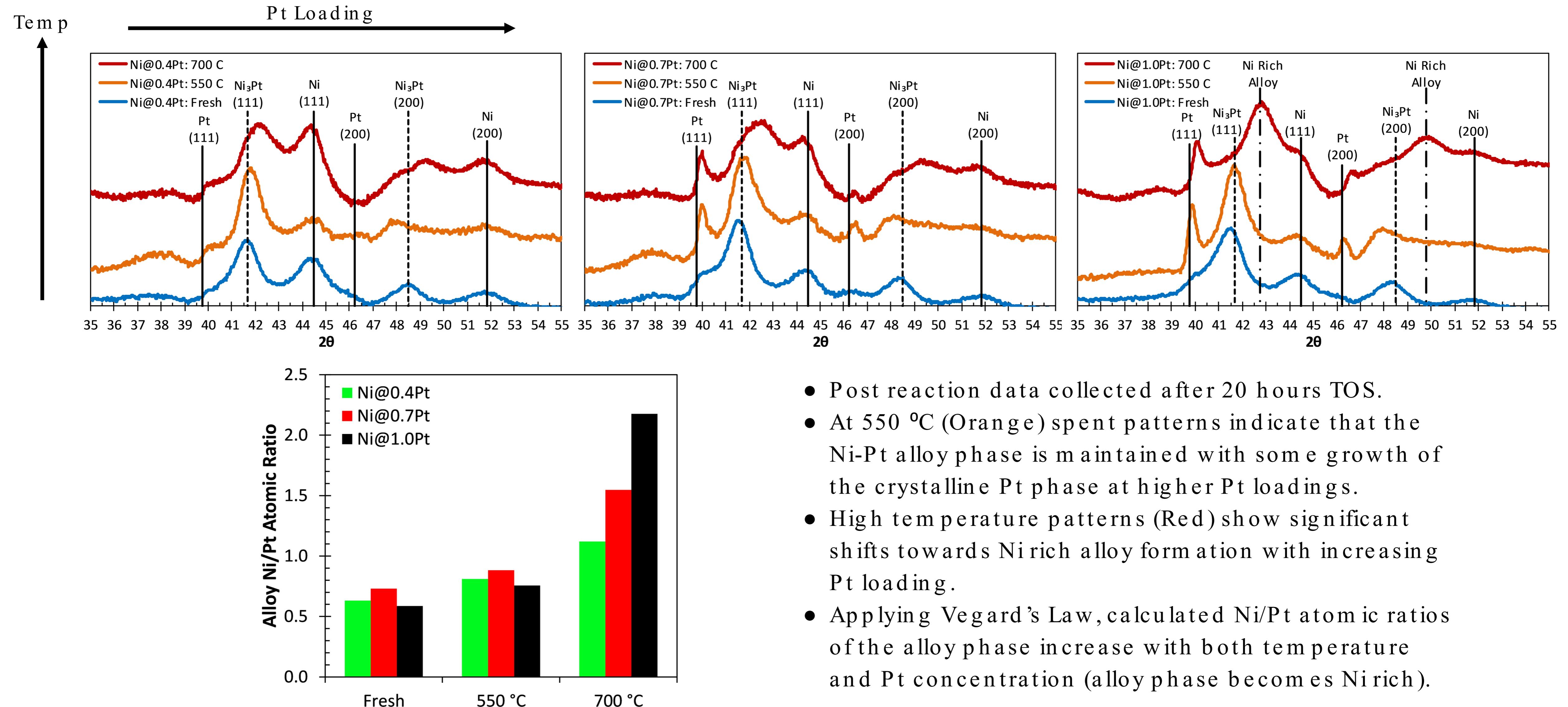
- CH<sub>4</sub> / CO<sub>2</sub> / He = 1 / 1 / 2 fixed GHSV after 20 hours TOS.
- Pt shows a negative effect on pseudo steady state CH<sub>4</sub> conversion.
- As Pt loading increases, deactivation rates over the linear region (30-50 hrs TOS) also increase.

# Post Reaction Characterization



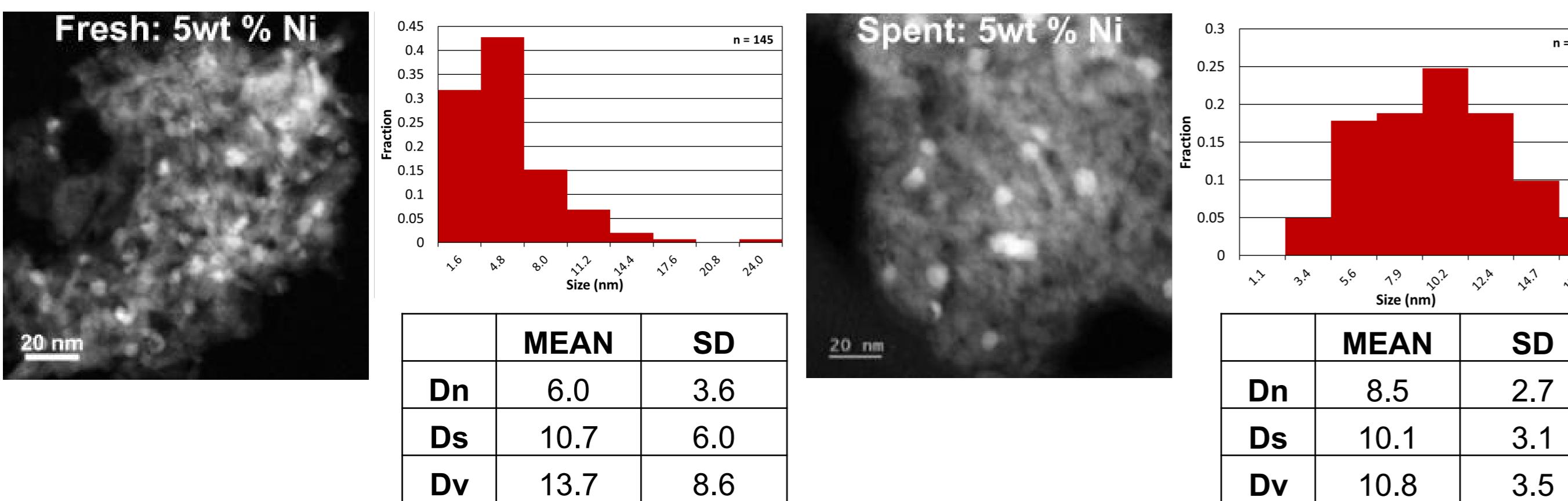
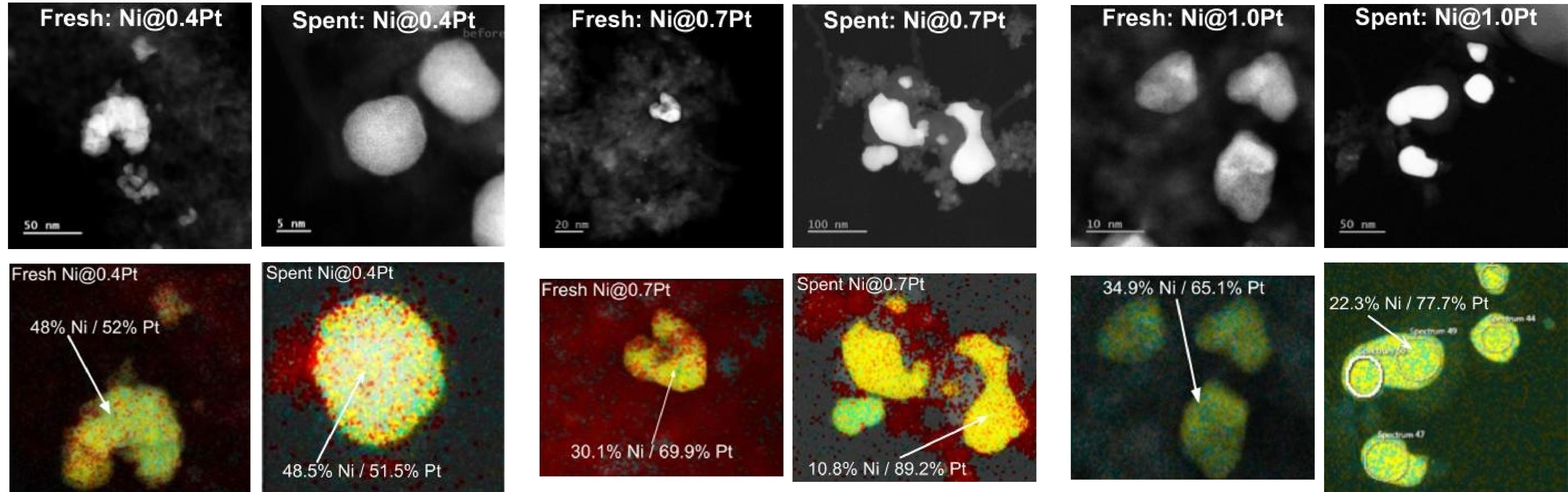
- Phase diagram suggests Ni-Pt separation at 630 °C.
- Spent XRD patterns (RHS) indicate a shift of the main alloy peak ( $41^{\circ}2\theta$ ) and growth of both the crystalline Ni and Pt phase.
- Additional Al-Ni-Pt peaks are observed in spent samples indicating Pt migration onto the alumina surface.

# Post Reaction Characterization



# Post Reaction Characterization

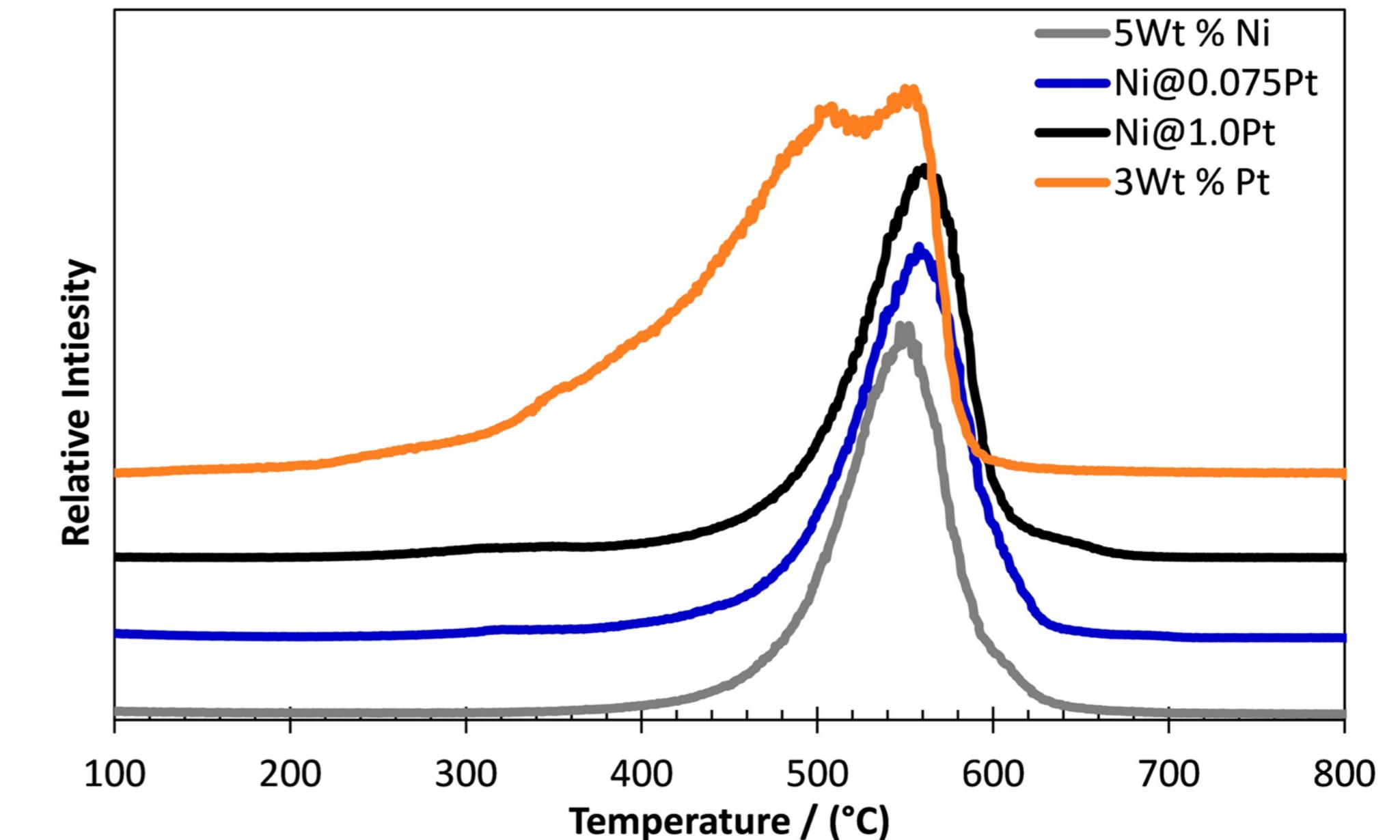
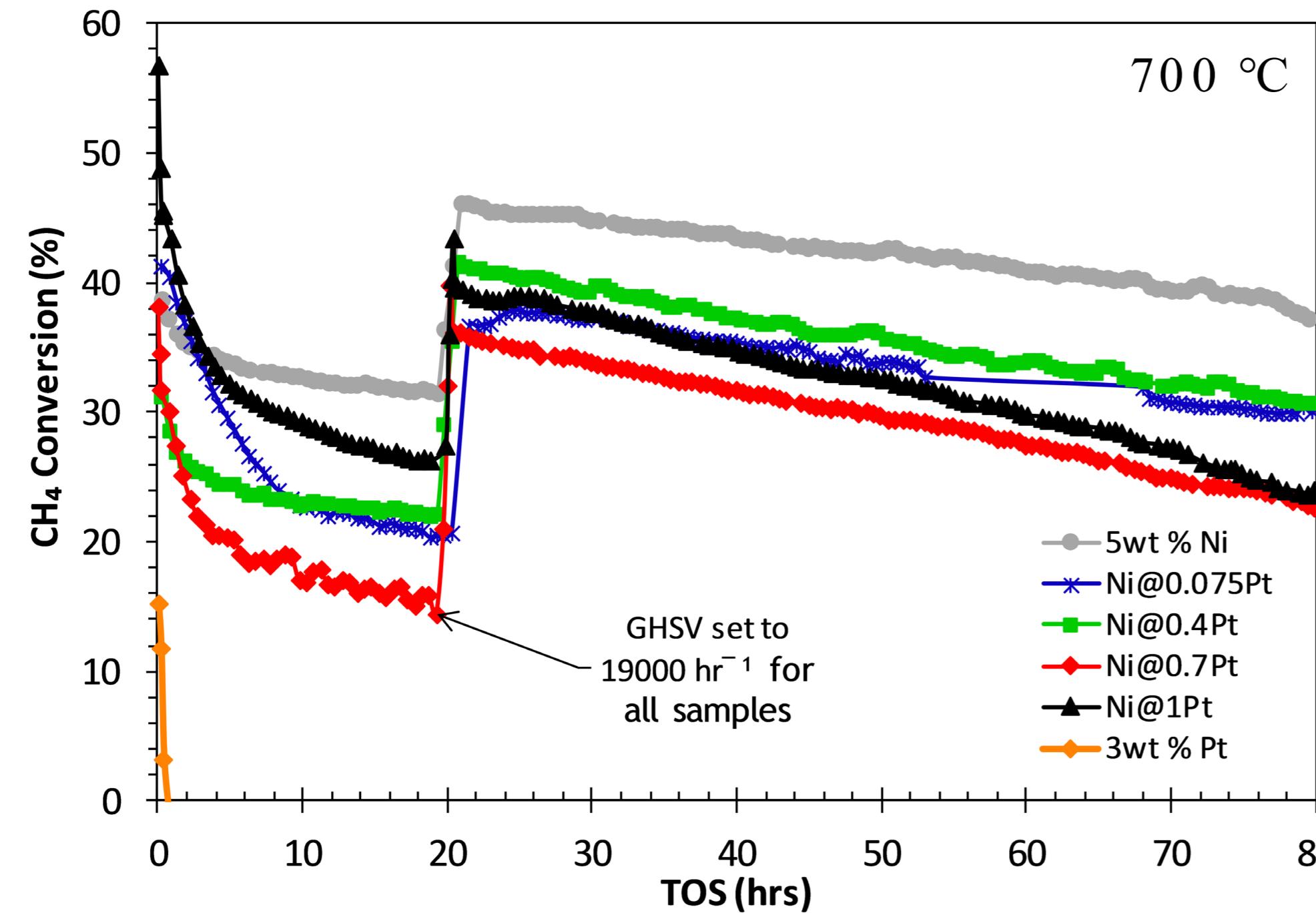
NOTE: "Spent" notation indicates samples were exposed to dry reforming for 80 hrs TOS.



## XRD Results

	Nickel		Ni-Pt Alloy			Platinum			
	Fresh	Spent (550)	Spent (700)	Fresh	Spent (550)	Spent (700)	Fresh	Spent (550)	Spent (700)
<b>5wt % Ni</b>	4.6	-	5	-	-	-	-	-	-
<b>Ni@0.075Pt</b>	4.6	-	6.3	-	-	-	-	-	-
<b>Ni@0.4Pt</b>	4.5	5.7	6.2	6.9	7.4	5	7.6	-	-
<b>Ni@0.7Pt</b>	4.1	6.5	6.1	6.7	7.5	4.8	8.5	20.8	21
<b>Ni@1.0Pt</b>	4.7	6.2	6.4	7.25	8.1	5.8	7.8	27.8	21
<b>3wt % Pt</b>	-	-	-	-	-	-	10.8	-	19.9

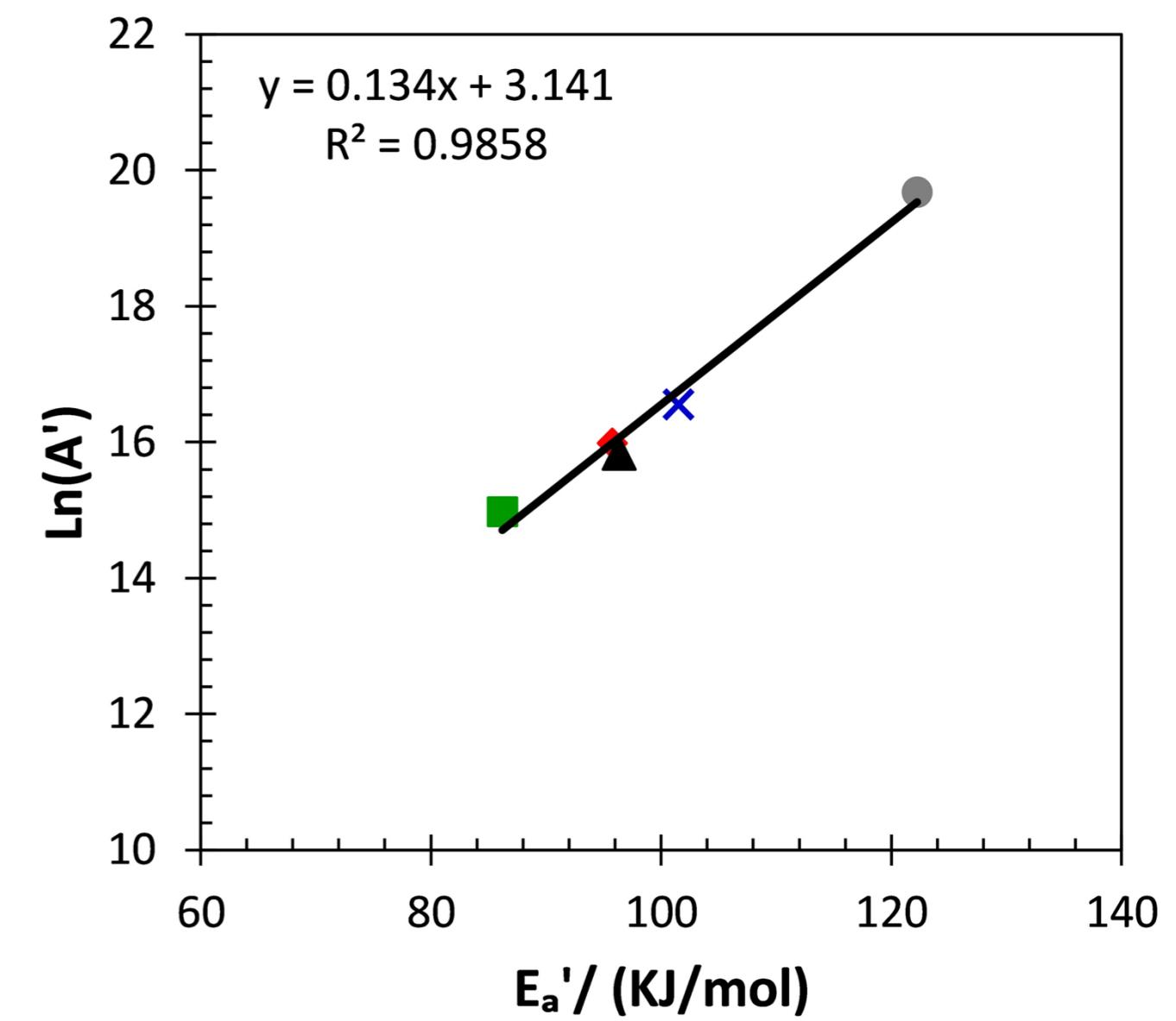
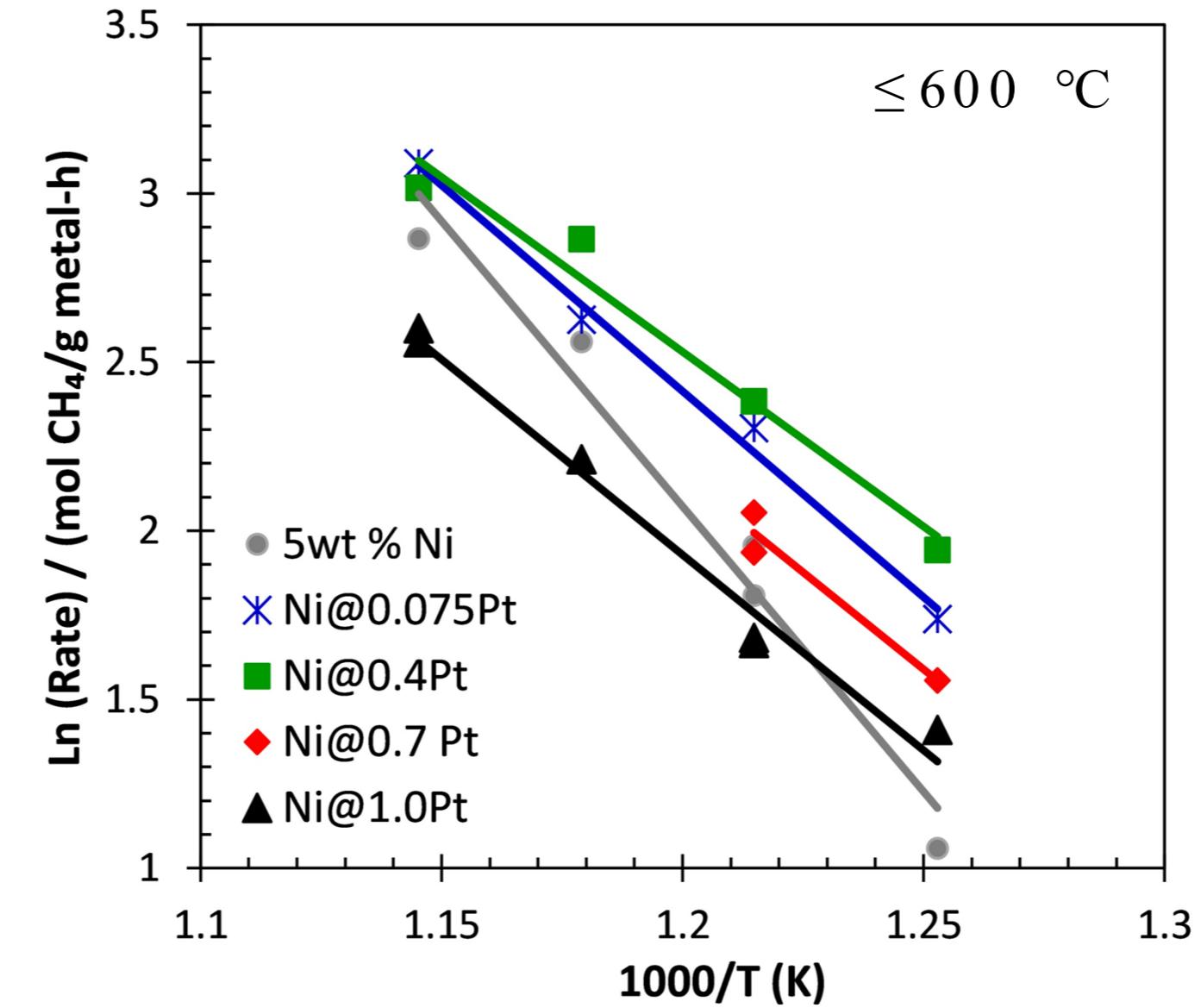
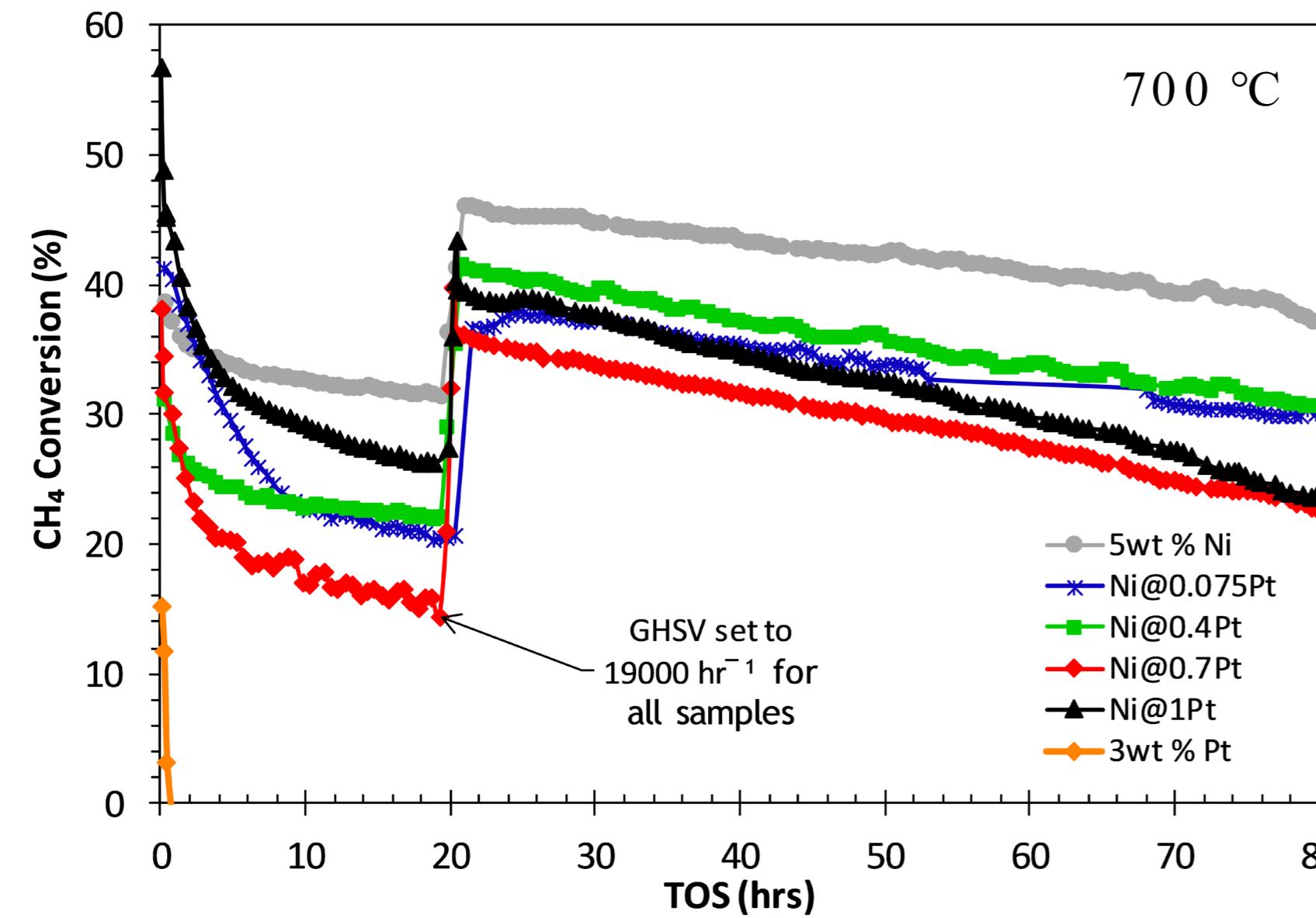
# Stability Conclusions



Catalyst	Ni/Pt Atomic Ratio	Deactivation rate (mmol CH <sub>4</sub> h <sup>-2</sup> g <sub>metal</sub> <sup>-1</sup> ) <sup>b</sup>	Coke formation (mmol C/g <sub>cat</sub> )
5wt% Ni	-	121.2	3.54 (150°)
Ni@0.075Pt	83.3	145.8	4.22 (150°)
Ni@0.4Pt	14.3	205.2	-
Ni@0.7Pt	8.8	242.1	-
Ni@1.0Pt	5.9	262.8	6.99 (110°)
3wt% Pt	-	6774	7.21 (20°)

- Elevated temperatures lead to separation of the Ni-Pt alloy forming large Pt ensembles.
- Pt enhances CH<sub>4</sub> decomposition increasing the rate of surface carbon formation.
- Ni sintering stabilizes within the first 20 hours TOS with minimal influence on long term deactivation.

# Activity Conclusions



- Above the isokinetic temperature ( $\theta$ ) the preexponential factor offsets the apparent activation energy.
- Isokinetic temperature (625 °C) is in close proximity to the Ni-Pt phase separation point (630 °C).
- Literature suggests the compensation effect results from a change in electronic structure.

$$k_0 = (A'_0) \exp(-E'_a/RT)$$

$$\ln(A') = \alpha + \frac{E'_a}{R\theta}$$

$$\theta = 625^\circ C$$

# Acknowledgements

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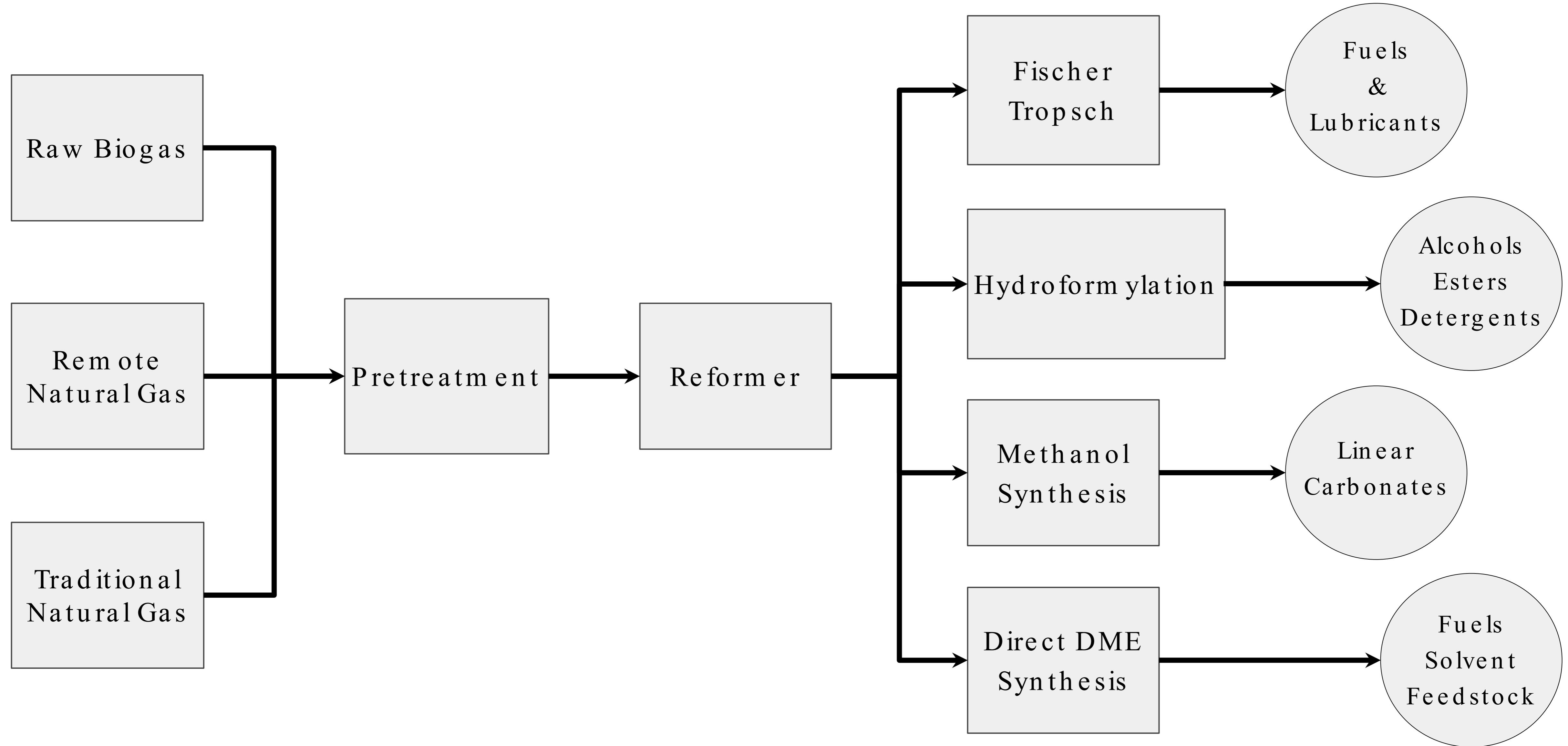




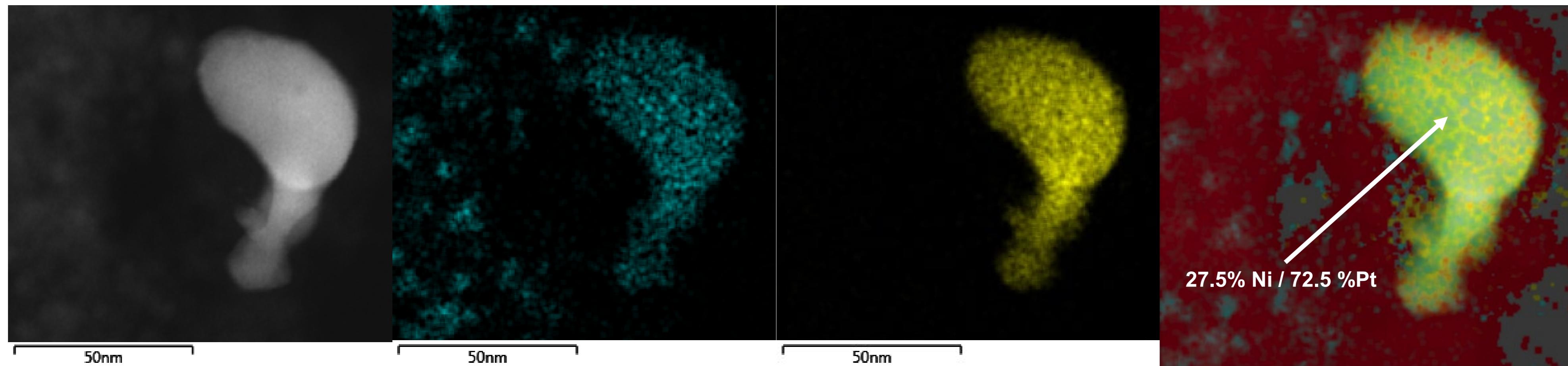
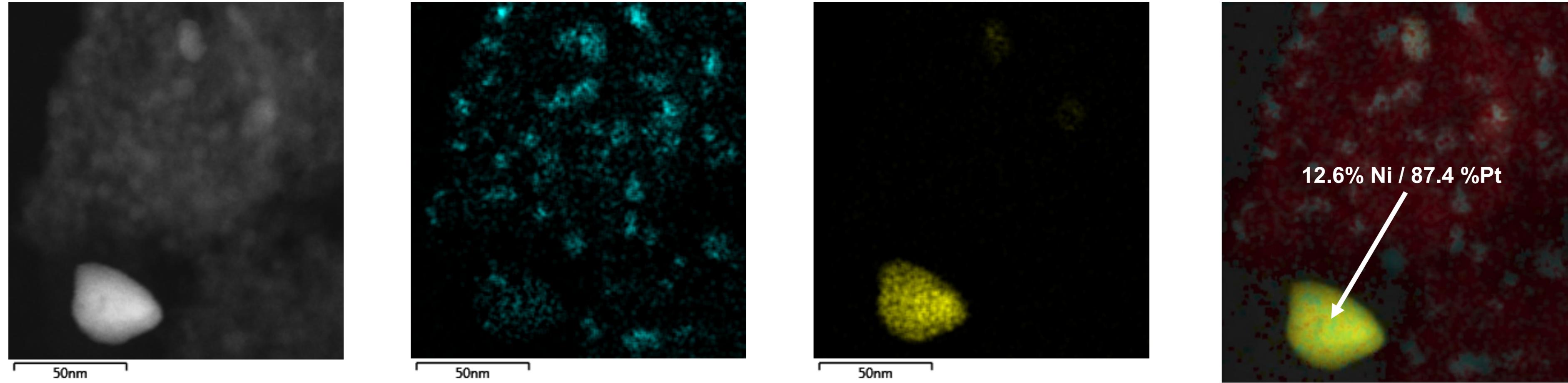
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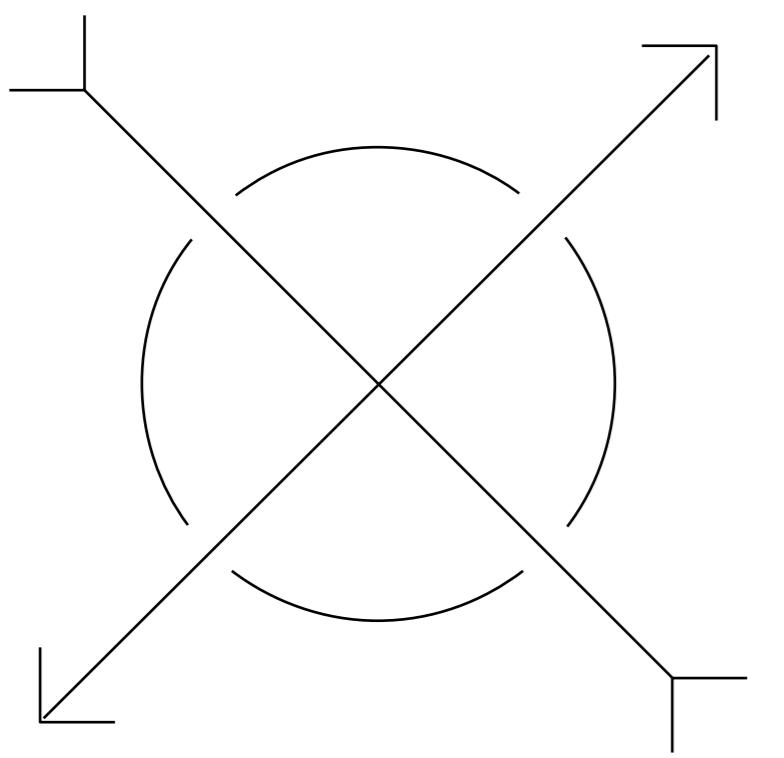
# Questions?

# Dry Reforming Applications



# Ni@0.7Pt Spent Samples





# Final Thoughts

1. Electroless deposition can place Pt directly on Ni seed sites to form an alloy phase.
2. Ni-Pt alloys show thermodynamic instability above 600 °C.
3. Large Pt ensembles increase the rate of surface carbon deposition increasing deactivation rates.
4. Differences in activities for the Ni-Pt literature can be explained by a compensation effect illustrating the importance of studying kinetics across a wide temperature range.