Toward Realization of ideal H_2 Society
~ What Can We 'Organic Chemists' Make a Contribution? ~

Lit.seminar
10/07/07
M2. Yutaka SAGA

0. Introduction

(1) Features of H_2

- Reported as independent substantial by H. Cavendish in 1766.
- Named as 'Hydrogen' by Lavoiser.
- The lightest element ↔ the heaviest element 'U' as nuclear energy.
- Harber-Bosch process: $N_2 + 3H_2 \leftrightarrow 2NH_3$ • Trans fat synthesis
- **Expected as a promising energy carrier in future energy system.**

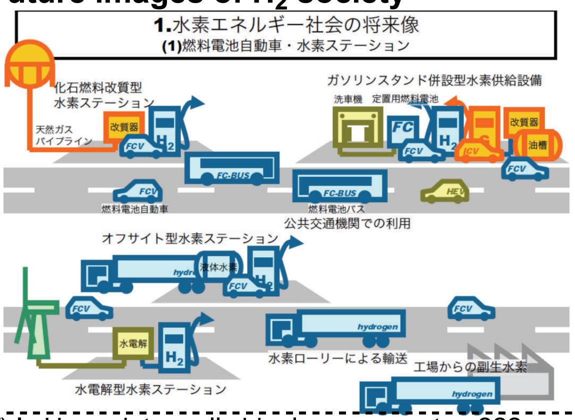
<advantages>

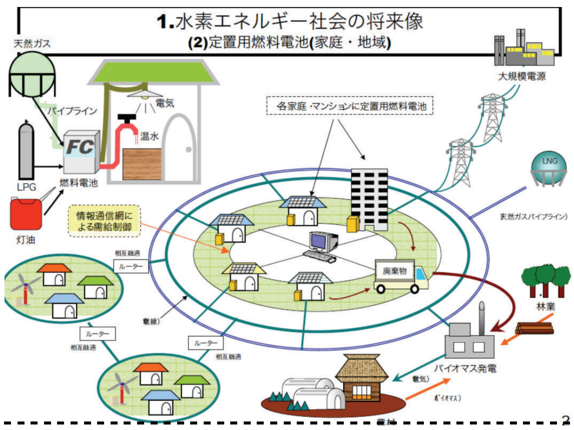
- Genuine **clean energy** ↔ CO_2
- The most **abundant** fuel
- Produced by extensive sources
- The highest energy **per kg**
- **Availability**

<disadvantages>

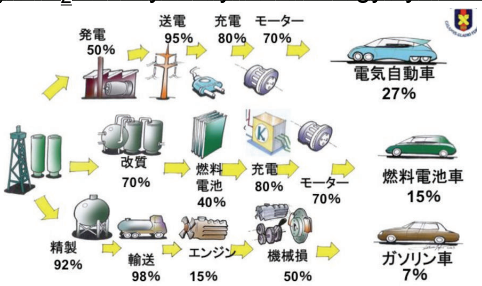
- Clean but **higly cost** for storage or deliver
- Abundant but **not easy to extract** from sources
- Not so high energy **per L**
- **Dangerous** (take care for fire or reeking)

(2) Future images of H_2 society

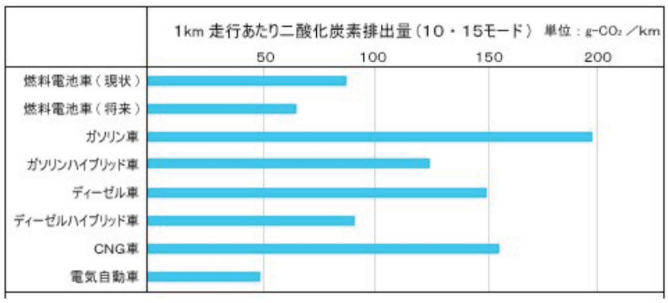




cf) Is H_2 society really ideal energy system???



電気自動車、燃料電池車、ガソリン車のエネルギー効率



For example: In the case of 'Hydrogen Cars'

Officially : • the biggest reduction of greenhouse gas
• economical and energy-saving device

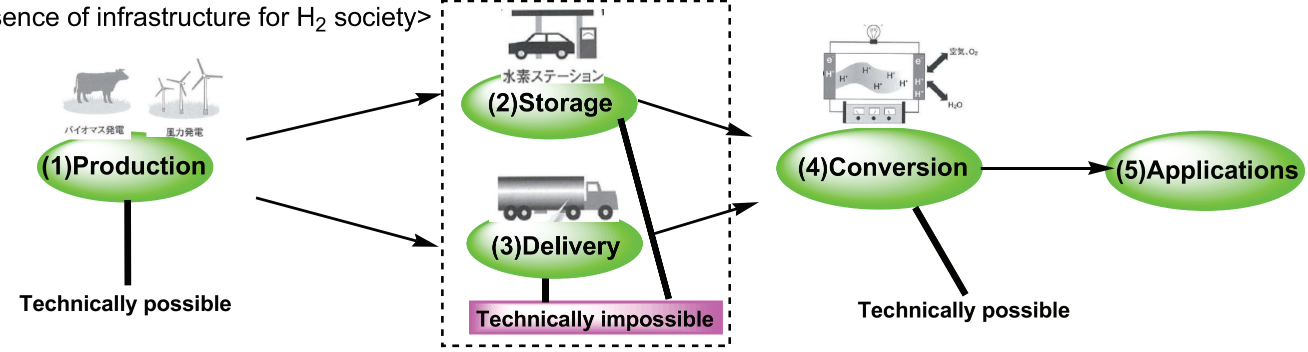
Current condition
: Almost all the aspects are **inferior to electric vehicle.**

⇨

- Many techinical obstacles
- **Political reasons???**

(Oil-coal system should be favorable.)

<Essence of infrastructure for H_2 society>



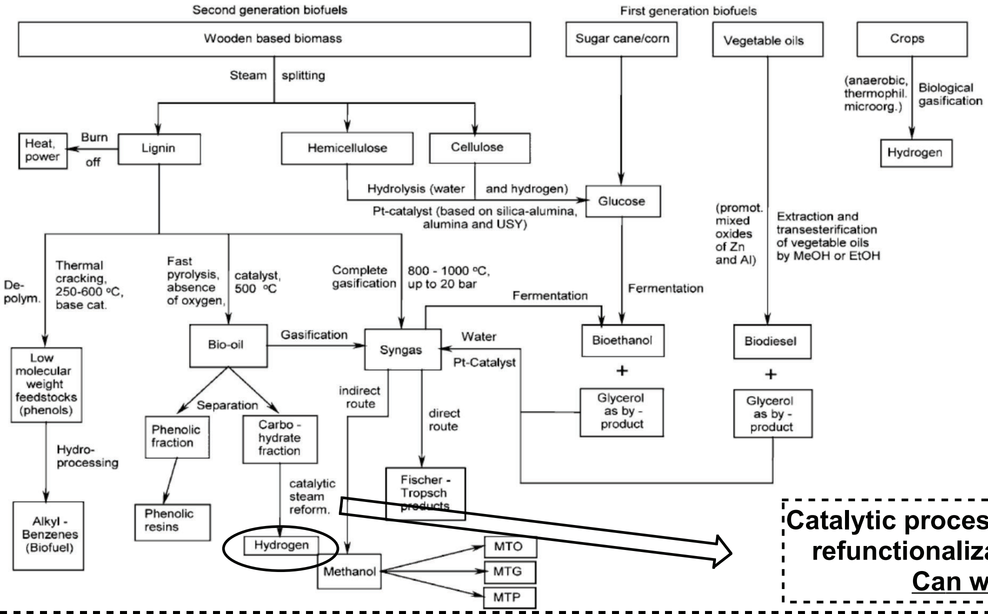
(1) production

Fossil resource-derived
: **CO_2** is the deepest energy sink.(Oil, coal, natural gas, MeOH...) ⇨ Inevitable CO_2 emmision
: Highly avoided method

H_2O electrolysis-derived
: Novel technology is continuously developed. ⇨ Energy source should be clean one.
: Solar energy, wind energy etc

Biomass-derived
: **Recyclable and carbon-neutral**

Ref)
review: *Angew. Chem.Int. Ed.* **2008**, *47*, 9200



Catalytic process for the selective de- and refunctionalization is highly demanded.
Can we contribute???

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(2) Storage (3) Delivery :Today's main topic
(4) Convesion : Mostly relies on **fuell cell**

Fascinating precedent of artificial H_2O electrolysis

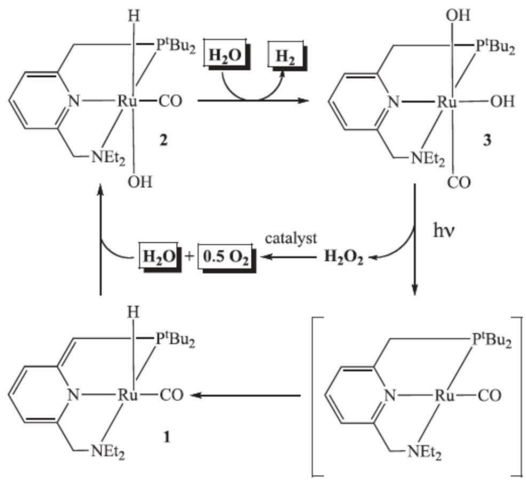
Milstein *et al Science.* **2009**, *324*, 74

> Ru-pincer ligand complex
(No change in the metal oxidation)

See: Mr.Kimura's lit.seminar(10/04/21)
Milstein *et al Science.* **2007**, *317*, 790
Milstein *et al J. Am. Chem. Soc.* **2005**, *127*, 10840
Pioneering work:
Brookhart *et al J. Am. Chem. Soc.* **1998**, *120*, 7143

> Stepwise generation:
H_2 thermally and O_2 photochemically

> Future model of artificial fuel cell - **Can we contribute???**



<Today's contents>

- **0. Introduction**
- **1. Properties of H_2 Storage**
- **2. Methodologies for H_2 Storage**
- **3. What Can We Contribute to This Field ?**
  ~ Organic Chemistry Approach ~
- **4. Perspectives**

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1. Properties for H_2 Storage

Review: *Angew. Chem.Int. Ed.* **2009**, *48*, 2
Chem. commun. **2008**, 681

1-1. Difficulities of H_2 Storage

1. Most difficult challenge
: **H_2 Storage must be simulated as real applications in vehicles(infrastructures)**
> Portable applications, then stationary applications, finally transportation purposes

2. Weight and volume
> H_2 has **lowest energy density (< 1/ 3000 of gasoline)**
> Naturally **harsh conditions** are required (High pressure, law temperature)
> Desired **as compact as possible** for application in vehicles

3. Efficiency = reversibility

> Energy efficiency is required **in order not to waste away the efficiency of fuel cell**
> How to process **byproducts**
> Recyclable devices = with **reversible ability** to uptake/release H_2

4. Applicability

> Durability:
Devices are needed that allow H_2 storage systems with **a lifetime of 1500 cycles.**
↔ semipermanent for gasolines
> Cost ← low boiling point
> Safety = How to handle with dangerous H_2 (fire, reeking)
when accidents (also for shock, change of temperature etc)

5. Analysis

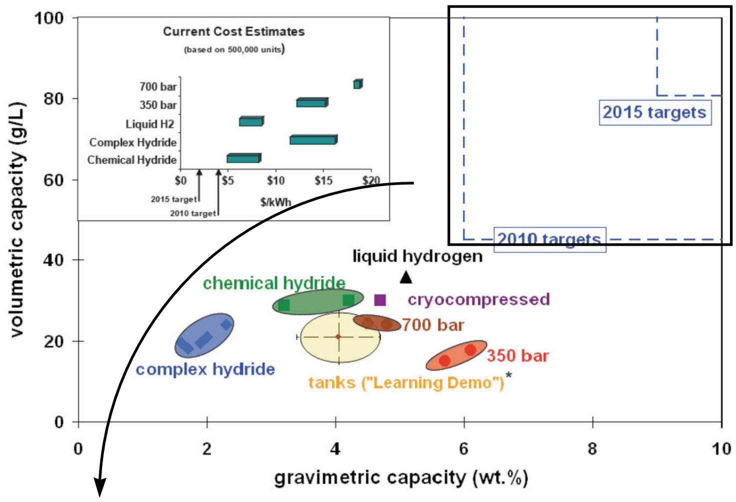
> There is **a lack of analyses** of the life-cycle cost and efficiency for H_2 storage systems.

1-2. Current situations for H_2 Storage

DOE set goals for each point

Storage Parameter	Units	2010	2015	Ultimate
System Gravimetric Capacity				
Usable, specific-energy from H_2	kWh/kg	1.5	1.8	2.5
(net useful energy / max system mass) [a]	(kg H_2/kg system)	(0.045)	(0.055)	(0.075)
System Volumetric Capacity				
Usable energy density from H_2	kWh/L	0.9	1.3	2.3
(net useful energy / max system volume)	(kg H_2/L system)	(0.028)	(0.040)	(0.070)
Storage System Cost [b] (and fuel cost) [c]	\$/kWh net (\$/kg H_2) \$/gge at pump	4* (133) 2-3	2* (67) 2-3	TBD* 2-3
Durability / Operability				
Operating ambient temperature [d]	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
Min/max delivery temperature	°C	-40/85	-40/85	-40/85
Cycle life (1/4 tank to full) [e]	Cycles	1000	1500	1500
Cycle life variation [f]	% of mean (min) at % confidence	90/90	99/90	99/90
Min delivery pressure from storage system; FC = fuel cell, ICE = internal combustion engine	Atm (abs)	4FC / 35 ICE	3FC / 35 ICE	3FC / 35 ICE
Max delivery pressure from storage system [g]	Atm (abs)	100	100	100
Charging / Discharging Rates				
System fill time (for 5 kg H_2)	min (Kg H_2/min)	4.2 min (1.2 kg/min)	3.3 min (1.5 kg/min)	2.5 min (2.0 kg/min)
Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
Start time to full flow (20 °C) [h]	s	5	5	5
Start time to full flow (-20 °C) [h]	s	15	15	15
Transient response 10%-90% and 90% - 0% [i]	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage) [j]	% H_2	99.99 (dry basis)		
Environmental Health & Safety				
Permeation and leakage [k]	Scc/h	Meets or exceeds applicable standards		
Toxicity	-			
Safety	-			
Loss of useable H_2 [L]	(g/h)/kg H_2 stored	0.1	0.05	0.05

However...

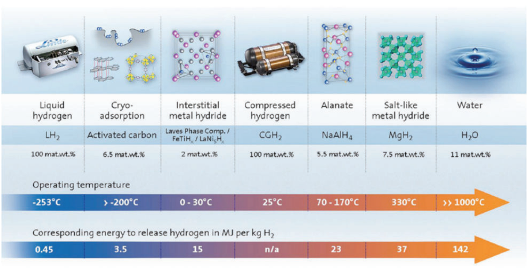


> Despite many developed methods,
none has yet reached the goals set by DOE.
> Goals should be **simultaneously achieved.**
> All have several advantages but also disadvantages.

1-3. Classifications of available methodologies for H_2 Storage

Physical Storage
: No strong chemical bonds

- **1. CGH2(Compressed Gaseous Hydrogen)**
- **2. LH (Liquid Hydrogen)**
- **3. Material-based Storage**
  - **1. Cryoadsorption**
  - **2. Carbon Materials**
  - **3. MOFs**



Chemical Storage
: Covalent bonds to metals

- **1. Inorganic approach**
  - **1. Hydrolytic systems**
  - **2. Metal Hydrides**
  - **3. Complex Hydrides**
- **2. Organic approach**
  - **1. FLP**
  - **2. N-B containing materials**
  - **3. Combination or New Entry**

We ' Organic chemists' can enter these fields to exploit our aquired skills!!!

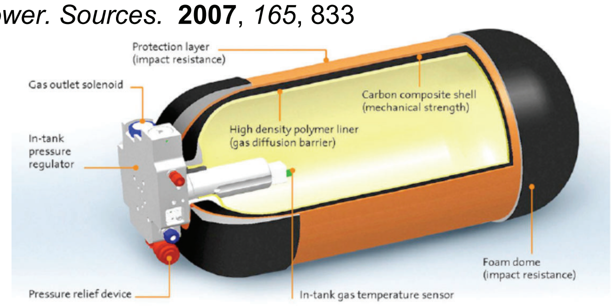
2. Methodologies for H_2 Storage

2-1. Physical Storage : **No strong chemical bonds** between hydrogen and a host compound are involved.

2-1-1. CGH2 (Compressed Gaseous Hydrogen)

> Compressed H_2 **greater than 70MPa**
> To store about **5-6 Kg** to achieve vehicles with a range of **500 km.**
> **The best overall technical performance to date.**

J. Power. Sources. **2007**, *165*, 833



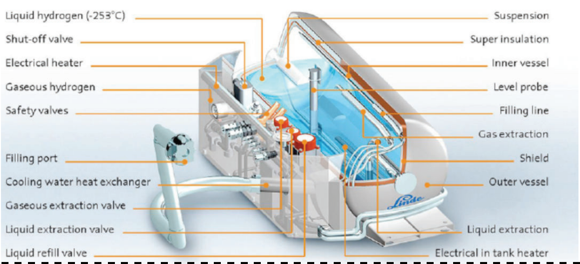
<Advantages>
- **Highest energy density**
- Feasible to refill H_2 completely **within 3 min**

<Disadvantages>
- **Special vessel design** to work with > 70MPa

> Cylindrical design is essential.
> **Three-vessel carbon composite unit**
(135 kg↔ 600kg with steel system)

2-1-2.LH2 (Liquid Hydrogen)

J. Power. Sources. **2007**, *165*, 833

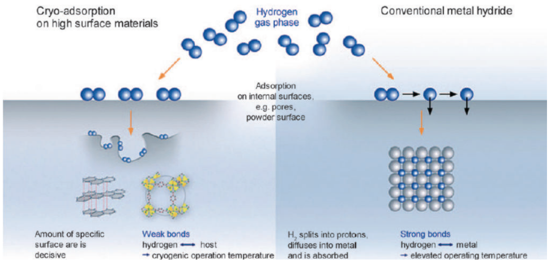


> **–253 °C, 0.1 MPa**

<Advantages>
- **Highest energy density**

<Disadvantages>
- Significant **hydrogen loses**(on-board + at infrastructure)
  > heat flowing→ increased pressure→H_2 vented
- **Special vessel design** to work with < –253°C

2-1-3.Material-based Storage



> Relatively **weak interactions with H_2**
(van der Waals interactions etc)
> H_2 is **molecularly adsorbed**, not dissociated
> H_2 uptake is controlled by **SSA(Supecific Surface Area), pore size**
> Zeolites, carbon matrials, **MOF(Metal-Organic Frameworks)**
<Disadvantages>
- **Low energy density**

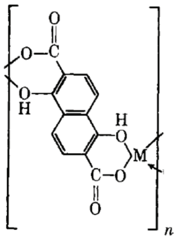
@ MOF(Metal-Organic Framework)

: porous solids where **inorganic building units are joined by organic links**

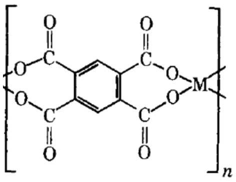
Review: *Nature.* **2003**,423, 725
Chem. Soc. Rev. **2009**, *38*, 1284

> provide **shape/size selectivity** with functionalized pores
> gas purification, gas separation, **H_2 storage**

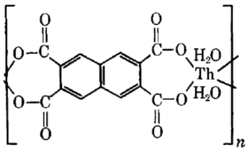
In 1965, birth year of MOFs



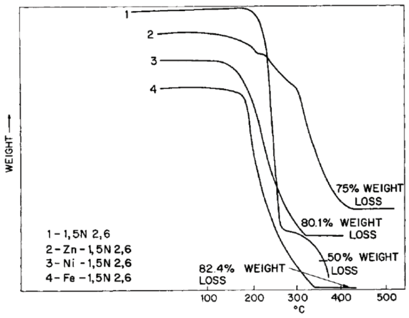
> 6-membered chelate
> with Zn, Ni, Fe

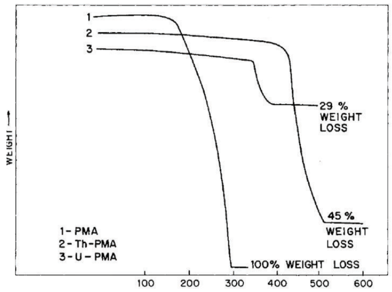


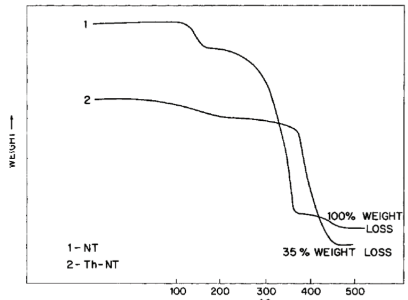
> 7-membered chelate
> with Th, U



> 8-membered chelate
> with Th



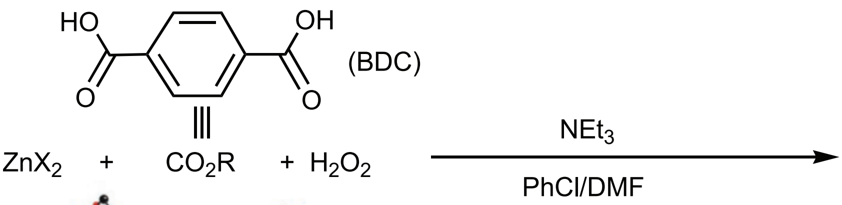


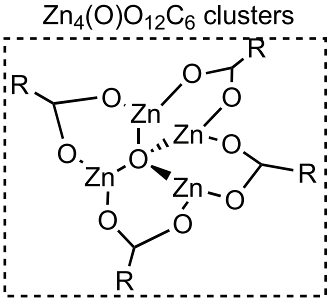


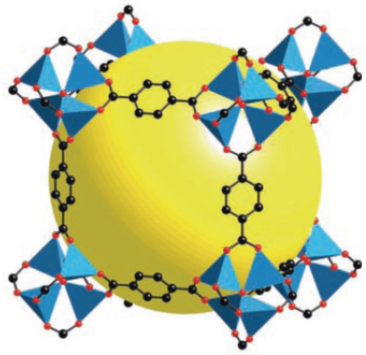
> **Only thermal stabilities were tested.**

J. Appl. Polym. Sci **1965**, *9*, 3745

Pioneering work by O.M. Yaghi *Nature*. **1999**, *402*, 279

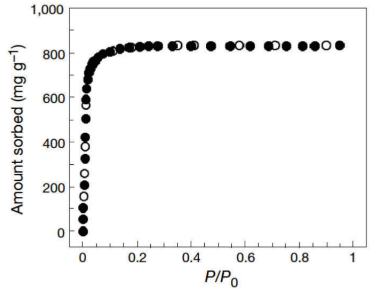






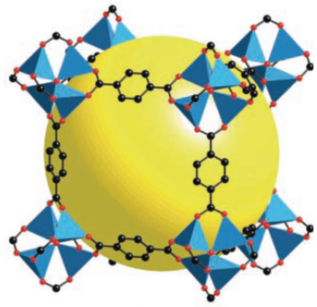
> **Stable without solvent in pores**
> Without loss of framework **at 300°C**
> Higher **surface area and pore volume**
> **Reversible sorption of gases** (N_2, $CHCl_3$ etc)

→ Univesal design for gas storage application

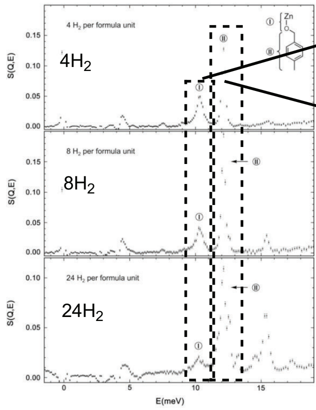


Ralated work by O.M.Yaghi *Science*. **2003**, *300*, 1127

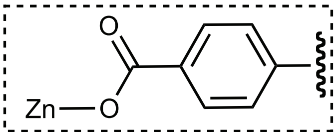
> With the same MOF or derivatives



> H_2 4.5 wt% at 77K, 0.8 bar
> H_2 1.0 wt% at r.t., 20 bar



H_2 binding site: **Zn cluster**



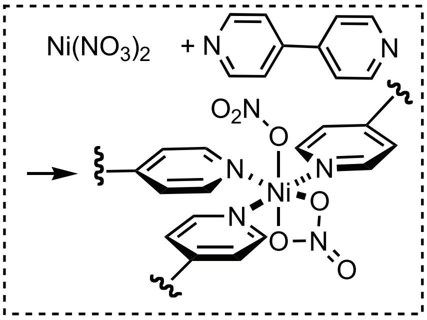
H_2 binding site: **Ligand**

> Determination of H_2 binding site by **INS**

INS :

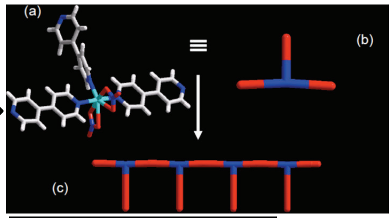
> Clear surface/uptake relationship
> Two binding sites are determined.

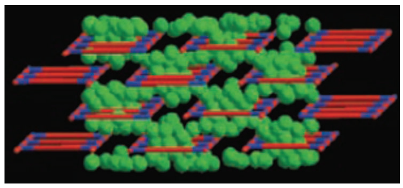
Gated absorption

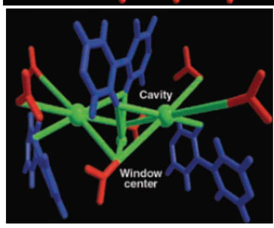


MOF structure
J. Am. Chem. Soc. **2002**, *124*, 9574

Thomas *et al*. *Science*. **2004**, *306*, 1012

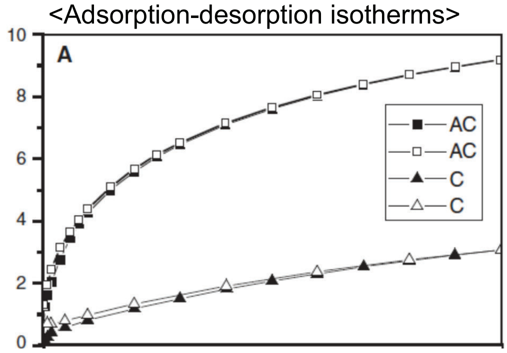


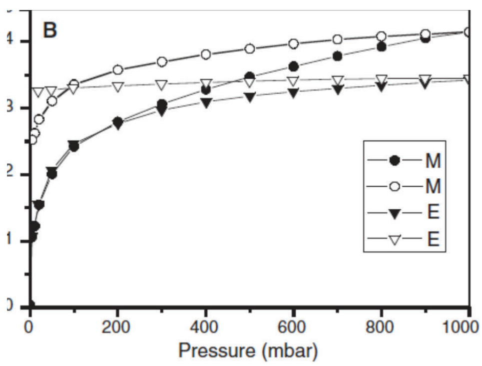




> Cavities and connected windows
(cavities >> windows)
> **Dynamical opening of windows**

<Adsorption-desorption isotherms>





AC: Activated Carbon
C: Control MOF
M, E: Gated absorption MOF

Material	Window Size /Å	Pore Cavity Cavity Size /Å	Total Pore Volume/ cm^3 g^{-1}
AC	-	-	0.44
E	2.32 x 2.75	5.4 x 5.2 x 4.1	0.149
M	2.5 x 4.9	4.3 x 5.3 x 8.3	0.181
C	8.5 x 8.5	13.7 x 10.7	0.63

> **Hysteresis**
: kinetic phenomena where a sample is loded at high pressure and becomes metastable
> **Absorbed at high pressure and stored at lower pressure** given the flexibility of frameworks

<Advantages>

- **Youngest** in the class of porous materials
- **Fully reversibility** by pressure or other control
- Recharging can proceed **within minutes**
- **Organic chemistry can enter the field???**

> We can approach through **complex ligand design,** compared to feasible ligands(BP, DC) generally utilized.

cf) Dr.Oisaki's work: *J. Am. Chem. Soc.* ASAP: **Covalently linked MOFs** by NHCs

<Disdvantages>

- **Significant lack of H_2 capacity**
- Still at the **basic research phase**
- Large pore volume to **enhance H_2 storage capacity** vs **decrease in the strength of the interaction**

2-2. Chemical Storage

2-2-1. Inorganic Approach

2-2-2-1. Hydrolytic systems

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x,$$

$$M + \frac{x}{2}H_2O + \frac{x}{2}e^- \leftrightarrow MH_x + \frac{x}{2}OH^-$$

: Upon reaction with metal and water , hydrogen is released with metal hydroxide or oxide.

> Any metals can be considered as **H_2 storage system**
(any metals with a redox potential below that of H^+/H_2 system)

> Best = **$NaBH_4$**

$$NaBH_4 + 4H_2O \xrightarrow{\text{Ru cat.}} NaOH + H_3BO_4 + 4H_2 \ (\mathbf{7.3\ wt\%})$$

<Advantages>

- Relatively **high energy density**
- Reasonably **stable** to be stored
- **Liquid** fuel = conventional gasoline

<Disdvantages>

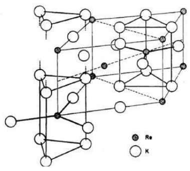
- **$NaBO_2$** cannot be removed from vehicles
- **Irreversible**

2-2-2-2. Metal hydrides

@ classical metal hydrides : **$K_2[ReH_9]$**

Inorg. Chem. **1964**, *3*, 555

Inorg. Chem. **1964**, *3*, 558



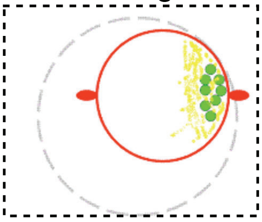
> 2.0 wt % H_2
> Due to **high atomic weight**

@ Alloys : **AB_5 ($LaNi_5$)** (expensive) ; **AB_2** (A= Ti, Zr, Mg; B = V, Fe)

@ Best metal hydrides : **MgH_2 with ball-milling**

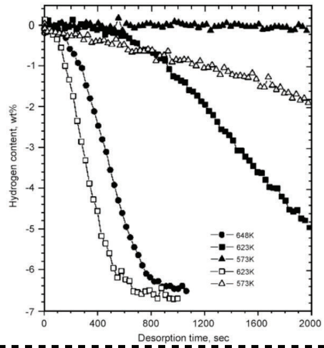
Ball-milling : Grinder used to grind materials into extremely fine powder
円筒体の胴体に粉砕したいものと一緒に金属球やセラミック球を入れ胴体を回転させて粉砕する

<Ball-milling>



Critical factor = **Metal surface**

> **Increased surface area and creation of defects on the surface**
> **Faster hydrogen desorption kinetics**: Milled (white) vs Unmilled (black)



<Advantages>

- **High storage capacity** : 7.7 wt%
- **Low material cost**
- **Good reversibility**

<Disdvantages>

- High-temperature metal hydride : **> 300°C** with 0.1 MPa
- High reactivity toward **air and O_2**

Int. J. Hydrogen. Energy. **2007**, *32*, 1121

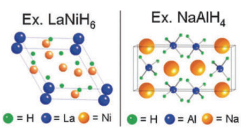
2-2-2-3. Complex hydrides

: A complex anion = **H covalentry bound to a metal**
> BH_4^-, AlH_4^-, NH_2^-

+

A metal cation > Li, Na, Mg

@ First report in 1940 **Synthesis of $LiBH_4$**
H. C. Brown *et al. J. Am. Chem. Soc.* **1940**, *62*, 3429
> Not considered for reversible H_2 storage



@ Pioneering work in 1997: **Doping system**
J. Alloys. Compd. **1997**, *253*, 1

$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2$ (3.7 wt%)
$Na_3AlH_6 \rightarrow 3NaH + Al + 1.5H_2$ (1.9 wt%)
$3NaH \rightarrow 3Na + 1.5H_2$

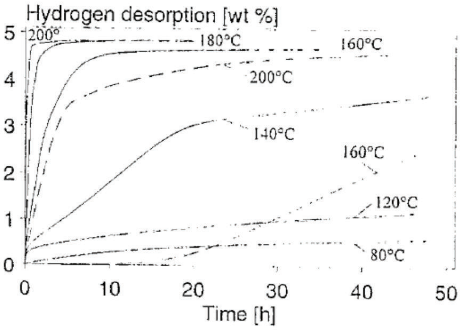
> **Irreversible**
: Rehydrogenation required too harsh condition.

Ti dopants

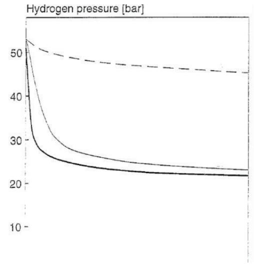
$$3NaAlH_4 \rightleftharpoons Na_3AlH_6 + 2Al + 3H_2$$

Ti = $TiCl_3$ or $Ti(O^tBu)$

> can be used as a **reversible** H_2 storage material



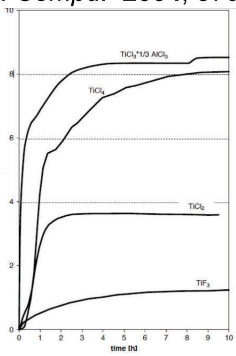
•••• : Undoped
—— : Ti-doped



> About **the ability to supply H_2**
> At undoped system, even at 200 °C, it takes 24h to supply H_2
> At Ti-doped system, it takes only 1h.

> About **the ability to resupply H_2** (rehydrogenation)
> **Dramatic improvement on the rate and the extent** of rehydrogenation

J. Alloys. Compd. **2004**, *370*, 104



$$x\mathrm{NaAlH_4} + \mathrm{TiCl_2} \xrightarrow{\text{b.m.}} (x-2)\,\mathrm{NaAlH_4} + \mathrm{Ti} + 2\mathrm{Al} + 2\mathrm{NaCl} + 4\mathrm{H_2}\uparrow \quad (5)$$

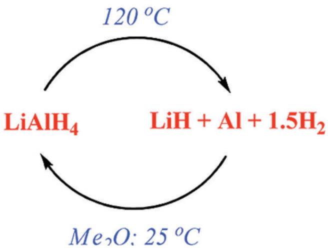
$$x\mathrm{NaAlH_4} + \mathrm{TiCl_4} \xrightarrow[\text{at } 25\,^{\circ}\mathrm{C}]{\text{stirring}} (x-4)\,\mathrm{NaAlH_4} + \mathrm{Ti} + 4\mathrm{Al} + 4\mathrm{NaCl} + 8\mathrm{H_2}\uparrow \quad (6)$$

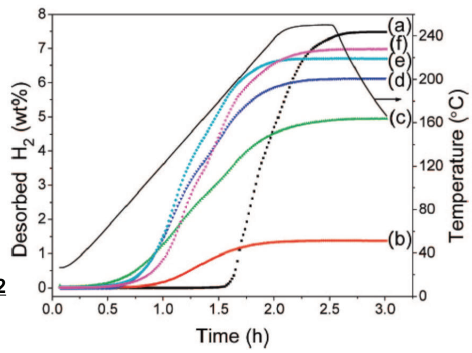
$$x\mathrm{NaAlH_4} + (\mathrm{TiCl_3})\tfrac{1}{3} \xrightarrow{\text{b.m.}} (x-4)\,\mathrm{NaAlH_4} + \mathrm{Ti} + 4\tfrac{1}{3}\mathrm{Al} + 4\mathrm{NaCl} + 8\mathrm{H_2}\uparrow \quad (7)$$

> Ti with **different oxidation states** gives different amounts of H_2
($TiCl_4$→8 mol/Ti, $TiCl_3$→6 mol/Ti, $TiCl_2$→4 mol/Ti)

> Formal Ti valence is **zero-valent**
> Alloy of $TiAl_3$?

J. Am. Chem. Soc. **2009**, *131*, 5032





> $LiAlH_4$ contains **> 40% more H_2**
→ **Irreversibility**
> Ti-doped $LiAlH_4$

> Reversible H_2 storage
> 7.5 wt% release and uptake at **remarkably mild condition**
> Due to solvent **Me_2O** effect (Me_2O and Li^+ interaction?)
> **Cat.loading of Ti** is relevant to the stability
> Not new materials, but **new processes**

@ Summery - qualitive evaluation

	Energy density(wt %)	Refilling/reversibility	Cost	Safty/mildcondition
1. CGH2				
2. LH				
3. MOF				
1. Hydrolytic systems				
2. Metal hydrides				
3. Complex hydrides				
1. FLP				
2. N-B				

> Prototype fuel-cell-powered cars(**smaller-scale storage) are based on CGH2.**
> For larger volume storage, **LH is the most promising option.**
> **Other promising materials** may be discovered → no materials has yet reached a satisfactory level.
> Combination?

3.What Can We Contribute to This Field?
~ Organic Chemistry Approach~

3-1. FLP(Frustrated Lewis Pairs)

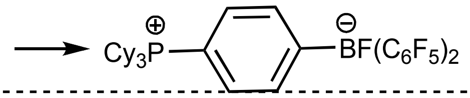
: **Unquenched Lewis acids and Lewis bases**
by steric and electronical frustration

Review: *Angew. Chem. Int. Ed.* **2010**, *49*, 46
Org. Biomol. Chem. **2008**, *6*, 1535

Classical Lewis Adducts

$B(C_6F_5)_3 + PMe_3 \longrightarrow [Me_3P{\rightarrow}B(C_6F_5)_3]$

Frustrated Lewis Pairs

$B(C_6F_5)_3 + PCy_3 \longrightarrow$ 

@ First report in 1964 — *J. Organometal. Chem.* **1964**, *2*, 245

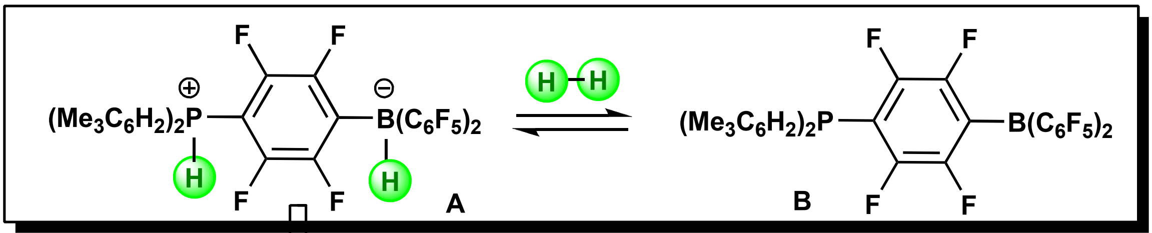
$B(C_6F_5)_3$ + PPh_3 or Py or NEt_3 $\longrightarrow$ $[B(C_6F_5)_3][PPh_3]$ or $[B(C_6F_5)_3][Py]$ or $[B(C_6F_5)_3][NEt_3]$

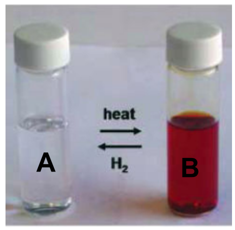
> Adducts were **only synthesized**
> Afterward several reports utilizing for **protection of silyl group** or **hydrosilylation**

cf) *J. Org. Chem.* **1999**, *64*, 4887 ; *Org. Lett.* **2000**, *24*, 3921

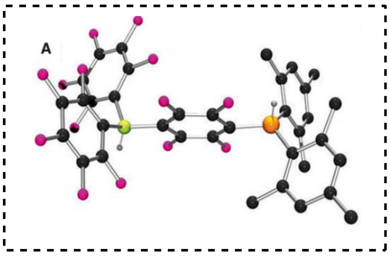
@ Pioneering work by Stephan *et al*

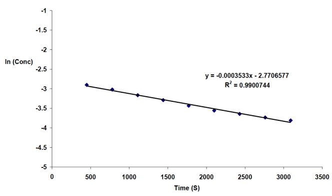
Science. **2006**, *314*, 1124





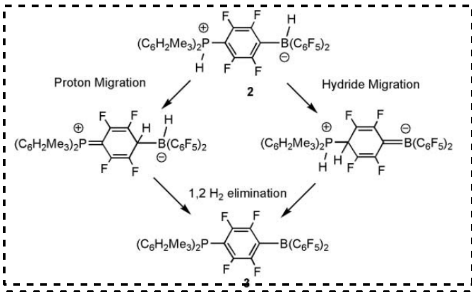
> **First report with no-metal system** for **reversible** H_2 activation
> $P(Mes)_3$ is a key : **too bulky to cooedinate $B(C_6F_5)_3$**





> First order process
= **Intramolecular process**

Mechanism



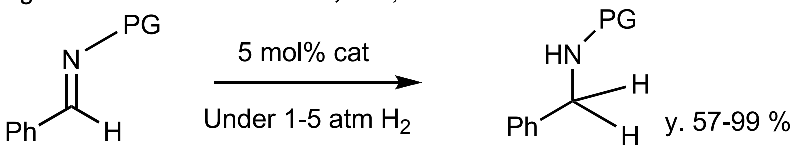
@ Studies for LA-LB combination
J. Am. Chem. Soc. **2007**, *129*, 1880

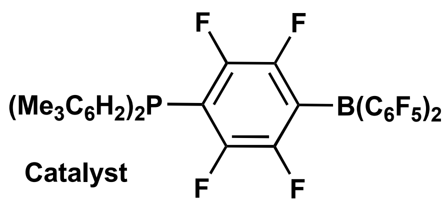
$P(Mes)_3$ + B**Ph_3**
P**$(C_6F_5)_3$** + $B(C_6F_5)_3$
P**tBu** + B**Mes_3** $\longrightarrow$ **N.R**

P**Ph_3** + $B(C_6F_5)_3$
P**Me_3** + $B(C_6F_5)_3$ $\longrightarrow$ **LA-LB adduct**

> FLP' s key = **Adequate combination of LA and LB for steric or electric properties**

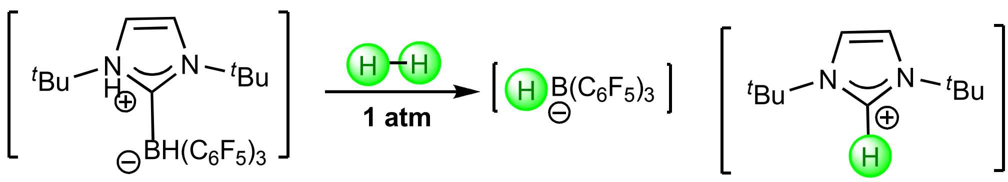
@ Application for metal-free hydrogenation
Angew. Chem. Int. Ed. **2007**, *119*, 8196





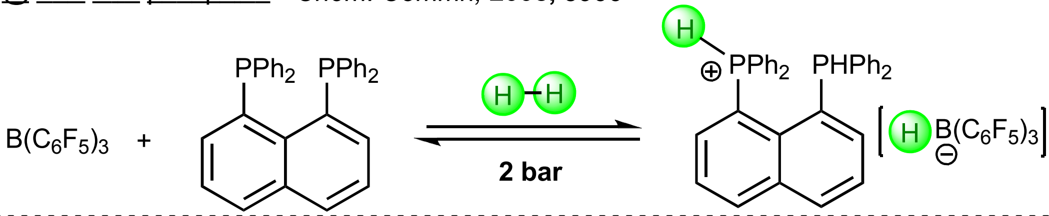
@ Related studies

<FLP with carbene> — *Angew. Chem. Int. Ed*, **2008**, *47*, 7433



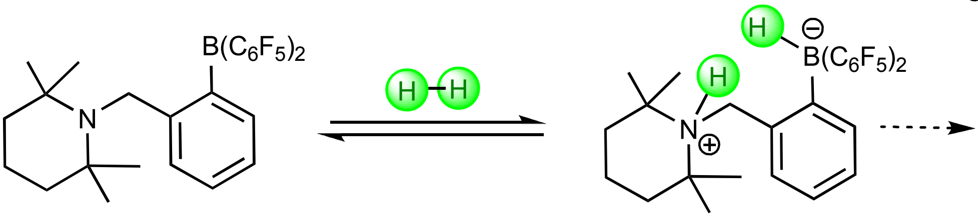
> Appropriate bulkiness
= **tBu** substituents

@ FLP with phosphine *Chem. Commn*, **2008**, 5966

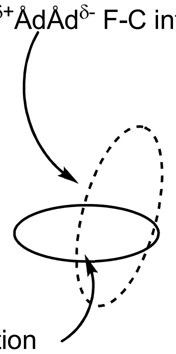


> Second reported system
> Uptake at 2 bar, 25 °C
> **Release at 60 °C**
> Utilized for hydrogenation of enolsilylether

@ FLP with amine *J. Am. Chem. Soc*, **2008**, *130*, 14117



C-H $^{\delta+}$ÅdÅd$^{\delta-}$ F-C interaction



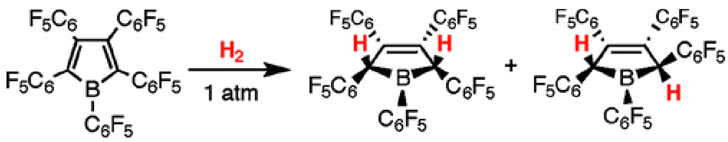
N-H$^{\delta+}$ÅdÅd$^{\delta-}$ H-B interaction

> Adequate **sterical property** → Unquenched generation of FLP
> **C-F•••H-C interaction** + **N-H•••H-B interaction** → Stability
> **H_2 splitting pocket**

<Advantages>
- **Low cost, safty, easy handling**
- **Reversibility at mild condition**
- Several combinations of LA/LB
- **Steric and electric tuning** = Diversity
→ We can appoach **through ligand** design??
- Combination of metals???

<Disdvantages>
- **Low energy density**
- Stability
- LA only **$B(C_6F_5)_3$ for acceptor???**

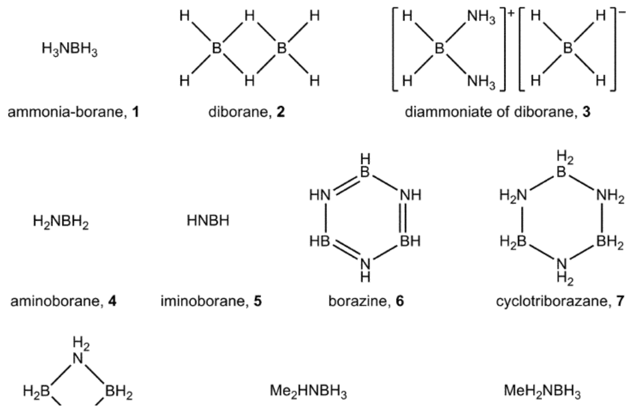
J. Am. Chem. Soc, ASAP



> **No Lewis base** was employed
> Driving force= **Strong Lewis acidity + antiaromaticity**
> **New entry**

3-2. N(Nitrogen)-B(Borane) Containing Material

Review : *Dalton. Trans*, **2007**, 2613
Angew. Chem. Int. Ed, **2007**, *46*, 8116



> **Hydridic B-H bond** and **protic N-H bond**

	H_3NBH_3	H_3CCH_3
$[XH_4][YH_4] \rightarrow H_3XYH_3 + H_2$	−70.3	64.96[a]
$H_3XYH_3 \rightarrow H_2XYH_2 + H_2$	−21.3	136.4
$H_2XYH_2 \rightarrow HXYH + H_2$	131.4	175.8
$HXYH \rightarrow XY + H_2$	562.1	609.9

[a] Value calculated from the heats of formation supplied in the *NIST Thermochemical Tables*[107] for the equation: $2CH_4 \rightarrow H_3CCH_3 + H_2$.

<Advantages>
- **Highest energy density** (19.6 wt%)
- Thermally **stable** at ambient temperature
- **Chemical conversion** to uptake/release H_2

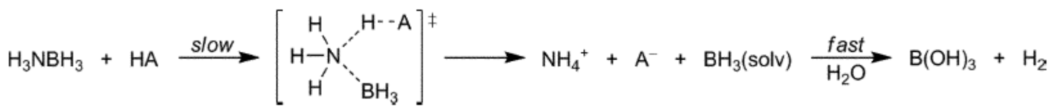
<Disdvantages>
- Actual density **in solvent** is significantly lowered
- **Irreversiblity** : Regeneration is rather difficult
> Dehydrogenetion
= **enthalpically and entropically favorable**
- **Volatile by-products** (borazine etc)

@ H_2 release

1. Solvolytic H_2 release

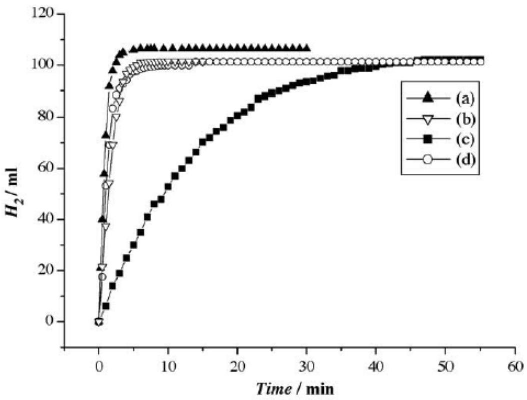
$$\boxed{NH_3BH_3 + H^+ + 3H_2O \rightarrow B(OH)_3 + NH_4^+ + 3H_2}$$

Catalyzed by Lewis/Bronsted acid (HCl, $B(C_6F_5)_3$)



> Toward practical use in vehicles = **solid and gaseous acid**

J. Power sources, **2006**, *159*, 855



(a) Dowex (sulfonic acid + functional groups)
(b) Amberlyst (sulfonic acid + functional groups)
(c) Control
(d) Nafion (sulfonic acid + functional groups)

>With solid acid the rate of H_2 release is **greatly enhanced**
> The reaction rate **depends on the type** of solid acids.

> Controlled flow system???
H_2 is generated **only when AB is in contact with the acids**

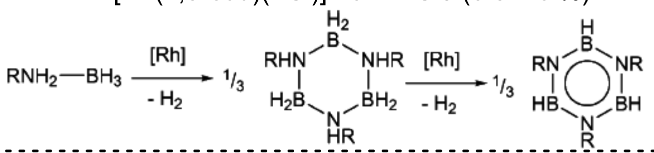
Drawbacks:
> **Solubility** is problematic : **19.6 wt % → <7 wt %**
> **Volatile NH_3** poisons fuel cells

2. Direct dehydrogenation by metal complexes

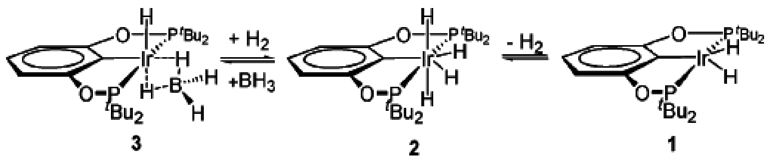
> First report by transition metal

Chem. commun, **2001**, 962
J. Am. Chem. Soc, **2003**, *125*, 9424

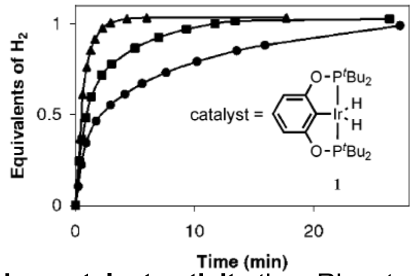
Rh = [Rh(1,5-cod)(í-Cl)]2 or RhCl3 (0.5 mol%)



> **Ir-pincer type ligand complex** with higher activity
J. Am. Chem. Soc, **2006**, *128*, 12048

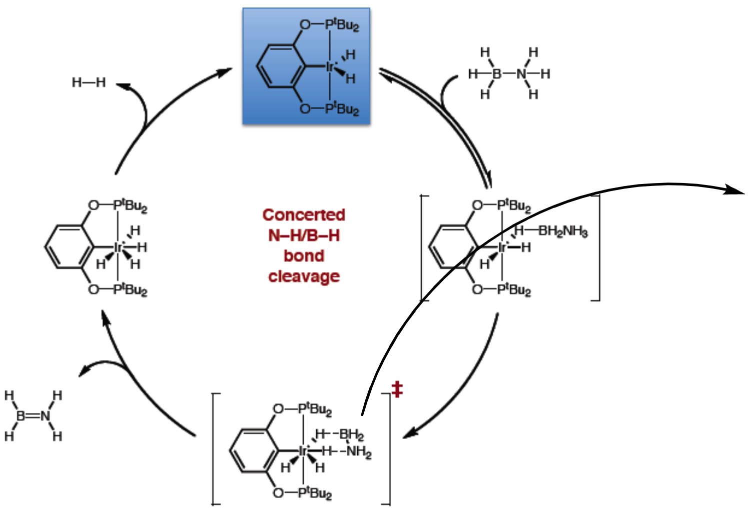


> Utilized for **alkane dehydrogenation**
J. Am. Chem. Soc, **2004**, *126*, 1804
Science, **2006**, *312*, 257

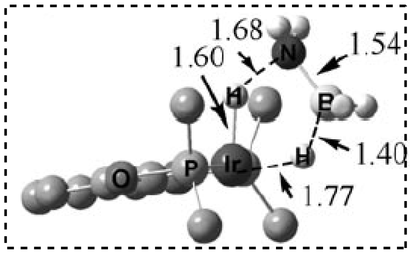


> **Higher catalyst activity** than Rh cat
0.5 mol %, 14 min vs 0.6 mol % 2-4 days

> Theoritical analysis
Angew. Chem. Int. Ed, **2007**, *46*, 8153



> **Concerted** H_2 transfer

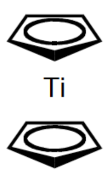


> **Stable 5-membered ring** TS

> Concerted mechanism is due to **dissimilar natures** of H
(**protone donor + hydride donor**)

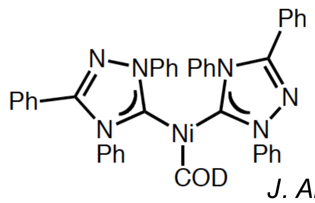
cf) ethane

> Other examples



> Initial **N-H cleavage**

Organometallics, **2007**, *26*, 3597



> NHC ligand
> Intial **B-H cleavage**

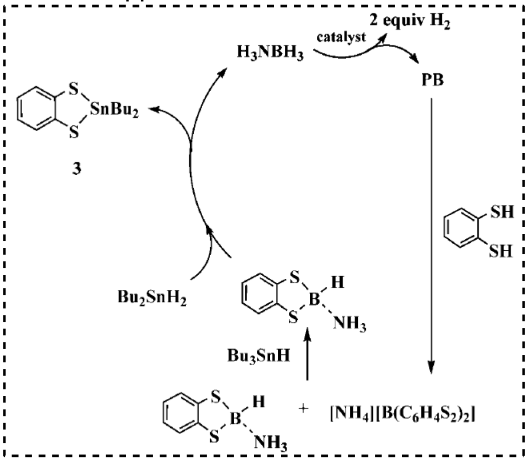
J. Am. Chem. Soc, **2007**,*129*, 1844

@ Regenaeration

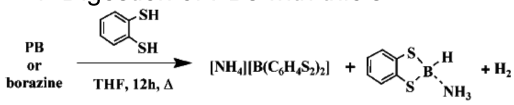
> **Enthalpically and entropically unfavorable**
> Stronger B-O bond or B-N bond
> Requiring **stronger reductant**

> Novel approach

Angew. Chem. Int. Ed, **2009**, *48*, 6812



<1. Digestion of PBs with thiols>

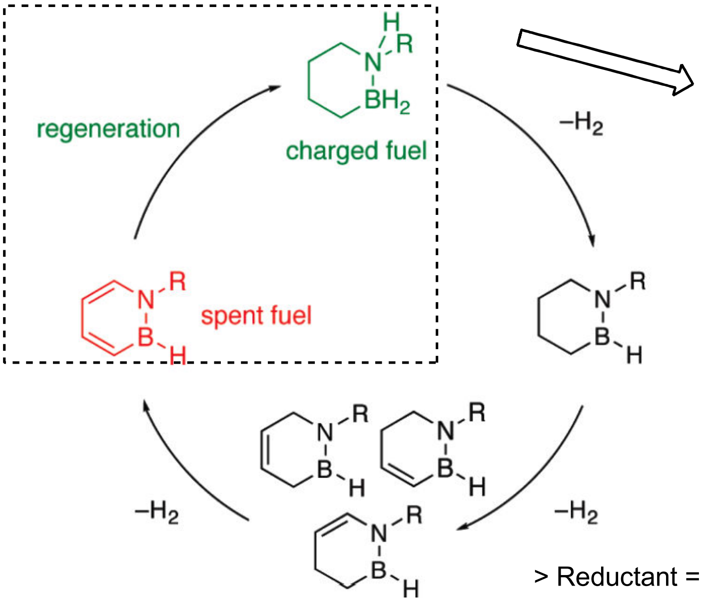


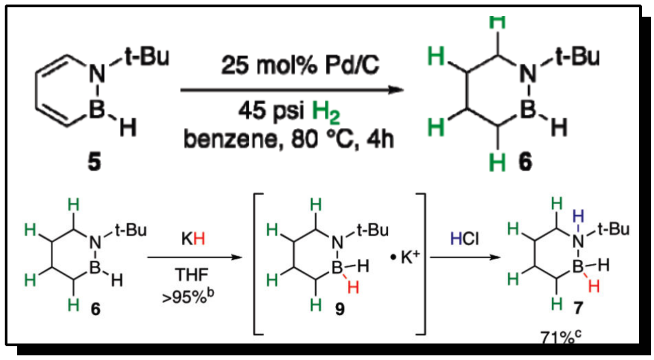
<2. Reduction with tins>

> **Thiols** as first reducing reagent = **weaker B-S bond**
> **Sn** reagent as second reductant
> Other hydride sources failed
> **All reagents and byproducts are recycled**

> Fascinating example of C-B-N heterocycle compound

J. Am. Chem. Soc, **2010**, *132*, 3289





> Reductant = H_2 itself

f¢G ~ 0 kcal/ mol

Exothermic dehydration of B-N
+
Endothermic dehydration of C-C
⇩
Reversible H_2 uptake/release

4. Future Prospects

> So far comprehensively most reliable way = **Liquid N_2 and CGH2**
: We are unlikely to make a contribution...

> What is the goal? : Practical H_2 storage in vehicles or new reaction/ligand design ?
Organic approach involves many methodologies/materials.
But **large gaps between practical use and experimental success**
cf) Industrial supply of complex molecules
> **Low cost**: Not precious metals (Pt, Ru, Rh)
Reversibility : Chemical conversion at mild condition

→ **New catalyst system**

> Our strong point =

We can synthesize compounds freely as we expect