Hydrogen Storage Research Capabilities

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Unique High-Pressure Mechanochemistry Capability

Magnetic ball-mill

**Mechanical milling (details)**
- Temperatures (-30 °C to R.T.)
- Intensity controlled by rotation and magnetic field
- Impact and/or shear mode – Switched by magnet placement
- Ambient, inert or high-P reactive environment.

Precise control over the delivery of mechanical energy
High-pressure, High-Energy (Programmable) Milling

Planetary style micro mill (PULVERISETTE 7, Fritsch)

- Dry or liquid grinding at gas pressures up to 350 bar.
- Rotation speed up to 800 rpm
- Programmable milling

High-pressure vessels (vials)

- Designed up to 350 bar H₂ pressure
- In-situ monitoring of P and T during milling (1-300 bar, 23-100 °C)
- 316 steel resistant to H embrittlement
- 440C steel sleeve for wear resistance

Knowledge of critical events during mechanochemical processing
Cryomilling

- Rapid nanostructuring
- Microstructural refinements
- New light-weight alloys

Can introduce H$_2$ capability!

Milling at 77 K under H$_2$ atm. is unprecedented!
Understand Mechanochemistry

• Lack of analytical methods to monitor MTs in real time ≡ lack of basic understanding of the mechanisms

• Develop analytical tool to facilitate in-situ neutron diffraction characterization of MTs in real time (Bragg and total scattering), in collaboration with ORNL-SNS

  • Science we are after
    ✓ Identify changes at the atomic length scale
    ✓ Deduce atomistic mechanisms of MTs critical to BES mission

  • Start with VULCAN; later integrate with NOMAD

Potential for a broad use by H-storage community
High-Pressure Mechanochemistry: Alane via Metathesis

\[ 3\text{LiAlH}_4 + \text{AlCl}_3 \xrightarrow{\text{RT, no ether}} 4\text{AlH}_3 + 3\text{LiCl} \]

All Al is 6-coordinated indicating formation of AlH\(_3\)

\[ ^{27}\text{Al NMR} \]

Adduct- free alane

Gas pressure during ball-milling can alter reaction pathways!
Quantitative SS-NMR

- Deconvolute SS-NMR spectra collected under quantitative conditions
- High-resolution reveals key features
- Simulated spin dynamics addresses quadrupolar coupling

\[ 4\text{LiAlH}_4 + \text{AlCl}_3 = 3\text{LiCl} + 4\text{AlH}_3 + \text{LiAlH}_4 \]

\[ ^{27}\text{Al} \]

**DPMAS experiment**

Deconvolution & QM simulations

Recover quantitative information

\[ \alpha\text{-AlH}_3 + \alpha'\text{-AlH}_3 \]

Fully quantitative SSNMR is critical for mechanistic developments
Solid-State (Dynamic Nuclear Polarization) NMR

DNP-NMR installed in July 2014 (9.4 T, 263 GHz)

Electron Spin-Resonance (ESR) to excited nuclei enhancements up to $\gamma_e/\gamma_H \approx 660$ or $\gamma_e/\gamma_N \approx 6500$

$\varepsilon = 61$ time saving $\approx 3700$

$13^C$ scan of catalytic moieties on silica

DNP-NMR $^{15}N$ and $^{17}O$ spectra at natural abundance

$^{15}N$ NMR

$^{17}O$ NMR

SS-NMR: $^{13}C$ or $^{15}N$ signal is enhanced by $^1H$ via cross-polarization (CP), yielding $\varepsilon$ of 4 ($^{13}C$) or 10 ($^{15}N$)

DNP NMR: DNP combined with CP can yield $\varepsilon$ of $\approx 2640$ ($^{13}C$) or $\approx 6500$ ($^{15}N$)

✓ Unique DNP-enhanced NMR provides unparalleled environmental information
SENSITIVE INSTRUMENTS FACILITY (SIF): Advanced Suite of Instruments

SIF advanced capabilities potentially available for H-storage research

ADVANCED E-BEAM Characterization Instruments

• FEI Teneo LoVac Field Emission SEM (FE-SEM)
• FEI Helios G3 UC Dual-Beam Focused Ion Beam (FIB) and FE-SEM
• FEI Tecnai G2 F20 Scanning TEM (STEM)
• FEI Titan Themis 300 Cubed 300 STEM/TEM
Theoretical Capabilities at Ames Lab

- **Surface Catalytic Reactions**
  - Defect-mediated Alane formation on Ti-doped Al(111)

- **Thermal Annealing for Structural Predictions**
  - NaAlH$_4$ and AlCl$_3$ reaction intermediate

- **Proper Solid-State Nudged Elastic Band for Solid-Solid Transitions**
  - Transformation pathway for Alane polymorphs

- **Configurational Thermodynamics for Nanoalloy with Adsorbates**
  - Simulating adsorption isotherm (hydrogen evolution reaction, HER)
Defects play significant roles

- Ti helps dissociate $H_2$ to facilitate $AlH_3$ formation
- $Al$ adatom with vacancy make $AlH_3$ formation exothermic
- Confirmed ball-mill formation under 344 bar of $H_2$ (a 30-fold reduction of $P_{H_2}$!)
- Coupling theory and experiment to achieve understanding of mechanism
Solve Unknown Reaction Intermediate

- NaAlH$_4$ + AlCl$_3$ → NaAl$_2$Cl$_3$H$_4$

✓ Knowledge of intermediates is critical for progress, especially in multi-step reactions.

- Thermal annealing with *ab initio* MD
- PEGS (Eric Majzoub)
Some NEB models decouple DOF that should not be!

Original NEB minimizes forces – purely local
Trinkle et al. PRL 91 025701 (2003)

Rapid Nuclear Motion – purely cell distortion
Casperson & Carter PNAS 102, 6738 (2005)

Alternative NEB models are not CELL INVARIANT!

Transition states are not always SADDLE-POINTS!

Multi-scale modeling for hydrogen storage materials

CdSe: rock-salt to wurtzite

• **α** phase is the most stable against decomposition
• Cell deformation gives edge-sharing Al-H octahedra
• Complex transformation pathways with intermediates for just alane polymorphs
Alloyed Nanoparticle (NP) Configurational Change

PdRh NP core-shell reversal in oxidizing/reducing gas

Shell conc. ($C_{\text{shell}}$)

AP-XPS


Unique Theoretical Capabilities for Ab Initio Prediction
✓ Alloy configurational thermodynamics for NP with adsorbates
✓ Simulating adsorption isotherm on low-coordinated alloy sites

L.-L. Wang, T. L. Tan and D. D. Johnson
PRB 86, 035438 (2012); JPCC. 117, 22696 (2013);
Nano Lett. 12, 4875 (2012); Nano Lett. 14, 7077 (2014);
ACS Catalysis 5, 2376 (2015); PCCP 17, 28103 (2015)

INCLUDES: Shape, size, stability, and design of nanolloy catalysts in working condition, for systems with Component (M) and Site (N)
Simulated Adsorption Isotherm

- Fully first-principles predicted isotherms that include correlation effects from low-coordinated alloy sites
- H-adsorption isotherm on alloyed Al nanostructures

Ames Laboratory H-Capabilities at a Glance

1. State-of-the-art mechanochemistry:
   → $P_{\text{H}_2} = 300-350$ bar with T,P monitoring
   → Real-time, in-situ analysis of processes with neutrons (under development)

2. Unique solid-state NMR →
   → Quantitatively accurate
   → DNP-enhanced

3. Accurate theory →
   → Thermodynamics/adsorption isotherms
   → Transformation pathways and intermediates

Questions?
Examples of scientific achievements enabled by DNP – SS-NMR studies were never before possible:

- 1D and 2D $^1$H-$^{15}$N DNP spectra determined the host-guest interactions between metal ions ($\text{Pt}^{2+}$ and $\text{Cu}^{2+}$) and a metal-organic framework (MOF).

- DNP surface-enhanced NMR spectroscopy was extended to the $^{17}$O nuclide, allowing the facile measurement of undistorted lineshapes, 2D $^{17}$O NMR spectra, and $^1$H-$^{17}$O distances at natural abundance.

- DNP-enhanced $^{15}$N SSNMR was used to describe the mechanism of solid-state thermolysis of ammonia borane.

- DNP-enhanced $^{29}$Si SSNMR was used to characterize isolated (-$\text{AlO})_3\text{Si(OH)}$ sites deposited on the $\gamma$-$\text{Al}_2\text{O}_3$ catalyst via atomic layer deposition.

- Molecular binding intermediates on metal nanoparticles were identified, for the first time, by DNP $^{13}$C-$^{13}$C SSNMR.

- Most recently, $^{27}$Al SSNMR spectra of surface Al species were detected on alumina thin film of the size on the order of $\sim 1$ cm$^2$.

Ames Laboratory’s DNP-enhanced NMR is the only system dedicated to materials studies.