Awareness-cum-Capacity Building Programme on
Hydrogen Production and Energy Uses (ACBHPE-2022)
June 8 – June 10, 2022

Hydrogen Production from Liquid Hydrogen Carriers

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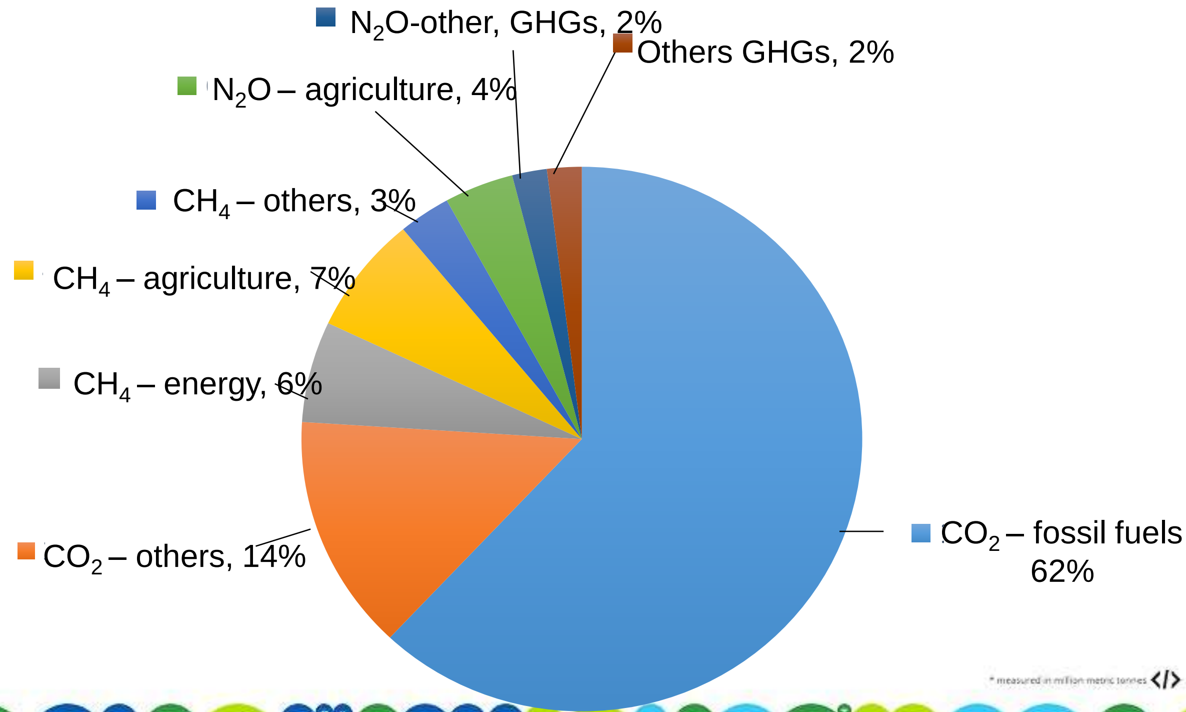
United Nations Framework Convention on Climate Change (UNFCCC)

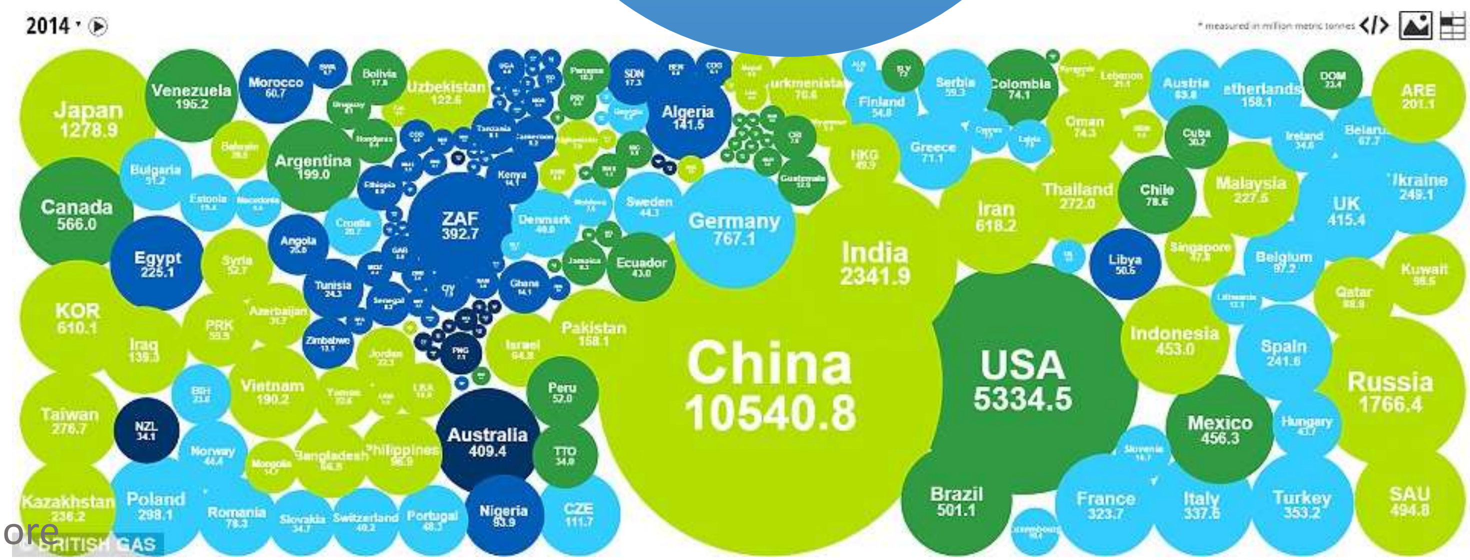
India's commitment towards Net Zero Emissions

"Prime Minister Narendra Modi announced that India will aim to attain net zero emissions by 2070. He also announced that India will draw 50% of its consumed energy from renewable sources by 2030, and cut its carbon emissions by a billion tonnes by the same year."

- to reduce emissions intensity economy-wide by 33 to 35 per cent below 2005 levels,
- to generate 40 per cent of electricity from renewable energy sources, and
- to create a carbon sink capable of absorbing 2.5 to 3 billion metric tons of carbon dioxide (through additional forest and tree cover).

Global Scenario of CO_2 emission





CO_2 emission and Global warming

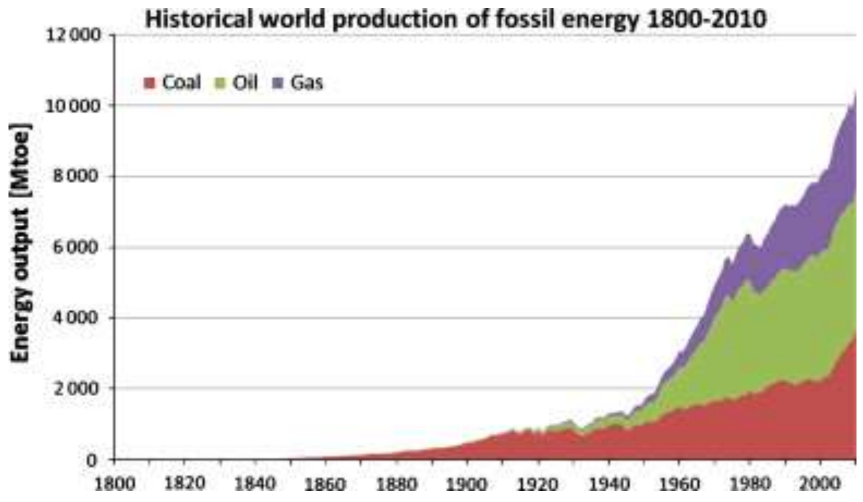
Transport sector contributed 138 TMT of CO_2 in 2007-08
contribution could rise to 346 TMT by 2022 in a business-as-usual case, an increase of about 150%

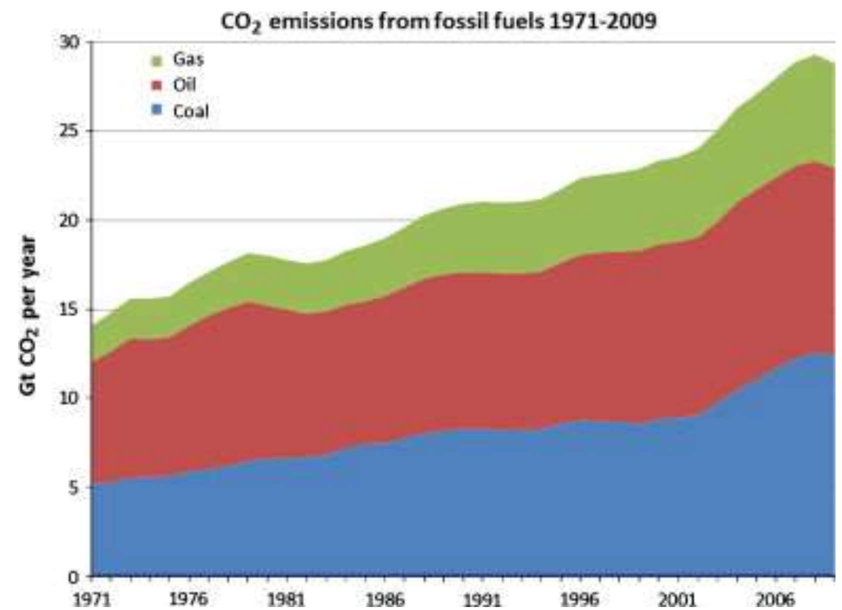
10% ethanol (E10) and 3 % methanol (M3) blends by 2025, and by 2030 industry could make specific vehicles compatible with 20% ethanol (E20) blended gasoline

3.045 million NGVs (India stands 3rd)

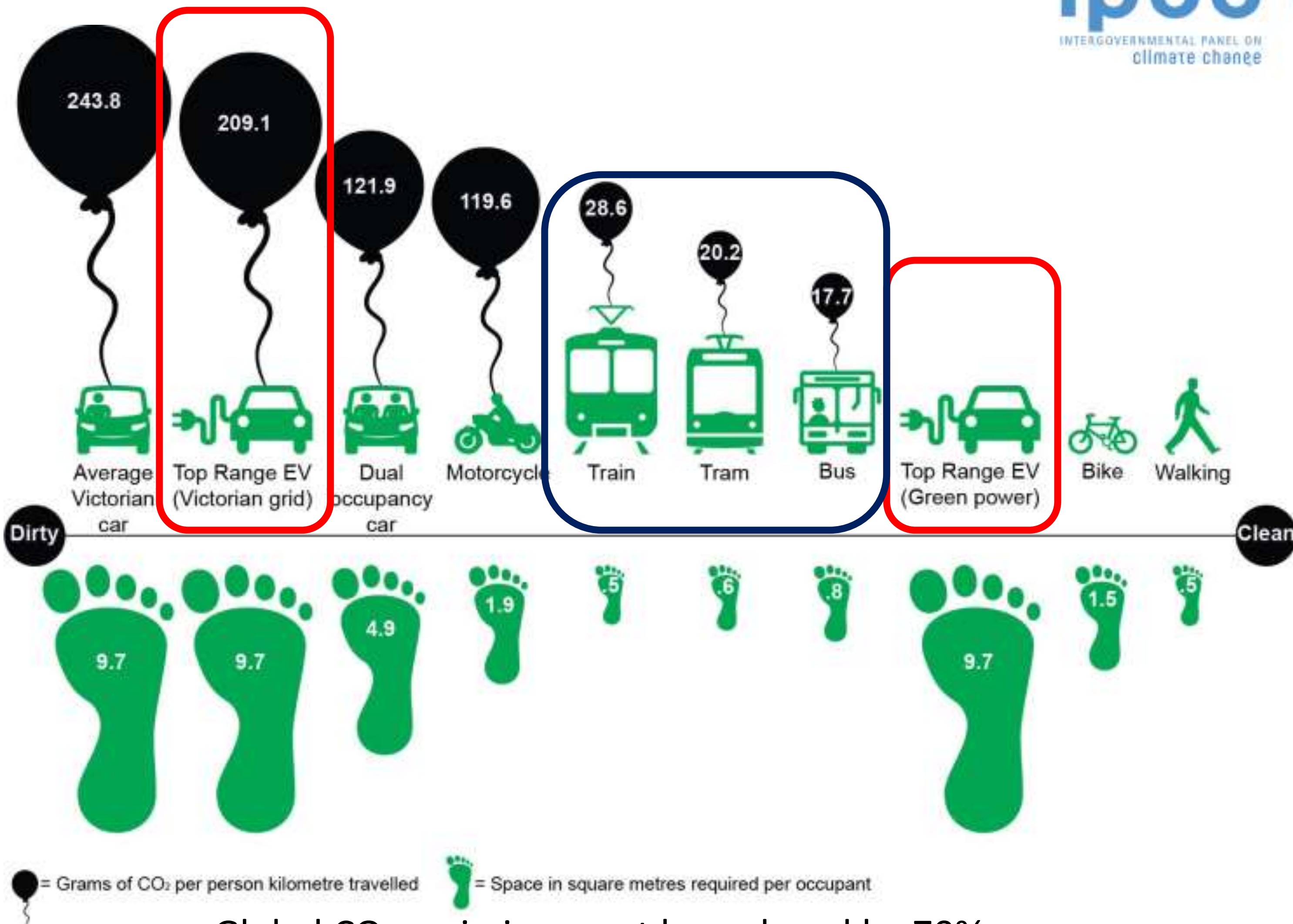
10,000 CNG stations will be required by 2030 for 20 million CNG vehicles

Alternative fuels:
Biofuel (its production in energy consuming)
Electricity for EVs (in India most of the power plants are heavily dependent on coal)





Carbon Footprint



Global CO_2 emission must be reduced by 70% to bring the temperature below 2 °C climate goal

https://blogvivinstrada.wordpress.com/2018/09/17/which-automobile/

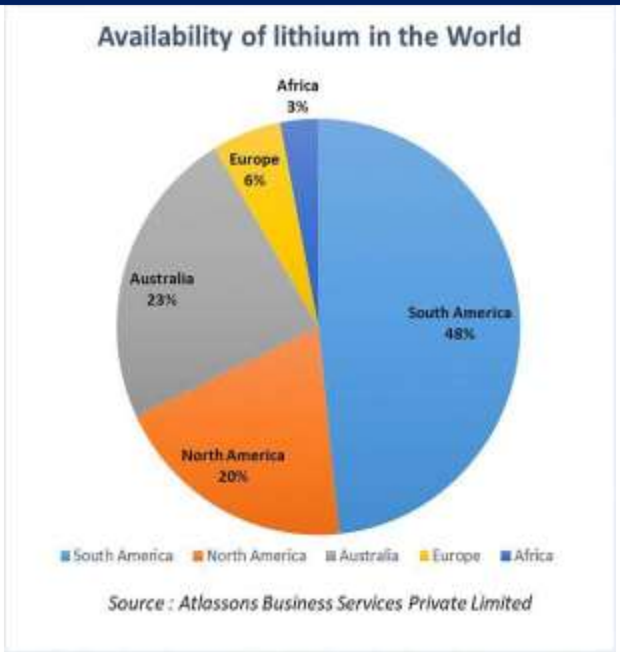
India’s potential in sustainable energy

The cost of electricity generated from wind and solar has been reduced significantly, respectively by 50% and 80%

Electric vehicles - for sustainable energy

https://www.hydrogenfuelnews.com/

Lithium-ion battery



Due to **lack of Lithium reserves in India**, dependency on other countries for Lithium source will greatly influence the India's efforts towards EV based vehicles

Nickel mines

Lithium mines

The mining of Lithium and other components from open mines affects a huge amount of natural resources, deforestation, and **causes a lot of carbon emissions**.

Hydrogen (H_2)

"Hydrogen is well balanced with efficient energy content for CO_2 free transportation to cater global energy demand, reduce oil dependency, greenhouse gas emissions and air pollution."

Nature, **2010**, *464*, 1262-1264

Hydrogen: Fuel of the future

Energy content of H_2 (130 MJ/kg) >> Energy content of fossil fuels (~46 MJ/kg)
33.6 kWh/kg (H_2) >> 12-14 kWh/kg (diesel)

Water is the only byproduct during utilization of H_2 as fuel

Hydrogen and Fuel Cell technologies could achieve a 33-35 % reduction in greenhouse gases by 2030 of its 2005 level apart from co-benefits in terms of lower levels of air pollution, affordability, sustainable transportation.

Agriculture sector is the largest user of hydrogen (as nitrogenous fertilizer), with 49% of hydrogen being used for ammonia production.

However, volumetric energy density is rather low and therefore storage of hydrogen is a challenge, as compared to the storage of liquid fossil fuels

11000 L tank will be required to run a Hydrogen fueled vehicle for 100 km

Hydrogen-based Society

Hydrogen Production

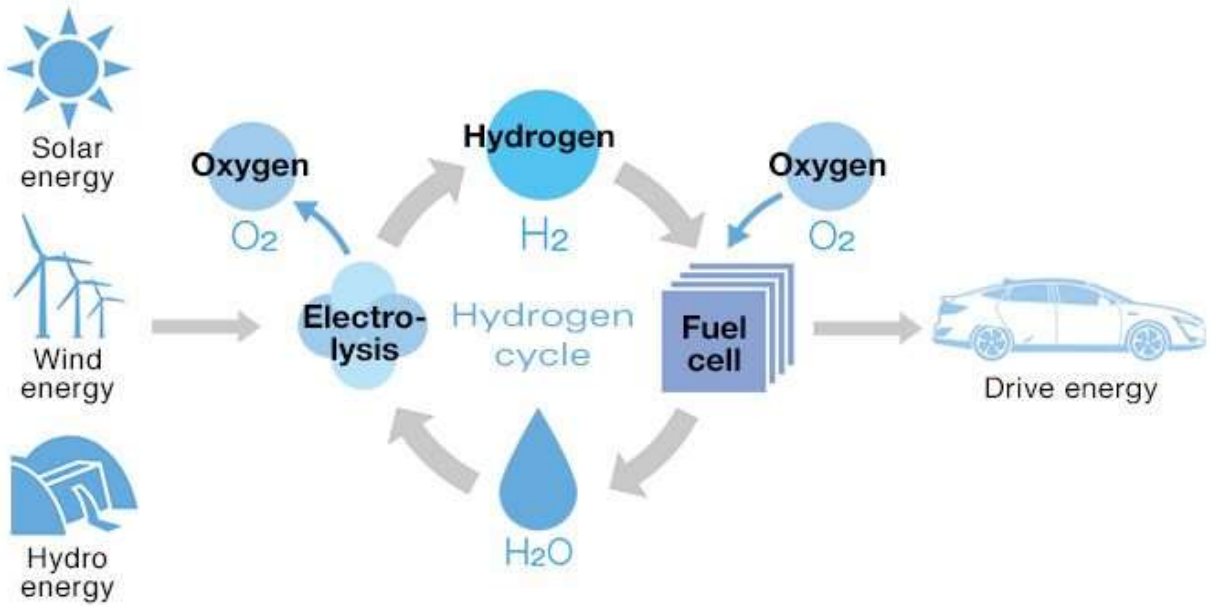
- Biological route
- Electrolysis of water
- Chemical production
- Steam reforming
- Coal gasification
- Thermo chemical

Hydrogen Storage

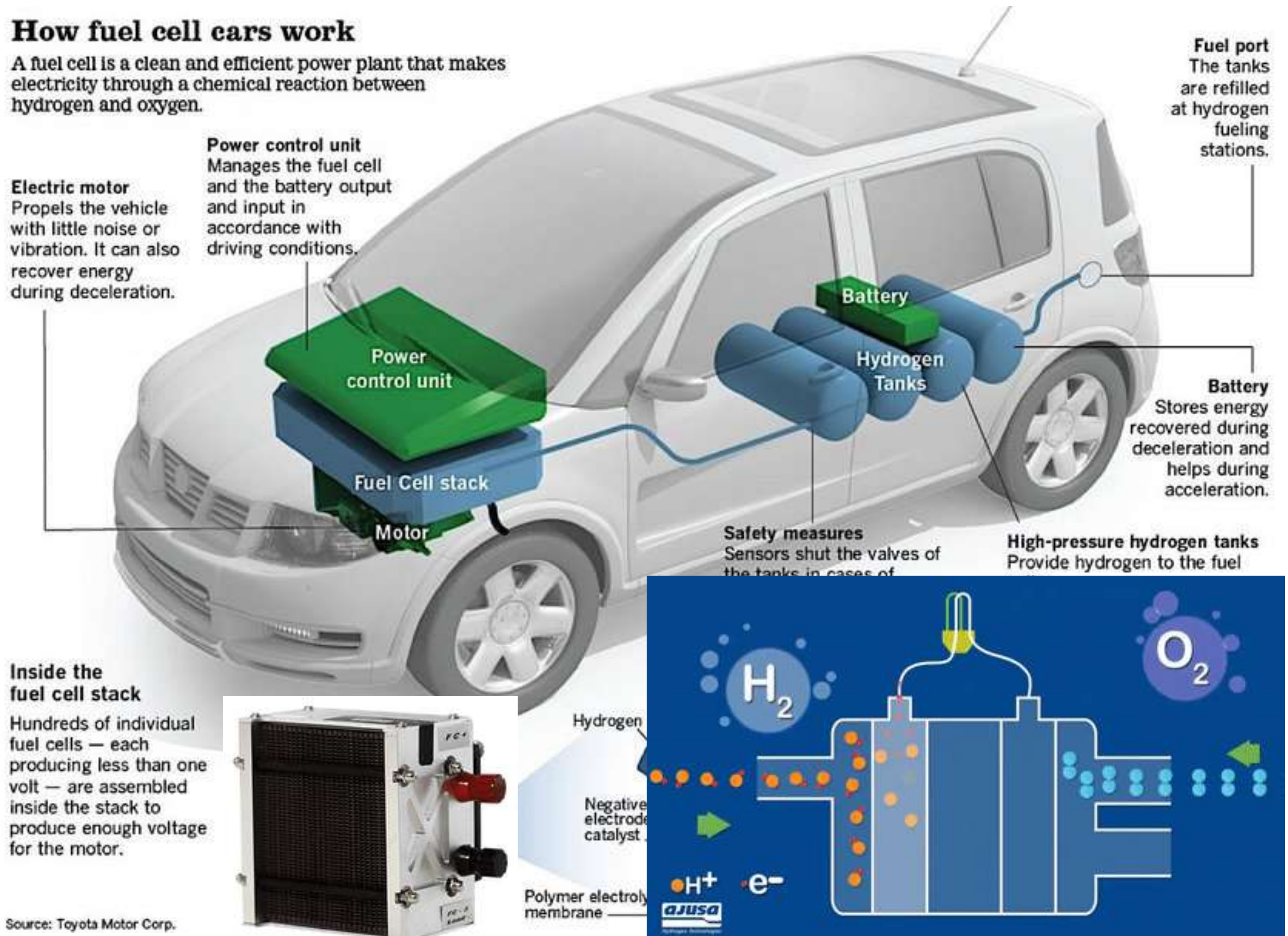
- Conventional technology
- Solid state material
- LOHC

Hydrogen Utilization

- Fuel Cell
- Automobile
- Electricity generation



Fuel Cell Electric Vehicle (Source: Toyota)



https://gfycat.com/discover/fuel-cell-industry-gifs

Advantages and Limitations with Hydrogen Fueled vehicles

Hydrogen vehicles are operating at US, JAPAN, Europe, China, South Korea.

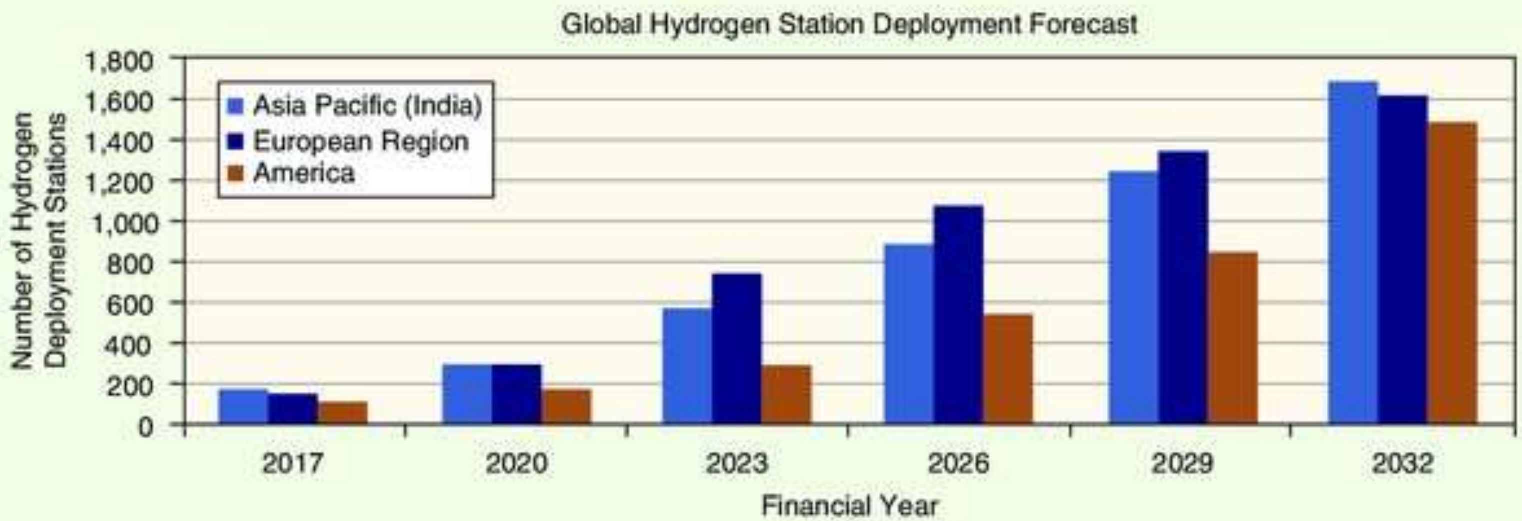
Advantages of hydrogen fueled vehicles:

- Toyota, Honda and Hyundai manufactured Hydrogen cars' mileage equivalent to 28 km/L of petrol
- Hydrogen fueled buses 300-450 km than EV buses (~250 km)
- H_2 fuel filling time is equivalent to petrol (EVs charging time 4-6 hours)

Limitations:

- A very few hydrogen-fueled vehicles are available worldwide and are costly (twice than EVs)
- Poor infrastructure: high cost of Hydrogen fuel stations (Twice than petrol/diesel fuel stations)

Global footprint of Hydrogen Fuel stations



DOI: 10.1109/MELE.2017.2784633

Global preparedness for Hydrogen-based Society

Image source: internet

Global initiatives for using Hydrogen as fuel...



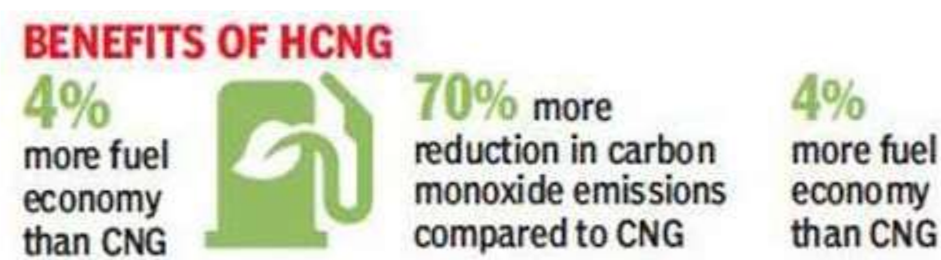
Indian initiatives towards Hydrogen based society

Council of Scientific and Industrial Research and **KPIT indigenously developed fuel cell**.

Trains to be run on Hydrogen Fuel Cell-Based hybrid system

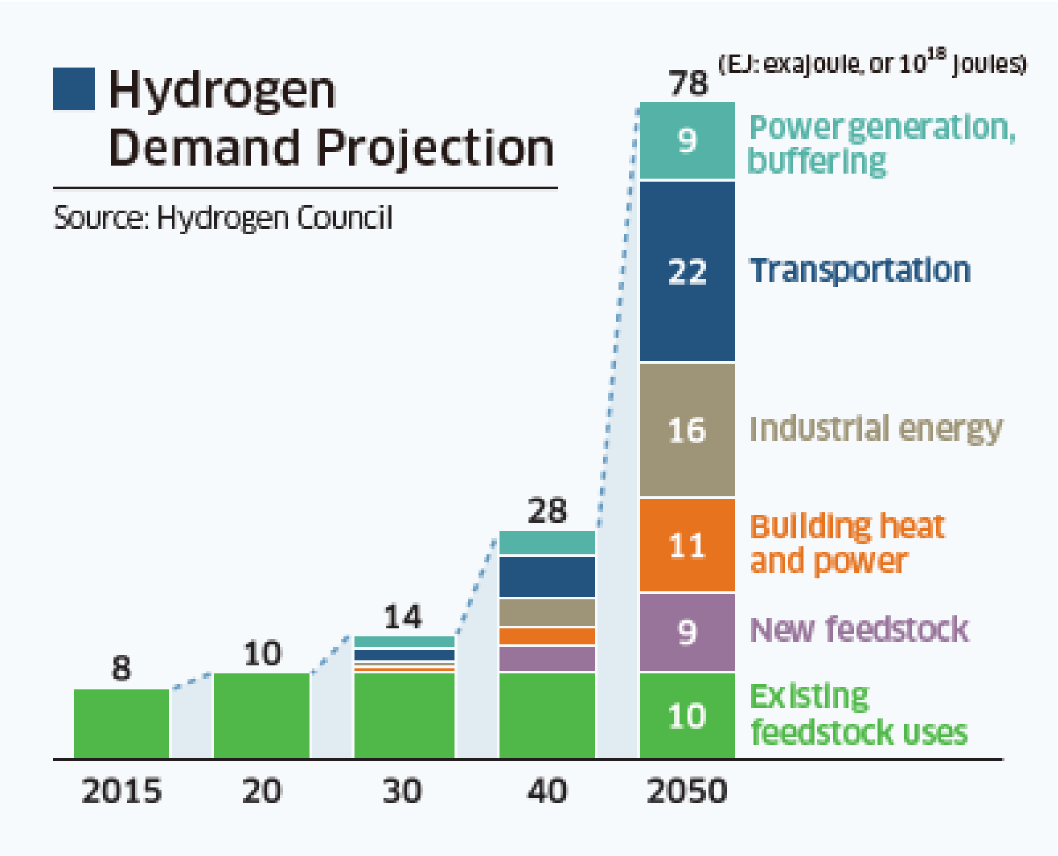
Hydrogen blended CNG (HCNG)

HCNG (18-23% Hydrogen blended CNG) can reduce CO emission by 70% and green house gas emission by 15-20%, with minor modifications in existing CNG vehicles



https://www.insightsonindia.com/2020/09/29/hydrogen-enriched-compressed-natural-gas-hcng/

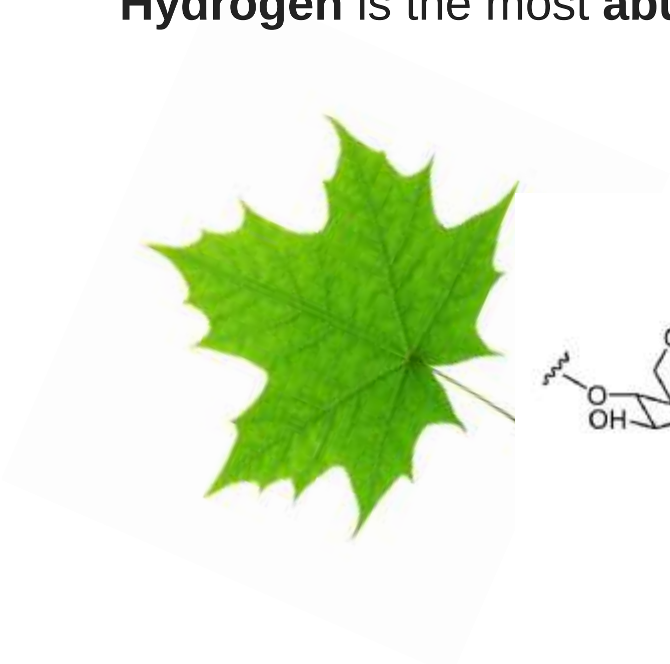
Global Hydrogen Demand

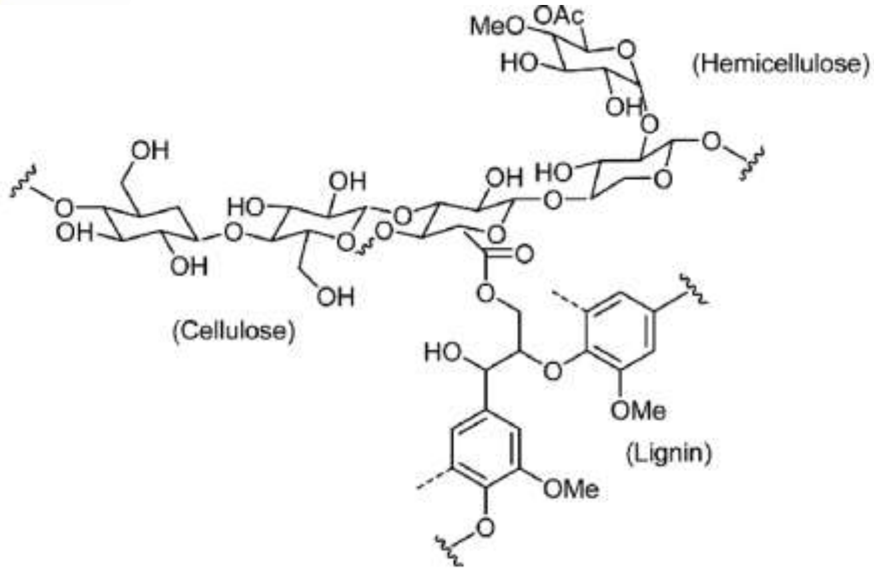


https://global.kawasaki.com/en/stories/articles/vol67/

“Hydrogen is everywhere but nowhere”

Hydrogen is the most **abundant** chemical substance in the universe.





There is only a small amount of **hydrogen gas** is present in the **Earth’s** atmosphere, and it makes up less than **one part per million (< 1ppm).**

Ways for Hydrogen production

Ammonia Cracking

$2NH_3 \rightarrow N_2 + 3H_2$

Thermo-catalytic Cracking of Methane

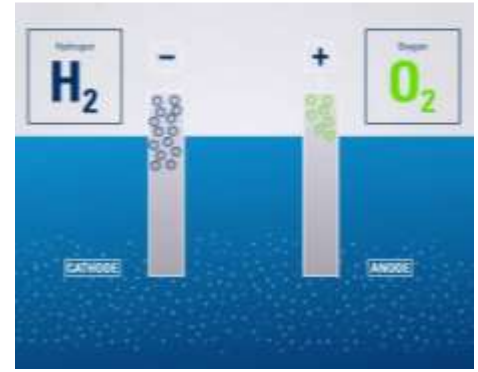
$CH_4 \rightarrow C + 2H_2$ $\Delta H° = 74.85$ kJ/mol

Methanol reforming (200- 350°C)

$CH_3OH \leftrightarrow CO + 2H_2$, $\Delta H = 90.1$ kJ/mol

Water gas shift reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -41.2$ kJ/mol



(electrolysis of water)

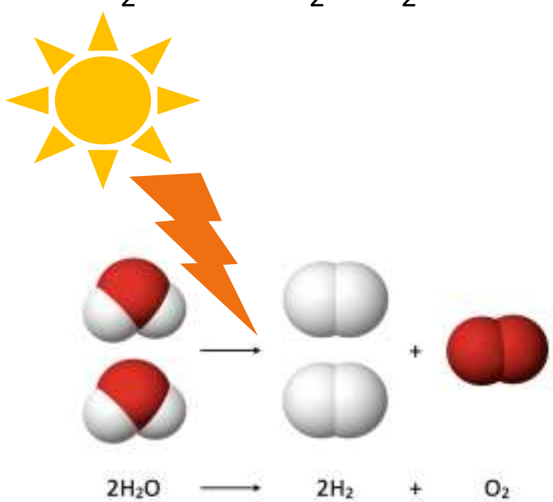
a highly energy intensive (4.5-6.5 kWh/Nm^3) process

high capital investment,

less preferred for commercial purposes

Challenges:

corrosion and poisoning of the electrolysers by inadvertent incursion of CO_2



(water splitting)

Over 95% of hydrogen produced globally is from hydrocarbons and only about 4% is produced through electrolysis of water.

Type of Hydrogen

Low Carbon

Zero Carbon

Blue Hydrogen

Produced from CH_4, CO_2 is captured and stored

Green Hydrogen

Produced from renewable sources, No CO_2 emission

Brown Hydrogen

Produced from Coal, CO_2 released in atmosphere

Grey Hydrogen

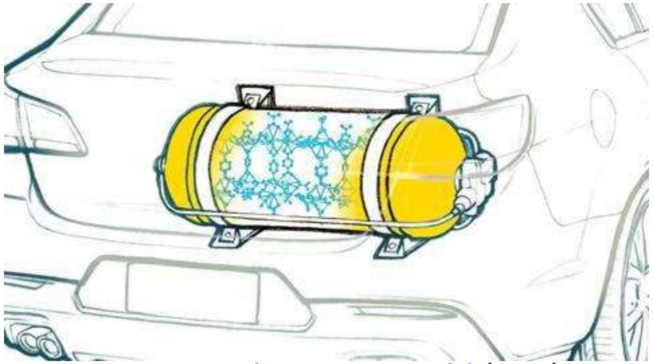
Produced from CH_4, CO_2 released in atmosphere

High Carbon

Challenges with Hydrogen

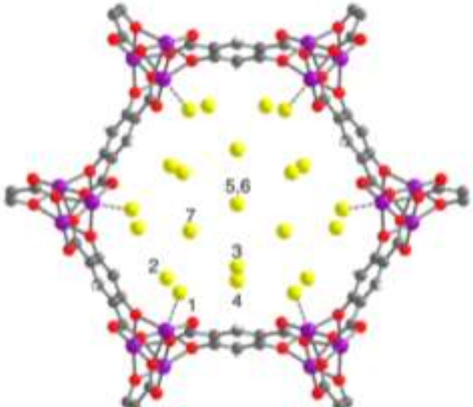
Cost effective and sufficient hydrogen production to meet global demand

Safe and efficient storage of hydrogen for on-board application (700 bar)



source: chemistryworld (RSC)

"Gaseous hydrogen can be highly explosive, and is difficult to store due to its low energy density, therefore the transportation of H_2 from one place to another is not easy"



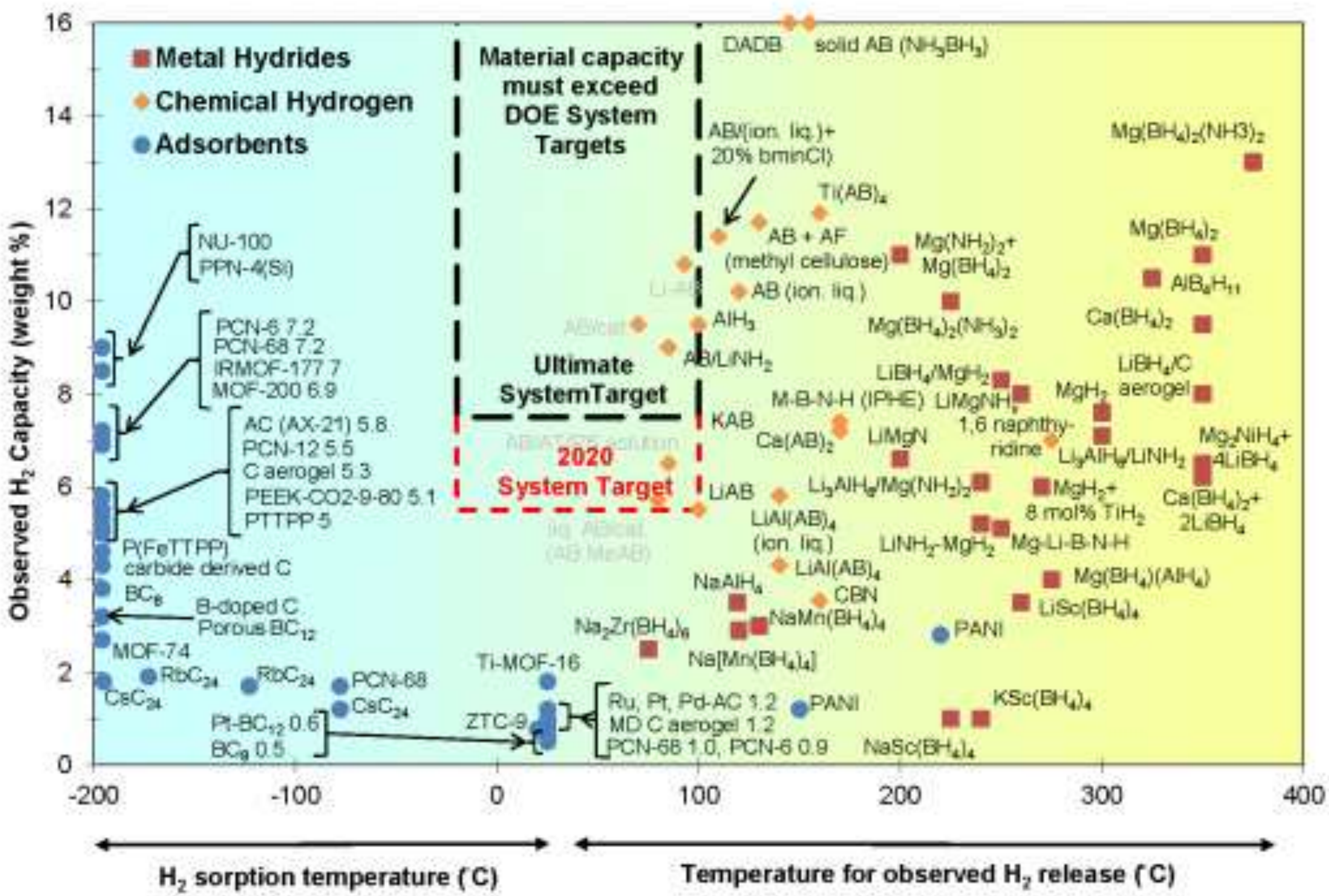
Chem. Mater. 2018, 30, 22, 8179–8189

Storing H_2 gas in large pores of Metal Organic Framework (MOF) at room temperature and 100 bar.

Establishing that Hydrogen is equally or even much safer than petrol

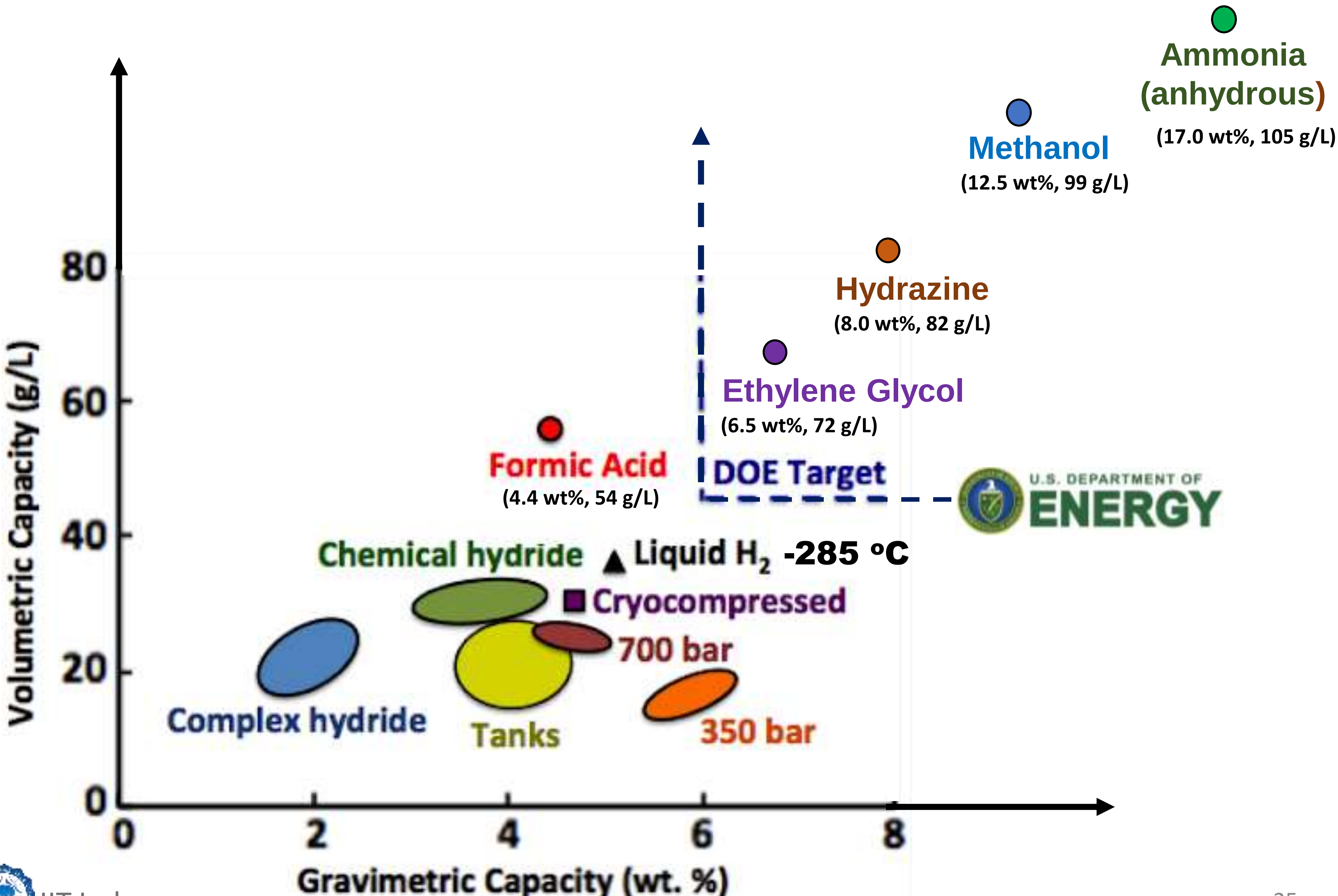
source: www.history.com

Hydrogen Storage Materials



https://www.energy.gov

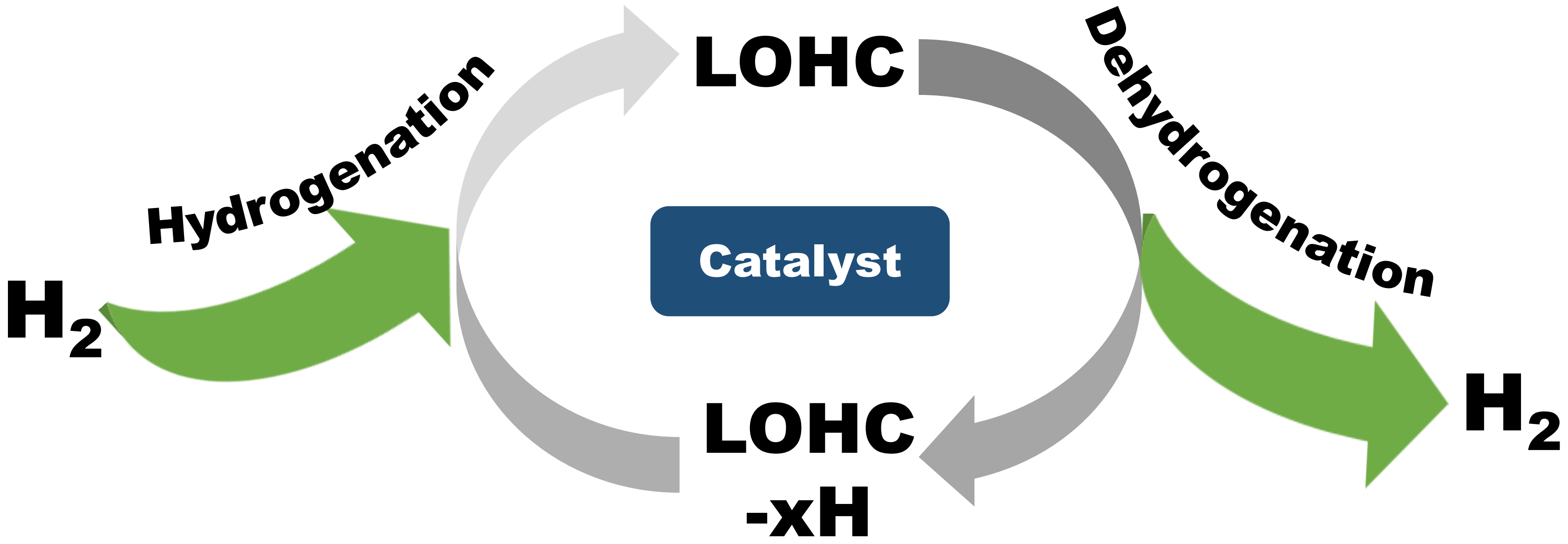
Liquid Hydrogen Storage Materials



http://large.stanford.edu/courses/2013/ph240/yoo1/

Liquid Hydrogen carriers / Liquid organic hydrogen carriers (LOHC)

These are organic compounds that can absorb and release hydrogen through chemical reactions, usually with the intervention of a catalyst.



Advantages:

- ❑ Being liquid, storage, transportation and dispensing using current infrastructure (of petroleum) is possible.
- ❑ On-demand Hydrogen production

Liquid Hydrogen carriers / Liquid organic hydrogen carriers (LOHC) For on-board and stationary hydrogen production application

N_2H_4 (Hydrazine)

CH_3OH (Methanol)

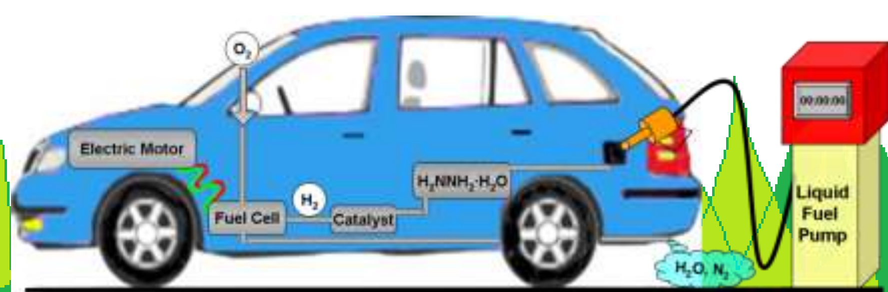
CH_2O (Formaldehyde)

$(CH_2OH)_2CHOH$ (Glycerol)

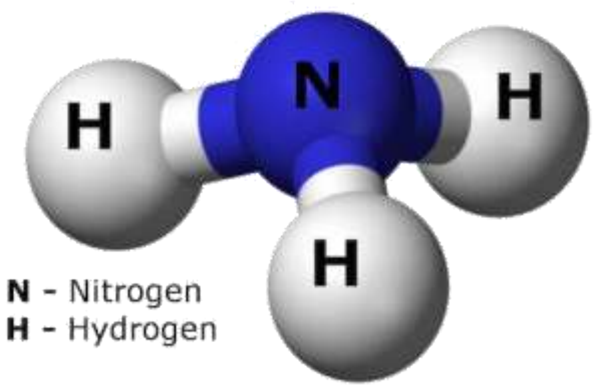
HCOOH (Formic acid)

C_2H_5OH (Ethanol)

CH_2OHCH_2OH (Ethylene glycol)



Ammonia – A promising zero-carbon liquid hydrogen storage carrier



$NH_3(g) \rightarrow 1/2\ N_2(g) + 3/2\ H_2(g)\ \Delta H = +46\ kJ/mol$

Highest gravimetric and volumetric hydrogen storage capacity of 17 wt% and 105 g/L

Release hydrogen at a very high temperature 600 – 1000 °C

Adverse physical and chemical properties: high coefficient of thermal expansion, high vapor pressure at ambient conditions, propensity for reacting with water, reactivity with container materials and high toxicity of the vapor if released into the air.

Proton electrolyte membrane (PEM) cannot tolerate ammonia: Since PEM fuel cells require ammonia concentrations below 0.1 ppm, significant purification will be necessary. Even at 900 °C, 1500 ppm unconverted NH_3 at 10 bar as far as current processes are involved.

US Department of Energy

Hydrazine – Toxic for humans, but satellites love it

N_2H_4 (Hydrazine)
Rocket Fuel

Hydrazine is a very attractive

Zero-carbon hydrogen source.

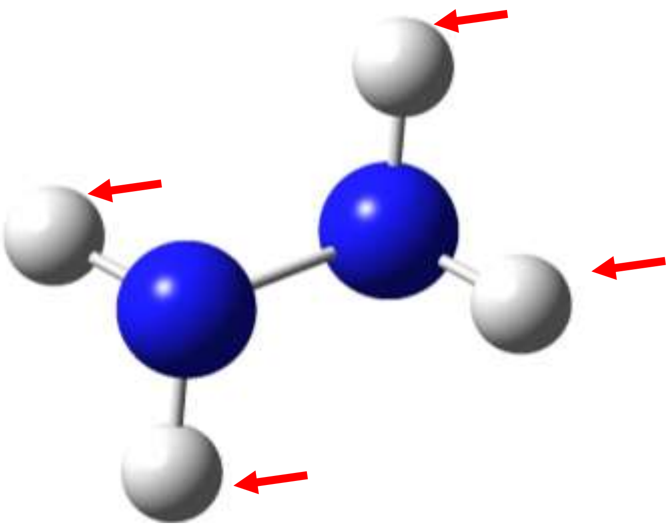
it is extremely toxic, caustic, and carcinogenic

spontaneously explode

neurotoxin

Why Hydrazine...?

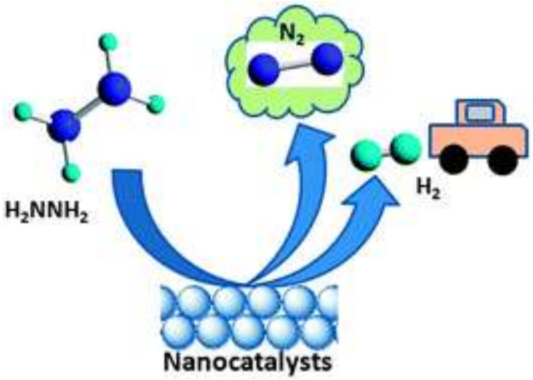
- High Hydrogen content for release (8.0 wt%) (Hydrazine monohydrate, $N_2H_4 \cdot H_2O$)



- Only N_2 as by-product (needs no recycling)

- Liquid, can be easily recharged using current available recharging facilities.

$H_2NNH_2 \cdot H_2O$
M.W. 50.06
density 1.032 g/ml at 25 ºC
b.p. 120 ºC
m.p. -51 ºC



Complete decomposition:

$$H_2NNH_2 \rightarrow 2H_2 + N_2 \ \Delta H = -95.4 \text{ kJ/mol}$$

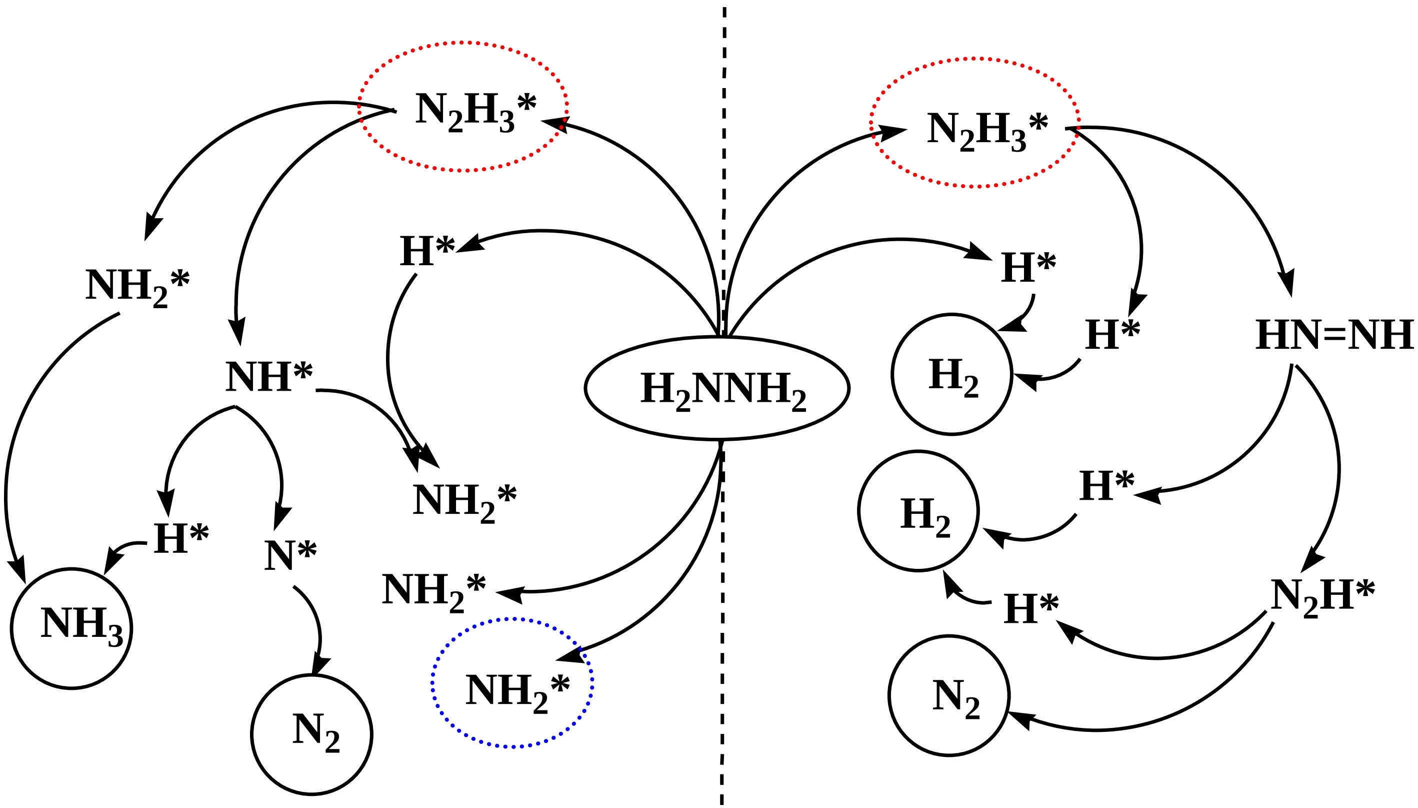
√

Incomplete decomposition:

$$3H_2NNH_2 \rightarrow N_2 + 4NH_3 \ \Delta H = -157 \text{ kJ/mol}$$

X

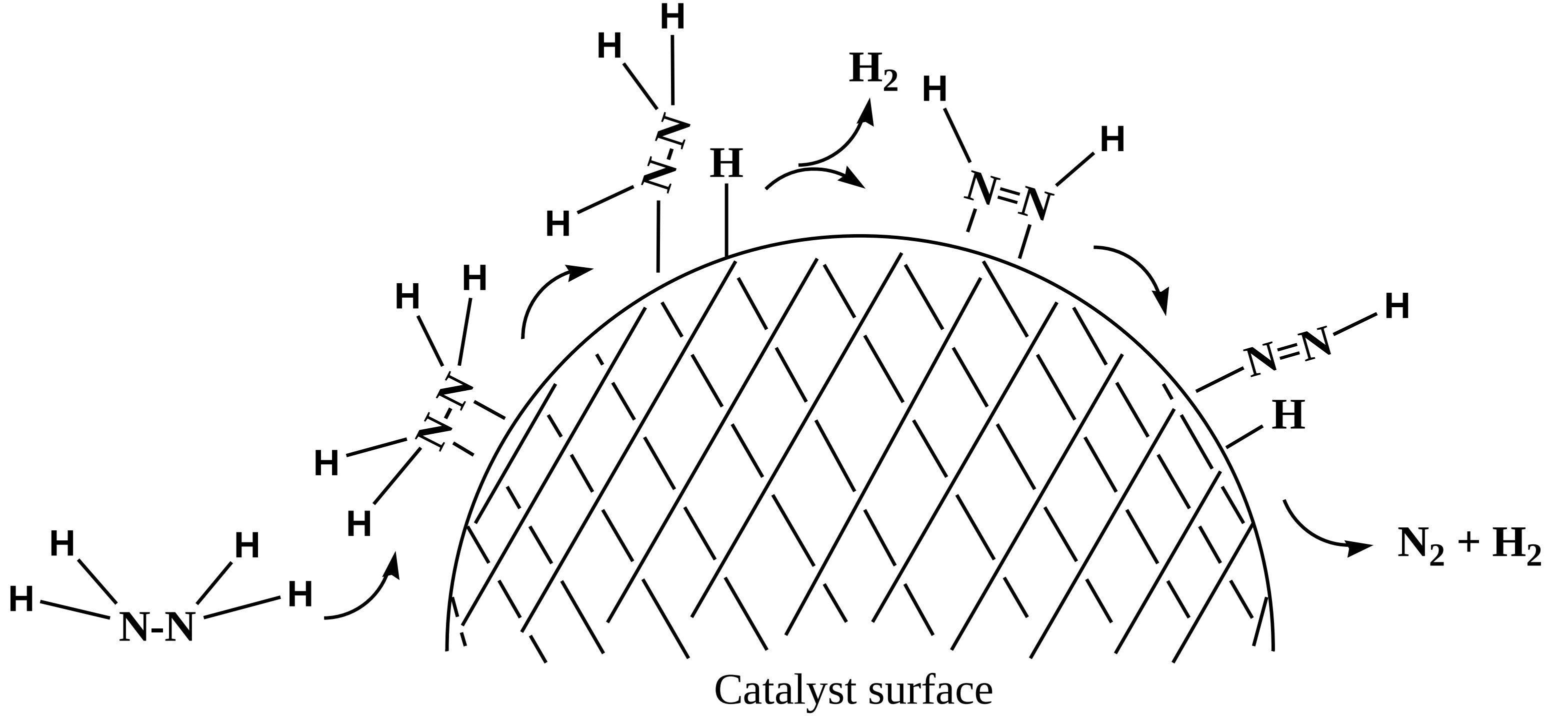
Reaction pathways for hydrazine decomposition



$H_2NNH_2 \longrightarrow 1/_3N_2 + 4/_3NH_3$

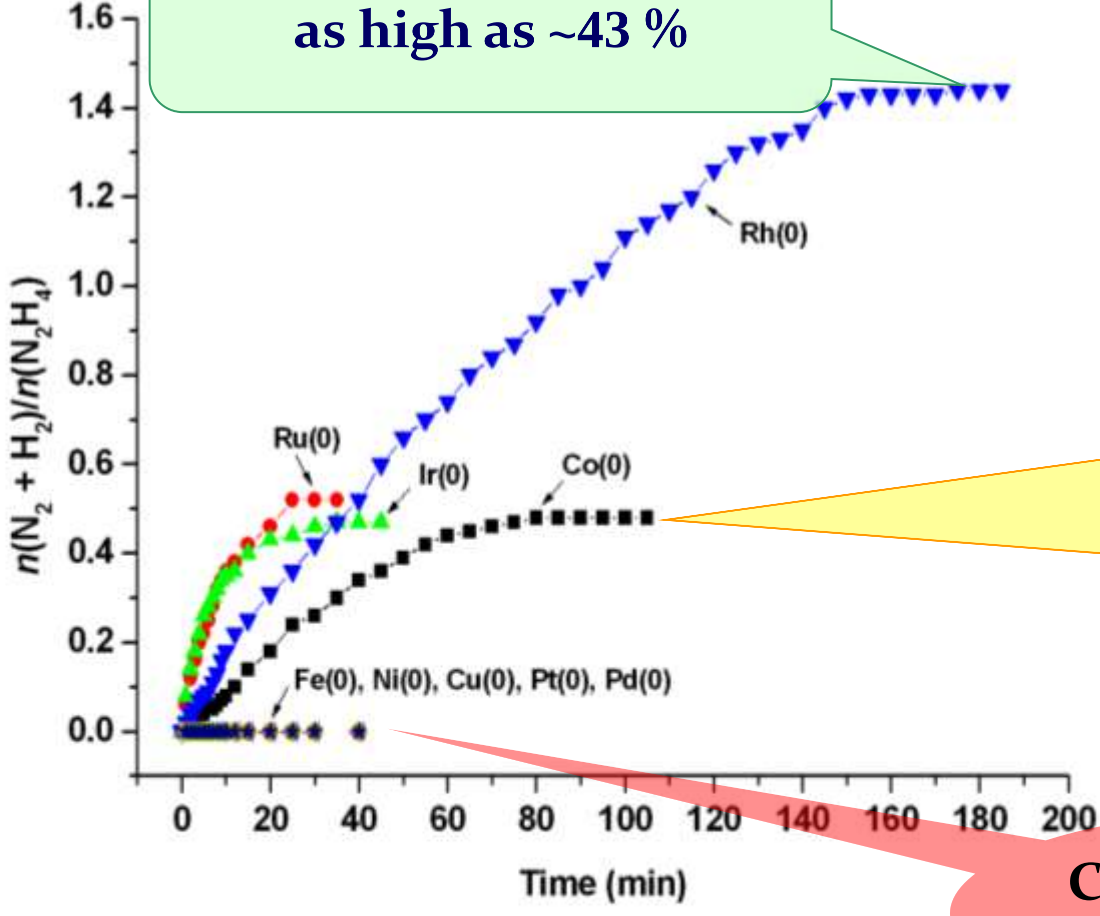
$H_2NNH_2 \longrightarrow N_2 + 2H_2$

Mechanism for hydrazine to H_2 production over catalyst surface



Based on: (a) Santos, J. B. O.; Valença, G. P.; Rodrigues, J. A. J. *J. Catal*. 2002, *210*, 1-6.
(b) de Medeiros, J. E.; Valença, G. P. *Braz. J. Chem. Eng*. 1998, *15*, 126-131.

Screening monometallic nanoparticle catalysts



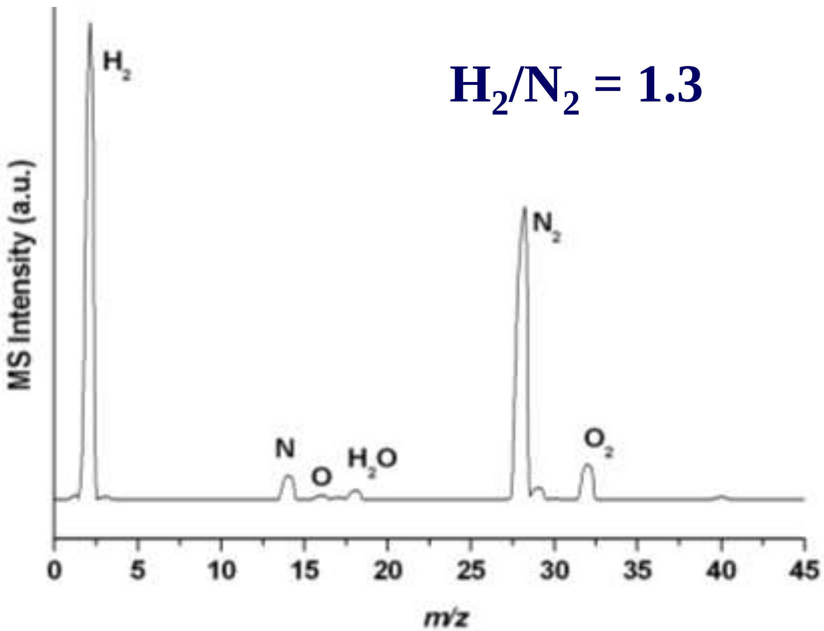
With Rh, H_2 selectivity as high as ~43 %

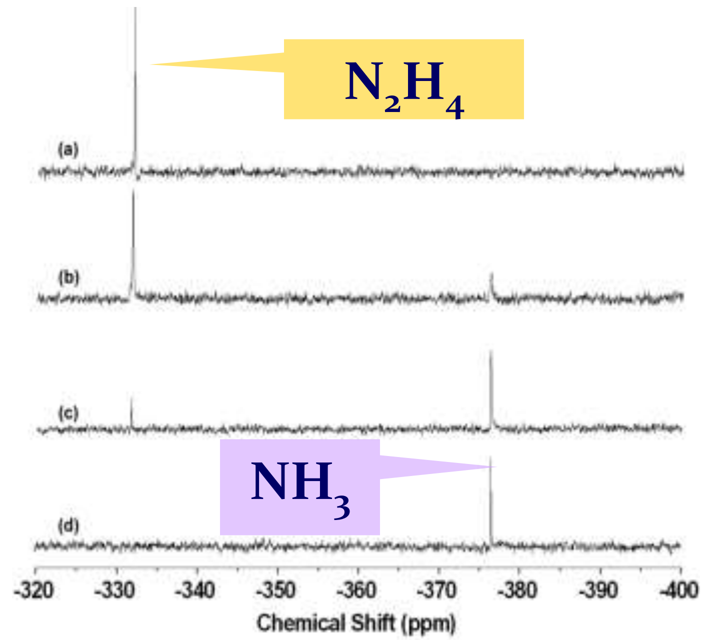
With Co, Ru and Ir, H_2 selectivity as low as ~7 %

Cu, Ni, Fe, Pt and Pd are inactive

Singh et al., J. Am. Chem. Soc., 2009, 131, 9894

Mass and ^{15}N NMR spectral analysis of the reaction products



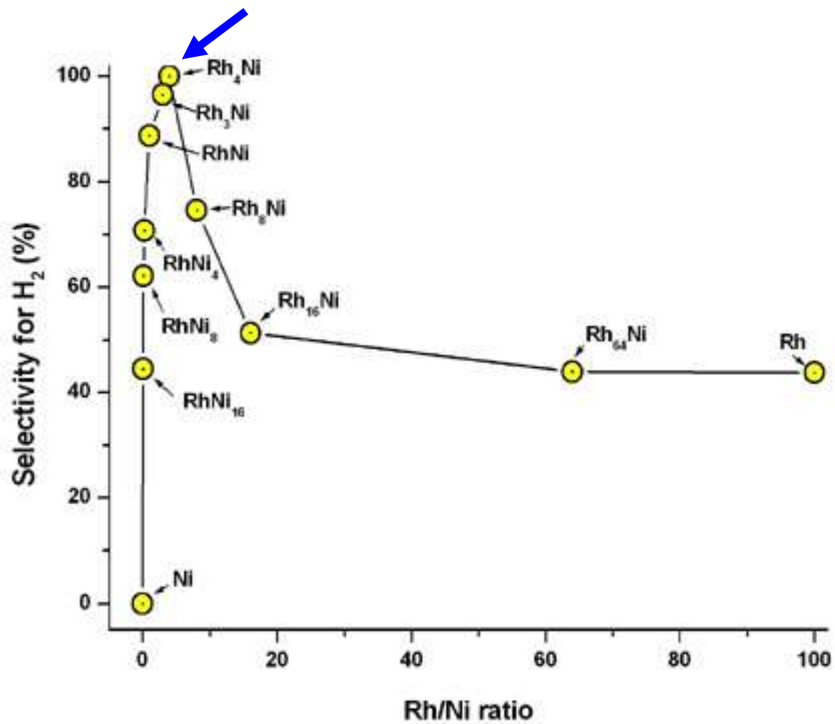


With Rh catalysts, the overall reaction for the decomposition of hydrous hydrazine is

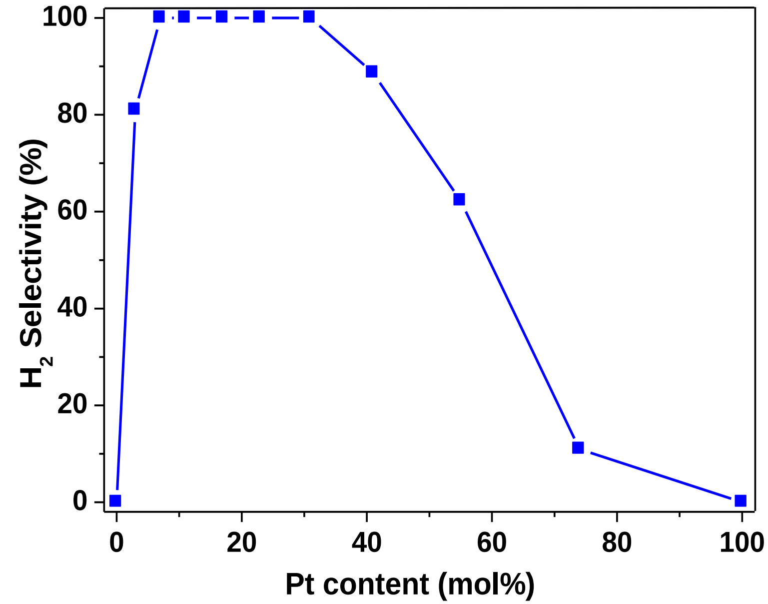
$$H_2NNH_2 \rightarrow 0.63N_2 + 0.88H_2 + 0.75NH_3$$

Screening of Alloy Catalysts

Hydrogen production from hydrous hydrazine

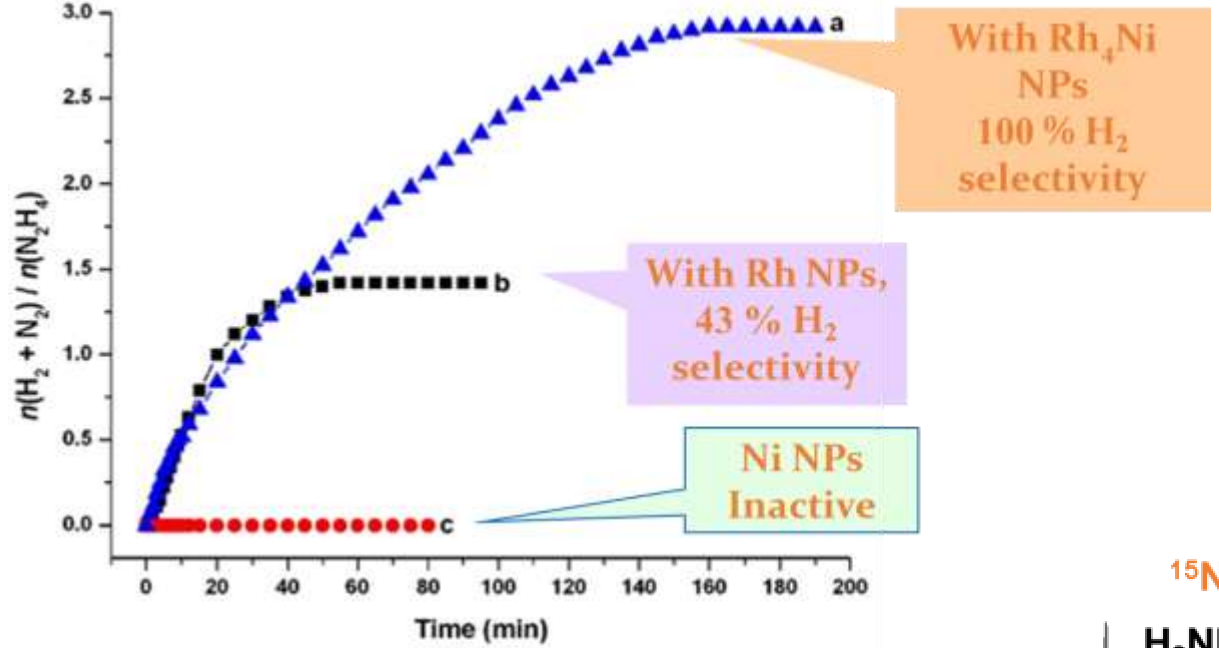


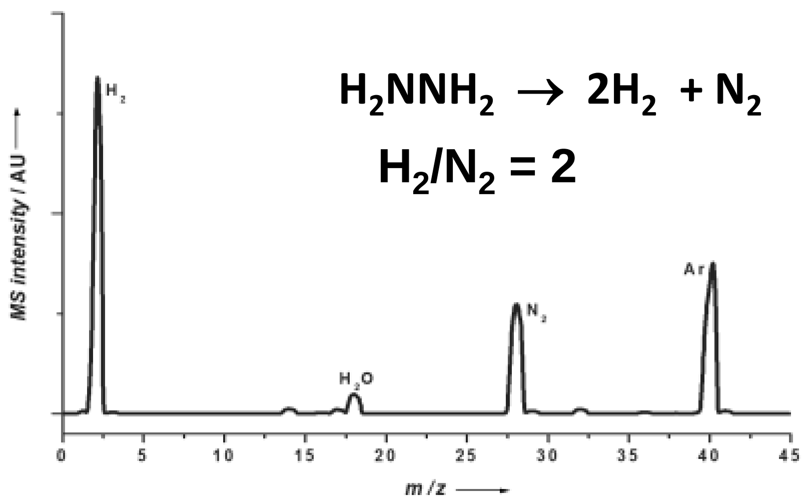
H_2 selectivity plot for hydrous hydrazine decomposition over Ni, Rh and Rh_xNi_y NPs.

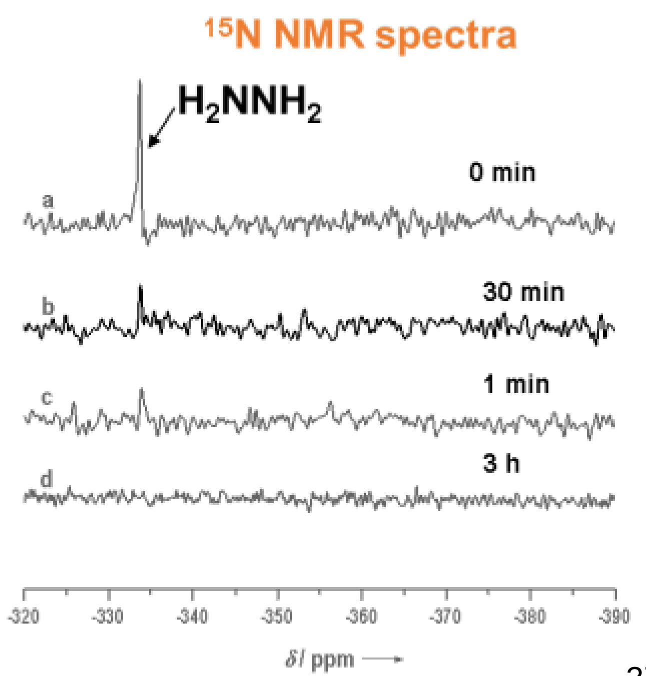


Selectivity for hydrogen generation by decomposition of hydrous hydrazine (0.5 M) catalyzed by Ni, Pt and $Ni_{1-x}Pt_x$ (x = 0.03 ~ 0.74) nanocatalysts at room temperature (catalyst = 0.017 g; $N_2H_4 \cdot H_2O$ = 0.1 mL).

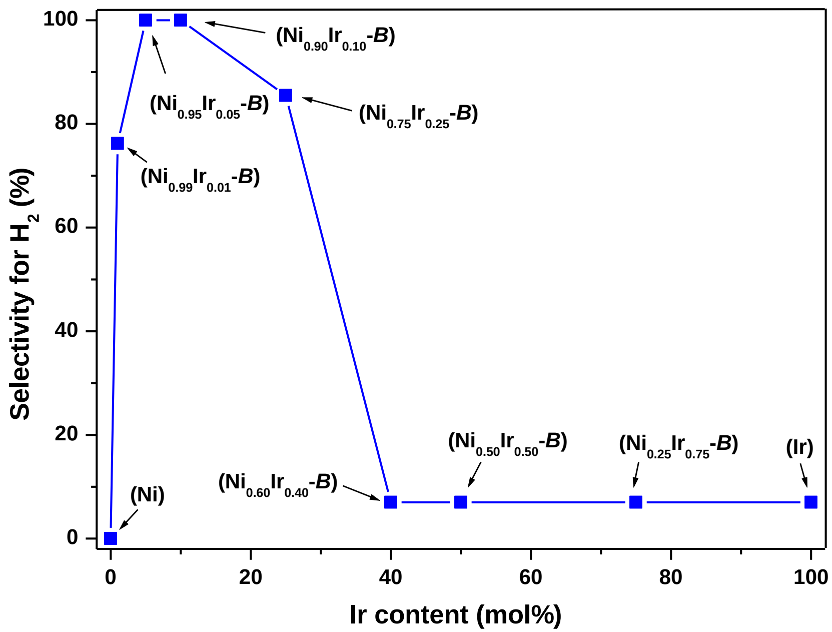
Rh_4Ni catalyst for hydrazine to hydrogen

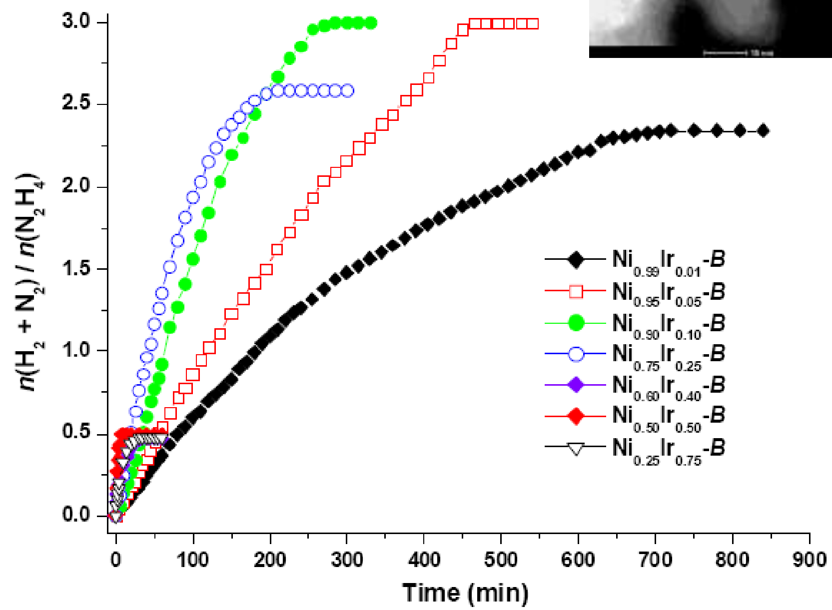


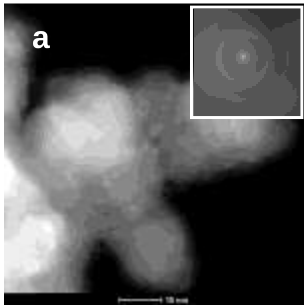




Ni-Ir catalyst for hydrazine to hydrogen





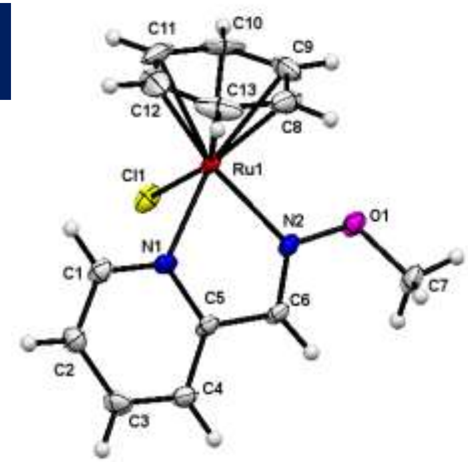


Reverse hydrogen spillover

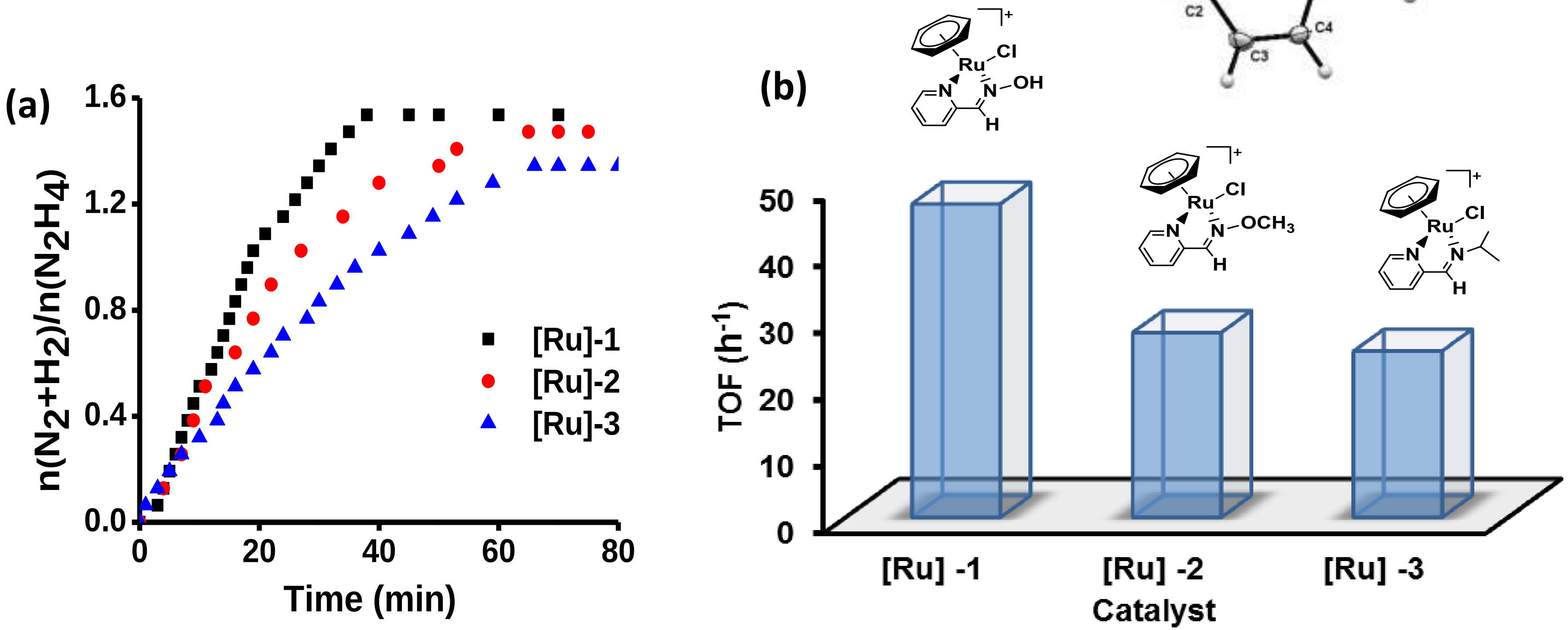
Activation of N-H bond over Ni, H-atoms spillover to Pt/Ir to recombine and release

Singh et al, Chem. Commun., 2010, 46, 6545

Activation of Hydrazine over the catalyst



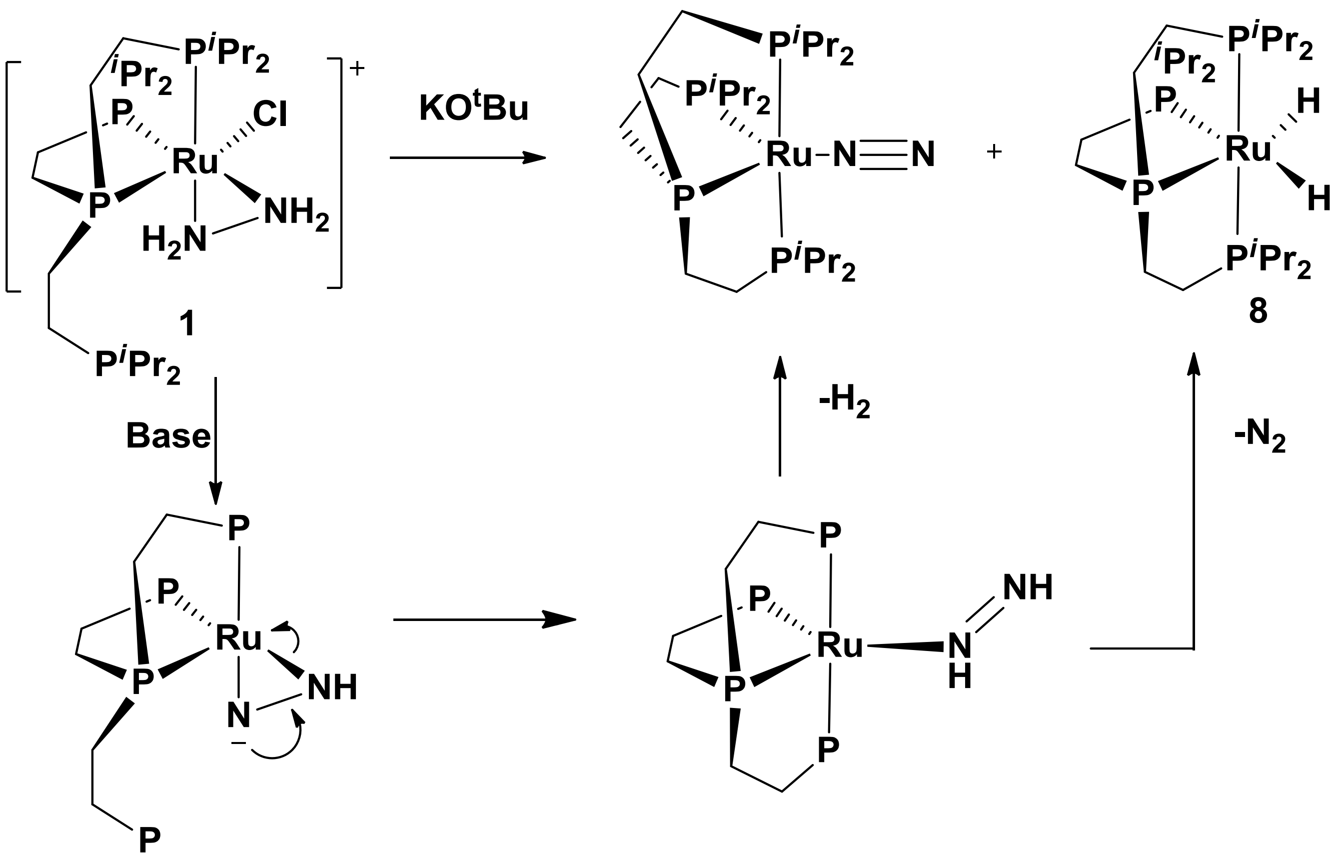
$$H_2NNH_2 \rightarrow 2H_2 + N_2$$



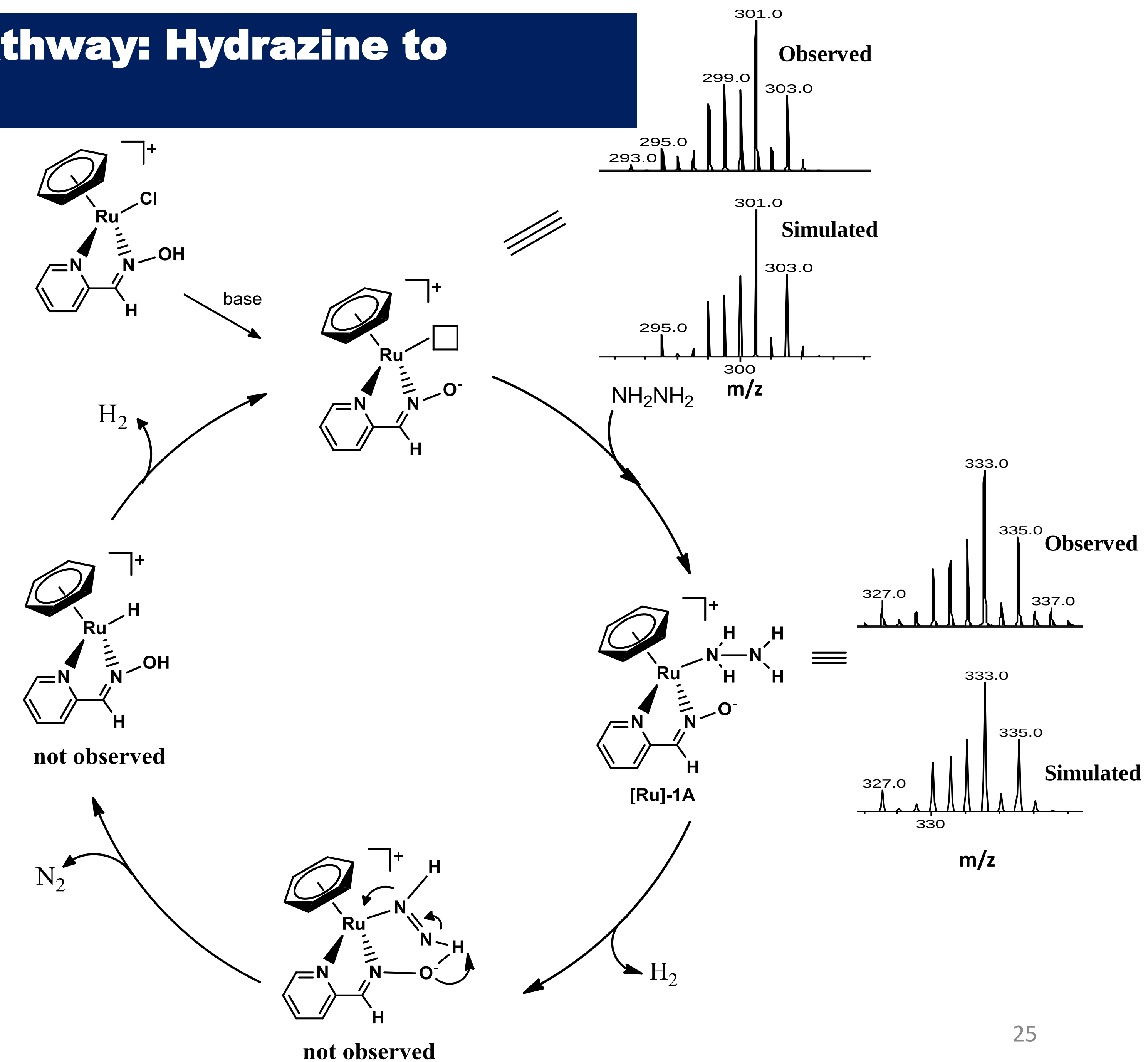
(a-b) Comparative catalytic efficacy (a) mmol of gas released *vs* time and (b) TOF (h^{-1}) for the dehydrogenation of hydrazine over ruthenium-arene catalysts. Reaction condition: hydrazine (1.0 mmol) over various ruthenium catalysts (2.5 mol%) in the presence of K^{t}OBu (2.5 mol%) in THF/methanol (5.5 mL, 10:1 v/v) at 80 °C.

Singh et. al., Chem. Asian J., 2018, 13, 1424-1431

Base induced dehydrogenation of ruthenium hydrazine complex

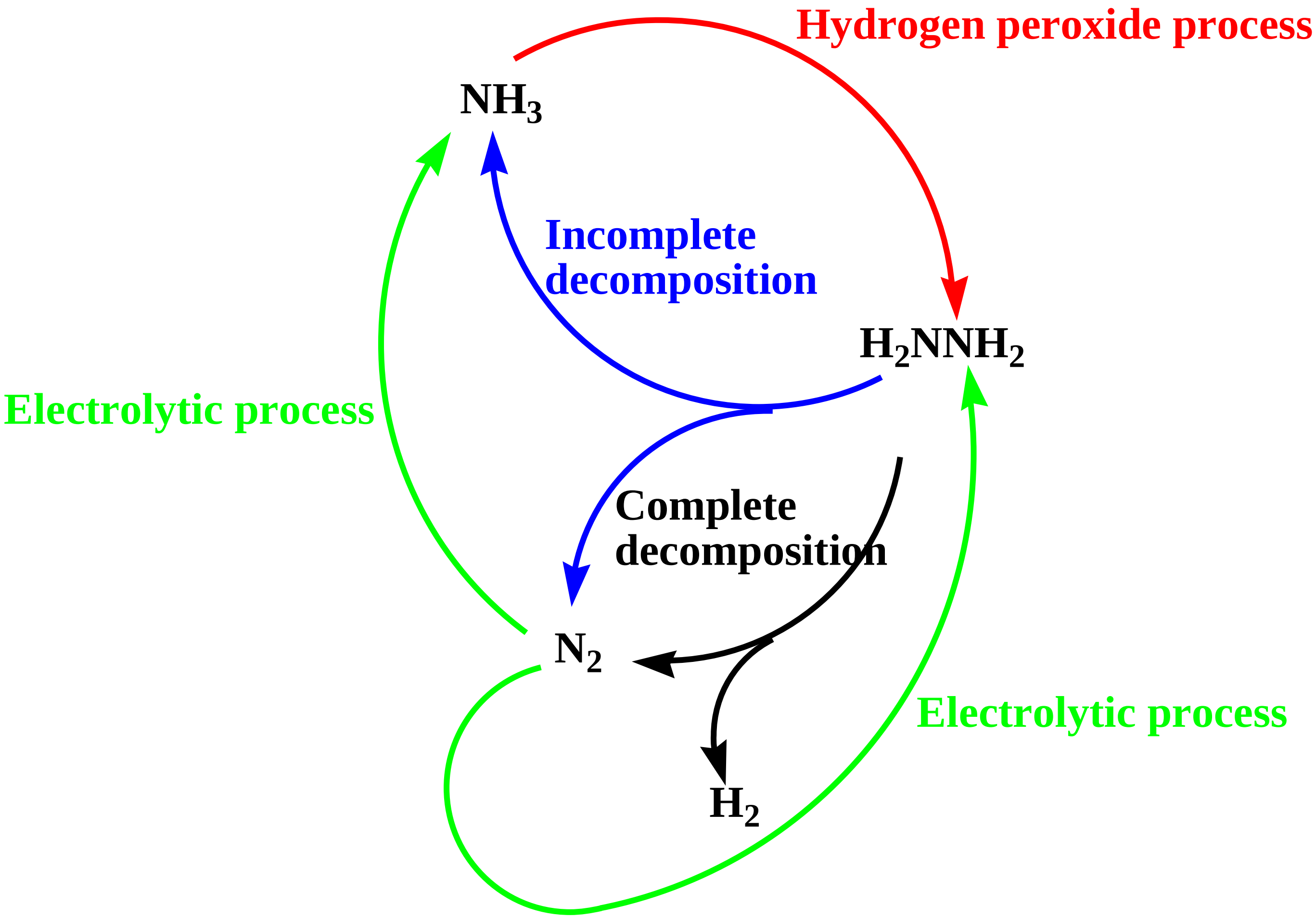


Plausible pathway: Hydrazine to hydrogen

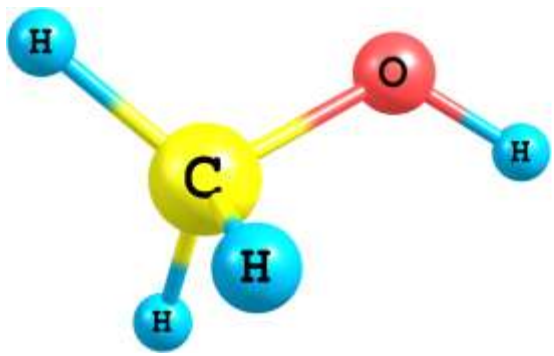


Recycling by-products: N_2 to N_2H_4

Recycling N_2



Hydrogen Production from methanol



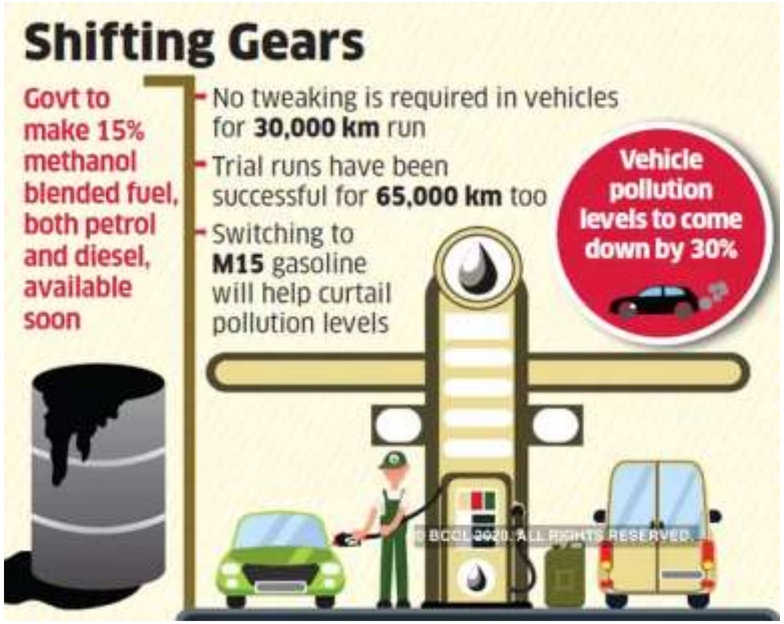
Methanol is produced from petroleum product (synthesis gas) via hydrogenation of CO and CO_2, and reversed water—gas shift reaction

Advantages with Methanol

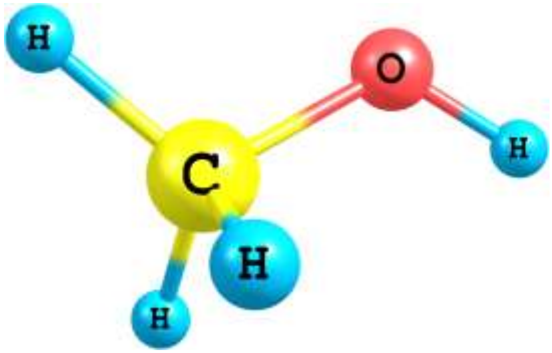
Methanol is a liquid at room temperature and has a high H_2 content (12.6 wt%)

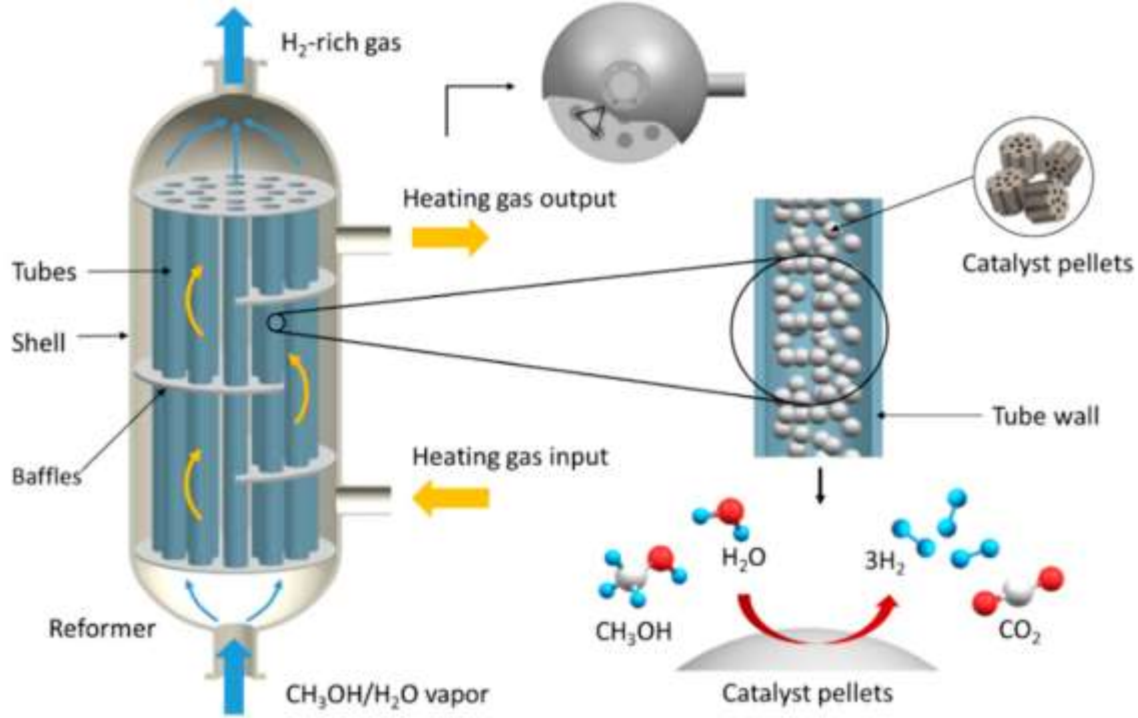
Easy to store and hydrogen can be released with the help of a suitable catalyst

No C-C bond cleavage is required for H_2 release.



Hydrogen Production from methanol





Methanol Reforming (200 - 350°C)

$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$ ΔH_r 48.9 kJ mol^{-1}

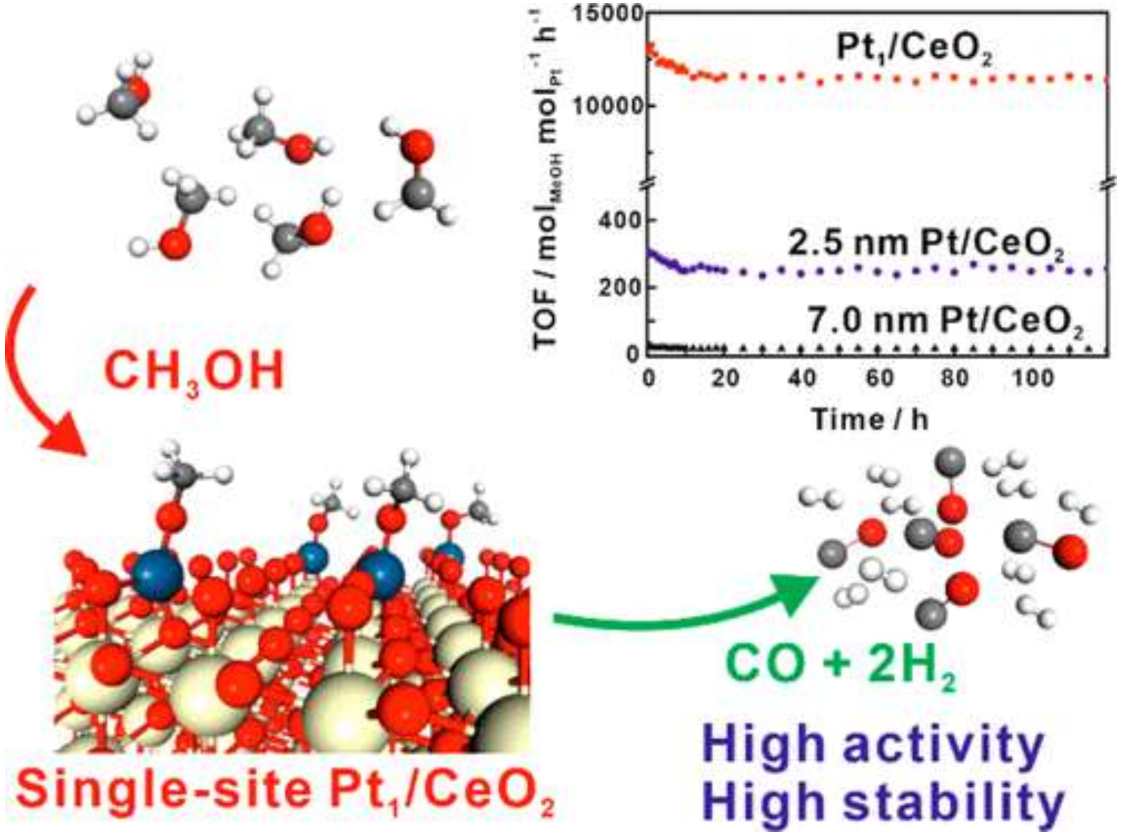
$CH_3OH + H_2O \rightarrow HCOOH + 2H_2$ **ΔH_r = 53.3 kJ mol^{-1}** (eq. 1)

$HCOOH \rightarrow CO_2 + H_2$ **ΔH_r = −14.5 kJ mol^{-1}** (eq. 2)

Ways to utilize methanol as Hydrogen Production source

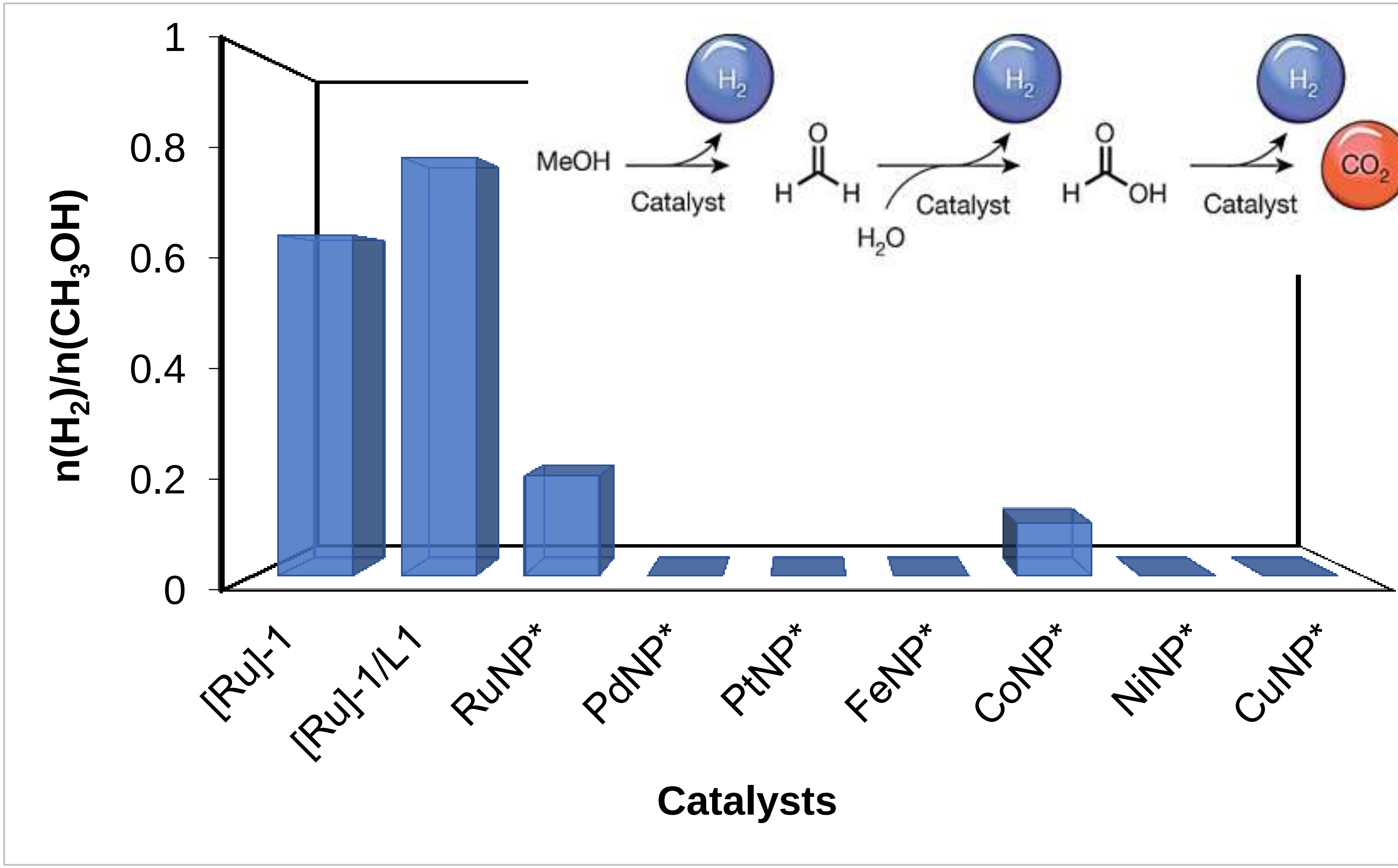
Low temperature hydrogen production (current process >150 ^{0}C)
Development of effective inexpensive catalysts
Complete conversion of methanol

"Hydrogen on-demand"



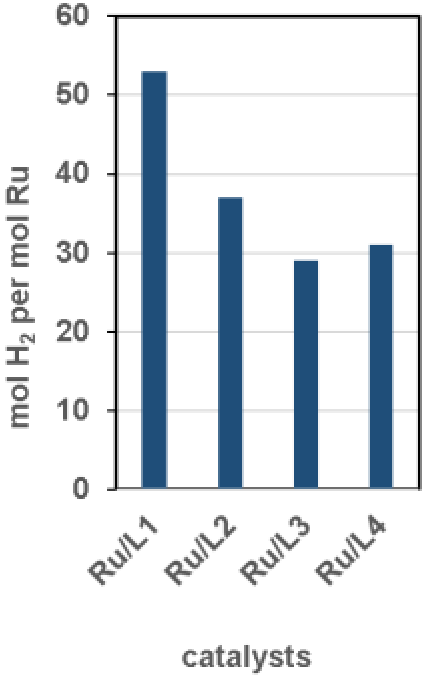
J.Am.Chem.Soc. 2019, 141, 17995−17999

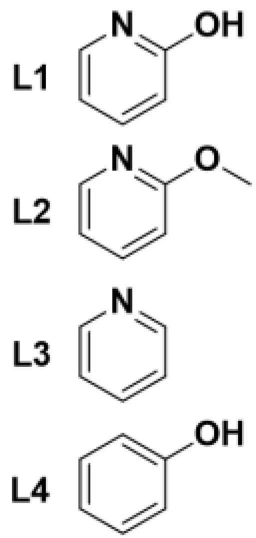
Catalysts for low temperature hydrogen production from methanol: Catalyst screening

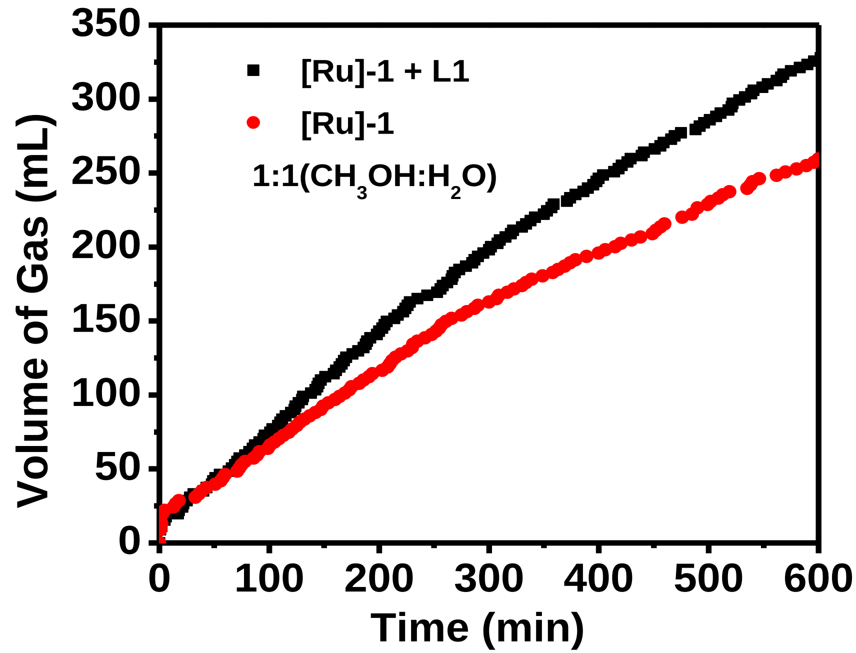


Singh et. al., Indian Patent 201921040586

Effect of ligands on the ruthenium catalyzed hydrogen production from methanol

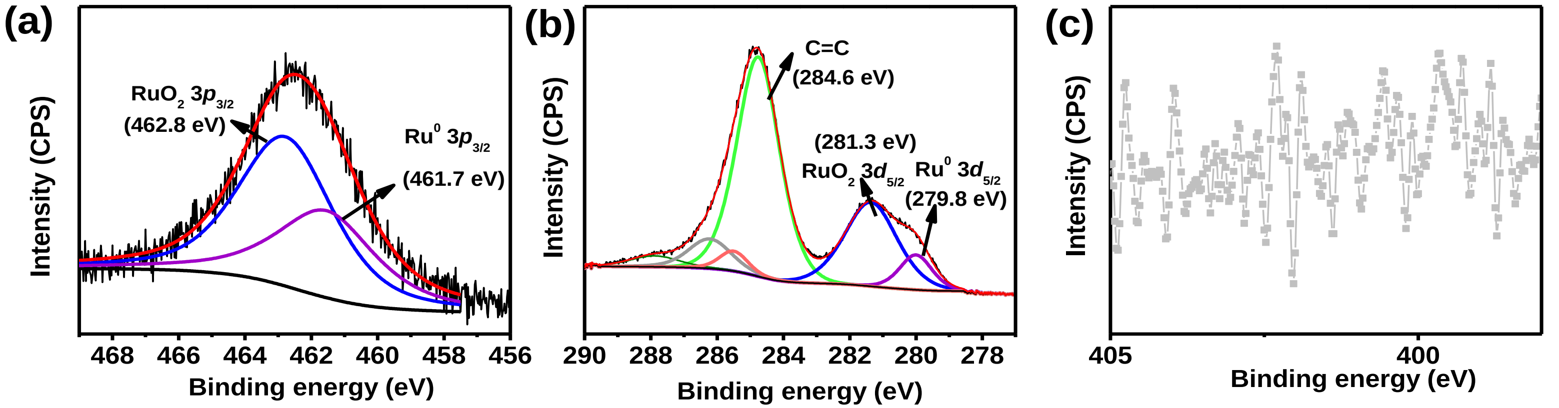




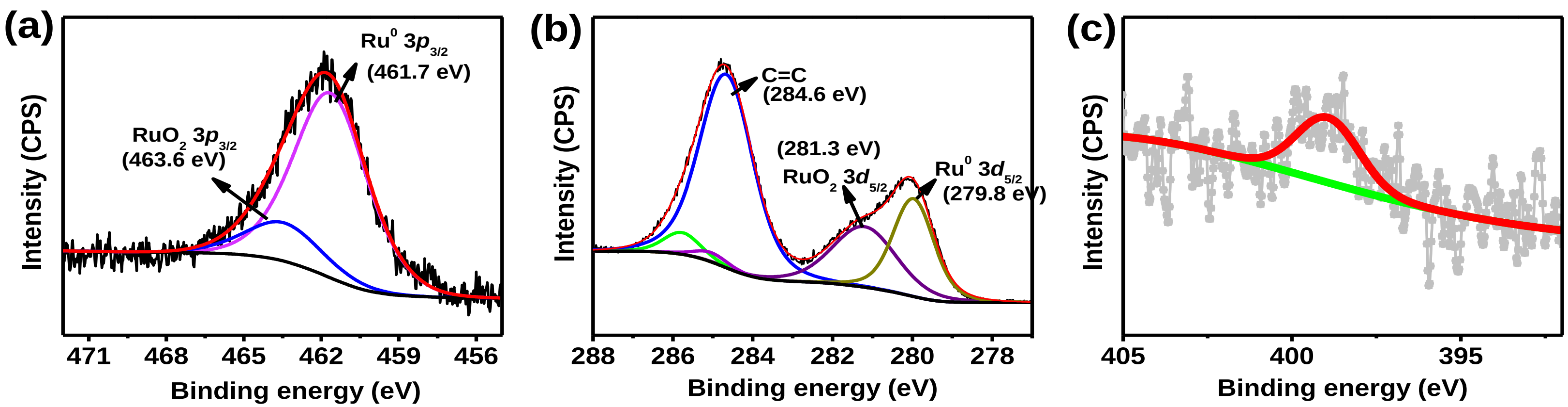


Reaction condition: methanol (16.08 mmol), Ru/Ligand catalyst (0.625 mol%, *n*(**[Ru]-1**)/*n*(Ligand) = 1:2), KOH (1.2 equiv.), water (1 equiv.), 3 h, 110 °C, Argon

Catal. Sci. Technol., **2021**, *11*, 136-142

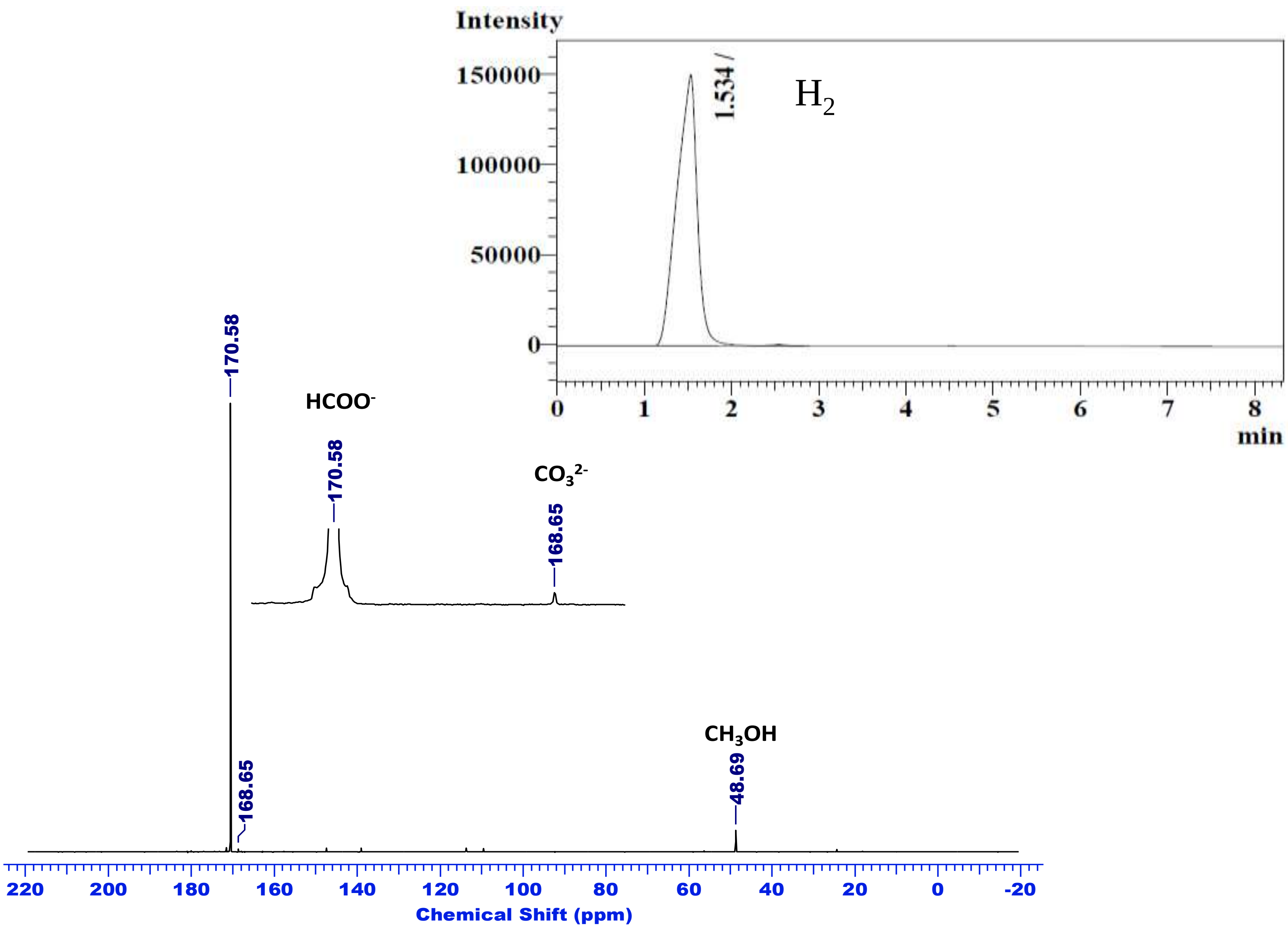


XPS spectra corresponding to the (a) Ru $3p_{3/2}$ (b) Ru $3d_{5/2}$ and (c) N 1s core levels of **Ru** catalyst



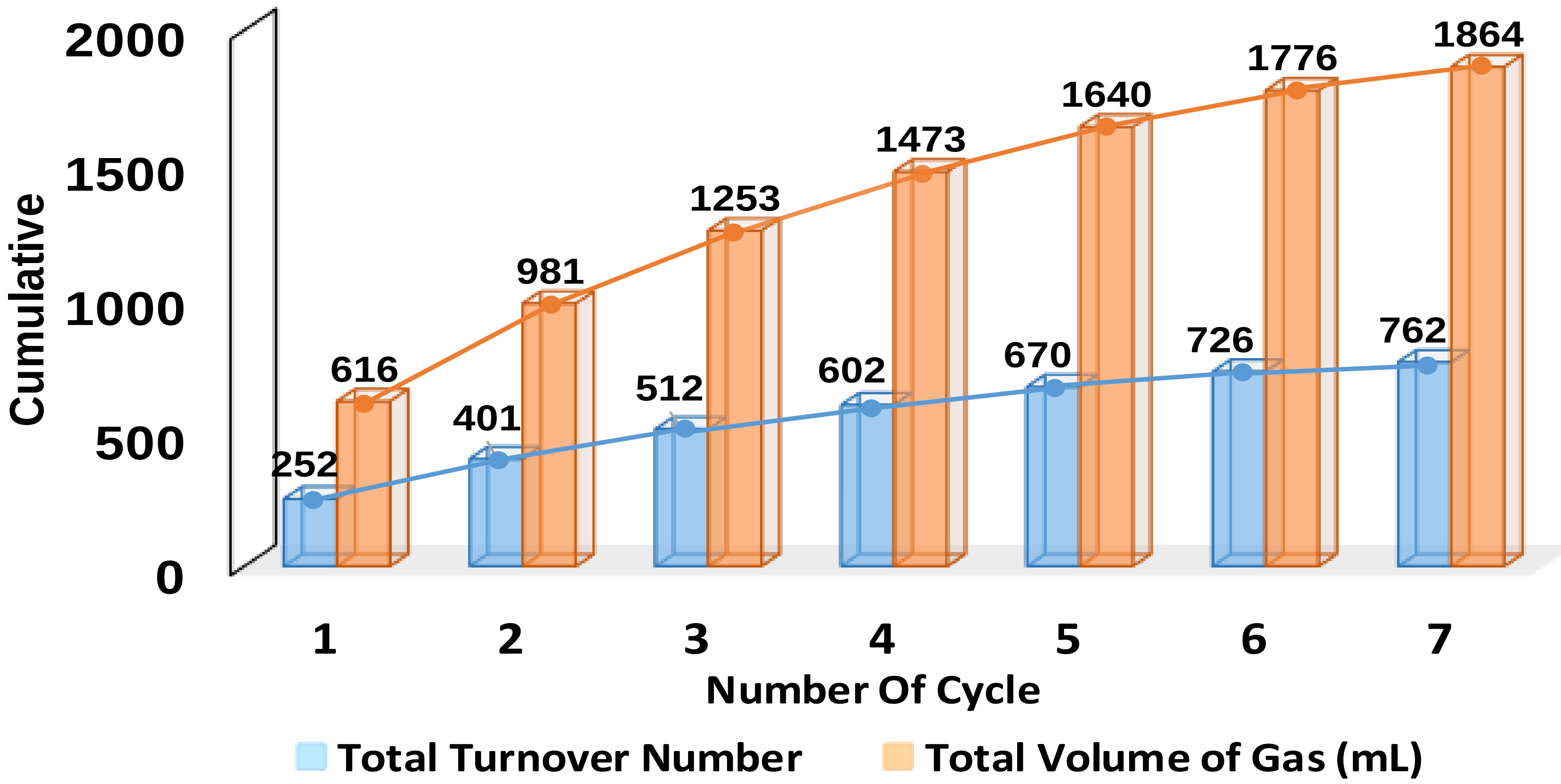
XPS spectra corresponding to the (a) Ru $3p_{3/2}$ (b) Ru $3d_{5/2}$ and (c) N 1s core levels of **Ru/L9** catalyst

Methanol to H_2

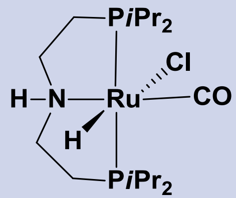


Indian Patent Application number 201921040586

Long term bulk production of hydrogen from methanol

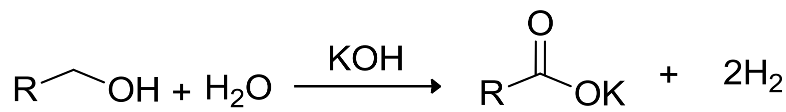


Performance evaluation of the catalyst for low temperature hydrogen production from methanol

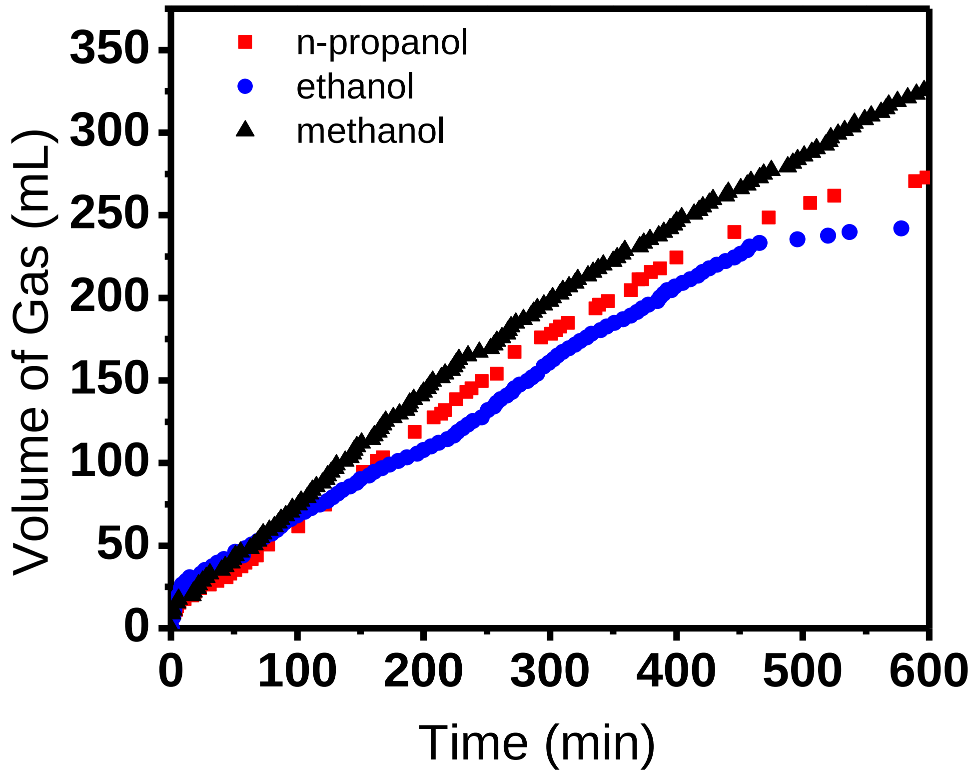
S. No.	Nature, 2013, 495, 85–89	Nature, 2017, 544, 80–83	Our work
Catalysts		0.2wt%Pt/α-MoC	in-situ generated Ru/C
Catalyst phase	Homogeneous	Heterogeneous	Heterogeneous
Temp (°C)	90	190	130
Solvent	Water	Water	Water
$n(H_2)/n(MeOH)$	0.28	0.20	1.4 (1 kg H_2/13 L MeOH)
H_2 purity	3.2:1 (H_2/CO_2) with 4 ppm CO	H_2 with CO_2 and 0.14% CO	>99% H_2
Estimation of catalyst usage to produce 1 kg H_2 per hour (in a commercial PEMFC vehicle) Toyota Mirai 2017 vehicle are 1 kg H_2 per 100 km (at a speed of about 100 km h^{-1})	-	6g Pt (~3 kg of 0.2%Pt/α-MoC catalyst)	6g Ru (~0.015 kg of [{(η^6-benzene)$RuCl_2$}$_2$] catalyst with 0.006 kg of 2-hydroxypyridine)

Singh et. al., **Indian Patent Application number 201921040586**

Catalysts for low temperature hydrogen production from other alcohols



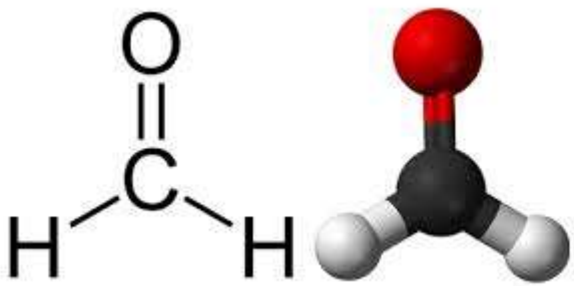
R= H, CH_3, C_2H_5

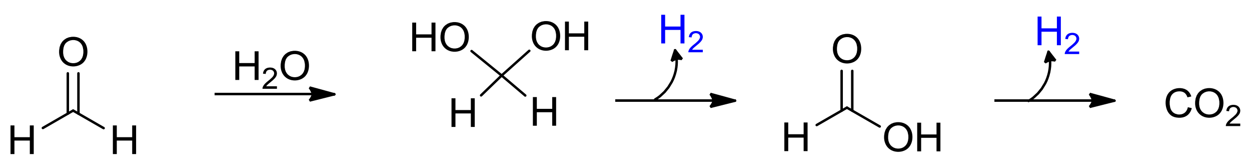


1 kg /40 L Ethanol (110 ^oC)

Singh et. al., Indian Patent Application number 201921040586

Formaldehyde to H_2

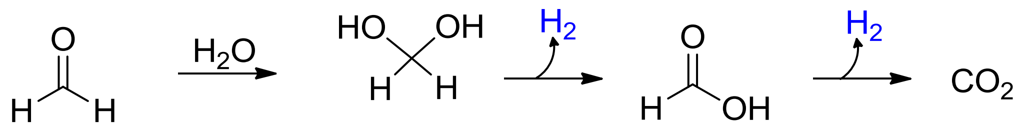


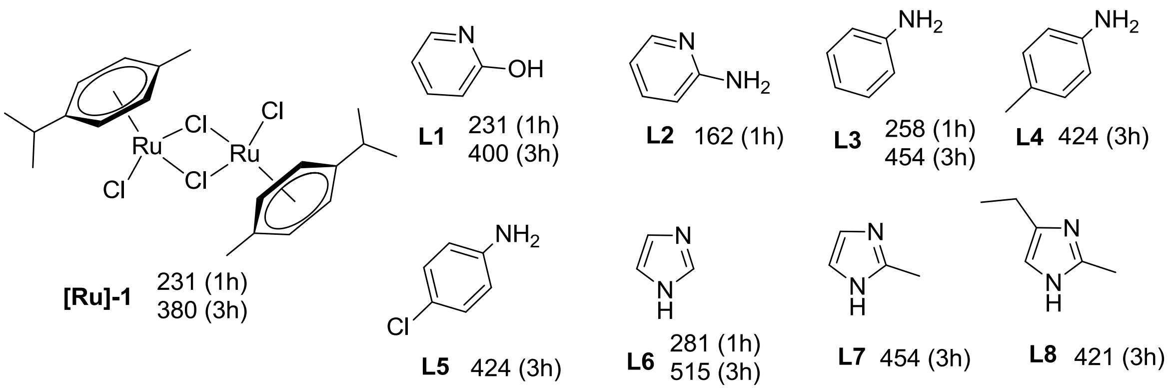


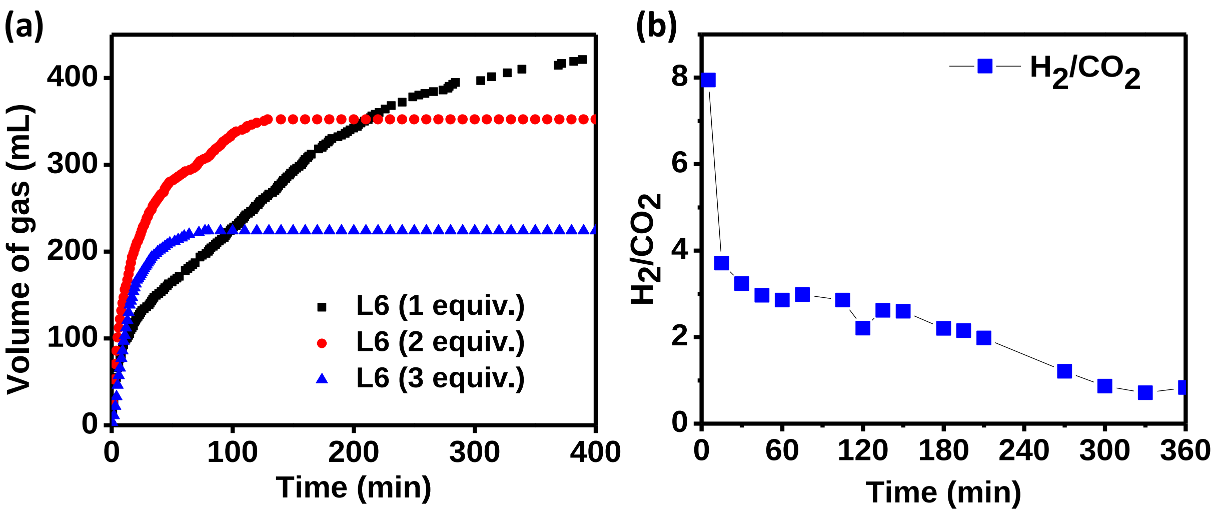
Formaldehyde
8.2 wt% H_2 content

Aq. formaldehyde
5.0 wt% H_2 content

Catalysts for hydrogen production from formaldehyde

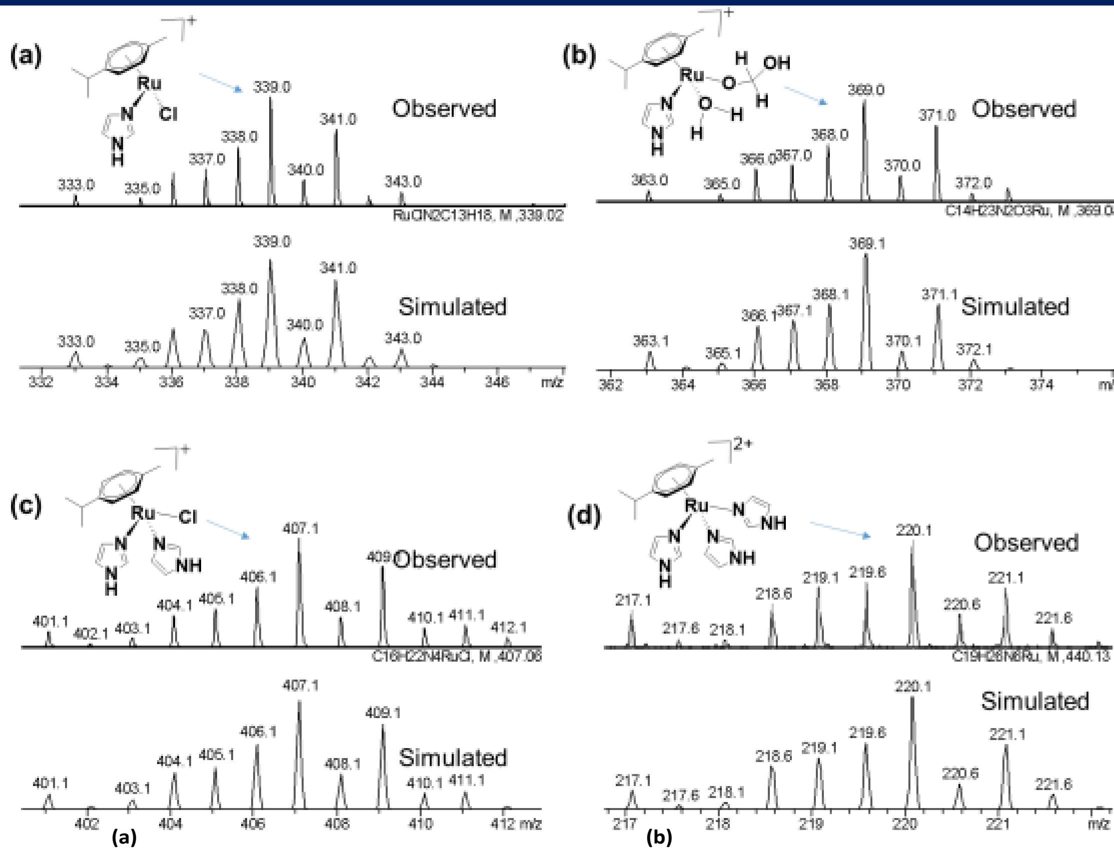


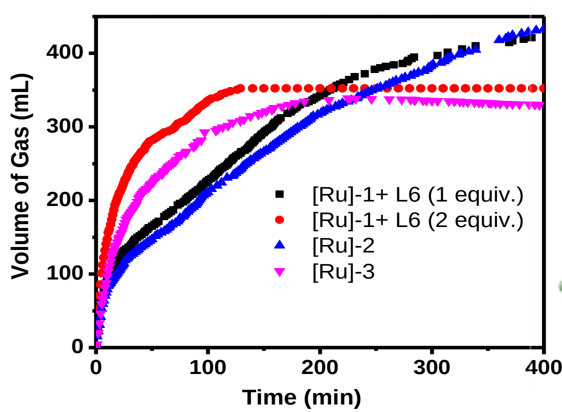


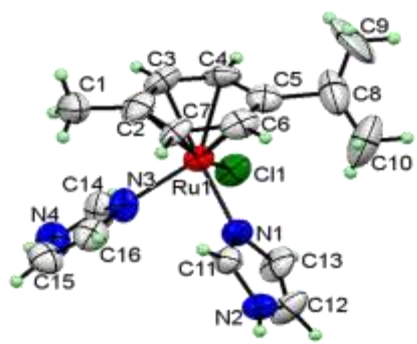


Singh et. al., Sustain. Energy Fuels, 2021

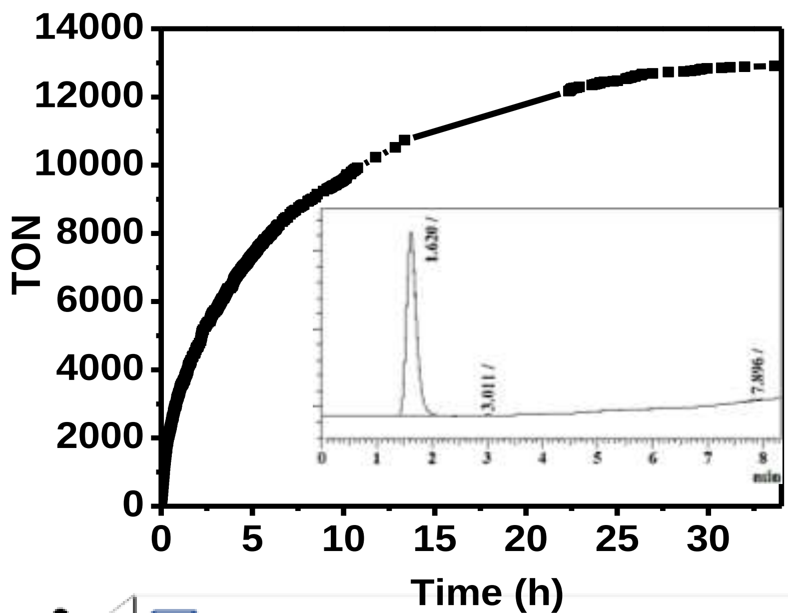
Formaldehyde to H_2: Mechanistic pathway

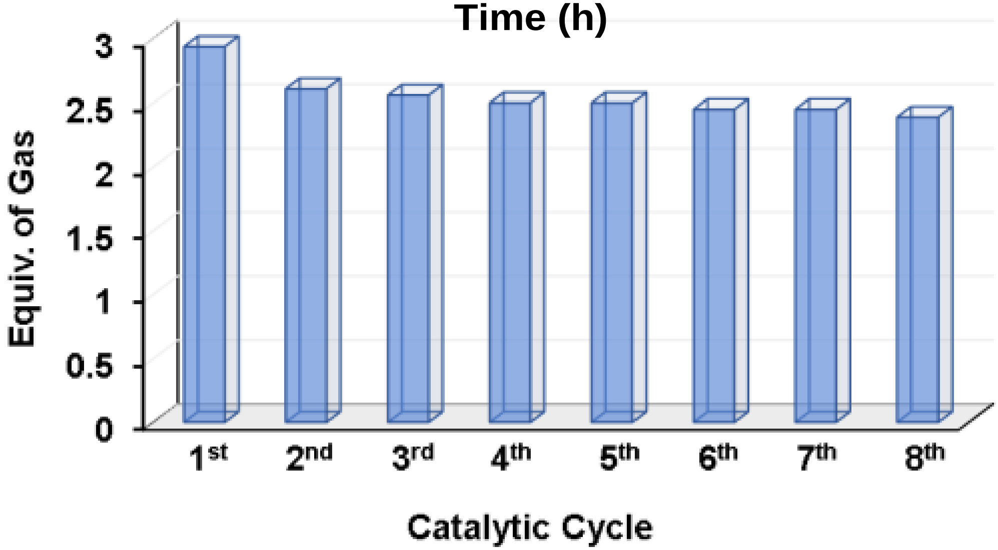






Formaldehyde to H_2: Bulk production and recyclability

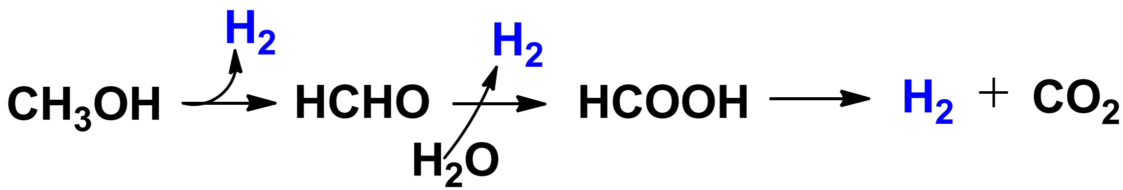


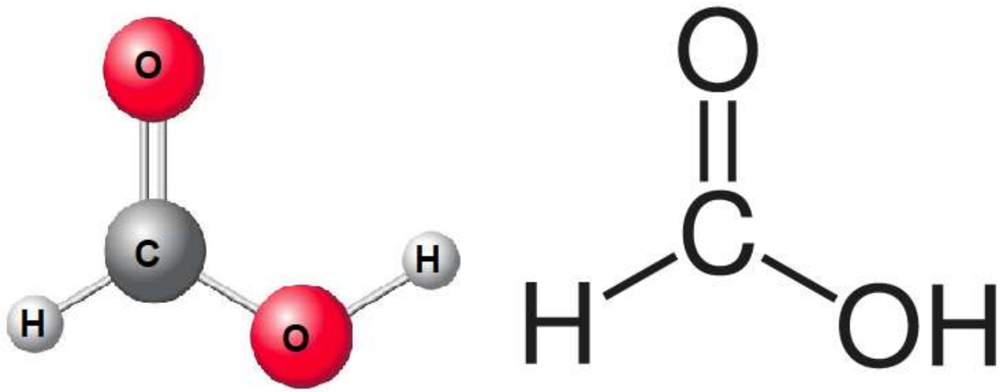


Reaction conditions: paraformaldehyde-water (1.5 mol L^{-1}, 40 mL), catalyst **[Ru]-1** (2.5 μmol) and imidazole (5 μmol) at 95 °C

1 kg /37 L aqueous formaldehyde (95 ^oC)

Liquid Organic Hydrogen Carriers: Formic acid



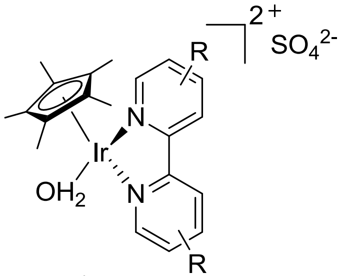


Formic acid (HCO_2H)

4.4 wt% H_2 content

Liquid, easy to handle and transport

Hydrogen production from Formic acid: Catalyst Screening



Himeda *et al.*

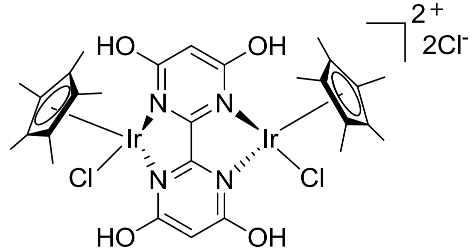
1: R= H

2: R= 4,4'-$(OH)_2$

3: R= 6,6'-$(OH)_2$

TON = 11000

TOF = 5440 h^{-1}

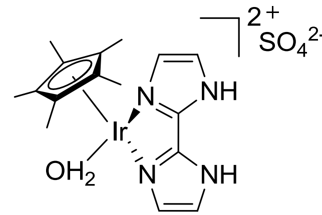


Fujita *et al.*

4

TON= 165000

TOF= 228000 h^{-1}

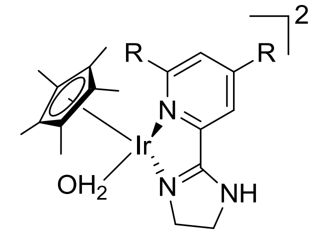


Himeda *et al.*

5

TON= 10000

TOF= 34000 h^{-1}



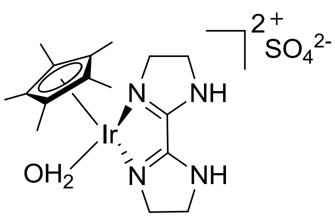
Himeda *et al.*

6: R= H

7: R= OH

TON= 68000

TOF= 322000 h^{-1}

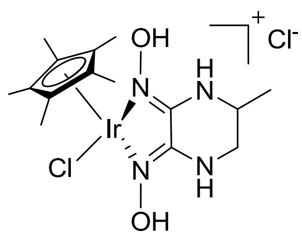


Himeda *et al.*

8

TON= 47000

TOF= 487500 h^{-1}

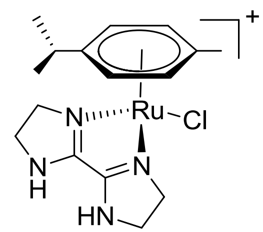


Li *et al.*

9

TON= 3900000

TOF= 6500 h^{-1}

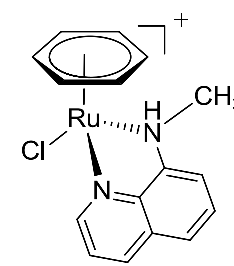


Huang *et al.*

10

TON= 350000

TOF= 12000 h^{-1}



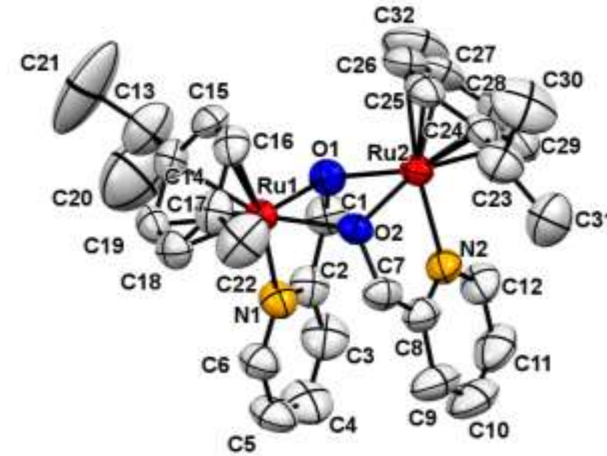
Singh *et al.*

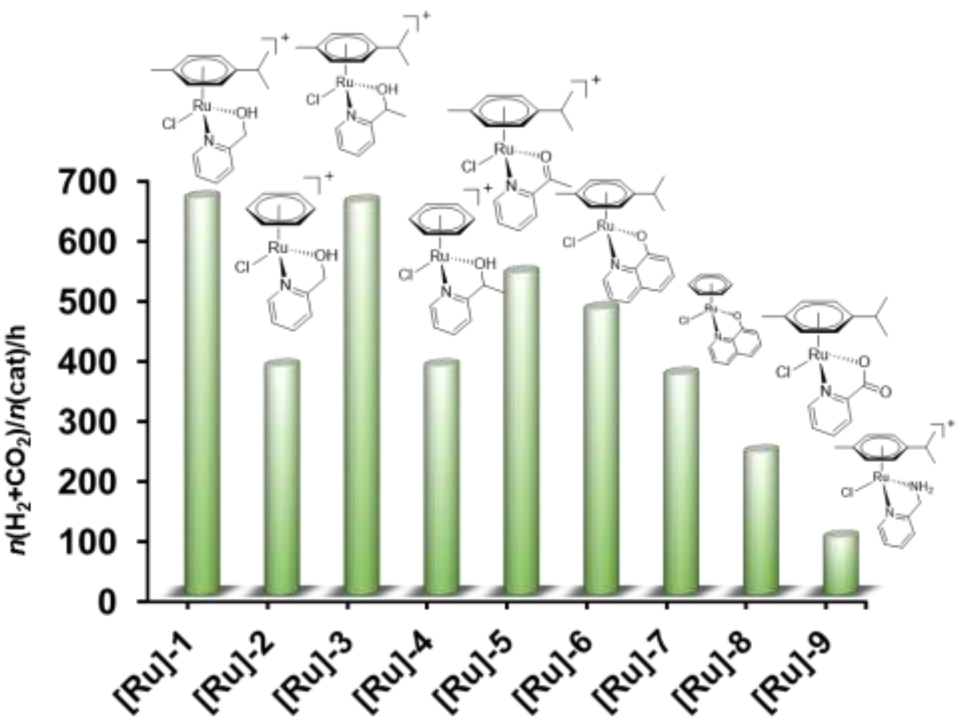
11

TON= 2248

TOF= 940 h^{-1}

$$HCOOH \xrightarrow[\text{HCOONa (0.05 mmol), } H_2O \text{ (2.5 ml), 90 °C}]{\text{1 mol\% [Ru]-complex}} H_2 + CO_2$$



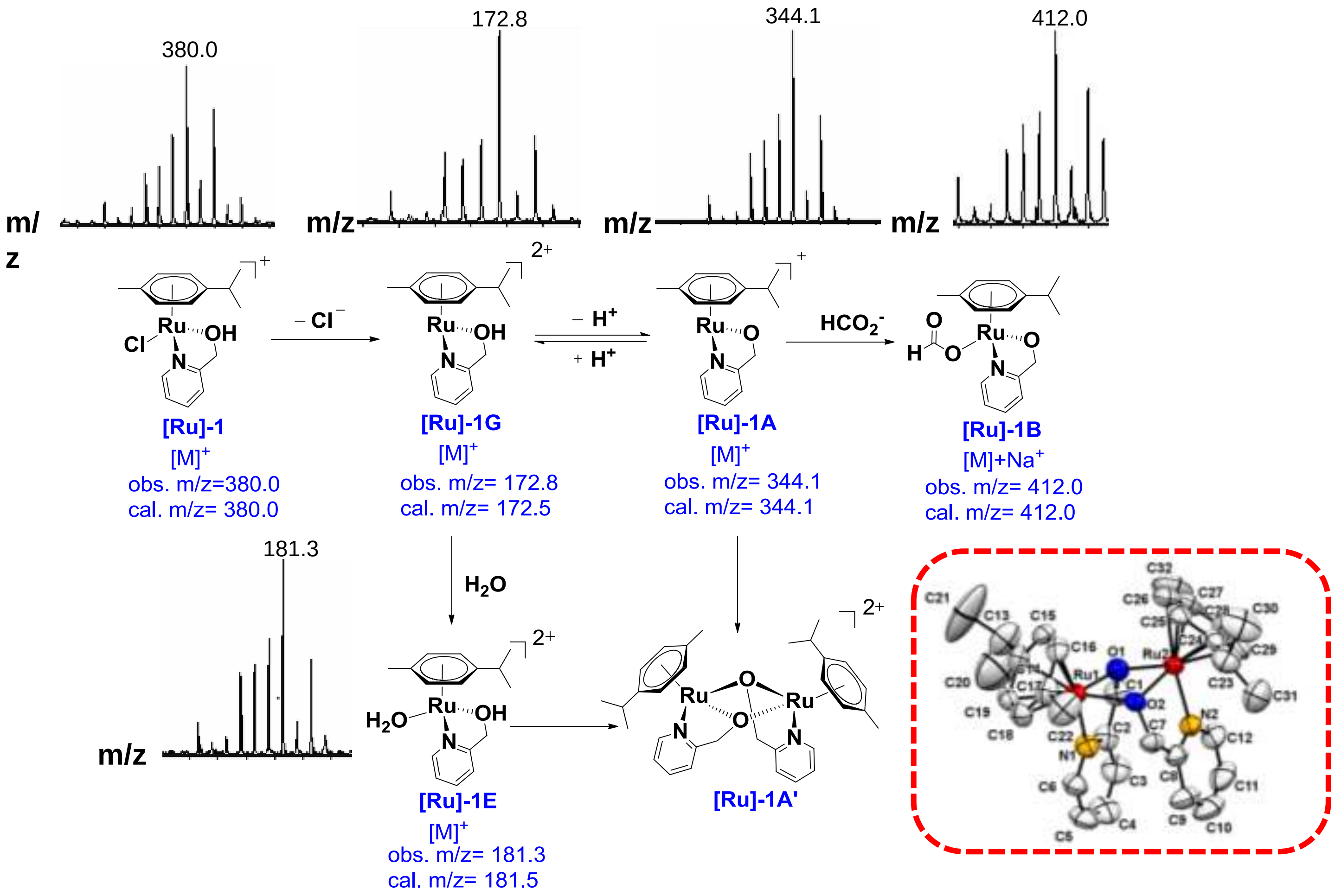


[HCOOH]/[HCOONa] 1:2

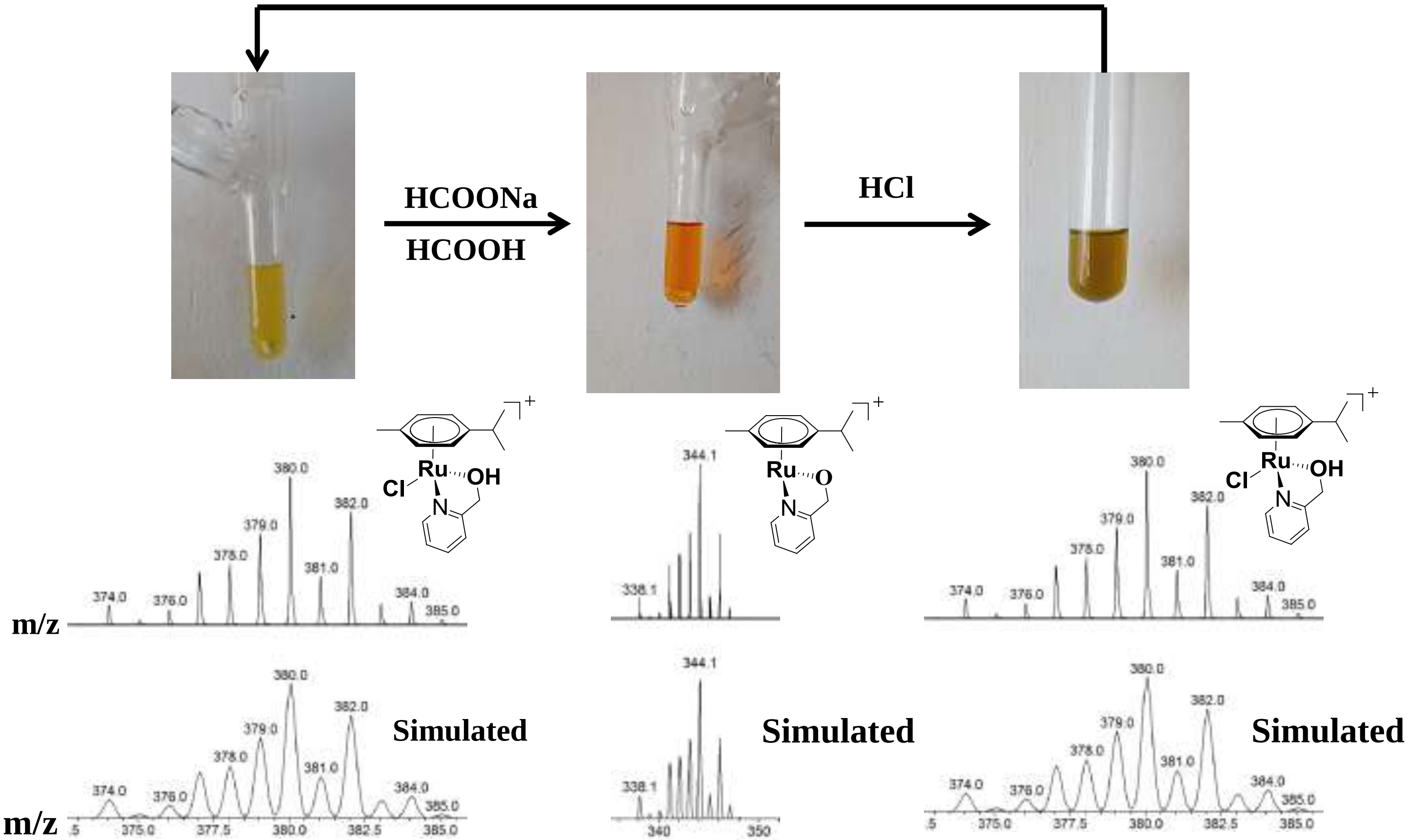
pH 4.4

Singh *et al*., *Inorg. Chem*. **2020** (under review)

Active Organometallic Species in Formic acid to H_2

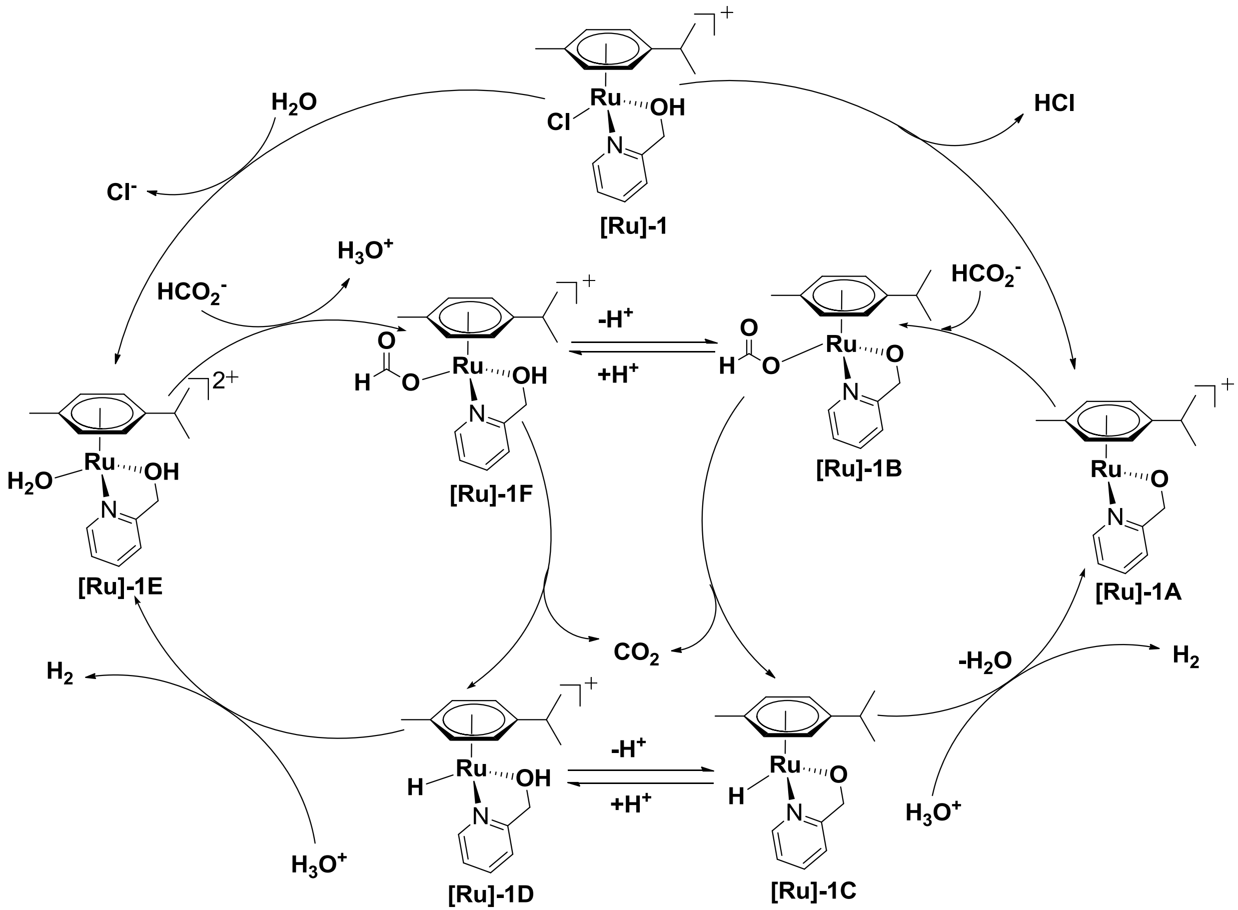


Active Organometallic Species in Formic acid to H_2

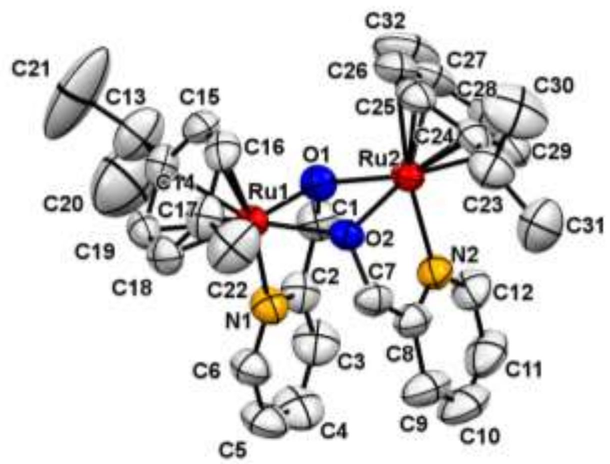


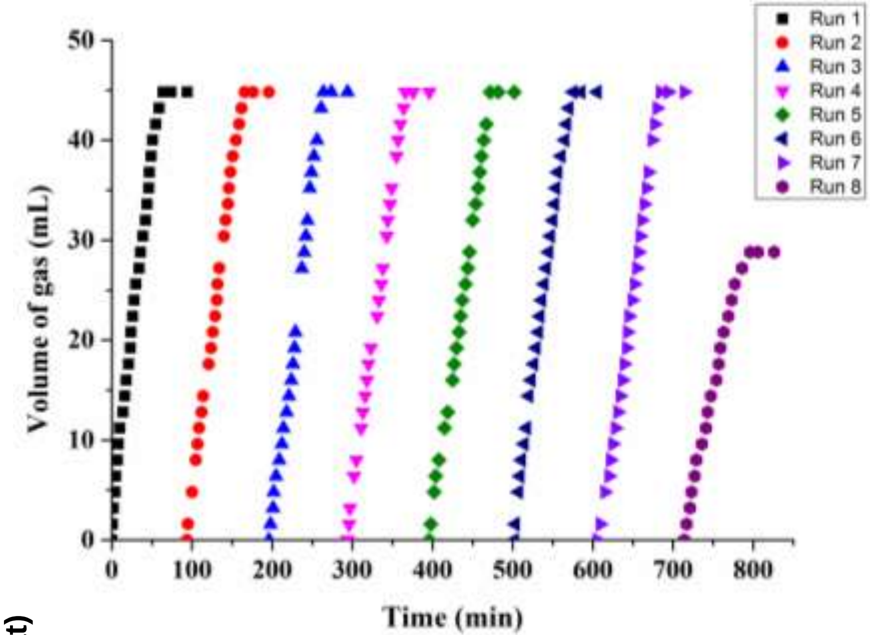
Transformation of colour and mass analysis after the orange red solution was treated with HCl

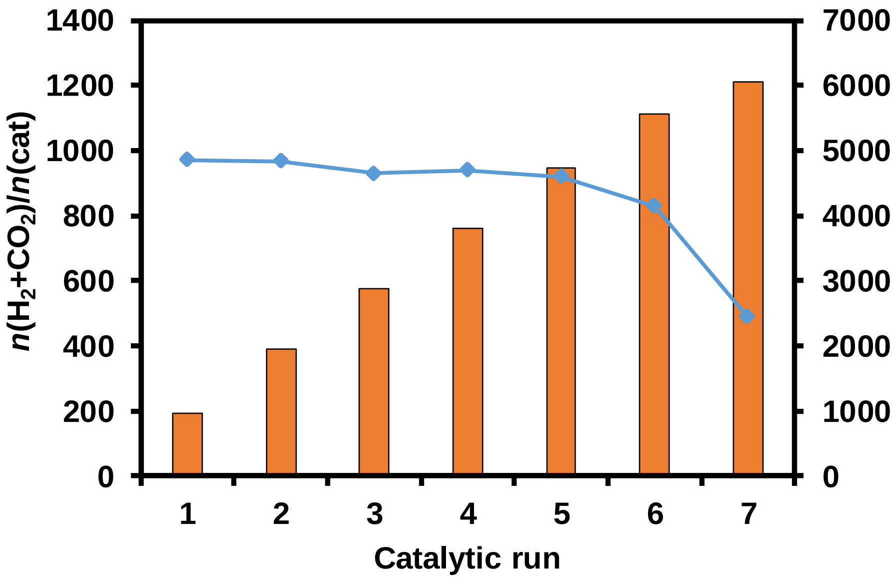
Plausible Mechanism for Formic acid to H_2

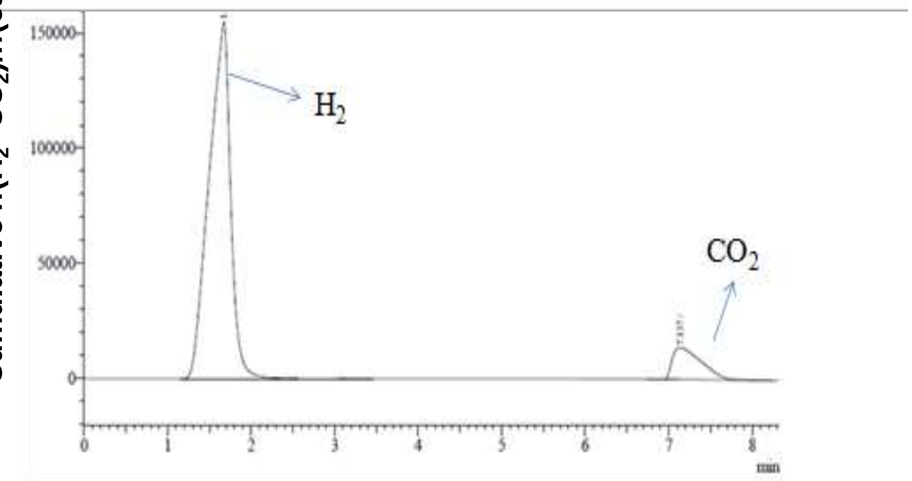


Turn over number (TON) of 6050 and a maximum initial TOF of 1548 h^{-1}









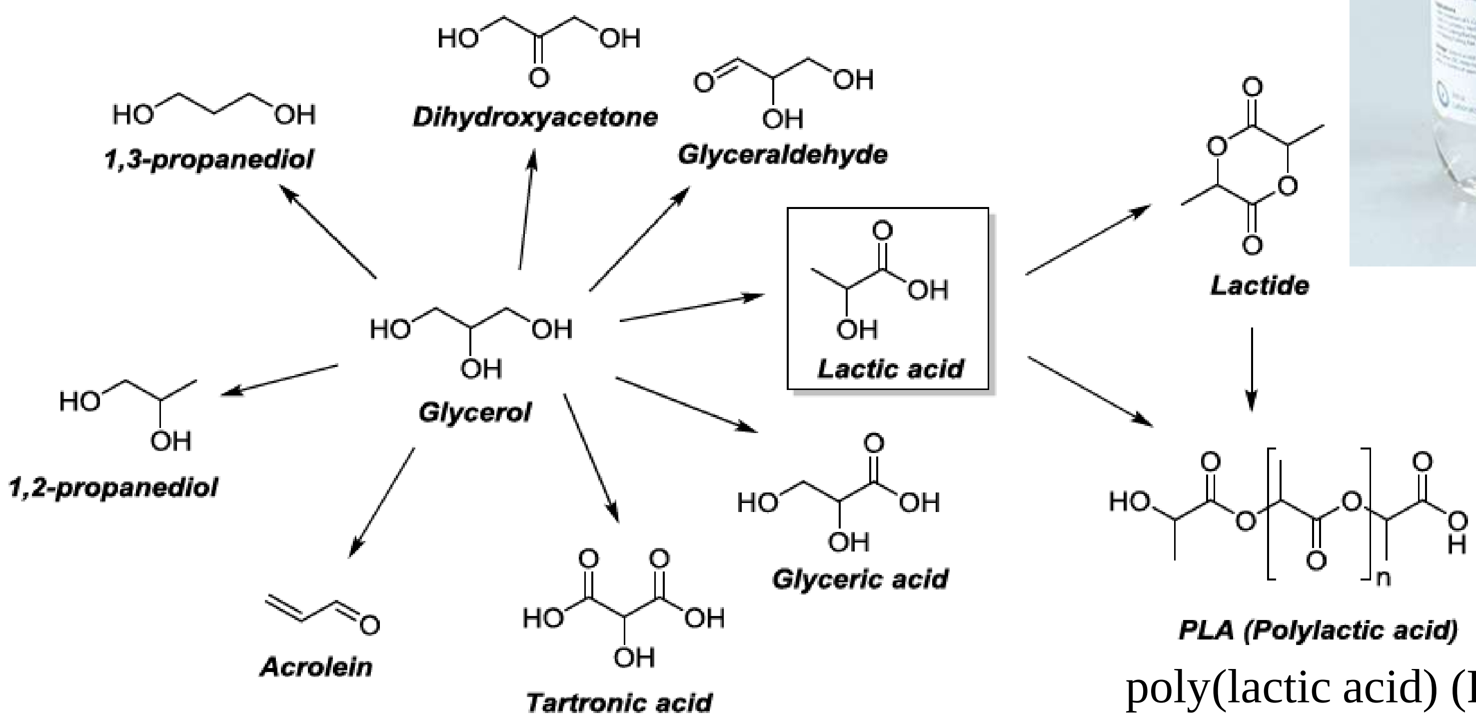
IIT Indore

Singh *et al*., *Inorg. Chem*. **2020**

Glycerol to H_2 gas

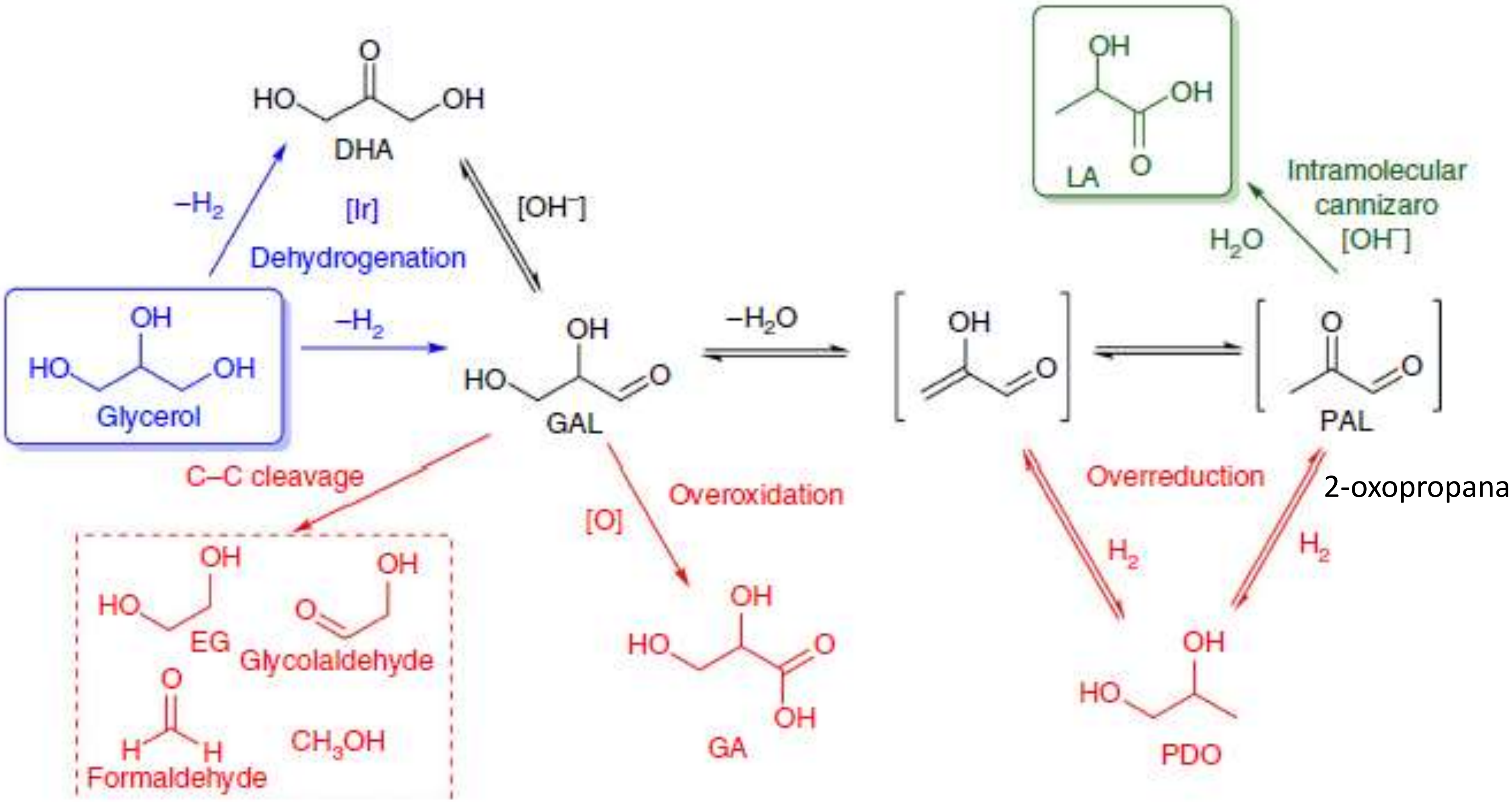
Glycerol is a byproduct of biodiesel, and constitutes about 10% of the weight of crude biodiesel.

Acceptorless dehydrogenation of glycerol leads to the production of H_2 gas

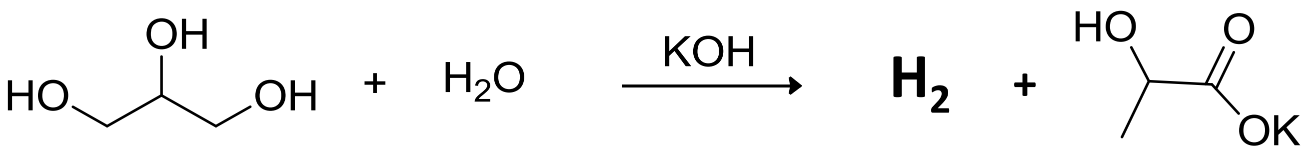


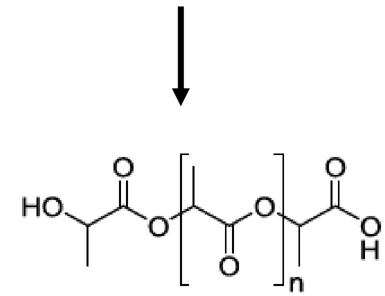
poly(lactic acid) (PLA)
a biodegradable polymer

Pathway for glycerol dehydrogenation



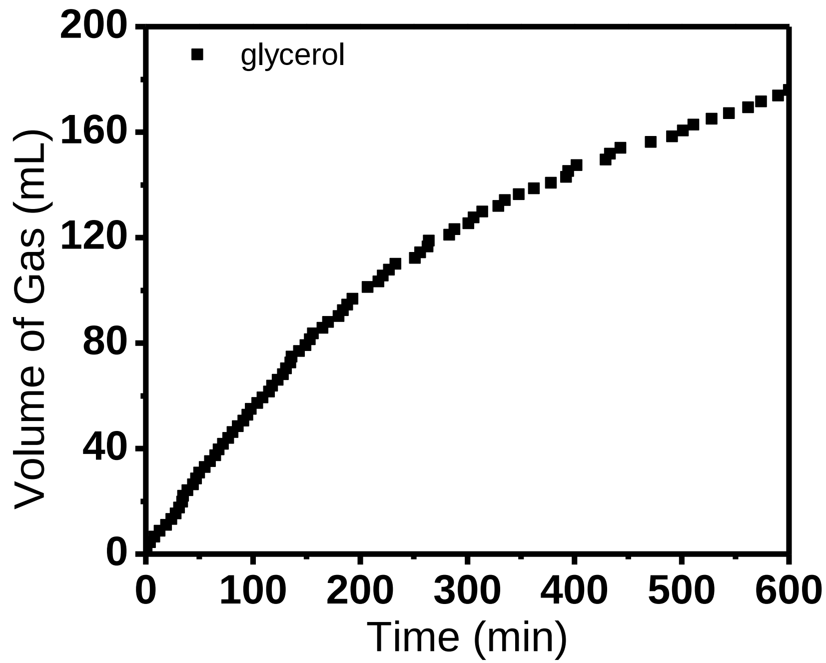
Catalysts for low temperature hydrogen production from glycerol





PLA (Polylactic acid)

Glycerol is a byproduct of biodiesel, and constitutes about 10% of the weight of crude biodiesel.



1 kg /52 L glycerol (110 ºC)

poly(lactic acid) (PLA)
a biodegradable polymer

Additional benefit:
with 1 kg H_2 production:
64 kg of Lactic acid (₹160/kg)

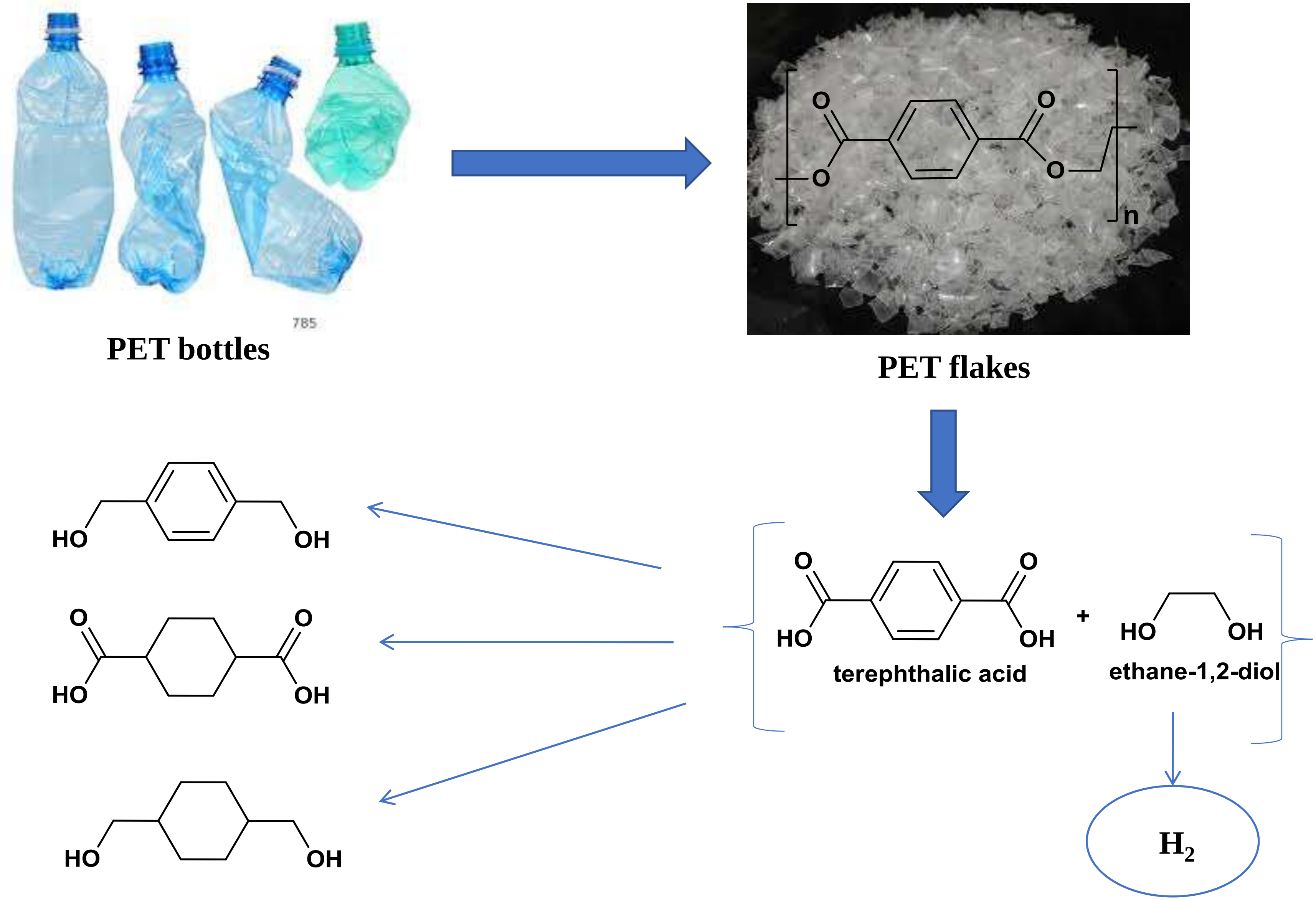
Singh et. al., Indian Patent Application number 201921040586

Environmental pollution due to PET waste

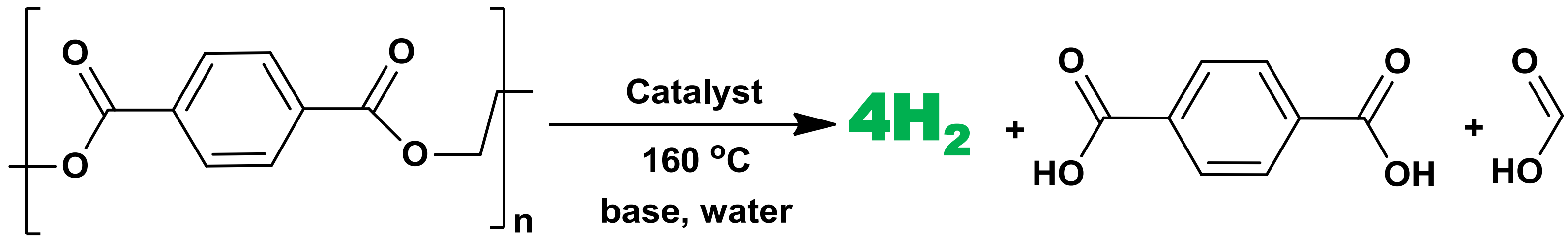
emro.who.int

blog.nus.edu.g

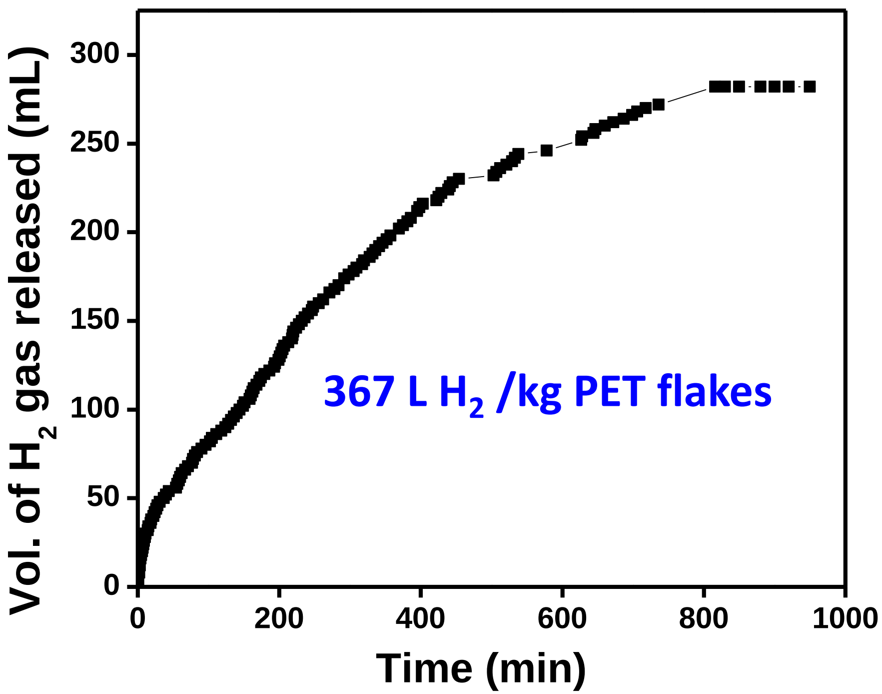
Hydrogen production from PET waste



Hydrogen production from PET waste



Polyethylene Terepthalate (PET)



1 kg H_2 can be produced from ~33 kg of PET waste

Additional benefit:

with 1 kg H_2 production:

40 kg of Terephthalic acid (₹93/kg)

33 kg of Potassium formate (₹208/kg)

Singh et. al., Indian Patent Application No. 202021020639

Liquid Hydrogen Storage Materials

For on-board and stationary hydrogen production application

GREEN H_2

NH_3 (Ammonia)
N_2H_4 (Hydrazine)

CH_3OH (Methanol)
C_2H_5OH (Ethanol)
$HOCH_2CH_2OH$ (Ethylene Glycol)
$(CH_2OH)_2CHOH$ (Glycerol)

BLUE H_2

HCOOH (Formic Acid)

Take home message

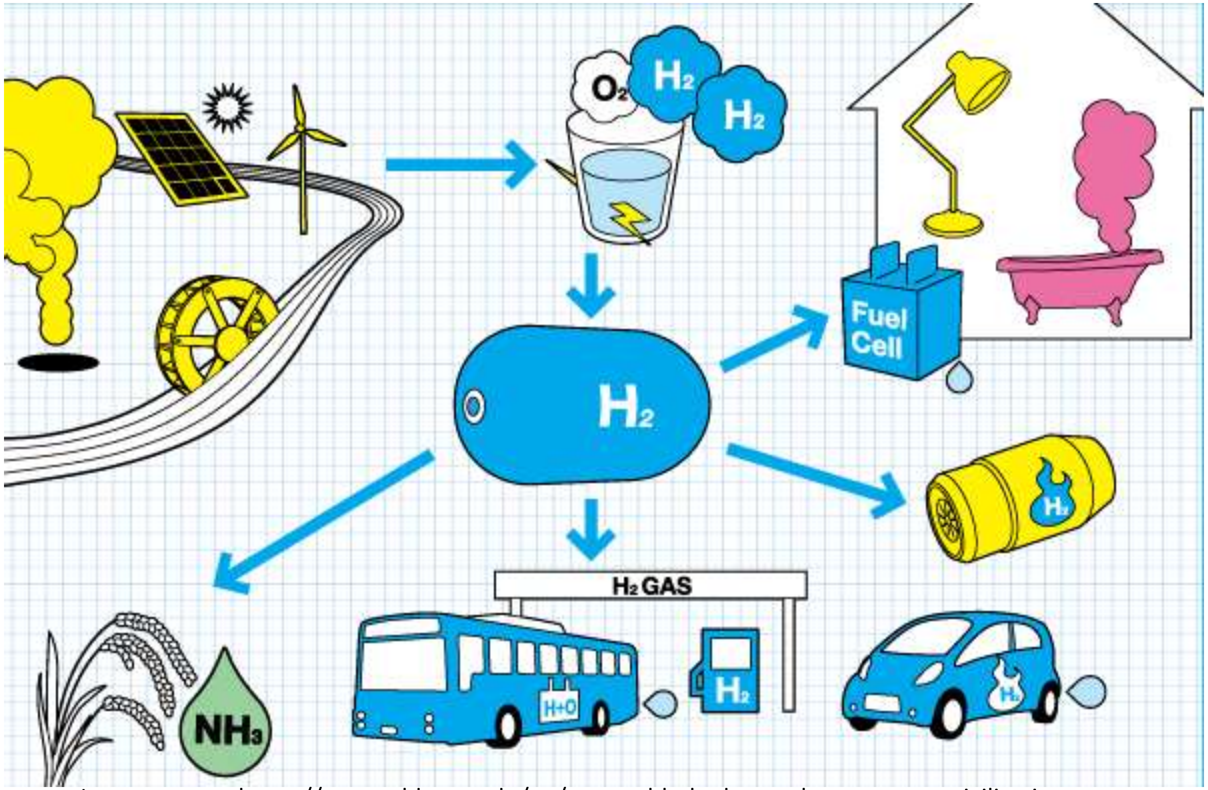


Image source: https://ourworld.unu.edu/en/renewable-hydrogen-key-to-a-new-civilization

Development of efficient technology by chemical intervention has created enormous opportunity to fulfill the global energy demand in a most efficient and cleaner way. In this regard, **H_2 based economy** is the ultimate solution at this point of time.

Acknowledgements

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SERB(DST) New Delhi

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SAIF, IIT Bombay

KIT, Germany

NTU, Singapore

AIST, Japan

Hokkaido University, Japan

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Department of Science and Technology (DST)
Govt. of India