Well-Dispersed Pt-Co Catalysts with Alloy Nanoparticles Using Electrostatic Adsorption and Electroless Co-Deposition Synthesis Methods

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Catalysis with Nanoparticles II

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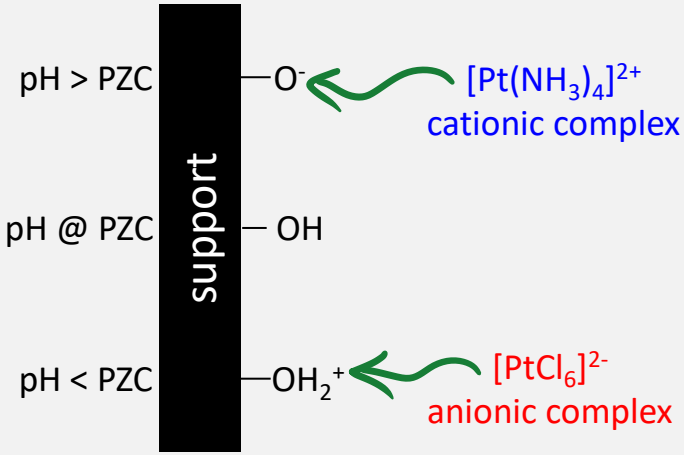
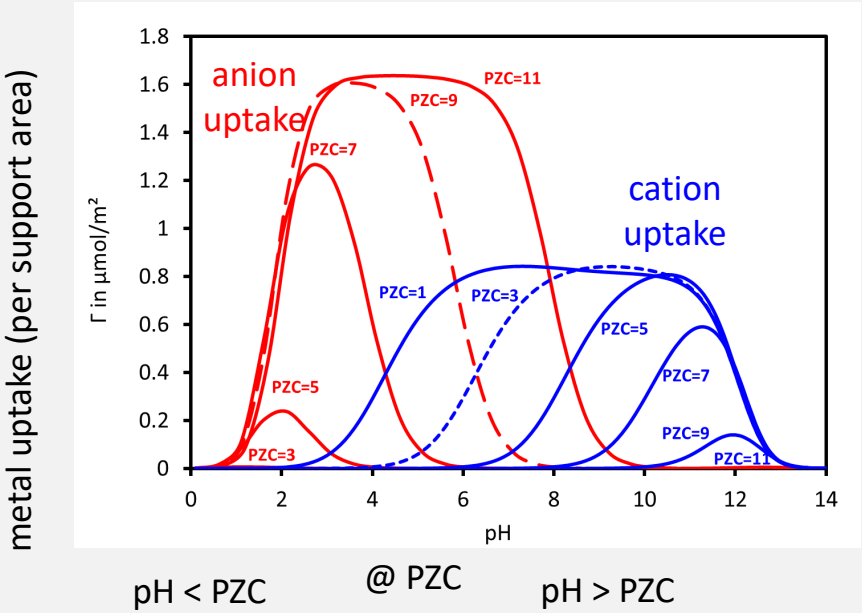
INTRODUCTION: STRONG ELECTROSTATIC ADSORPTION (SEA)

- Inducing surface charge on support by adjusting pH of impregnating solution
- SEA at incipient wetness is also called Charge Enhanced Dry Impregnation (CEDI)



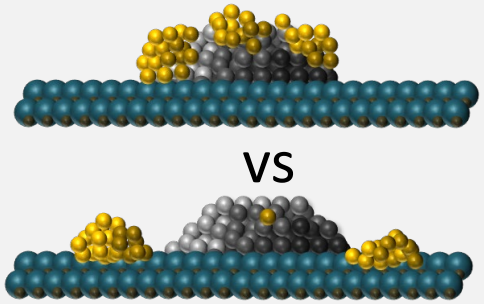


- resulting close packed monolayer of ionic complex (retaining hydration sheaths) with **strong interaction** with support

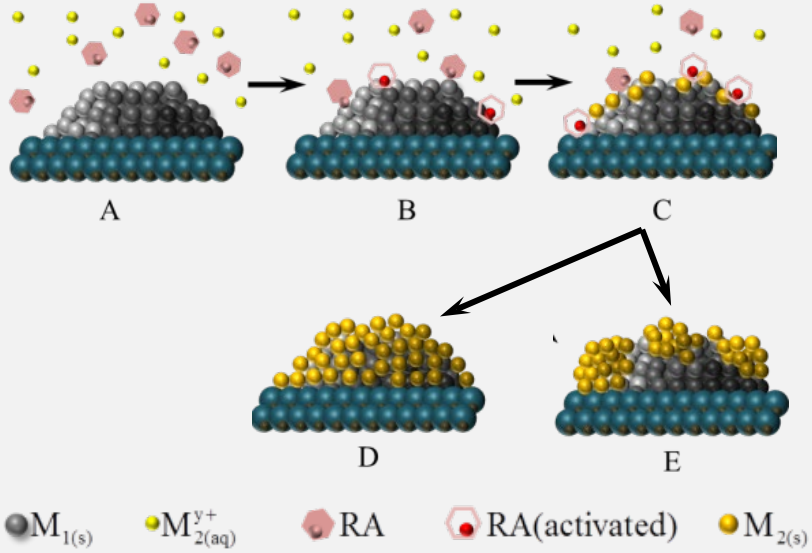
- decreased mobility of metal atoms result in smaller catalyst particles (compared to simple impregnation)

INTRODUCTION: ELECTROLESS DEPOSITION (ED) FOR BIMETALLIC CATALYSTS

- Addition of another metal can enhance catalytic activity through bimetallic effects: bifunctional, electronic, and/or ensemble.
- Usual method of co-impregnation does not ensure interaction between component metals



ED: Controlled deposition of secondary metal on the surface of primary/seed catalyst



A) Immersion of seed catalyst in ED bath
B) Activation of reducing agent (RA) on the surface of seed catalyst
C) Reduction and deposition of secondary metal
D) Catalytic deposition
E) Auto-catalytic deposition

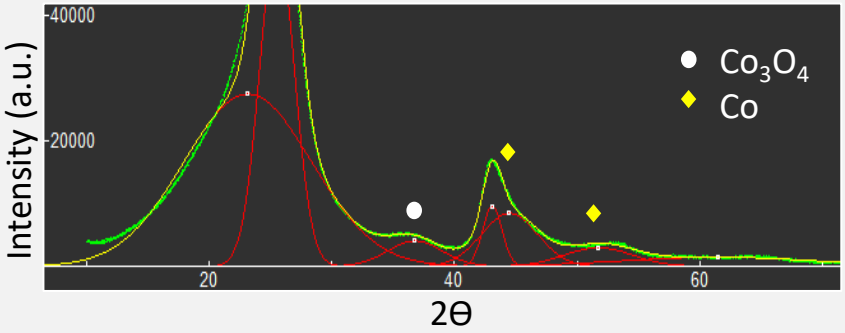
- Necessary to have proper combination of reducing agent, metal precursor, and ED conditions

PRIOR WORK: BATCH ED OF PLATINUM ON CARBON SUPPORTED COBALT

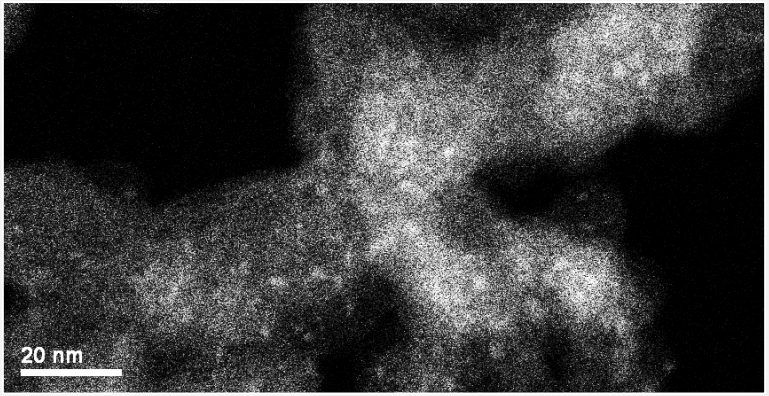
Base catalyst made by modified CEDI

Impregnation of Cobalt nitrate with Citric acid on Carbon Acethylene Black (**CB1**, PZC=3.4)
Annealing in He at 250°C for 4hrs, Reduction at 400°C for 1hr

Representative XRD profile of 2.5% Co/CB1



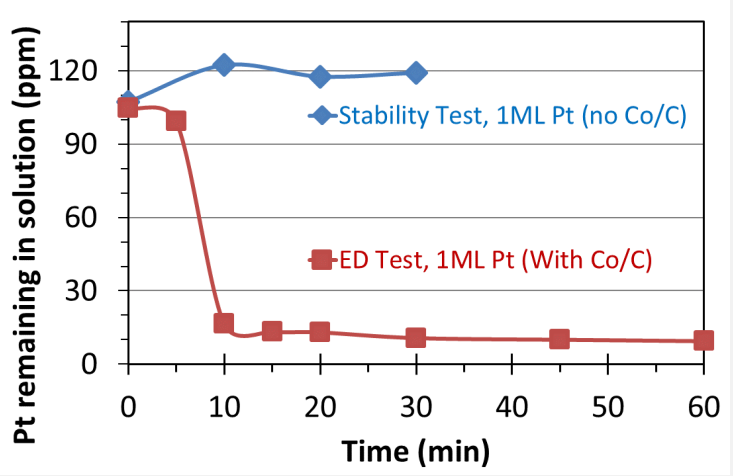
HAADF-STEM micrograph of 5% Co/CB1



Electroless Deposition in Batch Mode

Reducing Agent: Dimethylammineborane (DMAB)
Pt Precursor: Chloroplatinic acid, H_2PtCl_6
pH condition: basic – pH 10, above PZC of carbon support (3.7), to prevent adsorption of $[PtCl_6]^{2-}$ on carbon surface
Ethylenediammene added to improve bath stability
Pt:DMAB:EN = 1:5:4
T = 50°C
Theoretical Pt coverages used: 1.5ML, 3.0ML

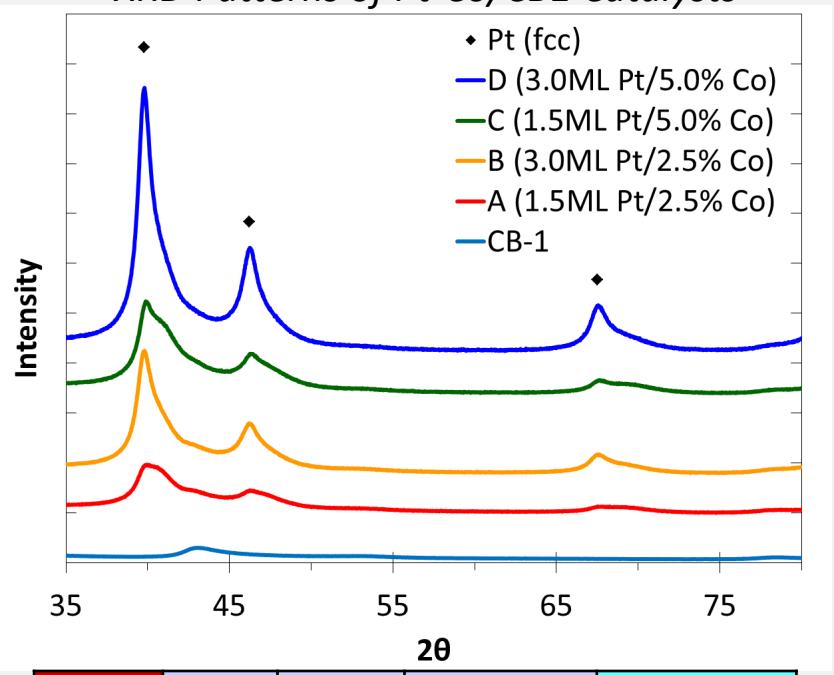
Trial deposition curves – Pt ED on Co/CB1



Catalysts 2016, 6(6), 83; DOI: 10.3390/catal6060083

PRIOR WORK: BATCH ED OF PLATINUM ON CARBON SUPPORTED COBALT

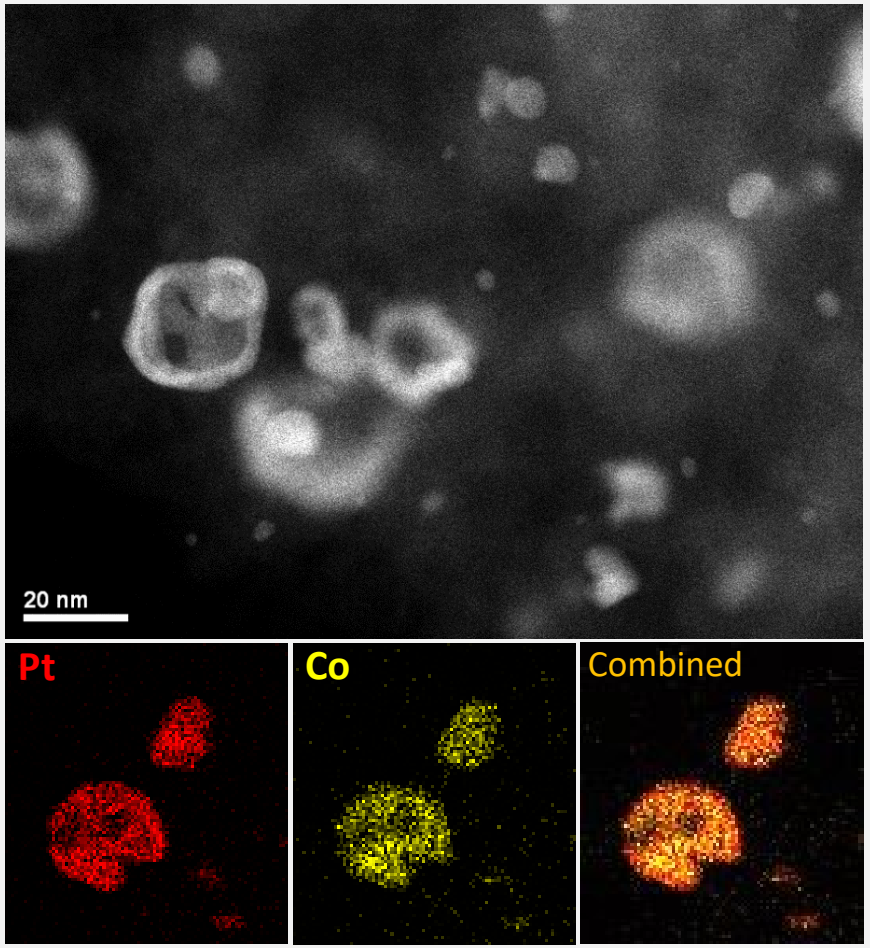
XRD Patterns of Pt-Co/CB1 Catalysts



Catalyst	Pt wt%	Co wt %	Bulk atomic Pt/Co	Alloy Lattice Param. (Å)
A	6.7	0.9	2.34	3.85
B	12.2	1.2	3.10	3.87
C	12.6	2.4	1.60	3.85
D	22.2	2.6	2.55	3.88
Pt				3.92
Co				3.55

Representative Micrographs and Maps of Pt-Co/CB1

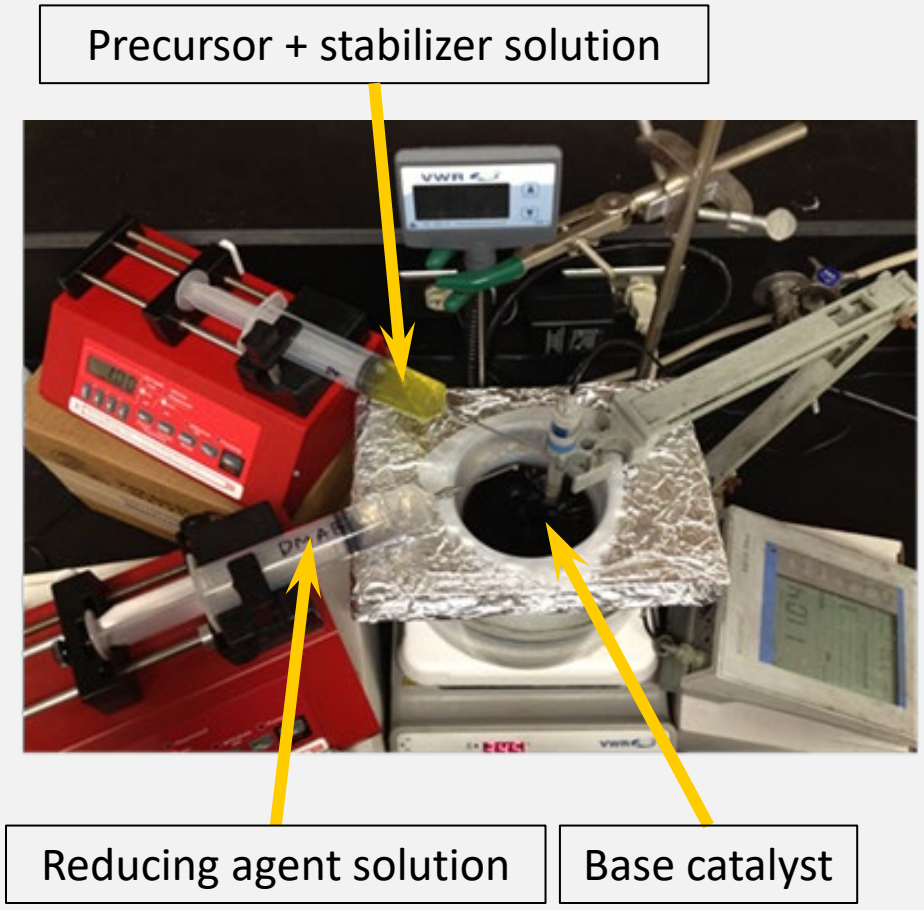
3.0ML Pt - 5.0% Cobalt on Carbon Black, reduced 200°C, 1 hr



- Shoulders to the right of Pt XRD peaks indicate alloy formation.
- Globules possibly from rapid decomposition of DMAB.
- Alloy formation from galvanic displacement of Co by Pt and re-deposition by ED (some of the Co dissolved in the bath).

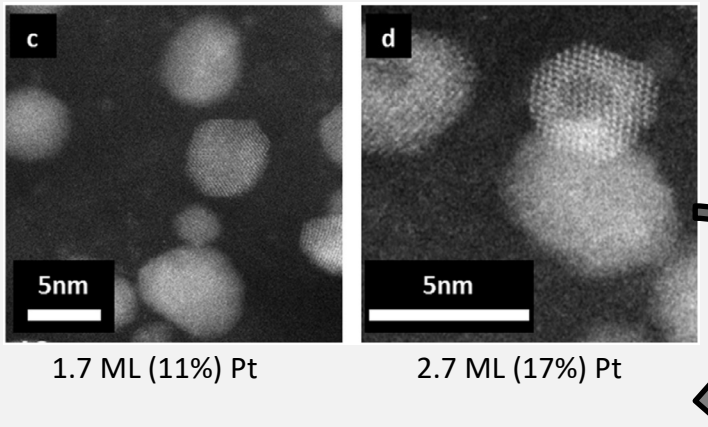
PRIOR WORK: SEMI-CONTINUOUS ELECTROLESS DEPOSITION OF PLATINUM

- By not loading all of the ED reactants initially in the bath, high concentrations are avoided and the rate of deposition is slowed down.



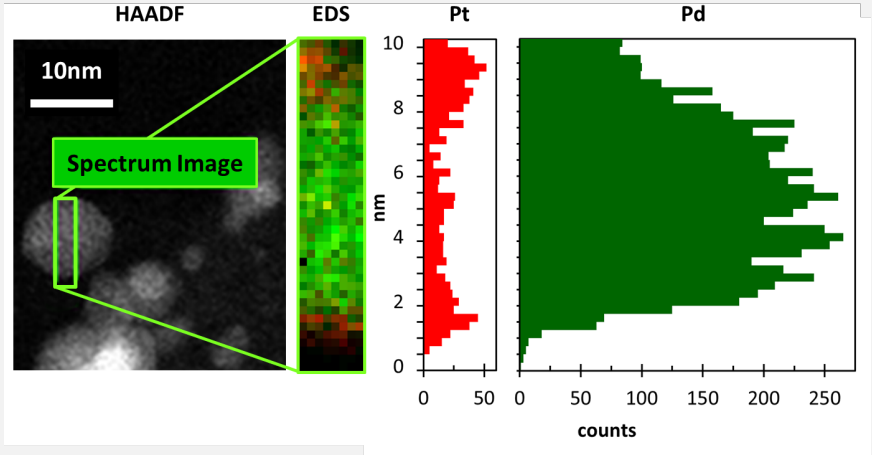
Pt on Pd/C by semi-continuous ED

30% Pd/C as base catalyst



1.7 ML (11%) Pt

2.7 ML (17%) Pt



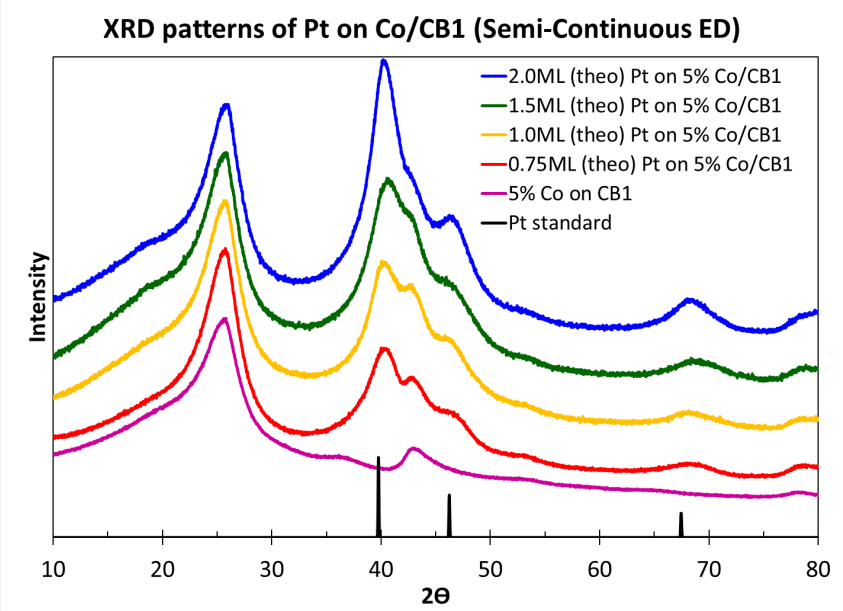
- Gradual addition of layers of secondary metal to higher loadings can be achieved.

Applied Catalysis B: Environmental 2016, 188, 367-375; DOI: 10.1016/j.apcatb.2016.02.022

APPLICATION OF SEMI-CONTINUOUS ED TO PLATINUM DEPOSITION ON CARBON SUPPORTED COBALT

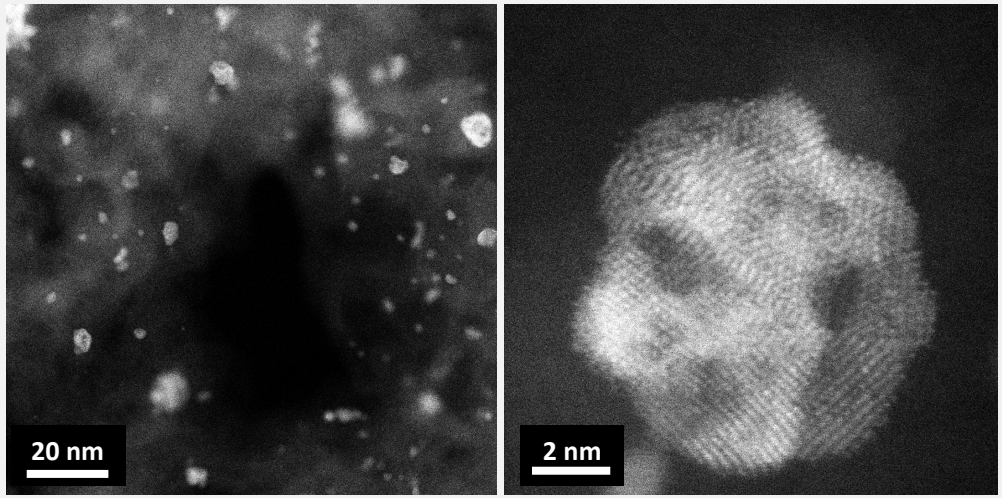
Akkarat Wongkaew, John Tengco, Yunya Zhang, John Regalbuto, John Monnier

- Same molar ratios of Pt precursor, EN stabilizer, and DMAB as batch system.
- Pt precursor and EN were pumped from a single reservoir while DMAB was added from another.



Representative Dark Field Micrographs Pt-Co/CB1

1.5ML Pt - 5.0% Cobalt on Carbon Black, reduced 200°C, 1 hr



- FCC peaks corresponding to Pt-Co alloy phase with lattice contraction (relative to Pt) was observed for all samples.
- No observed hollow globule type particles.
- Aggregates of smaller particles were observed in STEM.
- Grains/particles were speckled in Z-contrast imaging, due to intermixing of Co with Pt.

CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

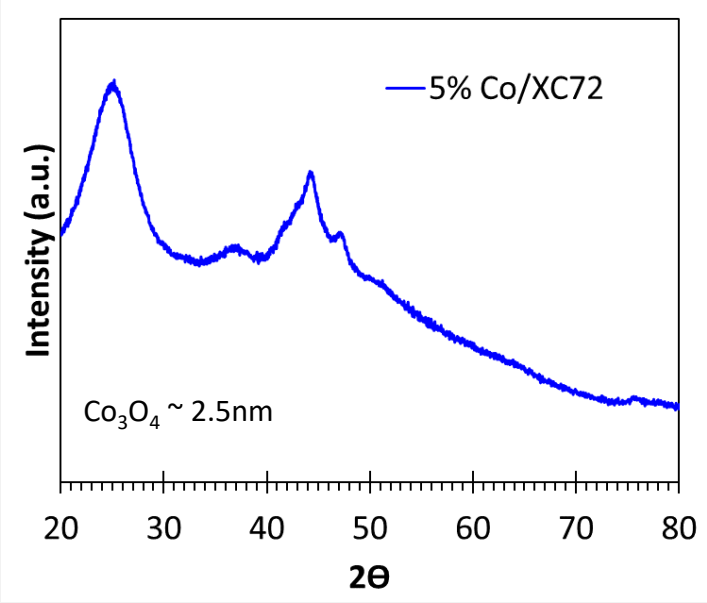
Base Co/C catalyst

- New base catalyst made on Vulcan XC72 carbon (BET SA = 250 m^2/g)
- 5% Co loading prepared by same modified CEDI method, annealed in He at 250°C for 4hrs, reduced at 400°C for 1hr.

co-ED Reagents

- Reducing Agent (RA): Dimethylammineborane (DMAB)
- Pt Precursor: Chloroplatinic acid, H_2PtCl_6 (CPA)
- Co Precursor: Hexamminecobalt chloride (CoHA)
- Ethylenediammene (EN) added to Pt solution

XRD pattern of Co base catalyst

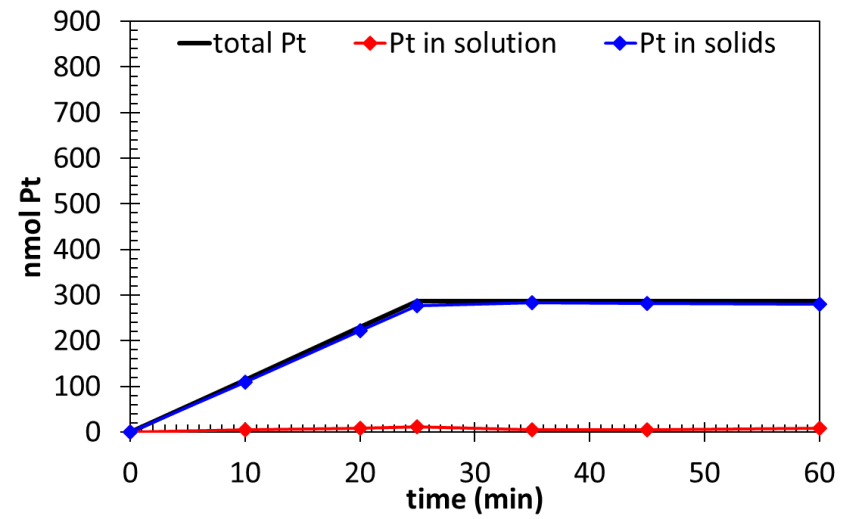


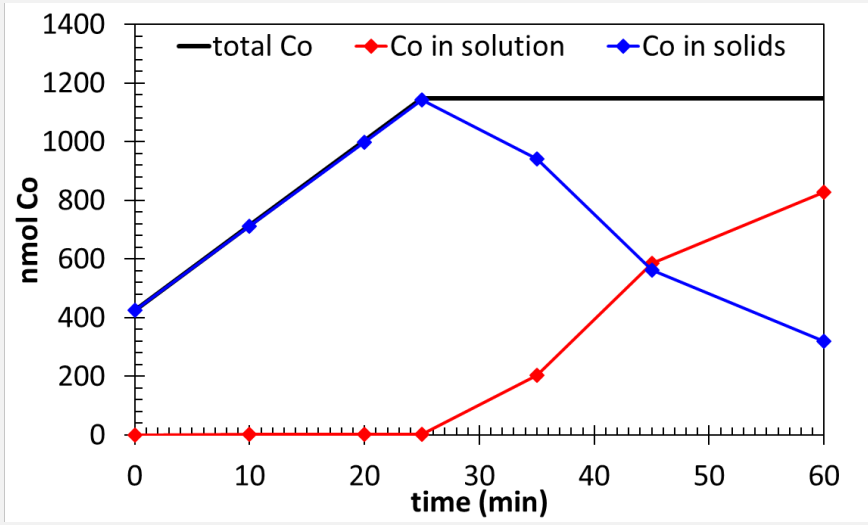
Semi-Continuous co-ED Parameters

Metal:RA = 1:5
Pt:EN = 1:4
Pt:Co = 3:1, 2:1, 1:1
Temp. = 50°C
pH = 10.0 to 10.5
Initial bath volume = 450 mL
CPA+EN volume = 50 mL
DMAB volume = 50 mL
CoHA volume = 50 mL
Pump rate = 2 mL/min
Run time = 25 min pump + 35 min rest

CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

Pt:Co = 1:3

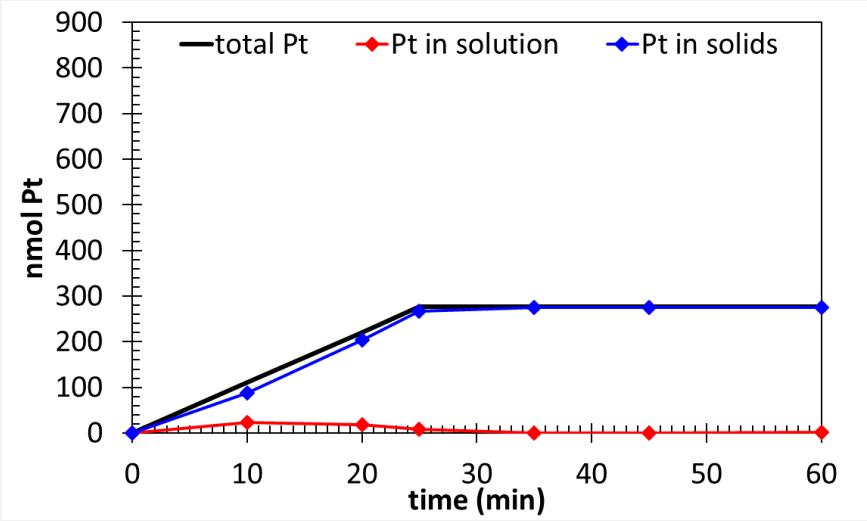


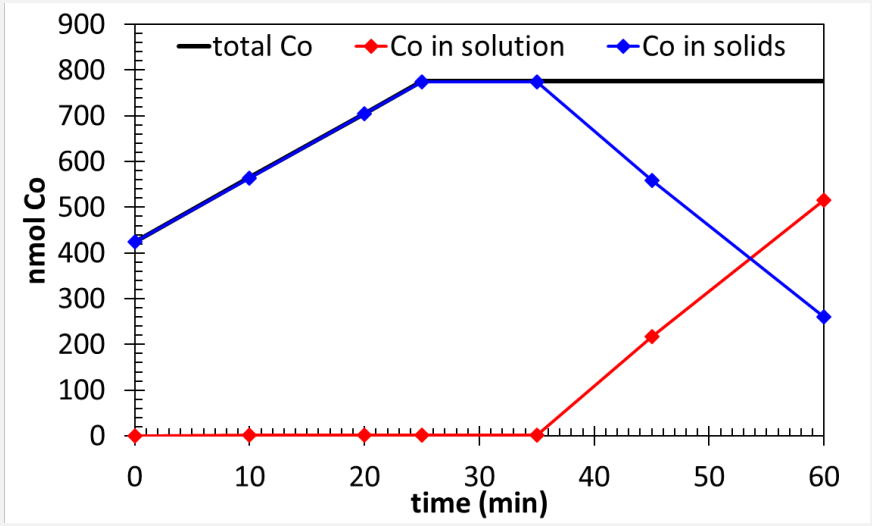


- Complete deposition of Pt was achieved, while Co deposition was complete during the pumping regime (25 min).
- Leaching of Co into solution after pumping of precursors and reducing agent has ended.
- More Co leaches out, eventually losing Co from the base catalyst.
- Increasing Pt:Co decreases Co leaching, possibly due to more corrosion resistant alloy being formed.

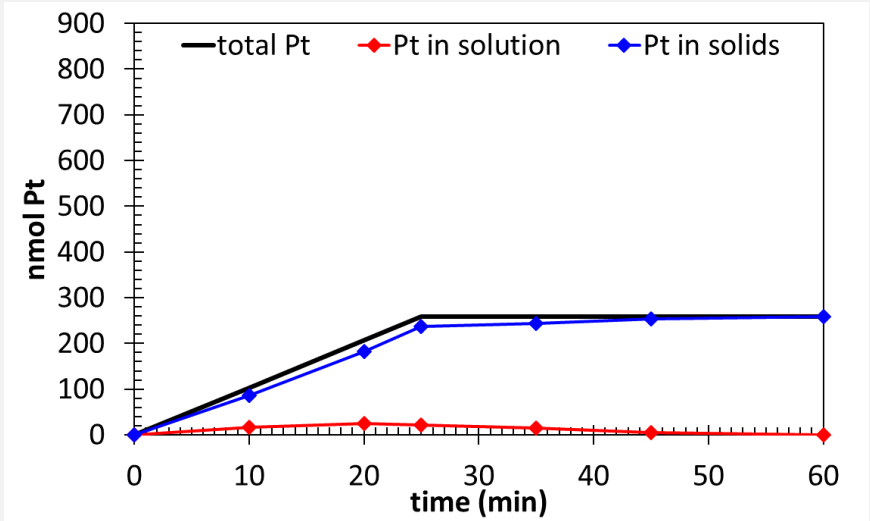
CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

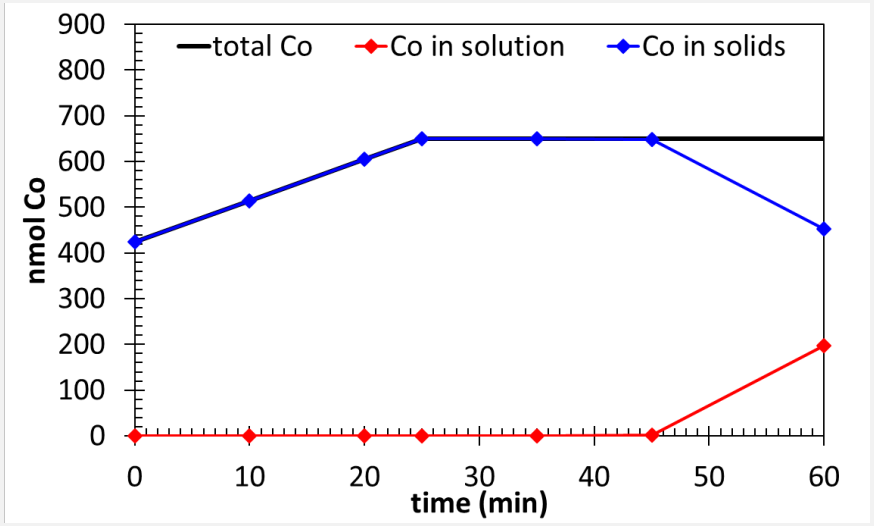
Pt:Co = 1:1.5





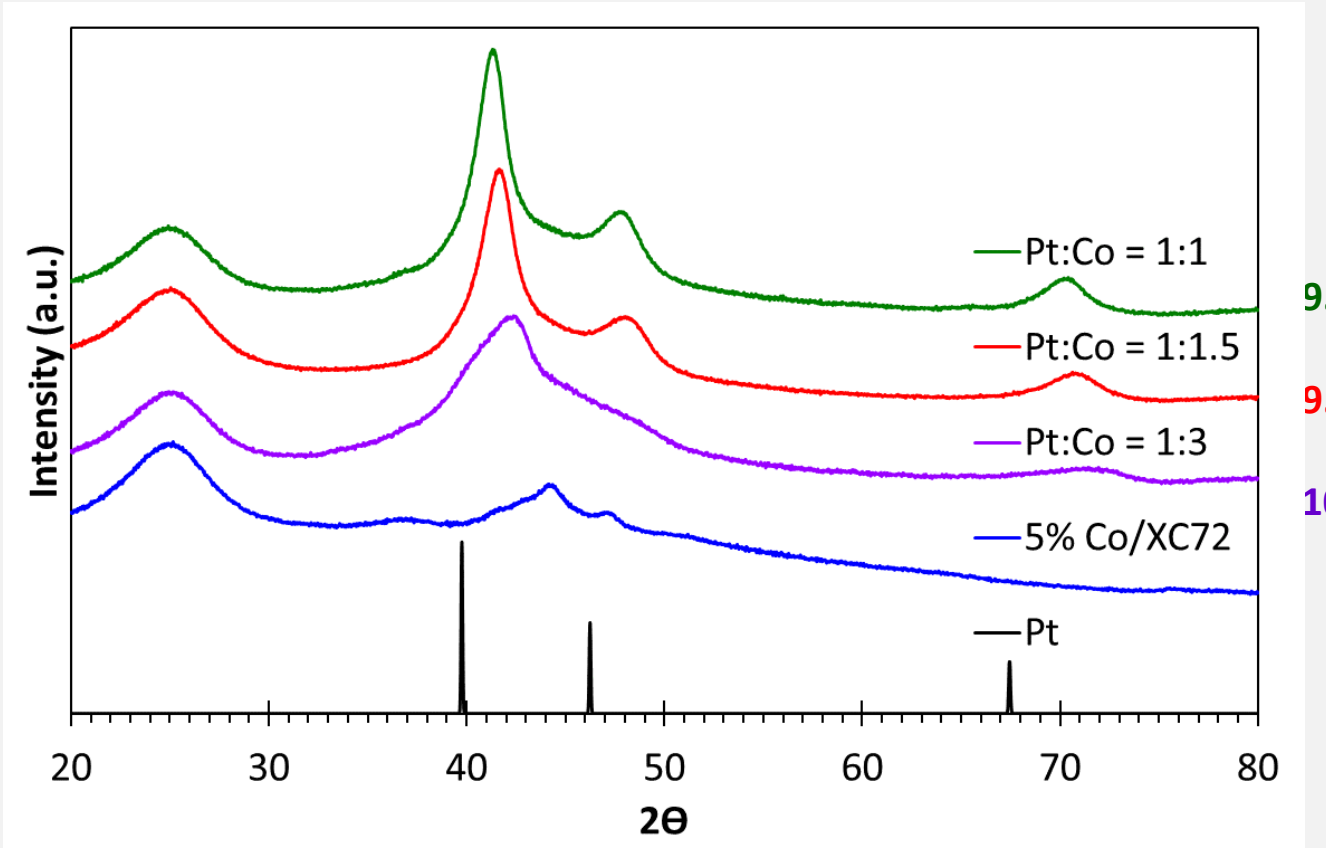
Pt:Co = 1:1





CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

XRD patterns of co-ED prepared Pt-Co/C catalysts



9.1% Pt – 4.8% Co

9.8% Pt – 2.8% Co

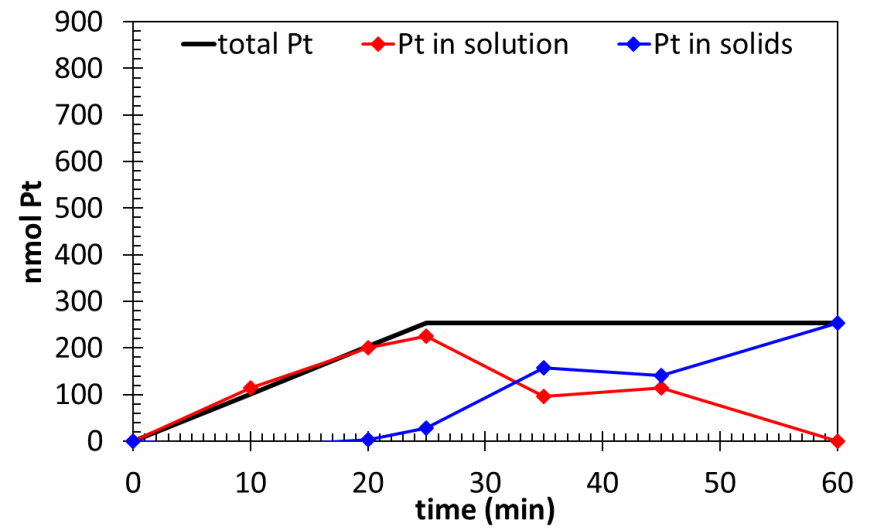
10% Pt – 3.4% Co

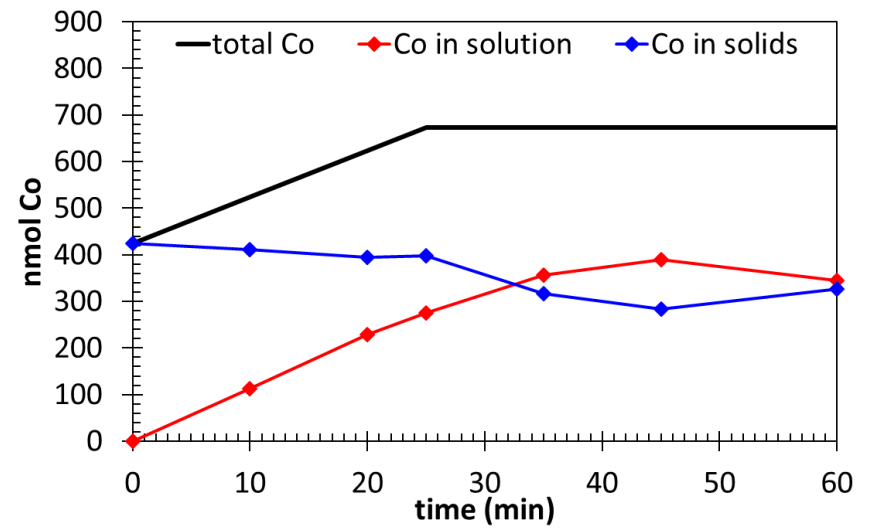
- FCC peaks corresponding to Pt-Co alloy phase with lattice contraction (relative to Pt) was observed for all samples.
- While all samples have resulting similar metal loadings, sample with feed ratio of Pt:Co = 1:1 gave the best dispersion based on XRD.
- Lattice parameter: 3.70 Å – 3.78 Å.
- Pending confirmation with STEM.

CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

Ethylenediaminetetraacetic Acid Disodium Cobalt as Precursor

Pt:Co = 1:1



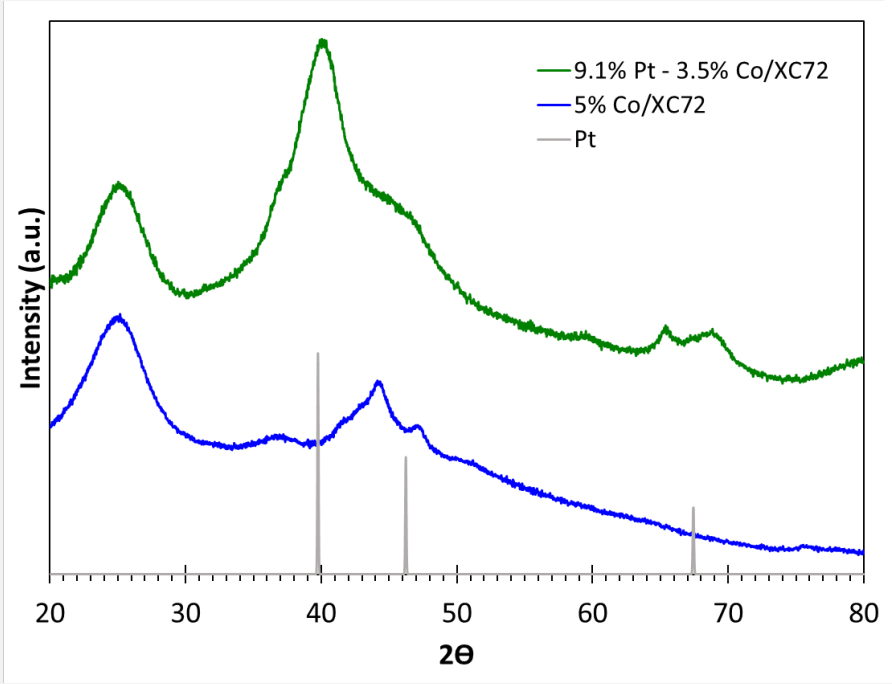


- CoEDTA complex substituted as precursor for Cobalt.
- Slower deposition of Pt was observed and virtually no net deposition of Co, possibly equal competing rates of displacement of Co (by Pt) and deposition.

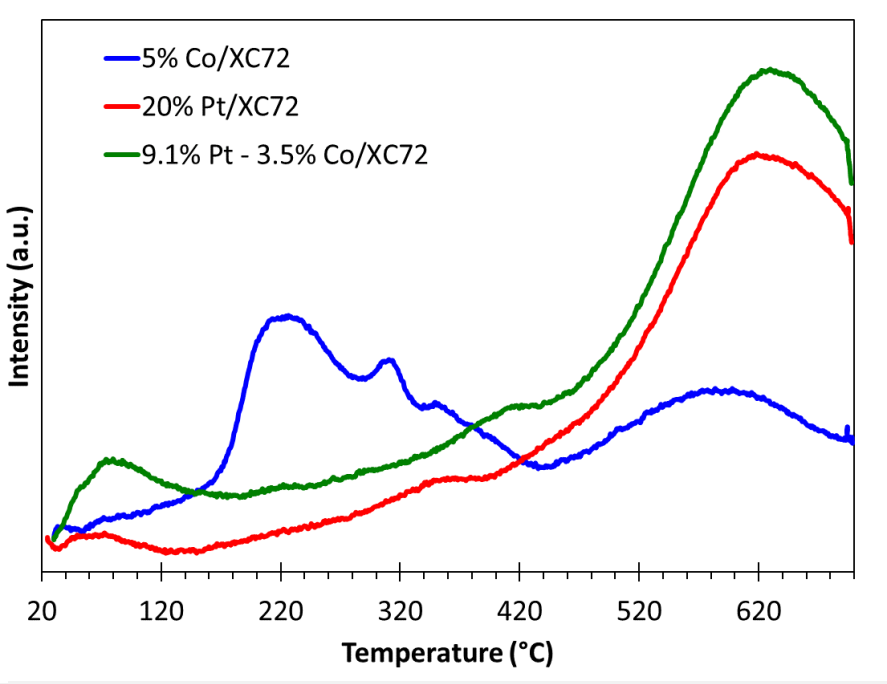
CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

Ethylenediaminetetraacetic Acid Disodium Cobalt (CoEDTA) as Precursor

X-ray Diffraction



TPR of O-pre-covered catalysts

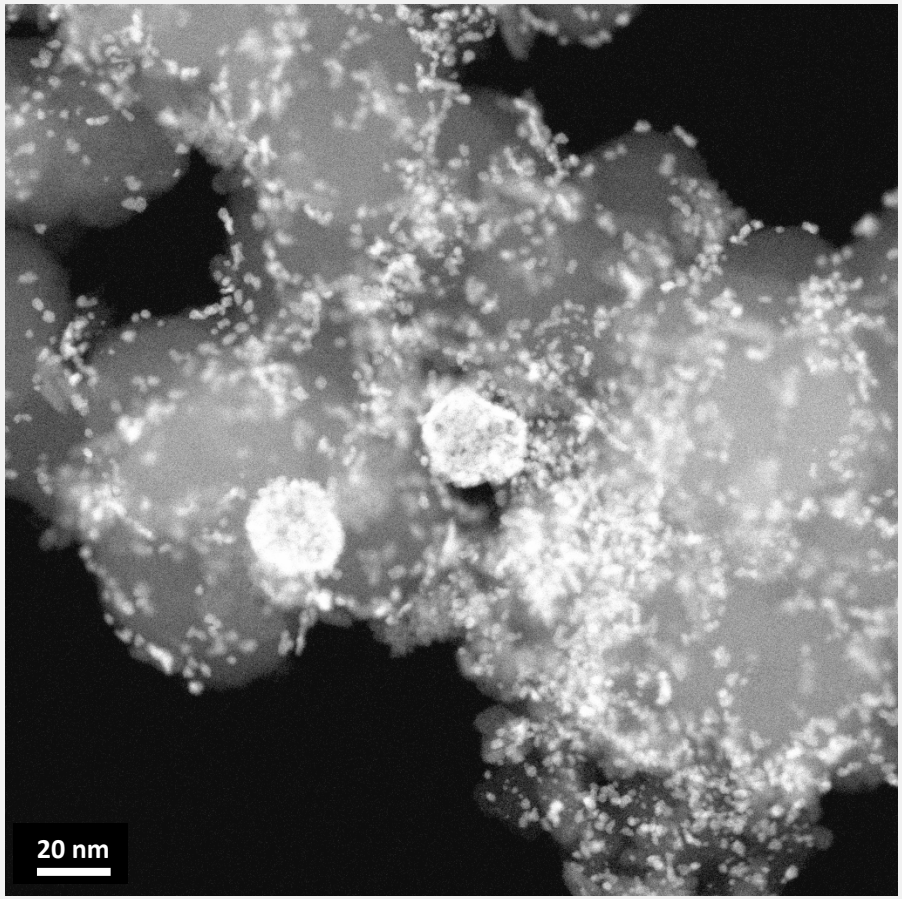


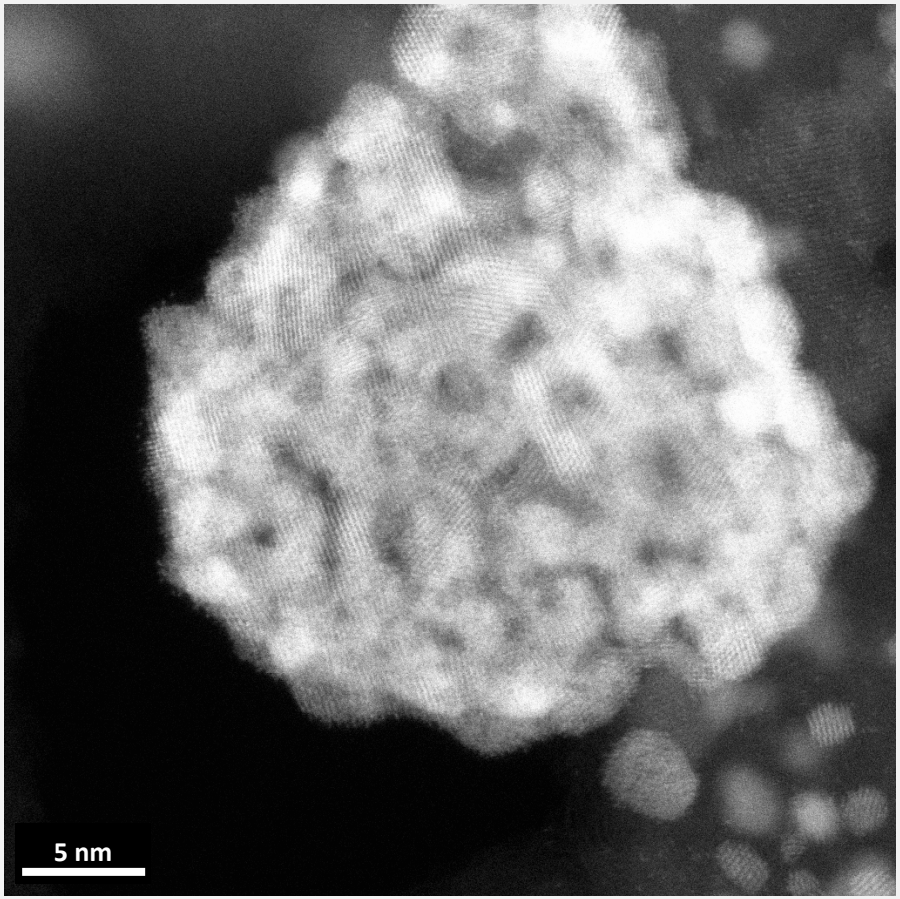
- XRD pattern still shows formation of well dispersed alloy nanoparticles (lattice parameter: 3.88 Å).
- TPR results indicate close contact between Pt and Co on the catalyst surface, resulting in lowering of reduction temperature due to Pt assisted reduction of surface Co-oxides.

CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

CoEDTA as Precursor

Representative Z-contrast Micrographs



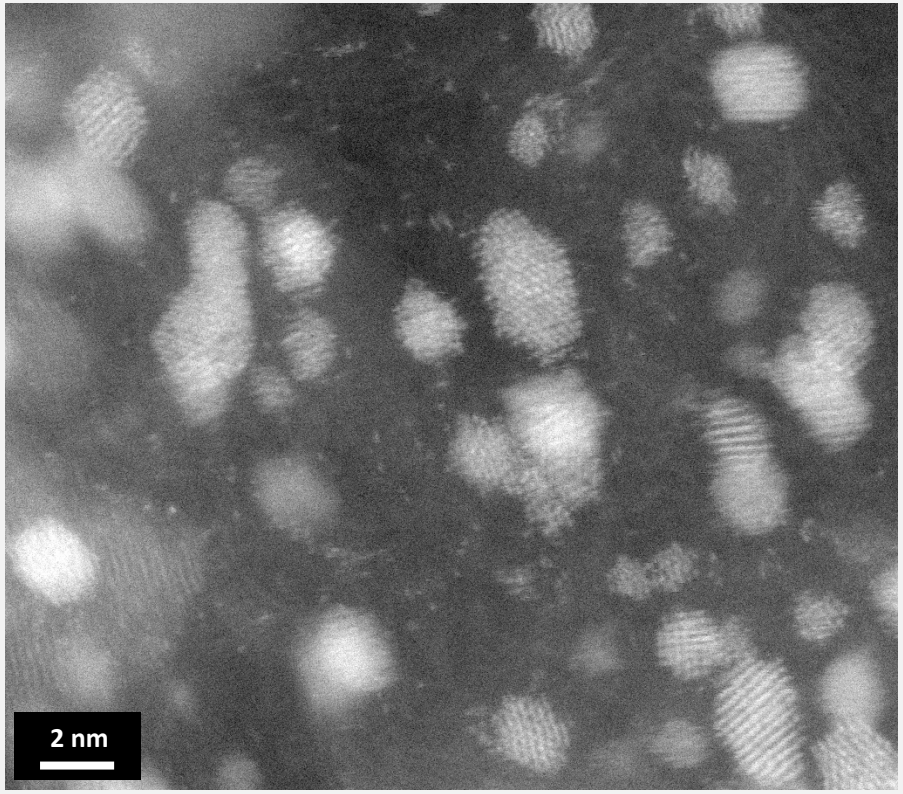


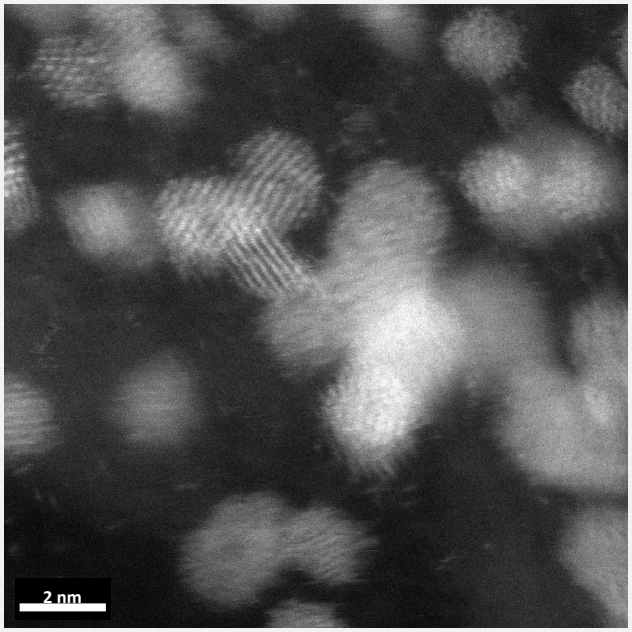
- Presence of agglomerated particles with distinct small grains.

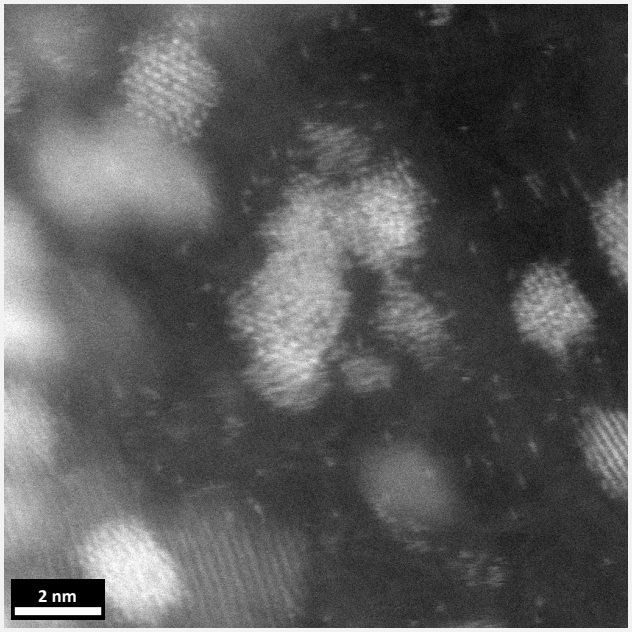
CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

CoEDTA as Precursor

Representative Z-contrast Micrographs





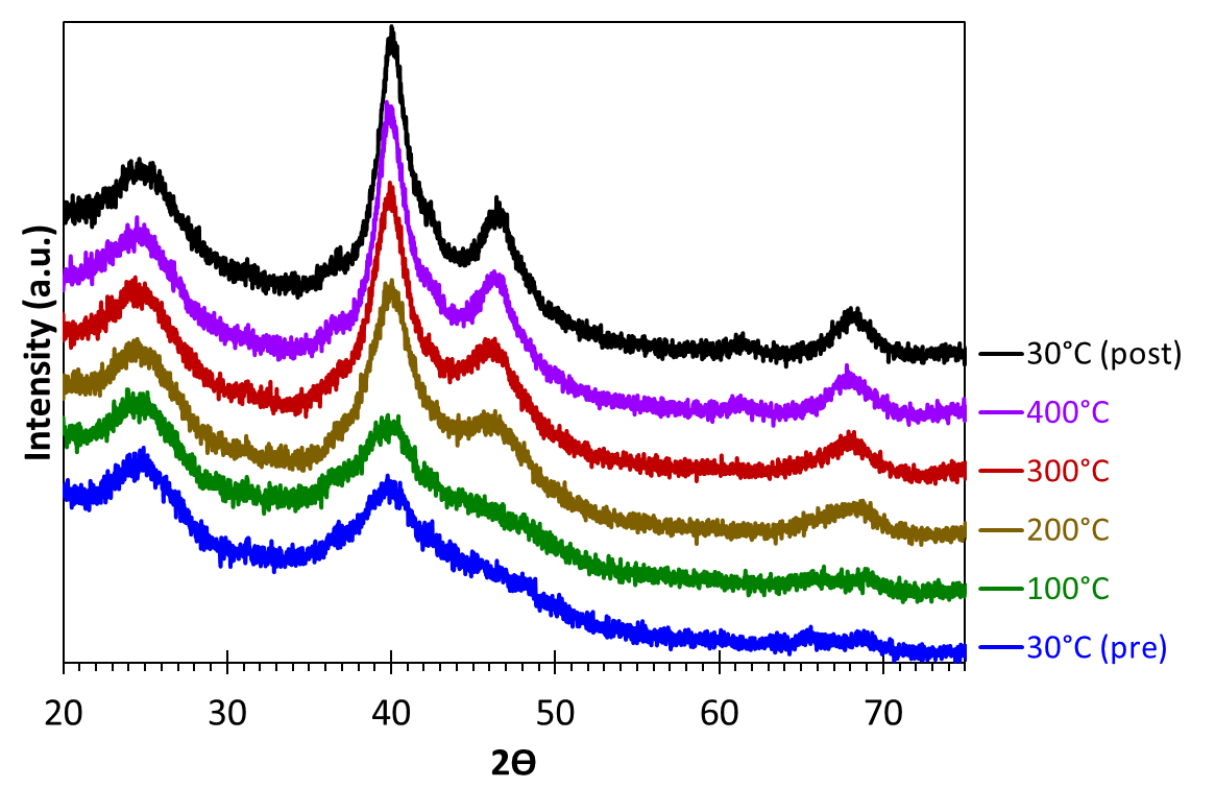


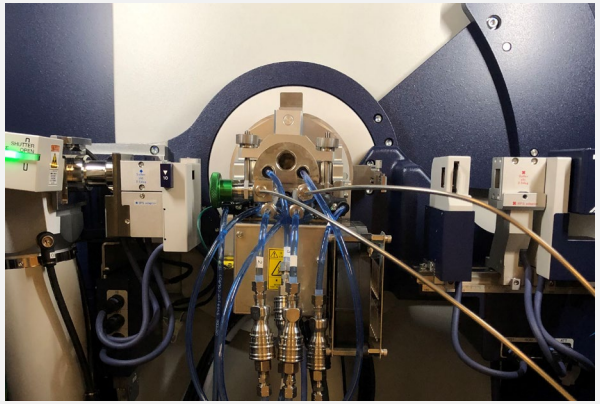
- Presence of dispersed single atom Pt.
- Speckling of nanoparticles (breaks in bright fringes) associated with alloy phase.

CO-DEPOSITION (co-ED) OF COBALT WITH PLATINUM

CoEDTA as Precursor

- In-situ XRD under N_2 flow using Rigaku Smartlab equipped with D/tex Ultra detector.
- 10°C/min heat rate, 5 min equilibration time at dwell temperatures, 5°/min XRD scan rate

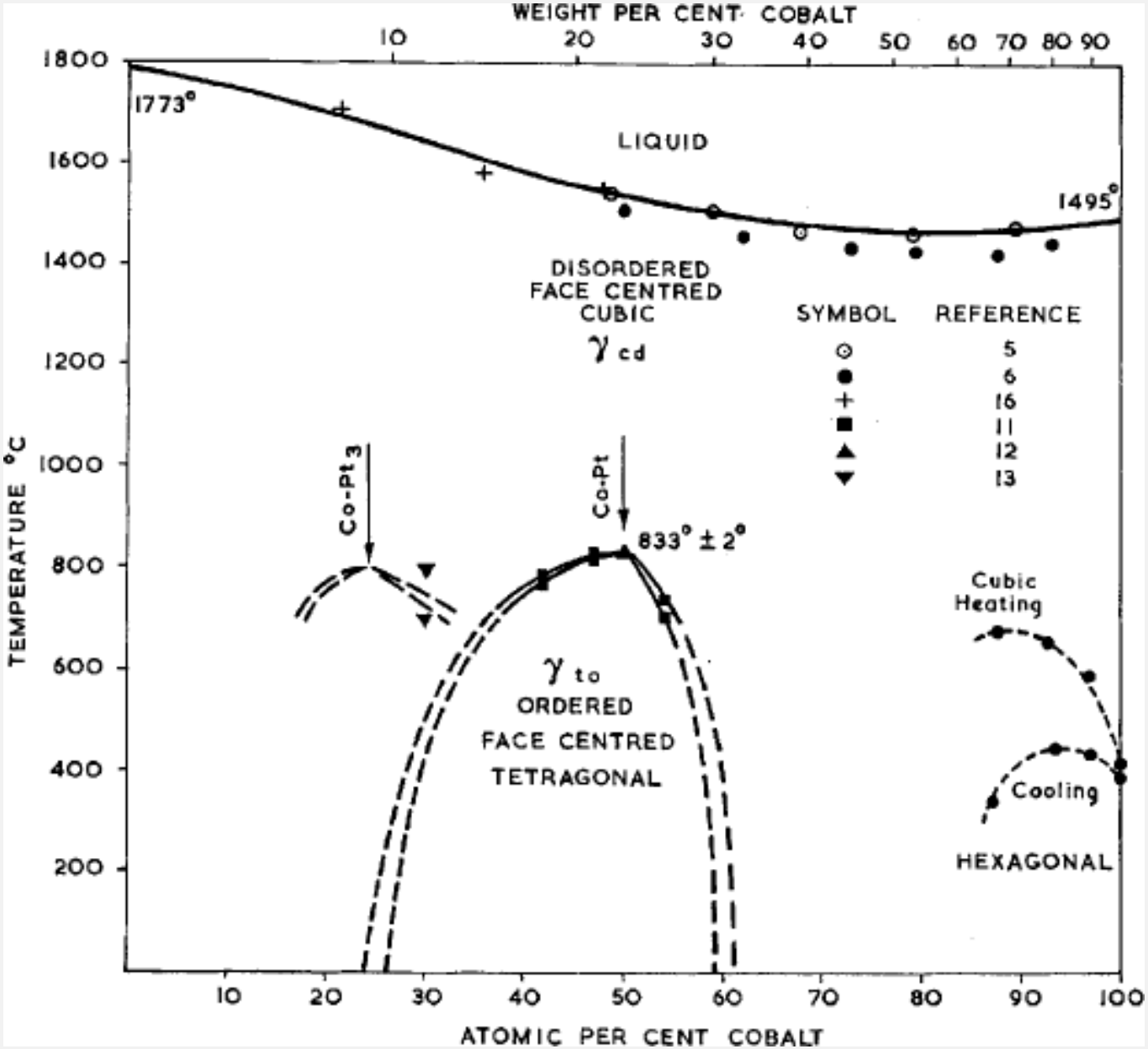




- Alloy phase begins to sinter at 200 °C.
- Shift towards higher 2Θ observed – further mixing with Co or lattice rearrangement?

Planned Work

- Repeat co-ED experiments, ensuring correct Pt concentration (Pt:Co = 3:1)
- Prepare base catalyst with co-impregnation Co-citrate + CPA → alloyed base catalyst?


WEIGHT PER CENT COBALT
10
20
30
40
50
60
70
80
90
1800
1600
1400
1200
1000
800
600
400
200
TEMPERATURE °C
1773°
LIQUID
1495°
DISORDERED
FACE CENTRED
CUBIC
γ cd
SYMBOL
REFERENCE
5
6
16
11
12
13
Co-Pt3
Co-Pt
833° ± 2°
γ to
ORDERED
FACE CENTRED
TETRAGONAL
Cubic
Heating
Cooling
HEXAGONAL
10
20
30
40
50
60
70
80
90
100
ATOMIC PER CENT COBALT