THIN LYAYRED MATERIALS AS A CATALYTIC SUPPOT

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Catalysts have been developed for a wide variety of reactions. These catalysts need to be supported by materials with high surface area, high surface area, high thermal stability, and a high degree of chemical inertness. A recent process has been developed which allows thin layered materials which possess these properties to be exfoliated into solution. This procedure creates 2-dimentional nanoscale sheets suspended in solution. Boron Nitride, graphene, and Molybdenum disulfide were the layered materials chosen in this study because of these properties and their classification as an insulator, conductor, and semiconductor respectively. The key to this project is the re-deposition of these materials into high surface area structures. To accomplish this goal exfoliated materials were mixed in varying ratios with other solutions and re-deposited. The resulting powders were initially tested using a BET surface area calculation with a physic-sorption technique. XRD was used to examine the crystal structure of the resulting powders and TEM images were taken to more closely examine the structure of these catalytic supports.

Thin-layered Materials as a Catalytic Support

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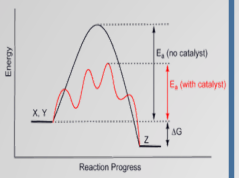
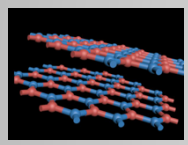
Background

◆Catalytic support

- Change in rate of a chemical reaction not consumed by the reaction itself
- Participate in multiple chemical transformations
- Catalytic reactions have a low rate-limiting free energy of activation



The Energy diagram of chemical reaction with catalyst



The view of Thin-layered material

◆Thin layered material

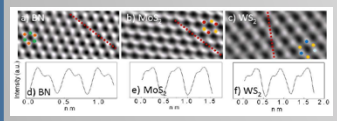
MoS2, WS2, MoSe2, MoTe2, TaSe2, NbSe2, NiTe2, BN, Bi2Te3, graphene

- 2-dimensional Structures
- Thermal stability & chemical stability

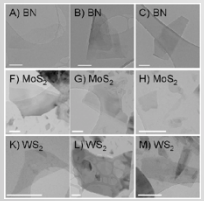
◆Peels off monolayer sheets of material

- Graphene, BN, MoS2,WS2
- Solvent dependent
- Don't want to involve surfactants
- Stable suspension formed

Photographs of dispersions



TEM image of thin- layered materials



SEM image of thin layered materials

*Jonathan N. Coleman, et al. Science **331**,568 (2011)*

Motivations

- Determine deposition methods that create porous material
- Examine the effects of mixing dispersions of different materials
- Develop a high surface area catalytic support by depositing nano-sheets of materials out of suspension

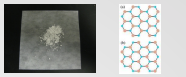
Methods

◆Materials

-Each layer is held together by strong covalent bonds

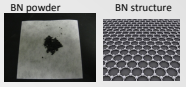
-Van der Waals forces hold separate layers together

- Boron Nitride (BN)
  Insulator material, white powder
- Graphene
  Conductor material, Black powder
- Molybdenum diSulfide (MoS_2)
  Semiconductor material, Dark gray powder



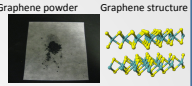
BN powder

BN structure



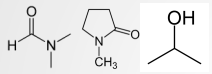
Graphene powder

Graphene structure



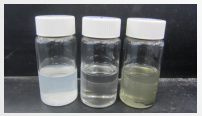
MoS_2 powder

MoS_2 structure



DMF NMP IPA

chemical structural formula



Dispersions BN, Grapnen,MoS2 in IPA

◆Solvent(boiling point[ºC])

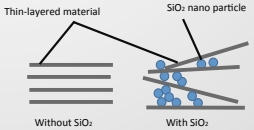
- IPA [C_3H_8O] (82.4)
- DMF [C_3H_7NO] (153)
- NMP [C_5H_9NO] (202)
- Water {pH5, pH9} [H_2O] (100)

◆Exfoliation

- Sonication crushing the materials
- Centrifugation separation of supernatant
- Decantation bulk and supernatant
- Evaporation getting material without boiling

◆SiO_2 nano particle mixture

- SiO_2 nanoparticles dispersed in water
- Mixed in different ratios with the BN with IPA solution
  →1:9, 5:5, 9:1 by volume
- Evaporated off the IPA/water to examine differences



Photograph off BET machine

◆BET Characterization

- Paper published by Brunauer, Emmett, & Teller in 1938
- Micromeritics ASAP 2010 unit
- Based off the Langmuir theory for monolayer molecular adsorption
- An adsorption isotherm is plotted which allows surface area calculations
- Samples de-gas at 250ºC until reaching 4 μm Hg

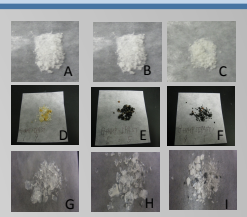
Results

◆Surface Area Data

- Data suggests Silica nanoparticles are controlling the surface area of the powders
- Since the Silica nanoparticles seem to be controlling the surface area we are examining exfoliated powders versus the bulk

BN:IPA-ST	1:9	5:5	9:1
Surface Area (m^2/g)	277	252	259
Pore volume (cm^3/g)	0.26	0.23	0.25

BET characterization



Material:SiO_2

1:9 5:5 9:1

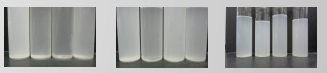
A, B, C : BN in IPA

D, E, F : Graphene in NMP

G, H, I : MoS_2 in DMF

◆We studied several processing parameters to increase amount of suspended BN Sheets

◆Solvent examination



in DMF in NMP in IPA

◆pH examination

- Water pH 5 and Water pH 9
- Very similar suspensions independent of pH

1day 3days later

◆Centrifugation speed examination

- The 0 RPM seems to be a reasonable suspension
- Some material crashes out in every sample
- Continued study of stability is necessary

1day 3days later

Conclusions

- It could be get some Resulting suspension and recovered materials
- Since the Silica nanoparticles seem to be controlling the surface area we are examining exfoliated powders versus the bulk
- We studied several processing parameters to increase amount of suspended BN Sheets

Acknowledgements

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