

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

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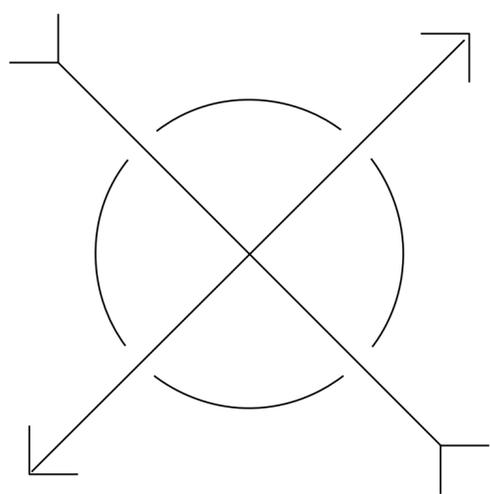
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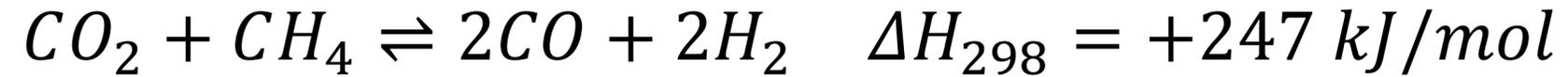
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Introduction

Dry Reforming of Methane



Side Reactions

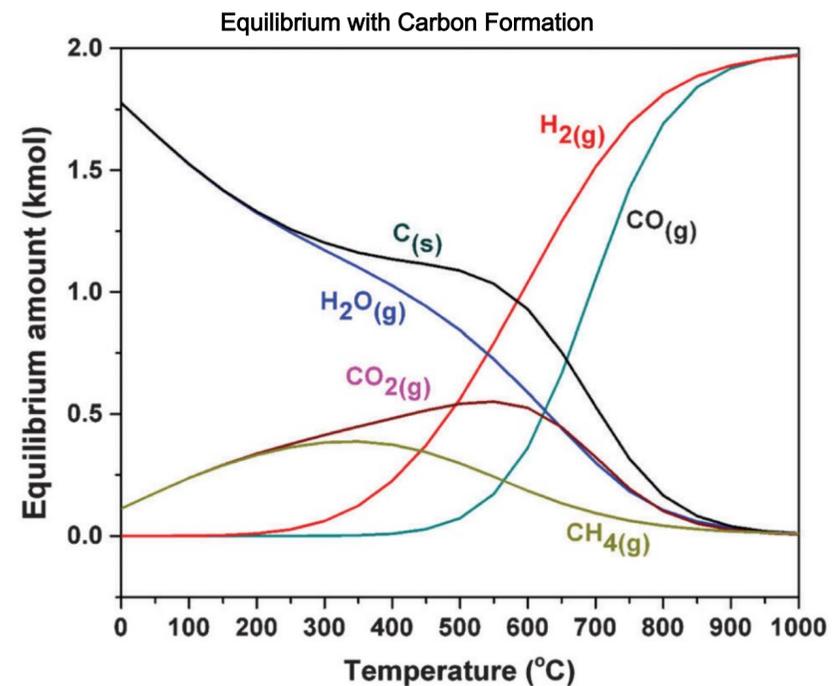
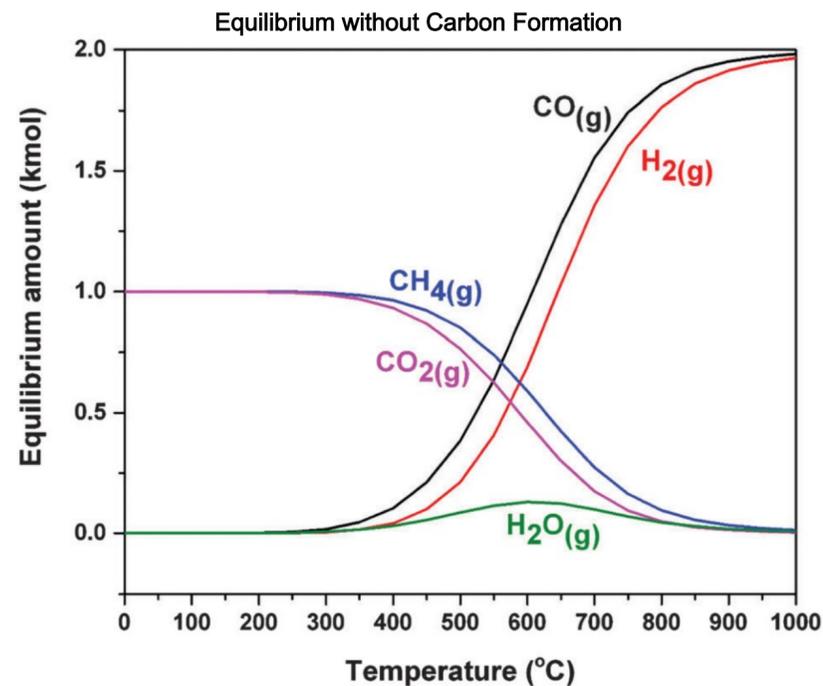
Reverse water -gas shift



Methane decomposition



Boudouard reaction



Introduction

01

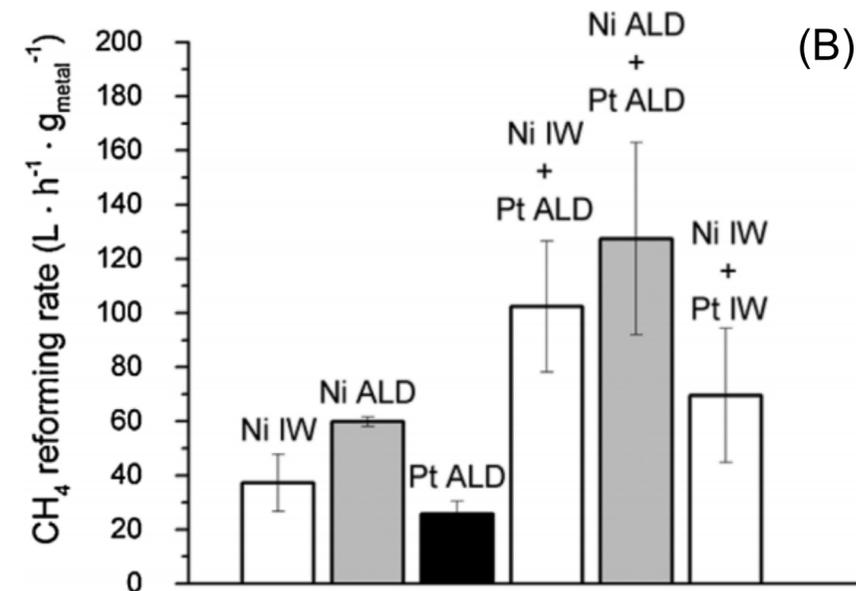
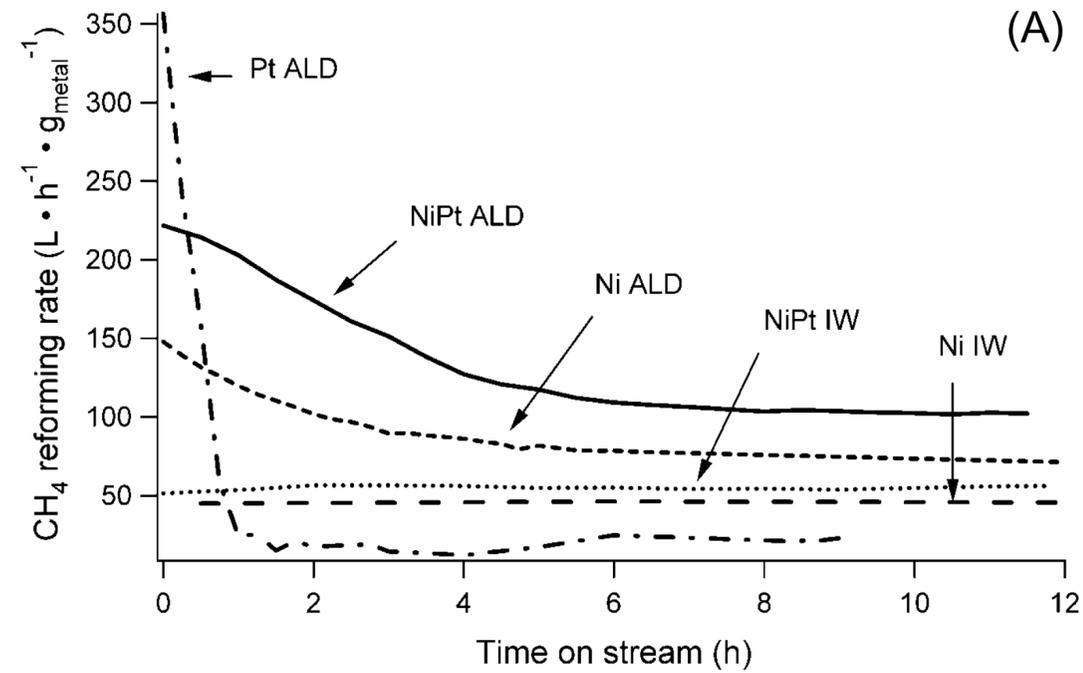
Ni-Pt: Atomic Layer Deposition

- 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 placed directly on the Nickel (Ni) maximizing bimetallic interaction.
- Final particle size and composition can be controlled to a target specification.

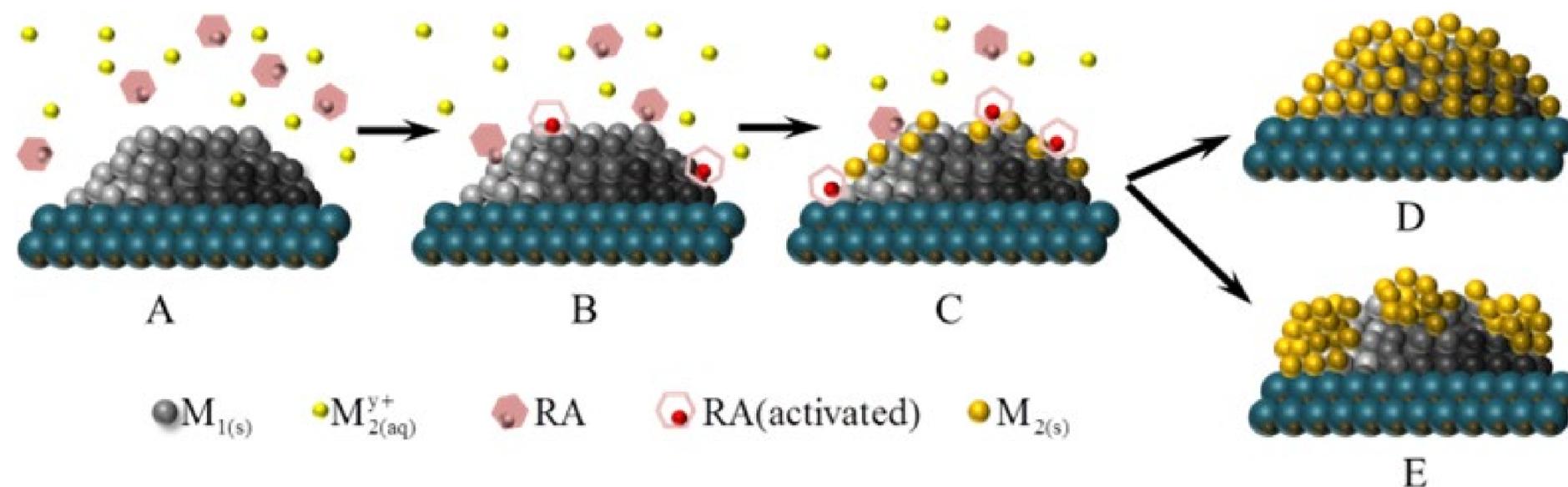


Electroless Deposition (ED)

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

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

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



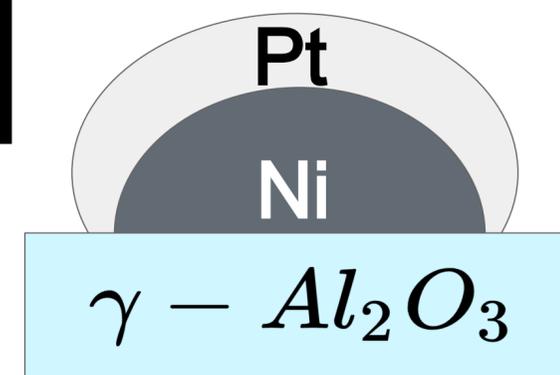
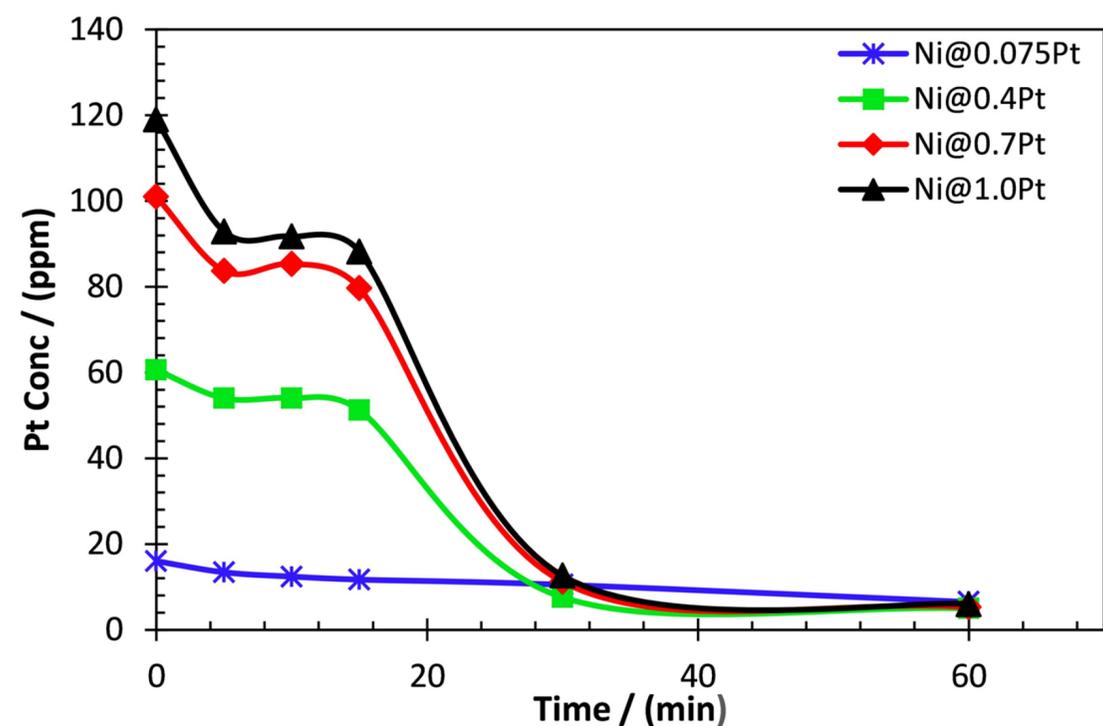
Synthesis

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

Dry Impregnation
($\text{Ni}(\text{NO}_3)_2$ on $\gamma\text{-Al}_2\text{O}_3$)
(1)

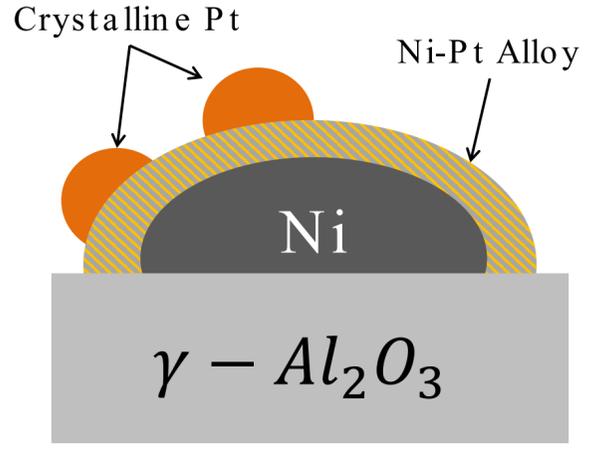
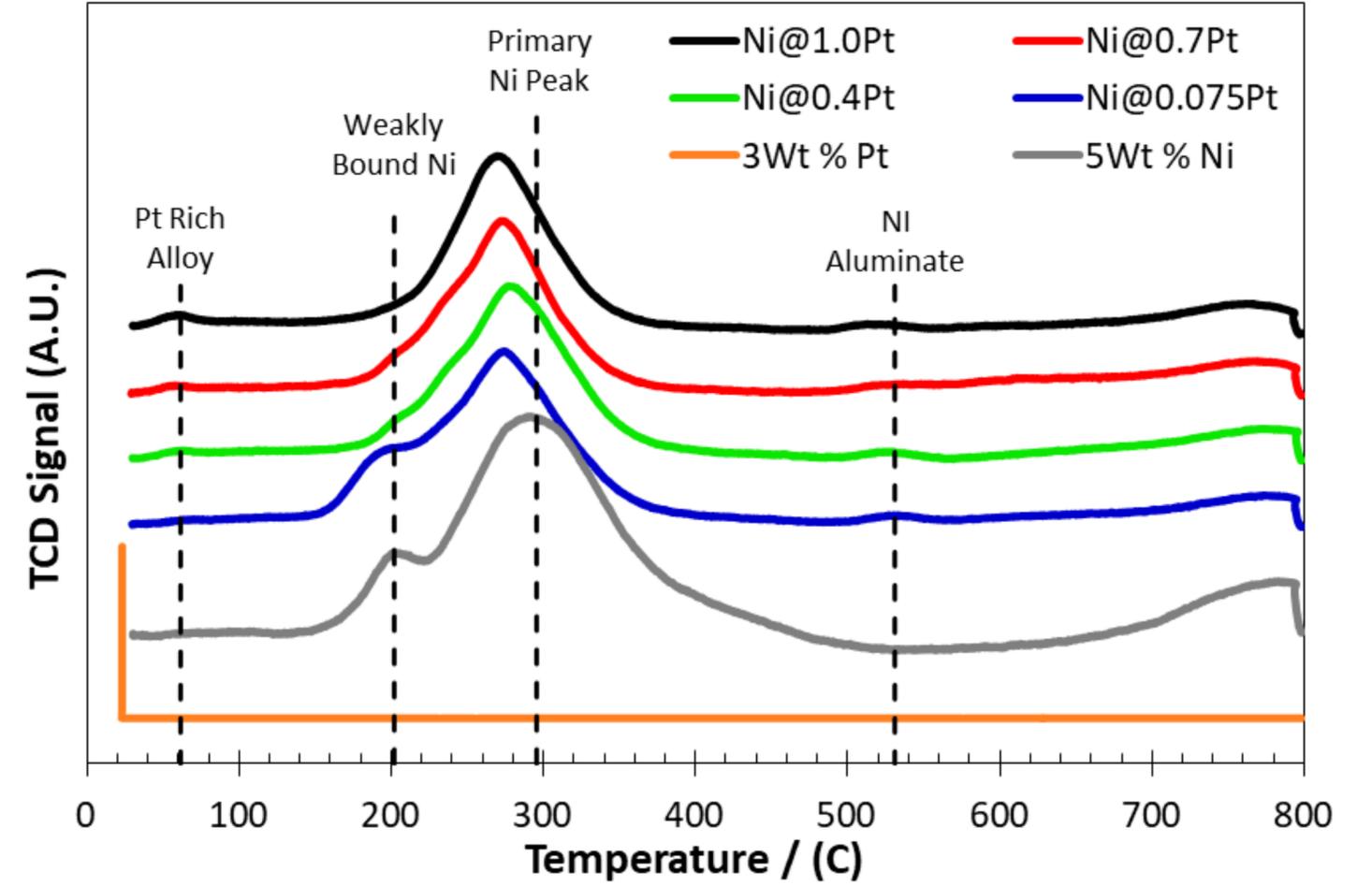
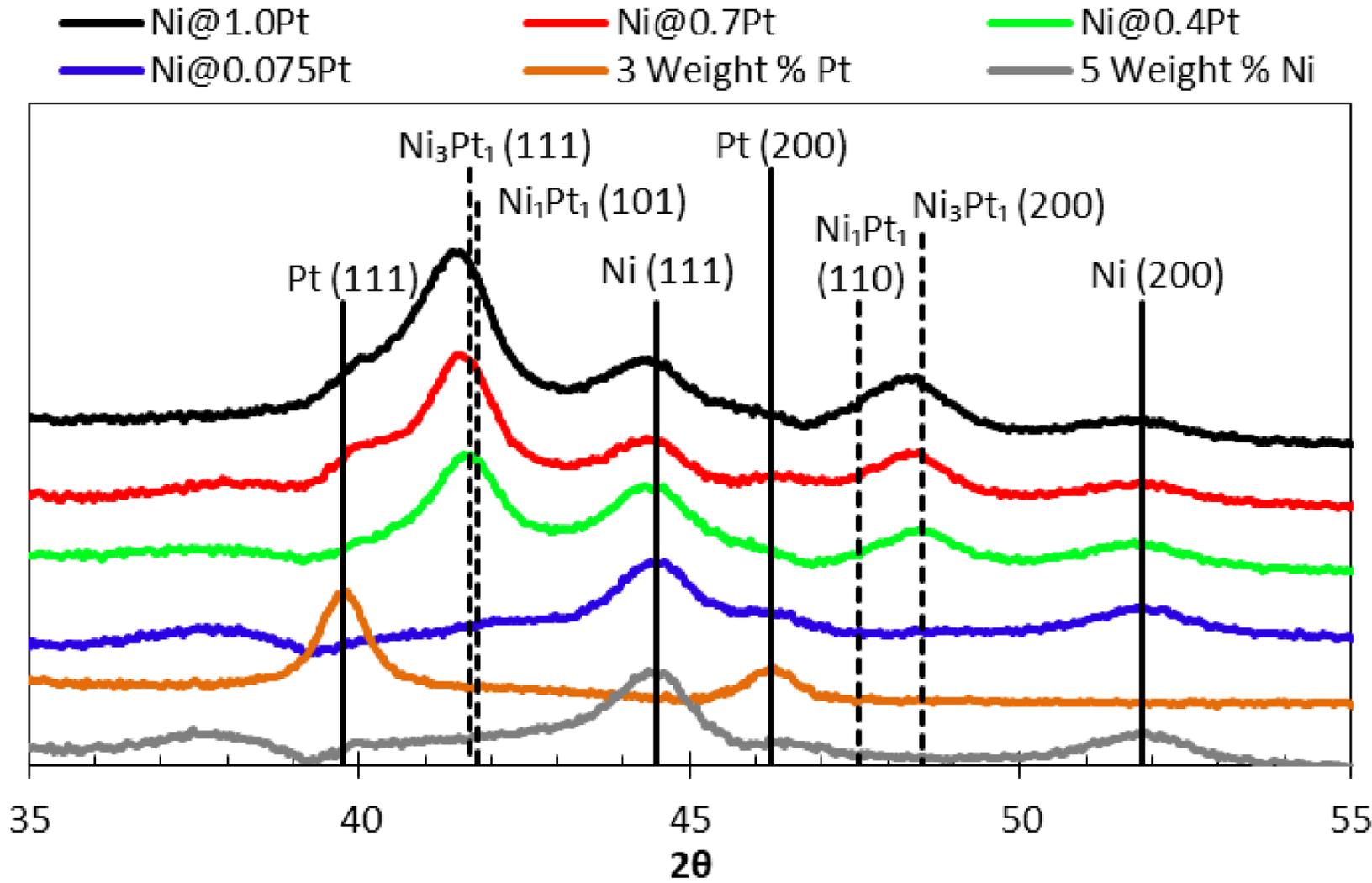
Ni Reduction
(600 °C)
(2)

Pt ED
(Precursor: H_2PtCl_6 , Reducing Agent: DMAB, Stabilizing Agent: Ethylene Diamine)



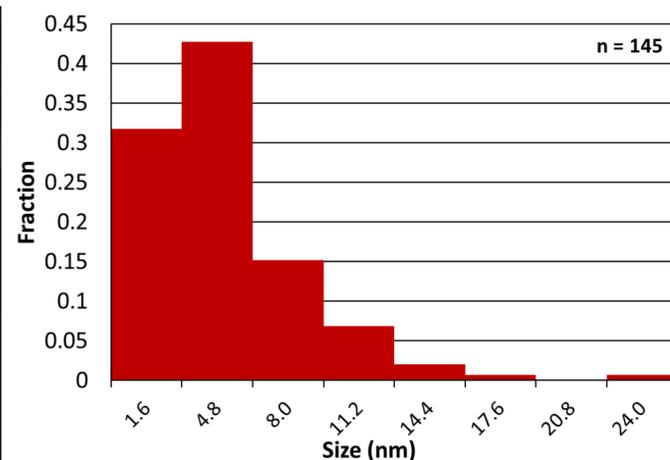
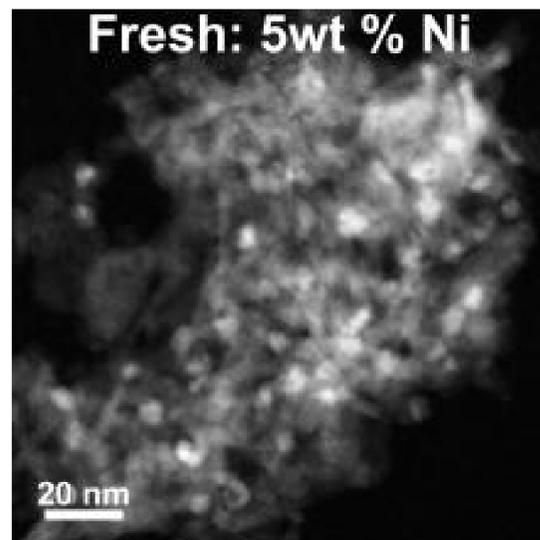
Pt Reduction
(300 °C)
(3)

Fresh Reduction Characterization



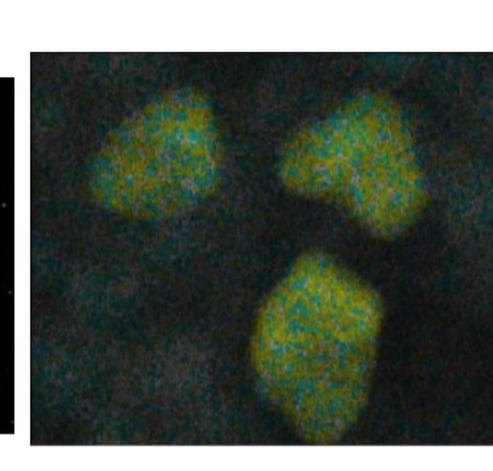
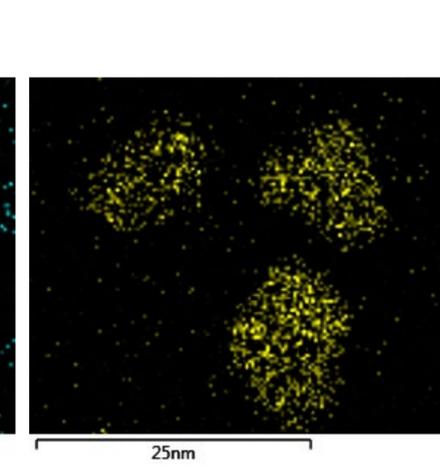
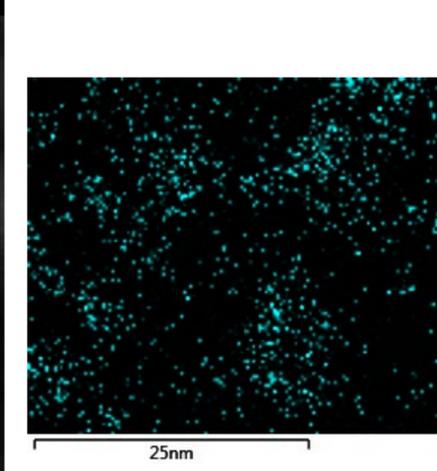
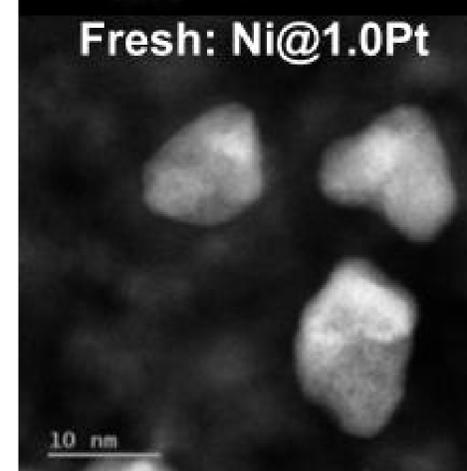
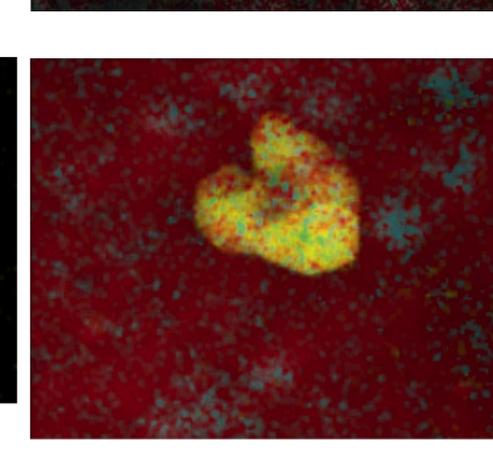
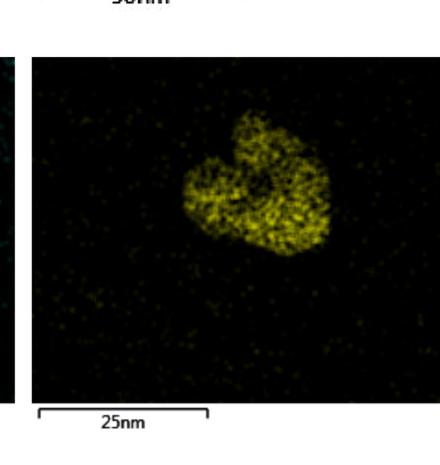
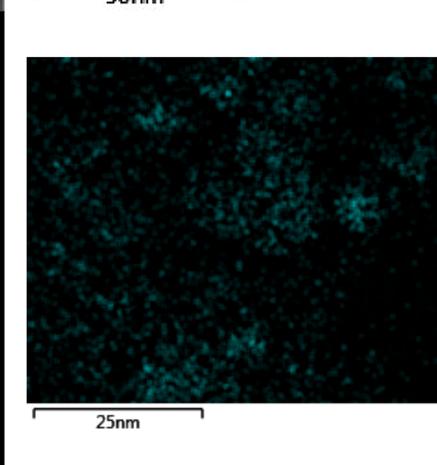
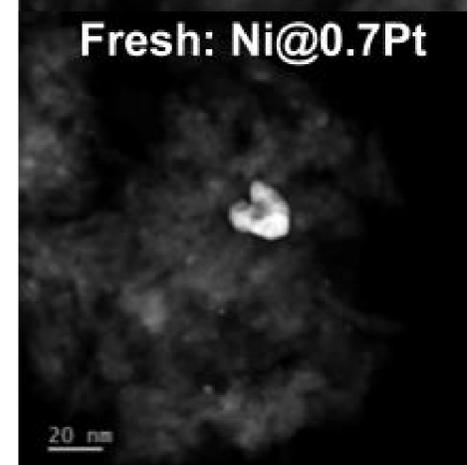
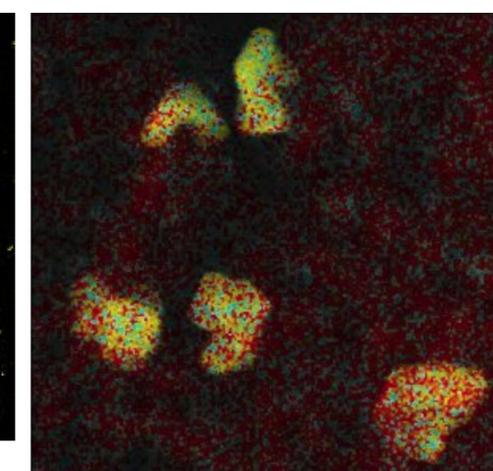
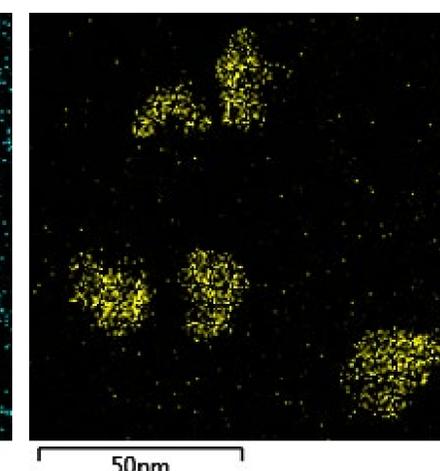
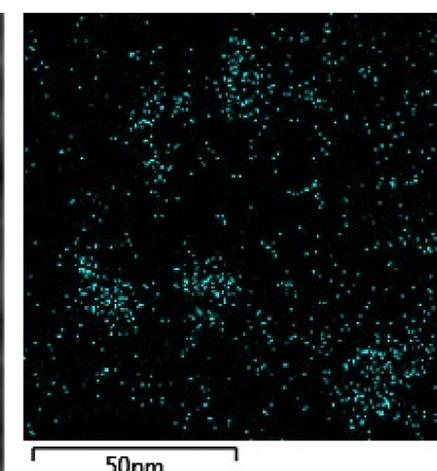
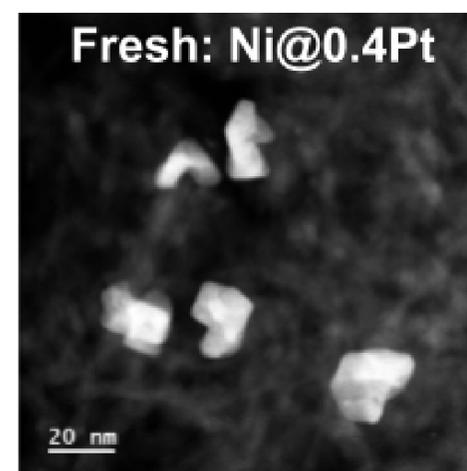
- XRD patterns indicate the formation of a Ni-Pt alloy with evidence of crystalline Pt sites.
- TPR results suggests that Pt assists the reduction of Ni compounds with a maximum difference of 30 °C at 1 monolayer Pt.

Fresh Reduction Characterization



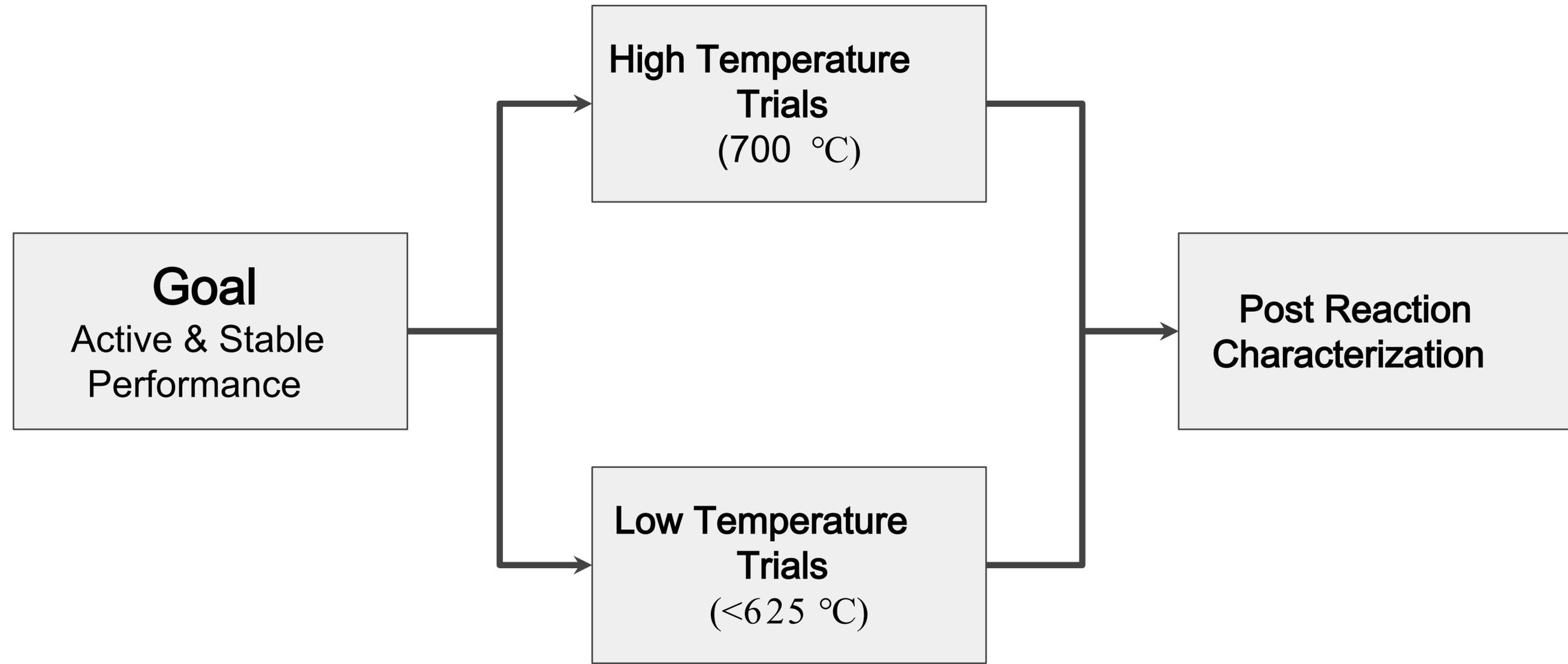
	MEAN	SD
Dn	6.0	3.6
Ds	10.7	6.0
Dv	13.7	8.6

- **Red:** Aluminum, **Blue:** Nickel, **Yellow:** Platinum
- A review of all captured images shows no evidence of metallic Pt on the $\gamma\text{-Al}_2\text{O}_3$ support.
- EDX suggests autocatalytic deposition of Pt forming crystalline sites on Ni seeds.

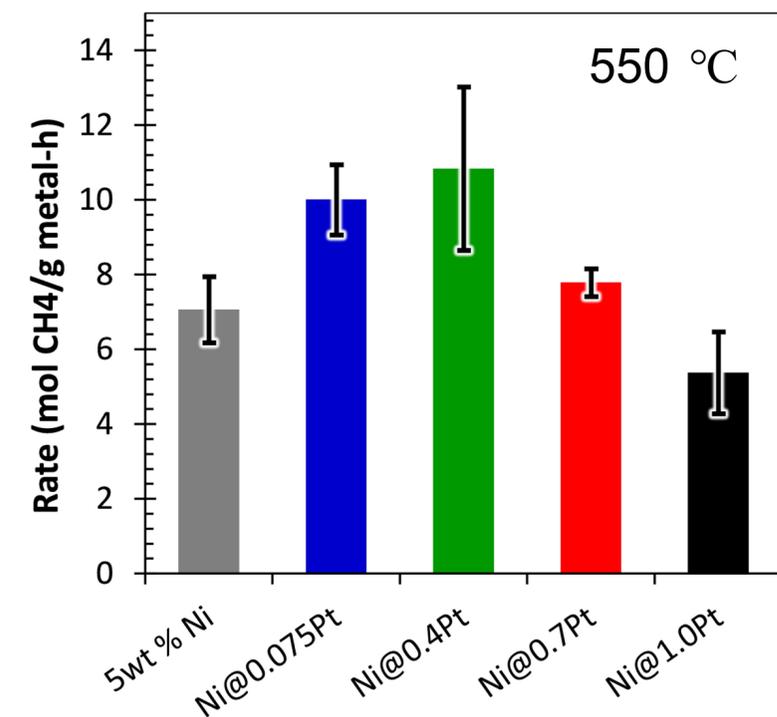
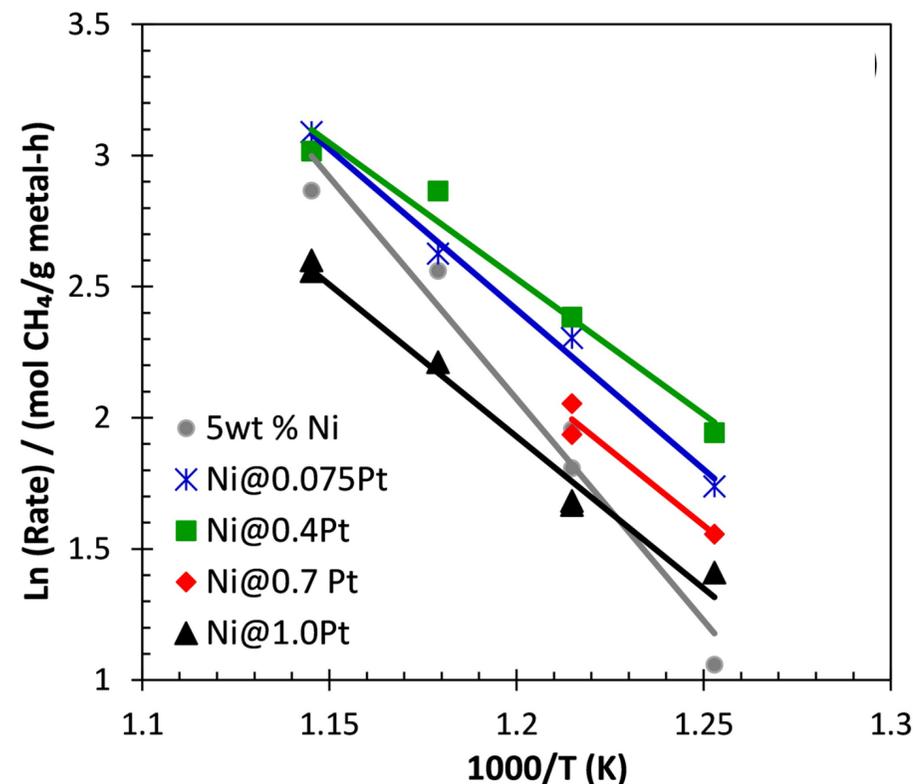
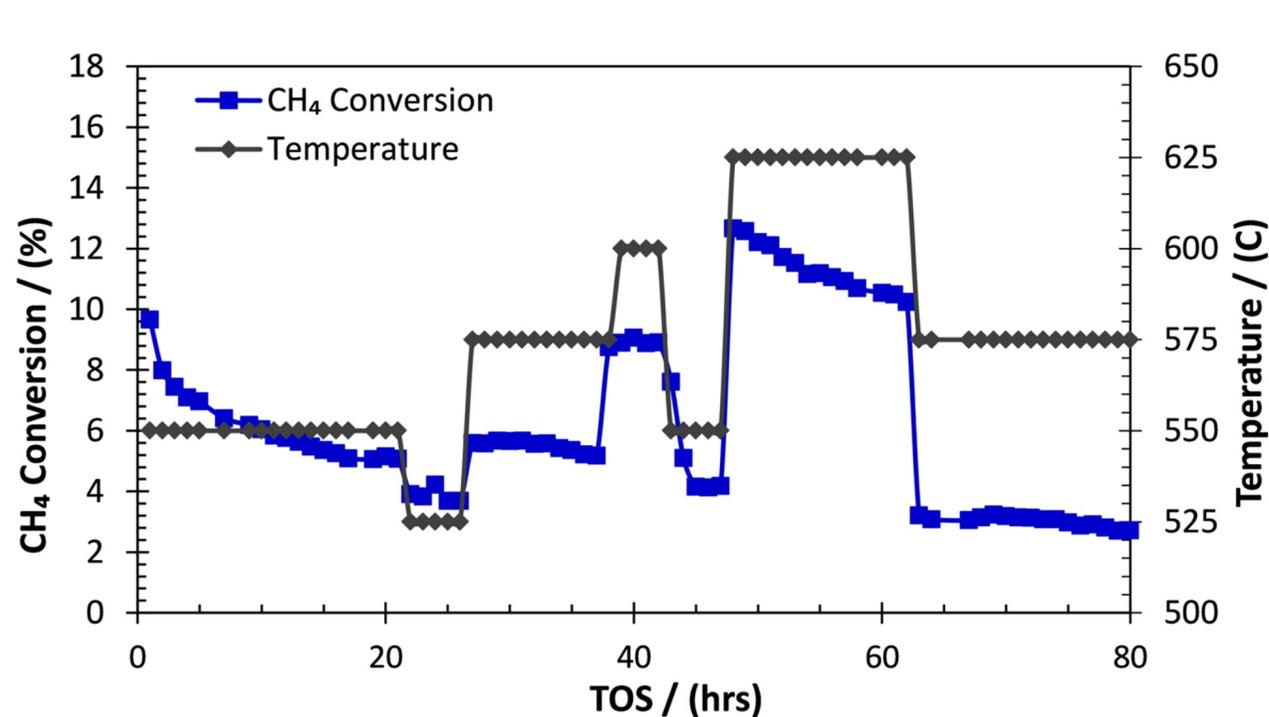


NOTE: "Fresh" notation indicates samples were reduced in H_2 at 600 °C (Ni) and 300 °C (Pt).

Evaluation



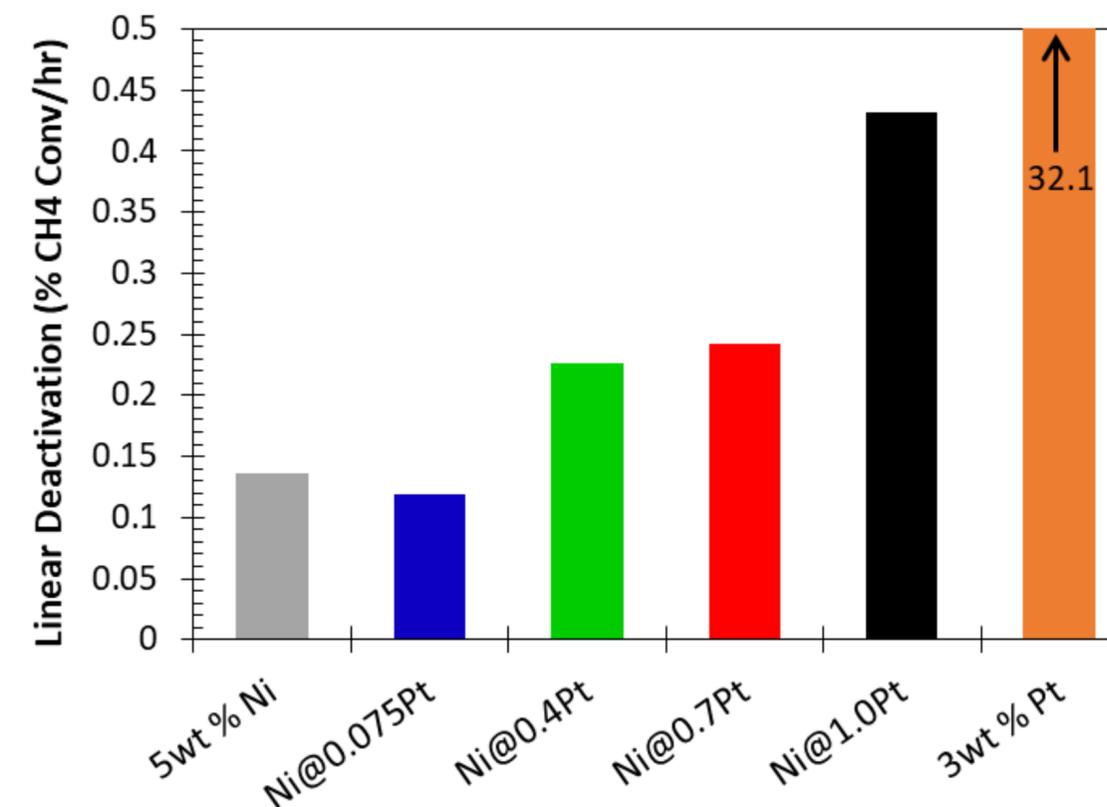
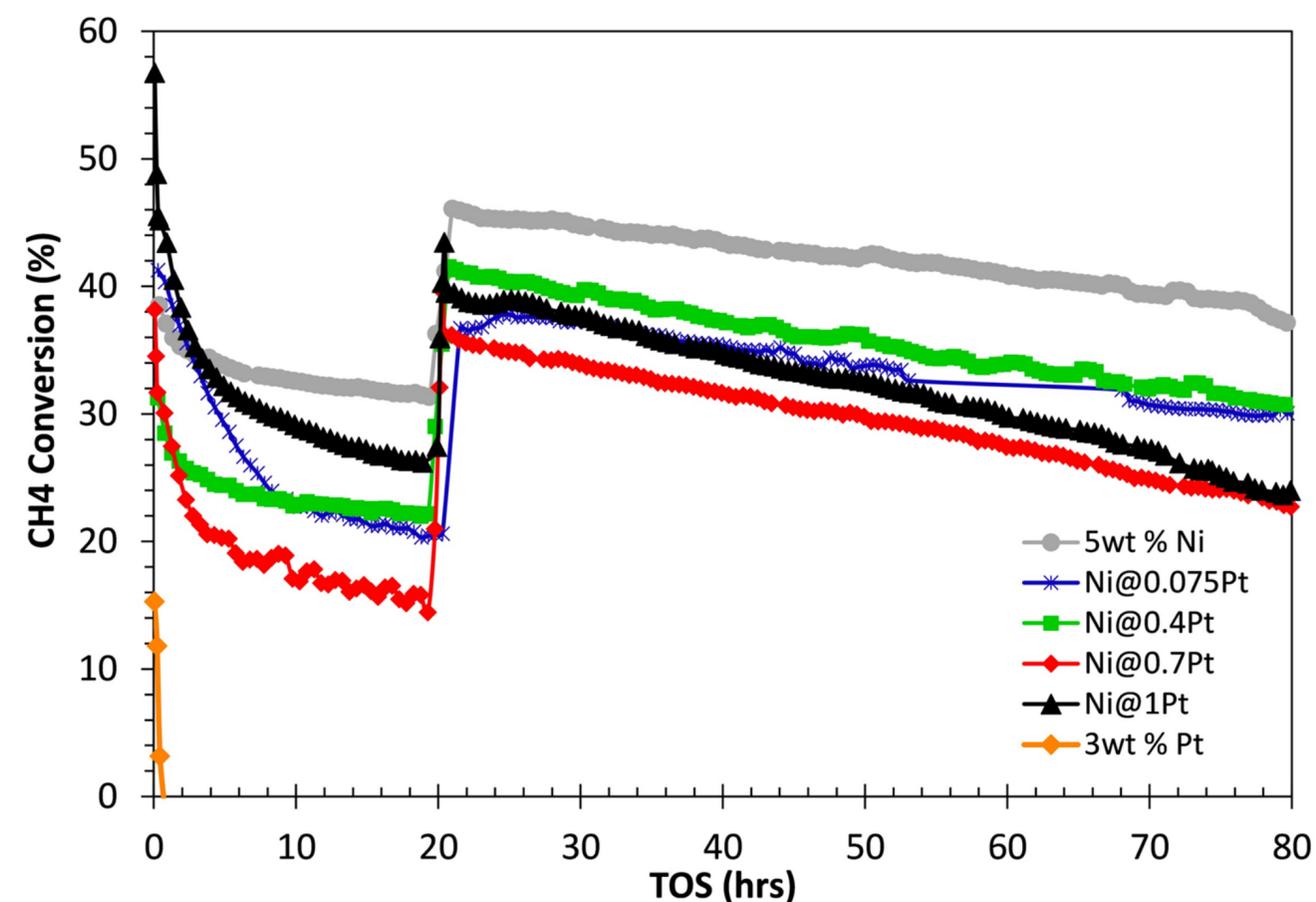
Low Temperature Results ($T \leq 600$ °C)



- 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 CH₄ conversion rates are increased with an optimum between 0.075 and 0.4 monolayers.

Catalyst	Ni/Pt Atomic Ratio	E_a' (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	-	-	-

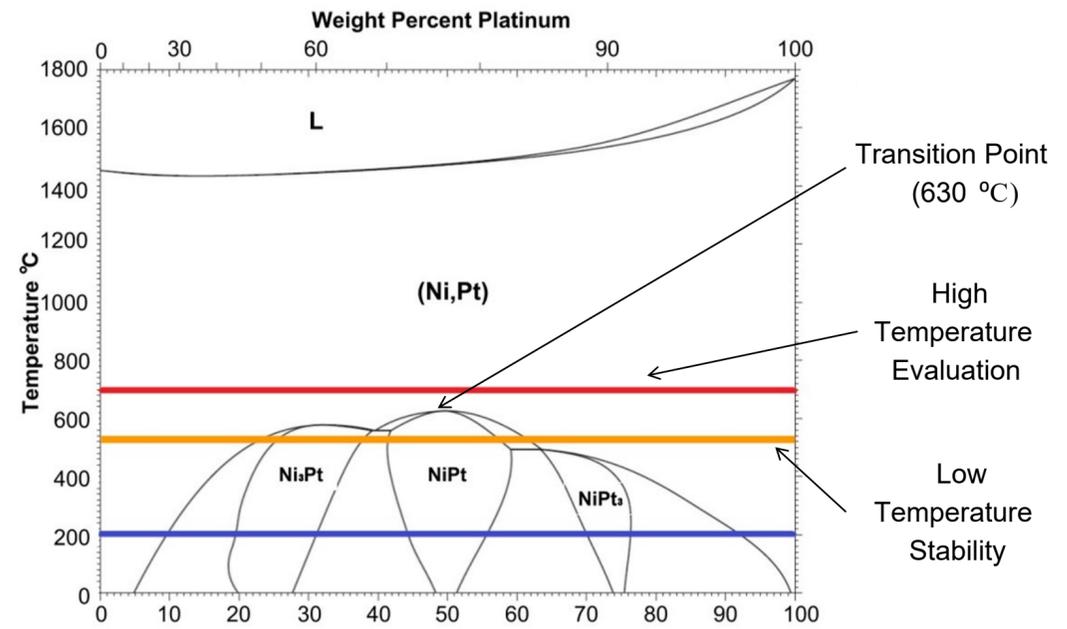
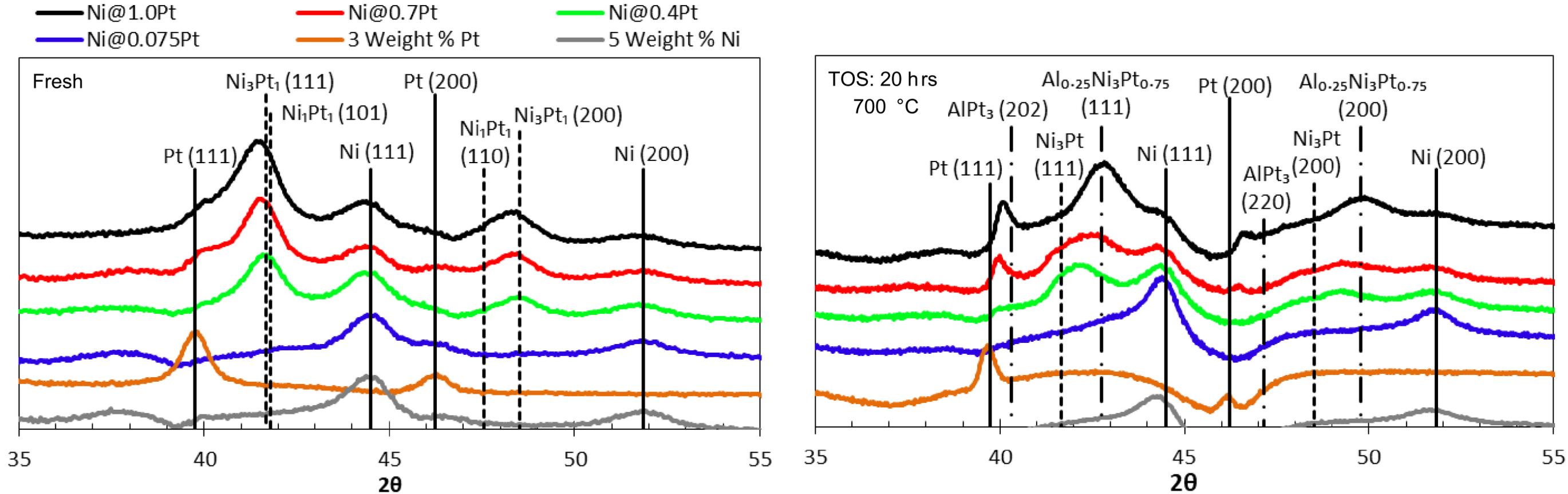
High Temperature Results (T=700 °C)



Catalyst	Ni/Pt Atomic Ratio	Deactivation rate ($\text{mmol CH}_4 \text{ h}^{-2} \text{ g}_{\text{metal}}^{-1}$) ^b
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

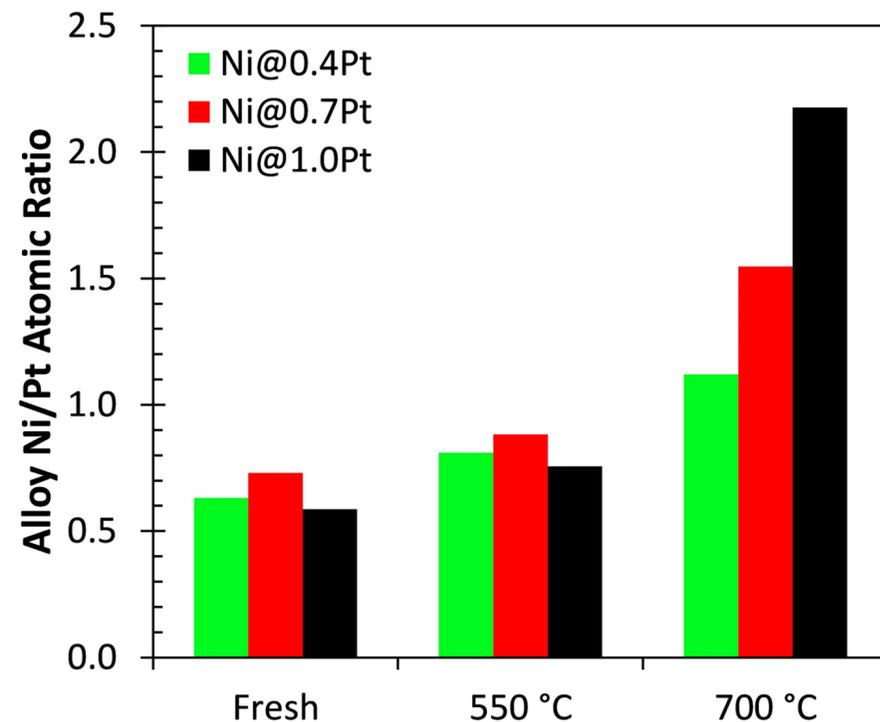
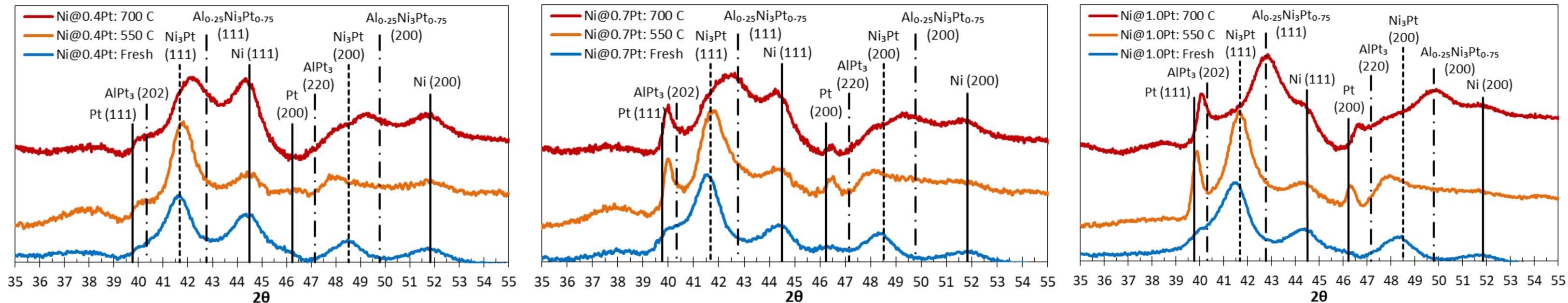
- $\text{CH}_4/\text{CO}_2/\text{He} = 1/1/2$ fixed GHSV after 20 hours TOS.
- Pt shows a negative effect on pseudo steady state CH_4 conversion.
- As Pt loading increases, deactivation rates over the linear region also increase.

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°2θ) 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.

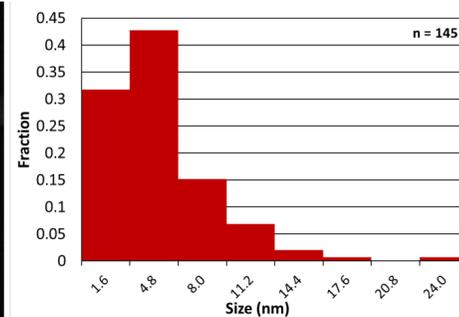
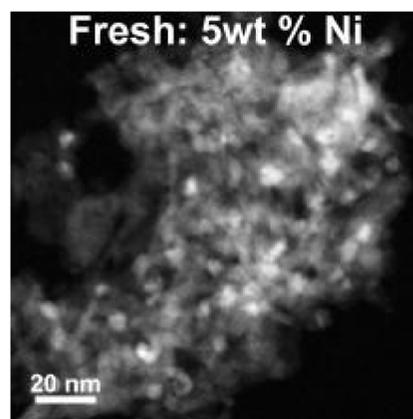
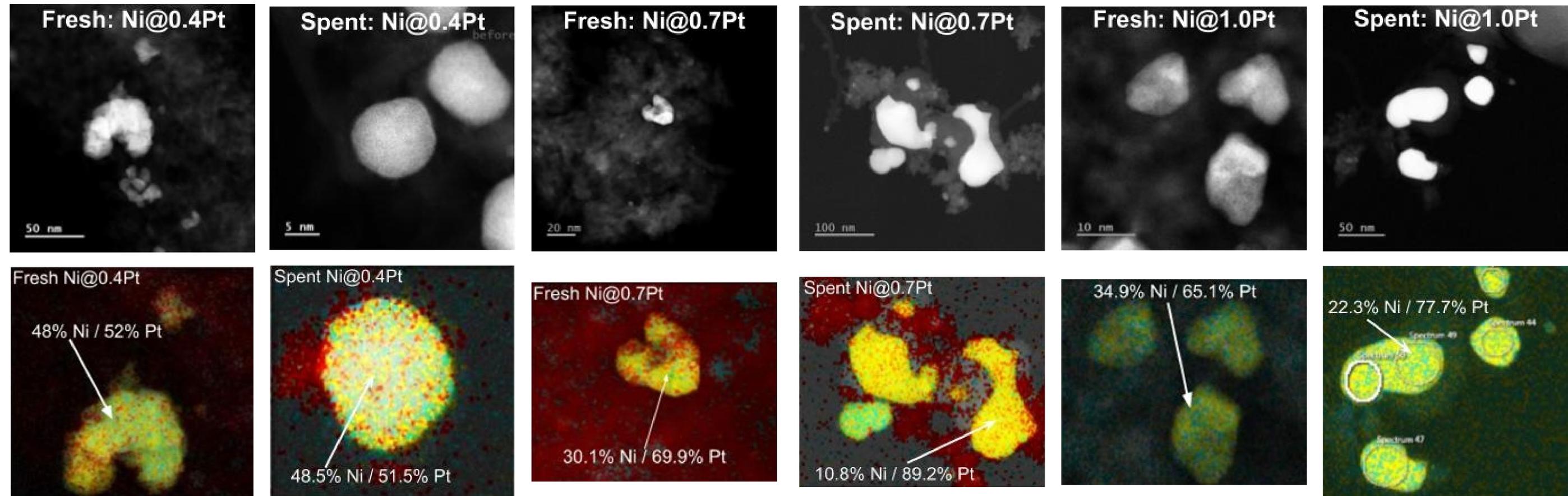
Post Reaction Characterization



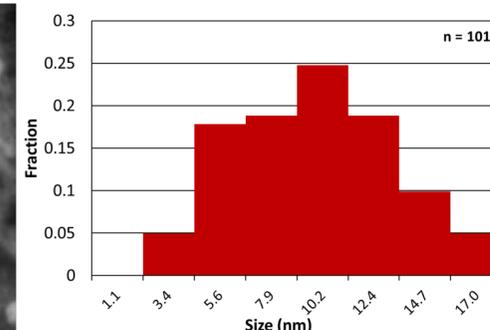
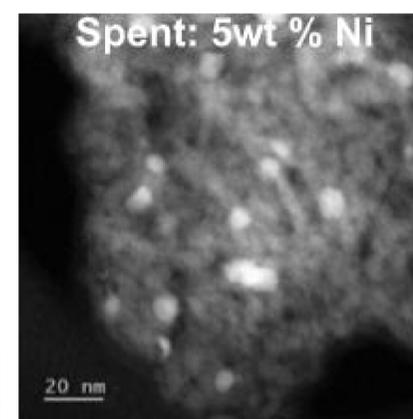
- Post reaction data collected after 20 hours TOS.
- At 550 °C (Orange) spent patterns indicate that the Ni-Pt alloy phase is maintained with some growth of the crystalline Pt phase at higher Pt loadings.
- High temperature patterns (Red) show significant shifts towards Al-Ni-Pt formation with increasing Pt loading.
- Applying Vegard's Law, calculated Ni/Pt atomic ratios of the alloy phase increase with both temperature and Pt concentration (alloy phase becomes Ni rich).

Post Reaction Characterization

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



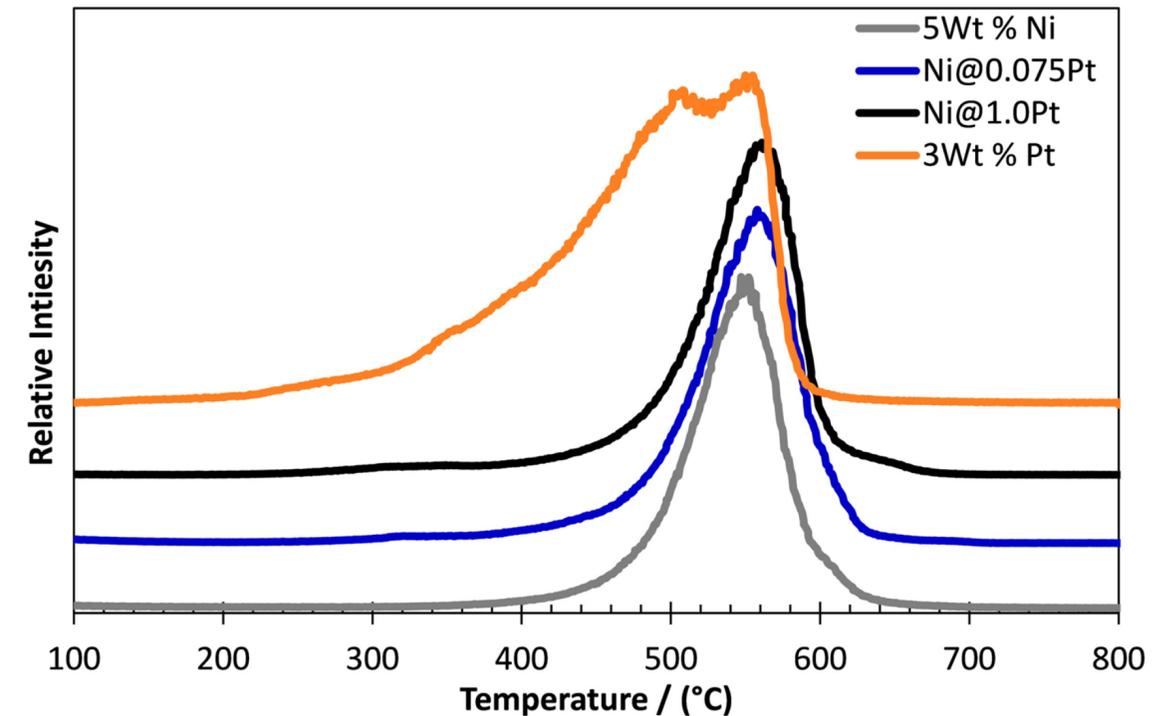
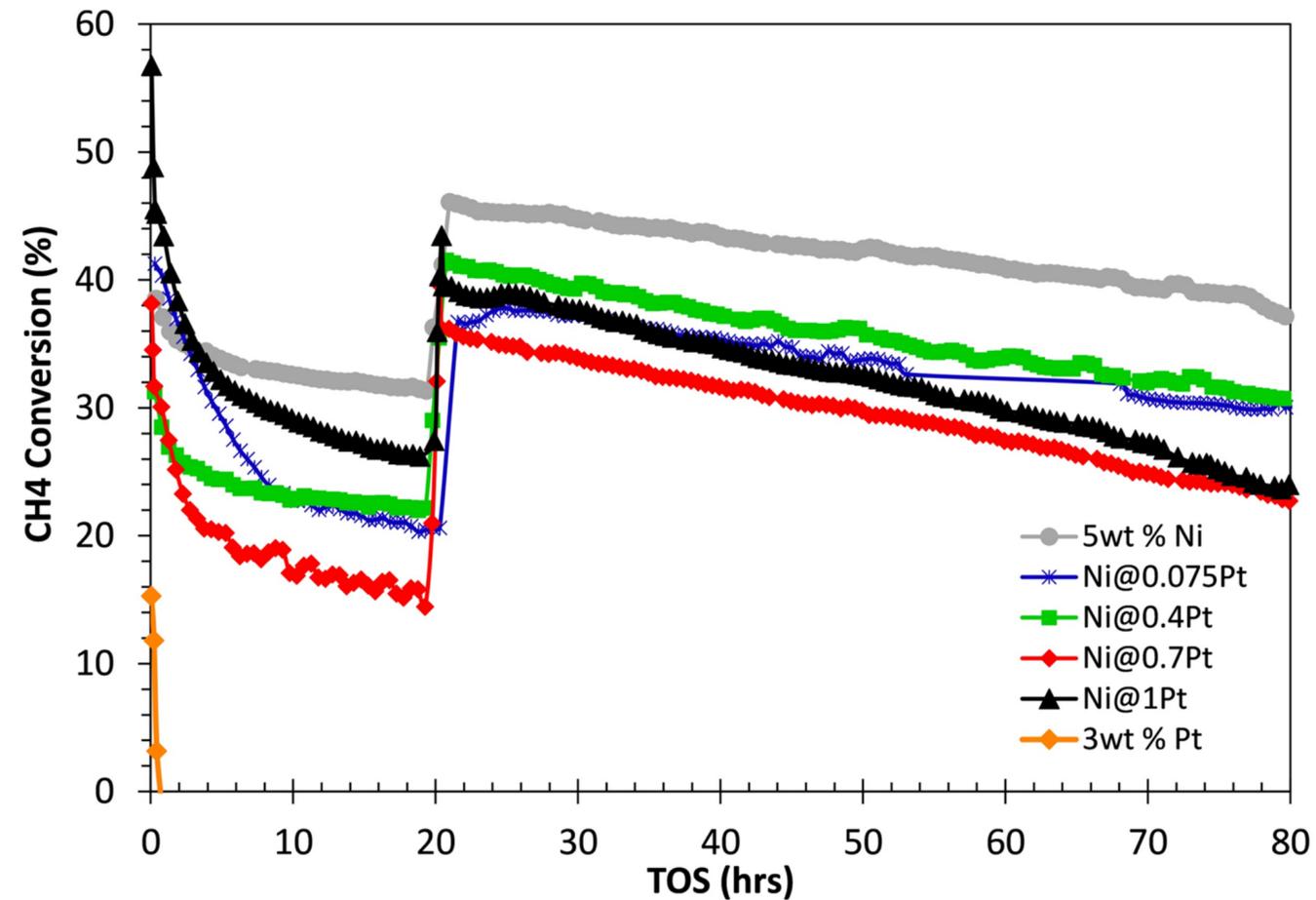
	MEAN	SD
Dn	6.0	3.6
Ds	10.7	6.0
Dv	13.7	8.6



	MEAN	SD
Dn	8.5	2.7
Ds	10.1	3.1
Dv	10.8	3.5

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

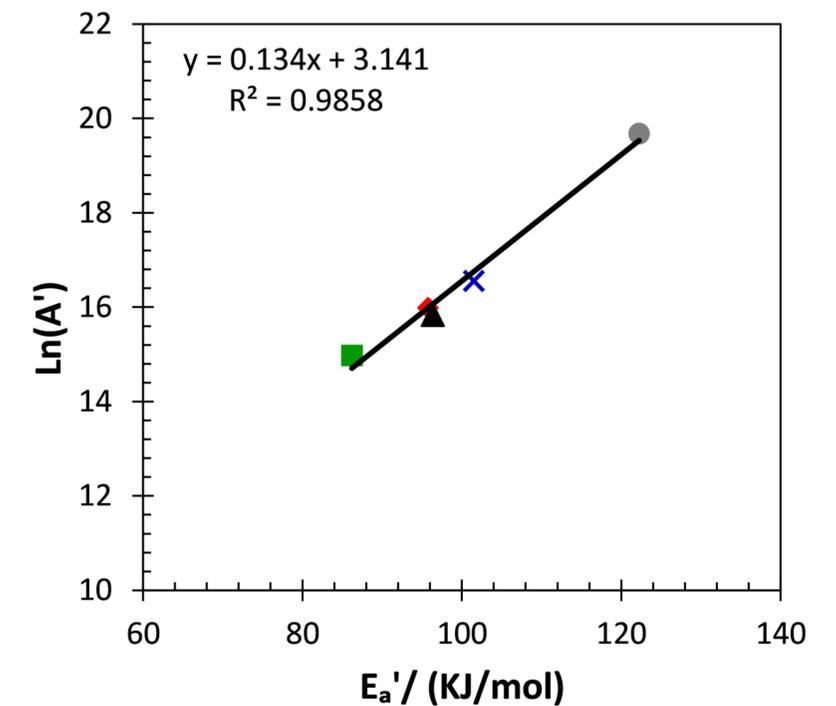
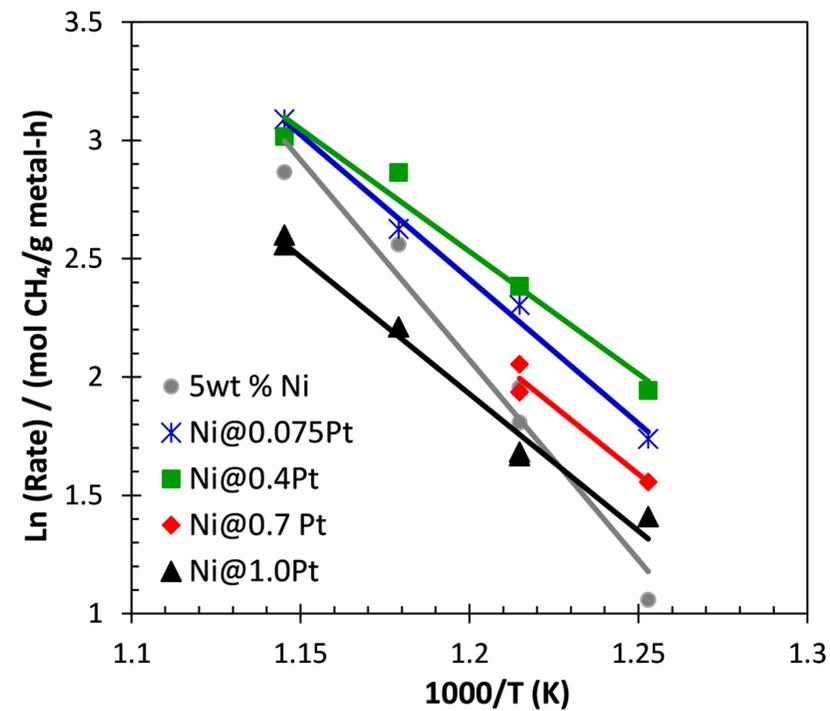
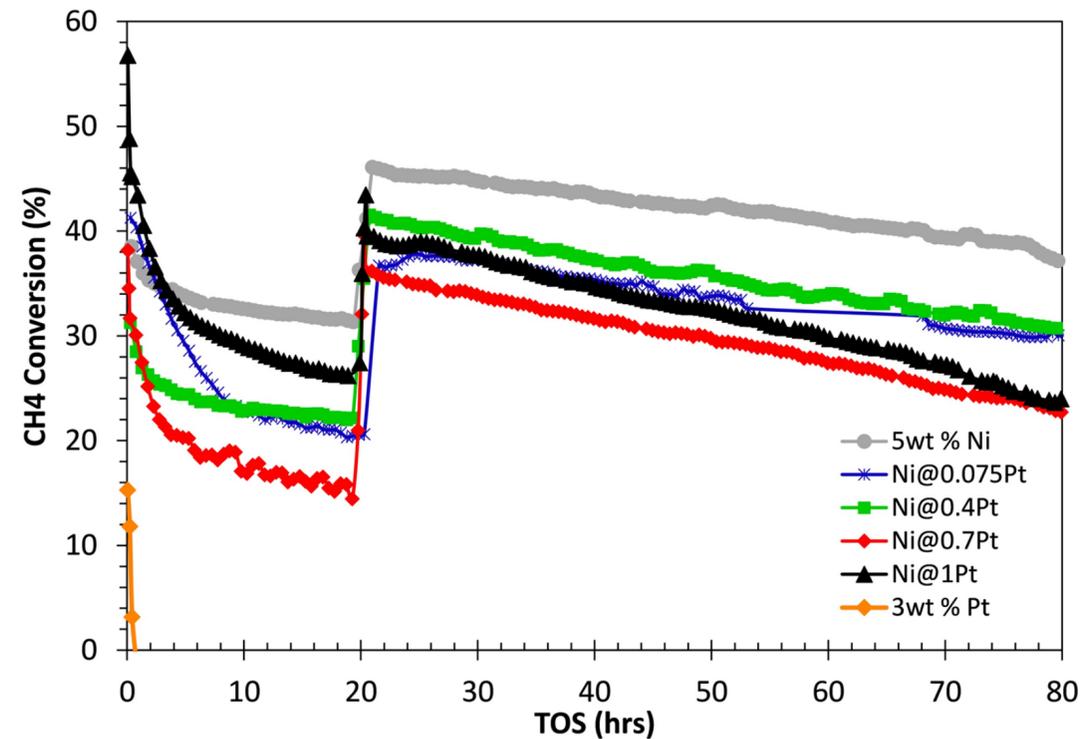
Stability Conclusions



Catalyst	Ni/Pt Atomic Ratio	Deactivation rate ($\text{mmol CH}_4 \text{ h}^{-2} \text{ g}_{\text{metal}}^{-1}$) ^b	Coke formation ($\text{mmol C/g}_{\text{cat}}$)
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 CH₄ 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 (θ) 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.

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

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

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

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.

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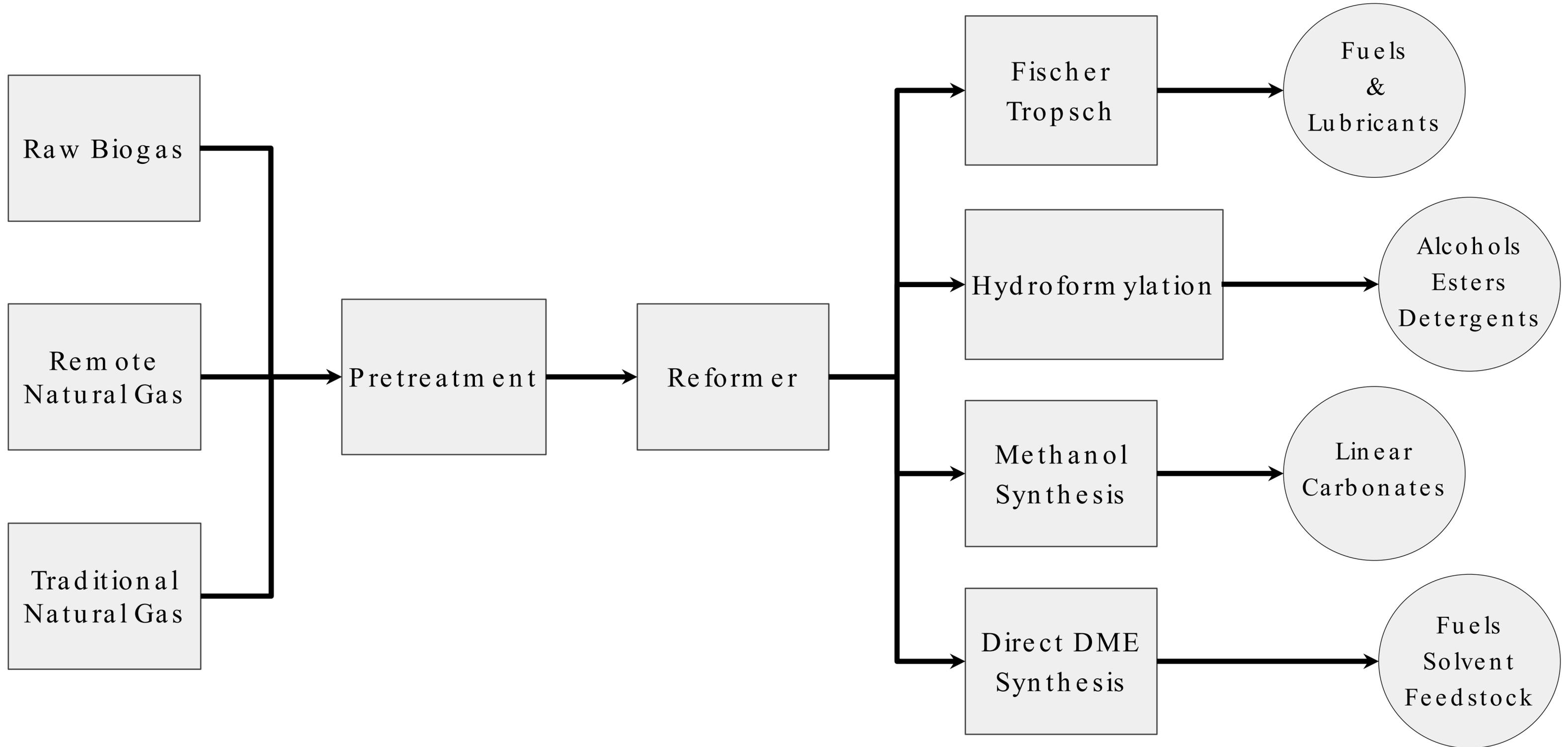




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Questions?

Dry Reforming Applications



Ni@0.7Pt Spent Samples

