Boron nitride: An effective support to synthesize very stable Pt-Ir catalyst for high temperature H_2SO_4 decomposition

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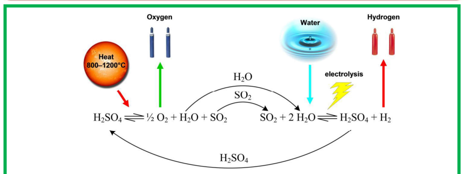
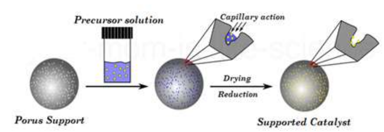
Background



- ❑ H_2SO_4 decomposition occurs catalytically at ≥800⁰C.
- ❑ As literature showed TiO_2 supported Pt-nanoparticles are effectively catalyze this decomposition reaction.
- ❑ However, at high temperature, platinum sinters and forms larger particles on TiO_2 that deactivates the catalyst.
- ❑ The sintering of Pt can be reduced by stabilizing support or replacing support with more stable one.
- ❑ Boron nitride (BN) exhibits higher thermal stability and oxidation resistance along with greater mechanical strength that could minimize Pt sintering at extreme conditions.

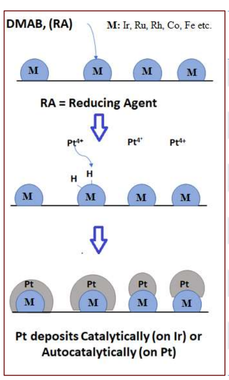
Experimental Methods

Monometallic Catalyst : Dry impregnation (DI)

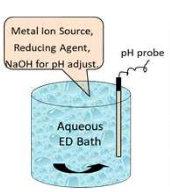


- ❑ **Drying:** Overnight atmospheric drying and then dried @80⁰C for 6h in maffle furnace.
- ❑ **Reduction:** @300⁰C for 2h in hydrogen flow (Fresh)
- ❑ **Calcination:** @800⁰C for 8h in static air (Calcined)

Bimetallic Catalyst : Electroless deposition (ED)



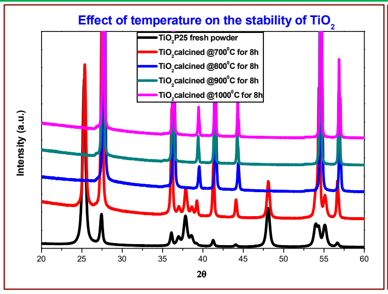
Metal	Surface free energy (ergs/cm²)
Cu	1934
Pd	2043
Ni	2364
Pt	2691
Co	2709
Rh	2828
Mo	2877
Fe	2939
Nb	2983
Re	3109
Ir	3231
Ru	3409

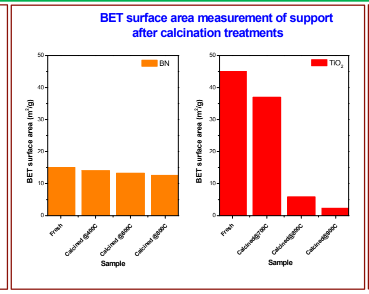


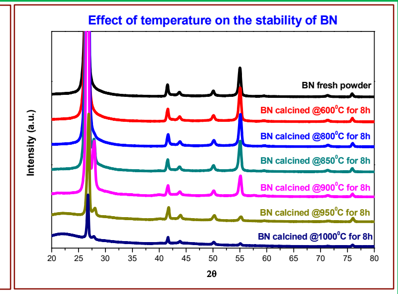
Parameters	
Temperature	50⁰C
Pt:DMAB:EN	1:5:4
Pt loading	1%
pH of ED bath	~10

- ❑ **Preparation:** Deposition of metals by a pre-existing metal (catalysis) or the metal which is being deposited (auto catalysis).
- ❑ **Washing**: Washed with DI-water to remove residual base
- ❑ **Drying:** Vacuum drying for 8-10 hrs (Fresh)
- ❑ **Calcination:** @800⁰C for 8h in static air (Calcined)

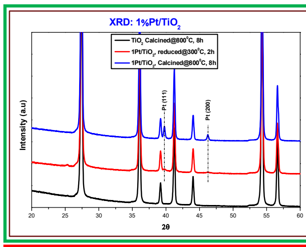
Stabilization of supports

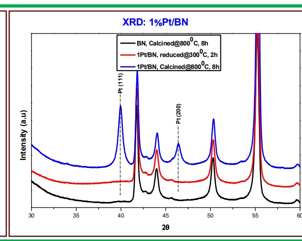






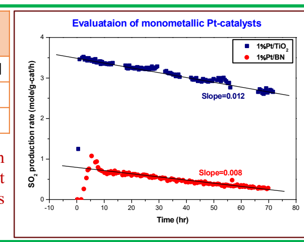
Results and Discussions

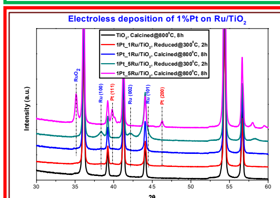


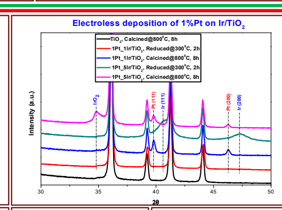


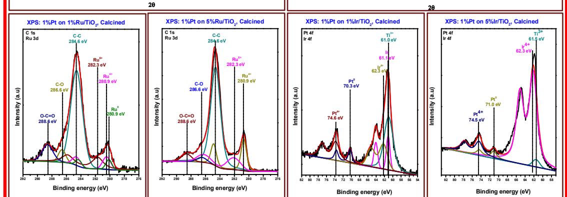
Catalyst	Particle size (nm)	
	Fresh	Calcined
1%Pt/TiO_2	11	34
1%Pt/BN	No peak	11

The rate of SO_2 production is higher for 1%Pt/TiO_2, but the rate of deactivation is lower for 1%Pt/BN

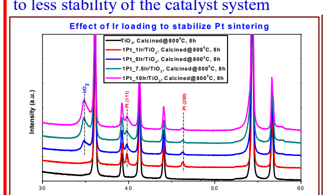


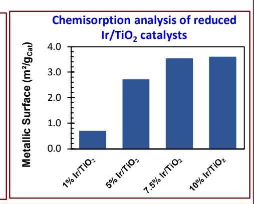




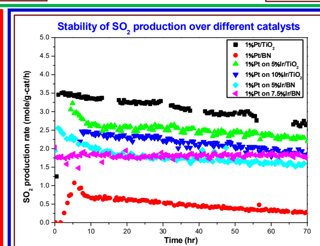


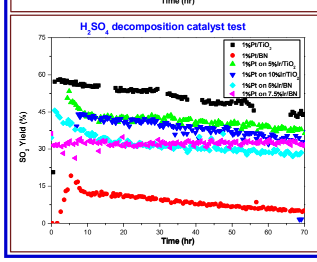
Both bimetallic catalysts are oxidize after calcination treatment but Ru is more quickly converted into RuO_2, which is more mobile species that can contribute to less stability of the catalyst system





Catalyst	Particle Size (nm)	
	Pt	IrO_2
1%Pt on 5%Ir/TiO_2, Calcined	23.4	10.0
1%Pt on 5%Ir/BN, Calcined	12.3	16.5
1%Pt on 7.5%Ir/TiO_2, Calcined	21.6	8.50
1%Pt on 7.5%Ir/BN, Calcined	10.5	10.2





Test conditions	
Temperature	800⁰C
Pressure	1 bar
H_2SO_4 concentration	75wt%
WHSV	532/hr

- ❑ **1%Pt/TiO_2** is the most active catalyst to produce SO_2, but the rate of deactivation is the highest.
- ❑ The activity of **1%Pt on 7.5%Ir/BN** is consistent in 72 hrs of testing, the rate of catalyst deactivation is <0.015%/hour
- ❑ The activity of catalysts are decreased with increasing loading of iridium.

Conclusion

- ❑ Almost 87% of the surface area has been lost for TiO_2 due to the calcination treatment at 800⁰C while BN is relatively stable.
- ❑ The surface area obtained after calcination of BN is as double as the surface area obtained for TiO_2.
- ❑ Ru is rapidly oxidize compare to Ir in high temperature oxidative condition and RuO_2 is more mobile specie that may reduce of catalyst activity.
- ❑ TiO_2 supported monometallic Pt-catalyst is the most active catalyst compare to any other catalysts prepared on both BN and TiO_2 support. However, the rate of deactivation is also high.
- ❑ The activity of the BN supported Pt-Ir catalysts is half of the activity of 1%Pt/TiO_2, but the activity is very stable over 72 hours of testing.

Acknowledgement

References

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