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Materials Chemistry and Catalysis

Debye Institute for Nanomaterials Science

Metal Hydride nanocomposites as transition metal free catalysts for ammonia synthesis

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NCCC, Noordwijkerhout

AMBHER

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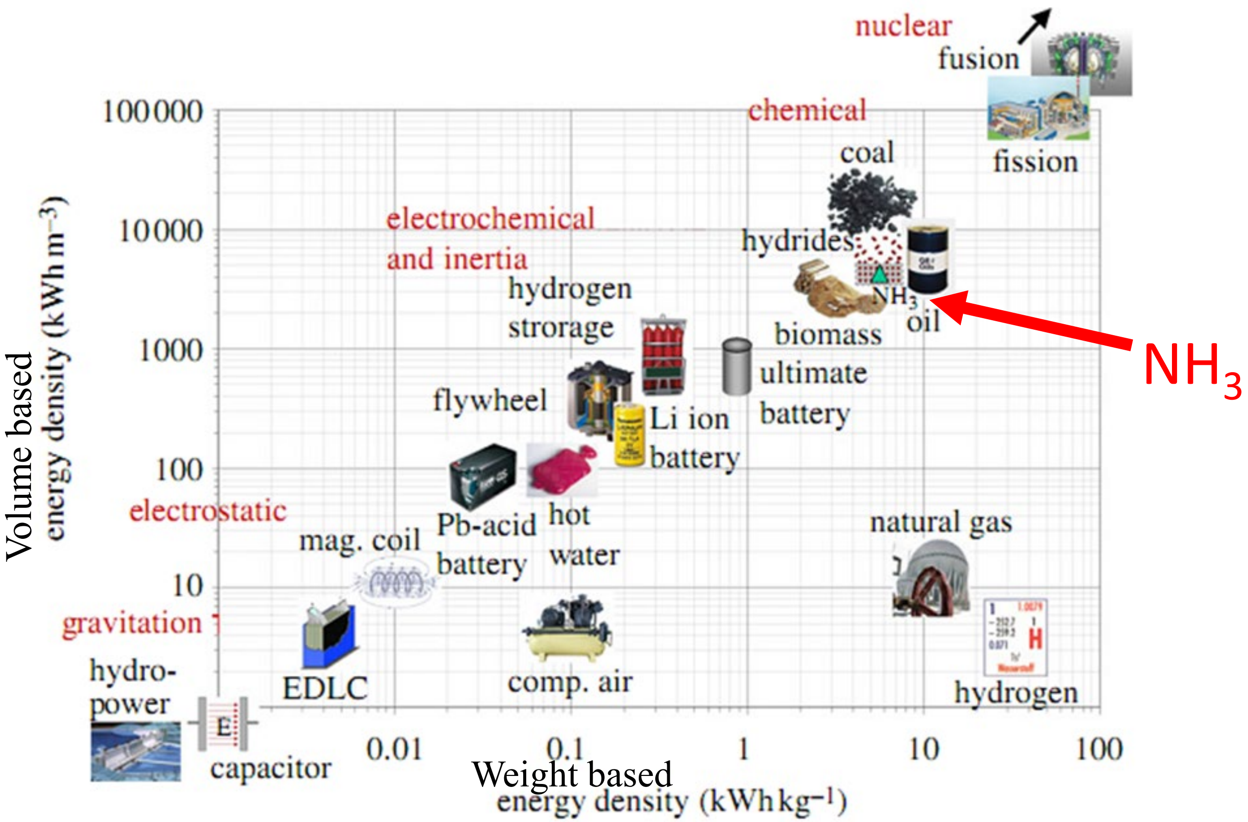
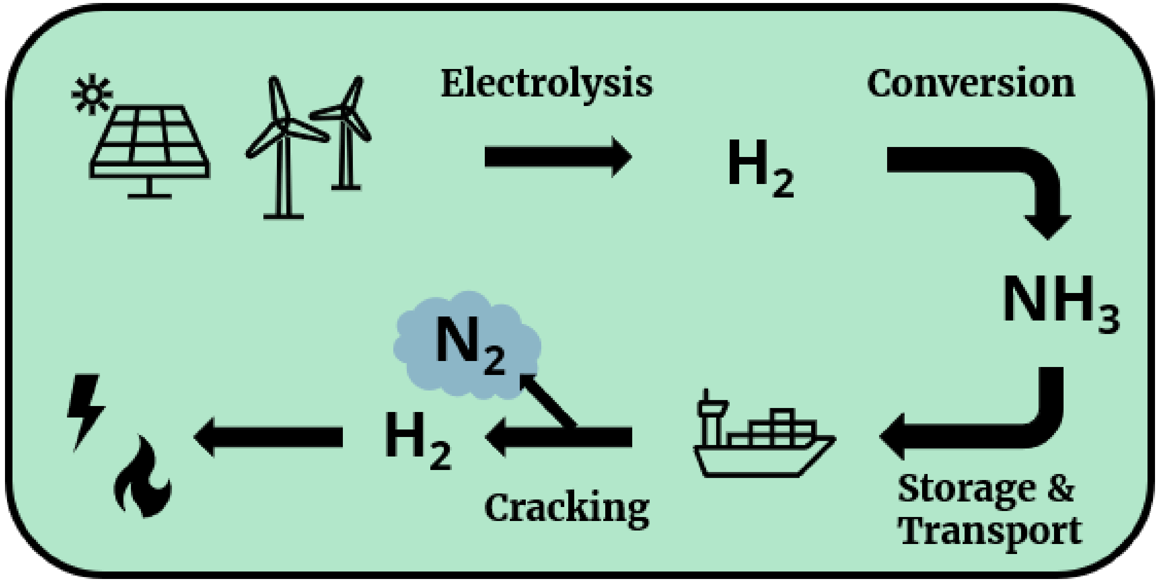
Ammonia as an energy carrier





Züttel *et al., Phil. Trans. R. Soc. A*, 2010, 368, 3329
Schüth et al., Energy Environ. Sci., 2012, 5, 6278

Ammonia is increasingly recognized as a highly viable chemical energy carrier.

Ammonia synthesis

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \quad \Delta H° = -92 \text{ kJ mol}^{-1} \quad \Delta S° = -198 \text{ J k}^{-1} \text{ mol}^{-1}$$

For high ammonia yield: low temperature and high pressure
(from thermodynamics)

For fast ammonia formation: high temperature
(from kinetics)

Catalysts

Efficient ammonia production
Reaction at temperatures as low as possible

Ammonia synthesis catalysts

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~ consumes 2% global energy production

Haber-Bosch process
(Fe based catalyst)

1st generation
(Haldor Topsoe)
$Fe_3O_4 + Al_2O_3 + K_2O + CaO$
350-525 °C, 100-300 bars

525 to 325 °C → 350 to 100 bar

KAAP Process
(Ru based catalyst)

2nd generation
(BP)
Ru-Ba-K/AC
325-450 °C, ≤ 100 bars

1913 — 1970 — 1992 — 2000 — 2012 — 2017 — 2022

Alkali metal-Ru
(Aika)

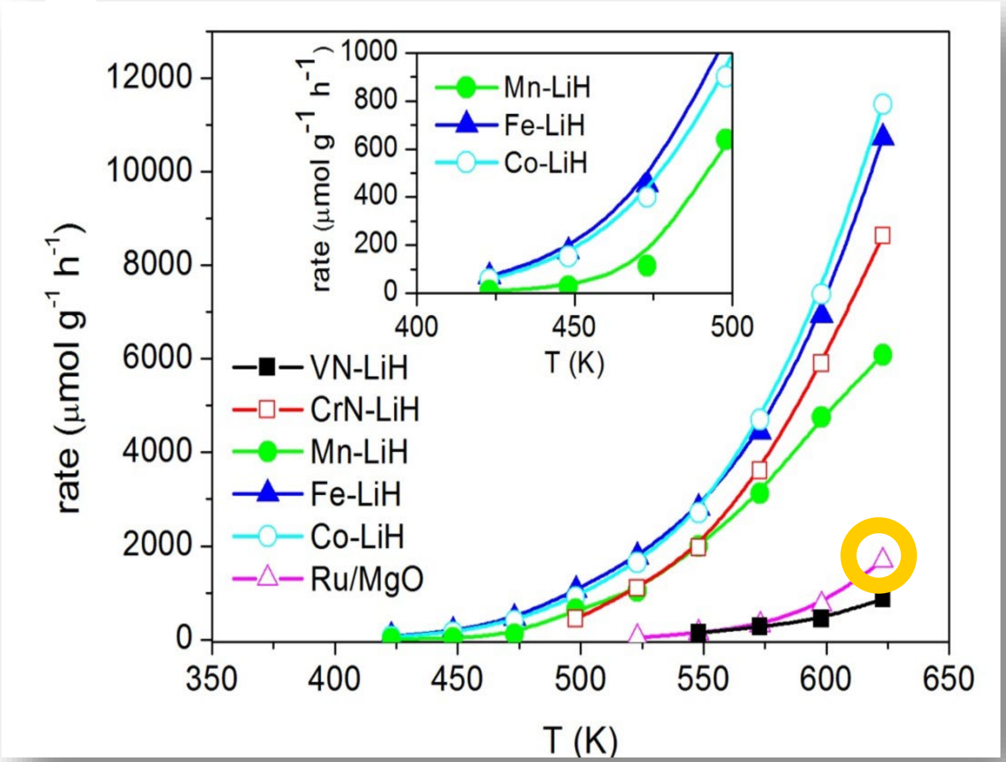
Co-Mo-N
(Aika & Jacobsen)

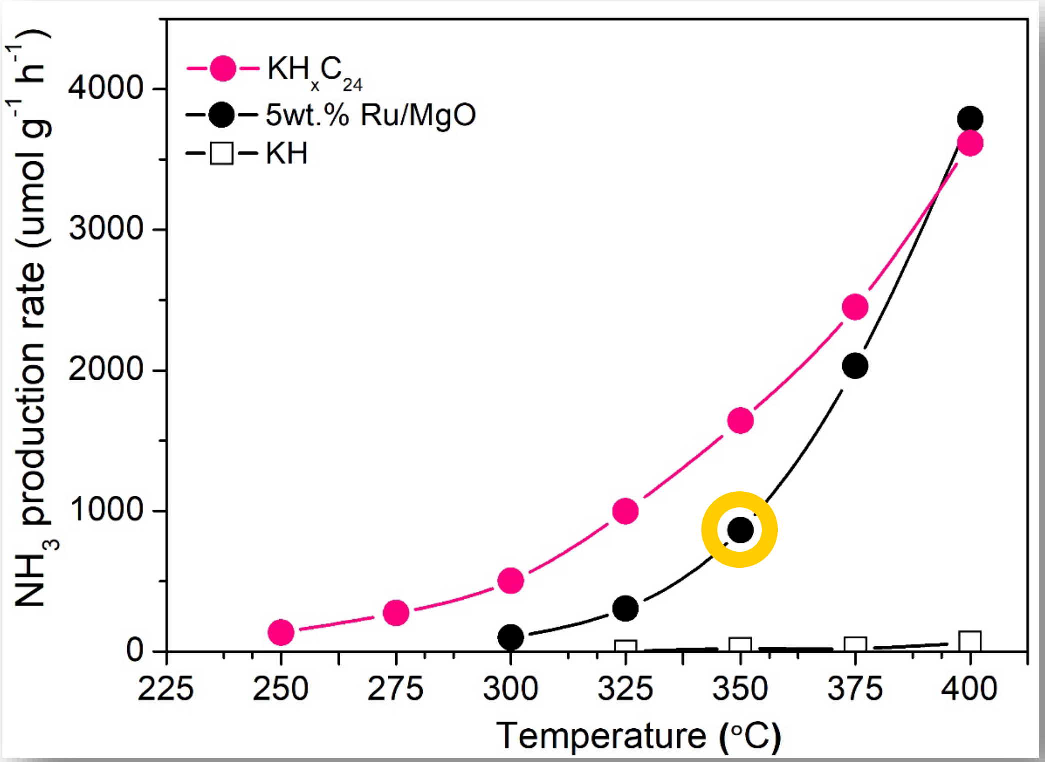
Ru/electride
(Hosono)

3d transition metal-alkali hydride
(Ping Chen)

Transition metal free

Alkali hydride mediated ammonia synthesis





- 3d TM+LiH composite catalysts achieved ammonia synthesis at a temperatures as low as 150°C
- KHC nanocomposites catalysts achieved ammonia synthesis at temperatures as low as 250°C

Wang, Peikun, et al. *Nature chemistry* 9.1 (2017): 64-70.
Chang, Fei, et al. *Nature Catalysis* 5.3 (2022): 222-230.

NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, $1N_2$:$3H_2$ and flow rate = 60,000 (left) – 36,000 (right) mL g_{cat}^{-1} h^{-1}.

Alkali hydride mediated ammonia synthesis

Are other alkali metal (hydride) carbide nanocomposites also active for ammonia synthesis?

How does the synthesis method affect the activity?

Chang, Fei, et al. *Nature Catalysis* 5.3 (2022): 222-230.

Alkali hydride carbide: melt infiltration

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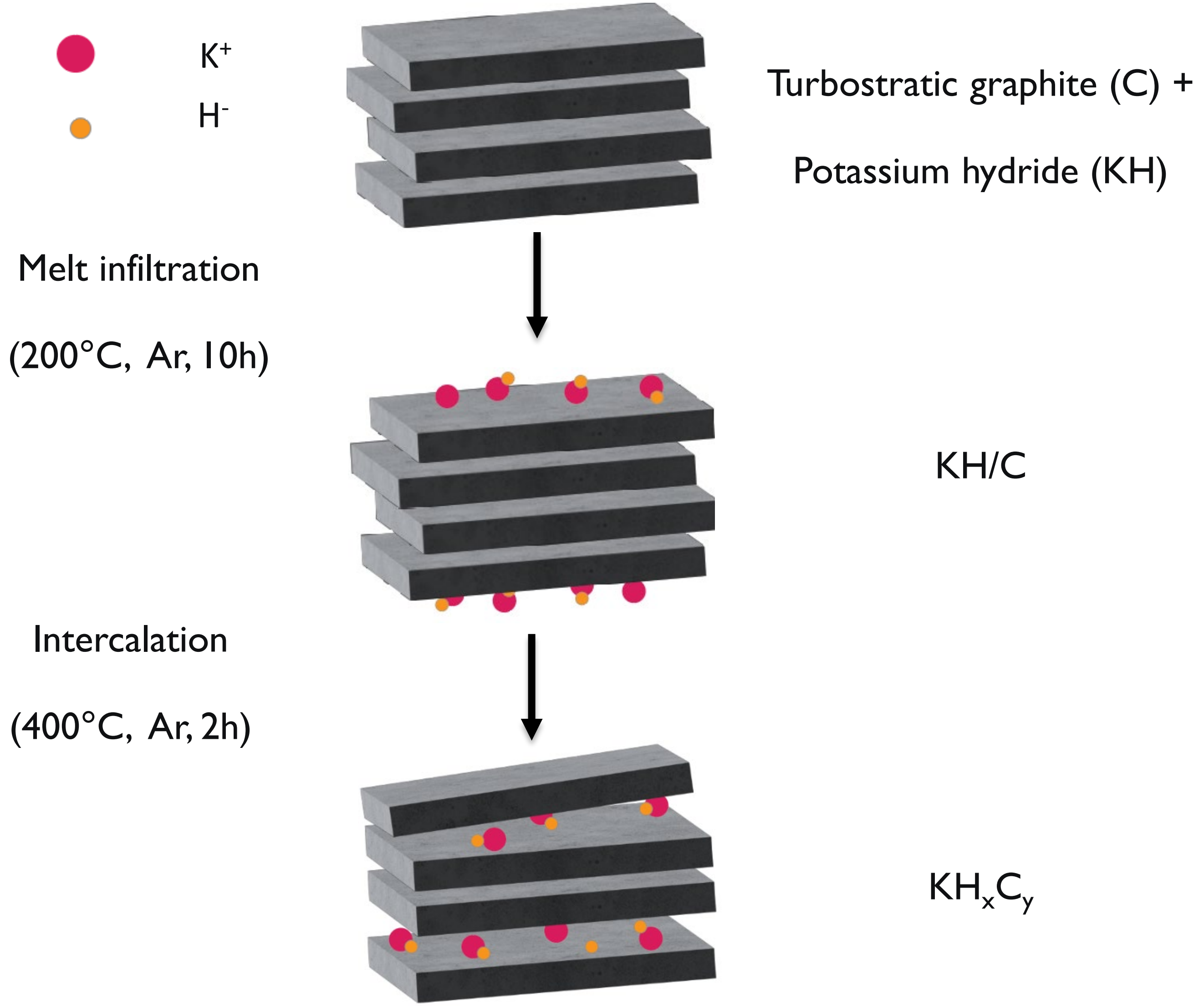

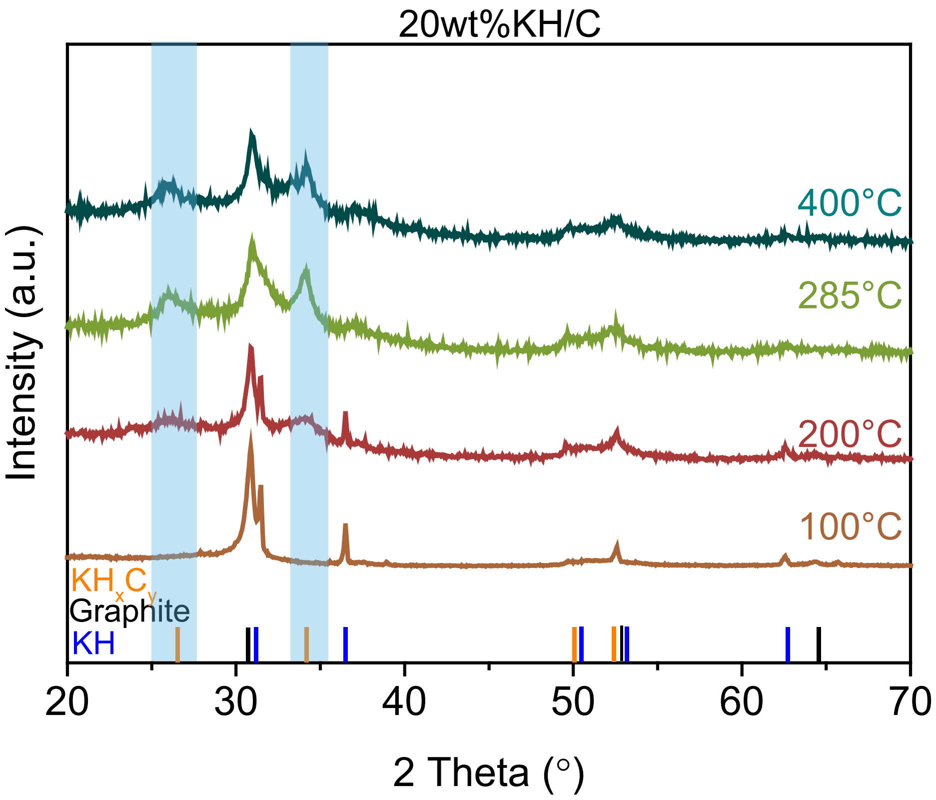

Chang, Fei, et al. *Nature Catalysis* 5.3 (2022): 222-230.

AH-Carbon for ammonia synthesis

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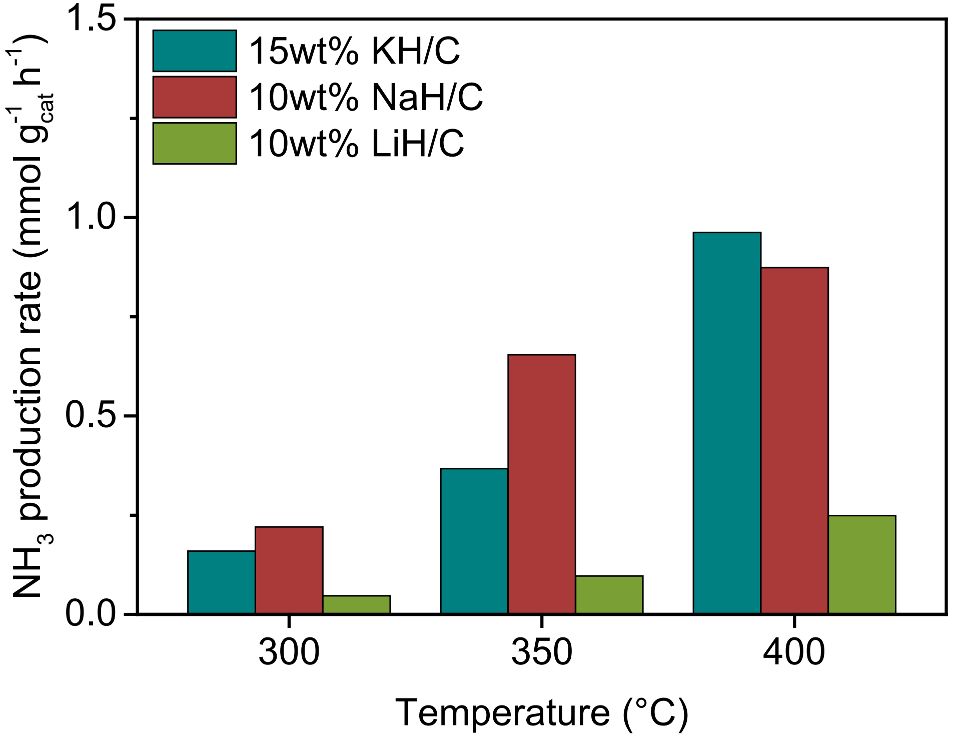
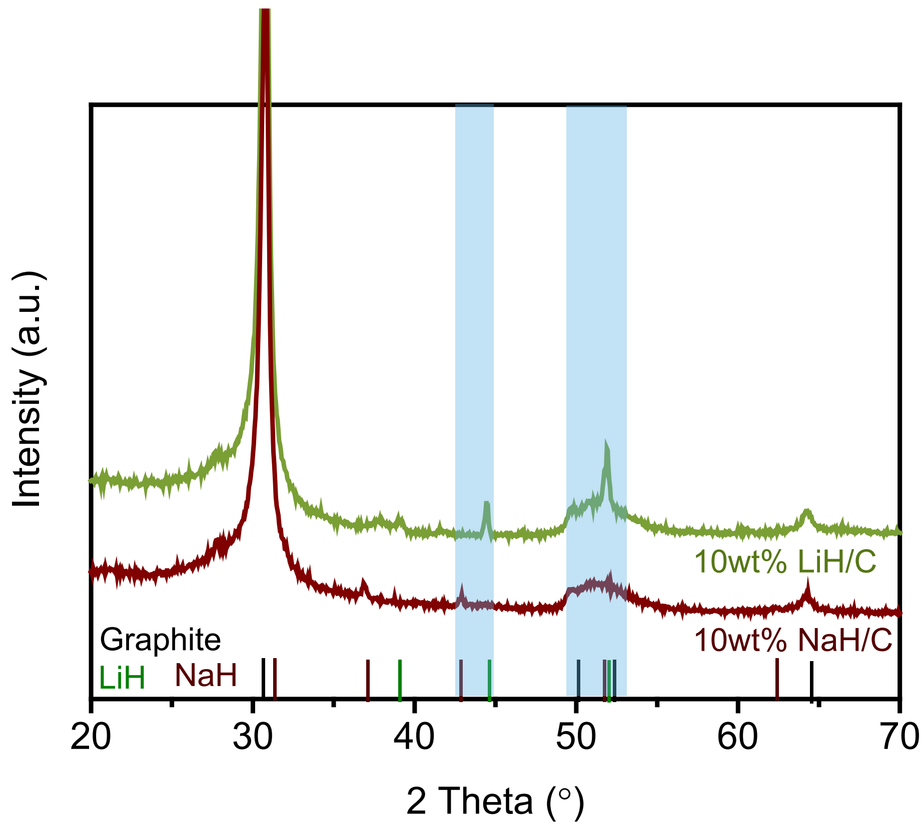
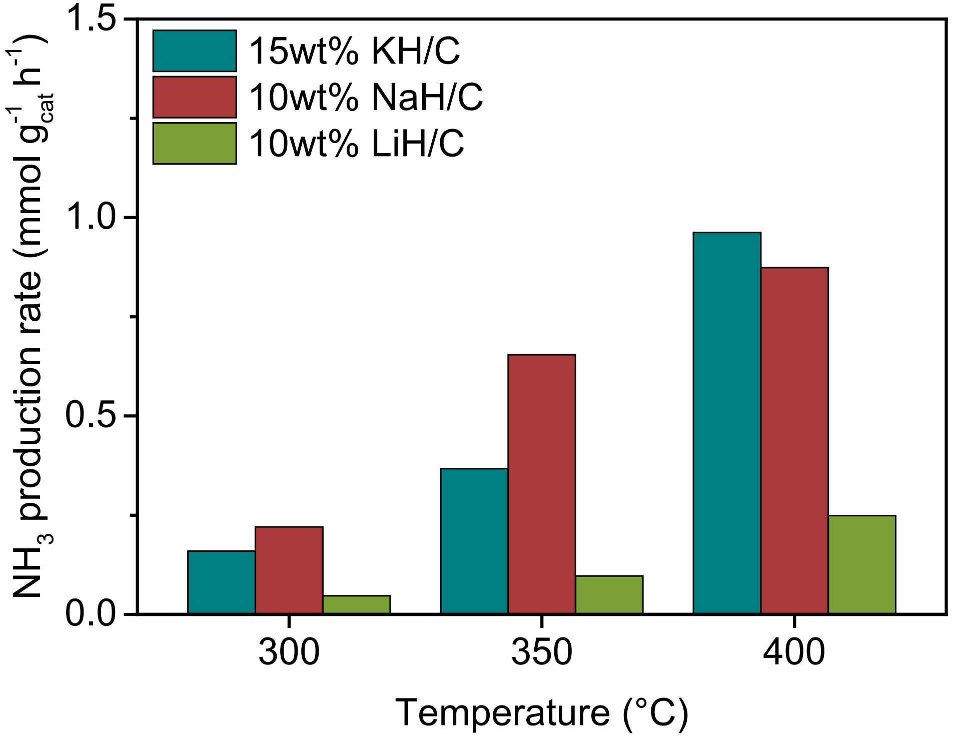


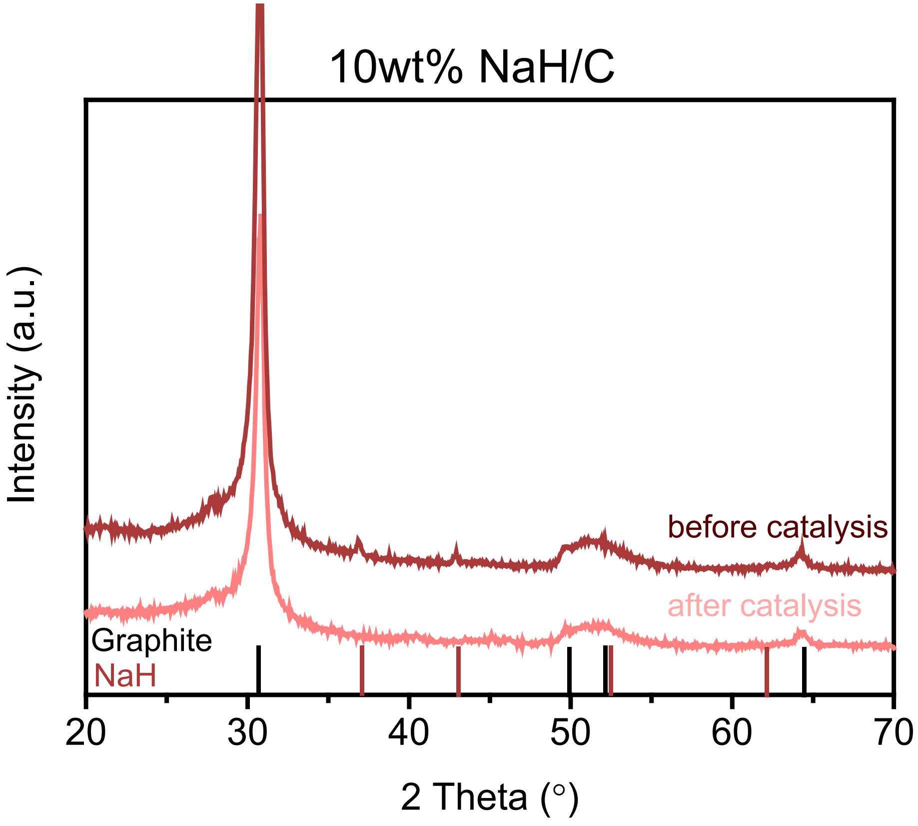


Besides KH, NaH & LiH based catalysts are also active towards ammonia synthesis

NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, 300-400 ℃, $1N_2$-$3H_2$ and flow rate = 60,000 mL g_{cat}^{-1} h^{-1}.

AH-Carbon for ammonia synthesis

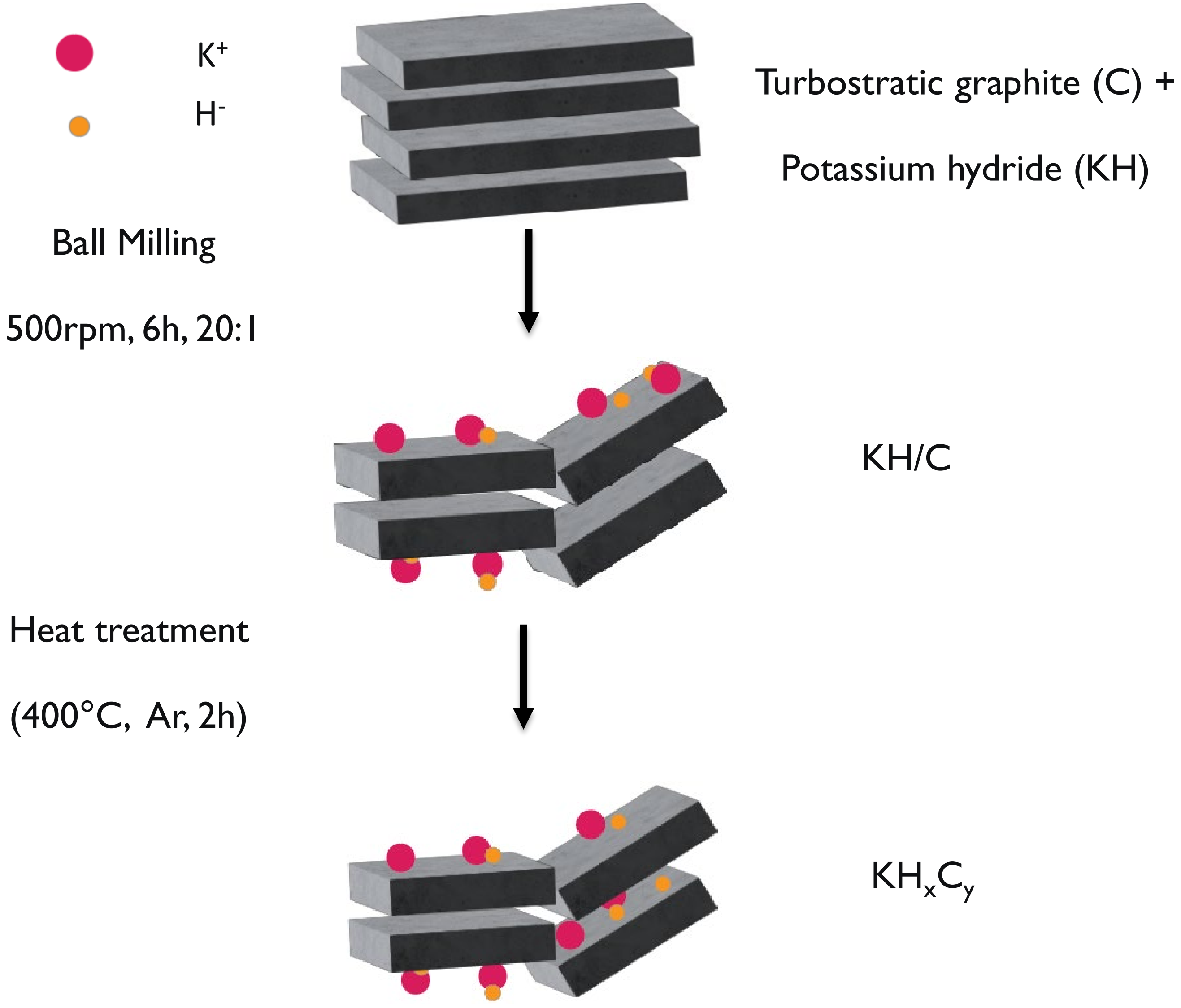


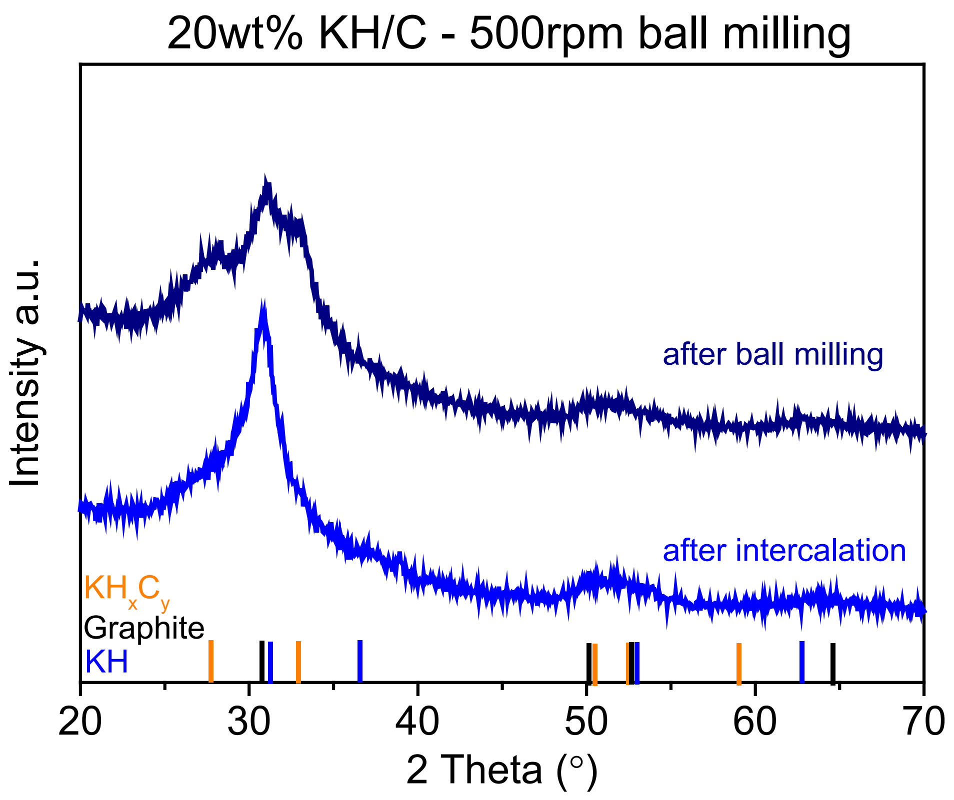


Intercalation might not be required for ammonia synthesis activity.

NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, 300-400 ℃, $1N_2$-$3H_2$ and flow rate = 60,000 mL g_{cat}^{-1} h^{-1}.

Alkali hydride carbide: ball milling





KH-C: BM effect on 20wt%KH

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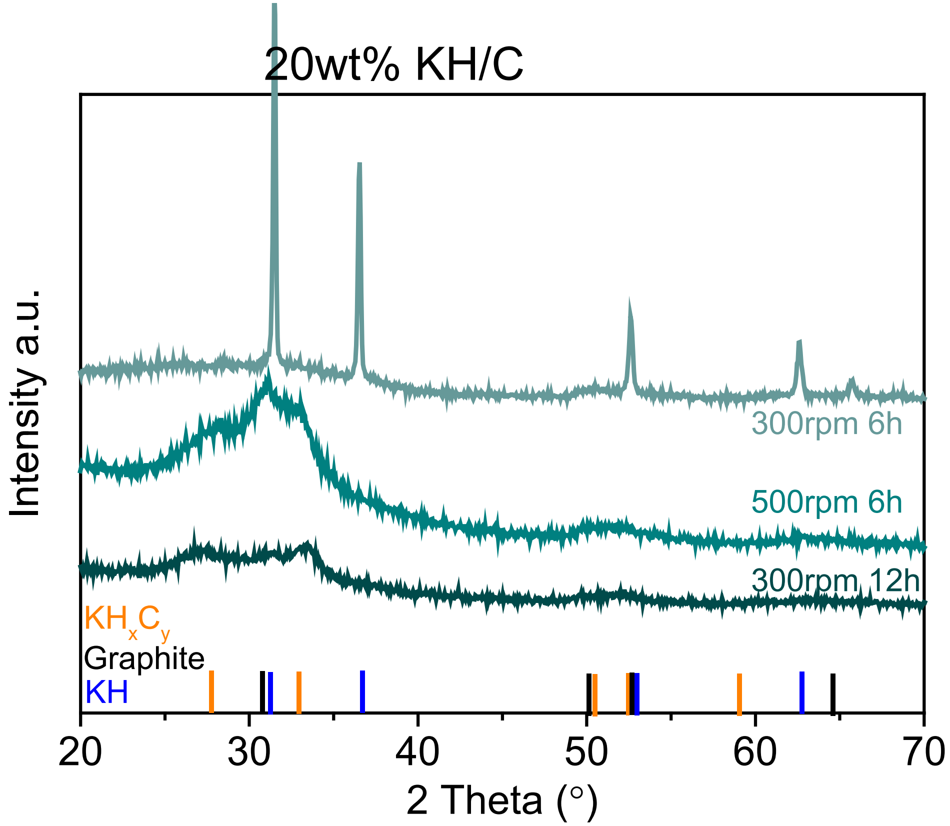

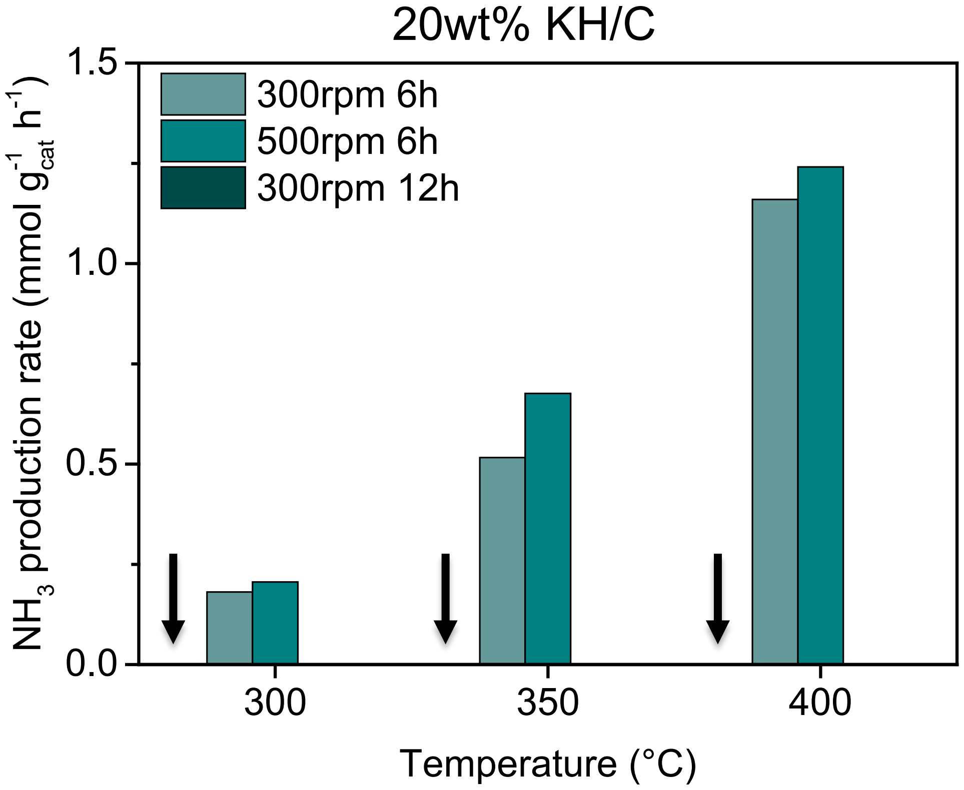

BM can be used to synthesize KHC ammonia catalyst, but prone to destruction

NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, 300-400 ℃, $1N_2$-$3H_2$ and flow rate = 60,000 mL g_{cat}^{-1} h^{-1}.

KH-C: BM effect on 20wt%KH

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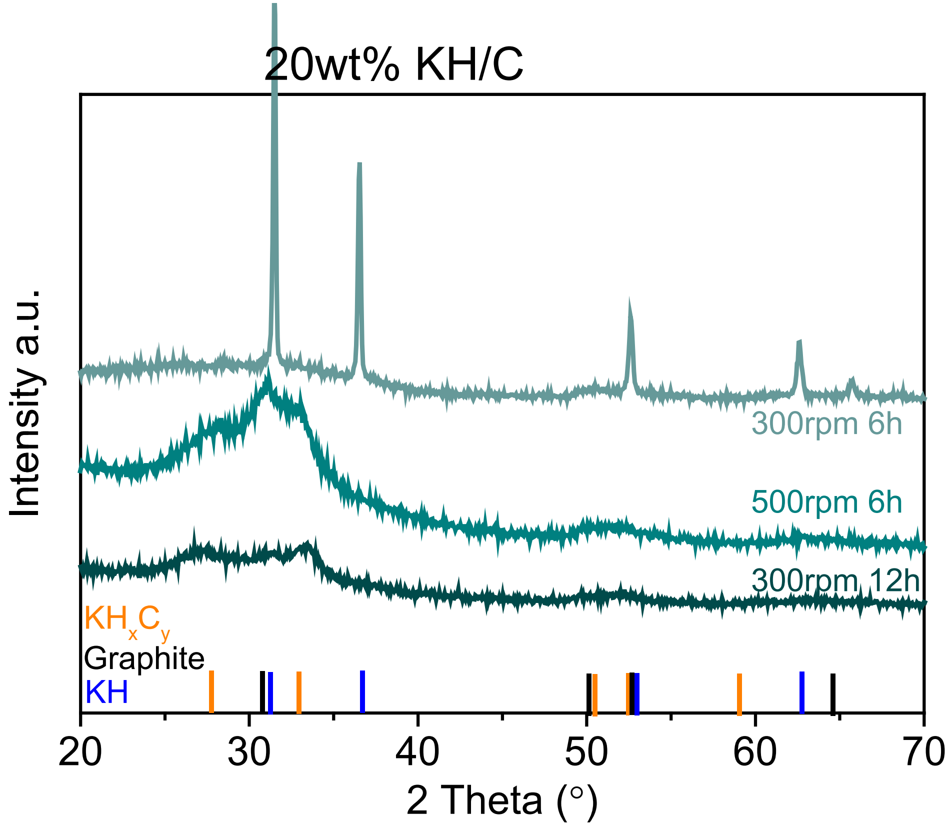

Sample	BET SA (m^2/g)	Pore volume (cm^3/g)	NH_3 activity @400°C, 10 bar (mmol NH_3 g^{-1} h^{-1})
300rpm 6h	238	0.26	1.16
500rpm 6h	9	0.02	1.24
300rpm 12h	75	0.09	0.00

BM can be used to synthesize KHC ammonia catalyst, but prone to destruction

NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, 300-400 °C, $1N_2$-$3H_2$ and flow rate = 60,000 mL g_{cat}^{-1} h^{-1}.

NaH-C: BM effect on 10wt%NaH

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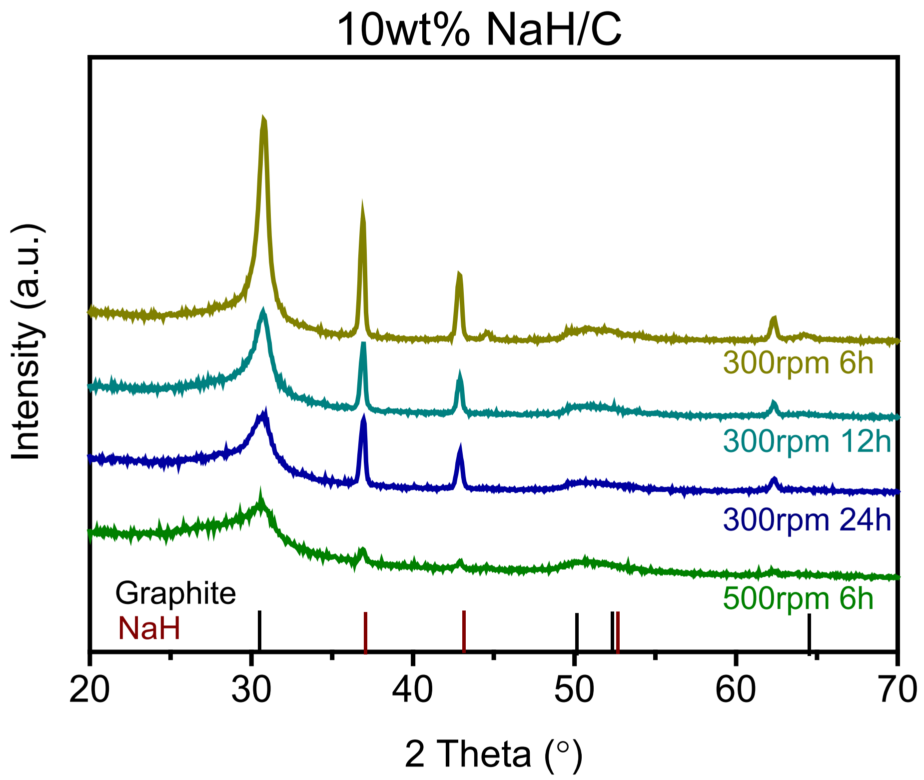
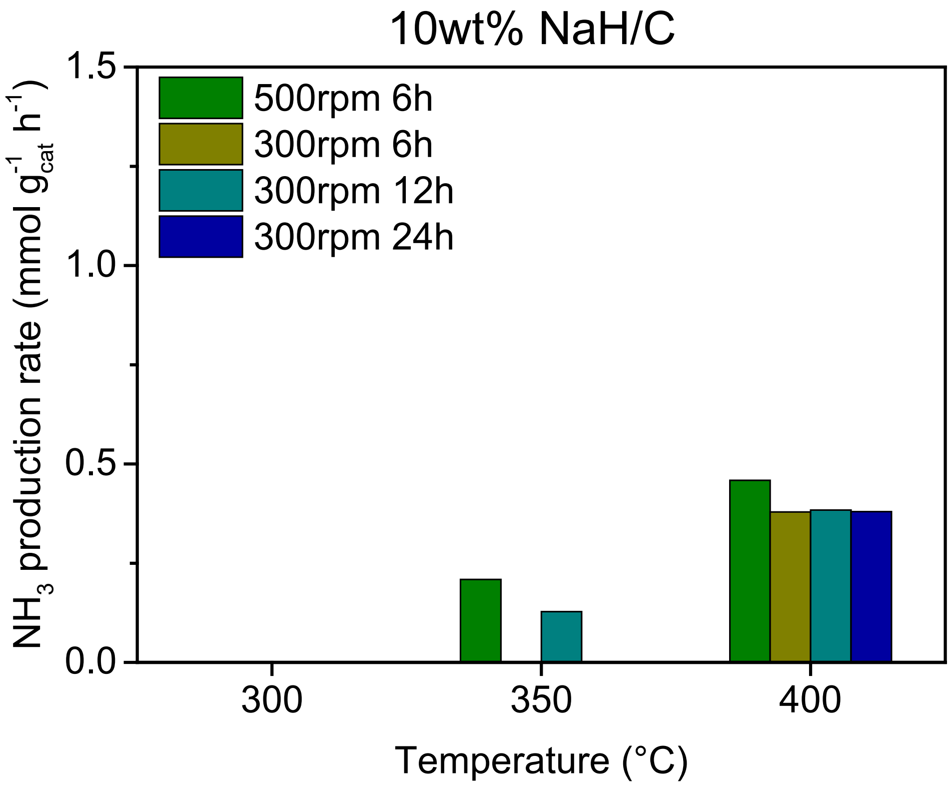
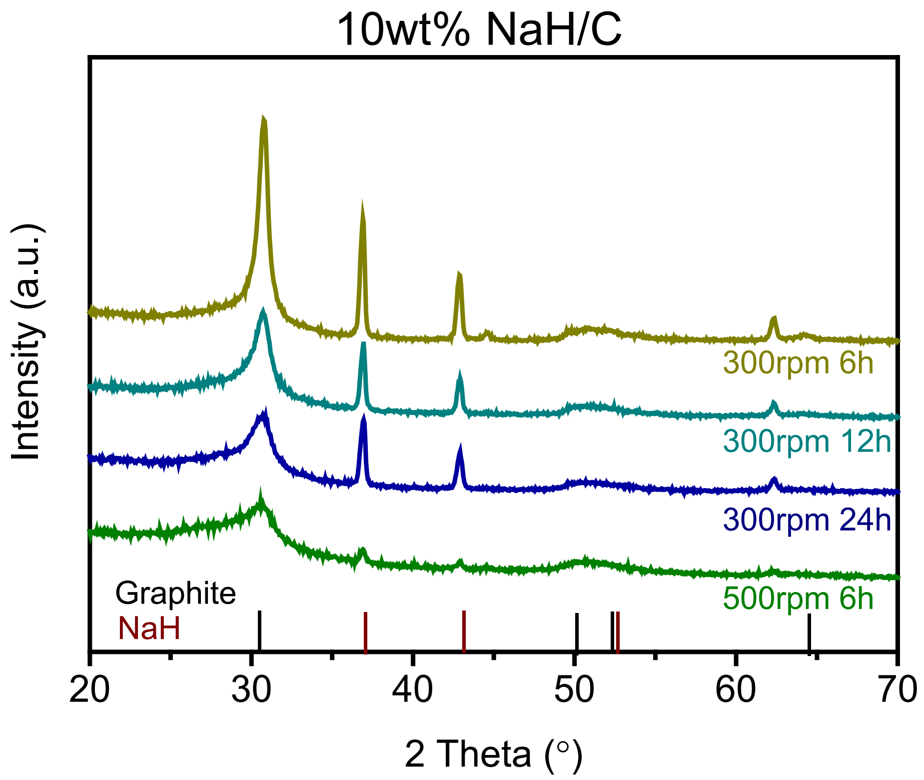




BM can be used to synthesize NaH/C ammonia catalyst, less prone to destruction in contrast to KHC

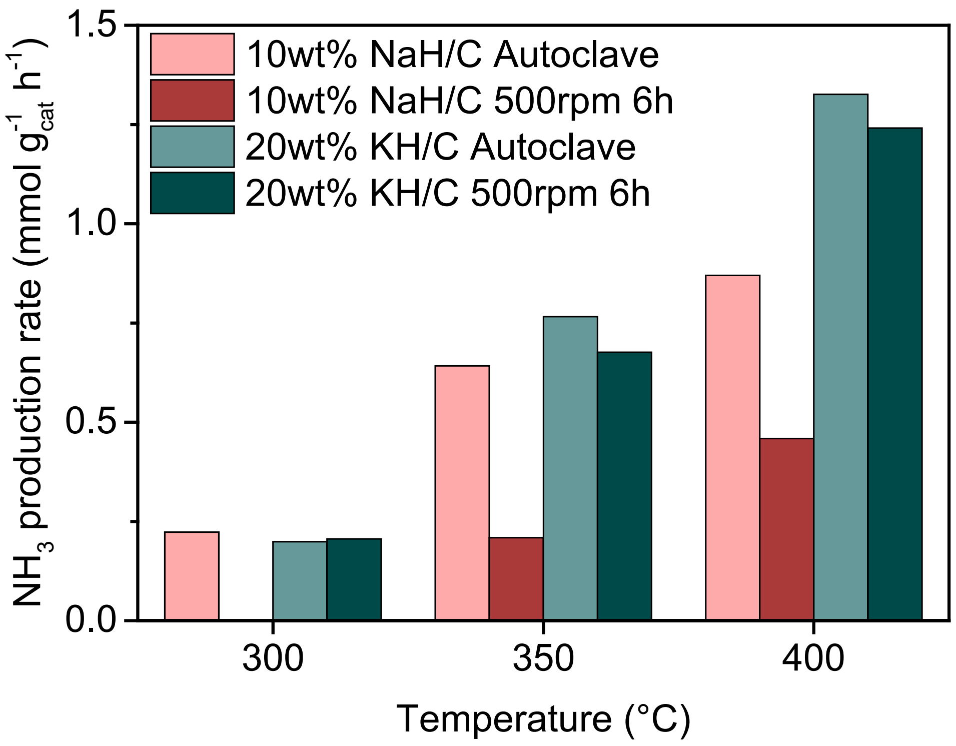
NaH-C: BM effect on 10wt%NaH

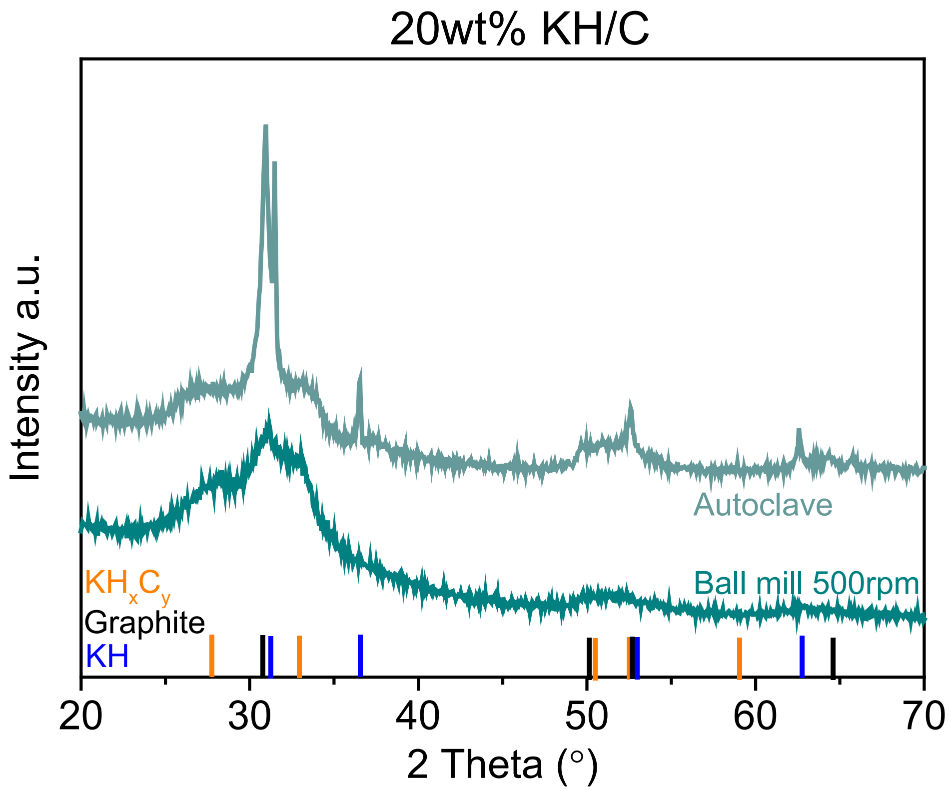


Sample	BET SA (m^2/g)	Pore volume (cm^3/g)	NH_3 activity @400°C, 10 bar (mmol NH_3 g^{-1} h^{-1})
300rpm 6h	452	0.67	0.38
300rpm 12h	477	0.52	0.38
300rpm 24h	542	0.66	0.33
500rpm 6h	360	0.33	0.46

BM can be used to synthesize NaH/C ammonia catalyst, less prone to destruction in contrast to KHC

AH-C: ball mill vs melt infiltration





NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, 300-400 ℃, $1N_2$-$3H_2$ and flow rate = 60,000 mL g_{cat}^{-1} h^{-1}.

Conclusion

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1. In addition to KH, **NaH and LiH based catalysts** are also active towards ammonia synthesis.

2. **Both ball milling and melt infiltration are suitable synthesis methods** for the synthesis of alkali hydride-based ammonia catalysts from alkali hydrides and graphitic carbon materials.

3. Intercalation might **not be required** for ammonia synthesis activity.

Acknowledgement

- Peter Ngene & Petra de Jongh
- Jan Willem de Rijk
- All of MCC

- European Union – AMBHER consortium

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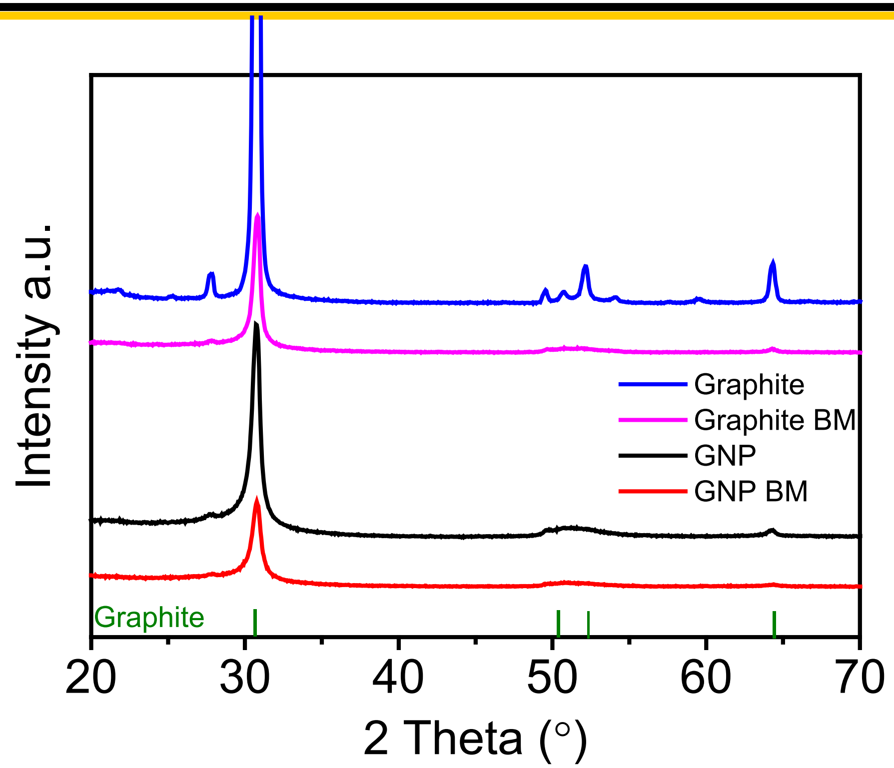
AMBH2ER

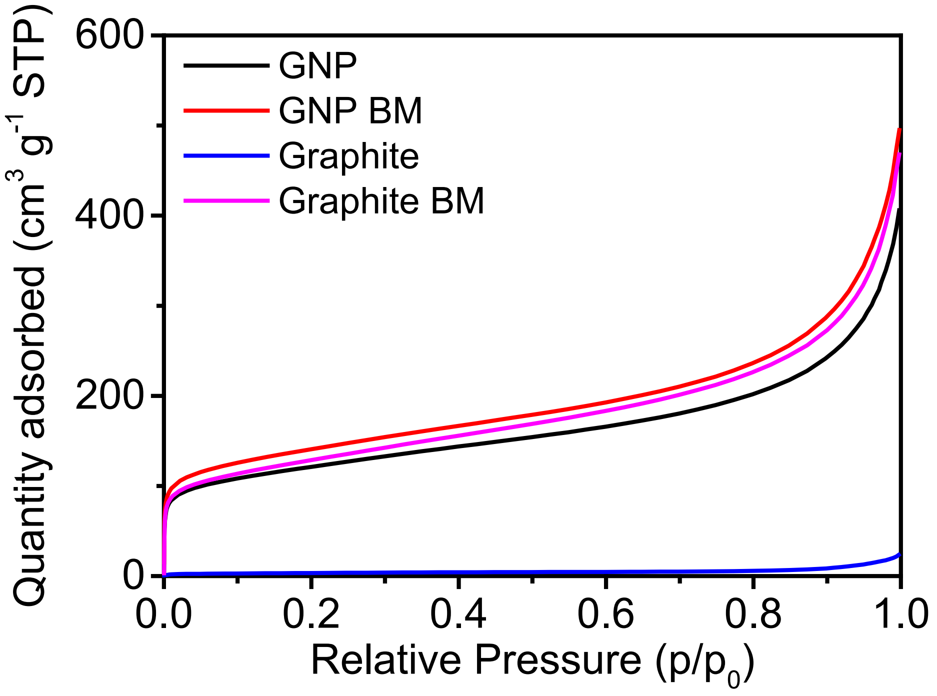
Ammonia and MOF Based Hydrogen storagE for euRope

Thank you for your attention

Funded by the European Union

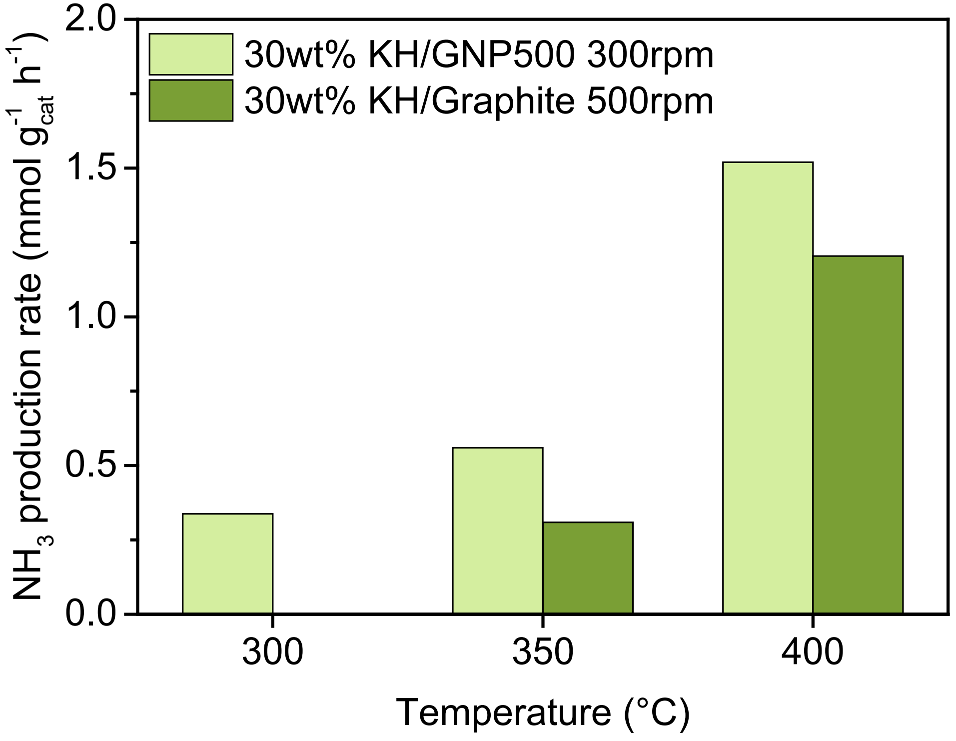
Graphite: XRD & N_2 physisorption





Sample	BET SA (m^2/g)	Pore volume (cm^3/g)
Graphite	12	0.03
Graphite BM	458	0.70
GNP500	434	0.61
GNP500 BM	505	0.74

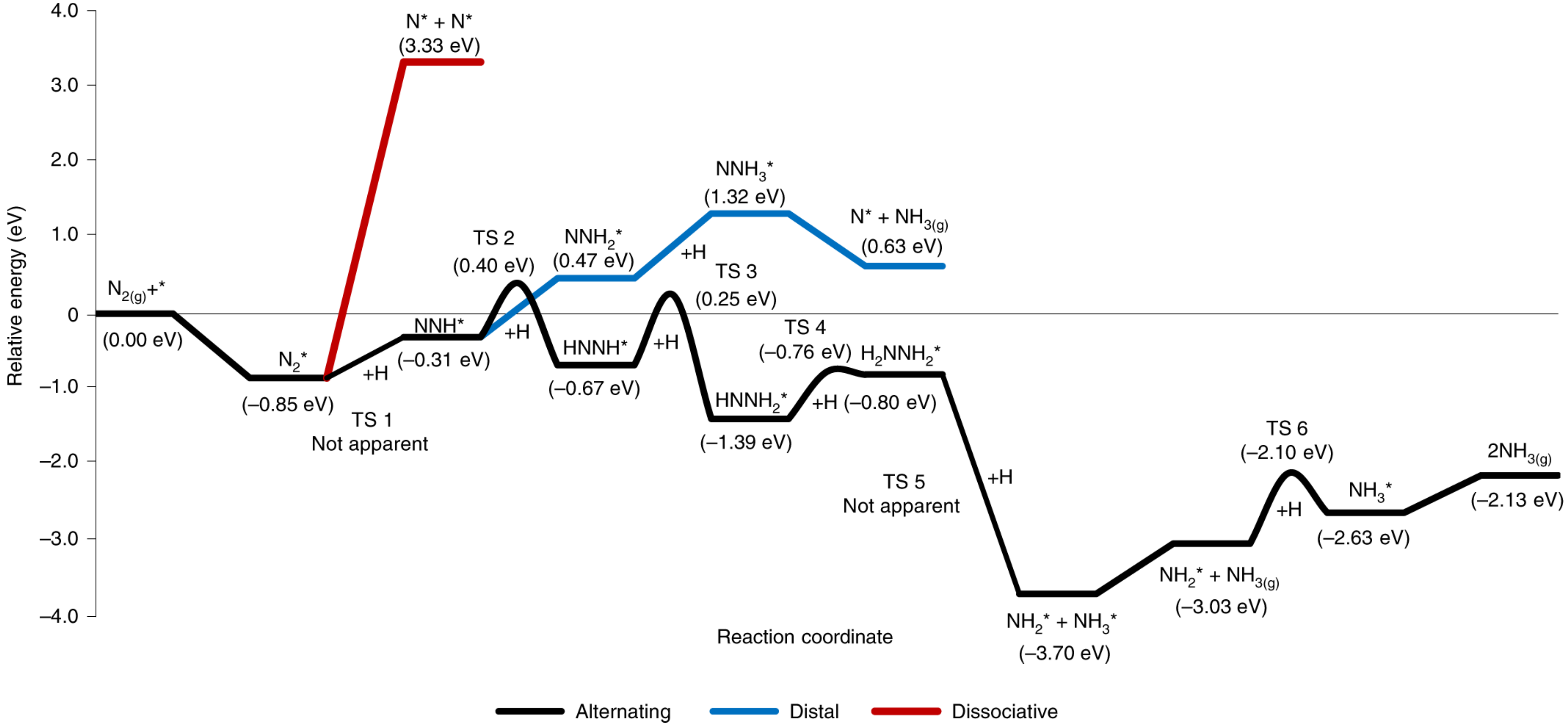
KH-GIC: BM 30wt%KH



Sample	BET SA (m^2/g)	Pore volume (cm^3/g)
KH+GNP500 300rpm 6h	37	0.05
KH+Graphite 500rpm 6h	10	0.02

NH_3 synthesis catalyzed by different catalysts under the conditions of 1 MPa, 300-400 ℃, $1N_2$-$3H_2$ and SV = 60,000 mL g_{cat}^{-1} h^{-1}.

Mechanism



The associative-alternating pathway is the most favourable pathway