

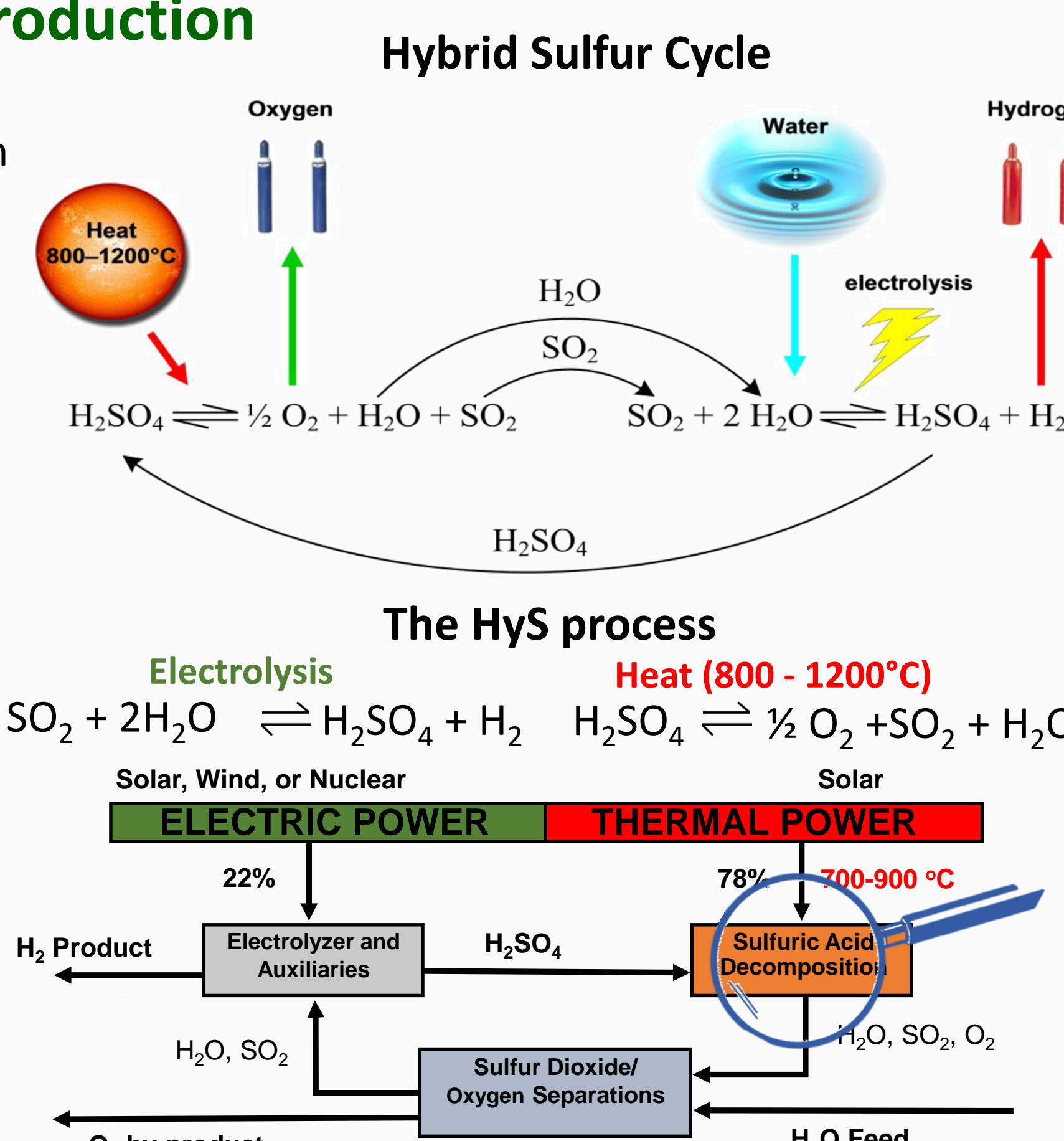
Design, synthesis, and evaluation of Ir@Pt bimetallic catalysts for high temperature decomposition of SO_3 to SO_2 in the HyS process for thermochemical H_2O splitting

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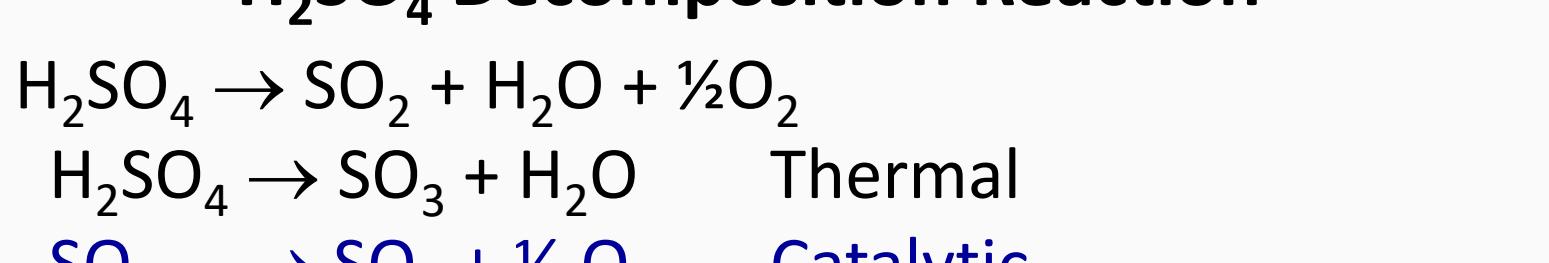
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Hydrogen use, potential, and production

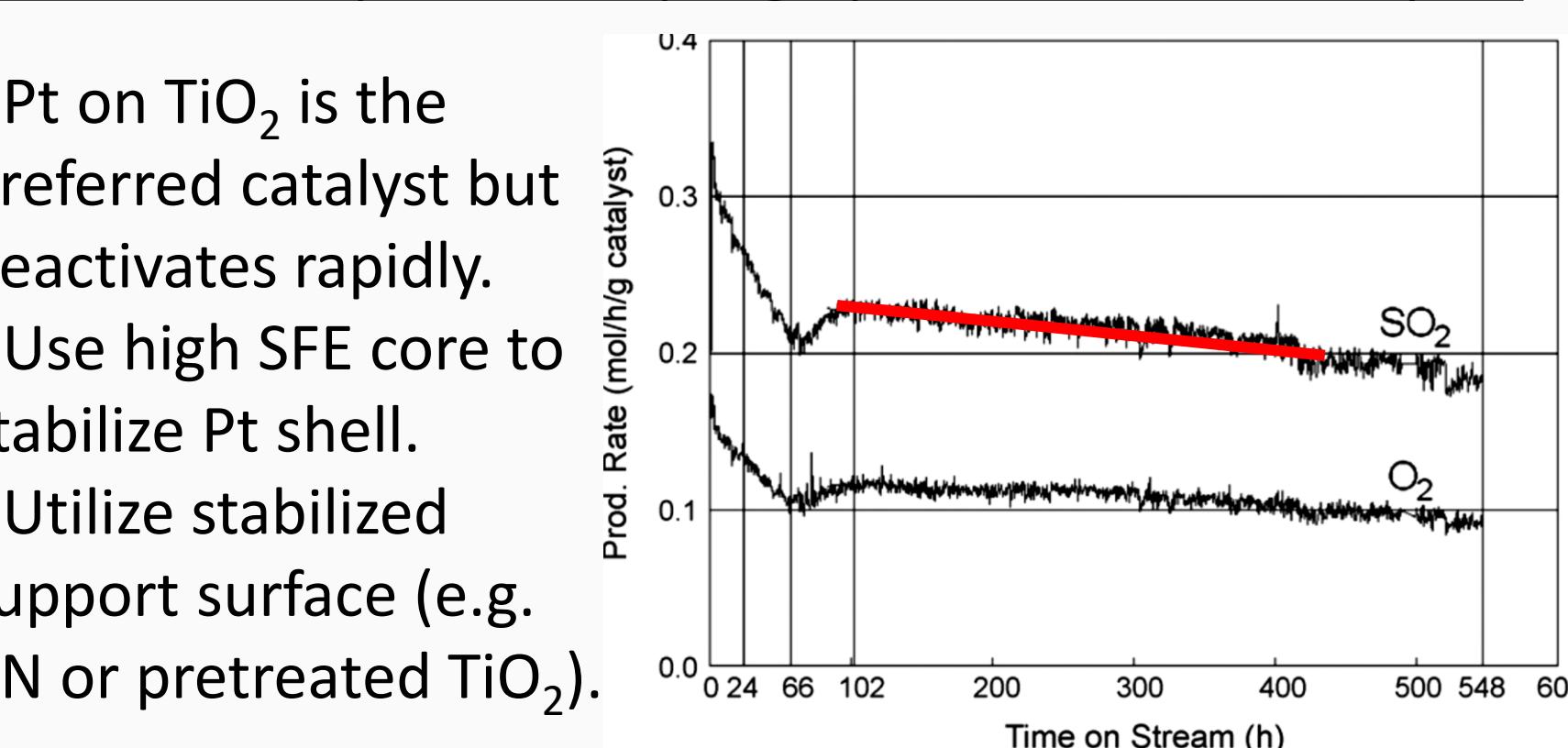
- Hydrogen demand
 - used in industrial chemical/fuel production
 - for advanced, environmentally sustainable vehicles where the exhaust contains only steam.
 - as a superior energy carrier to batteries.
- Currently from steam reforming of natural gas (CO_2 is a byproduct) or electrolysis (inefficient).
- Desirable advanced hydrogen technology should have low carbon footprint, high efficiency, and low production cost (\$2/kg H_2)
- Water splitting cycles: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$
 - Heat driven reactions: from solar or high temperature nuclear source.
 - Energy security: no dependence on imported oil or finite fossil fuels.
 - No CO_2 emissions.



H_2SO_4 Decomposition Reaction

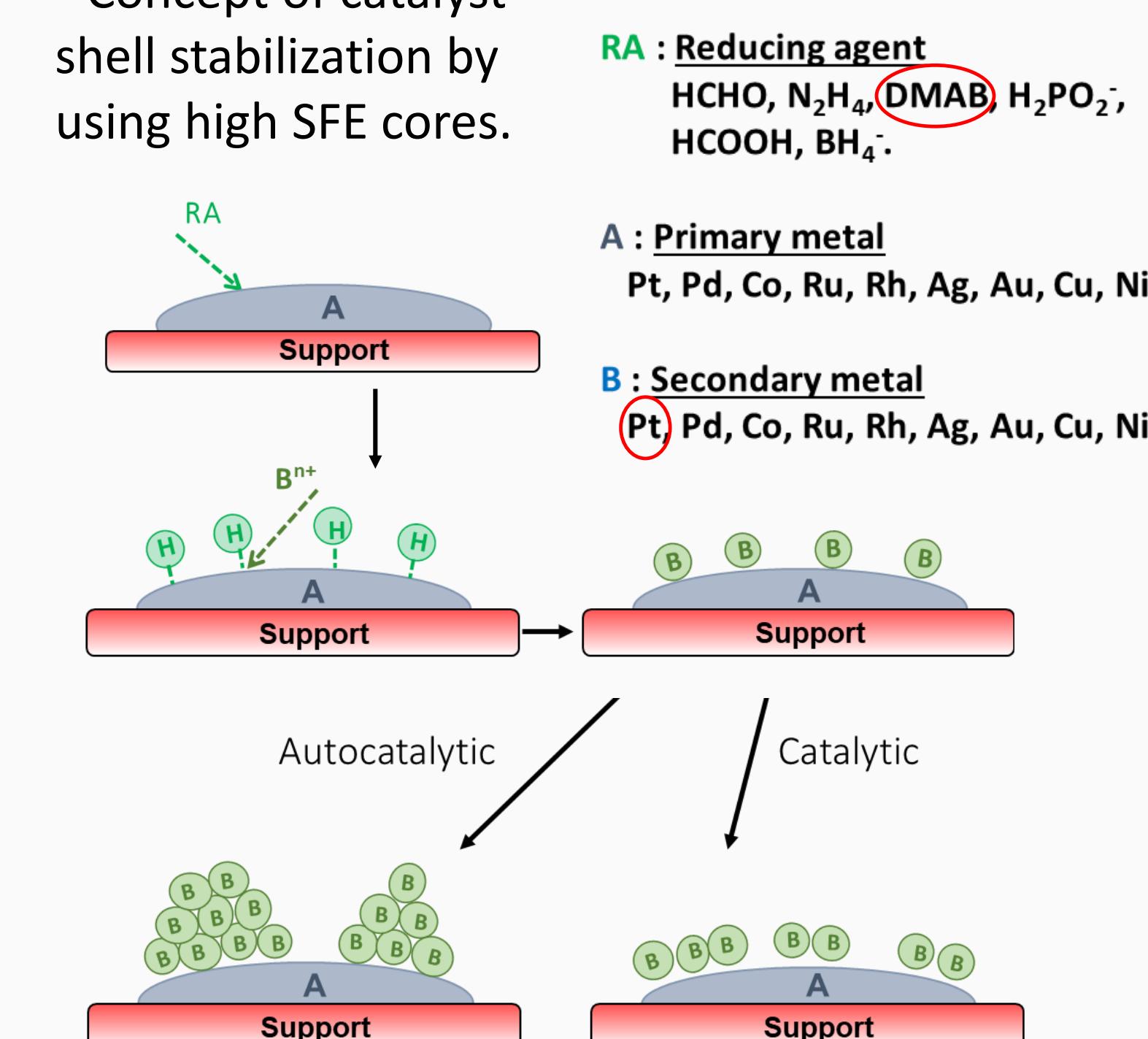


- High temperature catalytic reaction: 750 – 900 °C
- Equilibrium limited
- Highly endothermic
- Very harsh catalyst environment (high temp steam, O_2 , SO_2 , SO_3 , H_2SO_4 , and impurities)
- No catalysts known to withstand similar environment
- Goal: Identify or develop highly active, stable catalysts.
- Pt on TiO_2 is the preferred catalyst but deactivates rapidly.
- Use high SFE core to stabilize Pt shell.
- Utilize stabilized support surface (e.g. BN or pretreated TiO_2).



Electroless Deposition (ED) for Bimetallic Catalyst Synthesis

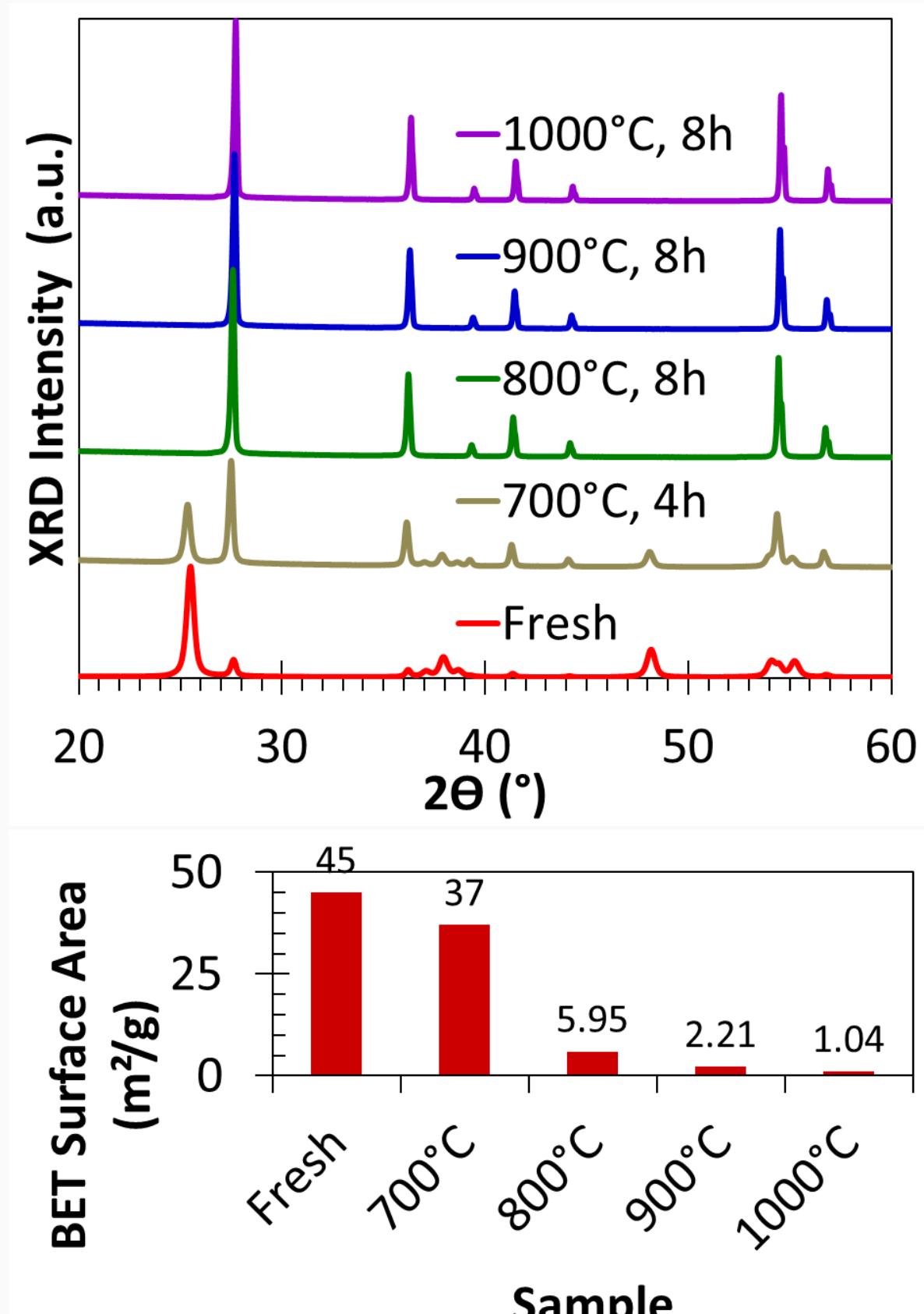
- Concept of catalyst shell stabilization by using high SFE cores.



Component	Surface free energy (ergs/cm ² surface)
Carbon	506
SiO_2	605
TiO_2	670
Al_2O_3	805
Ag	1302
Au	1626
Cu	1934
Pd	2043
Ni	2364
Pt	2691
Co	2709
Rh	2828
Mo	2877
Fe	2939
Nb	2983
Re	3109
Ir	3231
Ru	3409
W	3468

Catalyst Synthesis and Characterization

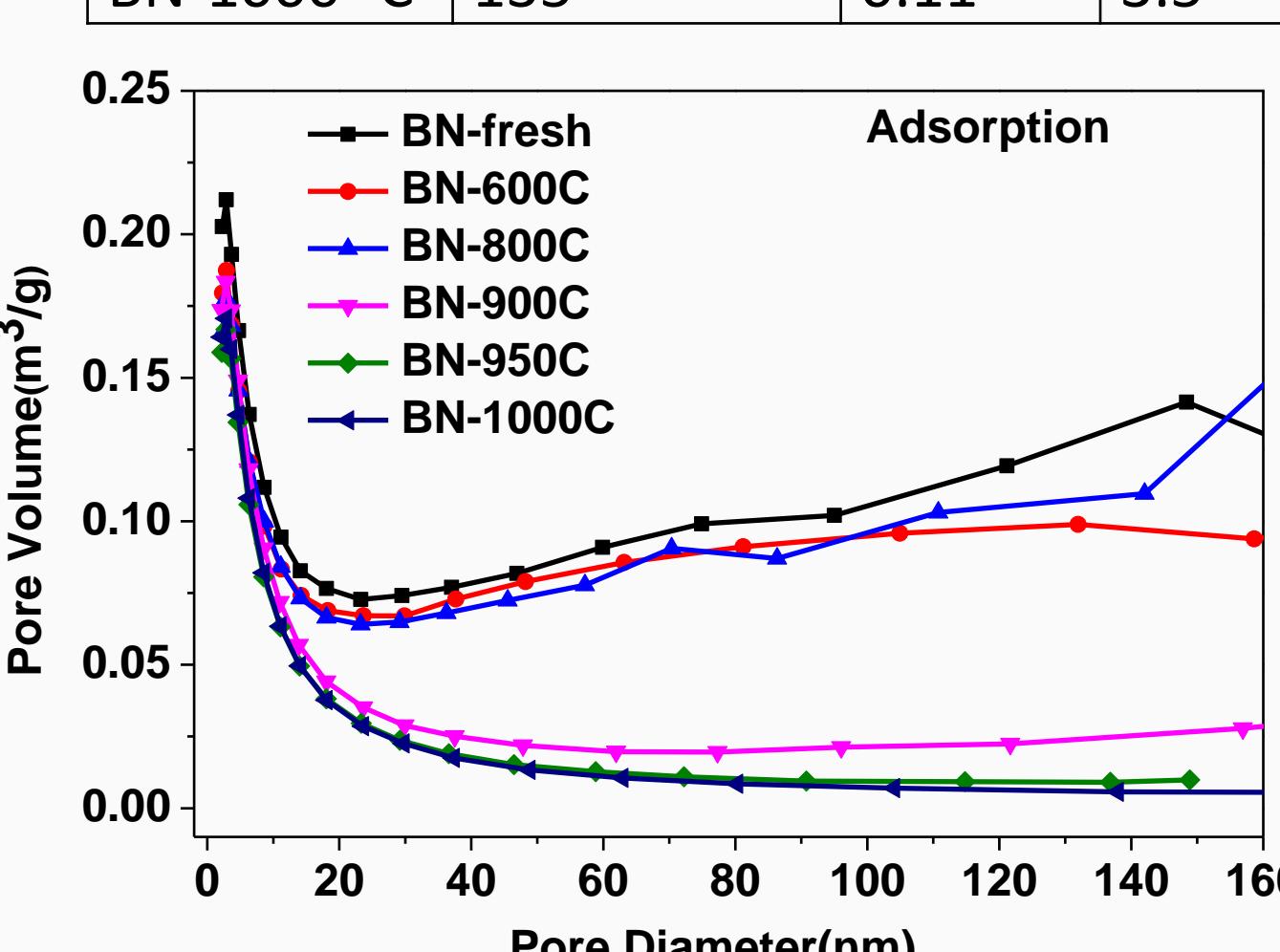
High Temperature Calcination of TiO_2



- Collapse of pores/surface as well as phase transition (anatase to rutile) around 700°C.
- Less surface area loss at high temperature calcination.
- Oxidation and material loss above 900°C

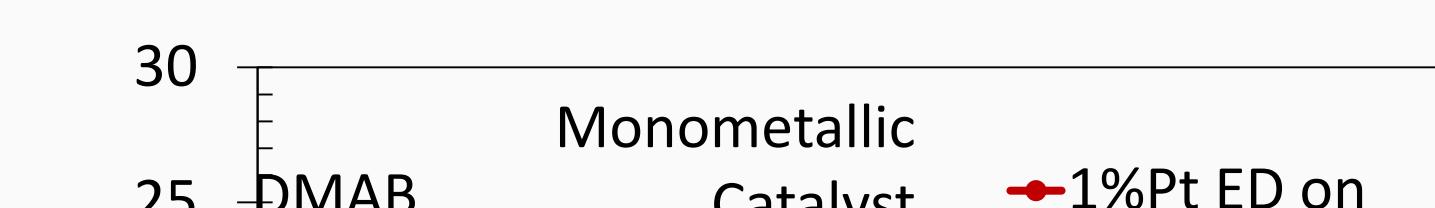
High Temperature Calcination of BN

Calcination (8 hr)	Surface area (SA, m ² /g)	V_{pore} (cm ³ /g)	D _{ave} (nm)
BN-fresh	61	0.21	13.7
BN-600 °C	54	0.18	13.8
BN-800 °C	53	0.17	13.1
BN-900 °C	73	0.13	7.4
BN-950 °C	100	0.11	4.6
BN-1000 °C	135	0.11	3.5



- Collapse of pores/surface as well as phase transition (anatase to rutile) around 700°C.
- Less surface area loss at high temperature calcination.
- Oxidation and material loss above 900°C

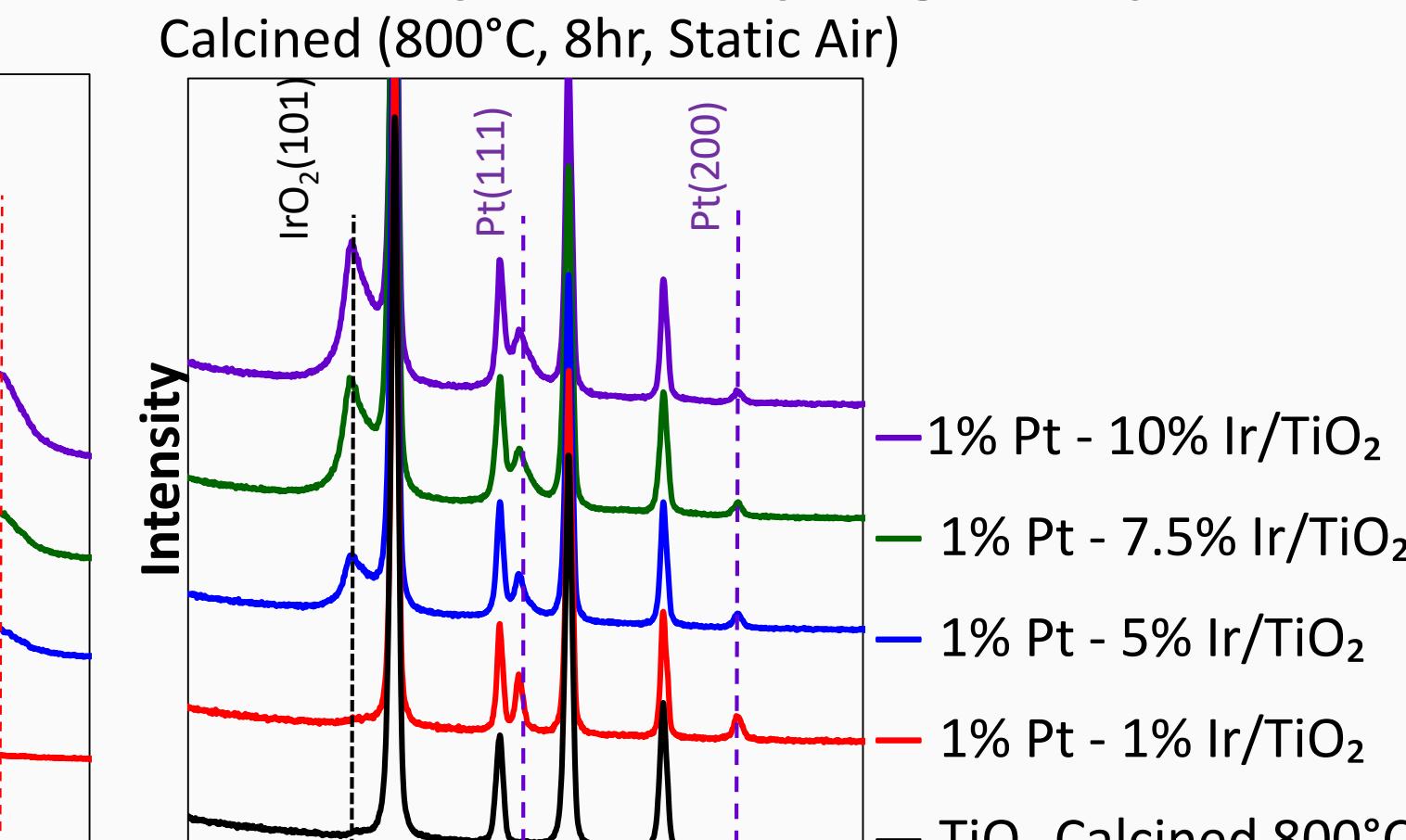
Electroless Deposition of Pt on Ir



ED parameters						
Temp (°C)	50					
Pt:DMAB:EN	1:5:4					
Volume (mL)	500					
Base Cat. Mass (g)	1					
Pt loading	1%					
Initial Pt (ppm) =	20.6					
Final Pt (ppm) =	0					

- Faster rate of Pt deposition on BN supported Ir compared to using Ir/TiO₂ base catalyst.

Catalyst Stability: High Temperature Calcination



Size estimate after calcination (nm)			
	Pt	IrO_2	
BN	12	24	15
TiO ₂	10		
1%Pt on 5%Ir	11	22	14
1%Pt on 7.5%Ir	11	22	14
1% Pt	15	34	N/A
			N/A

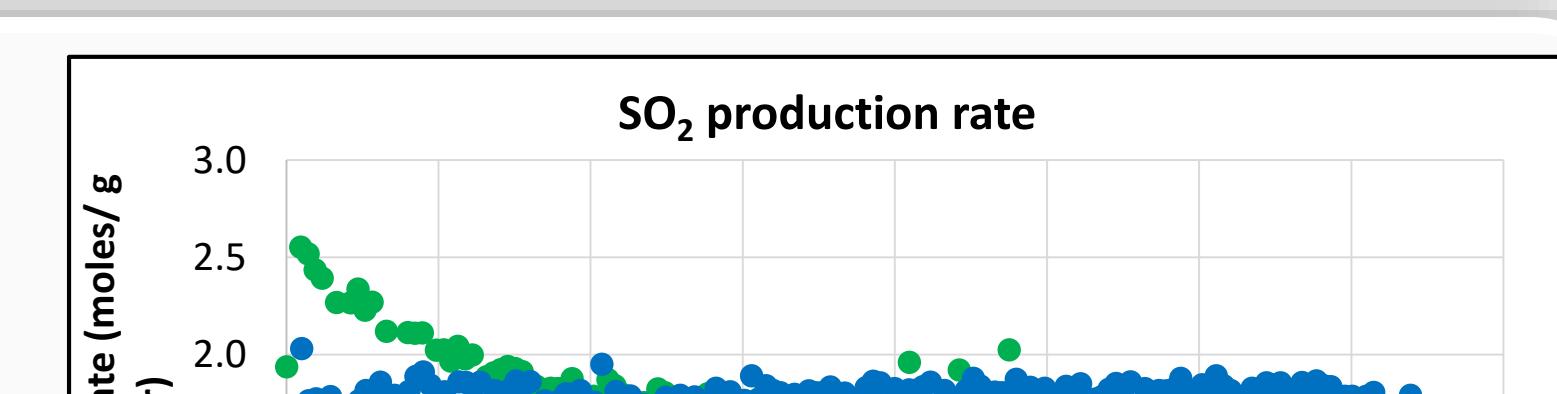
- Pt is more stable when deposited on Ir.
- Higher loading of Ir increases available surface for Pt anchoring.
- BN provides more stable support surface for metal nanoparticles.

Catalyst Evaluation

t = 72 hr
m = 0.025 g cat.
T = 801°C
WHSV = 524/hr



- Ir stabilizes Pt in oxidizing environment (air) at high temperature on TiO_2 .
- Pt-Ir/TiO₂ still deactivates fast in reaction conditions.



- Ir stabilizes Pt in oxidizing environment (air) at high temperature on TiO_2 .
- Increasing Ir content decreased deactivation rates.
- 1% Pt-7.5% Ir/BN gave nominal activity of 1.75 mol $\text{SO}_2/\text{h}\cdot\text{g}_{\text{Cat}}$ with deactivation rate of < 0.005%/hr.

Summary and Future Studies

- Pt is an effective catalyst for H_2SO_4 decomposition, but does not have long term stability.
- Electroless deposition of Pt containing bimetallic catalyst on BN appear to provide solution for catalyst stability.
- Strong metal-support and metal-metal interactions are key to catalyst stability.
 - ❖ Long term tests of catalysts (in excess of 500 hours).
 - ❖ Using Ni and other inexpensive substrate as core metal for Pt deposition.
 - ❖ Using co-ED deposition of Pt and core metal on BN supported core metal.

Acknowledgements

