

Catalytic Ammonia Decomposition with Supported Molten Salt Catalysts

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Low Temperature Molten Salts

Ionic liquids

- Organic cation + anion
- $T_m < 100\text{ °C}$
- $T_{\text{stable}} < 250\text{ °C}$ [1]

Low temperature molten salts

- Inorganic cation + organic anion
- Salt mixtures
- $100\text{ °C} < T_m < 250\text{ °C}$
- $T_{\text{stable}} > 250\text{ °C}$

High temperature molten salts

- Inorganic cation + anion
- $T_m > 400\text{ °C}$
- $T_{\text{stable}} \gg 400\text{ °C}$

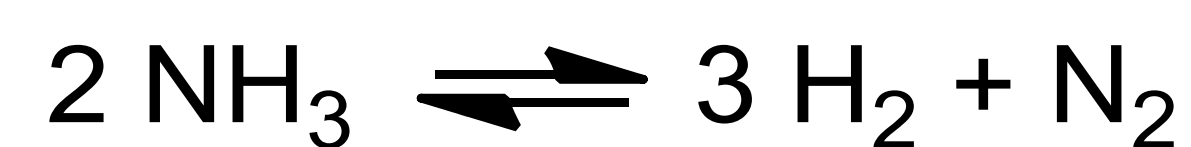
- Bridge the gap between ionic liquids and classical high temperature molten salts
- Novel class of reaction media for reactions at temperatures between 150 °C and 350 °C
- Enhanced reactivity
- Tuneable selectivity

	$\text{Cs}[\text{OAc}]$ Li[OAc]/K[OAc] Lithium Acetat/ Potassium Acetat/ Cesium Acetat (0.2/0.275/0.525) mol%	$\text{F}_3\text{C}-\text{S}(\text{O})_2-\text{N}(\text{Cs})-\text{S}(\text{O})_2-\text{CF}_3$ Cesium bis(trifluoromethyl- sulfonyl)imide
$T_m / \text{°C}$	119	120
$T_{\text{decomp}} / \text{°C}$	452	462
$\rho_{200\text{ °C}} / \text{g cm}^{-3}$	2.06	2.21
$\eta_{200\text{ °C}} / \text{mPas}$	42	15

Solid Catalyst with Molten Salt Layer

Test reaction

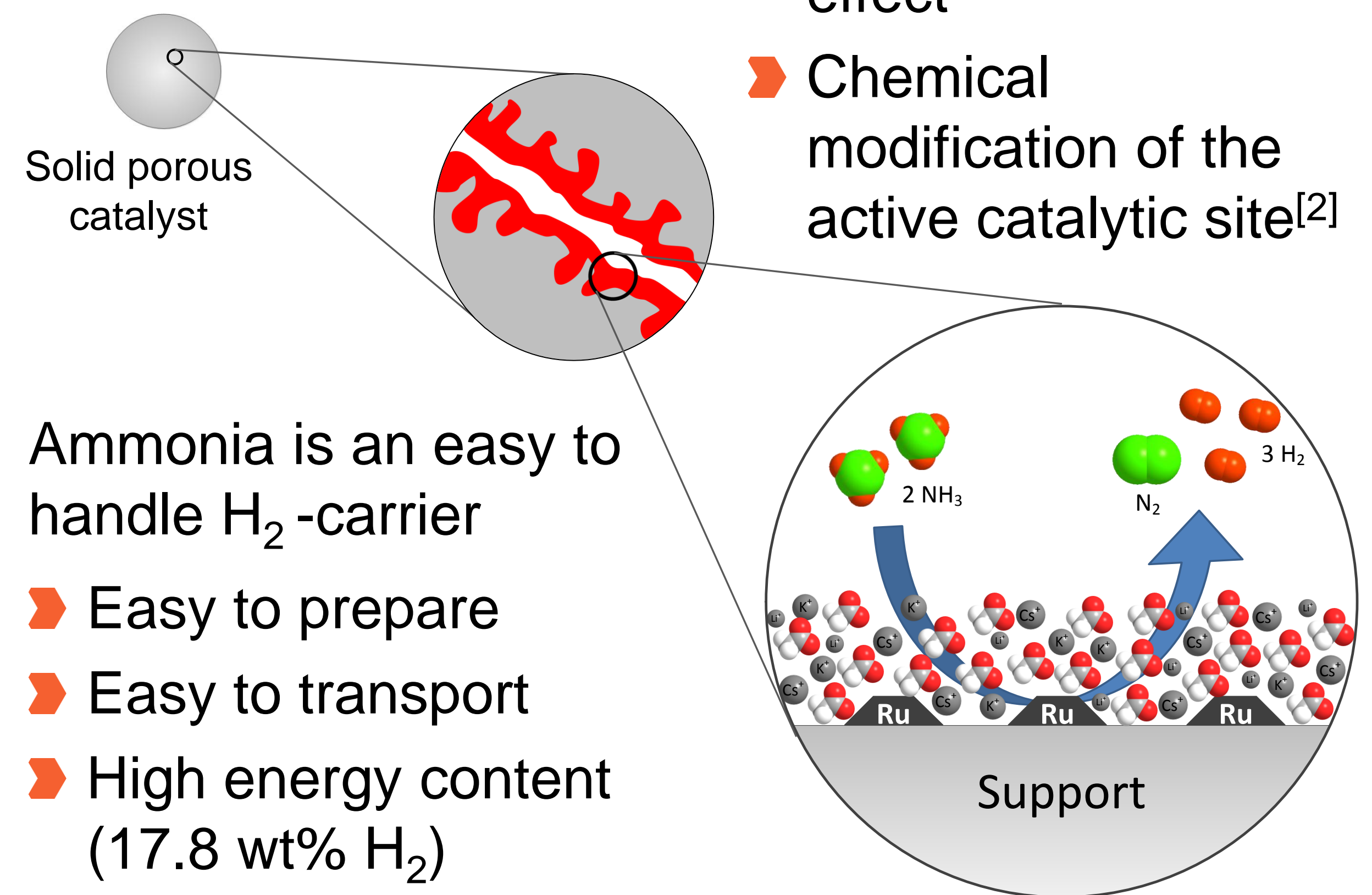
Ammonia decomposition



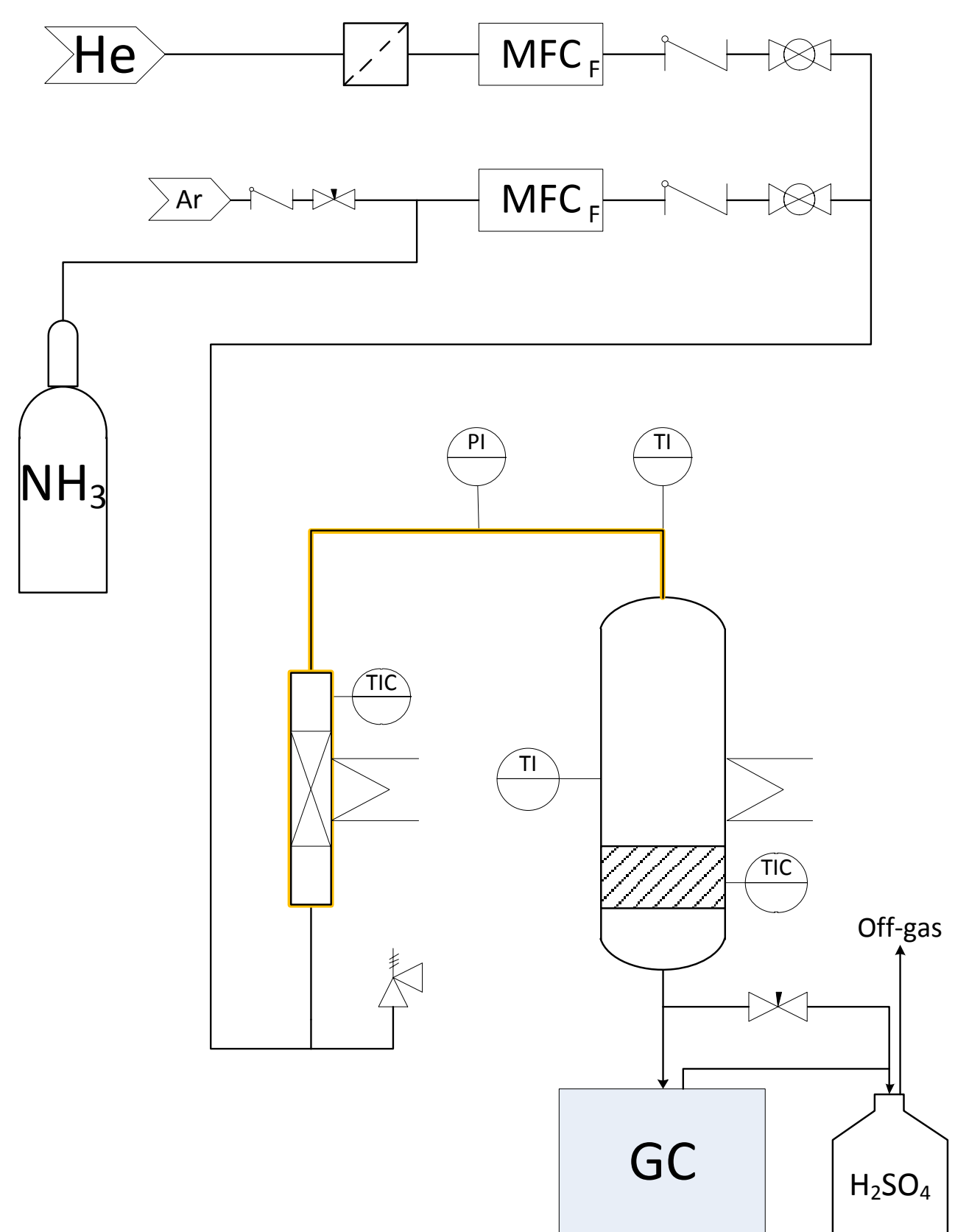
Molten salt layer on the surface of the pores

- Physical solvent effect

- Chemical modification of the active catalytic site^[2]



Experimental Rig and Setup



Continuous gas phase fixed bed reactor

- Up to 400 °C
- Atmospheric pressure
- Gas dosage via mass flow controller
- Inert gas: helium
- Sample analysis via online-GC



Catalyst system

- Ru (5 wt%) on alumina, Alfa Aesar – coated or uncoated

- Molten salt layer,

$$\text{pore filling degree } \alpha = \frac{V_{\text{salt}}}{V_{\text{pore},0}} = 0.2$$

Reaction conditions

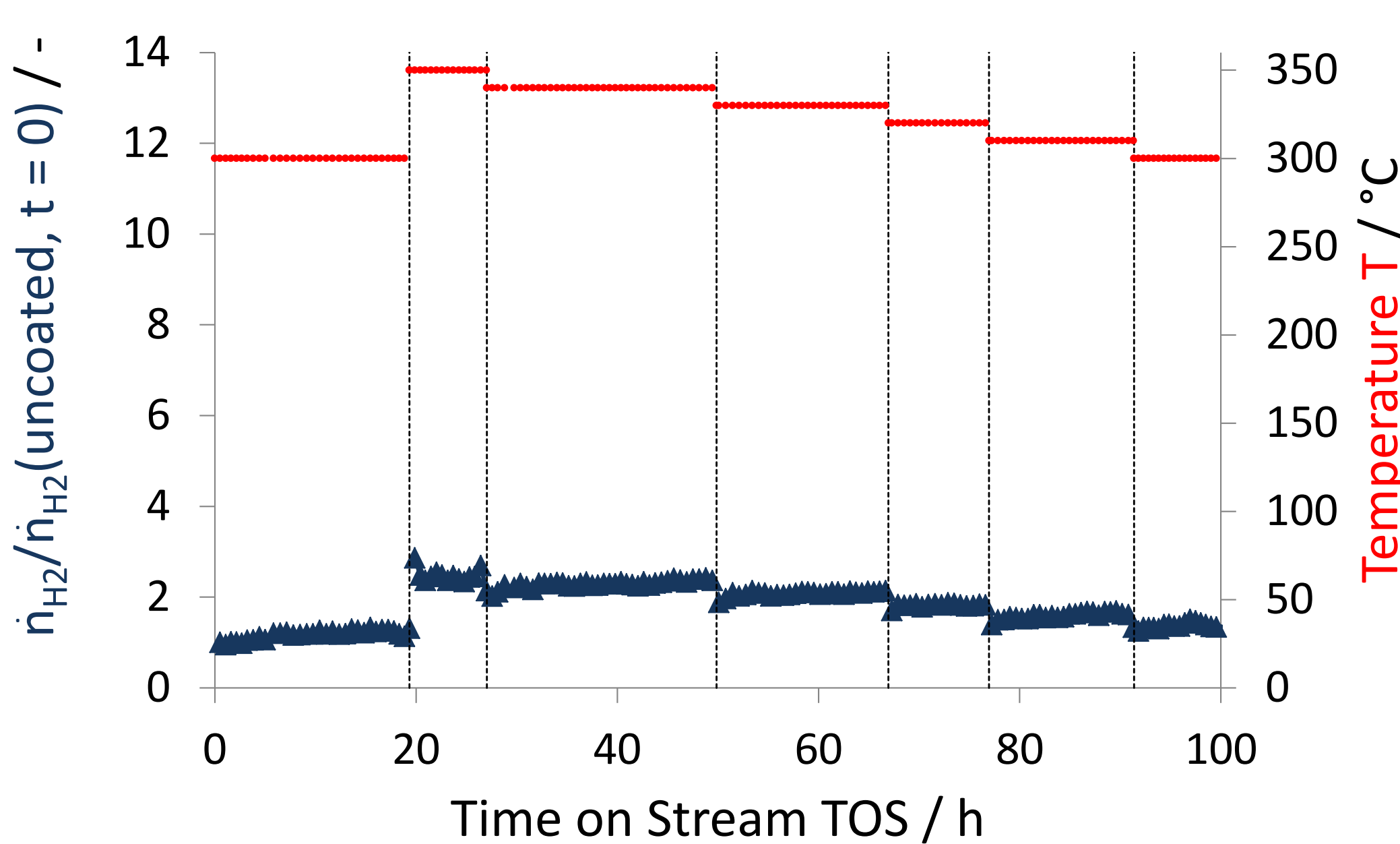
- Temperature variations from $300\text{--}350\text{ °C}$
- $p_{\text{total}} = 1\text{ bar}$
- $\dot{V}_{0,\text{total}} = 80\text{ ml min}^{-1}$
- $\text{NH}_3:\text{He} = 1:1\text{ to }5:1$



Fresh catalyst coated with Li/K/Cs[OAc] Catalyst with inert material after reaction

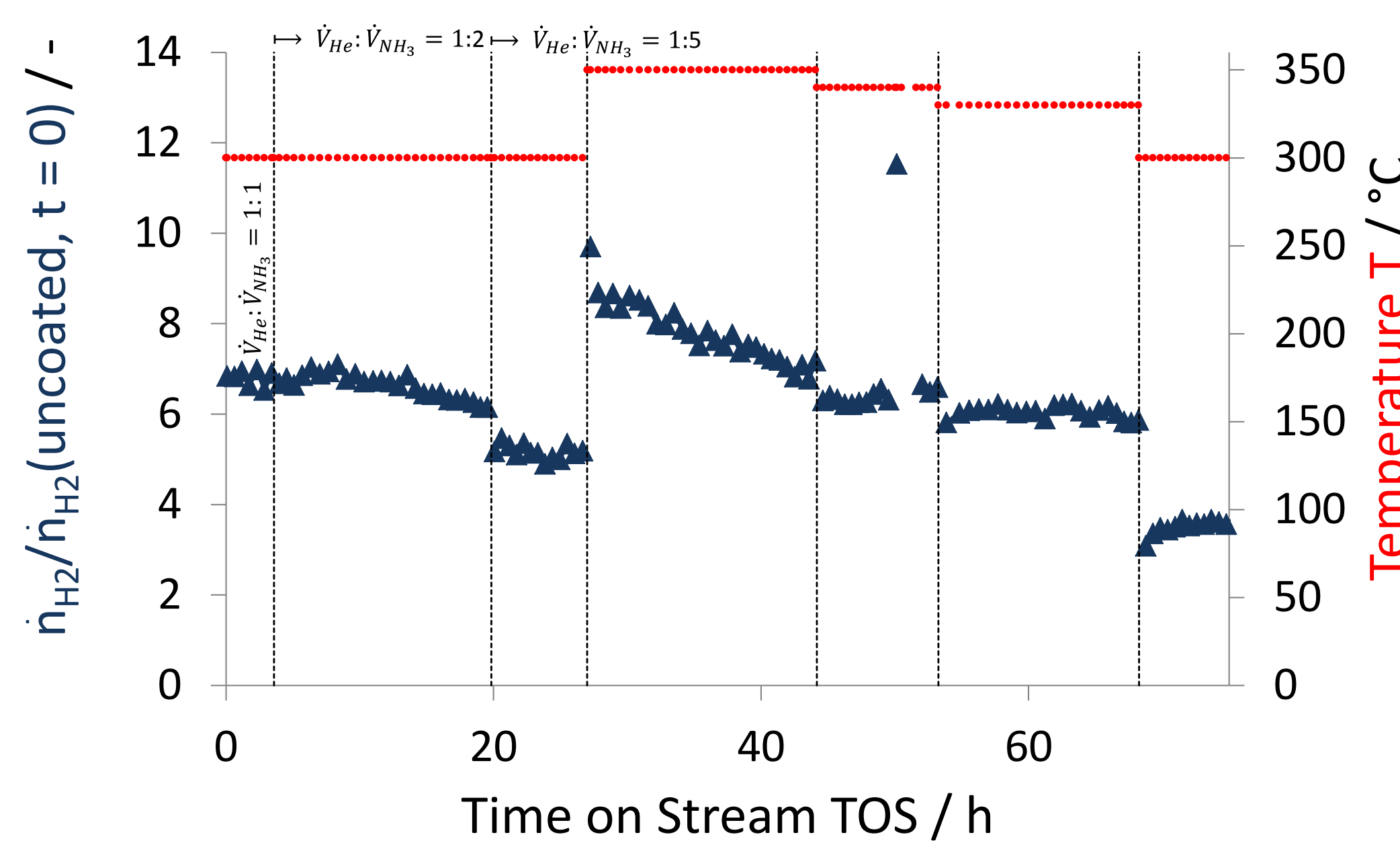
First Results

Uncoated



- Negligible activation phase
- Stable catalytic system

Coated with Li/K/Cs OAc



- Enhanced activity
- Deactivation at higher temperatures

Outlook

Further investigations of reaction parameters

- Variation of the molten salt layer
- Variation of the pore filling degree α
- Influence of the support material
- Variation of the catalytic active metal
- Kinetic measurements and evaluation
- CO-TPD measurements for evaluation of the active catalytic site

[1] S. Werner, M. Haumann, P. Wasserscheid, Annual Review of Chemical and Biomolecular Engineering 1 (2010) 203–230. [2] M. Sobota, M. Happel, M. Amende, N. Paape, P. Wasserscheid, M. Laurin, J. Libuda, Advanced Materials 23 (2011) 2617–2621.