$LaNi_5$ Metal Hydride as a Catalyst for Toluene Hydrogenation

Sung Ju Han, Jinwoo Kim, Young-Su Lee, Jae-Hyeok Shim, Young Whan Cho, Jin-Yoo Suh

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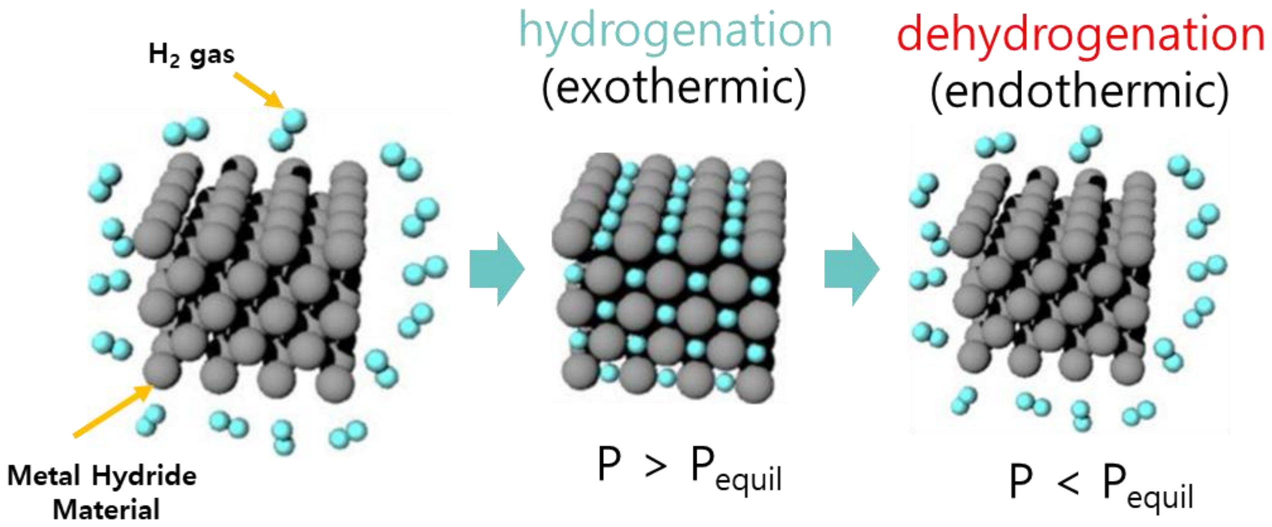
Metal Hydrides

Metal hydrides absorb and desorb hydrogen at specific temperature and pressure conditions.

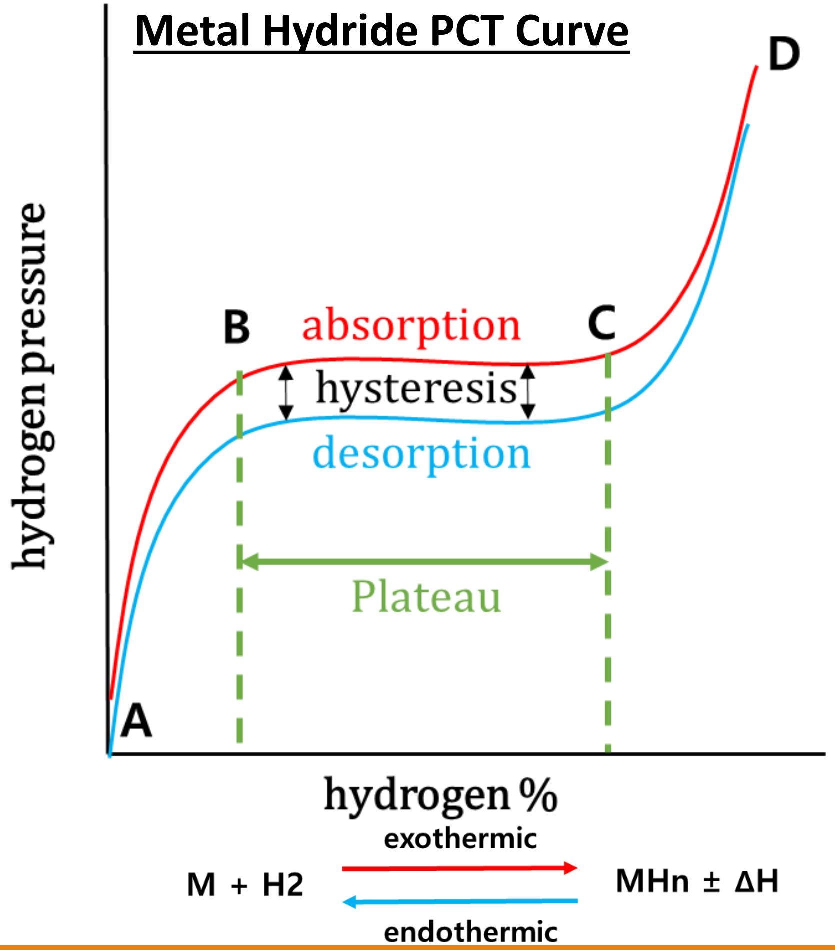
Hydrogenation and Dehydrogenation Process



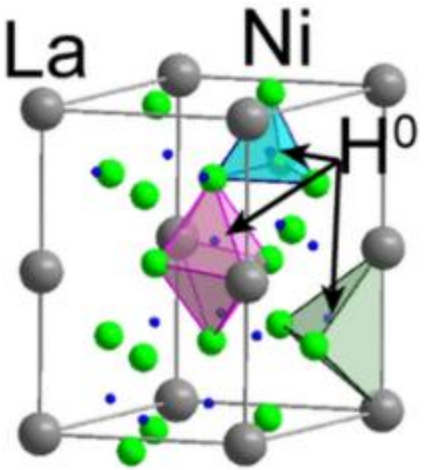
When $P > P_{equil}$,
the material absorbs hydrogen and stores hydrogen as a solid.

When $P < P_{equil}$,
that stored hydrogen is released back out as H_2 gas.

Metal Hydride PCT Curve

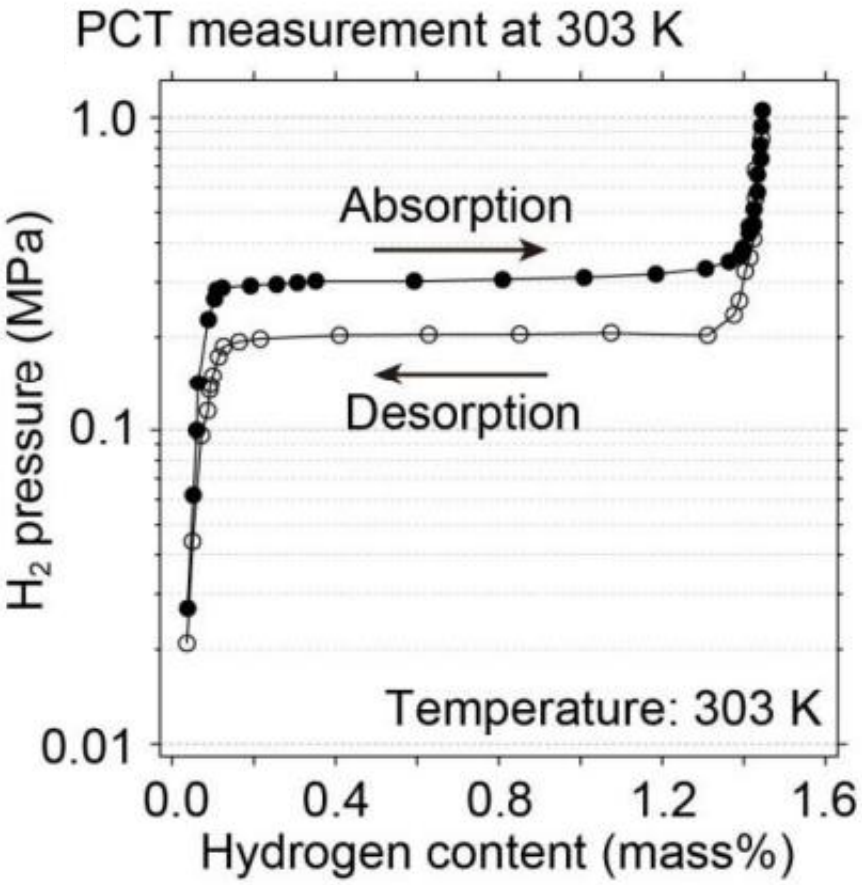


$LaNi_5$ Metal Hydride



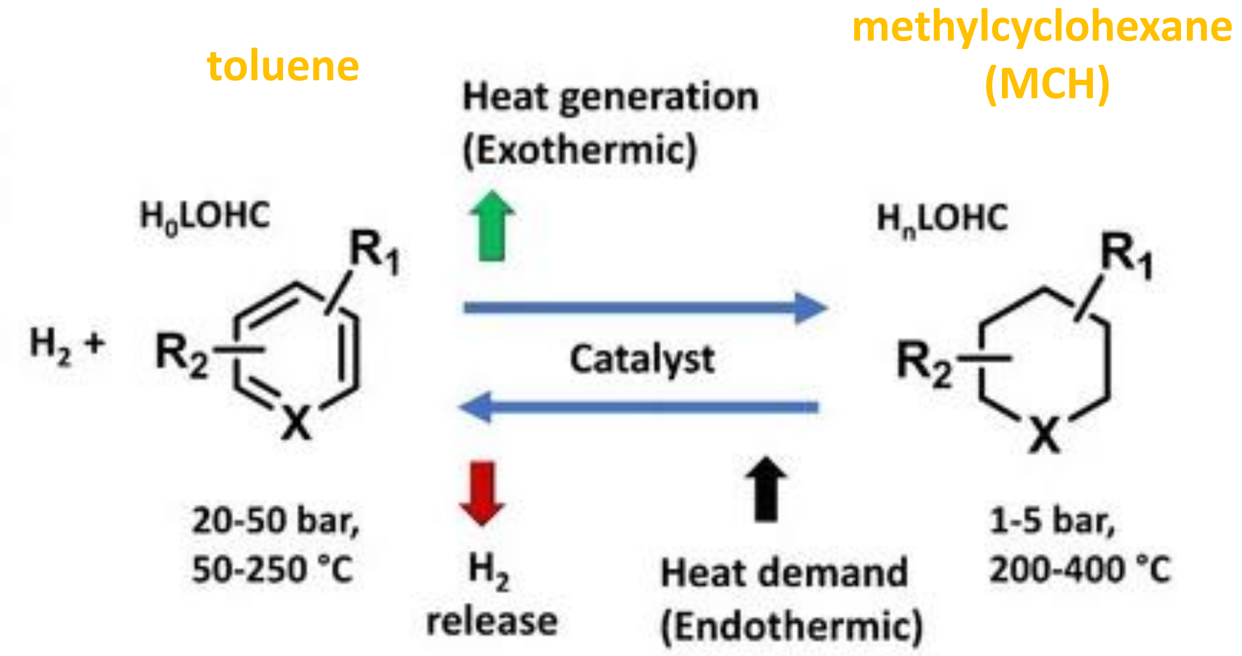
- $LaNi_5$ has been studied for a long time.
- It can operate in ambient conditions.
- easy activation
- $CaCu_5$ structure
- storage capacity : ~1.5 wt%
- hydrogenation at ambient : ~ 3 bar
- dehydrogenation at ambient : ~2 bar

Ref:Sato et al., “Hydrogen Absorption Reactions of Hydrogen Storage Alloy LaNi5 under High Pressure” (2023).



Well defined wide and flat plateau region

Liquid Organic Hydrogen Carriers

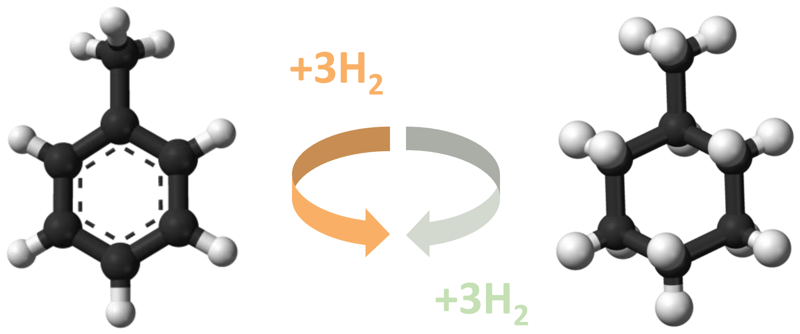


- **LOHCs are organic compounds that reversibly absorb and release H_2**
- **chemically stable – easy to handle**
- **the hydrogenation and dehydrogenation reactions require different conditions, use different catalysts, and operate in different reactors**

Toluene-MCH LOHC

toluene

methylcyclohexane (MCH)



C_7H_8 C_7H_{14}

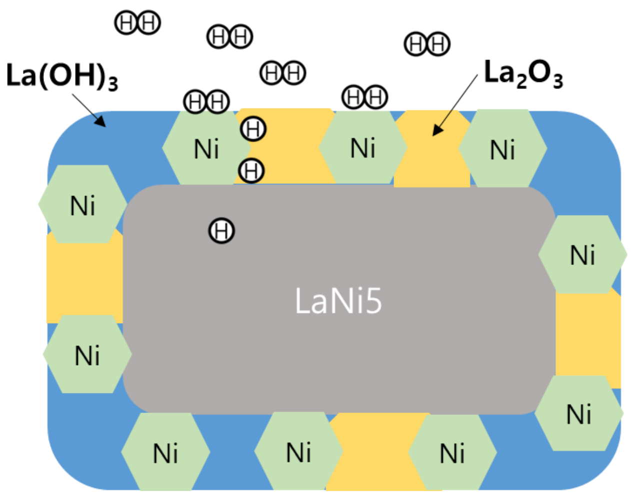
Catalysts	Conditions
Ni/Al_2O_3	150-210°C
Ni/C	290°C
Ru	30°C
Ir/Al_2O_3	60°C
Pt/zeolite	120°C
MoC	200°C
Ni-Co-Mo/zeolite	200°C

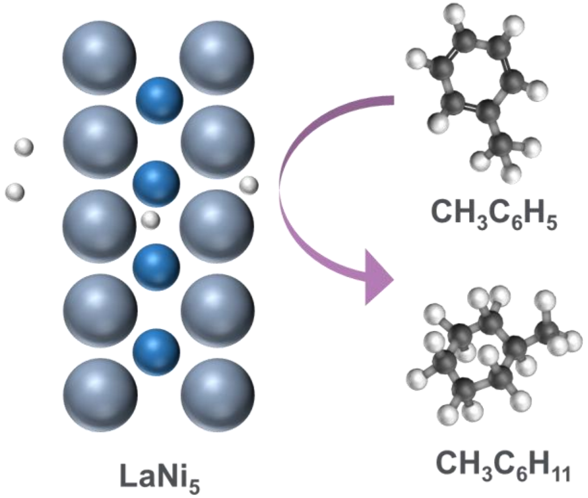
- **The benzene ring composes of alternating carbon double bonds & single bonds.**
- **adds 6 hydrogen atoms**
- **storage capacity : 6.2 wt%**
- **one of the best-known LOHC pairs**

- **either costly or the fabrication process is tedious**
- **how about metal hydrides?**

Could a metal hydride be used as a catalyst for the LOHC hydrogenation reaction?
(Could LaNi5 be used as a catalyst for toluene hydrogenation reaction?)

LaNi$_5$ as a Dual Purpose Storage Material





ACS APPLIED MATERIALS & INTERFACES
Research Article
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Thermochemical Energy Storage through De/Hydrogenation of Organic Liquids: Reactions of Organic Liquids on Metal Hydrides

Ulrich Ulmer,[*,†] Martin Cholewa,[‡] Thomas Diemant,[§] Christian Bonatto Minella,[†] Roland Dittmeyer,[‡] R. Jürgen Behm,[§] and Maximilian Fichtner[†]

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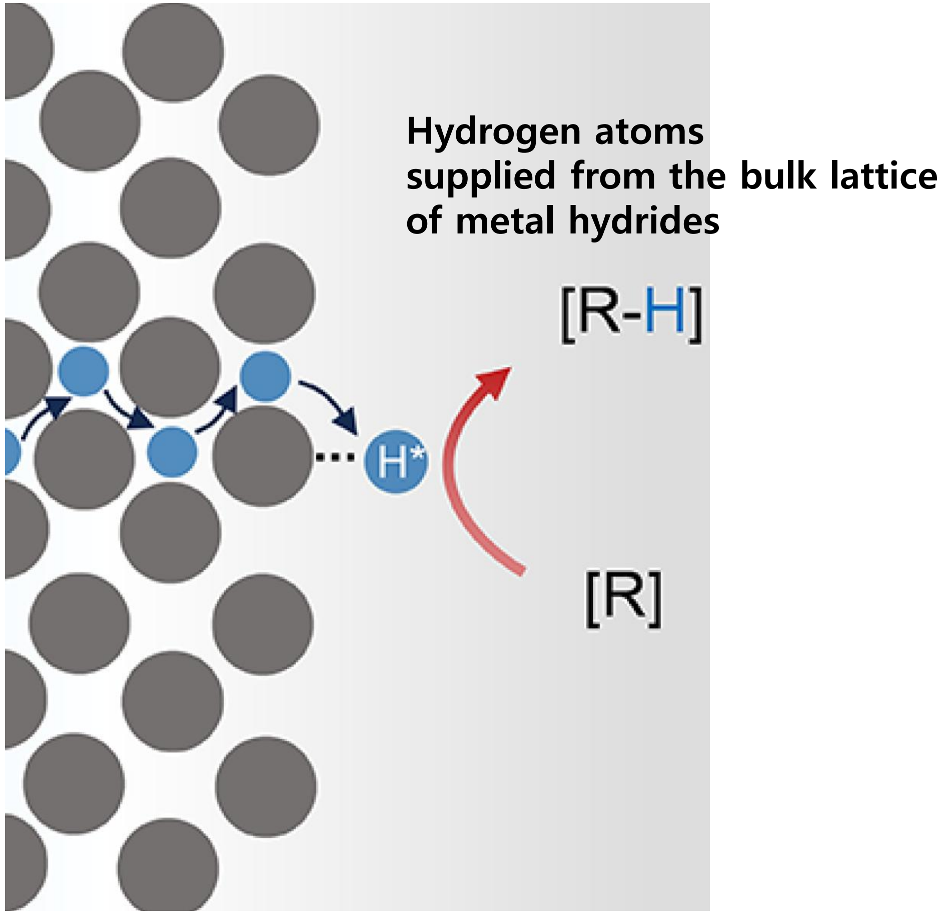
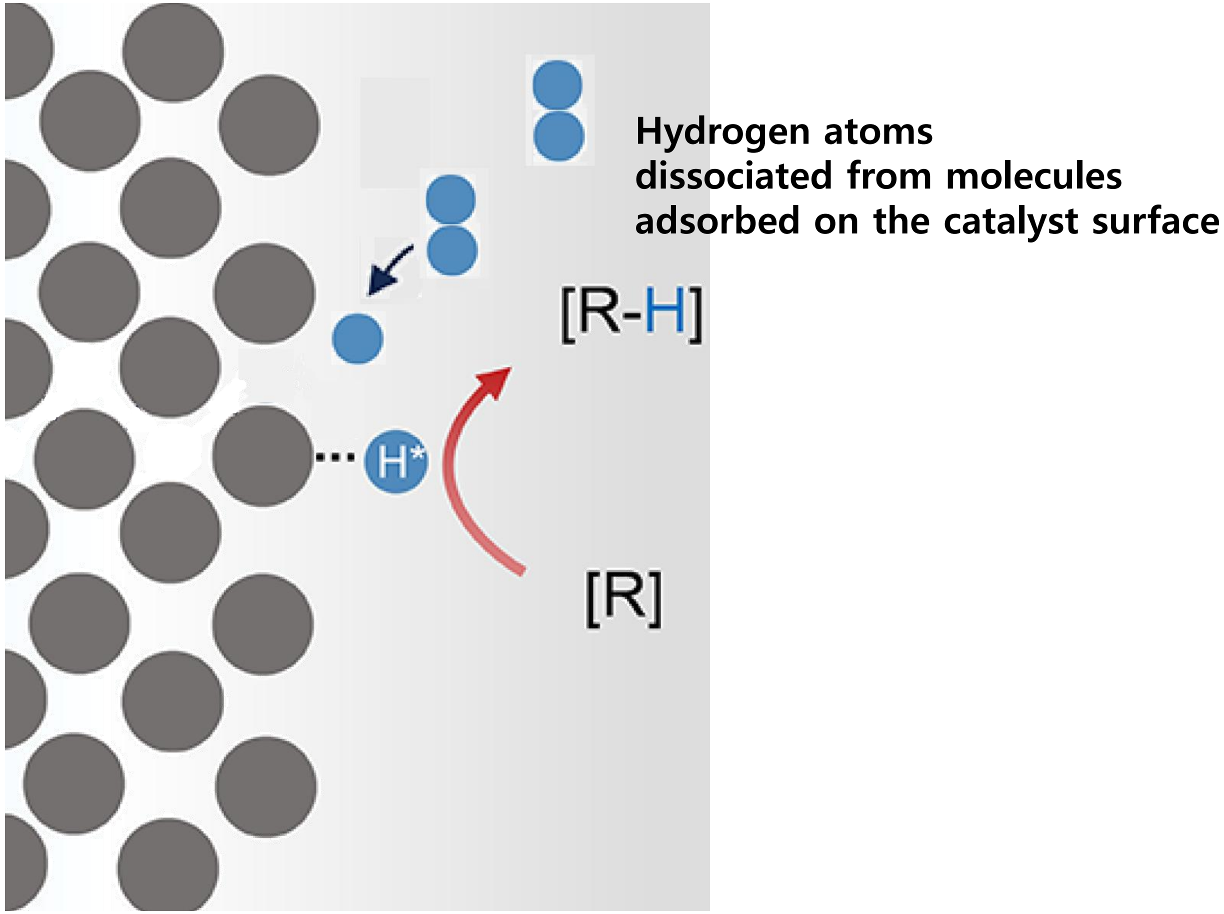
- compared AB (TiFe), AB$_2$ (Ti$_{0.95}$Zr$_{0.05}$Mn$_{1.49}$V$_{0.45}$Fe$_{0.06}$), and AB$_5$ (LaNi$_5$)
- XRD results – only LaNi$_5$ does not show hydride peaks
- no carbonaceous species on LaNi$_5$ surface
- LaNi$_5$ is not passivated by toluene.
  (The passivation layer blocks absorbed H atoms from desorption)

At the outermost surface of LaNi$_5$,
the La tends to oxidize while Ni forms some metallic clusters,
which we expect to provide a certain level of catalytic activity.

Key difference: Conventional vs. Metal Hydride Catalysts





We expect not only the catalytic effect from the metallic Ni clusters on the surface of $LaNi_5$, but also that the atomic hydrogen absorbed inside $LaNi_5$ would directly contribute to the hydrogenation of external compounds.

H_2 Solubility in Toluene & MCH

Procedures

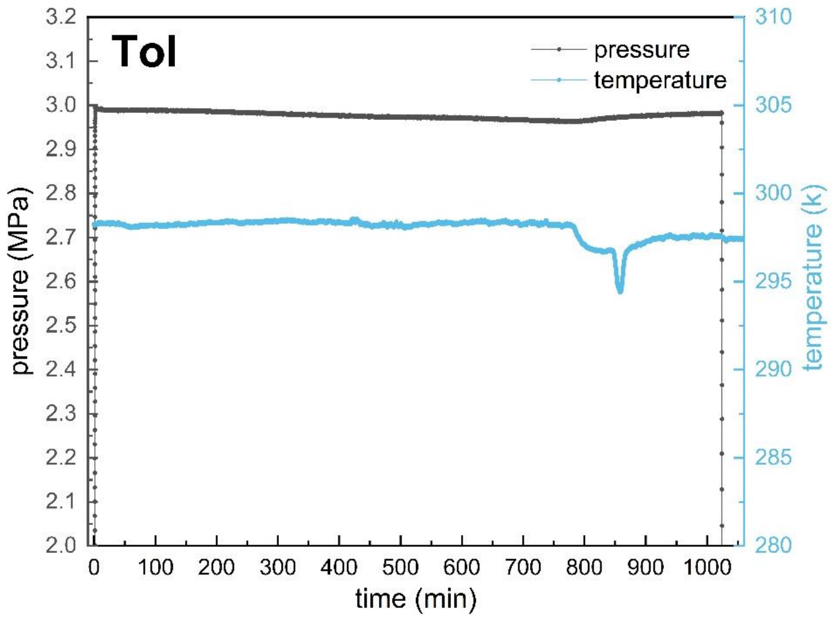
Toluene/MCH: 6.5 g

⬇

Hydrogenation
3 MPa, 17 hrs

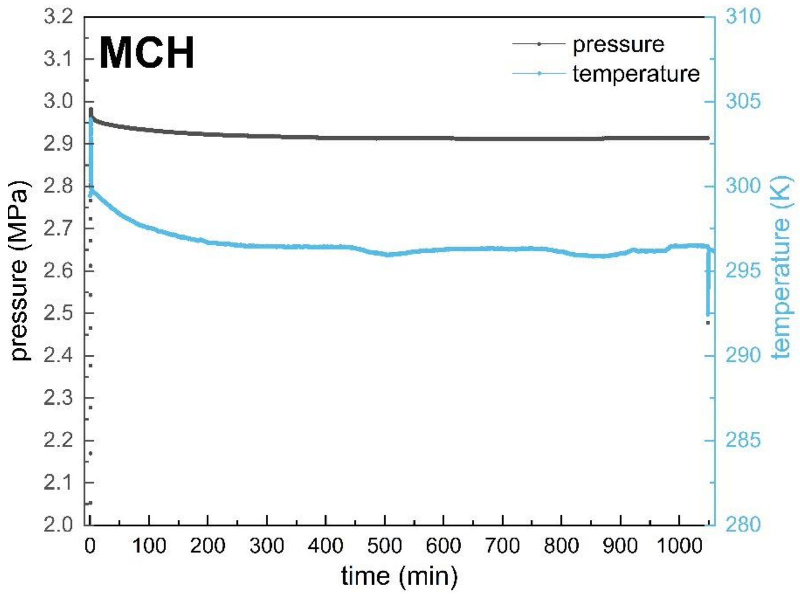
⬇

vent



2.997 MPa at 298 K → 2.983 MPa at 297 K
0.0003 mol H_2 dissolved

literature : **0.0007** mol



2.964 MPa at 299 K → 2.914 MPa at 296 K
0.0006 mol H_2 dissolved

literature : **0.0009** mol

No significant amount of hydrogen dissolution was observed.

$LaNi_5$ Hydrogenation under Tol & MCH

Procedures

$LaNi_5$: 5.0 g
Toluene/MCH: 6.5 g

⬇

$LaNi_5$ Activation 5 times
vacuum – H_2 30 bar – 30 min - vent

⬇

Toluene/MCH Insertion

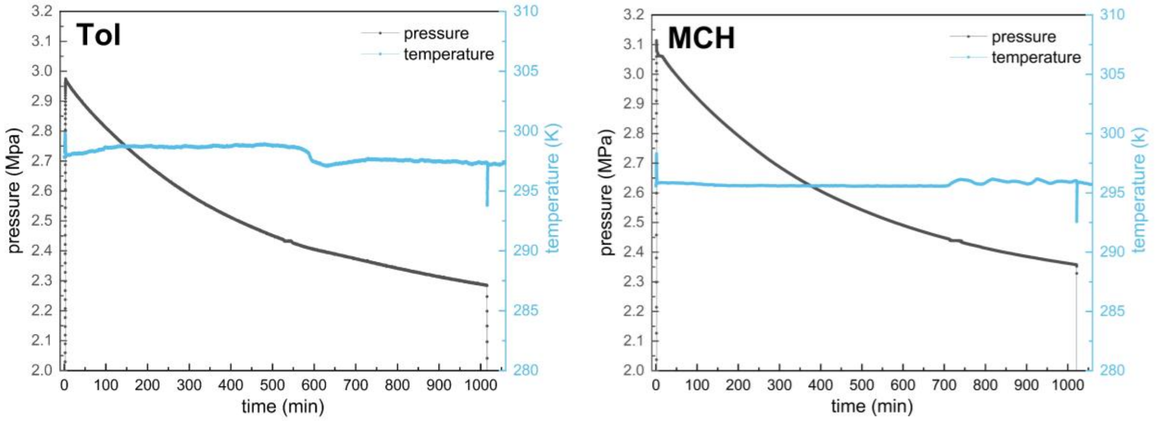
⬇

Hydrogenation
3 Mpa, 17 hrs

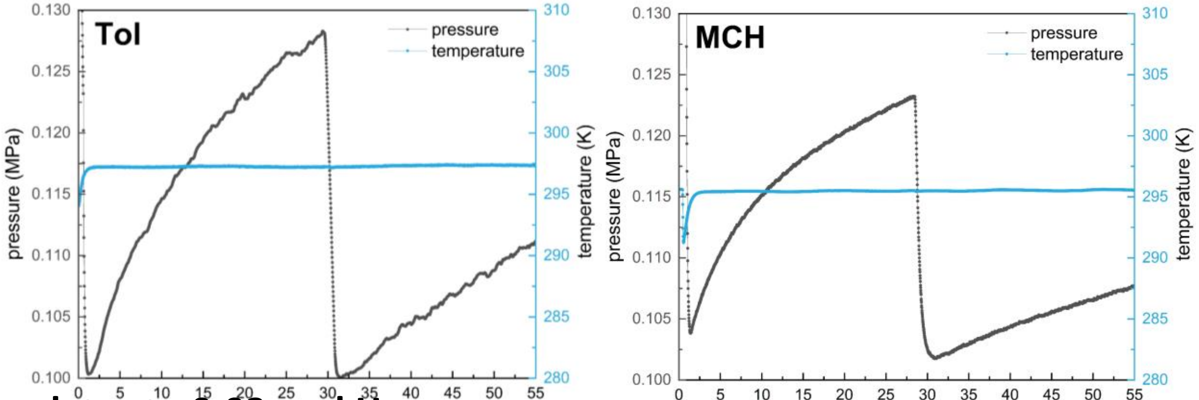
⬇

vent

Hydrogenation Curves



Post Dehydrogenation Curves

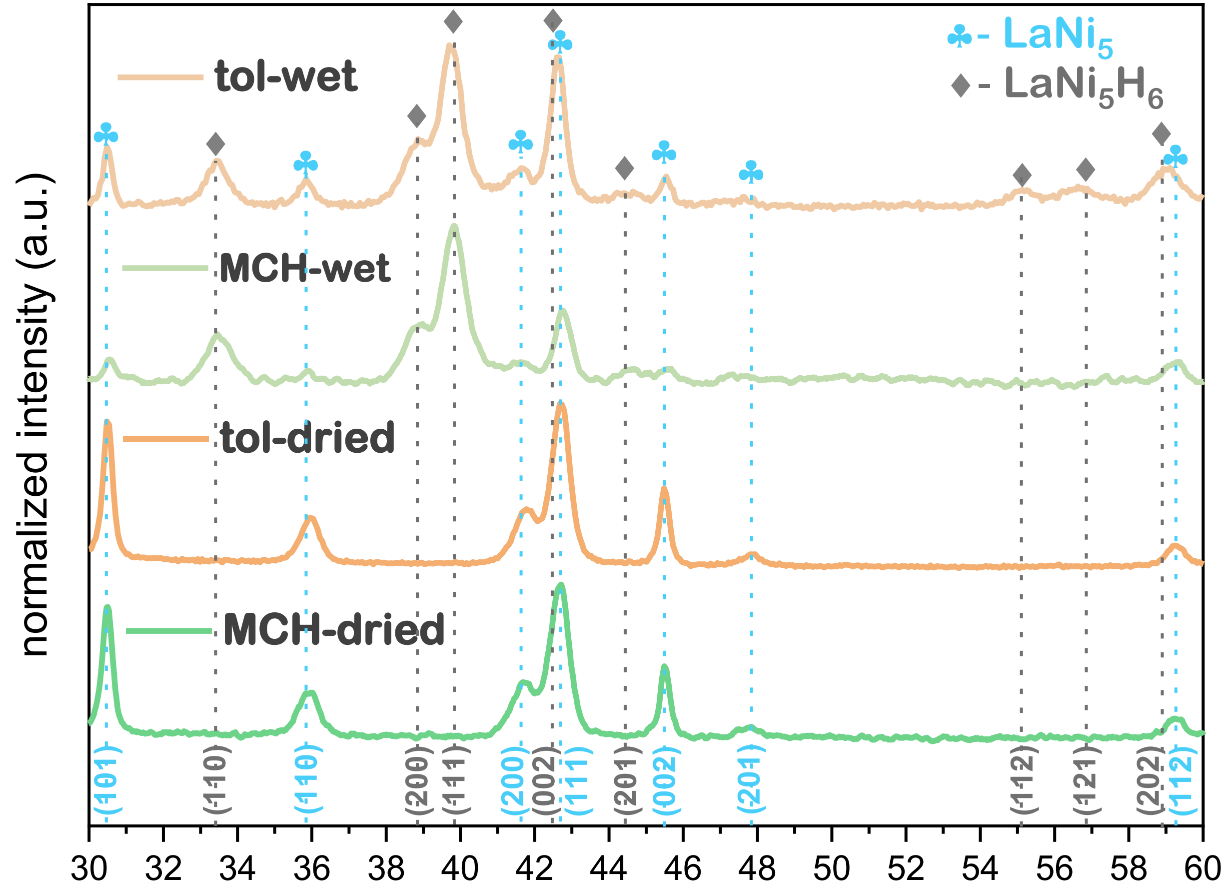


- **In both cases, ~0.7 Mpa drop was observed, which translates to 0.03 mol H_2**
- **The post dehydrogenation curves show that hydrogen can be desorbed from $LaNi_5$ even when immersed in tol/MCH.**

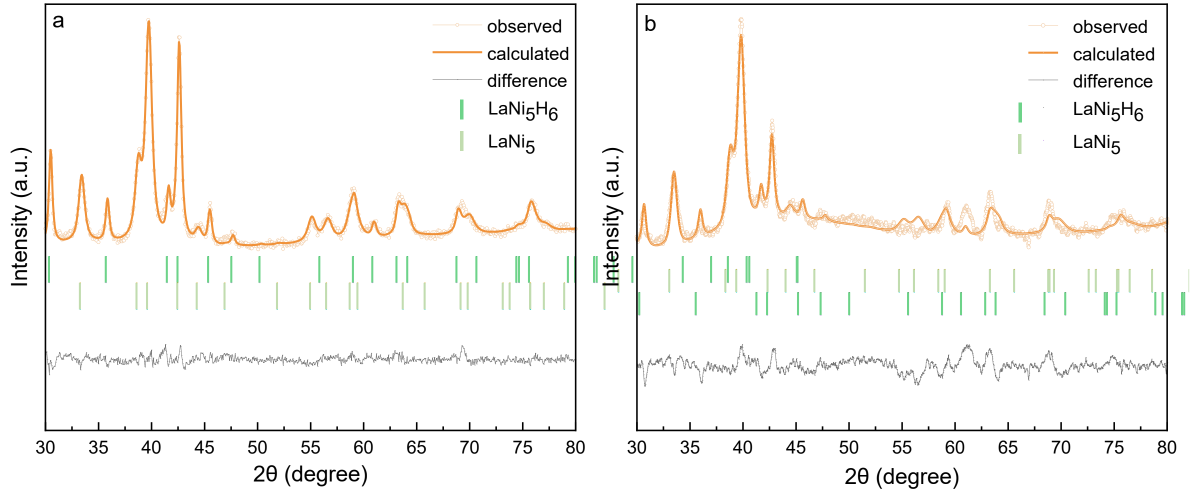
Hydrogen absorption and desorption take place even when LaNi5 is fully immersed in Toluene or MCH.

XRD Profiles after the Immersion

XRD Profiles of the Wet and Dried $LaNi_5$



Rietveld Refinement of $LaNi_5$



Toluene	**MCH**
solid solution : 28.85 %	solid solution : 25.35 %
hydride : 71.15 %	hydride : 74.65 %

Hydride phase disappeared during drying.

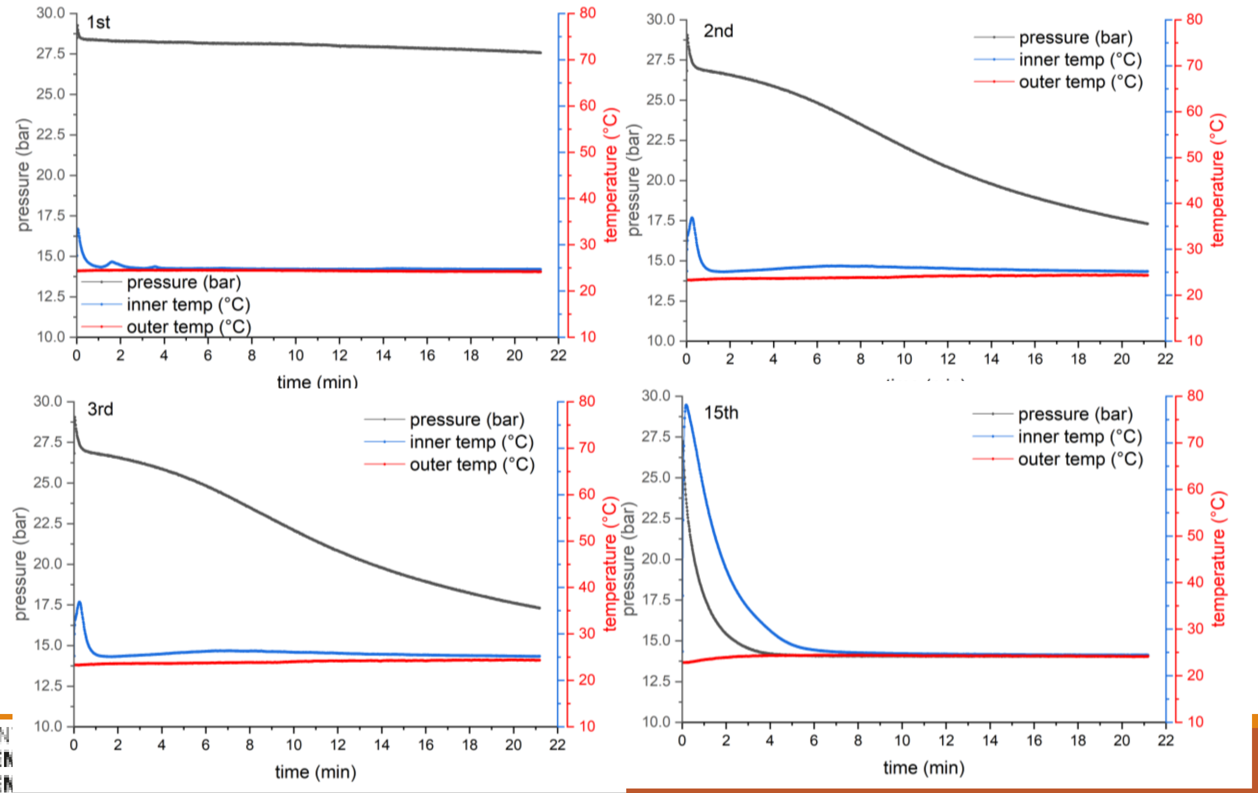
After hydrogenation in toluene or MCH,
$LaNi_5$ powder was collected and XRD was taken both in the
(i) solvent-wet state and (ii) again after complete drying.

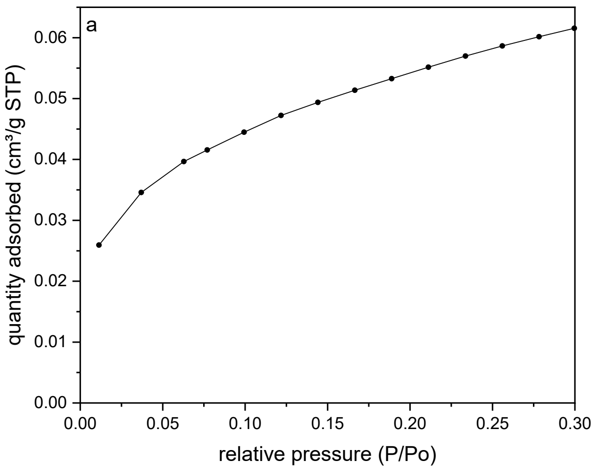
Hydrogen absorption and desorption take place even when LaNi5 is fully immersed in Toluene or MCH.

Catalyst Preparation by Cycling

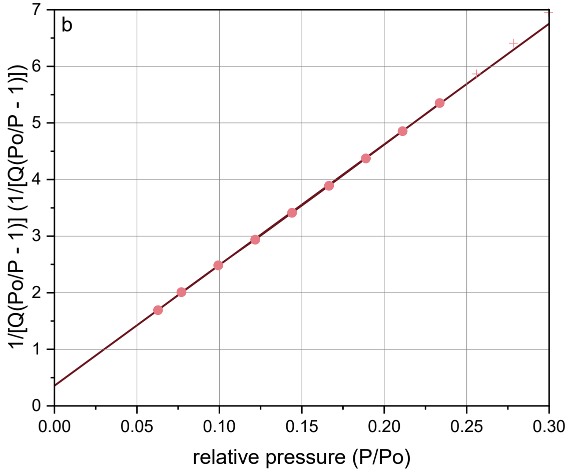
Size Control Method

1) 12 g of $LaNi_5$ is first loaded into a reactor connected to a custom-made cycling device.
2) 15 hydrogenation - dehydrogenation cycles at 3 Mpa are performed.
3) The sample is sieved with a 32 μm sieve.

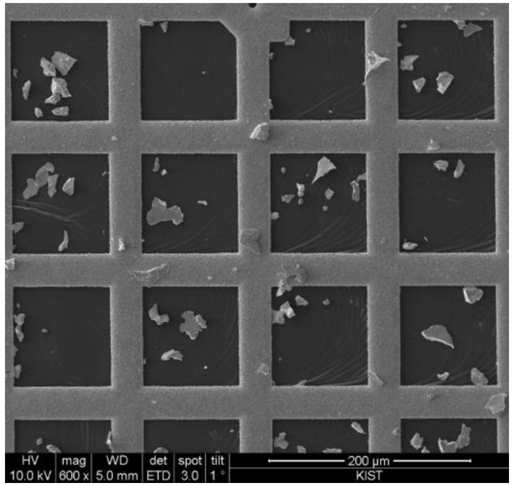




BET Isotherm Linear Plot



BET Surface Area Plot



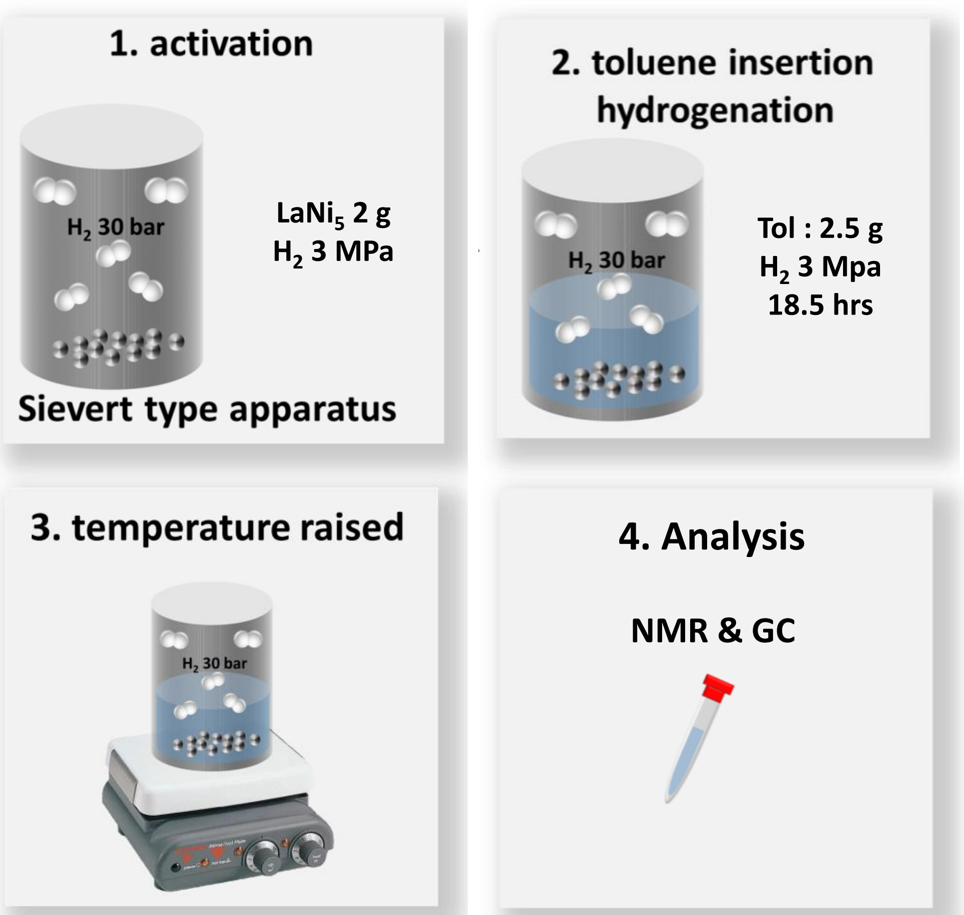
SEM Image

SEM diameter 10.2±7.05 μm
BET diameter 3.8 μm

1 μm 10 μm 30 μm

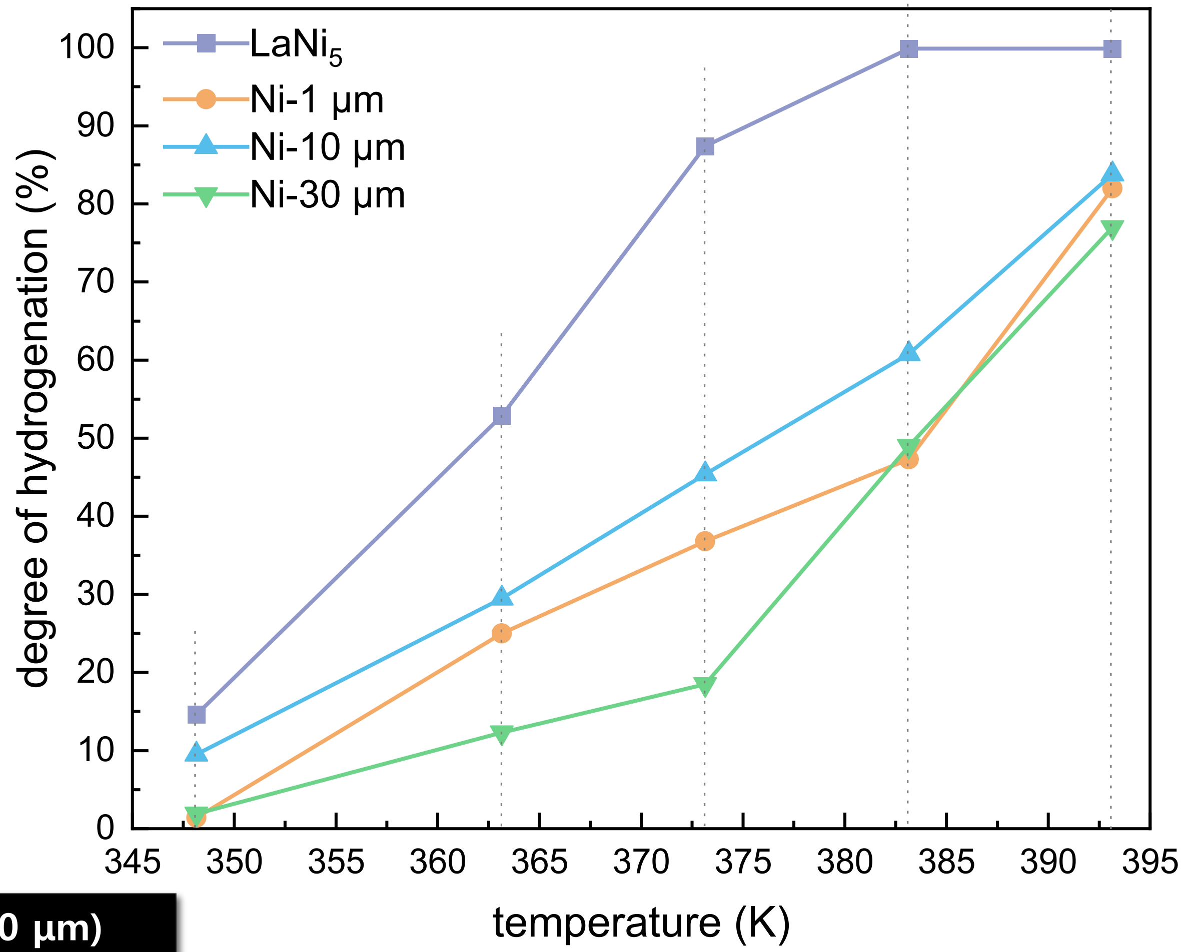
Ni particles for comparison

$LaNi_5$ vs Ni



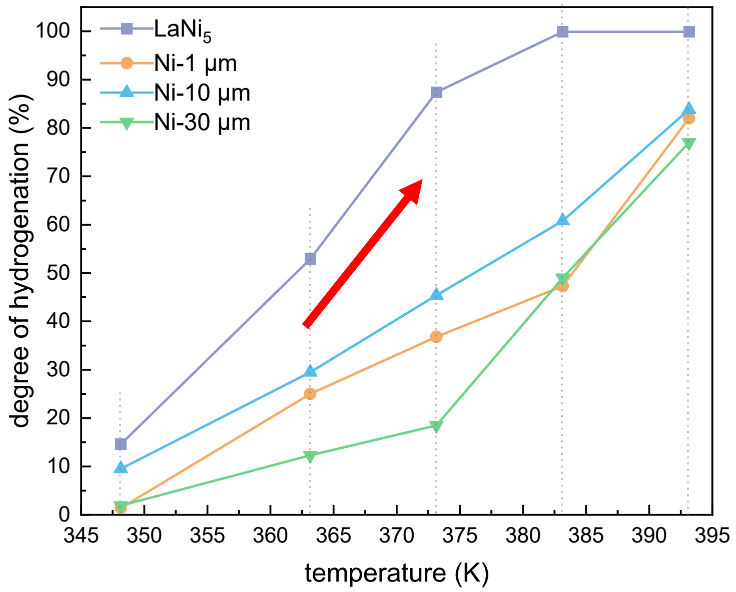
42.5 hours
at reaction temp.

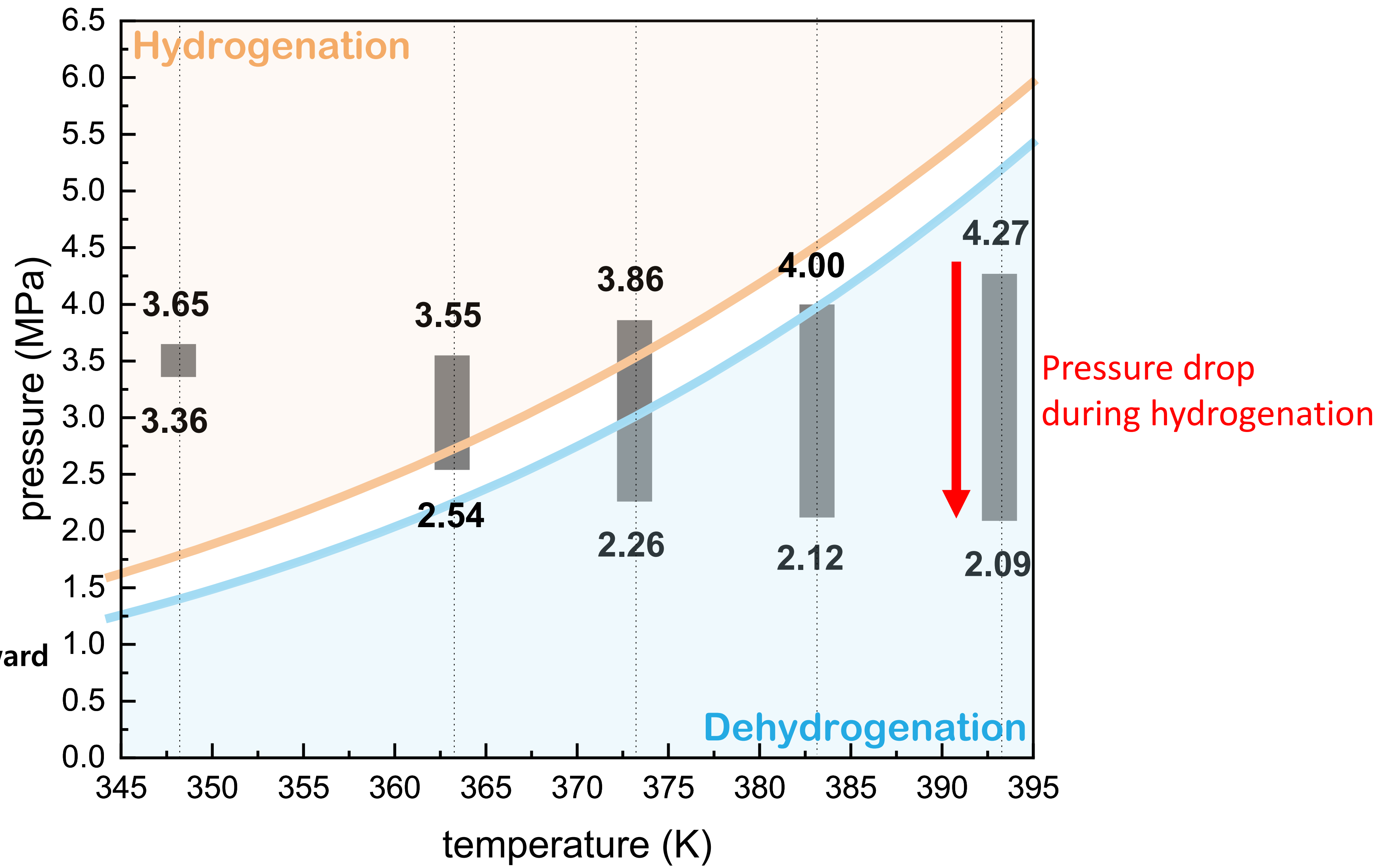
Pure Ni particles (1, 10, and 30 µm) were tested under identical conditions to compare with LaNi5 (~10 µm)



Selectivity : 0.999 ± 0.002

Experiment Conditions



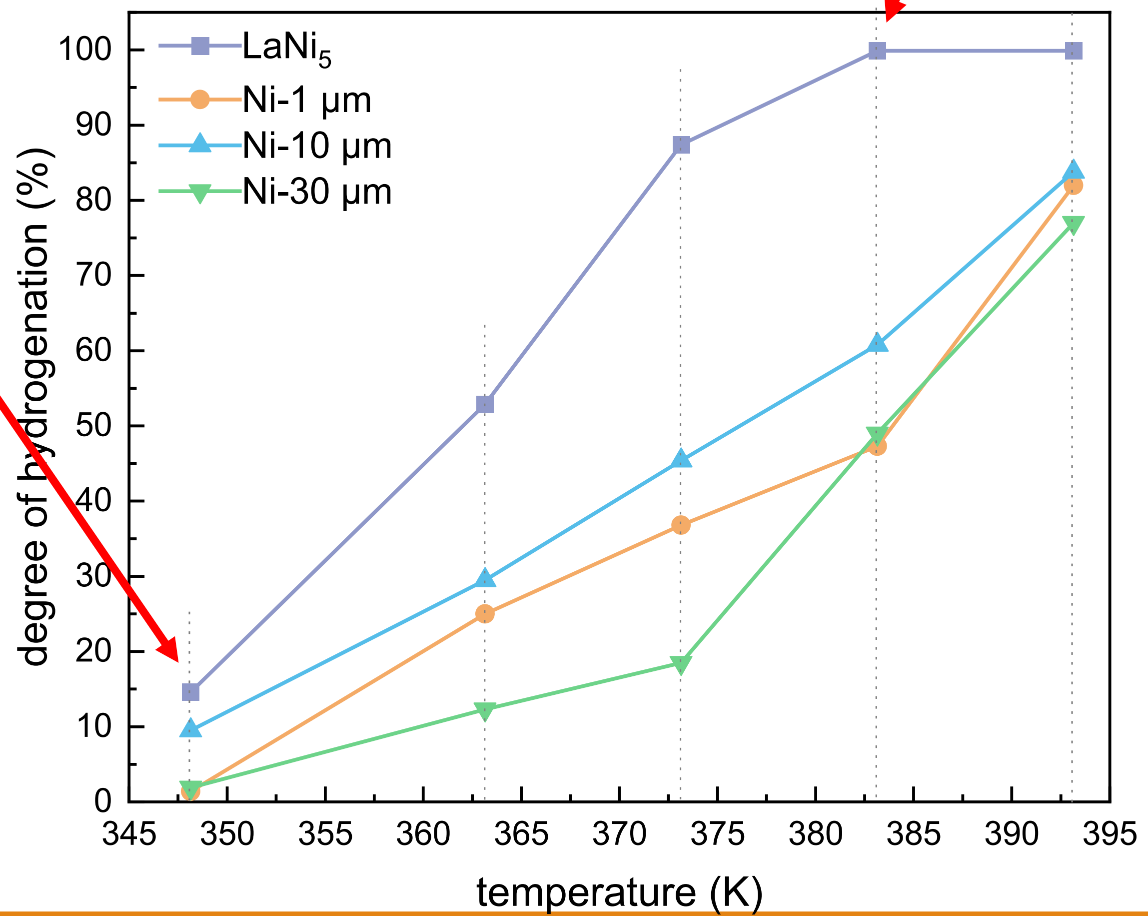


The conversion increase is driven not only by thermal activation but also by the metal hydride shifting toward a dehydrogenation-dominant regime at higher temperatures.

$LaNi_5$ vs Ni

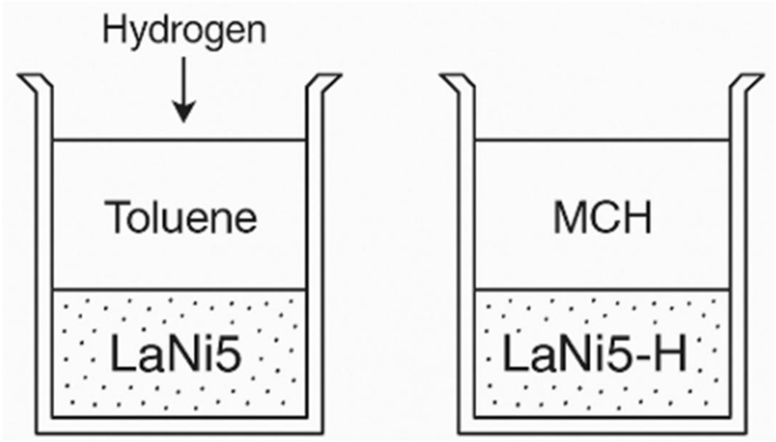
H2 stored in LaNi5: 0.024g
H2 disappeared by pressure drop: 0.023g
H2 consumed to convert Toluene to MCH: 0.024g
➔ Hydrogen stored in LaNi5H6 was not utilized during the reaction

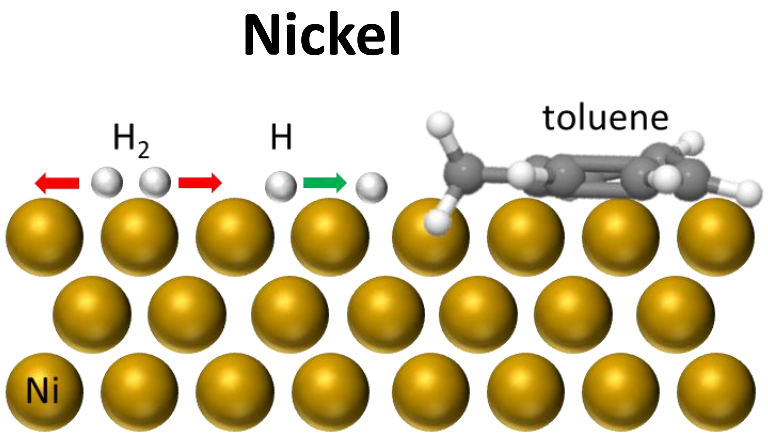
H2 stored in LaNi5: 0.024g
H2 disappeared by pressure drop: 0.134g
H2 consumed to convert Toluene to MCH: 0.164g
➔ the hydrogen stored in LaNi5 is supplied to toluene, enabling its complete conversion to methylcyclohexane

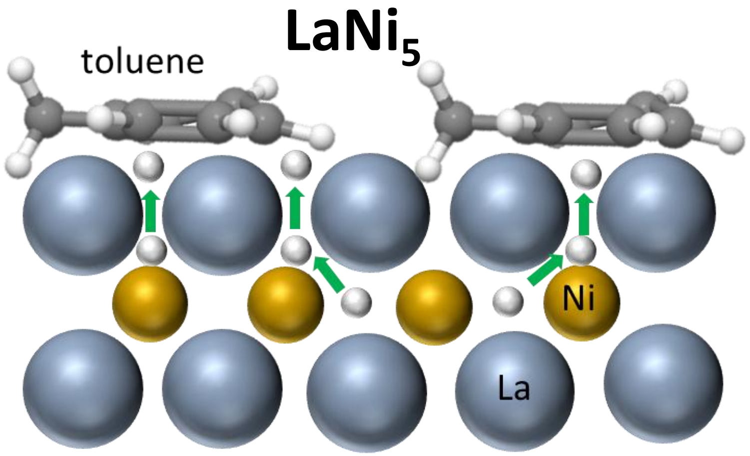


Summary

1. **Successfully demonstrated the proof-of-concept: when $LaNi_5$ was immersed in toluene under hydrogen pressure, both $LaNi_5$ and toluene were hydrogenated.**
2. **At 383 K, $LaNi_5$ achieved a 99.9 % conversion of toluene to MCH with an excellent selectivity of 99.9 % (GC).**
3. **$LaNi_5$'s catalytic performance is closely linked to its dual functionality: its hydrogen storage capability and unique surface properties. During the catalytic reaction, $LaNi_5$ acts as a hydrogen reservoir, storing atomic hydrogen and providing additional bonding sites to facilitate the hydrogenation process.**







Thank You for Your Attention.

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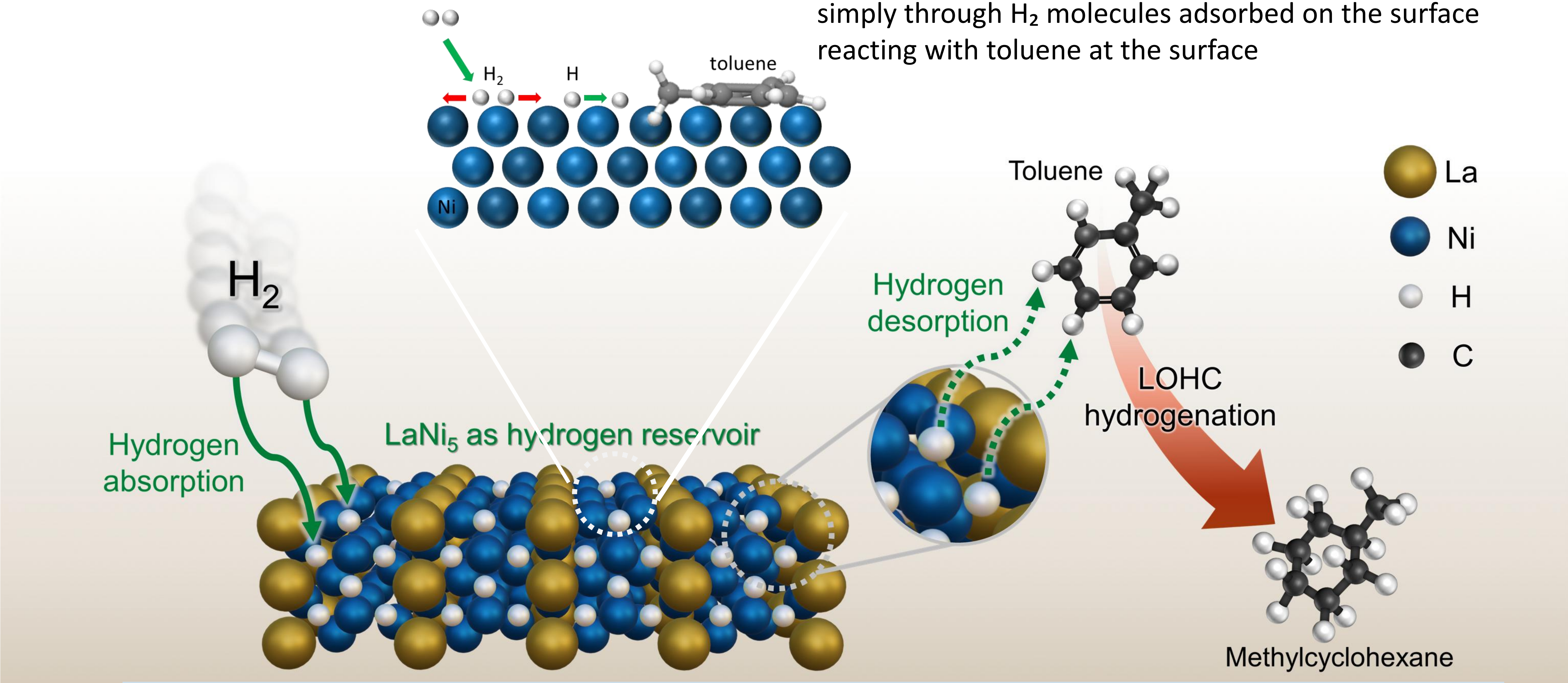
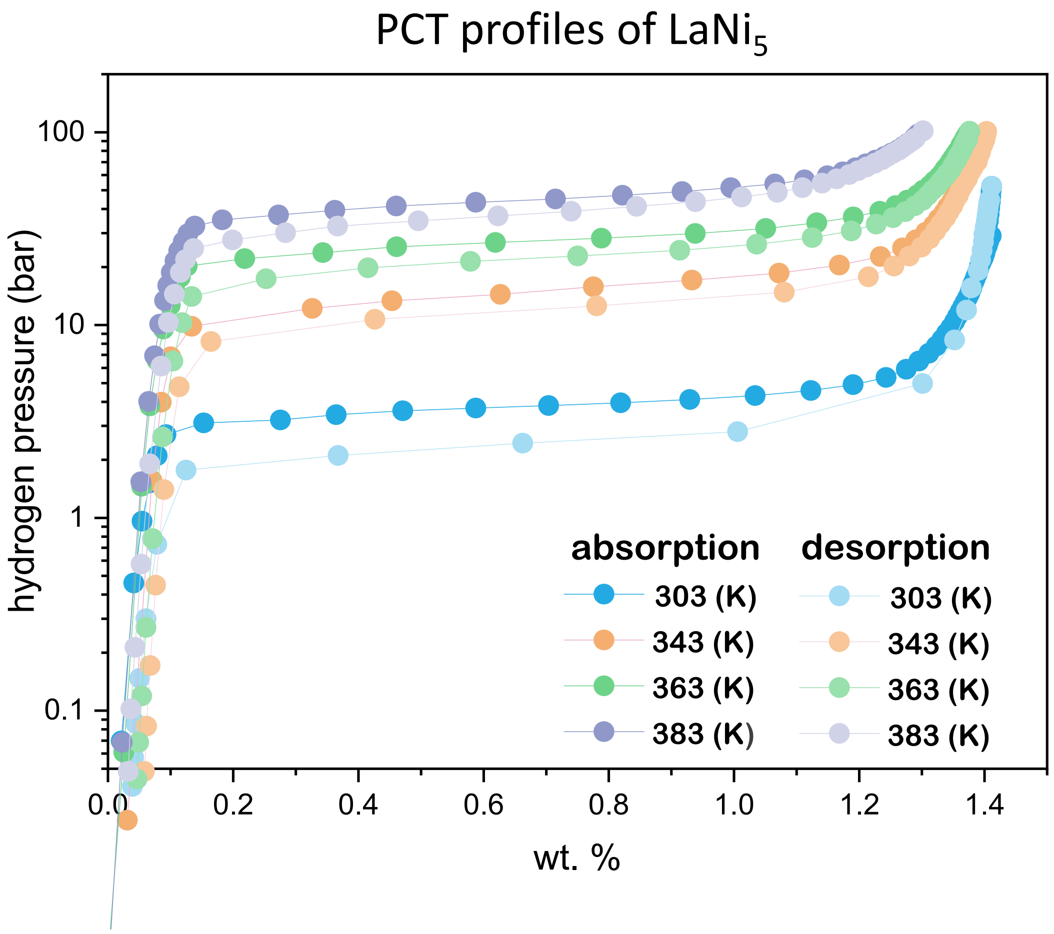
Study Concept

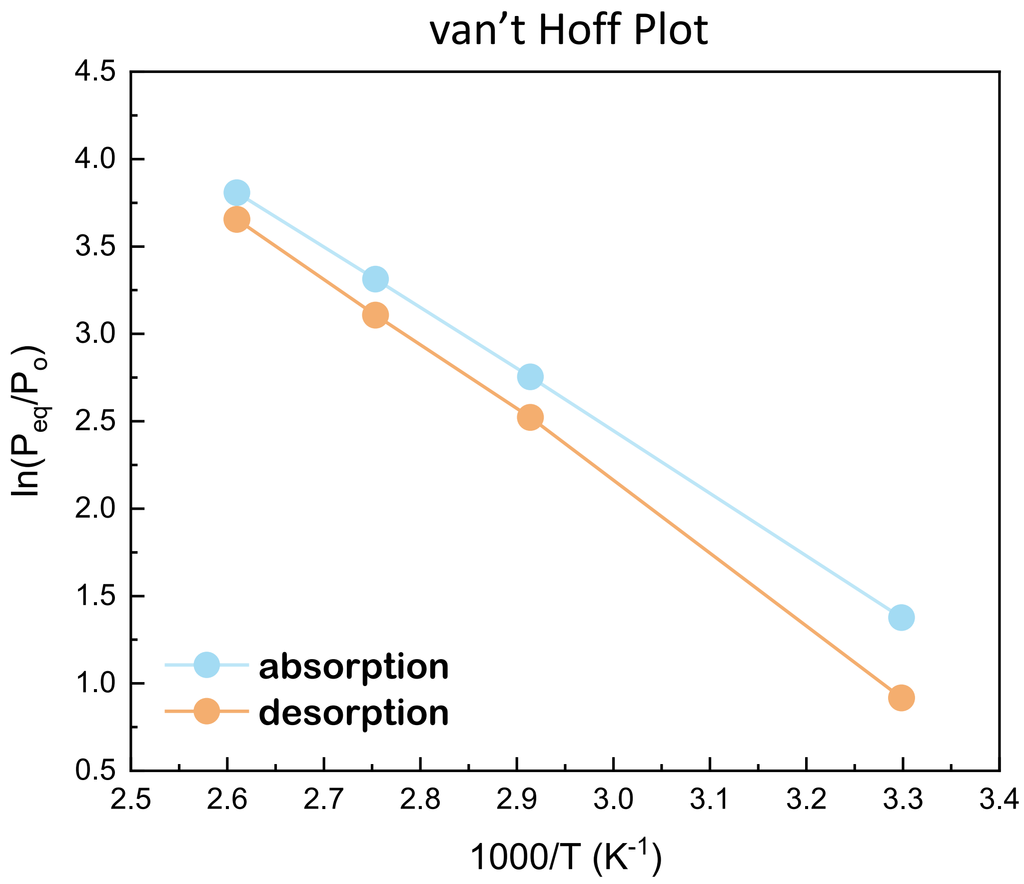
hydrogenation of toluene can occur
simply through H_2 molecules adsorbed on the surface
reacting with toluene at the surface



the atomic hydrogen absorbed inside $LaNi_5$ contributes directly to the hydrogenation of toluene

PCT Curves





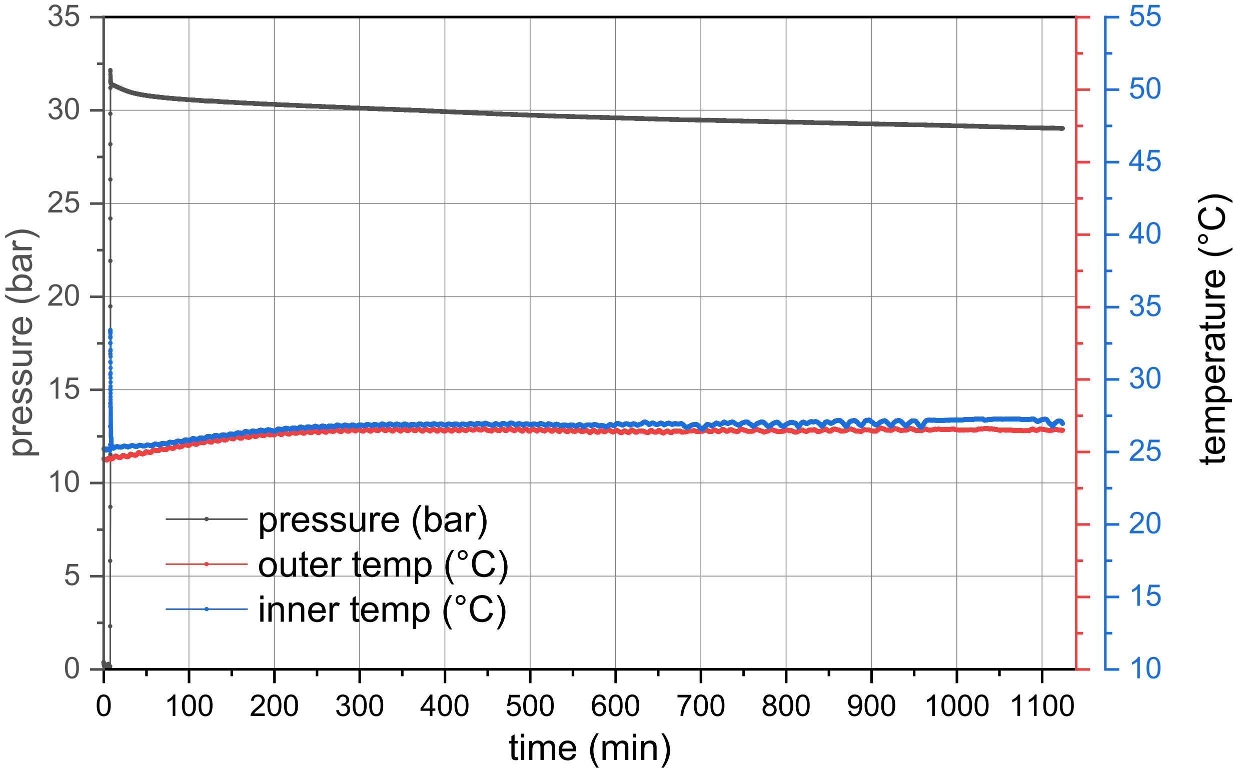
y = -3.98 x + 14.07 for absorption (R^2 = 0.99)

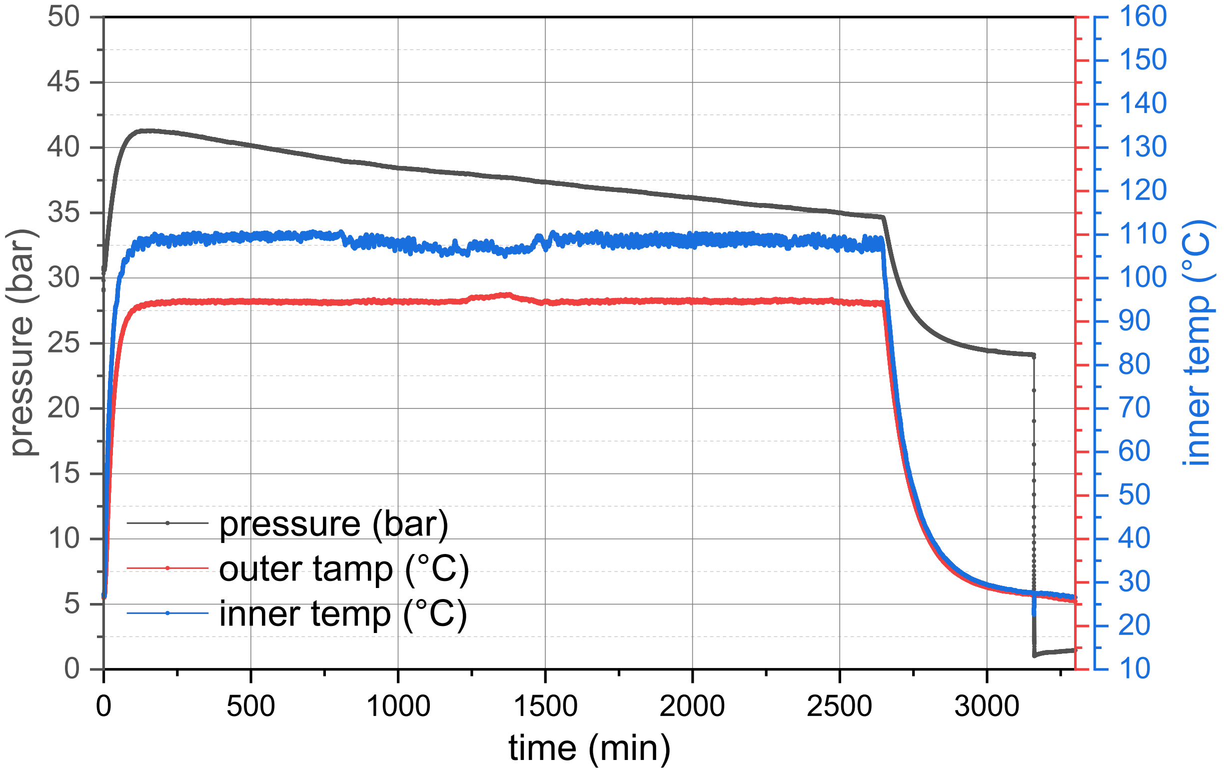
ΔH = −33.1 kJ mol^{-1}
ΔS = -117 J $mol^{-1}K^{-1}$

y = -3.54 x + 13.05 for desorption (R^2 = 0.99)

ΔH = 29.4 kJ mol^{-1}
ΔS = 109 J $mol^{-1}K^{-1}$

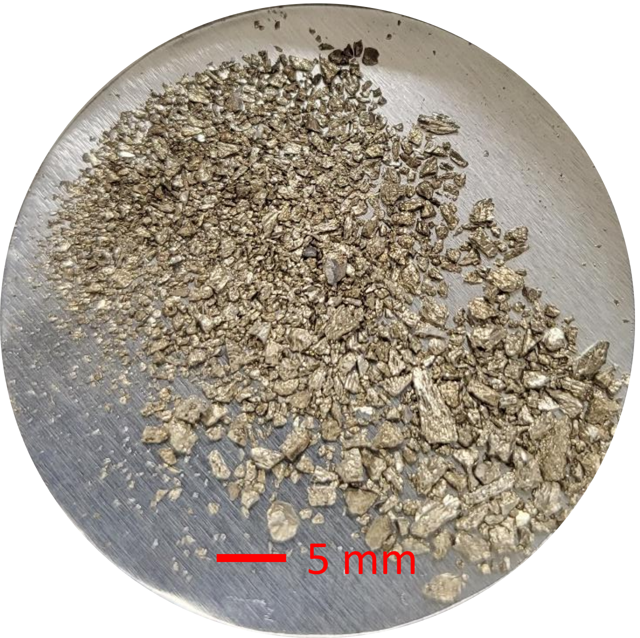
III. Toluene Insertion & Catalysis





The Morphology of $LaNi_5$ Particles after Hydrogenation

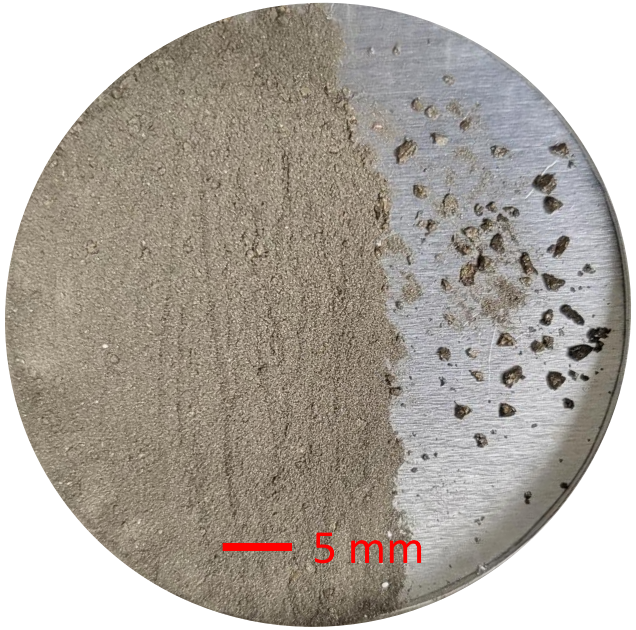
0 CYCLE



10 CYCLES

20 CYCLES

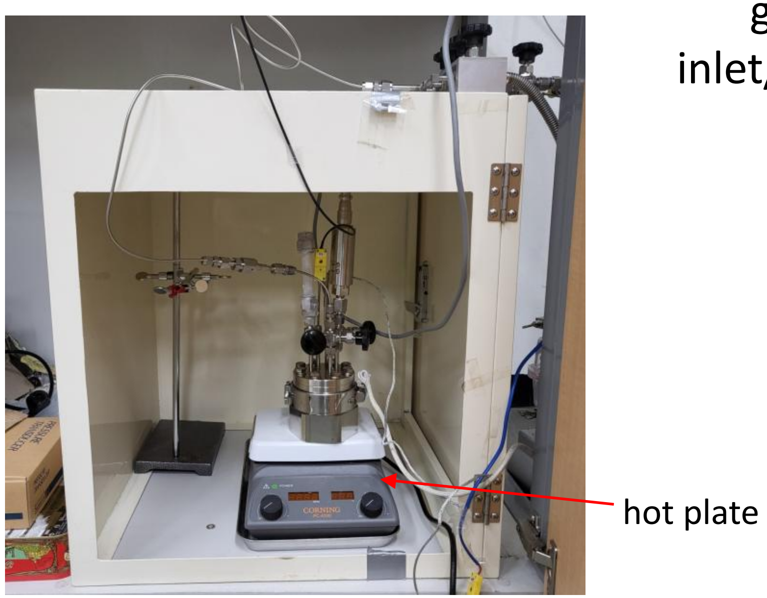
30 CYCLES



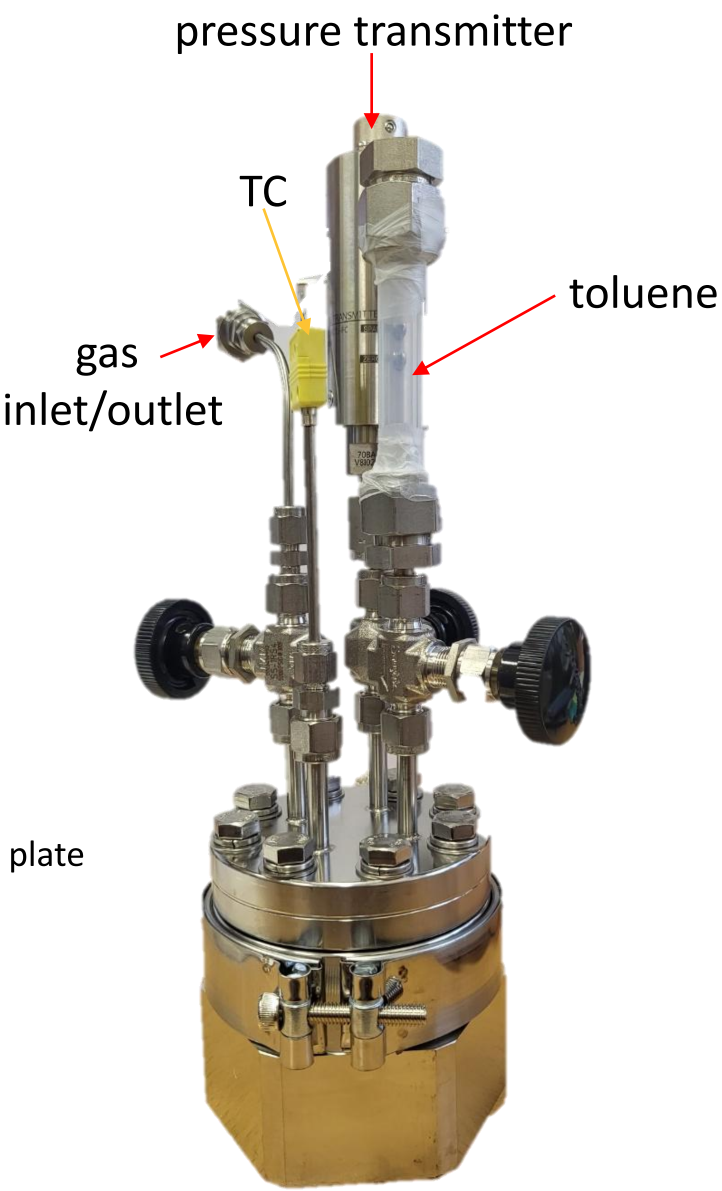
The Experiment Set UP

$LaNi_5$: 2.0 g

2.5 g of Toluene is inserted inside the glove box to prevent oxygen contamination.



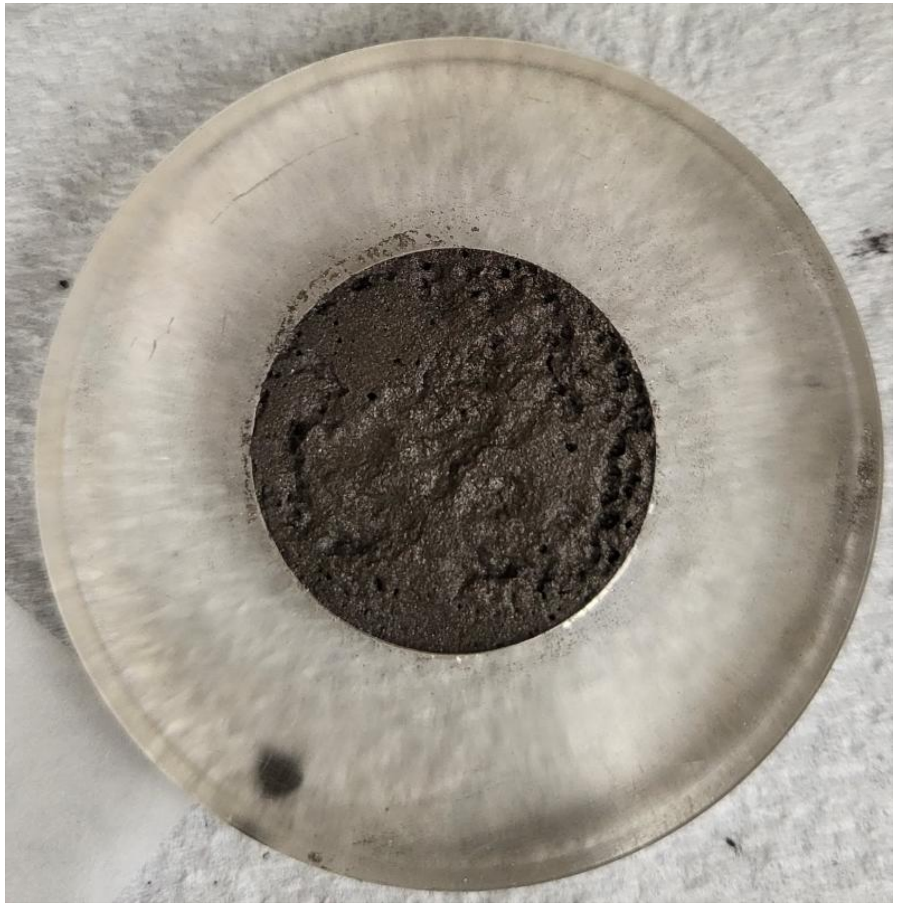
The Experiment Set Up



The Reactor

XRD of Toluene Immersed $LaNi_5$

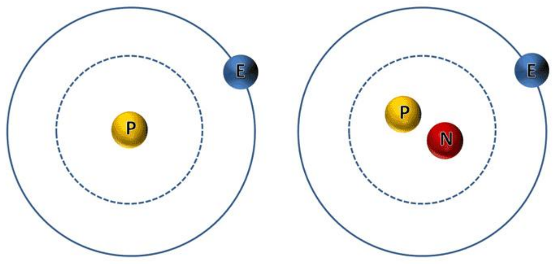
right after the experiment



XRD patterns of LaNi5 immersed in Toluene were obtained

Isotope Labelling Experiment

Hydrogen Isotopes



H
Hydrogen

D
Deuterium

1.0078 amu

2.0014 amu

Procedures

$LaNi_5$: 2.0 g
Toluene/MCH: 6.5 g

↓

$LaNi_5$ Activation 5 times
vacuum – **D_2 30 bar** – 1 hr – vent up to 15 bar

↓

Reactor Frozen to -60°C

↓

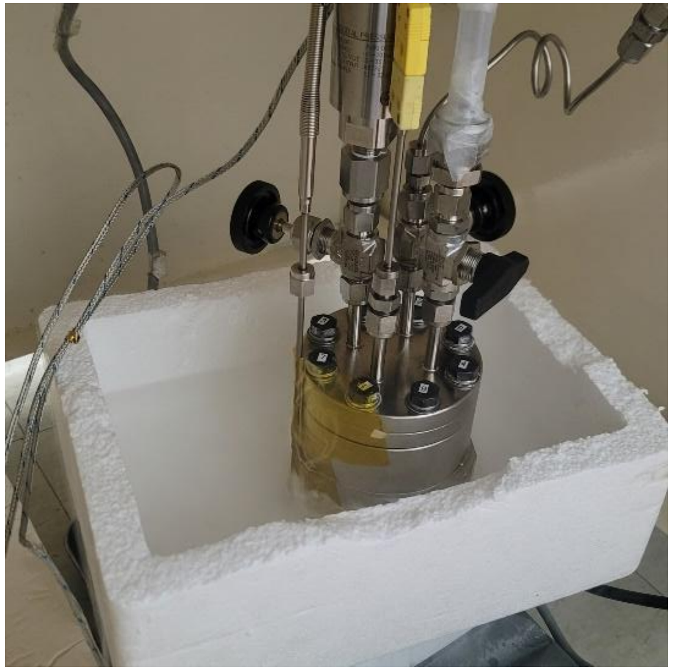
Vacuum + Toluene Insertion

↓

Toluene Hydrogenation
H_2 30 bar (ambient temp), raise temp to 120°C, maintain it for 42.5 hrs.

↓

Cooling and Venting



Isotope Labelling Experiment

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Promoting hydrogen absorption of liquid organic hydrogen carriers by solid metal hydrides†

Yong Wu, Hongen Yu, Yanru Guo, Yuxuan Zhang, Xiaojing Jiang, Bingxue Sun, Kai Fu, Jun Chen, Yue Qi, Jie Zheng * and Xingguo Li *

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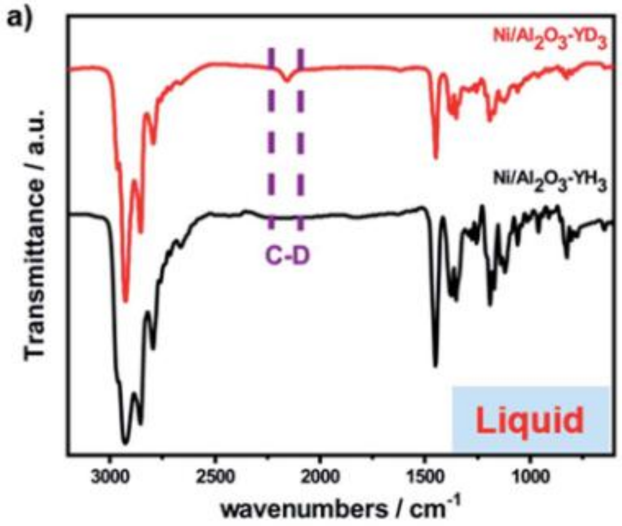
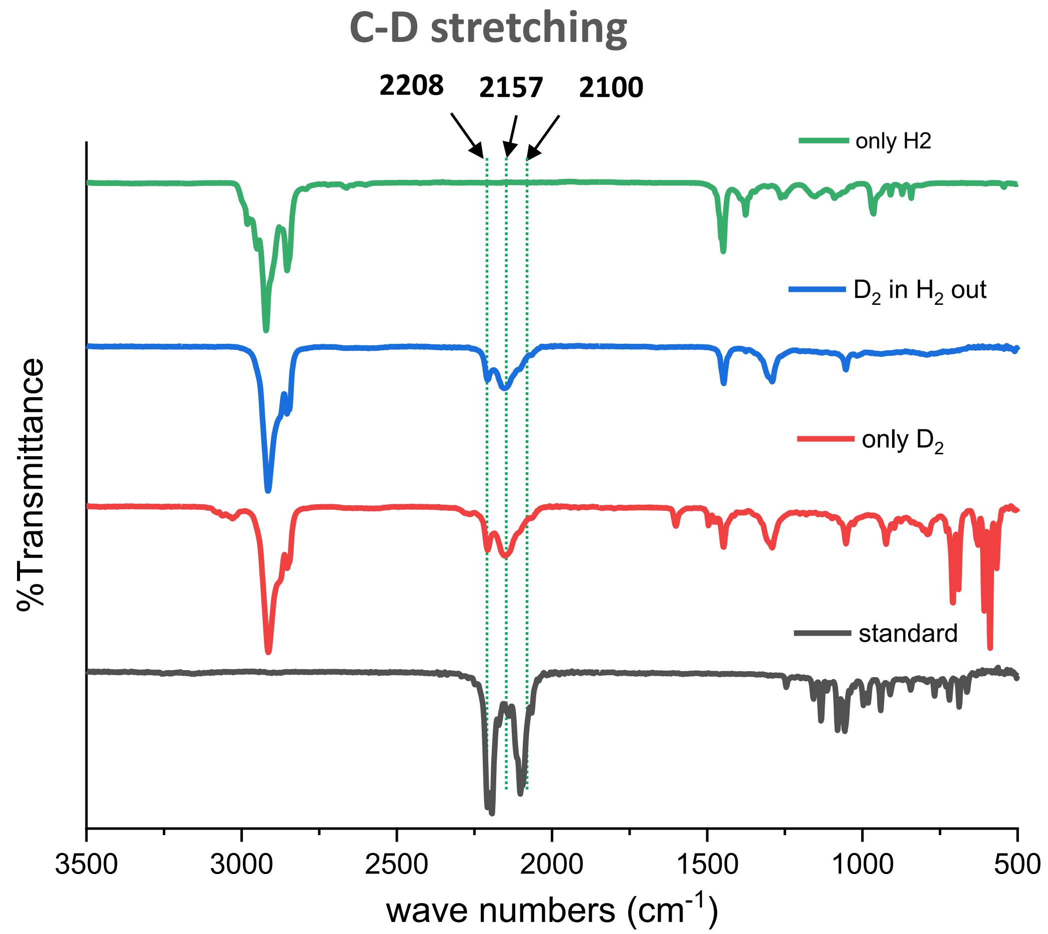
rsc.li/materials-a

analyzed. In the liquid product (12H–NEC, Fig. S7†), the peak at 2160 cm^{-1} in the FT-IR spectra (Fig. 2a) is the characteristic of C–D stretching, which is absent when YH_3 is used as the additive. Mass spectroscopy indicated that there was no D_2 or HD in



FTIR Spectra of Deuterium Substituted Samples



$LaNi_5$ Hydrogenation Video

when a metal hydride material is first hydrided, it breaks into very fine particles

Recent works with similar concept

Hydrogenation and the dehydrogenation of Liquid Organic Hydrogen Carriers (LOHCs)

Nano Energy 80 (2021) 105476

Contents lists available at ScienceDirect

Nano Energy

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Full paper

LaNi$_{5.5}$ particles for reversible hydrogen storage in N-ethylcarbazole

Hongen Yu [a], Xue Yang [b], Xiaojing Jiang [a], Yiman Wu [b], Shunpeng Chen [a], Wei Lin [b], Yong Wu [a], Lei Xie [c], Xingguo Li [a], Jie Zheng [a,d,*]

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[c] Sunan Institute for Molecular Engineering, Peking University, Building 6, Xianshi Road No.88, Changshu Hi-Tech Industrial Development Zone, Jiangsu 215500, China
[d] Guangdong Provincial Key Laboratory of Advance Energy Storage Materials, South China University of Technology, Guangzhou 510640, China

Rare Met. (2025) 44(3):2118–2127
https://doi.org/10.1007/s12598-024-02941-0

RARE METALS

LETTER

Efficient hydrogen transfer carriers: hydrogenation mechanism of dibenzyltoluene catalyzed by Mg-based metal hydride

Hai-Yu Deng, Li-Jun Jiang*, Shao-Hua Wang*, Wen-Quan Jiang, Yuan-Fang Wu, Xiu-Mei Guo, Shu-Mao Wang, Lei Hao

Ammonia synthesis

Journal of Materials Chemistry A

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AB$_5$-type intermetallic compounds as catalysts for ammonia synthesis†

Xi Chen,[a] Yichen Duan,[a] Jing Wang,[a] Xinhai Yuan,*[a] Lili Liu,[a] Yuhui Chen,[a] Lijun Fu[a] and Yuping Wu*[ab]

International Journal of Hydrogen Energy 167 (2025) 150891

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Dual functionality of $LaNi_5$ metal hydride as a catalyst for toluene hydrogenation

Sung Ju Han [a,c], Safira Ramadhani [b,d], Taejun Ha [e], Eun-Young Kim [b], Ju-hyun Baek [a], Dakyung Jeong [a], Gaeun Park [a], Jinwoo Kim [a], Young-Su Lee [a], Jae-Hyeok Shim [a,f], Young Whan Cho [a], Yongmin Kim [b], Hyangsoo Jeong [b,*], Heung Nam Han [c,**], Jin-Yoo Suh [a,***]