Pushing the Limits of Electrostatic Adsorption: Charge Enhanced Dry Impregnation of SBA-15

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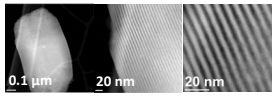
Introduction

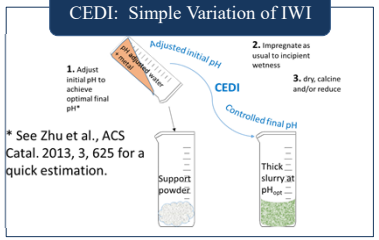
Charge enhanced dry impregnation (CEDI) is a method to synthesize supported metal nanoparticles which combines the simplicity of incipient wetness impregnation (IWI) with the small particle size obtained from electrostatic adsorption of metal precursors onto the oxide support. We have explored the utility of CEDI by applying it to a difficult to impregnate support – a largely one dimensional porous SBA-15 silica. Monometallic (Pt, Pd, Co, Ni, and Cu) catalysts at multiple metal loadings (1 – 20 wt%) as well as their bimetallic pairs were supported on mesoporous SBA-15 and characterized by high sensitivity powder XRD and in select formulations, with aberration-corrected z-contrast STEM imaging.

Figure 1. The mesoporous SBA-15 material at various magnifications.

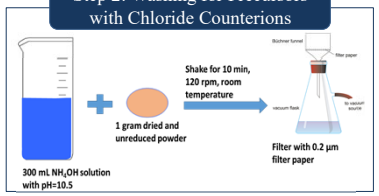


Methodology

CEDI: Simple Variation of IWI



Step 2: Washing for Precursors with Chloride Counterions



Composition and XRD Results

Effect of Counterions and pH

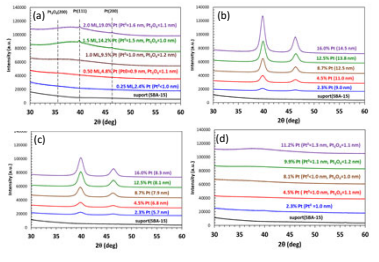


Figure 2. XRD patterns of PtTAOH and PtTACl derived nanoparticles on SBA-15: (a) CEDI – prepared series of PtTAOH, (b) DI - prepared series of PtTACl, (c) CEDI – prepared series of PtTACl, and (d) washed, Cl^- free samples from CEDI – prepared PtTACl.

CEDI Prepared Nanoparticles: Before and After Washing

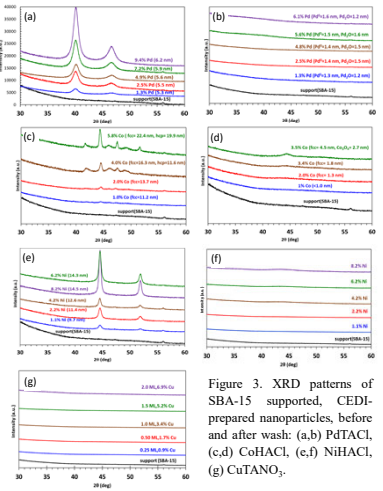


Figure 3. XRD patterns of SBA-15 supported, CEDI-prepared nanoparticles, before and after wash: (a,b) PdTACl, (c,d) CoHACl, (e,f) NiHACl, (g) $CuTANO_3$.

Particle Size & Metal Loss

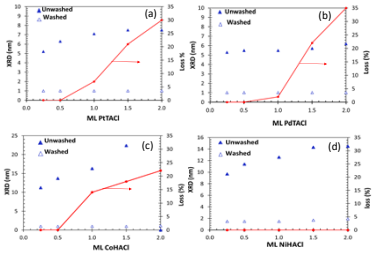


Figure 4. Metal particle size before and after wash with the metal loss (%) for the SBA-15 supported catalysts, CEDI-prepared: (a) Pt(PtTACl), (b) Pd(PdTACl)/SBA-15, (c) Co(CoHACl)/SBA-15, (d) Ni(NiHACl)/SBA-15.

Bimetallics Prepared using Different Methods and Support

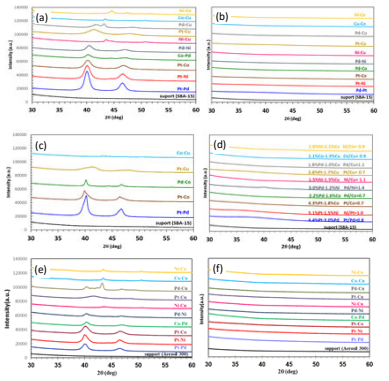


Figure 5. XRD patterns of SBA-15 supported bimetallic catalysts prepared by co-CEDI a) with no wash and b) with wash, c) prepared by co-DI and d) prepared by co-SEA; XRD patterns of Aerosil 300 supported bimetallic catalysts prepared by co-CEDI e) with no wash and f) with wash.

Effect of Nitrates Counterions

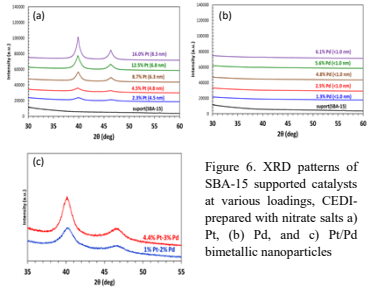


Figure 6. XRD patterns of SBA-15 supported catalysts at various loadings, CEDI-prepared with nitrate salts a) Pt, (b) Pd, and c) Pt/Pd bimetallic nanoparticles

Metal Loss Due to Washing (co-CEDI)

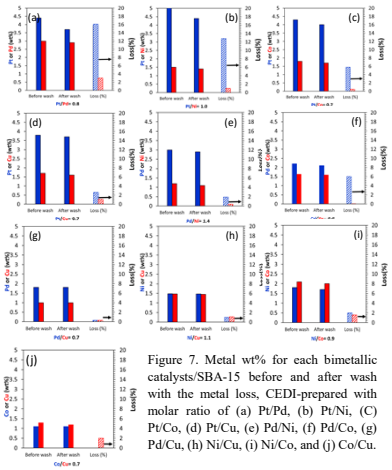


Figure 7. Metal wt% for each bimetallic catalysts/SBA-15 before and after wash with the metal loss, CEDI-prepared with molar ratio of (a) Pt/Pd, (b) Pt/Ni, (C) Pt/Co, (d) Pt/Cu, (e) Pd/Ni, (f) Pd/Co, (g) Pd/Cu, (h) Ni/Cu, (i) Ni/Co, and (j) Co/Cu.

STEM Results

Pt-Co Bimetallic Prepared using Different Methods

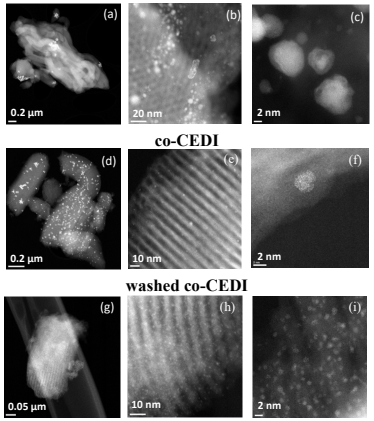


Figure 8. STEM images at low, medium, and high magnification of 4.3wt%Pt, 1.8wt%Co bimetallic nanoparticles synthesized by a, b, c) co-DI, d, e, f) co-CEDI and g, h, i) co-CEDI with washing.

Pt-Pd Bimetallic using Nitrates Salt Precursors

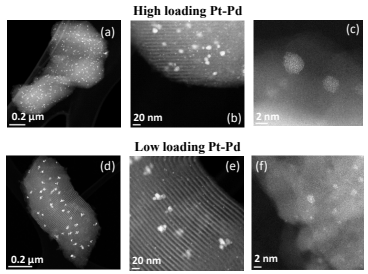


Figure 9. STEM images at low, medium, and high magnification of Pt-Pd bimetallic nanoparticles prepared by CEDI with nitrate salts for a, b, c) 1 ML precursor loading (4.3wt%Pt, 3.0wt%Pd) and d,e,f) lower loading (1wt% Pt, 2wt% Pd).

Conclusions

- Electrostatic interactions can be induced at incipient wetness.
  - Best results (smallest particles) with a hydroxide salt (no residual counterions).
  - Counterions can be removed with washing with little metal loss up to 1 ML of precursor; loss is significant above 1 ML.
  - Precursors with nitrate counterions give relatively small sizes at partial monolayer loadings with no washing; particles are bimodal as ionic strength limits the amount of precursor adsorbed
- The long aspect ratio of SBA-15 mesopores is no obstacle to SEA/CEDI

References

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Acknowledgements

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