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AmmoNia baseD membRane rEActor for green Hydrogen production - ANDREAH

Reaction kinetics of heterogenous catalysts. On the mechanism of hydrogen production from ammonia decomposition

2nd Edition of **Winter School** on "Membrane and Membrane Reactors",
1Cube Office (Microlab building), Eindhoven, 27-28 January 2025

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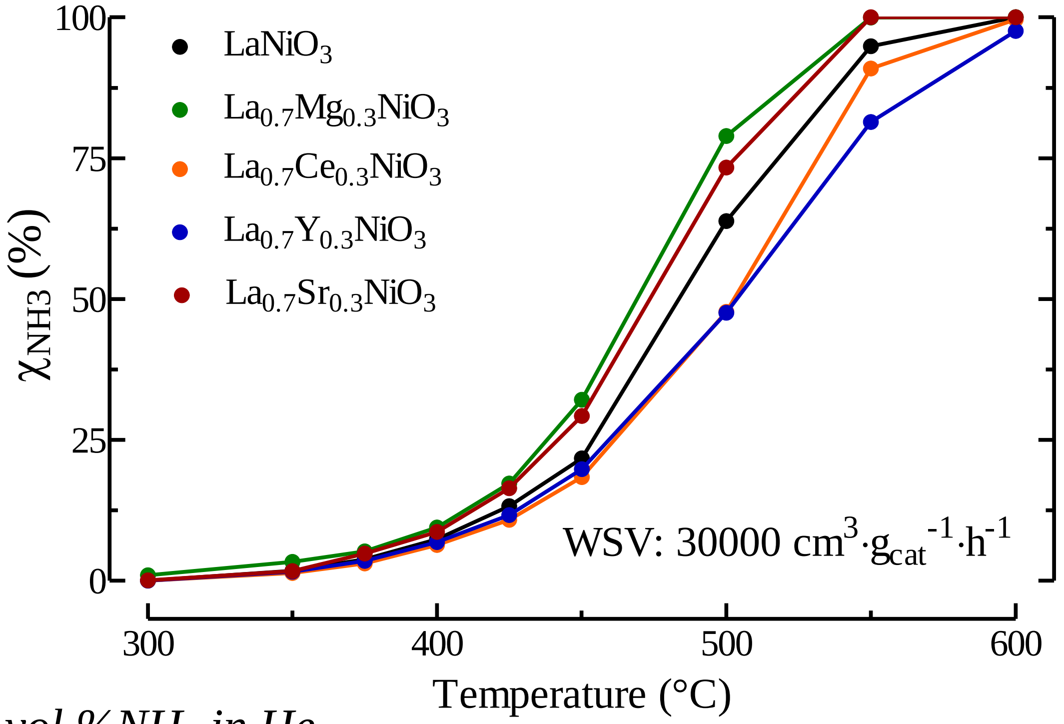
Outline

1) Preliminary Tests
2) Catalysts Synthesis and Characterization
3) Activity Tests & Kinetic Evaluation
4) Main Conclusions

PRELIMINARY TESTS

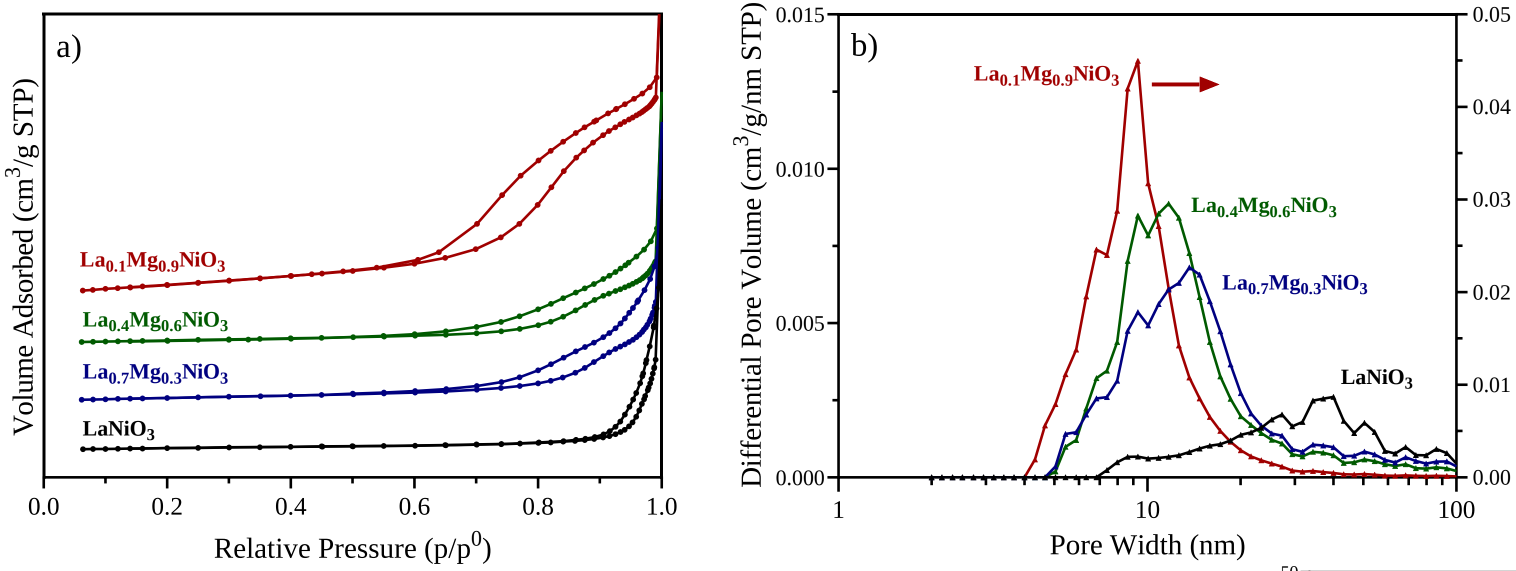


**50 vol.%NH_3 in He*

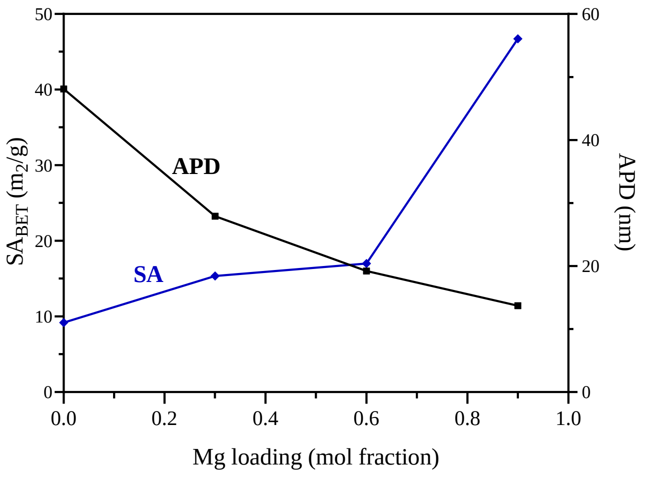
Sample	SA_{BET} (m_2/g)	NiO crystallite size from XRD (nm)
$LaNiO_3$	9	-
$La_{0.7}Mg_{0.3}NiO_3$	15	9.2
$La_{0.7}Ce_{0.3}NiO_3$	7	18
$La_{0.7}Y_{0.3}NiO_3$	8	7.6
$La_{0.7}Sr_{0.3}NiO_3$	7	13

Mg is the promoter selected for the subsequent kinetic evaluation

Characterization: N_2-Physisorption



Sample	SA_{BET} (m_2/g)	PV_{BJH}[a] (cm_3/g)	APD[b] (nm)
$LaNiO_3$	9.19	0.1104	48.1
$La_{0.7}Mg_{0.3}NiO_3$	15.35	0.1072	27.9
$La_{0.4}Mg_{0.6}NiO_3$	17.00	0.0814	19.2
$La_{0.1}Mg_{0.9}NiO_3$	46.71	0.1598	13.7



[a]*BJH desorption cumulative Pore Volume in the range 1.7-300 nm;*
[b]*Average pore Diameter from APD=4·PV/SA.*

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CHARACTERIZATION: XRD

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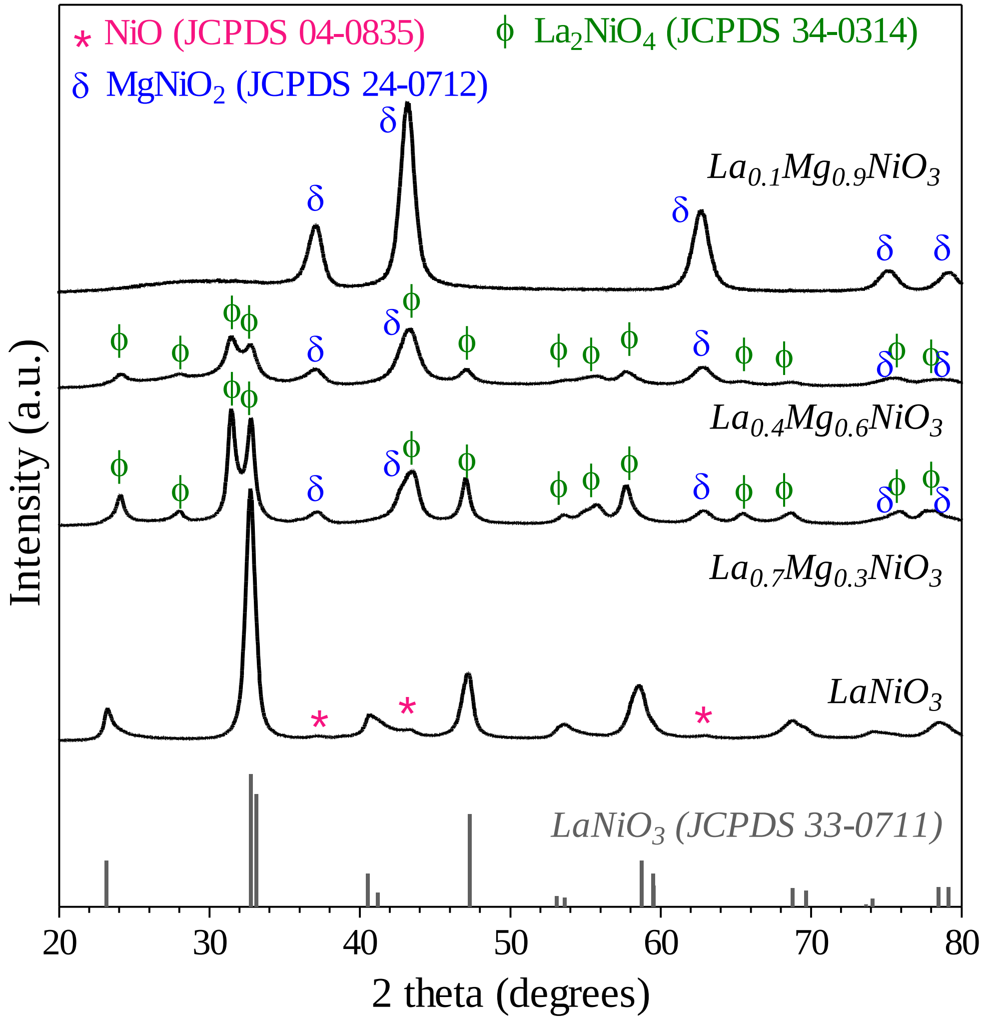
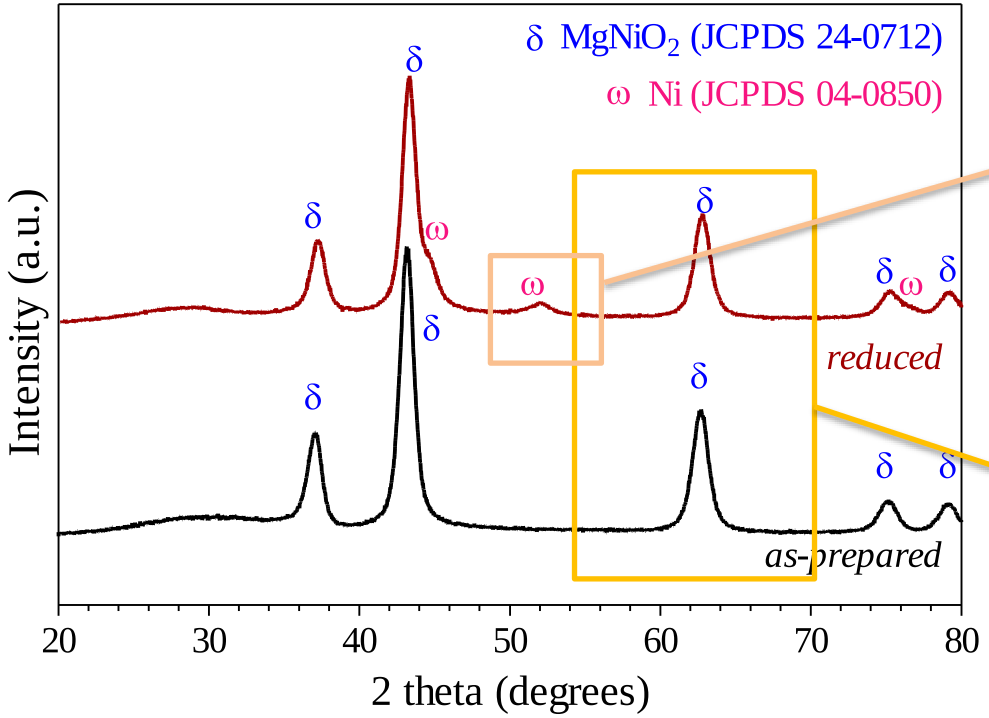


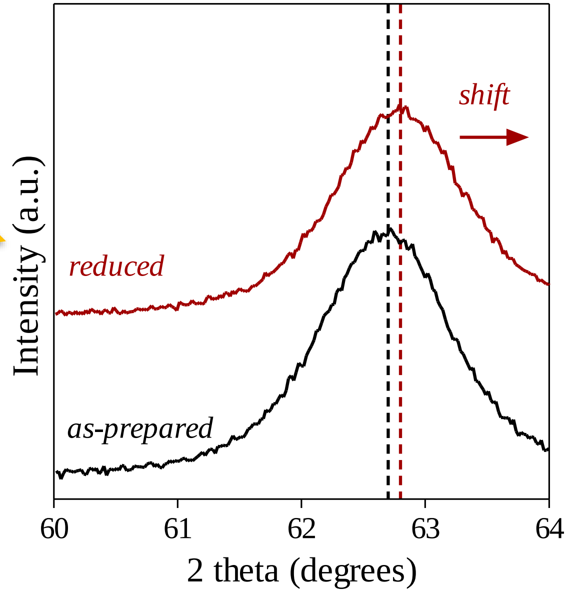
Sample	S-Q (wt.%)			
	$LaNiO_3$ (33-0711)	La_2NiO_4 (34-0314)	$MgNiO_2$ (24-0712)	NiO (04-0835)
$LaNiO_3$	99.3	-	-	0.7
$La_{0.7}Mg_{0.3}NiO_3$	-	89.0	11.0	-
$La_{0.4}Mg_{0.6}NiO_3$	-	72.2	27.8	-
$La_{0.1}Mg_{0.9}NiO_3$	-	-	100	-

CHARACTERIZATION: XRD



(200) crystal planes of metallic Ni (JCPDS 04-0859)

7.6 nm



Partial reduction of $MgNiO_2$ phase:
$MgNiO_2 + H_2 \rightarrow Ni + MgO\ H_2O$

$$r_{Ni^{2+}}^{(VI)} = 0.69\ \text{Å}$$

$$r_{Mg^{2+}}^{(VI)} = 0.57\ \text{Å}$$

Removal of larger Ni should cause reduction of the cell parameter and a shift to higher degrees!

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CHARACTERIZATION: H_2-TPR

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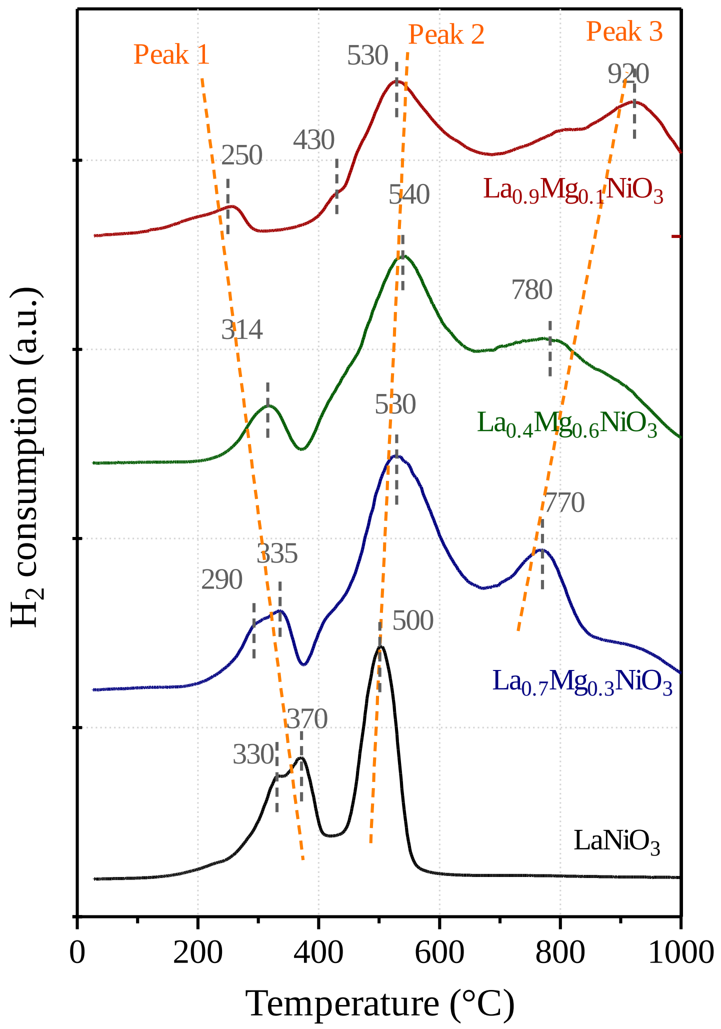
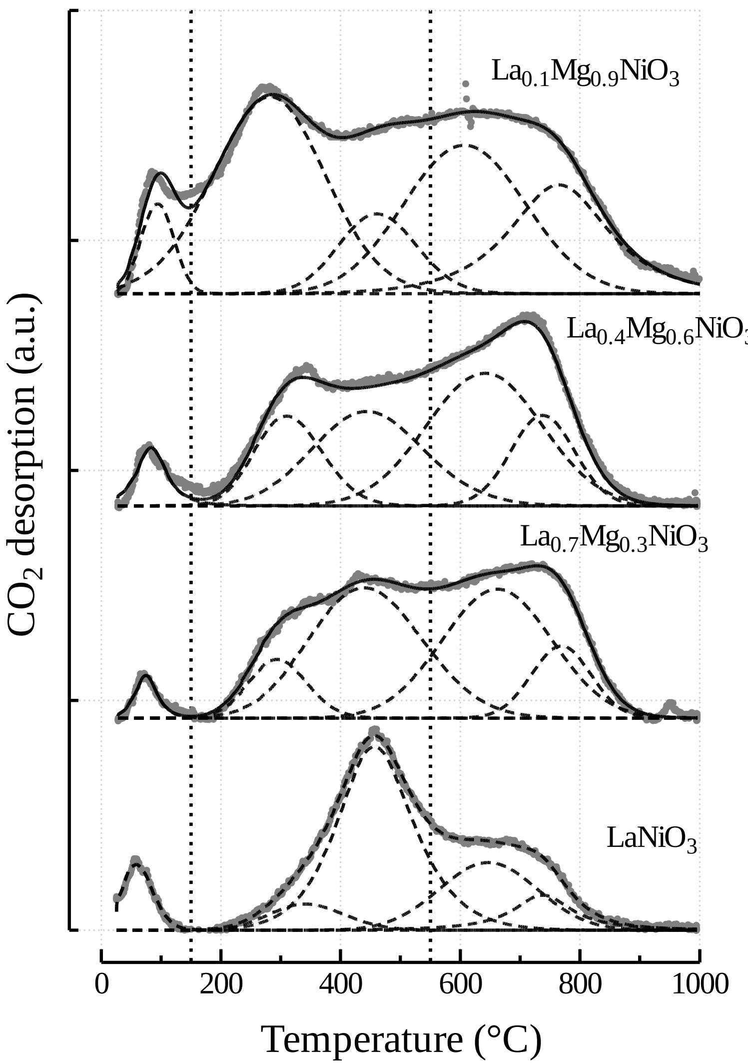


Sample	Hydrogen consumption (mmol/g)			
	Peak 1	Peak 2 (up to 600°C)	Total	Reducibility[a] (%)
$LaNiO_3$	2.83	3.26	6.09	98.9
$La_{0.7}Mg_{0.3}NiO_3$	0.54	2.36	2.90	91.2
$La_{0.4}Mg_{0.6}NiO_3$	0.48	2.73	3.21	75.9
$La_{0.1}Mg_{0.9}NiO_3$	0.39	2.31	2.60	31.1

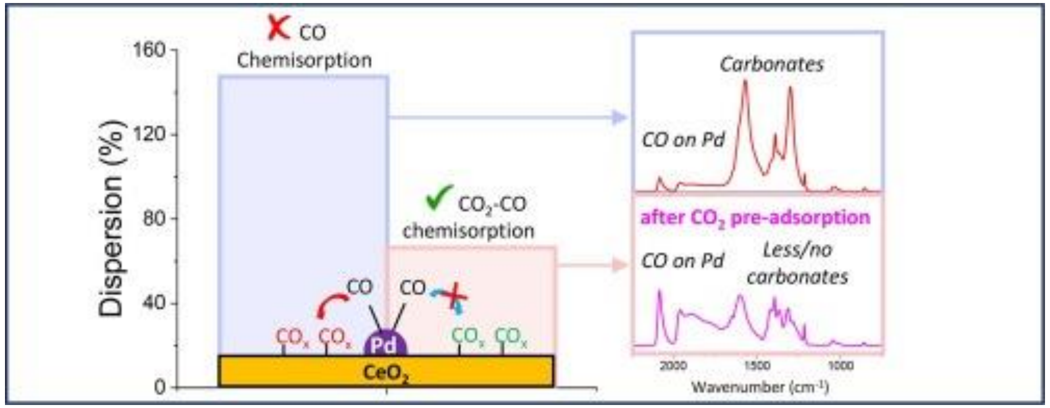
[a]*Calculated on the basis of XRD composition.*

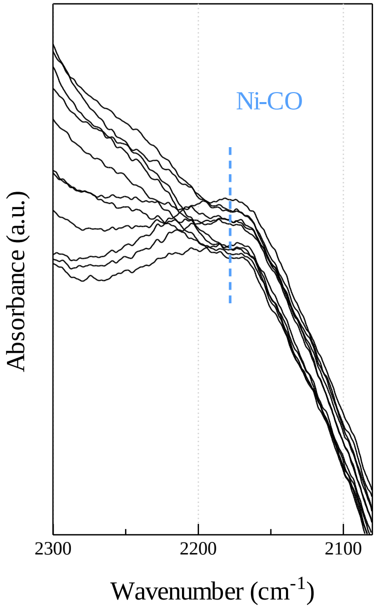
CHARACTERIZATION: CO_2-TPD

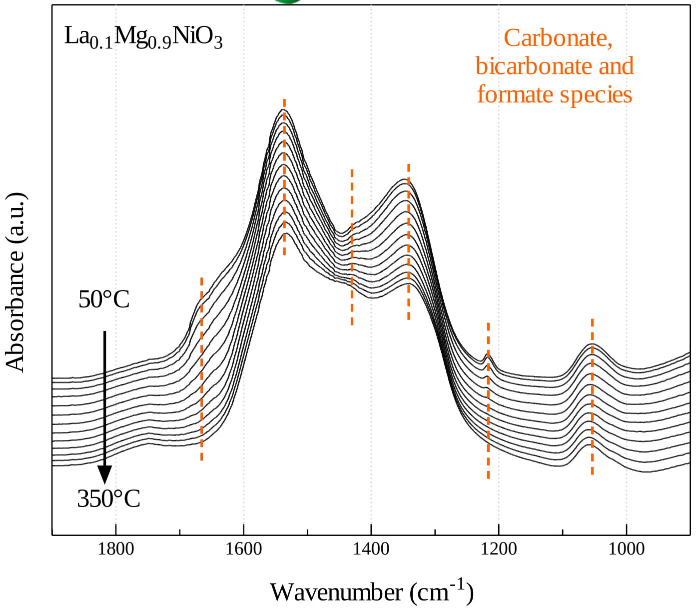


Sample	CO_2 desorption (µmol/g)			Total	
	Weak (<160°C)	Moderate (160-570°C)	Strong (>570°C)	µmol/g	µmol/m^2
$LaNiO_3$	13.6	105.6	64.7	183.9	9.2
$La_{0.7}Mg_{0.3}NiO_3$	6.6	121.9	116.2	244.7	15.4
$La_{0.4}Mg_{0.6}NiO_3$	12.5	119.7	124.1	256.3	17.0
$La_{0.1}Mg_{0.9}NiO_3$	35.0	218.7	150.1	403.8	46.7

CHARACTERIZATION: CO-CHEMISORPTION







Adapted CO chemisorption technique to measure Ni particle dispersion, avoiding carbonate formation over the support.

$$D_{Ni}(\%) = \frac{Ni_s}{Ni_t} = \frac{f_{CO/Ni} \cdot V_{CO} \cdot M_{Ni}}{22414 \cdot d_r} \cdot 100 = 8.1\ \%$$

12.5 nm

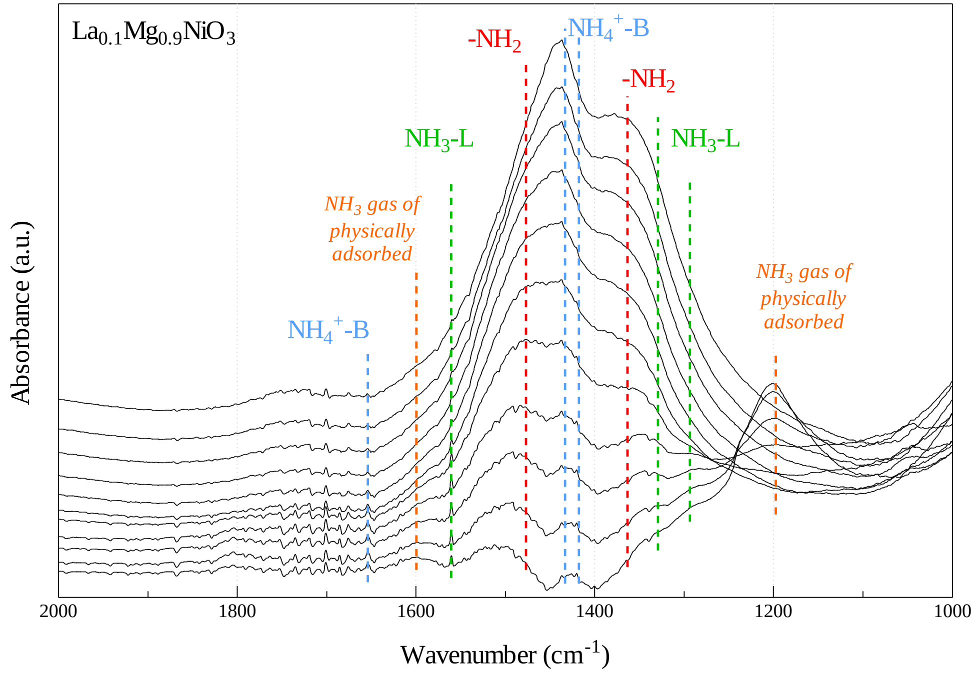
The Ni dispersion ($D_{Ni}(\%)$) was based on the simplified assumption that CO molecules are linearly chemisorbed on Ni (stoichiometric factor for CO chemisorption $f_{CO/Ni}$=1 is);
V_{CO} (4.95 cm^3/g_{cat}) is the amount of CO chemisorbed on Ni;
M_{Ni} (58.69 g_{Ni}/mol_{Ni}) is the molar mass of Ni;
L_{Ni} is the Ni content in the catalyst (from XRD;
d_r (0.16 g_{Ni}/g_{cat}) is the reduction degree of Ni calculated from H_2-TPR.

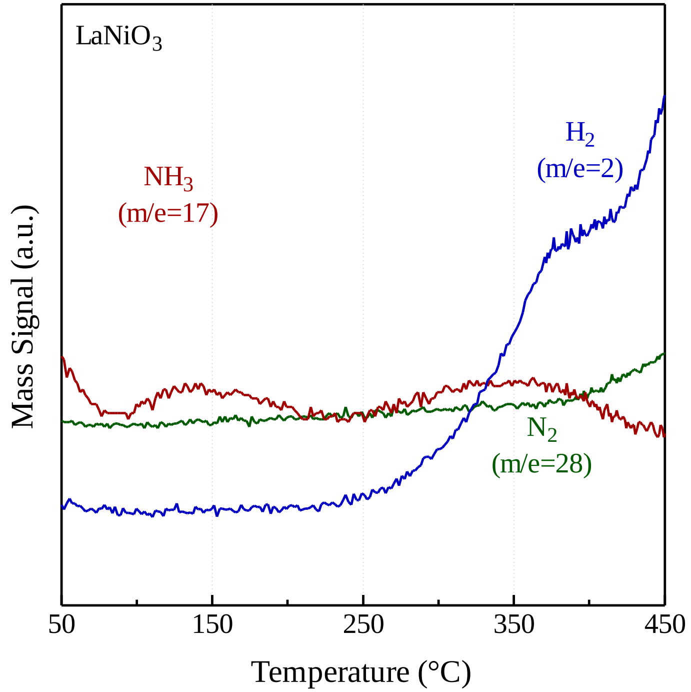
$$\text{TOF}= \frac{F_{NH3,in} \cdot \chi_{NH3}}{Ni_s}$$

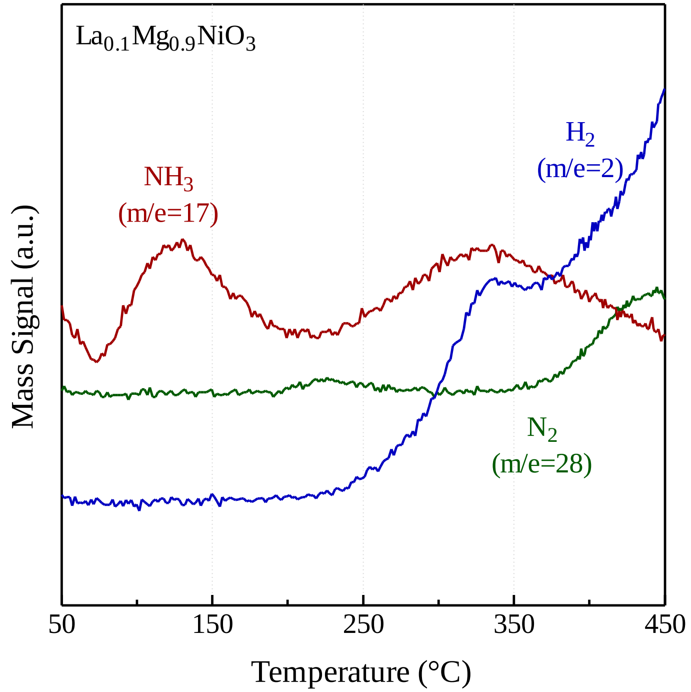
$$Ni_s = D_{Ni}(\%) \cdot Ni_t$$

$F_{NH3,in}$ is the inlet NH_3 flow ($mol_{NH3} \cdot g_{cat}^{-1} \cdot min^{-1}$);
χ_{NH3} is the conversion of NH_3;
Ni_s is the number of reduced surface Ni atoms (mol_{Ni}/g_{cat}, determined by CO-chemisorption);
Ni_t is the total number of reduced Ni atoms (mol_{Ni}/g_{cat}, determined by H_2-TPR).

CHARACTERIZATION: NH_3-TPD







CHARACTERIZATION: XPS

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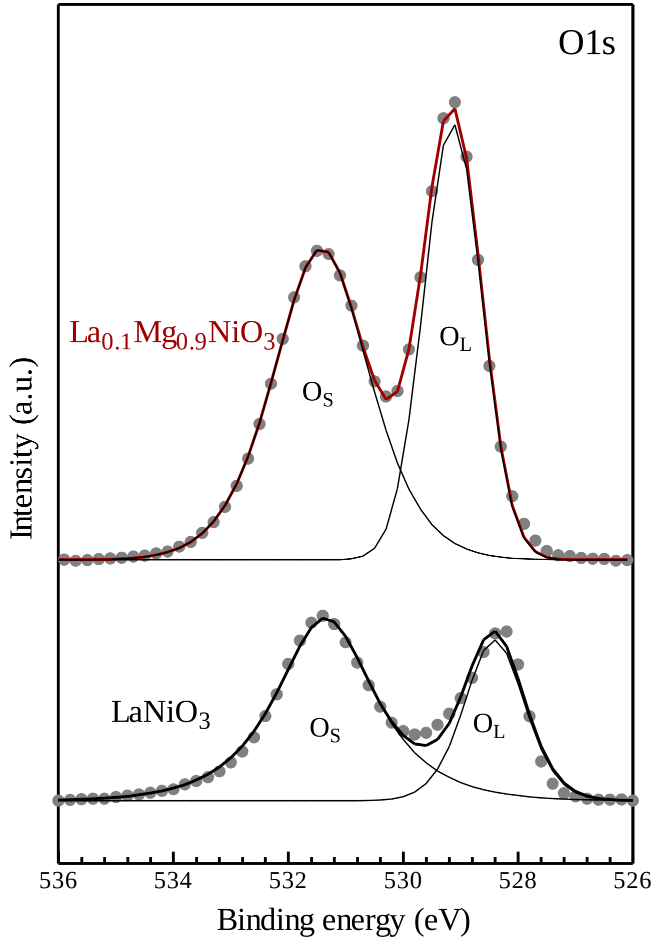
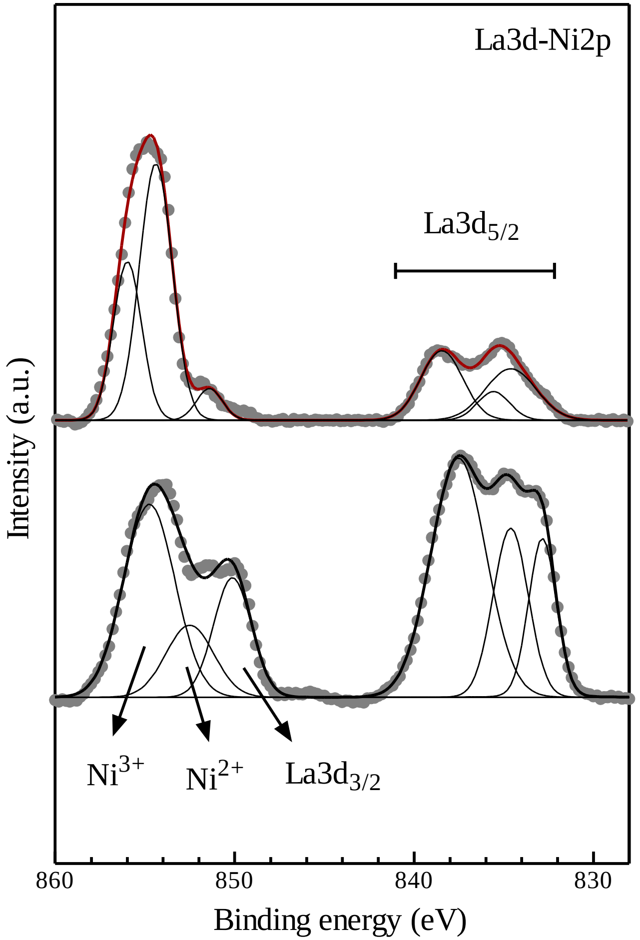




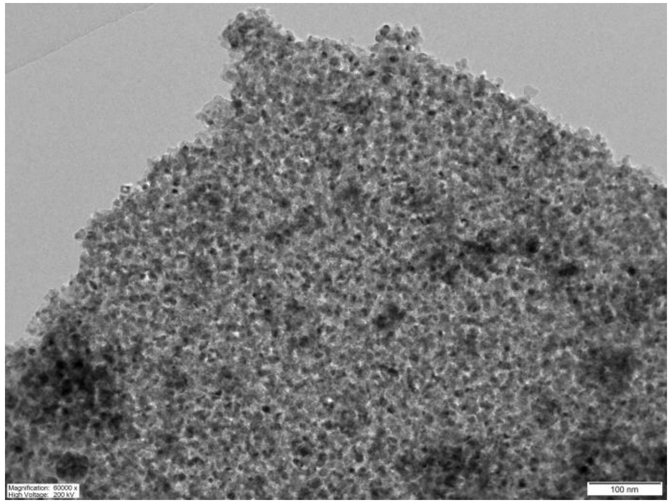
Fitting results od O1s, La3d and Ni2p photoelectron spectra.

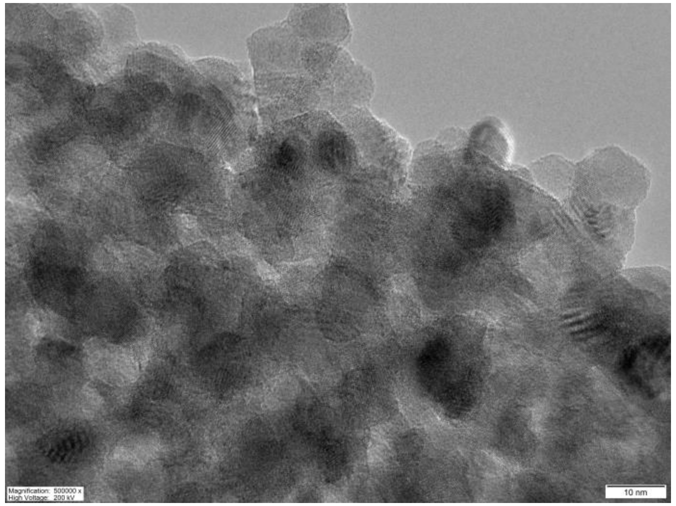
Peak BE (eV)		**Line**	**Assignment**
$LaNiO_3$	**$La_{0.1}Mg_{0.9}NiO_3$**		
528.4	530.0	1s	O^{2-} in lattice (O_L)
531.4	532.3	1s	O^{2-} in Ni/La hydroxide or oxygen vacancies (O_S)
832.8	835.5	$3d_{5/2}$	La_2O_3
834.6	836.5		Satellite
837.5	839.4	$3d_{5/2}$	$La(OH)_3$
850.1	852.3	$3d_{3/2}$	La_2O_3
852.5	855.3	$2p_{3/2}$	Ni (II) oxide
854.8	856.9	$2p_{3/2}$	Ni (III) oxide

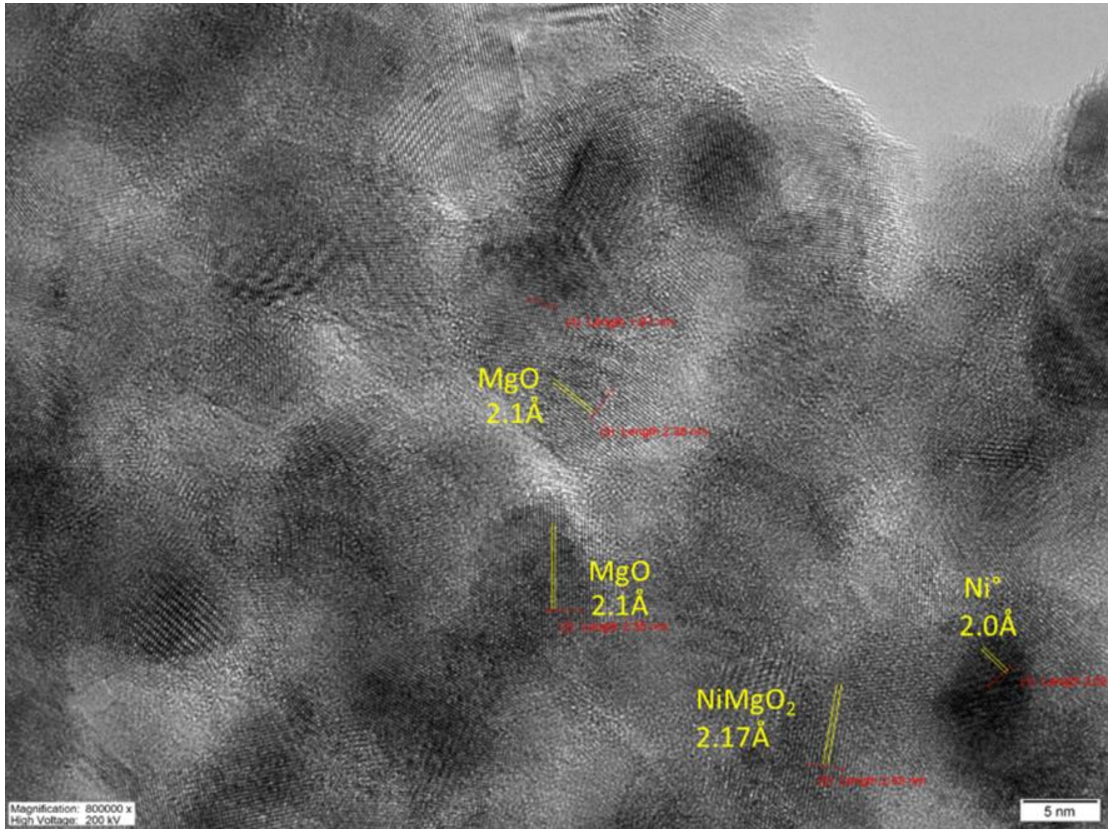
Summary of XPS analysis.

Sample	**Relative O content (%)**		**Relative Ni content (%)**	
	O_L	**O_S**	**Ni(II)**	**Ni(III)**
$LaNiO_3$	33.1	66.9	25.8	74.2
$La_{0.1}Mg_{0.9}NiO_3$	44.7	55.3	69.3	30.7

CHARACTERIZATION: TEM







$La_{0.1}Mg_{0.9}NiO_3$

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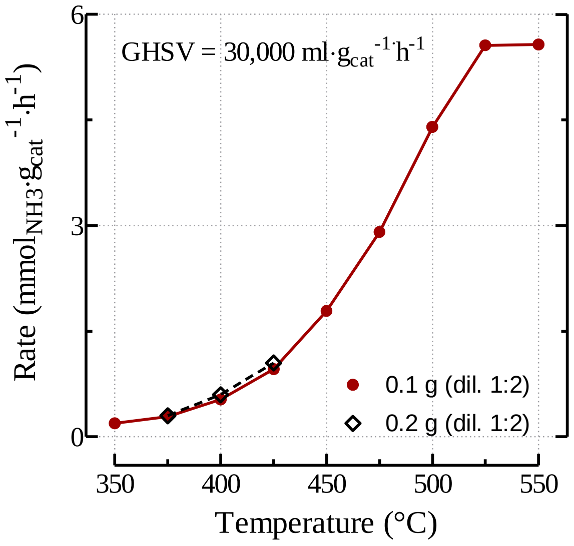
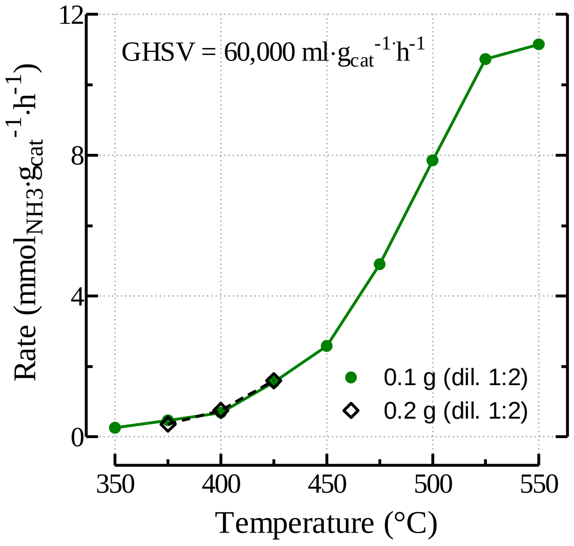
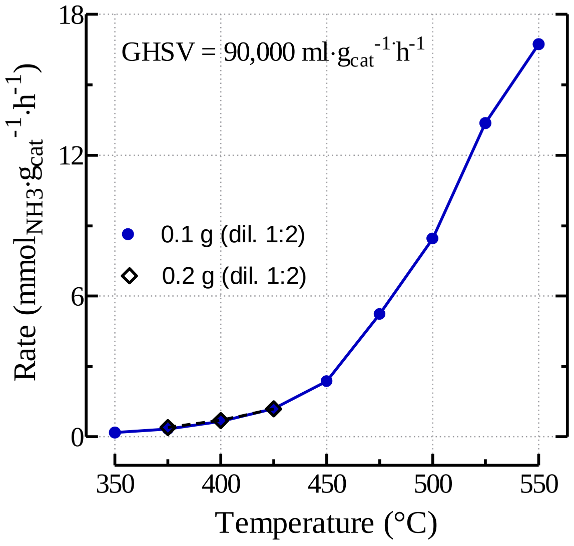
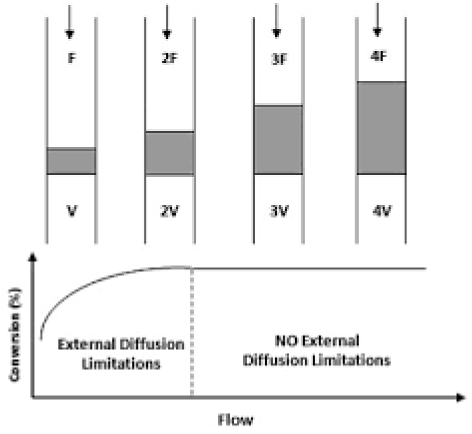
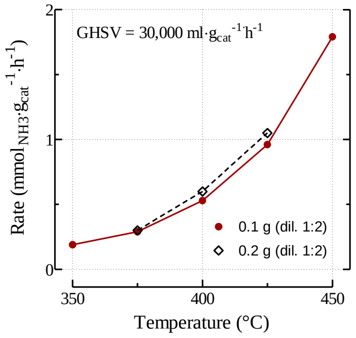
ACTIVITY TESTS: EXTERNAL DIFFUSION

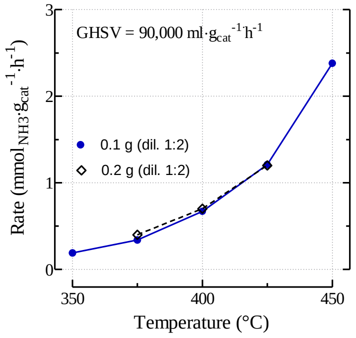


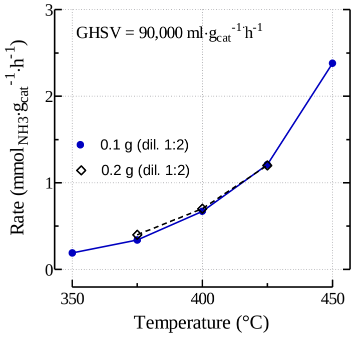








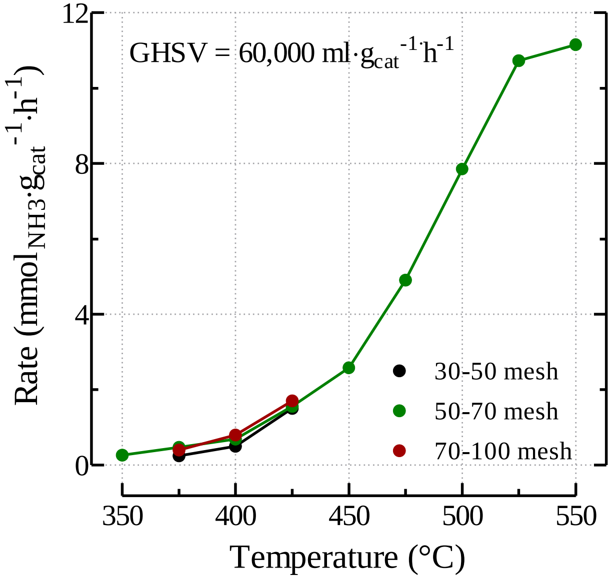


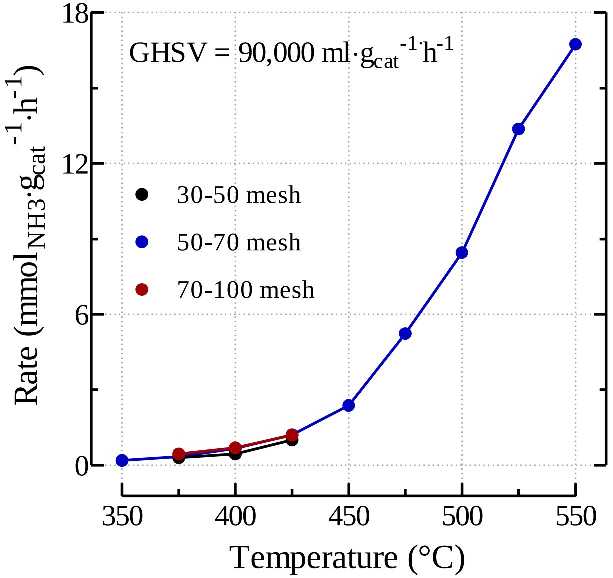


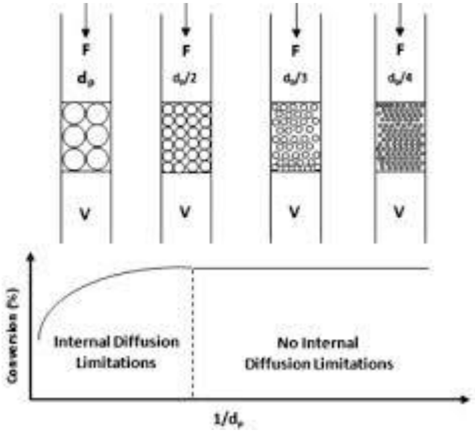
Selected conditions:
60,000 ml·g_{cat}^{-1}·h^{-1}
0.1 gr of catalyst (catalyst:quartz:1:2)

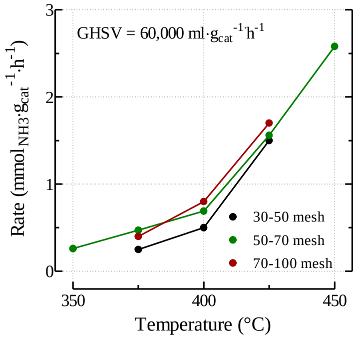
**25 vol.%NH_3 in He*

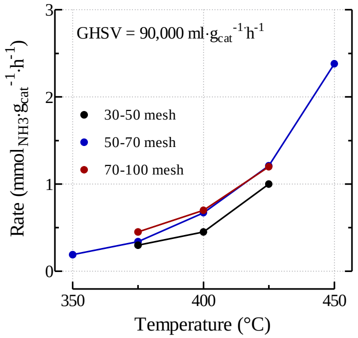
ACTIVITY TESTS: INTERNAL DIFFUSION











Selected conditions:
60,000 ml·g$_{cat}$$^{-1}$·h^{-1}
0.1 gr of catalyst (catalyst:quartz:1:2)
50-70 mesh

**25 vol.%NH_3 in He*

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ACTIVITY TESTS: GHSV

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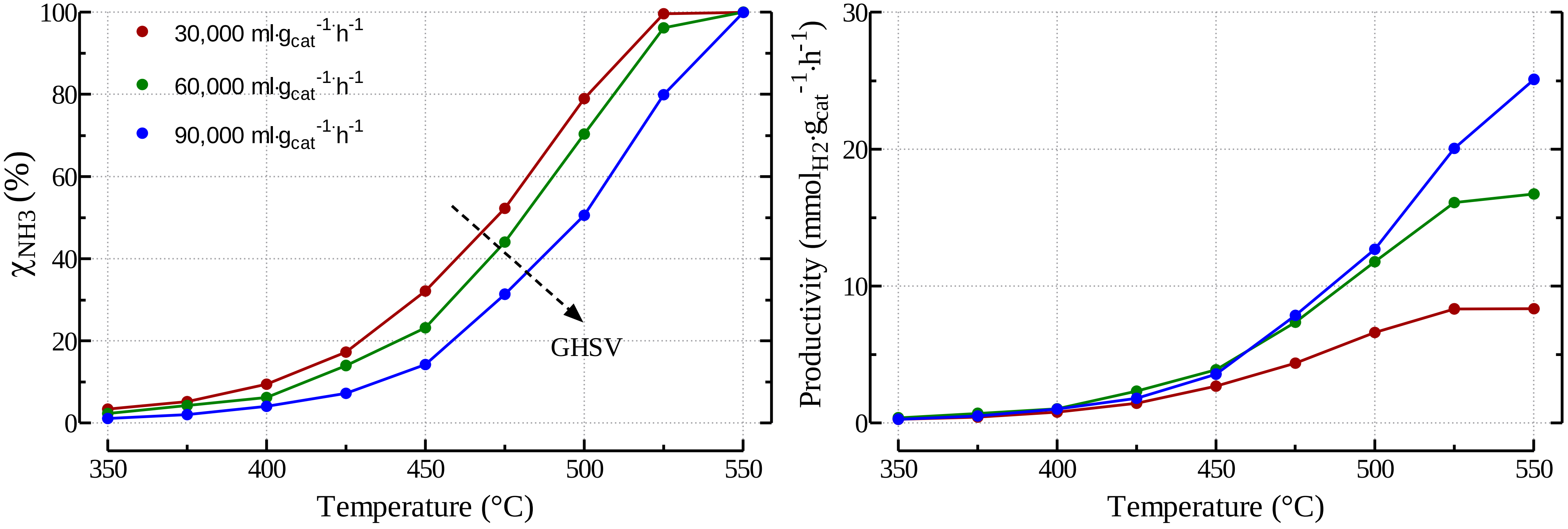

$*25$ vol.%NH_3 in He

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ACTIVITY TESTS: DETERMINATION OF KINETIC PARAMETERS

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The commonly accepted reaction mechanism includes the elementary steps of the chemisorption of ammonia, the consecutive dehydrogenation of ammonia, and the combinative desorption of hydrogen and nitrogen:

$$NH_3 + * \Leftrightarrow NH_3* \qquad \text{(i)}$$

$$NH_3* + * \Leftrightarrow NH_2* + H* \qquad \text{(ii)}$$

$$NH_2* + * \Leftrightarrow NH* + H* \qquad \text{(iii)}$$

$$NH* + * \Leftrightarrow N* + H* \qquad \text{(iv)}$$

$$2N* \Leftrightarrow N_2 + 2* \qquad \text{(v)}$$

$$2H* \Leftrightarrow H_2 + 2* \qquad \text{(vi)}$$

where * and X* denote an empty site and a species X bonded to the surface, respectively. Either step (ii) or (v) or both of them are generally agreed to be the rate-determining steps while the other reaction steps are in equilibrium

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ACTIVITY TESTS: ARRHENIUS PLOT

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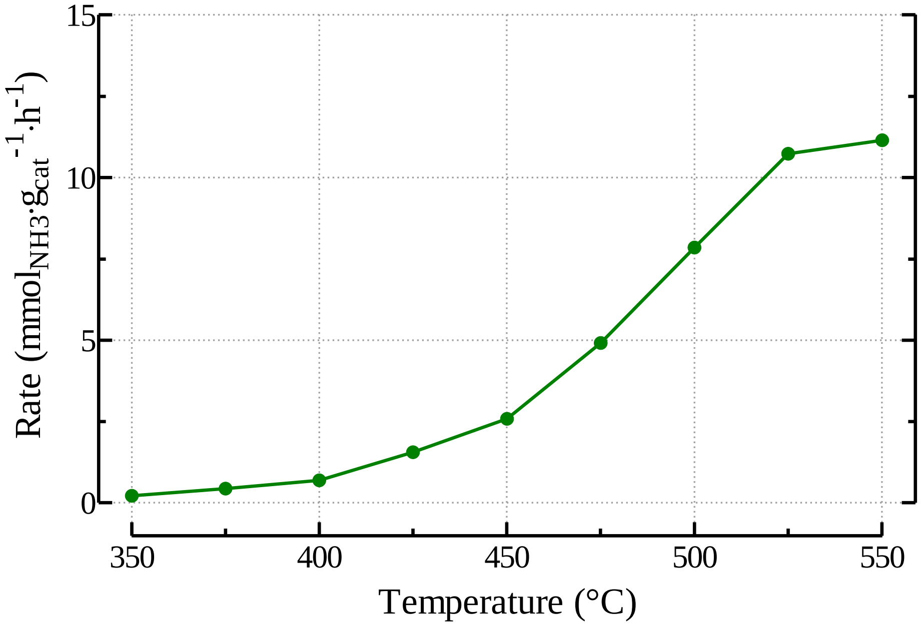

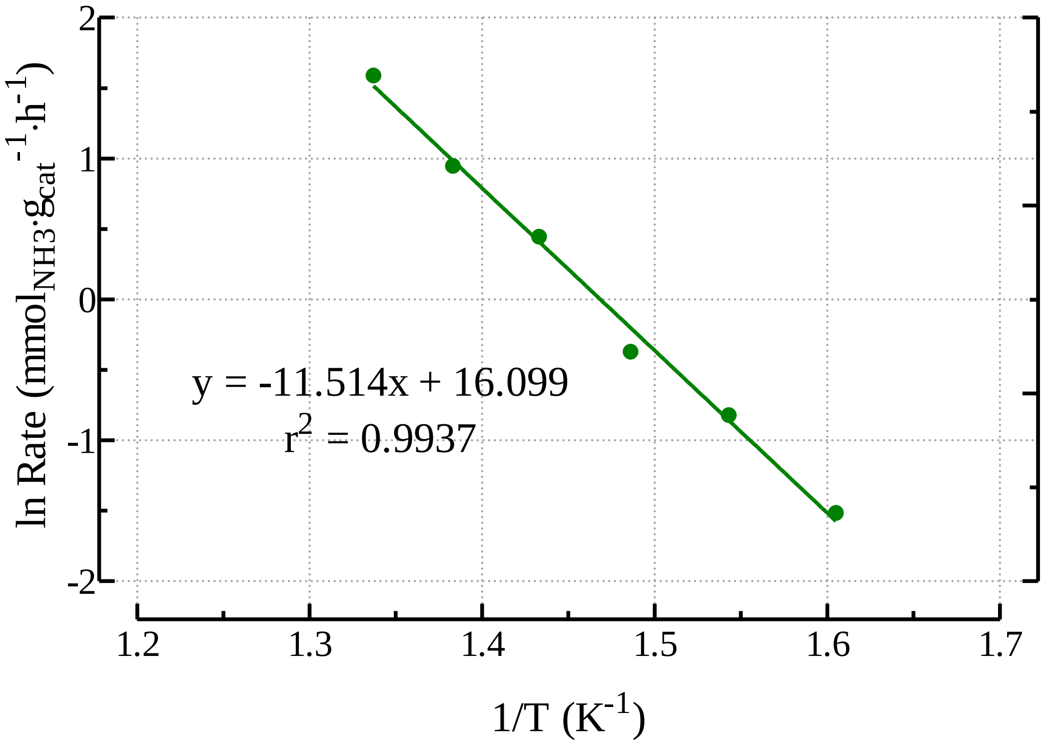

$$k = k_0 \, e^{-E_a/RT}$$

$$\ln r = -\frac{E_a}{RT} + \text{constant}$$

E_a = 95.7 kJ·mol^{-1}
k_0 = 9.81E+06 mmol$_{NH3}$·g$_{cat}$$^{-1}$·h^{-1}

**25 vol.%NH$_3$ in He*

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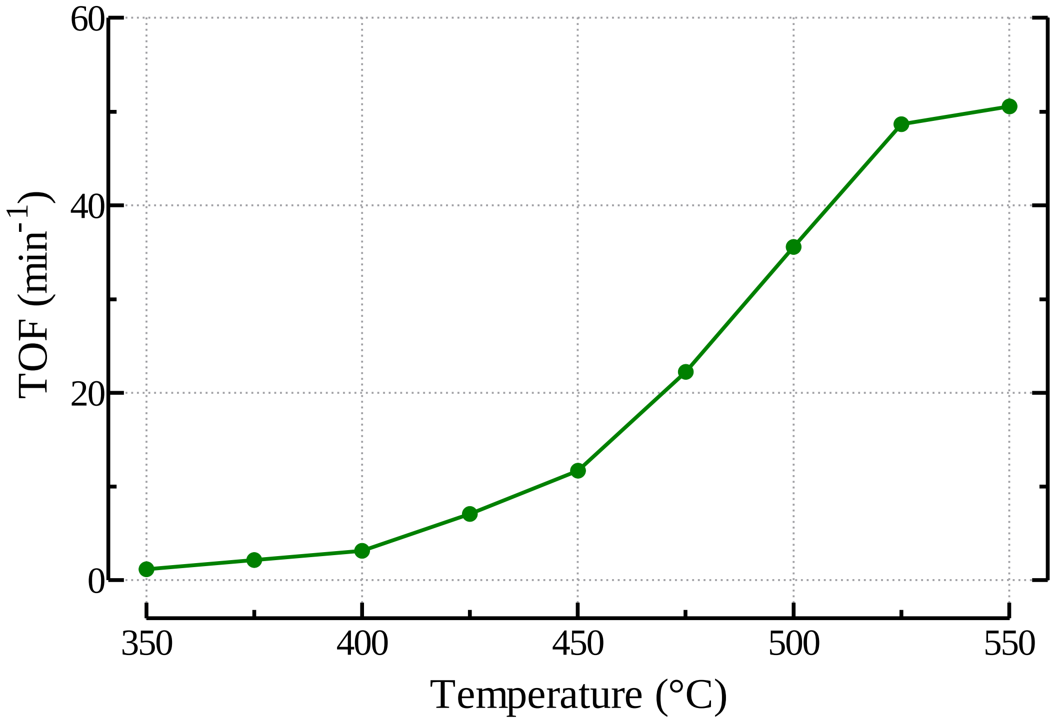
ACTIVITY TESTS: TOF



$$TOF = \frac{F_{NH3,in} \cdot \chi_{NH3}}{Ni_s}$$

$$Ni_s = D_{Ni}(\%) \cdot Ni_t$$

$F_{NH3,in}$ is the inlet NH_3 flow ($mol_{NH3} \cdot g_{cat}^{-1} \cdot min^{-1}$);
χ_{NH3} is the conversion of NH_3;
Ni_s is the number of reduced surface Ni atoms (mol_{Ni}/g_{cat}, determined by CO-chemisorption);
Ni_t is the total number of reduced Ni atoms (mol_{Ni}/g_{cat}, determined by H_2-TPR).

**25 vol.% NH_3 in He*

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ACTIVITY TESTS: POWER LOW MODEL

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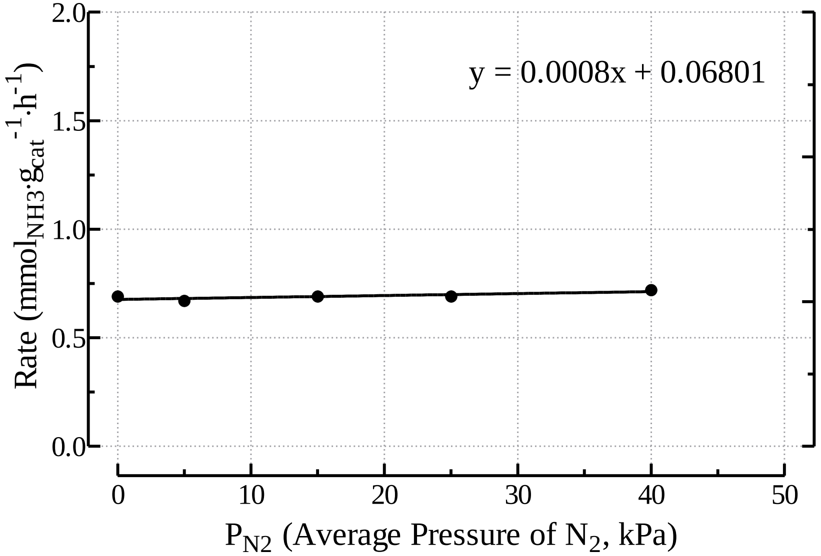
No dependence on partial pressure of N_2

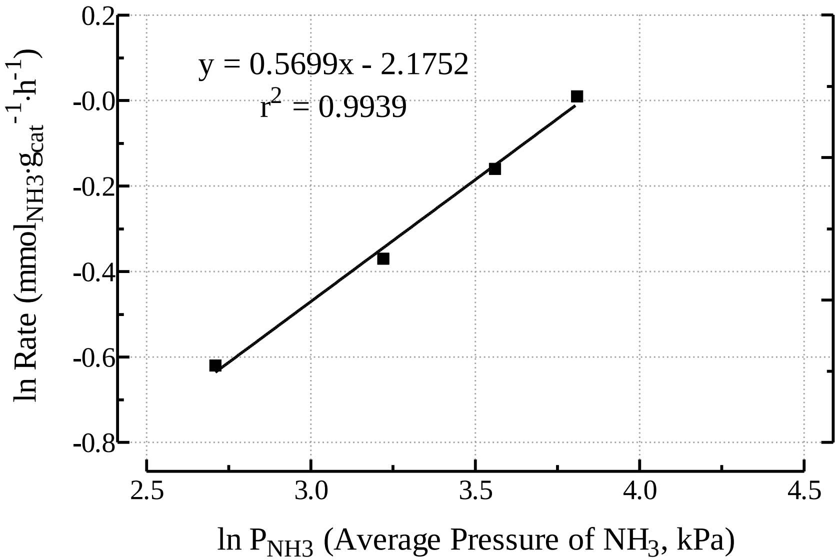


$$r_{NH_3} = kP^a_{NH_3} P^b_{H_2} P^c_{N_2}$$

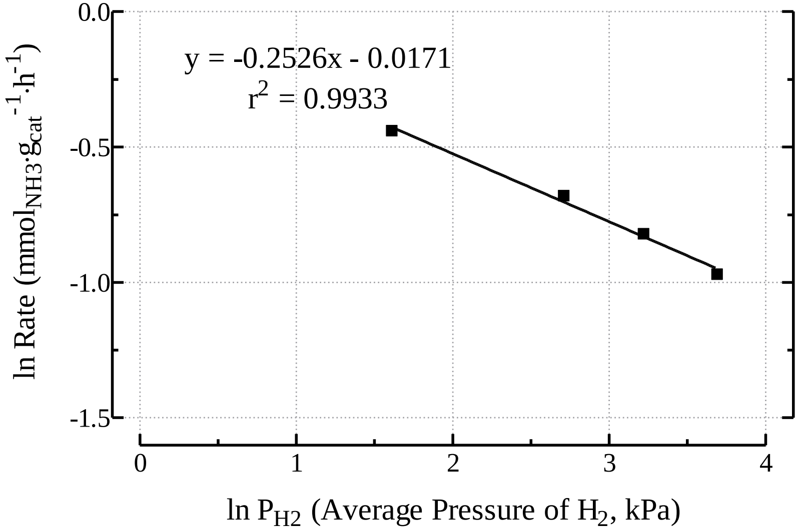
$$r_f = k' P^a_{NH_3} P^b_{H_2}$$

***25 vol.%NH$_3$ in He; 400 °C**

Positive order dependence on NH_3



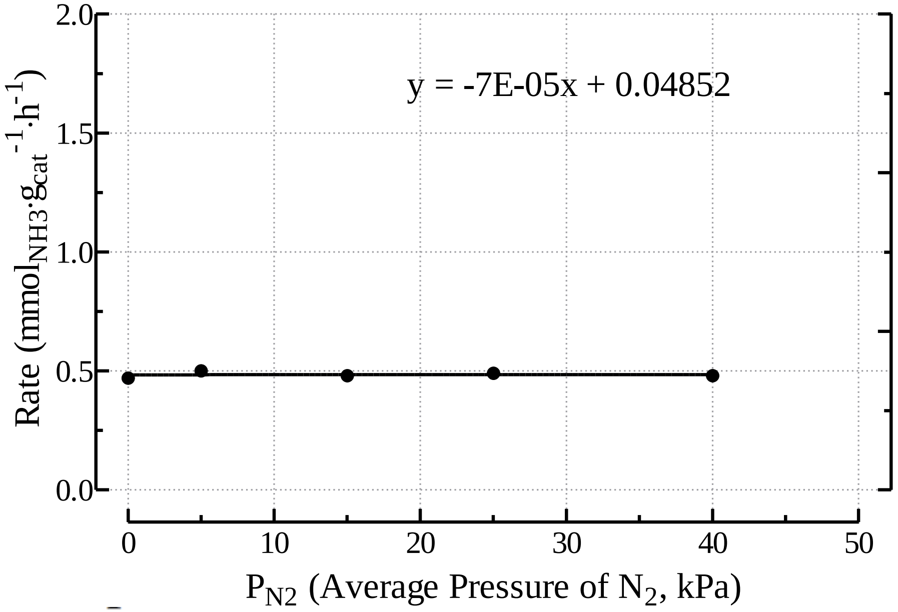
Negative order dependence on H_2



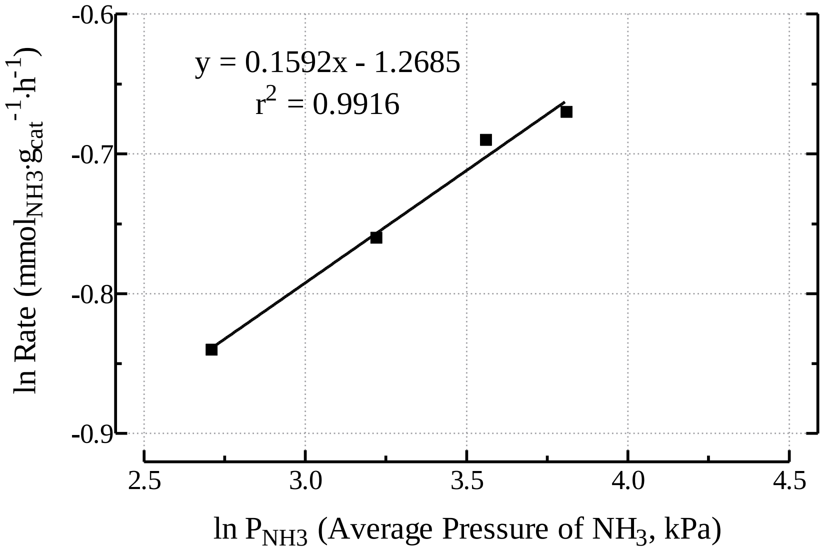
a = 0.57
b = -0.25
c = 0

ACTIVITY TESTS: POWER LOW MODEL

No dependence on partial pressure of N_2



Positive order dependence on NH_3

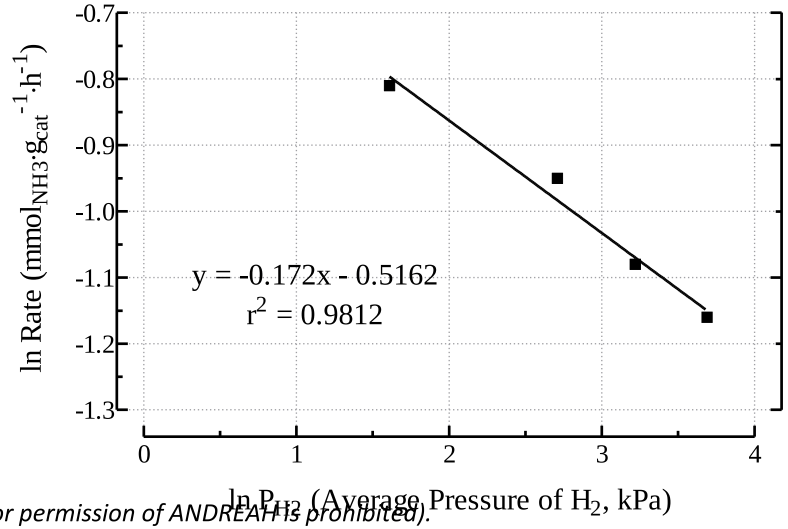


$$r_{NH_3} = kP_{NH_3}^{a} P_{H_2}^{b} P_{N_2}^{c}$$

$$r_f = k' P_{NH_3}^{a} P_{H_2}^{b}$$

a = 0.16
b = -0.17
c = 0

Negative order dependence on H_2



**25 vol.% NH_3 in He; 375 °C*

ACTIVITY TESTS: TEMKIN-PYZHEV MODEL

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$2\ NH_{3\,(g)} \leftrightarrow 2\ N^* + 3\ H_{2\,(g)}$

$2\ N^* \rightarrow N_{2\,(g)} + 2\ ^*$

$$r_A = k\left[\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{\beta} - \frac{P_{N_2}}{K_{eq}^2}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{1-\beta}\right]$$

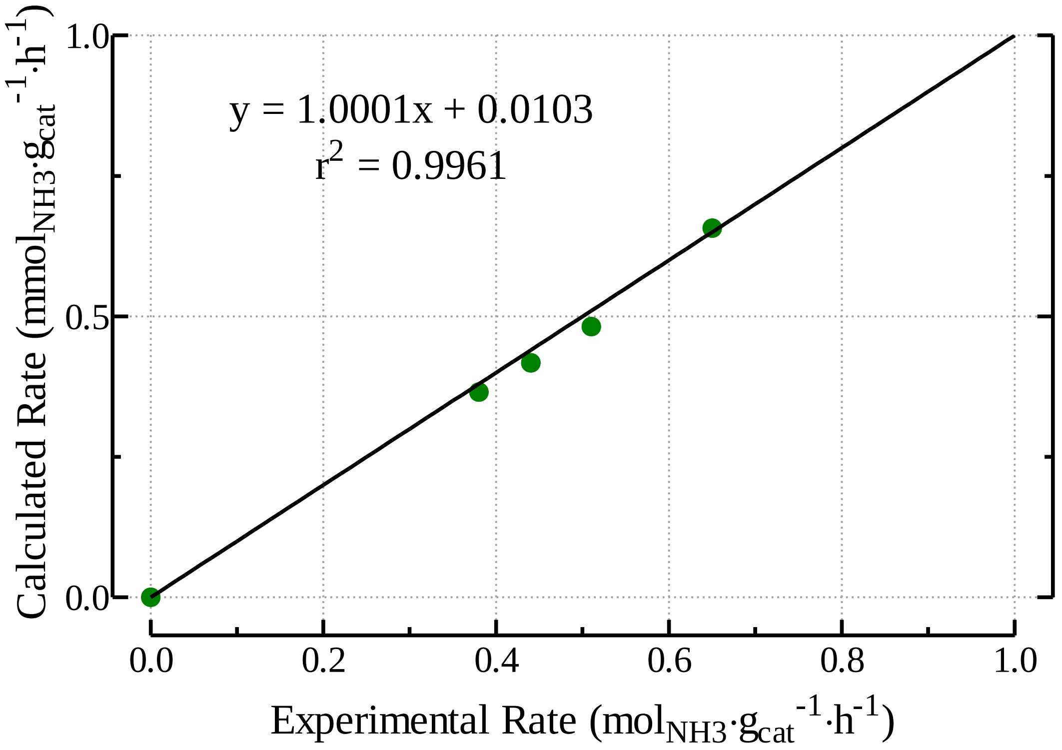
$$k = k_0\, e^{-E_a/RT}$$

Under the conditions employed, the value of approach to equilibrium (η) is always lower than 0.003:

$$\eta = \frac{[P_{N_2}]^{0.5}[P_{H_2}]^{1.5}}{[P_{NH_3}]} \times \frac{1}{K_{eq}}$$

$$r_f = k_f P_{NH_3}^a P_{H_2}^b = k_0\, e^{-E_a/RT}\left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{\beta}$$

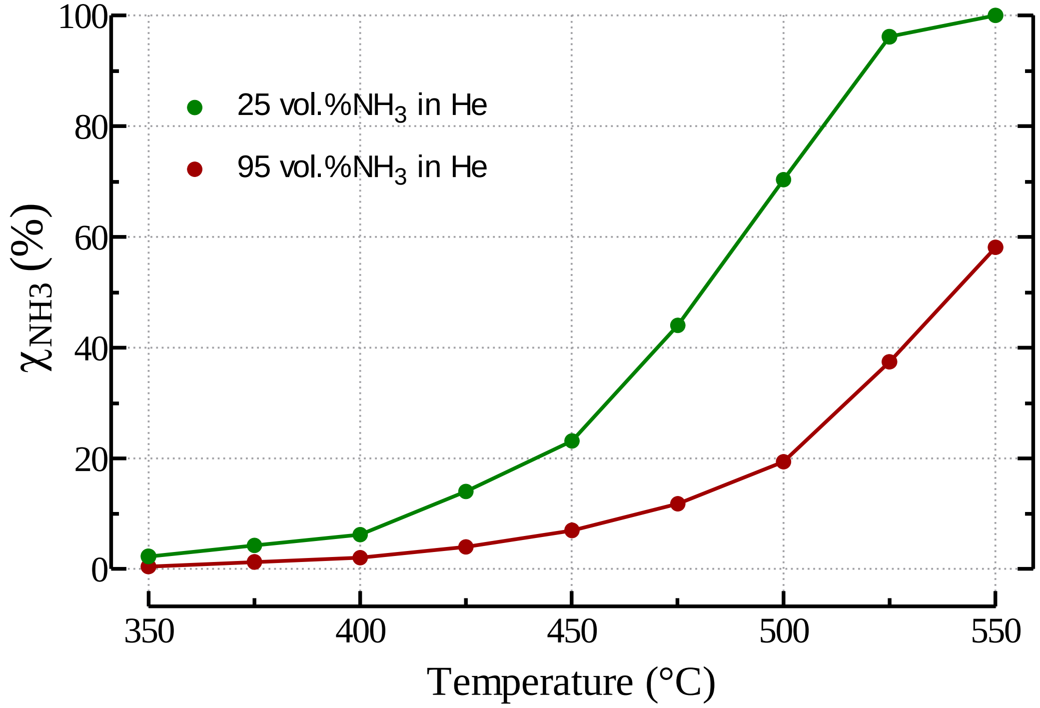
25 vol.%NH_3 in He; 400 °C

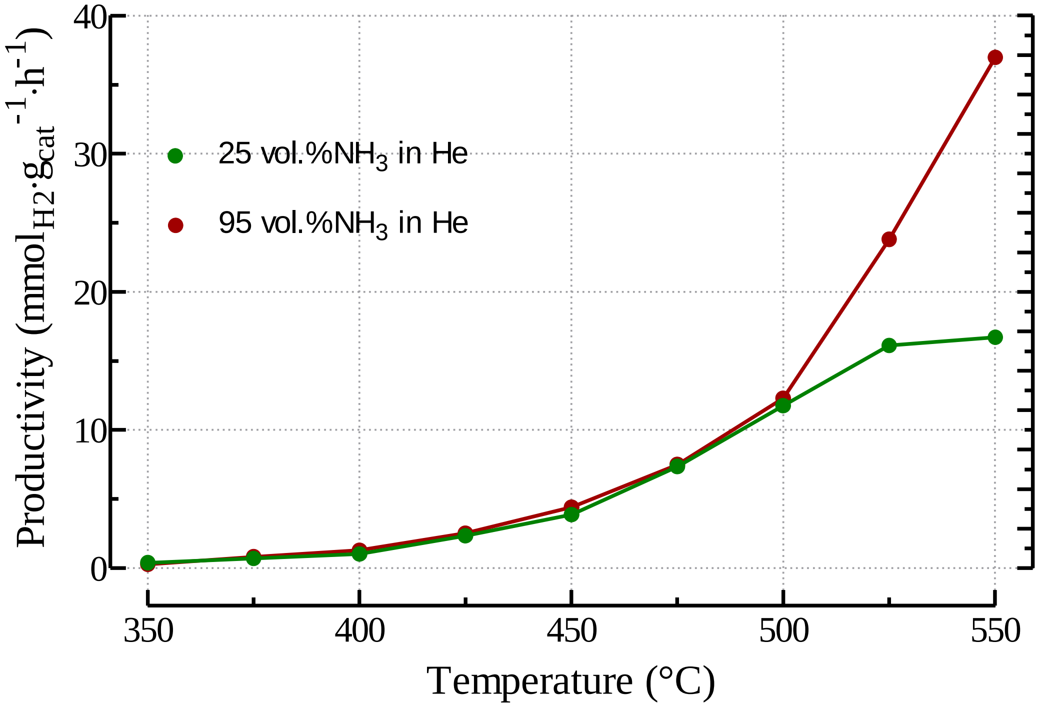


a = 0.57
b = -0.25
c = 0

β = 0.094
E_a = 95.7 $kJ\cdot mol^{-1}$
k_0 = 9.81E+06 $mmol_{NH3}\cdot g_{cat}^{-1}\cdot h^{-1}$

ACTIVITY TESTS: NH_3 CONCENTRATION





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MAIN CONCLUSIONS

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- The formation of the $MgNiO_2$ phase increases the stability of the $La_{0.1}Mg_{0.9}NiO_3$ catalyst (see TPR). The strong metal-metal interaction promotes the formation of small Ni particles after reduction (no sintering, see XRD and CO-chemisorption).

- The CO chemisorption performed via Tacheguchi (to avoid carbonates formation over the support, see IR) confirms the particle size obtained by XRD.

- Basicity is the key strength (see CO_2-TPD). The electron-donor property of Mg promotes the dehydrogenation and N_2 desorption stages.

- XPS evidences partial reduction of Ni^{3+} to Ni^{2+} (in agreement with XRD) and the presence of hydroxyl group of perovslyte structure

- N_2 desorption is the rate-determining step (RDS), as evidenced by the mass spectrometry coupled with IR.

- The kinetics of the NH_3 decomposition reaction has been investigated over $Na_{0.1}Mg_{0.9}NiO_3$ catalyst. Steady-state kinetic data reveals that this reaction proceeds according to the Temkin-Pyzhev mechanism, in which the recombinative desorption of N* acts as the rate-determining step.

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Thank you for your attention