Carbon Aerogels for Hydrogen Storage

T. F. Baumann, M. A. Worsley and J. H. Satcher, Jr.

Lawrence Livermore National Laboratory

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DOE Hydrogen Program

This presentation contains no confidential or proprietary information

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Project ID: stp_25_baumann

Project Overview

Timeline

- Project start: FY05
- Project end date: FY09
- Percent complete: 90%

Budget

- Total project funding (proposed): $1050K
- Funding received in FY08: $470 K
- Funding for FY09: $470 K
  - 0.5 FTE + 1.0 Post-Doc

Technical Barriers Addressed by Project

A. System Weight and Volume

C. Efficiency

P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- CalTech (Prof. Ahn)
  - H_2 adsorption measurements
- NIST (C. Brown)
  - Characterization by Neutron Scattering Experiments
- UNC-Chapel Hill (Prof. Wu)
  - Advanced NMR analysis
- HRL Laboratories (J. Vajo, MHCoE)
  - Scaffolds for Metal Hydrides

Project Objectives

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- Our objective is the design of novel aerogel materials that meet the DOE *system* targets (6 wt%, 45 g/L) for on-board vehicle H_2 storage
- Current focus in two areas:
  - Engineering of aerogel-based sorbent materials:
    - Optimize structure for enhanced H_2 uptake and improved kinetics
    - Storage at reasonable operating temperatures
  - Design of aerogel materials as porous scaffolds for light metal hydride systems:
    - Potential to improve kinetic and thermodynamic performance of metal hydrides

FY07	FY08	FY09
• Engineering undoped CAs • Evaluation of H_2 Sorption • Screening of CA Scaffolds	• Dopant Incorporation • Spillover/Kinetics Study • CA Scaffold Engineering	• Mechanistic Studies • Reversibility/Lifetime Studies for CA Sorbent and Scaffolds

Project Approach-Part 1

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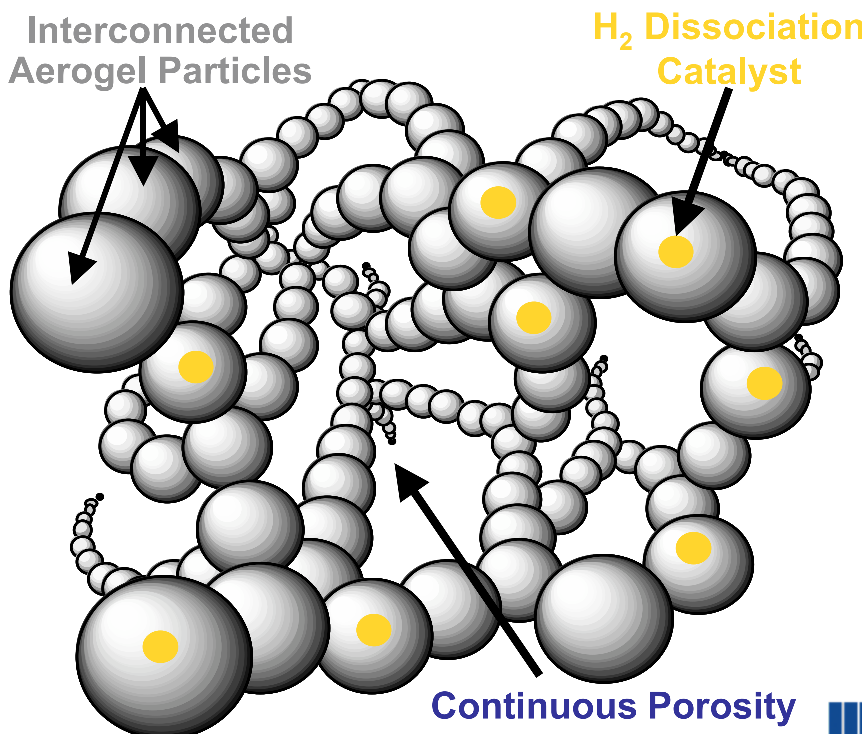
- Our approach is to utilize the flexibility of aerogel synthesis for the design new sorbent materials
- Aerogel synthesis allows for control over bulk properties (surface area, pore size, pore volume, composition, density) and for the homogeneous incorporation of modifiers (metal catalysts, organometallic species) into the matrix
- With this approach, we can control:
  - Surface chemistry and microstructure of the sorbent
  - Dispersion of the modifier (i.e. Pt nanoparticles for spillover)
- We can also use this flexibility to explore other sorbent materials with unique compositions
- Process is scaleable for production of monoliths or powders



Project Approach-Part 2

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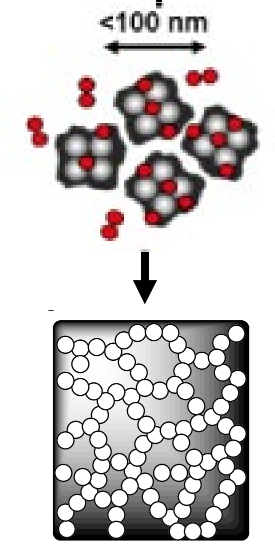
- Improved reaction kinetics for reversible H_2 storage in complex metal hydrides can be achieved through use of nanoporous scaffolds
  - Limits particles sizes and reduces diffusion distances
- We are fabricating aerogels as scaffolds for light metal hydrides (LMH), such as MgH_2, $LiBH_4$ and $NaAlH_4$
  - Work with HRL Laboratories (Metal Hydride CoE)
- Structural requirements for practical application of MH scaffolds:
  - Large pore volumes (minimize capacity penalty)
  - Small pore sizes (limit particle sizes)
  - Good thermal conductivity
  - Compatible surface chemistry
- We are using the flexibility of aerogel synthesis to design novel nanocomposites that possess the requisite structural, chemical and transport properties for metal hydride scaffolding

MH Nanoparticles



Porous Scaffold

Previous Accomplishments

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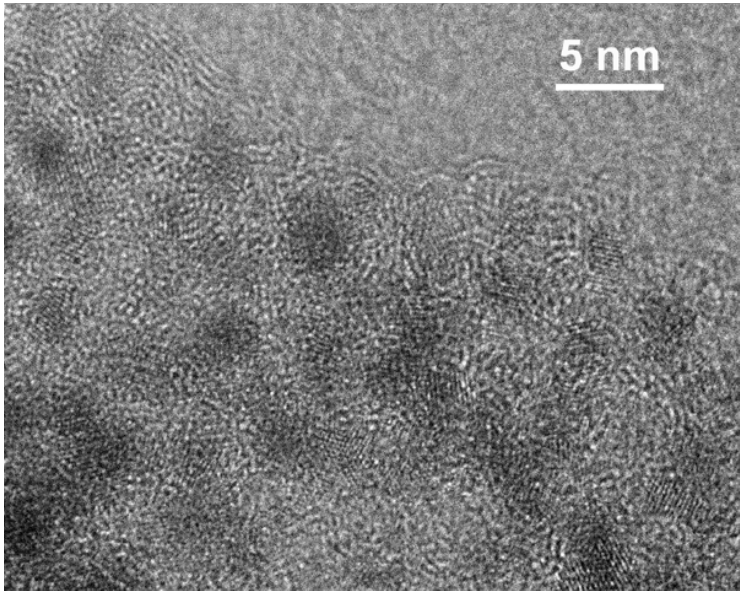
- Microporous CAs with surface areas in excess of 3000 m^2/g were prepared that exhibited surface excess H2 adsorption of up to 5.3 wt% and 29.2 g H_2/L at 77K
- These high surface area materials were used as supports for the design of new spillover materials with the goal of increasing overall H_2 capacity and improving uptake kinetics at room temperature
- Hydrogen dissociation catalysts (Ni, Pt) were incorporated into the aerogel supports by different methods to investigate the effects of catalyst dispersion and catalyst/support interface on H_2 uptake and kinetics
- Spillover systems derived from CAs exhibited significant issues with reproducibility for H_2 uptake at RT



HR-TEM of Pt-doped ACA (2400 m^2/g) prepared by atomic layer deposition

Technical Accomplishments:
Tailoring Surfaces of Spillover Materials

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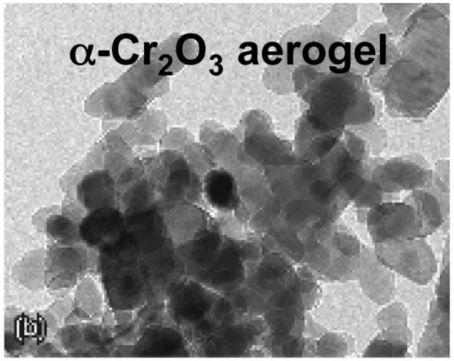
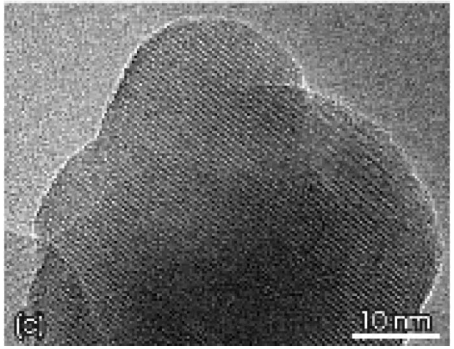
- We are examining the effects of surface chemistry of the carbon support on the spillover process:
  - Influence of oxygen-containing groups on catalyst performance, spillover kinetics, by-product formation (i.e. H_2O)
- Two approaches have been used to increase the oxygen content on the CA surface:
  1. Oxidation of CAs through activation in air at 450°C (SA ~ 1500 m^2/g)
     - Oxygen content: 20 wt% (vs. 3 wt% in ACA)
  2. Coating of activated CAs with sucrose (H_2O, H_2SO_4), followed by partial carbonization under N_2 at 400°C (SA ~ 2300 m^2/g)
     - Oxygen content: 11 wt%
- Pt nanoparticles have been incorporated into both types of modified CA using:
  - Impregnation (Yang, *J. Phys. Chem. C* 2007)
  - Microwave plasma deposition (Gennett, NREL)
  - Samples are currently being evaluated for RT H_2 uptake

Technical Accomplishments:
New Sorbent Materials

- **We have prepared a series of chromia aerogels as potential H_2 storage materials:**
  - **Previous work showed that Cr_2O_3 and ZnO can reversibly bind H_2 at appreciable binding energies[1]**
  - **Papers reported *enhanced* H_2 binding at low temperatures (77 K) and activated adsorption at elevated temperatures (> 50^oC) in α-Cr_2O_3**
- **Using sol-gel chemistry, high surface area amorphous and α-Cr_2O_3 aerogels have been synthesized for H_2 adsorption experiments (77 K and RT)**
  - **BET SAs: 500 m^2/g (amorphous)**
    70 m^2/g (crystalline)
  - **Uptake measurements at CalTech**
  - **Amorphous sample exhibits binding energy of ~6 kJ/mol at 77 K**
  - **Crystalline sample not yet tested**





[1]Weller/Voltz *JACS*, 1954, *76*, 4695; Burwell/Taylor *JACS*, 1936, *58*, 697.

Technical Accomplishments:
Functionalized Aerogels as Kubas Supports

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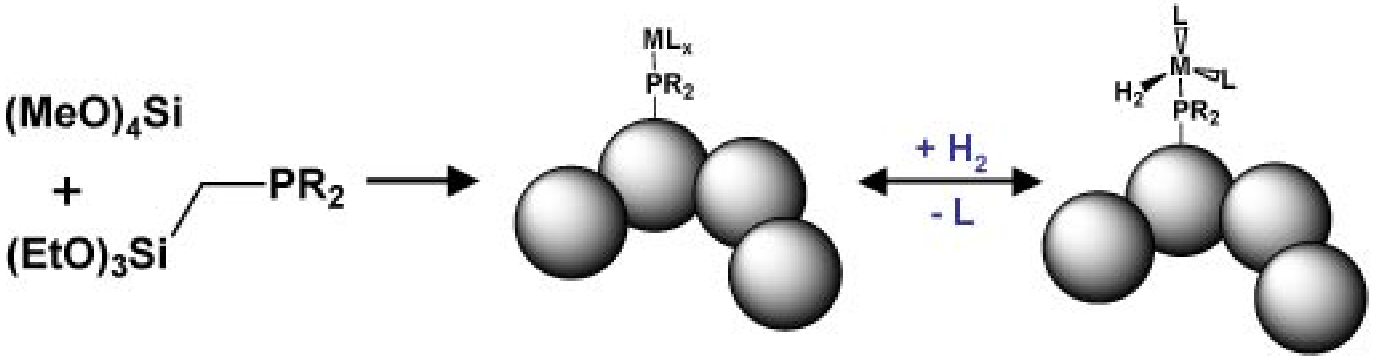
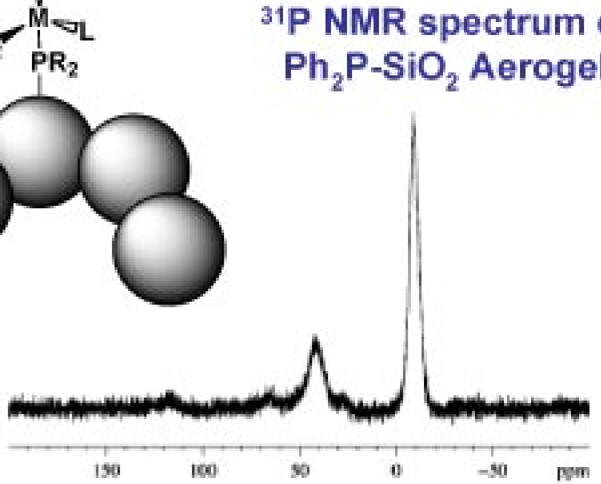
- Aerogel architectures can be utilized as high surface area supports for organometallic complexes that can reversibly bind H_2
- We have synthesized new aerogel substrates that are functionalized with ligands for the stabilization of organometallic complexes
  - Low-density SiO_2 aerogel (SA ~ 750 m^2/g) with pendant $-PPh_2$ groups
  - Prepared through co-condensation of $(MeO)_4Si$ and $(EtO)_3SiCH_2CH_2PPh_2$





- This material has been treated with organometallic Ni complexes and H_2 uptake behavior of the products are currently being tested

Technical Accomplishments:
Improved Scaffold Design

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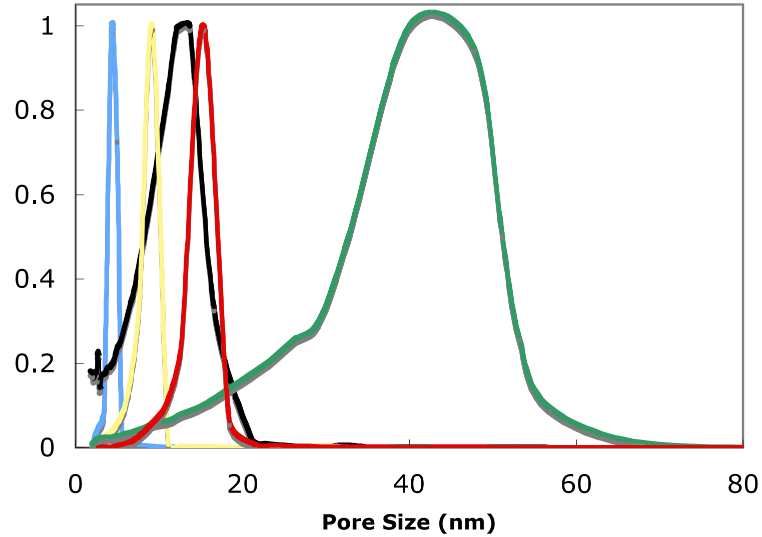
- **Improved synthesis methods have generated new scaffolds with smaller pore sizes and larger pore volumes:**
  - **Sacrificial template incorporated into aerogel matrix during the sol-gel reaction and removed during carbonization**
  - **Materials with pore volumes as large as 5 cm^3/g have been prepared**
  - **New material combines the large pore volumes of the our original CAs with the small pore size of HRL xerogels**

1st Generation
HRL Carbon Xerogel
APD ~ 13 nm
PV = 1.1 cm^3/g

LLNL CA
APD ~ 40 nm
PV = 2.7 cm^3/g



New CA Scaffolds
APD ~ 15 nm
PV = 2.6 cm^3/g

APD ~ 9.5 nm
PV = 1.1 cm^3/g

APD ~ 4 nm
PV = 0.5 cm^3/g

HRL LABORATORIES

METAL HYDRIDE CENTER OF EXCELLENCE

- **CA with small pore sizes (< 5 nm) delivered to NIST (Jack Rush) for $LiBH_4$ study (^{11}B and D studies)**
- **CA scaffolds also delivered to PNNL (Tom Autrey) for AB studies**

Technical Accomplishments:
Carbon Nanotube Composite Scaffolds

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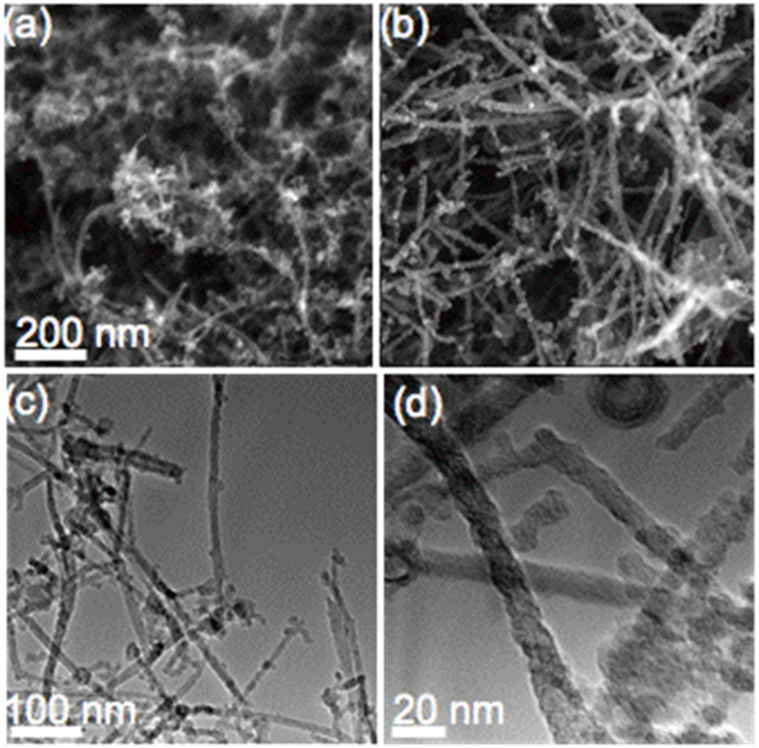
- We have prepared new carbon nanotube (CNT)-CA nanocomposites[1] as next-generation scaffold materials:
  - Improved thermal transport in these scaffolds
  - Facilitated H_2 transport (open-ended CNTs as “plumbing”)
  - CNTs can influence rates of hydrogen exchange



- Scaffolds prepared with single- and double-walled CNTs at various loading levels
- Composites exhibit enhanced thermal conductivities
- $LiBH_4$ composites prepared with these scaffolds exhibit unusually low dehydrogenation temperature:
  - Interaction of BH_4 with CNT surface may influence H_2 release
  - Residual metal catalyst (Ni/Y) may also play role in process

[1]M. A. Worsley,et al, *Appl. Phys. Lett.*, **2009**,*94*, 073115; *Langmuir*, **2008**, *24*, 9763.

Technical Accomplishments:
Scaffolds containing Destabilization Agents

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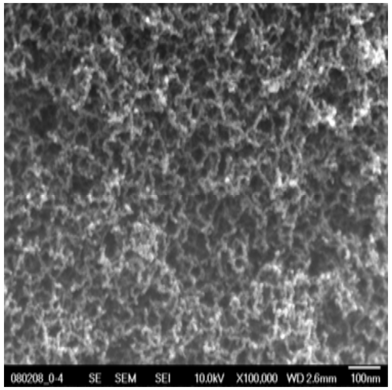
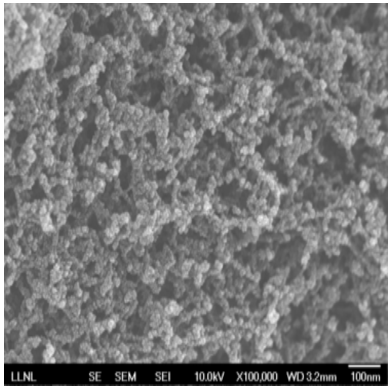
- **Performance of MHs can be improved through the introduction of catalysts and/or destabilizing agents into the bulk material**
- **Aerogel synthesis allows for controlled incorporation of these modifiers into these scaffolding architectures**
- **Titania has been reported to be a destabilizing agent for $LiBH_4$**
  - **Desorption temperatures of 150°C**
  - **Formation of $LiTiO_2$ as intermediate (*J. Phys. Chem. C*, 2008, *112*, 11059.)**
- **We have synthesized CA scaffolds coated with a thin layer of TiO_2:**



CA Scaffold

$Ti(OEt)_4$ →



TiO_2-coated CA (37 wt% Ti)

- **Large pore volumes are preserved after incorporation of TiO_2**
- **Loading of titania can be controlled through synthesis**
- **Performance as scaffolds currently being tested**

Collaborations

- **Partners:**
  - CalTech (Academic): H_2 uptake measurements in spillover materials as well as new sorbent systems
  - HRL Laboratories (Industry): Evaluation of aerogels as scaffolds for metal hydrides
  - NREL (Federal): (1) Performance evaluation of new spillover materials and (2) testing of functionalized aerogels as supports for organometallic species
  - NIST (Federal): (1) Characterization of H_2 uptake in sorbents and (2) evaluation of scaffolding effects on performance of metal hydride materials by Neutron Scattering experiments
  - UNC-Chapel Hill (Academic): Advanced NMR analysis of H_2 sorption in high surface area sorbents

Future Work

- Performance evaluation of spillover behavior in metal-doped CAs:
  - Tailored design of surface chemistry and microstructure of spillover support to improve uptake kinetics and reversibility
- Improved design of functionalized aerogels as supports for organometallic H_2 complexes:
  - Synthesis of high surface area R_2P-aerogels
- Evaluate RT H_2 uptake in new aerogel sorbents:
  - Determine binding energies and kinetics for H_2 uptake in high surface area Cr_2O_3 and reduced TiO_2 aerogels
- Optimization of aerogel scaffolds for metal hydrides:
  - Continued engineering of scaffold structure (porosity, composites)
  - Modify CA surface chemistry to improve MH wetting behavior
  - Incorporation of catalysts/destabilizing agents
- Evaluate reversibility and lifetime in these materials over multiple charge/discharge cycles

Project Summary

DOE Hydrogen Program

Relevance: Design of new aerogel materials for hydrogen storage

Approach: Incorporation of modifiers into high surface area aerogels to maximize H_2 uptake and increase binding energies

Technical Accomplishments:

- Fabrication of new spillover supports with tailored surface chemistry
- Synthesis of functionalized aerogels as supports for Kubas-type complexes as well as novel sorbent materials derived from Cr_2O_3
- Preparation of novel CA-CNT nanocomposites as scaffolds for metal hydride systems

Center Collaborations:

- Prof. Channing Ahn (CalTech): H_2 sorption measurements
- John Vajo (HRL, MHCoE): CA scaffolds for metal hydrides
- Craig Brown (NIST): Characterization of activated CA structure by NS techniques
- Prof. Yue Wu (UNC): Characterization of CA structure and H_2 uptake by advanced NMR techniques

Summary for CA Materials

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DOE On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 *System* Target	CA *Material* Results
Specific Energy	kWh/kg ($wt\% H_2$)	2.0 ($6 wt\% H_2$)	5.3 wt% at 77 K and 30 bar
Energy Density	kWh/L ($g H_2/L$)	1.5 ($45 g H_2/L$)	~29 $g H_2/L$