MAGNESIUM-DOPED LANTHANUM NICKELATE PEROVSKITES FOR AMMONIA DECOMPOSITION: KINETIC ANALYSIS AT LOW TEMPERATURES

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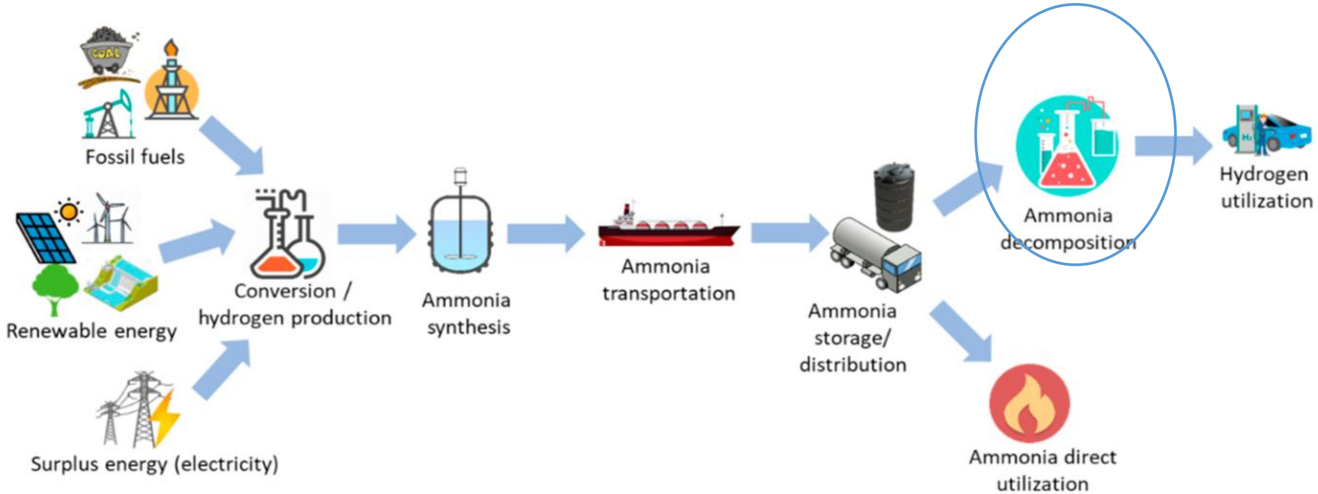
OUTLINE

- Introduction
- Preliminary Tests (optimal catalyst identification)
- Catalysts Synthesis and Characterization
- Activity Tests & Kinetic Evaluation
- Conclusions

INTRODUCTION

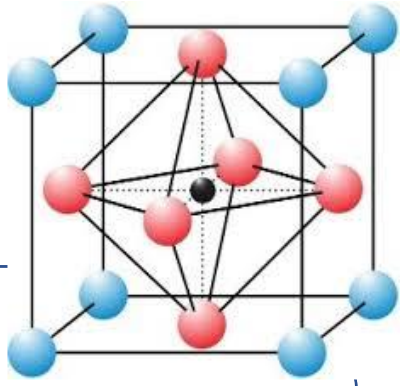
Ammonia Decomposition



Safe transportation
High energy density (4.25 kWh/L)
Easily liquifieble (8bar 20 ^{o}C)
C free Energy carrier

Energies **2020**, *13*(12), 3062

Perovskites



- Perovskite general formula ABO_3
- Metal exsolution: size controlled metal nanoparticles
- Incorporation of different dopants
- Facile preparation
- Strong metal support interaction
- uniform spatial distribution after reduction
- Precursor for transition metal based catalyst

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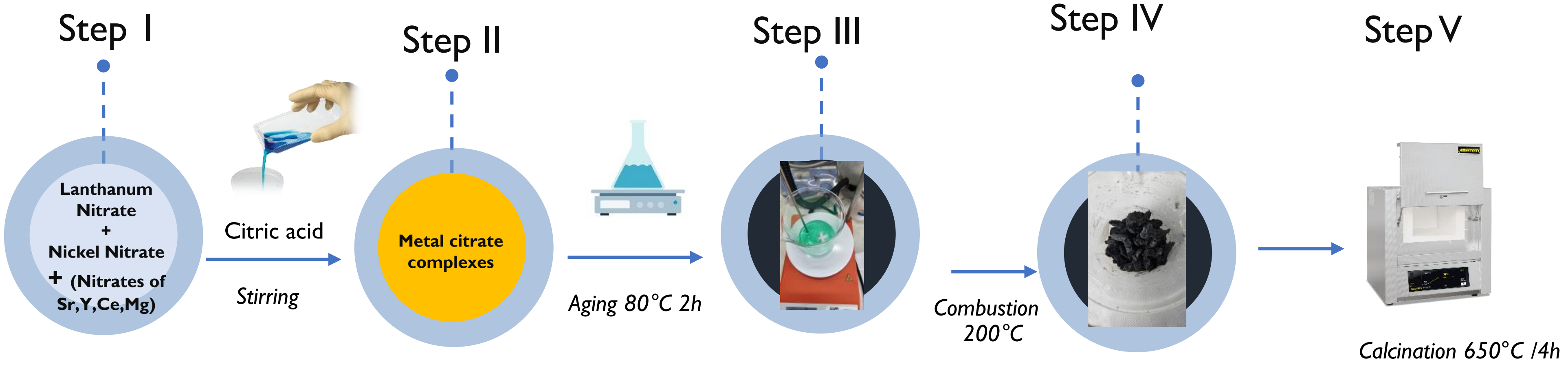
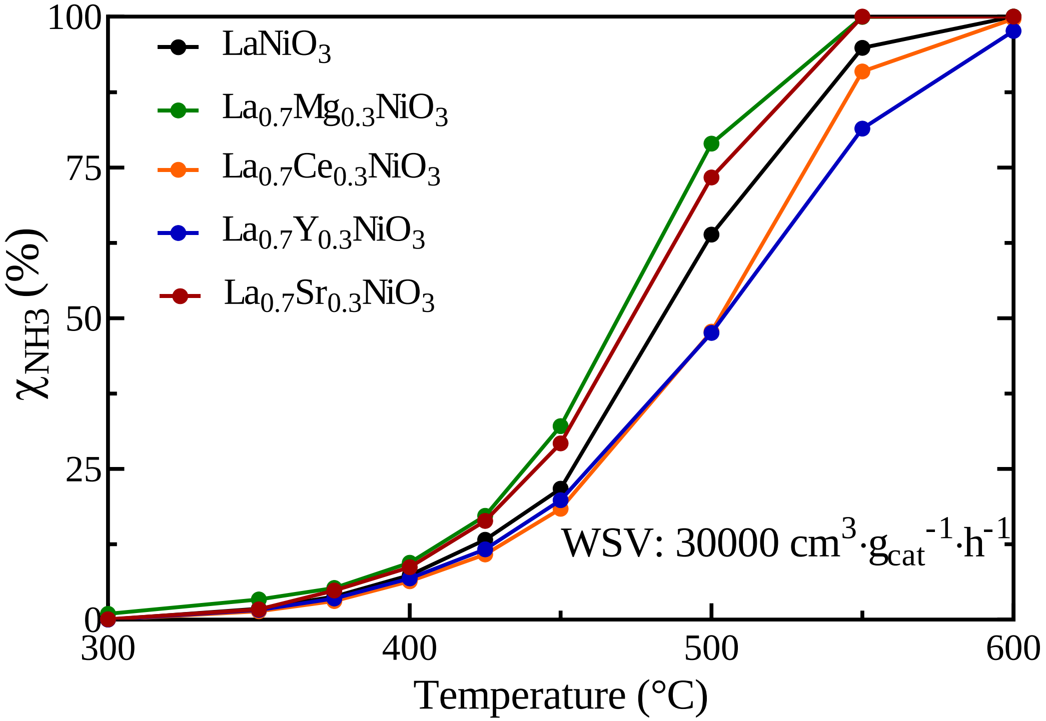
SYNTHESIS

- Preparation of novel (A-doped $La_xA_{1-x}NiO_3$ perovskites, A= Mg, Y, Ce, Sr) by **sol-gel combustion method**



Sr Precursor	Y Precursor	Mg Precursor	Ce Precursor	Liquid medium	Fuel
$Sr(NO_3)_2$ Strontium nitrate	$Y(NO_3)_3$ Yttrium nitrate	$Mg(NO_3)_2$ Magnesium nitrate	$Ce(NO_3)_2$ Cerium Nitrate	water	Citric acid

PRELIMINARY TESTS

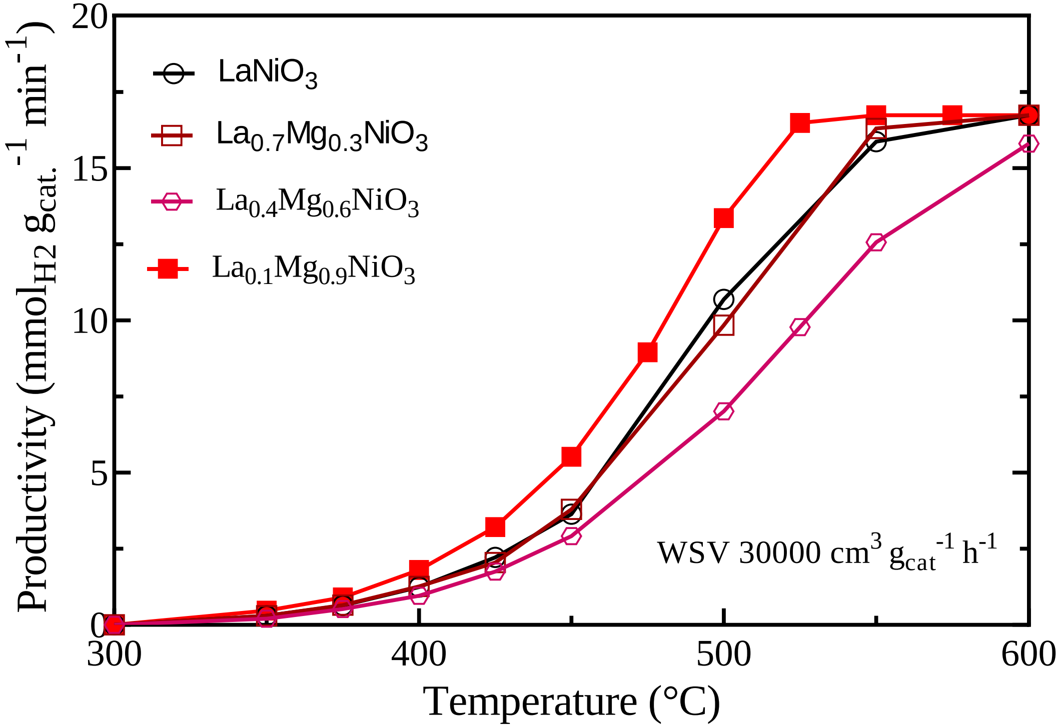


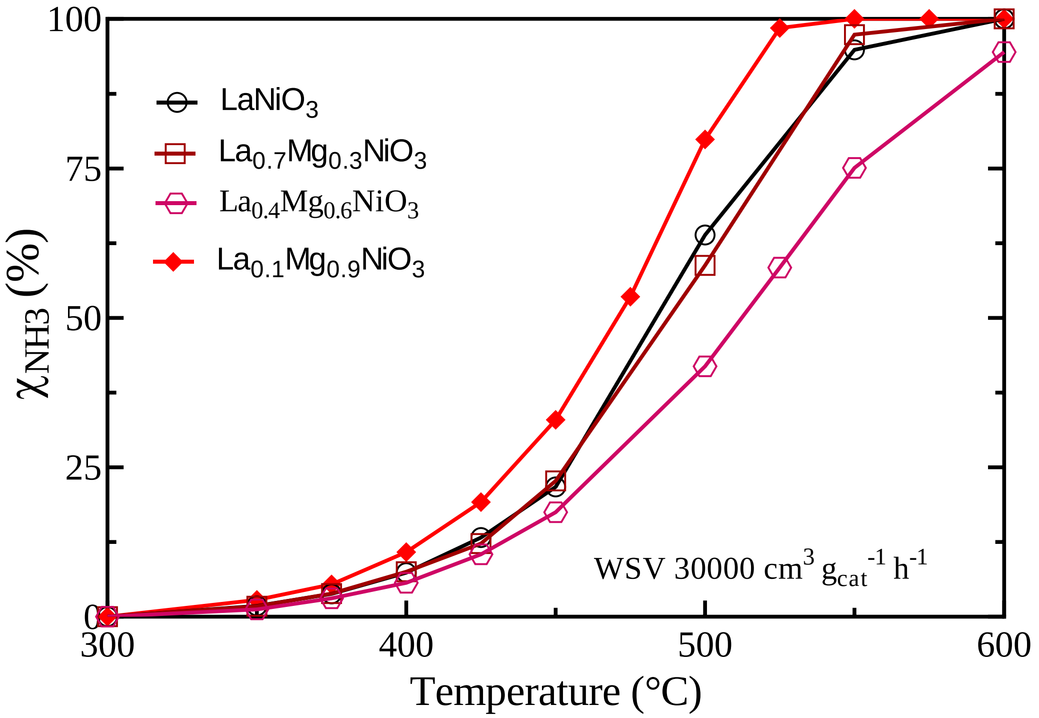
Sample	SA_{BET} (m_2/g)	NiO crystallite size from XRD (nm)
$LaNiO_3$	9	-
$La_{0.7}Mg_{0.3}NiO_3$	15	9.2
$La_{0.7}Ce_{0.3}NiO_3$	7	18
$La_{0.7}Y_{0.3}NiO_3$	8	7.6
$La_{0.7}Sr_{0.3}NiO_3$	7	13

**50 vol.%NH_3 in He*
200 mg (dilution ratio 1:1)

Mg is the promoter selected for the subsequent tests and evaluation

AMMONIA DECOMPOSITION

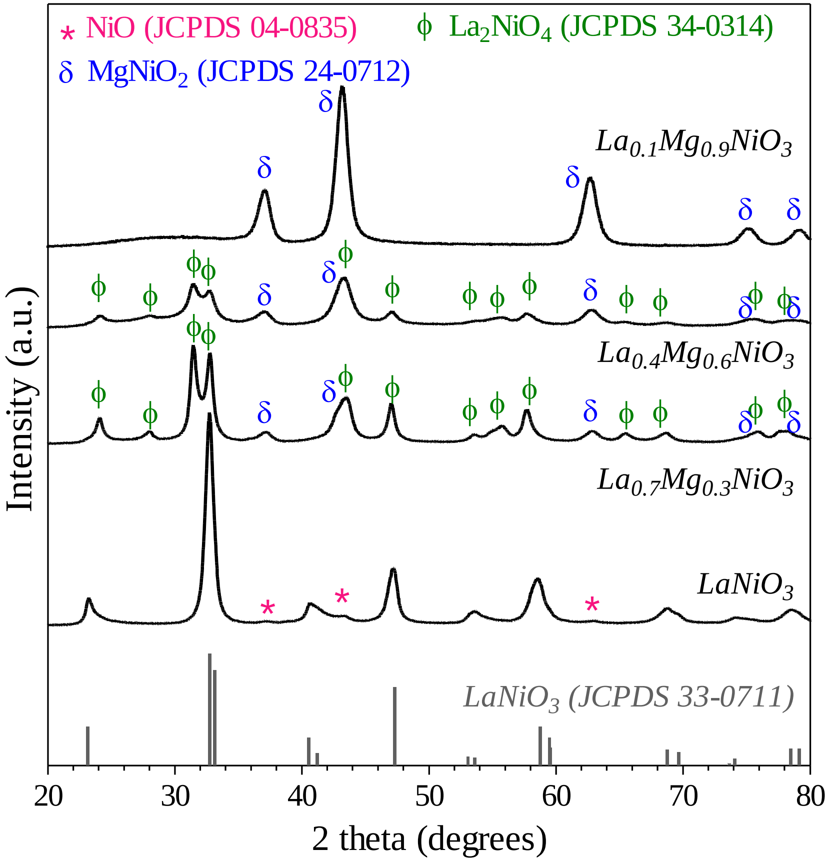




**50 vol.%NH$_3$ in He*
200 mg (dilution ratio 1:1)

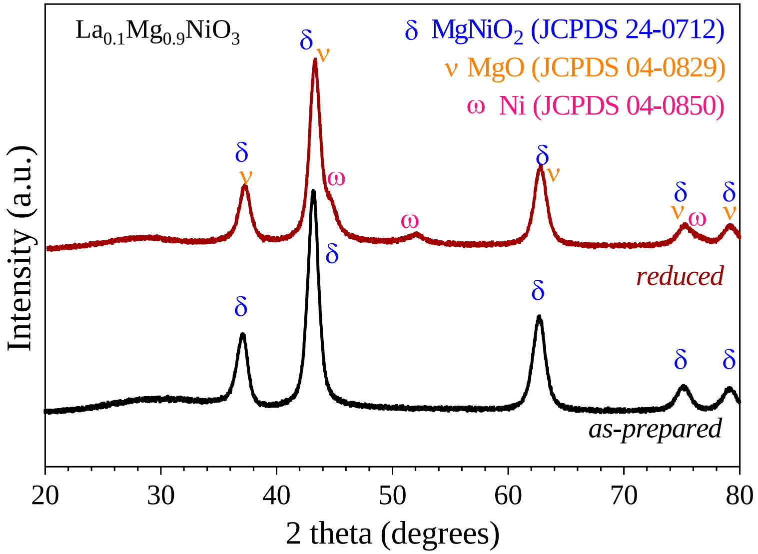
6 mmolH$_2$ gcat^{-1} min^{-1}, at 450 ^{o}C

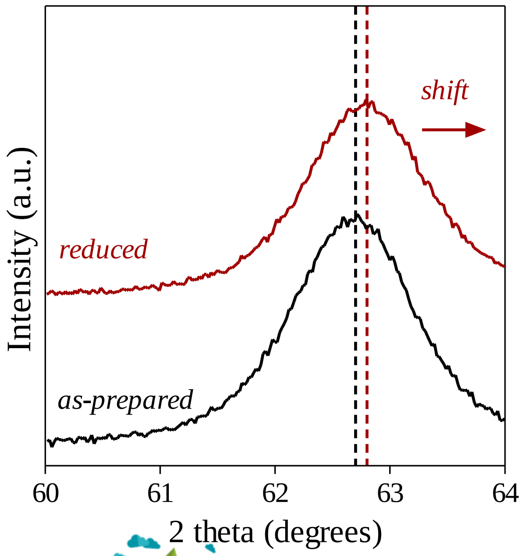
CHARACTERIZATION: XRD



phases :La_2NiO_4, $MgNiO_2$,NiO

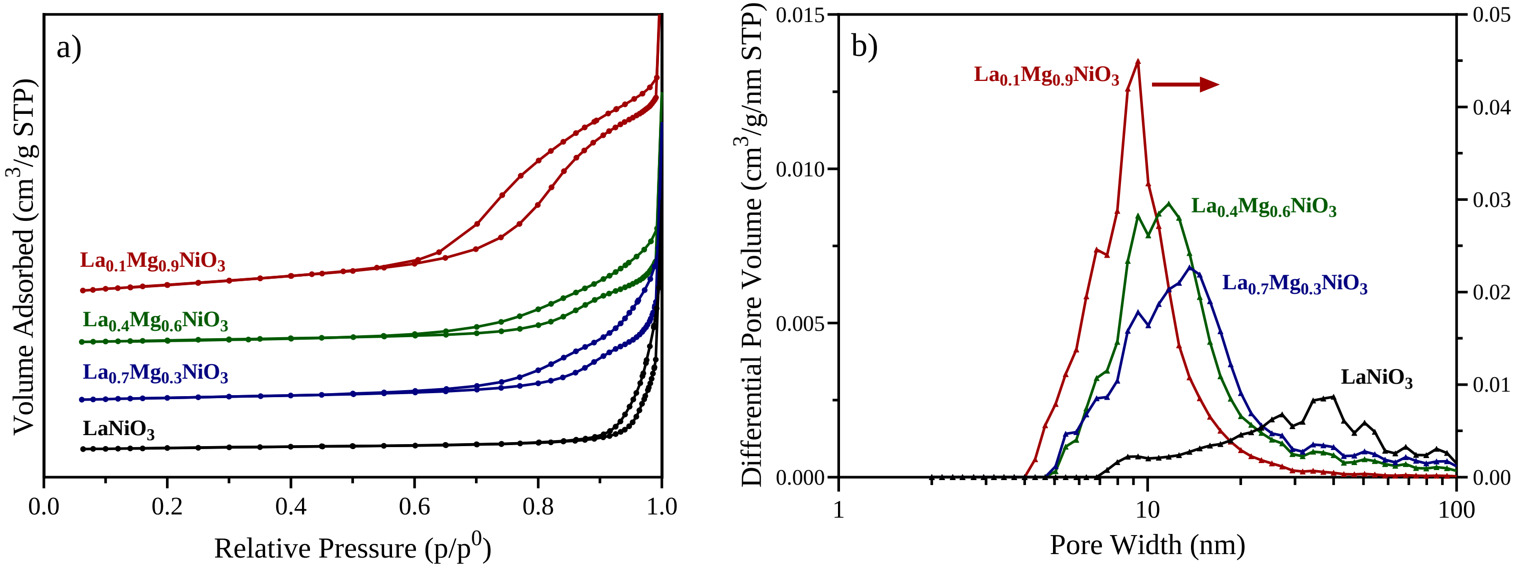
Sample	S-Q (wt.%)			
	$LaNiO_3$ (33-0711)	La_2NiO_4 (34-0314)	$MgNiO_2$ (24-0712)	NiO (04-0835)
$LaNiO_3$	99.3	-	-	0.7
$La_{0.7}Mg_{0.3}NiO_3$	-	89.0	11.0	-
$La_{0.4}Mg_{0.6}NiO_3$	-	72.2	27.8	-
$La_{0.1}Mg_{0.9}NiO_3$	-	-	100	-





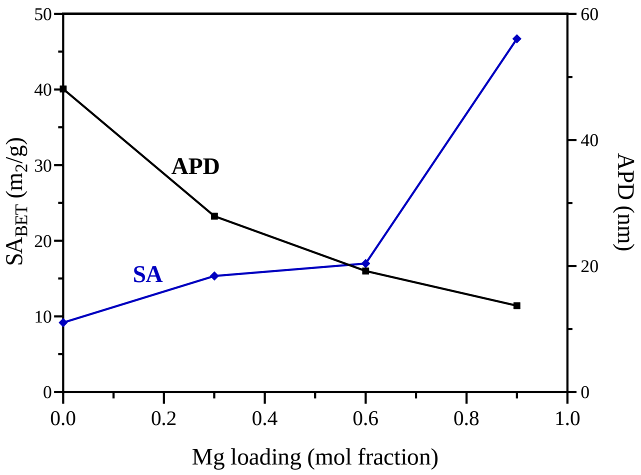
Crystallite size of Ni is 7.6 nm

N_2-PHYSISORPTION



Mg addition improved the surface area and pore characteristics

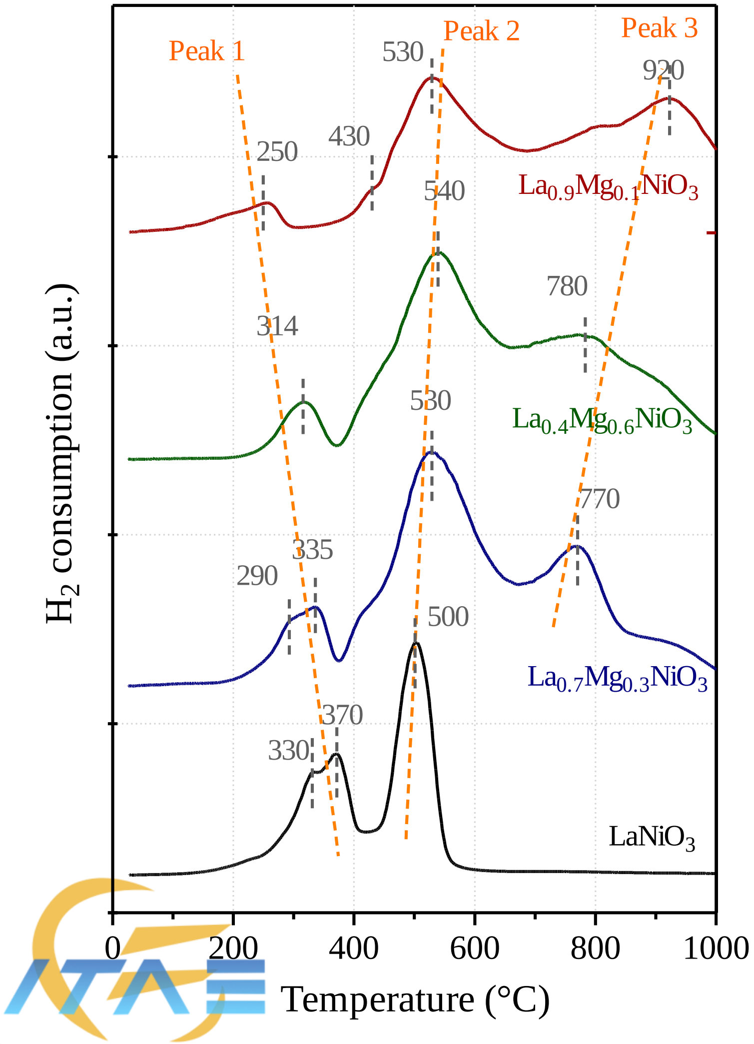
Sample	SA_{BET} (m_2/g)	$PV_{BJH}{}^a$ (cm_3/g)	APD^b (nm)
$LaNiO_3$	9.19	0.1104	48.1
$La_{0.7}Mg_{0.3}NiO_3$	15.35	0.1072	27.9
$La_{0.4}Mg_{0.6}NiO_3$	17.00	0.0814	19.2
$La_{0.1}Mg_{0.9}NiO_3$	46.71	0.1598	13.7



[a] *BJH desorption cumulative Pore Volume in the range 1.7-300 nm;*

[b] *Average pore Diameter from APD=4·PV/SA.*

H_2-TPR

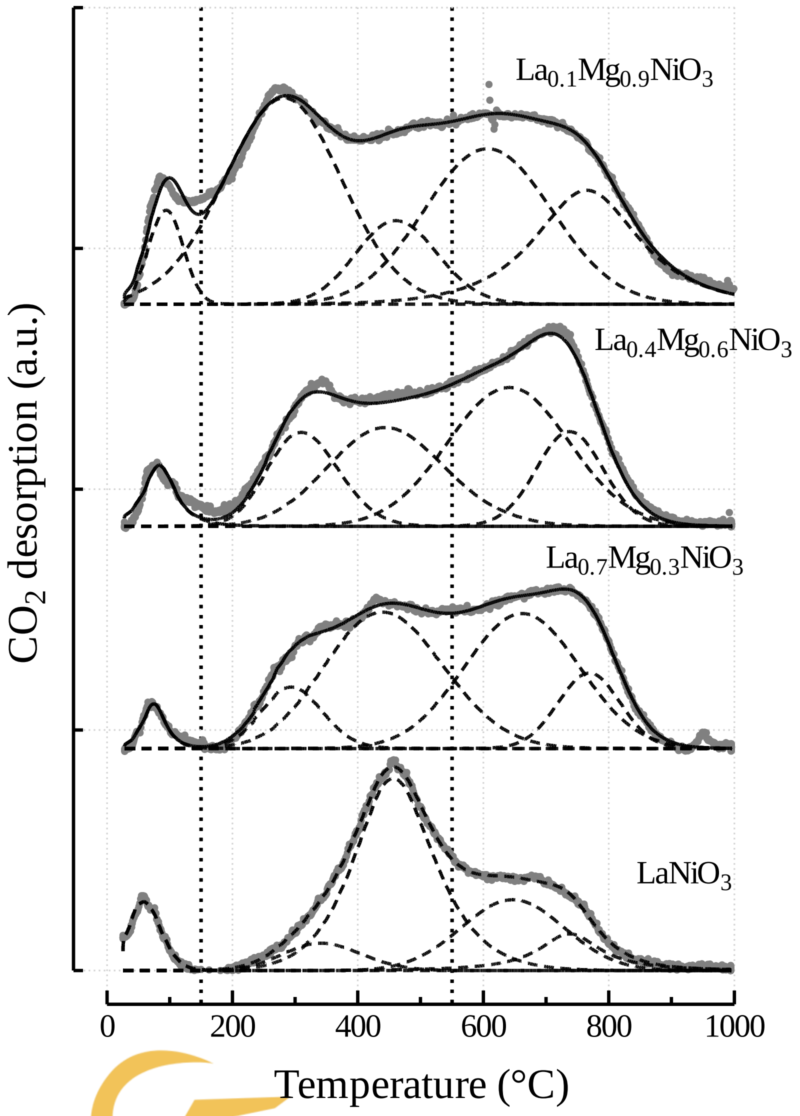


Sample	Hydrogen consumption (mmol/g)			
	Peak 1	Peak 2 (up to 600°C)	Total	Reducibility[a] (%)
$LaNiO_3$	2.83	3.26	6.09	98.9
$La_{0.7}Mg_{0.3}NiO_3$	0.54	2.36	2.90	91.2
$La_{0.4}Mg_{0.6}NiO_3$	0.48	2.73	3.21	75.9
$La_{0.1}Mg_{0.9}NiO_3$	0.39	2.31	2.60	31.1

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

- H_2 consumption decreased by increasing the content of Mg, due to the increased metal-support interaction
- The formation of $MgNiO_2$ increased the reduction temperature
- This interaction enhances Ni dispersion and prevents sintering—crucial for catalytic performance in ammonia decomposition.

CO_2-TPD



Sample	CO_2 desorption (µmol/g)			Total	
	Weak (<160°C)	Moderate (160-570°C)	Strong (>570°C)	µmol/g	$\mu mol/m^2$
$LaNiO_3$	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

- Formation of $La_2O_2CO_3$
- Monodentate carbonates formation on highly dispersed Mg-sites ($MgCO_3$)

Basicity increased with Mg doping

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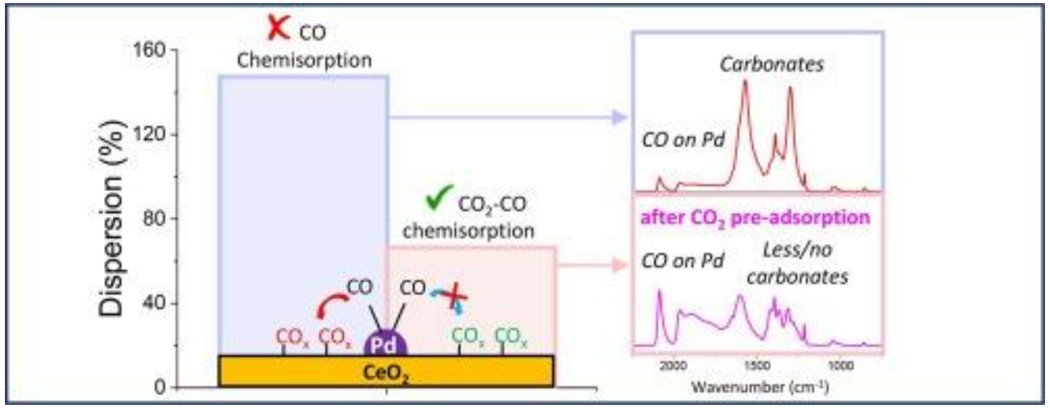
CO-CHEMISORPTION



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

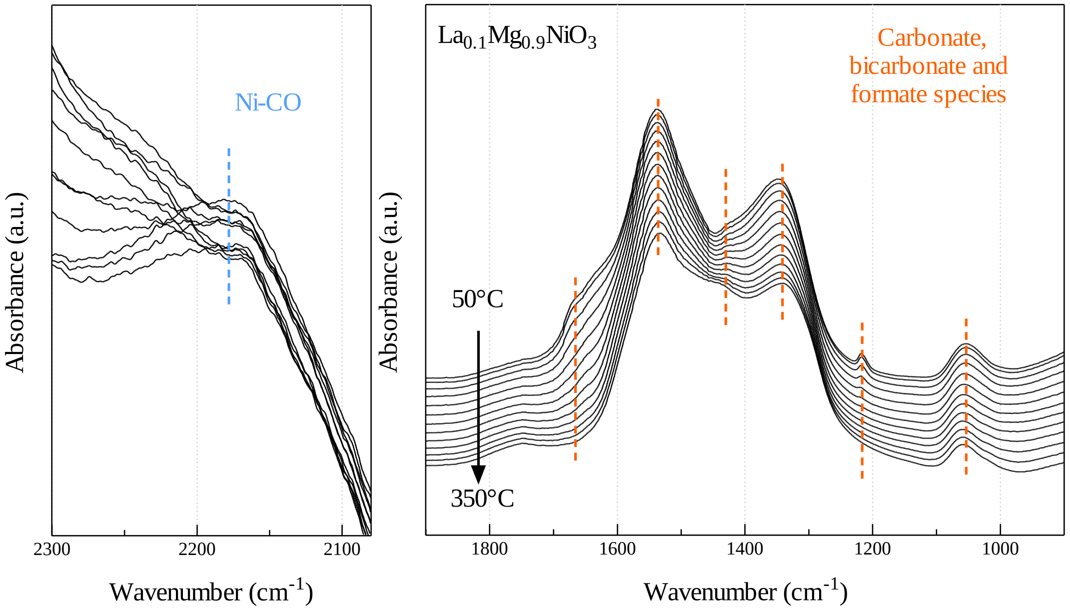
The Ni dispersion ($D_{Ni}(\%)$) was based on the simplified assumption that CO molecules are linearly chemisorbed on Ni (stoichiometric factor for CO chemisorption $f_{CO/Ni}$=1 is);

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 ($mol_{NH3} \cdot g_{cat}^{-1} \cdot min^{-1}$);

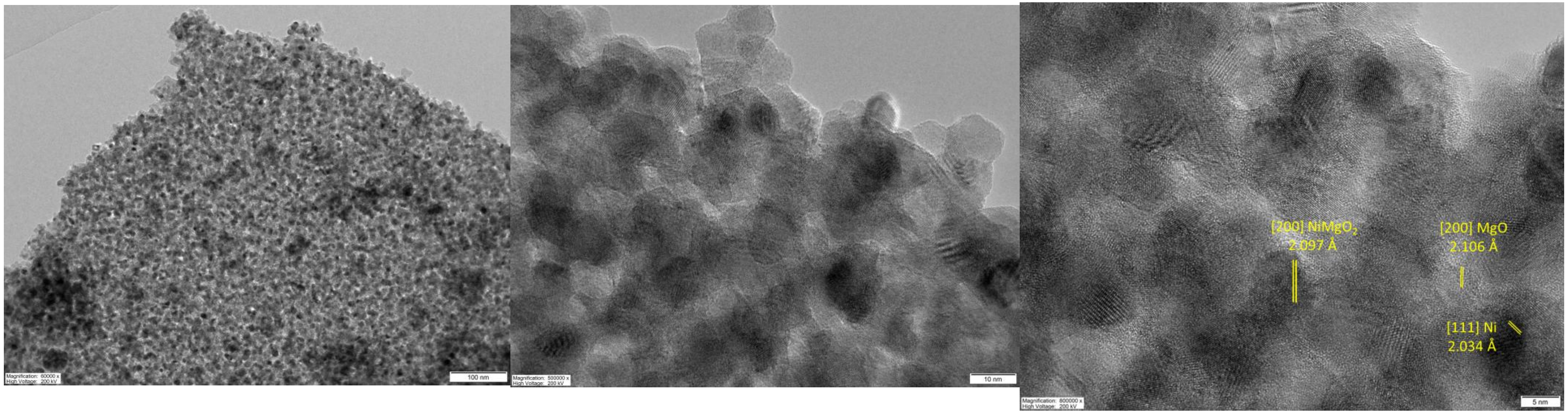
χ_{NH3} is the conversion of NH_3;

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: TEM

$La_{0.1}Mg_{0.9}NiO_3$



Unifrom distribution of Ni nano particle
MgO,Ni, $MgNiO_2$ phases in agreement with XRD

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DETERMINATION OF KINETIC PARAMETERS

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:

$$NH_3 + * \Leftrightarrow NH_3* \tag{i}$$

$$NH_3* + * \Leftrightarrow NH_2* + H* \tag{ii}$$

$$NH_2* + * \Leftrightarrow NH* + H* \tag{iii}$$

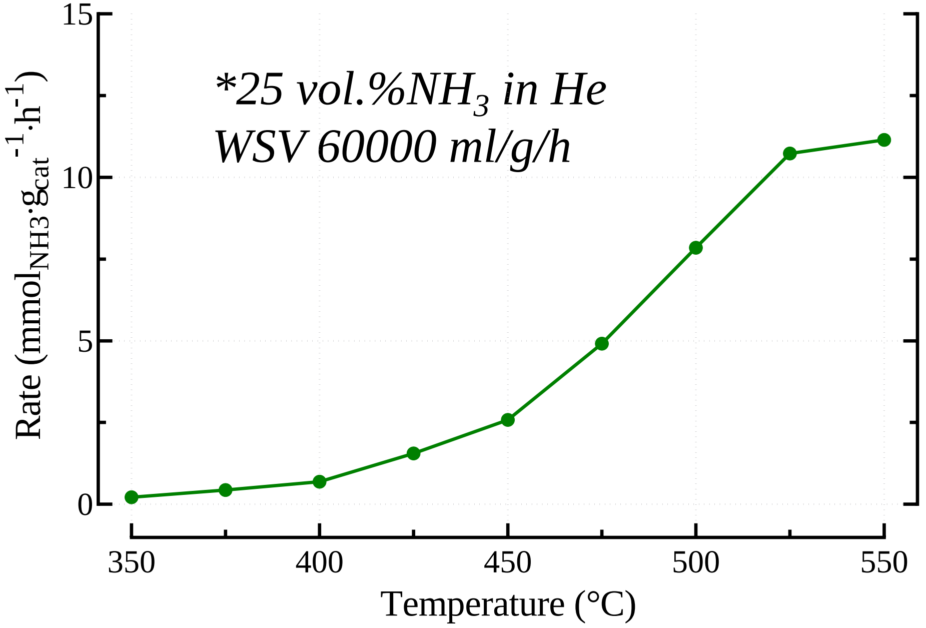
$$NH* + * \Leftrightarrow N* + H* \tag{iv}$$

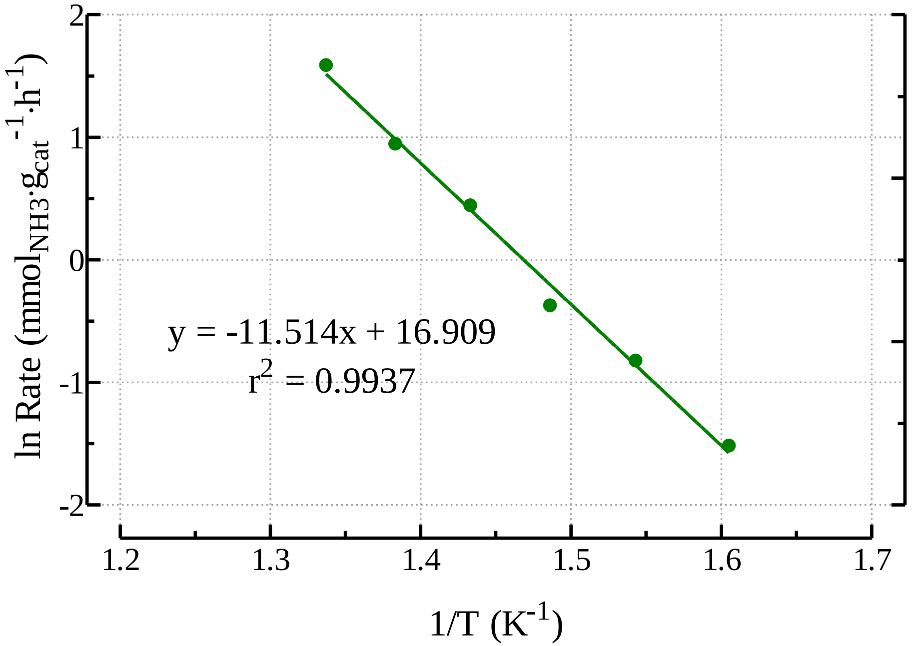
$$2N* \Leftrightarrow N_2 + 2* \tag{v}$$

$$2H* \Leftrightarrow H_2 + 2* \tag{vi}$$

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

KINETICS: ARRHENIUS PLOT





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

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

E_a = 95.7 kJ·mol^{-1}
k_0 = 2.21E+07 $mmol_{NH3}\cdot g_{cat}^{-1}\cdot h^{-1}$

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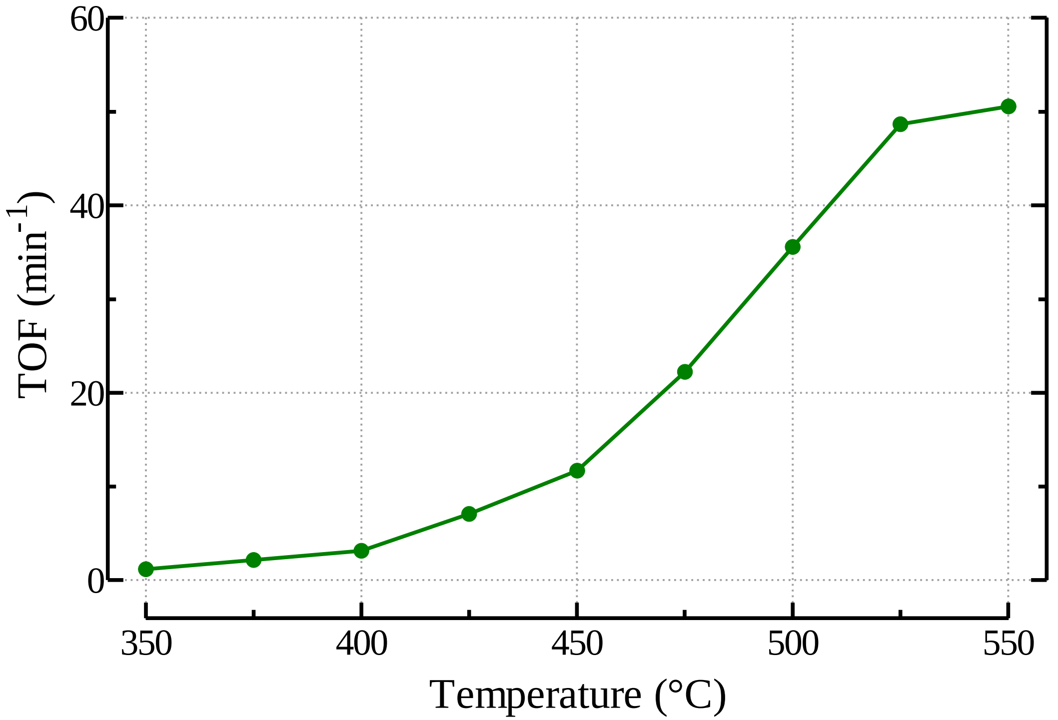
KINETICS : TOF



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

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

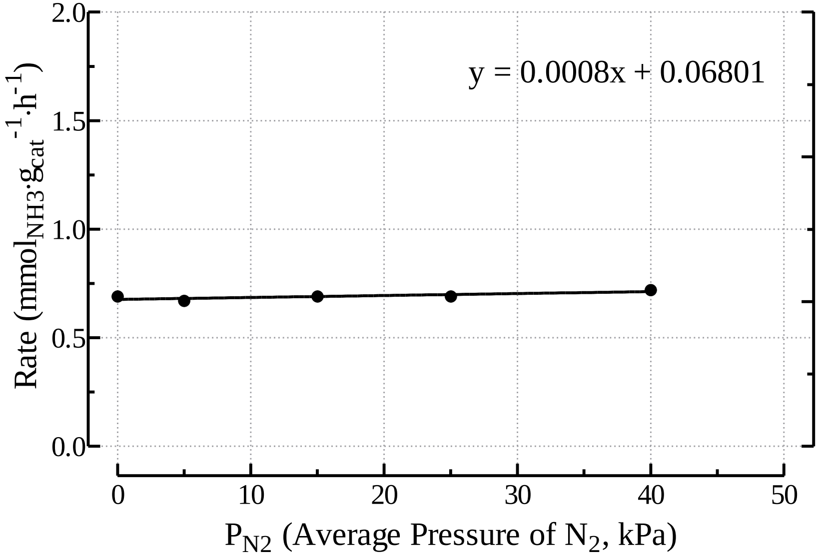
$F_{NH3,in}$ is the inlet NH_3 flow ($mol_{NH3} \cdot g_{cat}^{-1} \cdot min^{-1}$);
χ_{NH3} is the conversion of NH_3;
Ni_s is the number of reduced surface Ni atoms (mol_{Ni}/g_{cat}, determined by CO-chemisorption);
Ni_t is the total number of reduced Ni atoms (mol_{Ni}/g_{cat}, determined by H_2-TPR).

**25 vol.% NH_3 in He*

Winter School on “Membrane and Membrane Reactors”,

KINETICS: POWER LAW MODEL

No dependence on partial pressure of N_2

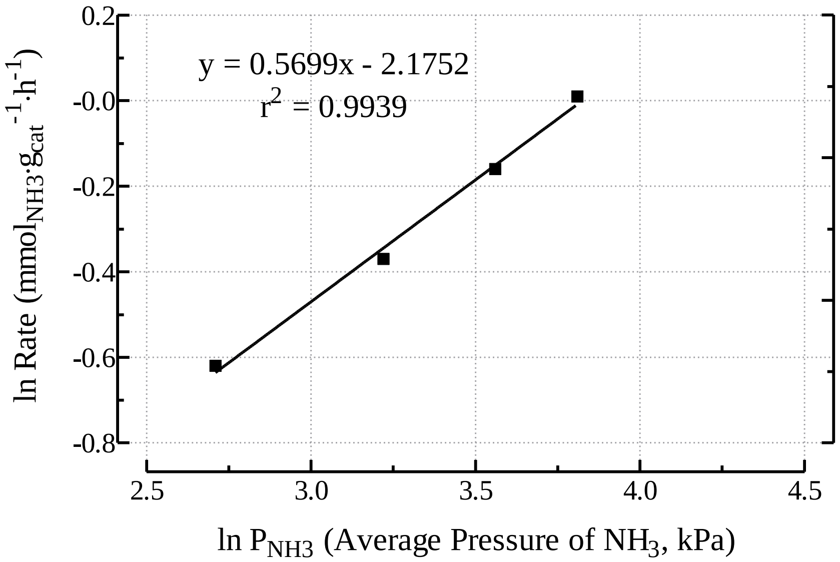


$$r_{\mathrm{NH_3}} = kP^{a}_{\mathrm{NH_3}}P^{b}_{\mathrm{H_2}}P^{c}_{\mathrm{N_2}}$$

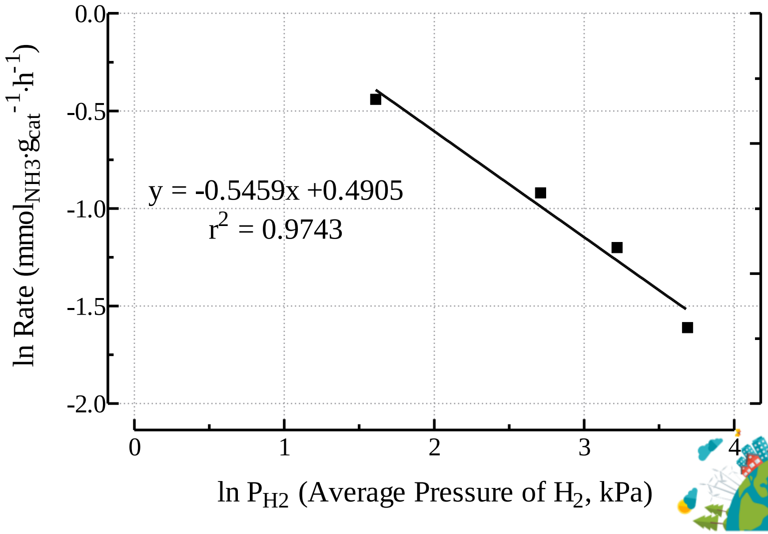
$$r_{\mathrm{f}} = k'P^{a}_{\mathrm{NH_3}}P^{b}_{\mathrm{H_2}}$$

**25 vol.%NH_3 in He; 400 °C*

Positive order dependence on NH_3



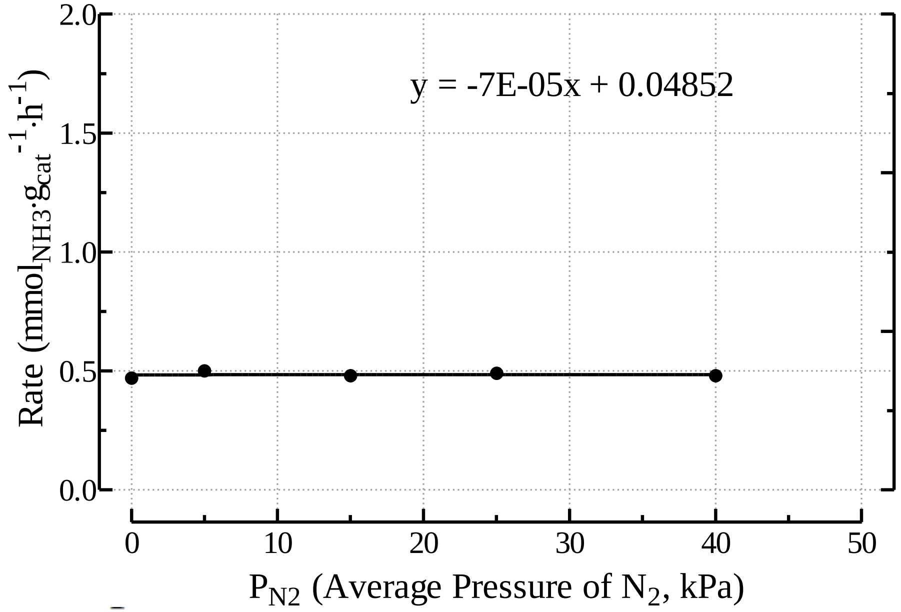
Negative order dependence on H_2



a = 0.57
b = -0.55
c = 0

KINETICS: POWER LAW MODEL

No dependence on partial pressure of N_2

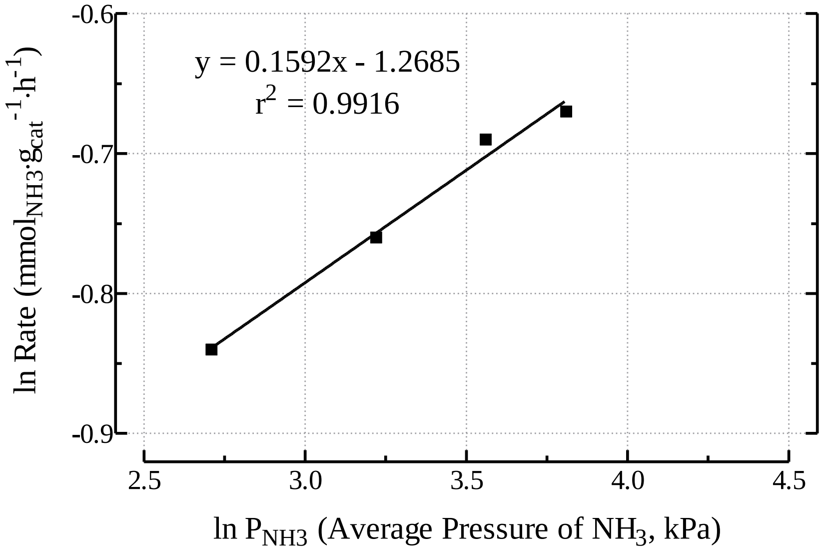


$$r_{NH_3} = kP_{NH_3}^{a} P_{H_2}^{b} P_{N_2}^{c}$$

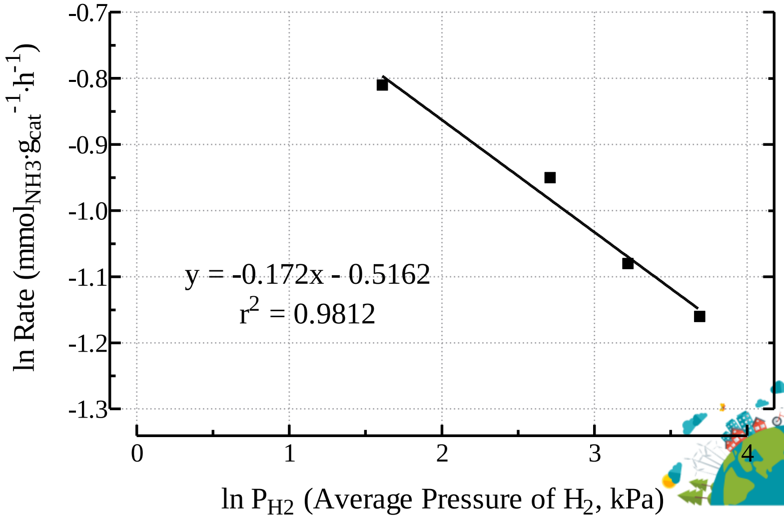
$$r_f = k' P_{NH_3}^{a} P_{H_2}^{b}$$

**25 vol.%NH_3 in He; 375 °C*

Positive order dependence on NH_3



Negative order dependence on H_2



$a = 0.16$
$b = -0.17$
$c = 0$

Numerous investigations have demonstrated that **H_2 partial pressure**, particularly at low temperatures, **inhibits the decomposition of NH_3**. The decomposition of NH3 is determined using the **Temkin-Pyzhev model**. The reaction rate is given by:

$$r_A = k\left[\left(\frac{P_{NH_3}^2}{P_{H_2}^2}\right)^{\beta} - \frac{P_{N_2}}{K_{eq}^2}\left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{1-\beta}\right] \Longrightarrow r_A = k_0 e^{-Ea/_{RT}}\left(\frac{P_{NH_3}^2}{P_{H_2}^2}\right)^{\beta}$$

where P_{NH3}, P_{H2}, and P_{N2} are partial pressures (Pa) of reagent and products. The rate constant is denoted by **k**. The fitted parameter in the Temkin-Pyzhev kinetic model is **β**. K_{eq} denotes the thermodynamic equilibrium constant.
The first term within the brackets is the NH_3 decomposition rate, while the second one is the rate of its reverse reaction (NH_3 synthesis). Under the adopted conditions, the second term can be neglected.

The Temkin–Pyzhev model is equivalent to the power law rate expression:

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

In the above equations, **k and k' follow an Arrhenius dependence** with temperature, **β is a constant related to the nonuniformity of the surface**, **a and b are the kinetic orders with respect to ammonia and hydrogen**.

Phys. Chem. Chem. Phys. 2013,15, 12104

KINETICS: TEMKIN-PYZHEV MODEL

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

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

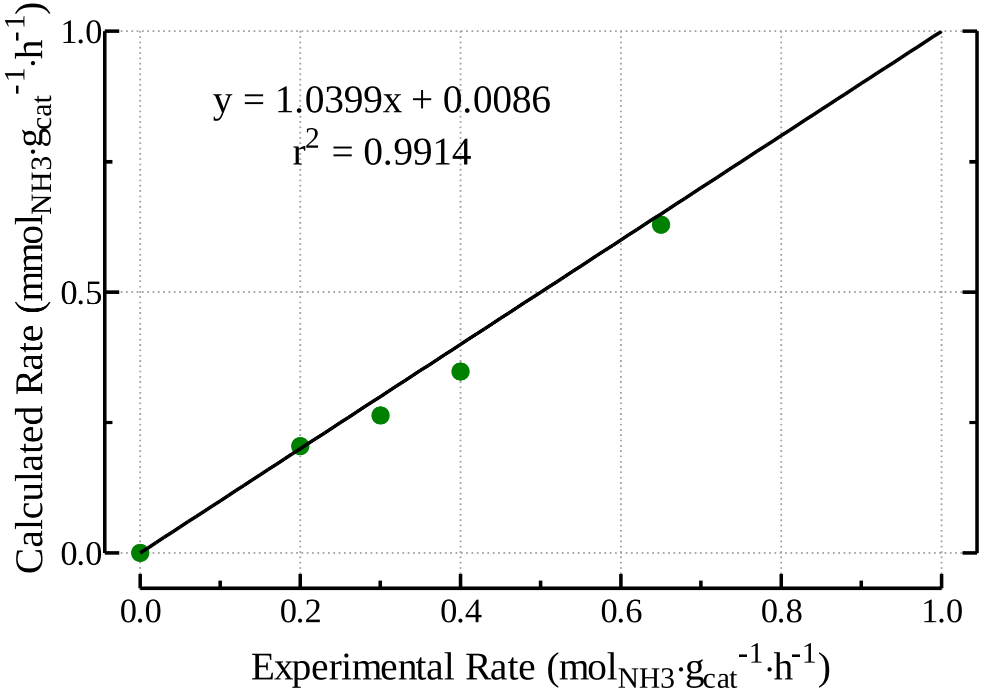
$$k = k_0\, e^{-E_a/RT}$$

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

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

$$r_f = k_f P^a_{NH_3} P^b_{H_2} = k_0\, e^{-E_a/RT}\left(\frac{P^2_{NH_3}}{P^3_{H_2}}\right)^{\beta}$$

25 vol.%NH_3 in He; 400 °C



a = 0.57
b = -0.55
c = 0

E_a = 95.7 $kJ\cdot mol^{-1}$
k = 0.21 $mmol_{NH3}\cdot g_{cat}^{-1}\cdot h^{-1}$
β = 0.18

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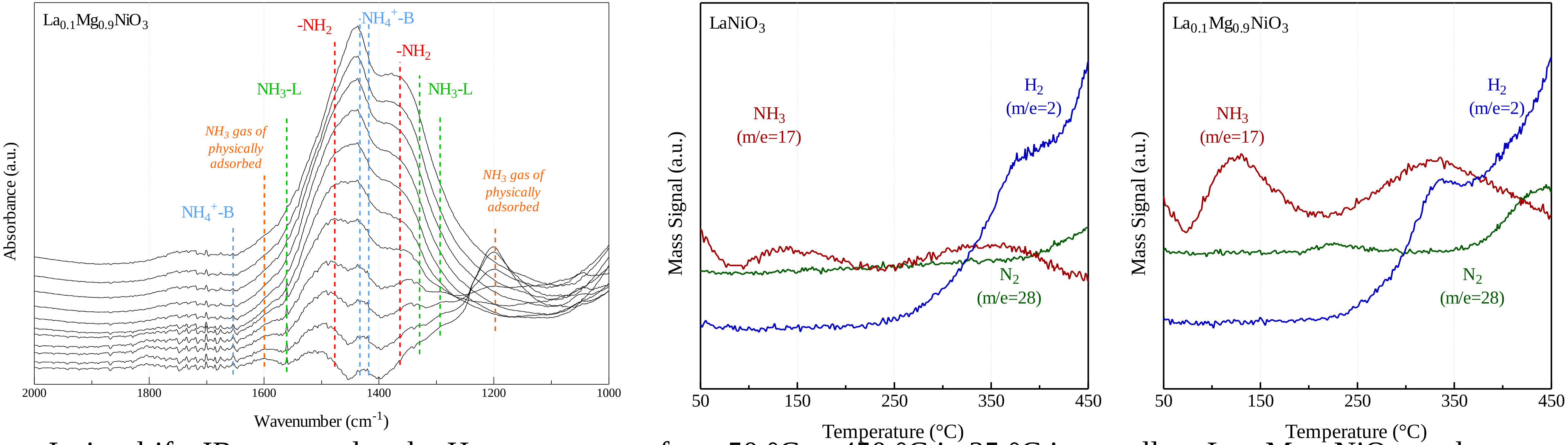
INSITU NH_3-TPD



Insitu-drifts IR measured under He temperatures from 50 °C to 450 °C in 25 °C interwell on $La_{0.1}Mg_{0.9}NiO_3$ catalyst after reduction.Insitu NH_3-TPD profiles of NH_3 (m/e=27, N2 (m/e=28), and H2 (m/e=2) over the reduced a) $LaNiO_3$ b) $La_{0.1}Mg_{0.9}NiO_3$

- The desorption of N_2 take place at higher temperature than the desorption of NHx species
- desorption of N_2 is the rate determining site.

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MAIN CONCLUSIONS

- The formation of the $MgNiO_2$ phase increases the stability of the $La_{0.1}Mg_{0.9}NiO_3$ catalyst . 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 confirms the particle size obtained by XRD.

- Basicity is the key strength The electron-donor property of Mg promotes the dehydrogenation and N_2 desorption stages.

- XPS evidences partial reduction of Ni^{3+} to Ni^{2+} 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 $La_{0.1}Mg_{0.9}NiO_3$ 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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