



**HAL**  
open science

# Influence of the rare earth (R) element in Ru-supported RScSi electrider-like intermetallic catalysts for ammonia synthesis at low pressure: insight into NH<sub>3</sub> formation mechanism

Charlotte Croisé, Khaled Alabd, Sophie Tencé, Etienne Gaudin, Antoine Villesuzanne, Xavier Courtois, Nicolas Bion, Fabien Can

## ► To cite this version:

Charlotte Croisé, Khaled Alabd, Sophie Tencé, Etienne Gaudin, Antoine Villesuzanne, et al.. Influence of the rare earth (R) element in Ru-supported RScSi electrider-like intermetallic catalysts for ammonia synthesis at low pressure: insight into NH<sub>3</sub> formation mechanism. *ChemCatChem*, 2023, 15 (3), e202201172 (12 p.). 10.1002/cctc.202201172 . hal-03992609

**HAL Id: hal-03992609**

**<https://hal.science/hal-03992609>**

Submitted on 16 Feb 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

# Influence of the Rare Earth (*R*) Element in Ru-supported *R*ScSi Electride-like Intermetallic Catalysts for Ammonia Synthesis at Low Pressure: Insight into NH<sub>3</sub> Formation Mechanism

Charlotte Croisé,<sup>[a]</sup> Khaled Alabd,<sup>[b]</sup> Sophie Tencé,<sup>[b]</sup> Etienne Gaudin,<sup>[b]</sup> Antoine Villesuzanne,<sup>[b]</sup> Xavier Courtois,<sup>[a]</sup> Nicolas Bion,<sup>[a]</sup> and Fabien Can<sup>\*[a]</sup>

This study investigates the influence of the rare-earth (*R*) element in Ru/*R*ScSi electride-like intermetallic catalysts for ammonia synthesis under mild conditions (300–450 °C; 1–5 bar). All materials present poor specific surface area and the grain size impacts the ammonia yield. The catalytic performances follow the La to Gd lanthanides series (Ru<sub>1.7</sub>/LaScSi = Ru<sub>1.7</sub>/CeScSi = Ru<sub>1.7</sub>/PrScSi > Ru<sub>1.7</sub>/NdScSi > Ru<sub>1.5</sub>/SmScSi > Ru<sub>1.3</sub>/GdScSi) and appear correlated with the formation of the hydride phase. Ru<sub>1.7</sub>/CeScSi shows remarkable catalytic activity

under moderate condition (0.58 mmol<sub>NH<sub>3</sub></sub>/h/g at 300 °C, 1 bar) associated with its reversible hydrogen storage–release properties. It is evidenced that *R*ScSi materials assist the N<sub>2</sub> dissociation in agreement with their electride character and that the hydrogen for NH<sub>3</sub> formation mainly comes from gaseous hydrogen and not primarily from the hydride phase. It is suggested that NH<sub>x</sub> formation could be the rate determining step rather than the N<sub>2</sub> cleavage over these catalysts.

## Introduction

Ammonia synthesis represents a major worldwide challenge since ammonia is one of the most synthesized chemicals in the world, with a production reaching almost 180 million tons per year.<sup>[1]</sup> The production continues to rise every year due to the important demand in organic and inorganic chemistry, especially as nitrogen source in fertilizers for agricultural crops. In recent years, NH<sub>3</sub> was also envisaged to be used directly as fuel in the next generation of more efficient fuel cells that do not emit CO<sub>2</sub>.<sup>[2]</sup> In addition, ammonia synthesis is a promising alternative way to store energy since NH<sub>3</sub> is easy to liquefy compared to H<sub>2</sub>. Ammonia could become a hydrogen carrier with a high H storage capacity and a higher volumetric H density than liquid H<sub>2</sub>.<sup>[3]</sup>

The Haber-Bosch process remains currently the main industrial technology for ammonia production thanks to the use of Fe-based catalysts. Although the reaction is exothermic (N<sub>2</sub> + 3H<sub>2</sub> → 2NH<sub>3</sub>; ΔH° = −92 kJ mol<sup>−1</sup>), high temperatures (400–600 °C) are necessary for the process to be efficient because the trivalent bond of the N<sub>2</sub> molecule is highly refractory (945 kJ mol<sup>−1</sup>). To compensate for the low yields achieved at high temperatures, high pressures (200 bar) are also applied.<sup>[4]</sup> It results in high energy consumption (1–2% of the world's annual energy supply) and thus in emission of greenhouse gases. The improvement of the Haber-Bosch process involves the development of catalytic materials active in the cleavage of the N≡N bond by electron donation, commonly recognized as the rate-determining step of ammonia synthesis. Supported ruthenium (Ru) catalysts are claimed to be good candidates for NH<sub>3</sub> synthesis and the back-donation of electrons to N<sub>2</sub> can be promoted by addition of alkali or alkaline earth metals.<sup>[5]</sup> However, despite these improvements, the operating pressure of the Haber-Bosch process remains high and the Ru metal is subject to hydrogen poisoning that lowers the efficiency of the reaction. Therefore, more efficient catalysts for sustainable ammonia synthesis are still expected.

Important efforts have been made to develop new active materials: metals nitrides, LiH support or amide-based samples were recently claimed to enhance the ammonia synthesis rate.<sup>[6]</sup> Another promising solution is the use of electride materials whose electron-donating effect is expected to promote the N<sub>2</sub> dissociation. Electrides are crystals that contain excess electrons periodically located in crystallographic sites throughout the lattice.<sup>[7]</sup> These extra electrons play the role of anions. Such materials were known as unstable until Matsuishi *et al.* discovered in 2003 the first stable electride, [Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>14+</sup>(e<sup>−</sup>)<sub>4</sub><sup>[8]</sup> that was successfully used in 2012 as an activator for the Ru-based

[a] C. Croisé, Dr. X. Courtois, Dr. N. Bion, Dr. F. Can  
Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP)  
Université de Poitiers, CNRS.  
4 rue Michel Brunet  
TSA 51106 86073 Poitiers Cedex 9 (France)  
E-mail: fabien.can@univ-poitiers.fr

[b] K. Alabd, Dr. S. Tencé, Dr. E. Gaudin, Dr. A. Villesuzanne  
Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026  
F-33600 Pessac (France)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.202201172>

This publication is part of a Special Collection on "French Conference on Catalysis 2022". Please check the ChemCatChem [https://chemistry-europe.onlinelibrary.wiley.com/doi/toc/10.1002/\(ISSN\)1867-3899.french-conference-catalysis-2022](https://chemistry-europe.onlinelibrary.wiley.com/doi/toc/10.1002/(ISSN)1867-3899.french-conference-catalysis-2022) homepage for more articles in the collection:

© 2022 The Authors. ChemCatChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

catalysis for ammonia synthesis.<sup>[9]</sup> These results demonstrate the very attractive potential of this type of materials for ammonia synthesis under mild conditions. Since, several intermetallic silicides such as La(Co,Mn,Fe)Si,<sup>[10]</sup> LaRuSi,<sup>[11]</sup> LaNiSi<sup>[12]</sup> or Y<sub>5</sub>Si<sub>3</sub><sup>[13]</sup> have been reported as active catalyst in NH<sub>3</sub> synthesis. Very recently, Wu *et al.* have demonstrated that the use of the electrone-like intermetallic phase LaScSi combined with Ru enables to reach one of the highest reported production rate of ammonia at ambient pressure (4.8 mmol/g/h at 400 °C, compared to 0.2 mmol/g/h for Ru/CaO with the same experimental conditions and Ru loading, at 1.5 wt%).<sup>[14]</sup>

The *RTX* intermetallics crystallizing in the CeScSi-structure type are usually composed of *R*=Y, La–Tm, Lu; *T*=Sc, Ti, Zr and *X*=Si, Ge, Sn, Sb<sup>[15]</sup> and can present a large capacity in hydrogen absorption. Indeed, their structure contains rare-earth tetrahedral voids [*R*<sub>4</sub>] as well as mixed rare-earth/transition metal or Sc octahedral voids [*R*<sub>2</sub>*T*<sub>4</sub>], both suitable for hydrogen insertion. *RTX* compounds with rare earths such as lanthanum (La), cerium (Ce), neodymium (Nd) and gadolinium (Gd) have been identified as promising candidates for hydride formation. The hydride character is claimed to avoid the poisoning of ruthenium by adsorbed H species due to surface H<sup>−</sup> ion mobility, that would play a major role in ammonia synthesis by providing a high catalyst durability for the Haber-Bosch process.<sup>[9,16]</sup> In particular, the hydrogenation properties of LaScSi, CeScSi, NdScSi, GdScGe or GdTiGe have been recently published.<sup>[17]</sup>

However, a systematic study of the impact of the rare earth element (*R*) in *RScSi* ternary intermetallics for the catalytic Haber-Bosch synthesis is still lacking. In fact, Gong *et al.*<sup>[18]</sup> recently noted the great potential of rare earth-containing catalysts for more efficient ammonia synthesis. In addition, ammonia production at the laboratory scale is usually monitored under steady-state conditions of temperature, by ammonia trapping in a sulphuric acid solution and subsequent analysis by ion chromatography. As a result, it is not possible to obtain crucial information on the evolution of the materials activity during temperature rise and catalysts activation.

In this paper, we investigate the influence of the rare earth element (*R*=La, Ce, Pr, Nd, Sm, Gd) in Ru supported *RScSi* electrone-like catalysts for ammonia synthesis under mild conditions of pressure and temperature. A specific attention is made on low temperature activity (300 °C, 1–5 bar) and new insights into NH<sub>3</sub> formation mechanism are considered using N<sub>2</sub> isotopic exchange measurements and transient flow experiments.

## Results and Discussion

### Catalysts characterization

The comparison of the powder XRD patterns of the as-cast and annealed samples confirms the formation of the main phase *RScSi* after annealing, with the presence of a few amount of the secondary phase Sc<sub>5</sub>Si<sub>3</sub> (less than 4 wt%). The SmScSi sample also has a small amount of Sm<sub>5</sub>Si<sub>3</sub> (approx. 3 wt%), and the GdScSi sample contains approximately 6 wt% of Gd<sub>2.45</sub>Sc<sub>2.55</sub>Si<sub>3</sub> solid solution. All patterns were indexed with the tetragonal space group *I4/mmm* with unit cell parameters in agreement with previous published data (gathered in Table 1).<sup>[14,17]</sup>

The ruthenium loadings in the studied materials, obtained from ICP analysis, are between 1.3 wt% and 1.7 wt% (Table 2). The ruthenium particle sizes were determined by TEM-EDX analysis. Histograms of the size distributions of Ru particles show irregular morphology (Figure S1 in the Supplementary Information file, and also illustrated in Figure 3A for Ru<sub>1.4</sub>/LaScSi). The average Ru particles size, depending on the intermetallic formula, are estimated between 5 nm and 18 nm, as presented in Table 2.

The dispersion values are calculated from different models, as described in the experimental part, to cover the full range of particle sizes. The dispersion ranges from 7 to 25 % depending on the involved intermetallic support. Note that the particle size and dispersion values also depend on the Ru loading, as illustrated by the comparison of Ru<sub>1.4</sub>/LaScSi and Ru<sub>1.7</sub>/LaScSi

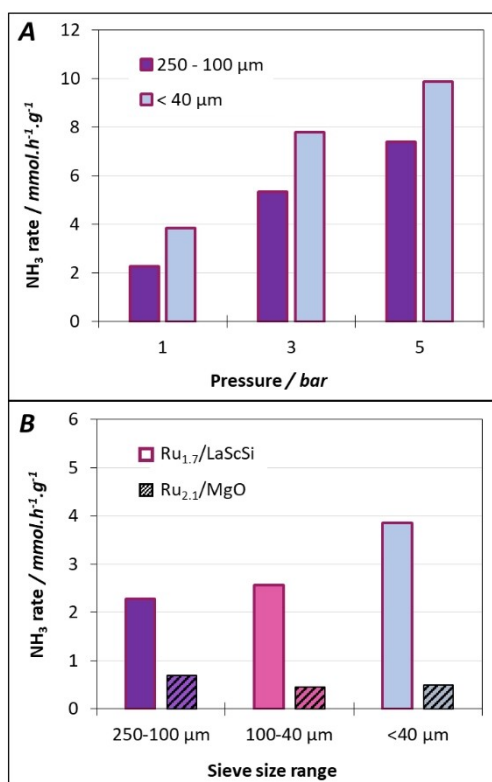
**Table 1.** Unit cell parameters from XRD data before and after catalytic tests at 400 °C (1, 3, and 5 bar) for different catalyst support, along with the phases found after the catalytic test.

intermetallic support	Cell parameters of the intermetallic phase before catalytic test	Phases found after catalytic test <sup>[a]</sup>	Cell parameters of the hydrides after catalytic test
LaScSi	a = 4.355(1) Å c = 16.031(1) Å	LaScSiH <sub>x</sub> <sup>[b]</sup>	a = 4.273(1) Å c = 17.045(1) Å
CeScSi	a = 4.337(1) Å c = 15.794(1) Å	CeScSiH <sub>x</sub> <sup>[c]</sup>	a = 4.246(1) Å c = 16.778(1) Å
PrScSi	a = 4.313(1) Å c = 15.690(1) Å	PrScSiH <sub>x</sub> <sup>[c]</sup>	a = 4.251(1) Å c = 16.453(3) Å
NdScSi	a = 4.295(1) Å c = 15.685(1) Å	NdScSi (20%) NdScSiH <sub>x</sub> <sup>[d]</sup> (80%)	a = 4.208(1) Å c = 16.576(2) Å
SmScSi	a = 4.262(1) Å c = 15.555(1) Å	SmScSi (47%) SmScSiH <sub>x</sub> <sup>[c]</sup> (53%)	a = 4.174(1) Å c = 16.436(2) Å
GdScSi	a = 4.239(1) Å c = 15.467(1) Å	GdScSi	

[a]: this only includes main intermetallic pristine or hydride phases with an estimation of their relative proportion (wt%), and does not include secondary phases like Sc<sub>5</sub>Si<sub>3</sub> or CeO<sub>2</sub>. [b]: x value lies between 1.2 and 1.5 based on hydrides characterized in [14] where LaScSiH<sub>1.5</sub> has the parameters a = 4.271 Å and c = 17.090 Å and LaScSiH<sub>1.2</sub> has the parameters a = 4.261 Å and c = 17.039 Å. [c]: the hydrides with these cell parameters were characterized for the first time. [d]: x is lower than 1.5 based on data from [17<sup>a,b</sup>] where NdScSiH<sub>1.5</sub> has the parameters a = 4.221 Å and c = 16.928 Å.

	Ru loading [wt%] <sup>[a]</sup>	Particle size [nm] <sup>[b]</sup>	Ru Dispersion hcp [%] <sup>[c]</sup>	Ru Dispersion spherical [%] <sup>[c]</sup>
Ru <sub>1.4</sub> /LaScSi	1.4	5.6	22.5	25.1
Ru <sub>1.7</sub> /LaScSi	1.7	13.0	11.0	10.2
Ru <sub>1.7</sub> /CeScSi	1.7	11.5	12.1	11.6
Ru <sub>1.7</sub> /PrScSi	1.7	15.5	9.5	8.6
Ru <sub>1.7</sub> /NdScSi	1.7	9.0	14.7	14.8
Ru <sub>1.5</sub> /SmScSi	1.5	18.1	8.4	7.3
Ru <sub>1.3</sub> /GdScSi	1.3	17.5	8.6	7.6
Ru <sub>2.1</sub> /MgO	2.1	1.8	53.4	73.9

[a]: the Ru content was determined by ICP-OES experiments. [b]: Particle size were determined by TEM analysis. [c]: dispersion was calculated assuming spherical metal particles or hexagonal close packed particles (hcp) model.

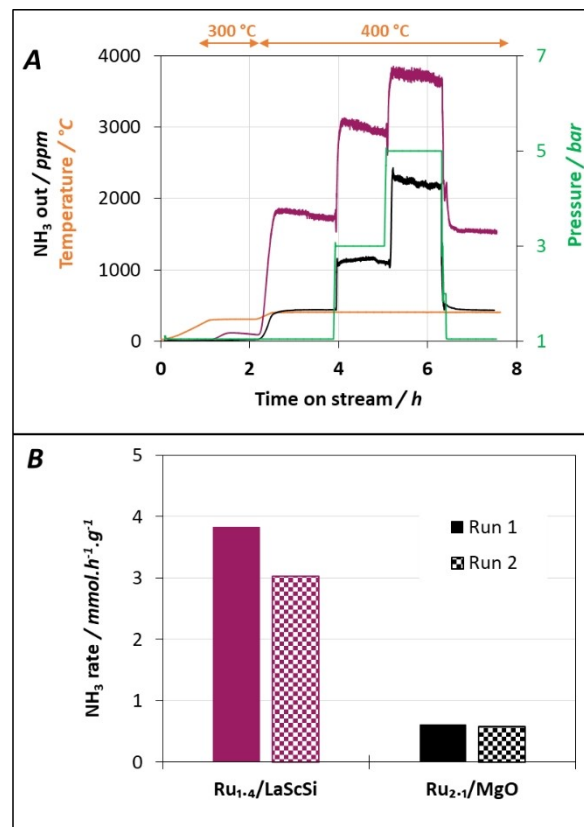


**Figure 1.** A: Impact of catalyst sieving on ammonia synthesis at 450 °C over Ru<sub>1.7</sub>/LaScSi depending on pressure; B: Focus at 1 bar (450 °C) for Ru<sub>1.7</sub>/LaScSi (□) and Ru<sub>2.1</sub>/MgO (□).

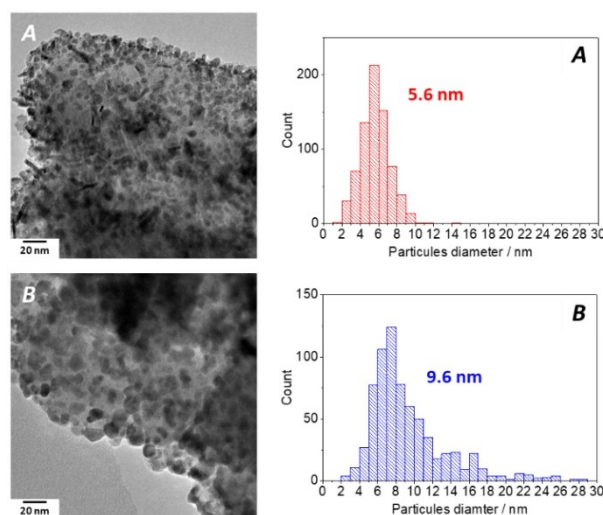
samples (Table 2). The effect of Ru particle size in NH<sub>3</sub> synthesis rate is discussed thereafter (Figure 4, Table 4).

### Catalyzed ammonia synthesis

In a first set of preliminary tests, the effect of catalyst sieving and catalyst stability as a function of time on stream were investigated on the Ru<sub>1.7</sub>/LaScSi intermetallic and compared to the Ru<sub>2.1</sub>/MgO reference material. A study on the sintering of



**Figure 2.** A: evolution of the ammonia production over Ru<sub>1.7</sub>/LaScSi (□) and Ru<sub>2.1</sub>/MgO (■) depending on the temperature and pressure. B: Effect of number of runs on ammonia synthesis at 400 °C and 1 bar for 100–40 μm over Ru<sub>1.4</sub>/LaScSi (□) and Ru<sub>2.1</sub>/MgO (■).



**Figure 3.** TEM images and particle size distribution of Ru<sub>1.4</sub>/LaScSi (100–40 μm). A: Before catalytic test. B: After 2 catalytic runs at 400 °C up to 5 bar.

ruthenium particles was also performed on the Ru<sub>1.4</sub>/LaScSi material.

Because of the extremely low porosity of intermetallic materials, the grain size of the samples should have a strong

**Table 3.** NH<sub>3</sub> emission /ppm for 1 hour of NH<sub>3</sub> synthesis at 300 °C and 400 °C over Ru/RScSi catalysts (100–40 μm) and N<sub>2</sub> equilibrium rate at 450 °C (from isotopic exchange measurements).

Temp. [°C]		1 bar	3 bar	5 bar	Return 1 bar	N <sub>2</sub> equilibrium rate at 450 °C, R <sub>q</sub> /10 <sup>22</sup> at.g <sup>-1</sup> .min <sup>-1(a)</sup>
400 °C	Thermodynamic	<b>3743</b>	<b>11066</b>	<b>18179</b>	<b>3743</b>	
	Ru <sub>1,4</sub> /LaScSi	2560	4577	5421	2361	
	Ru <sub>1,7</sub> /LaScSi	1710	2920	3650	1520	55.4
	Ru <sub>1,7</sub> /CeScSi	1600	2930	3720	1505	50.1
	Ru <sub>1,7</sub> /PrScSi	1559	2776	3584	1340	13.9
	Ru <sub>1,7</sub> /NdScSi	1367	2334	2976	1210	1.52
	Ru <sub>1,5</sub> /SmScSi	868	1275	1540	700	0.46
	Ru <sub>1,3</sub> /GdScSi	420	910	1200	314	4.42
	Ru <sub>2,1</sub> /MgO	420	1100	2170	434	0
300 °C	Thermodynamic	<b>17348</b>	<b>48769</b>	<b>76595</b>	<b>17348</b>	
	Ru <sub>1,7</sub> /LaScSi	95	470	650	65	
	Ru <sub>1,7</sub> /CeScSi	385	720	900	365	
	Ru <sub>2,1</sub> /MgO	2	2	2	2	

[a]: determined from the slope of the m/z = 29 curve at the beginning of the isothermal <sup>14</sup>N<sub>2</sub>/<sup>15</sup>N<sub>2</sub> nitrogen homomolecular isotopic exchange experiments.

**Table 4.** NH<sub>3</sub> production turn over frequency/min<sup>-1</sup> in NH<sub>3</sub> synthesis at 300 °C and 400 °C over Ru/RScSi catalysts (100–40 μm, average TOF for 1 h measurement).

Temp. [°C]		1 bar	3 bars	5 bars	Return 1 bar
400 °C	Ru <sub>1,4</sub> /LaScSi	2.0	3.6	4.3	1.9
	Ru <sub>1,7</sub> /LaScSi	2.4	4.1	5.1	2.1
	Ru <sub>1,7</sub> /CeScSi	1.9	3.5	4.4	1.8
	Ru <sub>1,7</sub> /PrScSi	2.6	4.6	5.9	2.2
	Ru <sub>1,7</sub> /NdScSi	1.4	2.3	3.0	1.2
	Ru <sub>1,5</sub> /SmScSi	1.9	2.7	3.3	1.5
	Ru <sub>1,3</sub> /GdScSi	1.0	2.2	2.9	0.8
	Ru <sub>2,1</sub> /MgO	0.1	0.2	0.4	0.1
300 °C	Ru <sub>1,7</sub> /LaScSi	0.1	0.7	0.9	0.1
	Ru <sub>1,7</sub> /CeScSi	0.5	0.9	1.1	0.5
	Ru <sub>1,3</sub> /GdScSi	0.0	0.0	0.0	0.0
	Ru <sub>2,1</sub> /MgO	0.0	0.0	0.0	0.0

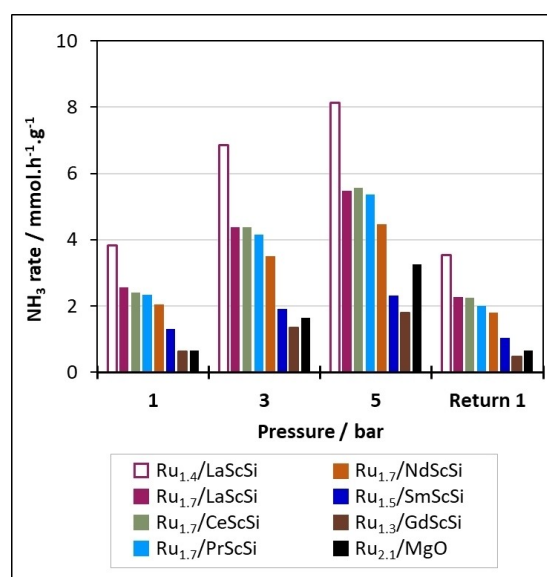
influence on the catalyst behavior since heterogeneous catalysis mainly involves surface reactions. It is worth noting that previous works reported by Kitano *et al.*<sup>[9]</sup> or Wu *et al.*<sup>[14]</sup> about the ammonia synthesis over intermetallic-based catalysts did not report the influence of this parameter (not specified in the experimental part of the corresponding paper).

The effect of catalyst grain size on the performance in NH<sub>3</sub> synthesis at 450 °C (H<sub>2</sub>:N<sub>2</sub> = 3; 1–5 bar) was examined by sieving the samples in three different ranges: 250–100, 100–40 and < 40 μm. Figure 1A show that, under similar reaction conditions, the ammonia production rate differs significantly depending on the selected grain size range. As expected, the ammonia rate increases with the decrease in the particle size, whatever the reaction pressure from 1 to 5 bar.

A comparison between the Ru<sub>1,7</sub>/LaScSi sample and the reference Ru<sub>2,1</sub>/MgO catalyst is presented in Figure 1B for experiments performed at 1 bar and 450 °C depending on the selected grain size range. It is clear that the effect of grain size is significantly less pronounced with a divided material like Ru<sub>2,1</sub>/MgO (with a specific surface area of about 21 m<sup>2</sup>g<sup>-1</sup>) compared to intermetallics which develop a very low surface area of 1 m<sup>2</sup>g<sup>-1</sup> (see experimental part). It also illustrates that

the reaction rate over Ru<sub>2,1</sub>/MgO was not limited by the intergranular diffusion. Finally, due to the uncertainty of the grain distribution in the lowest grain size range (< 40 μm), we have further selected the 100–40 μm range for the study (except mentioned otherwise).

The experimental set-up used to evaluate the performance of catalysts allows a continuous and fast monitoring of the NH<sub>3</sub> synthesis reaction as a function of time under controlled temperature and pressure. Our protocol usually includes a first step under N<sub>2</sub> + H<sub>2</sub> at 300 °C (1 bar during 1 h) and four consecutive measurements at 400 °C under 1, 3, 5 and 1 bar (1 h each). The results obtained with the Ru<sub>1,7</sub>/LaScSi material are presented in Figure 2A and compared to the reference catalyst Ru<sub>2,1</sub>/MgO. The step at 300 °C (between t = 1.2 h and t = 2.2 h) is carried out in order to evaluate the activities at low



**Figure 4.** Effect of rare earth (R: La, Ce, Pr, Nd, Sm, Gd) on Ru/RScSi (100–40 μm) catalysts on the NH<sub>3</sub> production rate/mm<sup>3</sup>.h<sup>-1</sup>.g<sup>-1</sup> at 400 °C.



temperature but also to promote the hydride formation of the catalysts in the case of intermetallics (this specific point is discussed thereafter in the study). Figure 2A shows that the Ru<sub>1.7</sub>/LaScSi catalyst (purple line) shows an activity at 300 °C with a formation of about 100 ppm of NH<sub>3</sub>, which is not observed for the Ru<sub>2.1</sub>/MgO sample (Table 3). The ammonia production is then studied at 400 °C from 1 to 5 bar. Whatever the gas inlet pressure, the intermetallic based catalyst systematically shows higher NH<sub>3</sub> yields than the sample supported on MgO. Moreover, it is also observed that ammonia formation on Ru<sub>1.7</sub>/LaScSi is pressure-dependent since the outlet ammonia concentration is doubled from 1 to 5 bar for Ru<sub>1.7</sub>/LaScSi, from 1710 to 3650 ppm, respectively. For Ru<sub>2.1</sub>/MgO, the amount of ammonia is multiplied by five (from 420 to 2170 ppm) (Table 3). These results are consistent with the work of Wu *et al.*<sup>[14]</sup> Figure 2A also points out that the ammonia production is not constant over Ru<sub>1.7</sub>/LaScSi during each stage of the test. A decrease with time was observed while the activity of Ru<sub>2.1</sub>/MgO appears more stable.

To study the stability of the Ru/LaScSi sample in ammonia synthesis compared to Ru<sub>2.1</sub>/MgO reference, each sample was submitted to two consecutive catalytic tests under the H<sub>2</sub>:N<sub>2</sub> flow (3:1) including the pretreatment at 300 °C (1 bar during 1 h) and four consecutive measurements at 400 °C under 1, 3, 5 and 1 bar (1 h each) before cooling to room temperature under nitrogen (1 h each) before cooling to room temperature under nitrogen (and one night without gas flow). For these experiments, another batch of Ru/LaScSi was used, with 1.4 wt% Ru (Ru<sub>1.4</sub>/LaScSi; activities of both catalysts are reported in Figure 4). Results presented in Figure 2B evidence a loss of activity for Ru<sub>1.4</sub>/LaScSi of about 20% between the first run and the second run. In contrast, the reference Ru<sub>2.1</sub>/MgO sample remains stable in similar conditions, but its activity was still significantly lower compared to Ru<sub>1.4</sub>/LaScSi. These results were assigned to a sintering effect of Ru particles revealed by TEM experiments performed over Ru<sub>1.4</sub>/LaScSi (Figure 3). Indeed, the mean size of the ruthenium particles from TEM analysis increases from 5.6 nm to 9.6 nm after two catalytic runs at 400 °C up to 5 bar. These results highlight the aggregation of Ru nanoparticles over the electride support which tends to cause a rapid decay of activity and thus a durability drawback. These observations confirm some previous results reported for Ru/intermetallics dedicated to ammonia synthesis. Indeed, the method of Ru deposition is a key point to obtain strong metal-support interaction in order to avoid Ru particles aggregation and facilitate electron transfer.<sup>[10a,19]</sup> As the ruthenium deposition method differs between Ru/RScSi samples and Ru/MgO (see experimental part), a specific study about the impact of the ruthenium deposition method on MgO support is reported in Supplementary Information (Figures S2 and S3).

The influence of the rare earth element (*R*) in Ru-supported RScSi electrides for ammonia synthesis is thereafter investigated. The catalytic performance of ruthenium catalysts depends on the loading and thus on the particle size distribution of Ru.<sup>[20]</sup> Consequently, the effect of the nature of the rare earth on the Haber-Bosch synthesis is compared with close ruthenium contents (1.3–1.7 wt%). As previously exposed,

the usual catalytic test includes a first step under N<sub>2</sub> + H<sub>2</sub> at 300 °C (1 bar during 1 h) and four consecutive measurements at 400 °C under 1, 3, 5 and 1 bar (1 h each). Figure 4 shows the mean NH<sub>3</sub> yields measured at 400 °C between 1 and 5 bar for the Ru supported RScSi-catalyst series sieved in the 100–40 μm range (*R*=La, Ce, Pr, Nd, Sm, Gd). The corresponding mean NH<sub>3</sub> emission (ppm) are reported in Table 3. The results are compared to the Ru<sub>2.1</sub>/MgO reference material. Note that no activity is observed in the absence of ruthenium, whatever the considered support.

With the exception of the Ru<sub>1.4</sub>/LaScSi catalyst which seems to exhibit a different behavior, the materials with a Ru content of 1.7 wt% supported on LaScSi, CeScSi and PrScSi show similar activities, with ammonia yields reaching 5.6 mmol.h<sup>-1</sup>.g<sup>-1</sup> at 5 bar (400 °C). On the opposite, the catalyst based on SmScSi support presents lower activities. Ammonia yields still always increase with pressure but to a limited extent, so that the reference material is more active at high pressure than Ru<sub>1.5</sub>/SmScSi. Ru<sub>1.3</sub>/GdScSi shows lower activities compared to other intermetallics, with limited NH<sub>3</sub> emissions compared to Ru<sub>2.1</sub>/MgO. The poor catalytic activity of the gadolinium containing catalyst is discussed thereafter in this study. Based on ammonia rate (Figure 4), Ru<sub>1.7</sub>/NdScSi sample shows an intermediate behavior. In addition, the two Ru/LaScSi samples with 1.4 wt% and 1.7 wt% Ru shows significantly different catalytic behaviors. The higher ammonia rate observed for Ru<sub>1.4</sub>/LaScSi (8.1 mmol.h<sup>-1</sup>.g<sup>-1</sup> at 5 bar, 400 °C) is attributed to the lower Ru particles size at 5.6 nm compared to 9–18 nm for other samples (Table 2). In fact, it is accepted that the NH<sub>3</sub> synthesis reaction is structure sensitive. For Ru-based catalysts, the B5-type surface sites are reported to be responsible for the activity.<sup>[21]</sup> These specific surface sites are expected to be favored over Ru crystallites exhibiting diameters in the 3–5 nm range.<sup>[22]</sup> In addition, Gong *et al.*<sup>[10a]</sup> recently showed that the transition metal in ternary La-TM-Si intermetallics (TM=Co, Fe, and Mn) intermetallics influences the ruthenium-support interactions.

Then, to overcome the Ru particle size effect and to highlight the impact of electride-hydride properties of Ru supported intermetallics catalyst, the ammonia formation rate is also expressed as turn over frequency (TOF) in Table 4. TOF is calculated as the number of moles of NH<sub>3</sub> emitted per time unit divided by the amount (mol) of surface ruthenium (estimated from the average Ru particle sizes measured by TEM, Figure S1 in the Supplementary Information file). Results presented in Table 4 firstly highlight that intermetallic supports allow significantly higher catalytic performance than the reference MgO materials. This result clearly highlights the specific role of electride-hydride properties and suggests that the intrinsic activity of the Ru catalyst is highly improved by the Ru/intermetallic interaction.

Comparison of data expressed as NH<sub>3</sub> production rate (Figure 4) and TOF (Table 4) shows slight differences. Although the supported LaScSi, CeScSi and PrScSi catalysts remain the most active materials, the Sm-based sample becomes close to NdScSi and GdScSi. Note that the Ru<sub>1.3</sub>/GdScSi remains the less active sample. Regarding the effect of Ru content on LaScSi, the

Ru<sub>1.4</sub>/LaScSi material, which has a higher NH<sub>3</sub> formation rate than Ru<sub>1.7</sub>/LaScSi (Figure 4), shows a lower TOF (Table 4).

This result can be explained by the sensitivity of the NH<sub>3</sub> synthesis reaction to the ruthenium structure. The TOF calculated here do not consider only the Ru particles between 3 and 5 nm (type B5) but the average size of the whole accessible Ru particles.

To highlight the specific activity of Ru supported intermetallics catalysts toward N<sub>2</sub> adsorption/dissociation, a study of <sup>14</sup>N<sub>2</sub>/<sup>15</sup>N<sub>2</sub> homomolecular exchange is described below as well as DFT and XRD characterizations.

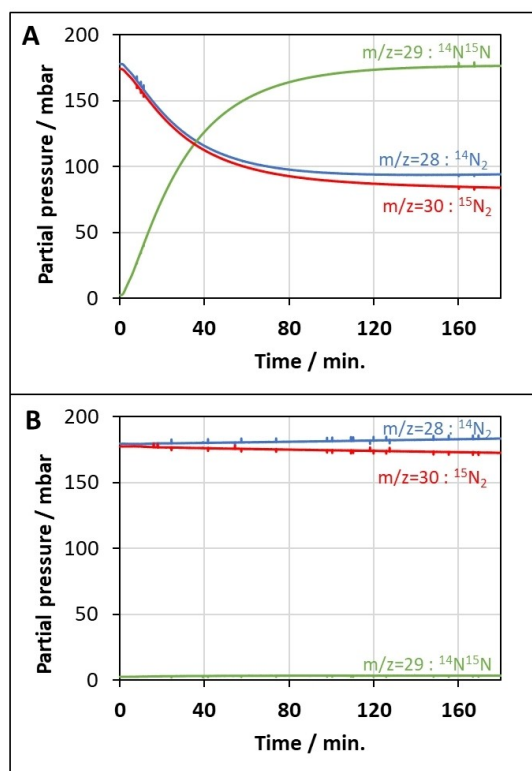
## N<sub>2</sub> activation and hydride characterization

Isothermal <sup>14</sup>N<sub>2</sub>/<sup>15</sup>N<sub>2</sub> nitrogen homomolecular isotopic exchange experiments (INHIE: <sup>14</sup>N<sub>2(g)</sub> + <sup>15</sup>N<sub>2(g)</sub> → 2<sup>14</sup>N<sup>15</sup>N<sub>(g)</sub>) were undertaken at 450 °C for the studied RScSi-supported Ru catalysts and the Ru<sub>2.1</sub>/MgO reference material. The INHIE reaction is an efficient indicator to evaluate the capacity of the catalyst to adsorb and dissociate the dinitrogen molecule. The dinitrogen profiles recorded with Ru<sub>1.7</sub>/LaScSi and Ru<sub>2.1</sub>/MgO are presented in Figures 5A and 5B, respectively. A pure homomolecular exchange occurs on Ru<sub>1.7</sub>/LaScSi, illustrated by a simultaneous decrease with time in the partial pressure of <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> and a concomitant increase in the partial pressure of <sup>14</sup>N<sup>15</sup>N. Similar trends are obtained for all intermetallics, but with various kinetics. In comparison, neither a consumption of <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub>

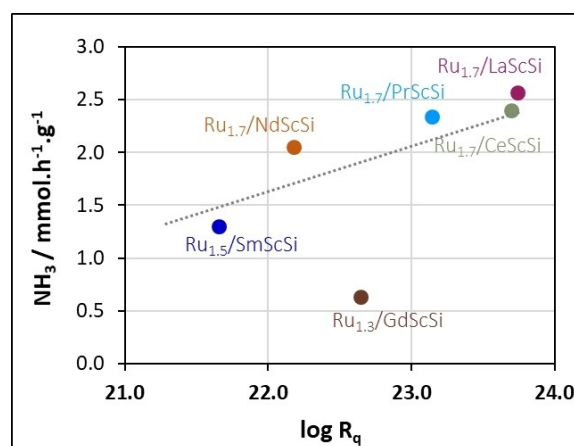
nor an increase in <sup>14</sup>N<sup>15</sup>N signal were observed with Ru<sub>2.1</sub>/MgO at 450 °C. The promotion of the homomolecular exchange reaction on Ru/RScSi samples indicates that the dissociation of N<sub>2</sub> on Ru is favored by intermetallics support compared to the reference Ru<sub>2.1</sub>/MgO material.

This result is in agreement with the reported electride character of intermetallics which are electron-donor materials.<sup>[9,14]</sup> A comparison of the Ru/RScSi behaviors for N<sub>2</sub> dissociation can be achieved by calculating the initial rate of homomolecular exchange (R<sub>q</sub>) from the slope of the m/z=29 curve at the beginning of the reaction (Eq. 1, experimental part). The results reported in Table 3 show that Ru<sub>1.7</sub>/LaScSi, Ru<sub>1.7</sub>/CeScSi and Ru<sub>1.7</sub>/PrScSi exhibit high equilibrium rates, at 5.54 × 10<sup>23</sup> at.g<sup>-1</sup>.min<sup>-1</sup>, 5.01 × 10<sup>23</sup> at.g<sup>-1</sup>.min<sup>-1</sup> and 1.39 × 10<sup>23</sup> at.g<sup>-1</sup>.min<sup>-1</sup>, respectively. For Ru<sub>1.7</sub>/NdScSi and Ru<sub>1.5</sub>/SmScSi, lower equilibration rates were observed, at 1.52 × 10<sup>22</sup> and 0.46 × 10<sup>22</sup> at.g<sup>-1</sup>.min<sup>-1</sup>, respectively. On Ru<sub>1.5</sub>/SmScSi, for which the equilibration was extremely low at 450 °C, a temperature-programmed analysis of the reaction was performed between 450 °C and 600 °C (Figure S4). This additional experiment shows that a temperature of 580 °C is required to obtain a significant rate of equilibration for this samarium containing sample. Finally, the Ru<sub>1.3</sub>/GdScSi sample exhibits an intermediate behavior with an initial equilibrium rate of 4.42 × 10<sup>22</sup> at.g<sup>-1</sup>.min<sup>-1</sup> at 450 °C.

The cleavage of the N<sub>2</sub> bond is commonly recognized as the rate-determining step of ammonia synthesis pathway. Consequently, a tentative of correlation between the ammonia yield at 400 °C and the equilibration activity measured at 450 °C is reported in the Figure 6. Interestingly, the Ru/RScSi catalysts with the highest ammonia production rate (Ru<sub>1.7</sub>/LaScSi and Ru<sub>1.7</sub>/CeScSi) also have the highest equilibrium rate, while the catalyst with the lowest ammonia formation rate (Ru<sub>1.5</sub>/SmScSi) shows the lowest N<sub>2</sub> equilibrium rate. However, Ru<sub>1.3</sub>/GdScSi does not follow this correlation with an intermediate N<sub>2</sub> equilibrium rate but a very low ammonia synthesis rate. Additionally, the reference Ru<sub>2.1</sub>/MgO catalyst presents no N<sub>2</sub>



**Figure 5.** Evolution of the nitrogen isotopomer partial pressures during a homomolecular (INHIE) experiment at 450 °C for A: Ru<sub>1.7</sub>/LaScSi, B: Ru<sub>2.1</sub>/MgO.

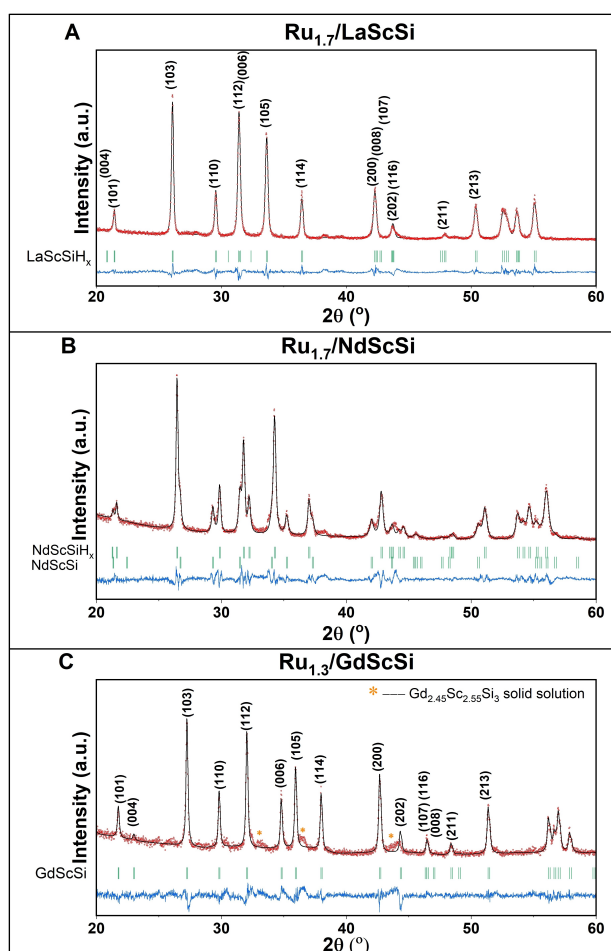


**Figure 6.** Correlation between the initial rate of equilibration at 450 °C and the ammonia production rate at 400 °C on Ru/RScSi samples. Ru<sub>1.7</sub>/LaScSi (Text/Zahl), Ru<sub>1.7</sub>/CeScSi (●), Ru<sub>1.7</sub>/PrScSi (●), Ru<sub>1.3</sub>/GdScSi (●), Ru<sub>1.7</sub>/NdScSi (●) and Ru<sub>1.5</sub>/SmScSi (●).

exchange activity at 450 °C. To go further insight in NH<sub>3</sub> synthesis route, DFT and XRD investigations are described thereafter.

To identify the possible phase changes during the catalytic tests performed at 400 °C, XRD patterns were collected at room temperature after the tests. The diffractograms of Ru/RScSi samples for R=La, Nd and Gd are shown in Figure 7 and the unit cell parameters of the phases obtained after catalytic tests are listed in Table 1 for all tested rare earths. From these results, it appears that LaScSi, CeScSi, and PrScSi samples exhibit only one single hydride phase after the catalytic test, while NdScSi and SmScSi show also the formation of a hydride phase but with remaining pristine material. The relative proportion of hydride phase, estimated by Rietveld refinement, decreases from Nd to Sm. Finally, GdScSi does not form any hydride phase and only the pristine intermetallic is present.

Therefore, this firstly evidences that the hydrogenation process differs depending on the rare earth nature and becomes more difficult when going from La to Gd lanthanides.



**Figure 7.** Full pattern matching of XRD patterns obtained after catalytic tests at 400 °C for three different samples (each was tested at 1, 3, and 5 bar). The Bragg peaks positions are marked with ticks and the indexations are given for single-phase samples. The difference curve between calculated and measured curves is shown below (blue curve). (A): Ru<sub>1.7</sub>/LaScSi after catalytic test at 400 °C. (B): Ru<sub>1.7</sub>/NdScSi after catalytic test at 400 °C. (C): Ru<sub>1.3</sub>/GdScSi after catalytic test at 400 °C.

Besides, as the catalytic performances tend to decrease from the lightest rare earths to the heavier ones, it also suggests that the formation of the hydride phase favors the catalytic activity of Ru/RScSi materials, likely by enhancing the electron-donating character of the support.<sup>[9]</sup> Note that those measurements were performed back to room temperature, meaning that *in-situ* XRD would be required to confirm the hydrogenation state during the catalytic tests. As previously noted, the Ru<sub>1.3</sub>/GdScSi sample exhibits different behavior compared to the other ones (Figure 6). The fact that no correlation is observed between the N<sub>2</sub> exchange and the ammonia production rate needs further experiments and DFT calculations to be understood.

Our previous theoretical works on GdScGe and NdScSi and their hydrides, using density functional theory (DFT), gave insights on the effect of both the nature of the rare earth and the presence of hydrogen, on features closely related to the electrone character.<sup>[17d,23]</sup> The electronic structure of GdScGe and NdScSi was found spin-polarized, which is expected from, at least, the significant magnetic moment from Nd and Gd 4f shells. Sc bands are thus spin-polarized too, especially since Sc and Gd/Nd are first-neighbors. Since the electrone charge density arises from the overlap of Sc s and p atomic orbitals,<sup>[14]</sup> the spin polarization of Sc bands lifts the degeneracy of spin-up and spin-down electrone states, thus removing at least half the electrone states from the vicinity of Fermi level. Also, the spin polarization induces a charge transfer from the minority spin toward the majority spin channel, likely to depopulate the electrone states.

Upon hydrogen insertion in the tetrahedral sites of the rare earth double layers, the spin polarization of Sc bands vanishes, and only 4f-character bands retain a magnetic moment, consistently with the loss of long-range magnetic ordering observed experimentally. This striking effect, due to the strong RE–H interactions competing with RE–Sc interactions, potentially restores the full electrone character, as in the non-magnetic LaScSi. However, two conditions are necessary for this electronic structure effect to actually achieve an electrone character: i) obviously, the octahedral R<sub>2</sub>Sc<sub>4</sub> sites should remain mostly hydrogen-free, since they host the electrone charge density. This condition is intrinsically satisfied in GdScGeH (GdScGeH<sub>1.5</sub> has never been observed); ii) hydrogen insertion goes along with a lowering of Fermi level, potentially depopulating the electrone states. Therefore, a second condition is that the electrone states remain populated, at the vicinity of Fermi level. Interestingly, GdScGeH meets this condition as well.<sup>[17d]</sup> From our preliminary calculations (to be published) we assume that GdScSi has a similar behavior.

In conclusion of this DFT part, the 4f-shell magnetic moment perturbs significantly the electronic structure near the Fermi level, and could strongly reduce the contribution of electrone states as electron donors in the catalytic process, as observed here (Figure 4), especially for Sm and Gd that carry the most populated 4f shells. Hydrogen insertion potentially solves this issue, and a complete DFT study is ongoing to address these aspects in intermetallics of interest here.



## Electride and hydride behaviors in NH<sub>3</sub> synthesis reaction; mechanistic insights

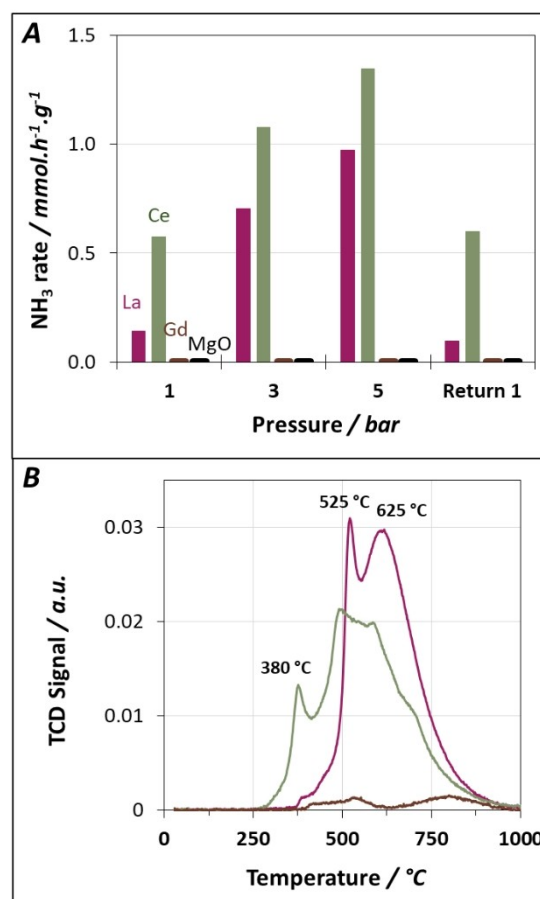
As a result, a specific study on Ru<sub>1.7</sub>/LaScSi and Ru<sub>1.7</sub>/CeScSi catalysts compared to Ru<sub>1.3</sub>/GdScSi and Ru<sub>2.1</sub>/MgO reference was undertaken in the following section to highlight the involvement of electride and hydride behaviors in NH<sub>3</sub> synthesis reaction.

First, the catalytic performances at very low temperature (300 °C) were determined over Ru<sub>1.7</sub>/LaScSi and Ru<sub>1.7</sub>/CeScSi in order to provide further information on the mechanism encountered on these electride samples. For sake of comparison, the Ru<sub>1.3</sub>/GdScSi sample which showed intermediate N<sub>2</sub> equilibration rate (Figure 6) and no hydride behaviors (Figure 7) was also evaluated, as well as the Ru<sub>2.1</sub>/MgO reference catalyst.

Figure 8A shows the performances of the selected materials in ammonia synthesis at 300 °C depending on the pressure. First the Ru<sub>1.3</sub>/GdScSi material and the Ru<sub>2.1</sub>/MgO reference sample present no activity at 300 °C even at 5 bar. To the opposite, the cerium-based catalyst shows remarkable activities with ammonia yield of 1.35 mmol.h<sup>-1</sup>.g<sup>-1</sup> (900 ppm) compared to 0.97 mmol.h<sup>-1</sup>.g<sup>-1</sup> (650 ppm) for Ru<sub>1.7</sub>/LaScSi at 5 bar. Note that 0.58 mmol.h<sup>-1</sup>.g<sup>-1</sup> is reached from 1 bar over Ru<sub>1.7</sub>/CeScSi. The higher ammonia synthesis performances at 300 °C of cerium-based intermetallic is also confirmed by the TOF calculation on Ru particles (Table 4).

H<sub>2</sub>-TPD experiments were then carried out to study the hydrogen-sorption properties of intermetallic samples. Note that Ru addition on RScSi has no effect in H<sub>2</sub>-TPD curve profiles and that no desorption was observed for the Ru<sub>2.1</sub>/MgO sample (results not shown). Figure 8B shows that very low H<sub>2</sub> desorption was recorded for Gd-based material. This result seems to indicate that the hydride-phase was not formed over GdScSi intermetallic during the adsorption phase performed at 350 °C. This particular behavior for R=Gd might be related to the inability of GdScSi phase to absorb H<sub>2</sub>, as previously highlighted by XRD analysis (Figure 7). Despite the electride character of this material, which promotes the transfer of electrons from Ru to the antibonding  $\pi$ -orbitals of N<sub>2</sub> (<sup>15</sup>N<sub>2</sub>/<sup>14</sup>N<sub>2</sub> equilibration experiments), the hydrogenation step is limited under the N<sub>2</sub>+H<sub>2</sub> reactional mixture. In addition to the strong magnetic moment of Gd which should perturb significantly the electride-type density in the Gd<sub>2</sub>Sc<sub>4</sub> site (DFT calculations previously discussed), the low activity of Ru<sub>1.3</sub>/GdScSi could also come from the partial poisoning of the Ru nanoparticles by the chemisorbed -H atoms that cannot migrate inside the interstitial sites of the intermetallic phase sites. Figure 8B also shows that the hydrogen release proceeds in different temperature ranges depending on rare earth elements in RScSi-based sample (R=La, Ce).

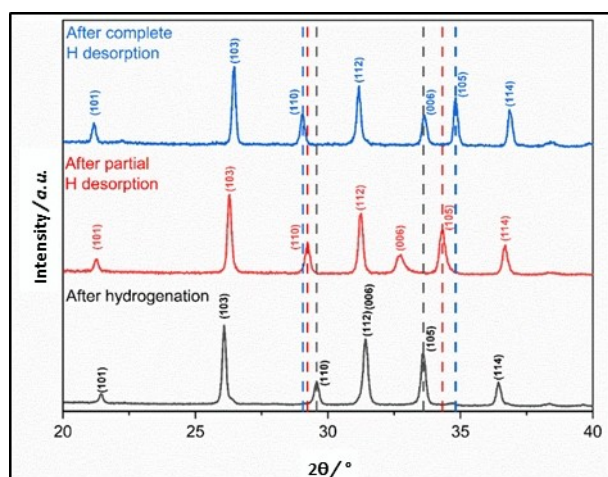
Both catalysts present two main desorption peaks centered at 380–560 °C and 525–625 °C for Ru<sub>1.7</sub>/CeScSi and Ru<sub>1.7</sub>/LaScSi, respectively. Note that the observation of two desorption peaks is in fair agreement with the existence of two different crystallographic sites able to store hydrogen species in the material, *i.e.* the [R<sub>4</sub>] tetragonal site and the [R<sub>2</sub>Sc<sub>4</sub>] octahedral site corresponding to 1H/f.u. and 0.5 H/f.u., respectively. The



**Figure 8.** shows the performances of the selected materials in ammonia synthesis at 300 °C depending on the pressure. First the Ru<sub>1.3</sub>/GdScSi material and the Ru<sub>2.1</sub>/MgO reference sample present no activity at 300 °C even at 5 bar. To the opposite, the cerium-based catalyst shows remarkable activities with ammonia yield of 1.35 mmol.h<sup>-1</sup>.g<sup>-1</sup> (900 ppm) compared to 0.97 mmol.h<sup>-1</sup>.g<sup>-1</sup> (650 ppm) for Ru<sub>1.7</sub>/LaScSi at 5 bar. Note that 0.58 mmol.h<sup>-1</sup>.g<sup>-1</sup> is reached from 1 bar over Ru<sub>1.7</sub>/CeScSi. The higher ammonia synthesis performances at 300 °C of cerium-based intermetallic is also confirmed by the TOF calculation on Ru particles (Table 4).

relative ratio of both peaks suggests that hydrogen is released from the octahedral cavity first, then from the tetrahedral cavity, in accordance with the fact that the latter is reported to be more stable than the octahedral one.<sup>[14]</sup>

To confirm the hydrogen desorption process, XRD patterns were recorded on Ru<sub>1.7</sub>/LaScSi at three different steps of the desorption curve: (i) after the hydrogen absorption at 350 °C, (ii) after the first desorption peak at 550 °C and (iii) after the complete desorption process up to 1000 °C (Figure 9). The diffractogram obtained before the beginning of the hydrogen release process confirms the presence of the hydride phase LaScSiH<sub>1.5</sub> with the unit cell parameters  $a=4.270$  Å and  $c=17.072$  Å. As expected, the pristine phase LaScSi with higher  $a$  and much lower  $c$  values ( $a=4.348$  Å and  $c=15.984$  Å) is recovered after the complete heating up to 1000 °C. After the first H<sub>2</sub>-TPD desorption peak, the sample was kept 1 hour at 550 °C and the corresponding diffractogram shows the presence of only one phase with intermediate unit cell parameters



**Figure 9.** XRD patterns at room temperature after different stages of the H<sub>2</sub>-TPD for Ru<sub>1.7</sub>/LaScSi. Below (black): after hydrogenation. Middle (red): after the first desorption peak at 550 °C. Above (blue): after complete desorption up to 1000 °C. The dashed lines emphasize the evolution of the (110) and (105) peaks evidencing the increase of the *a* parameter and the decrease of the *c* parameter upon hydrogen desorption.

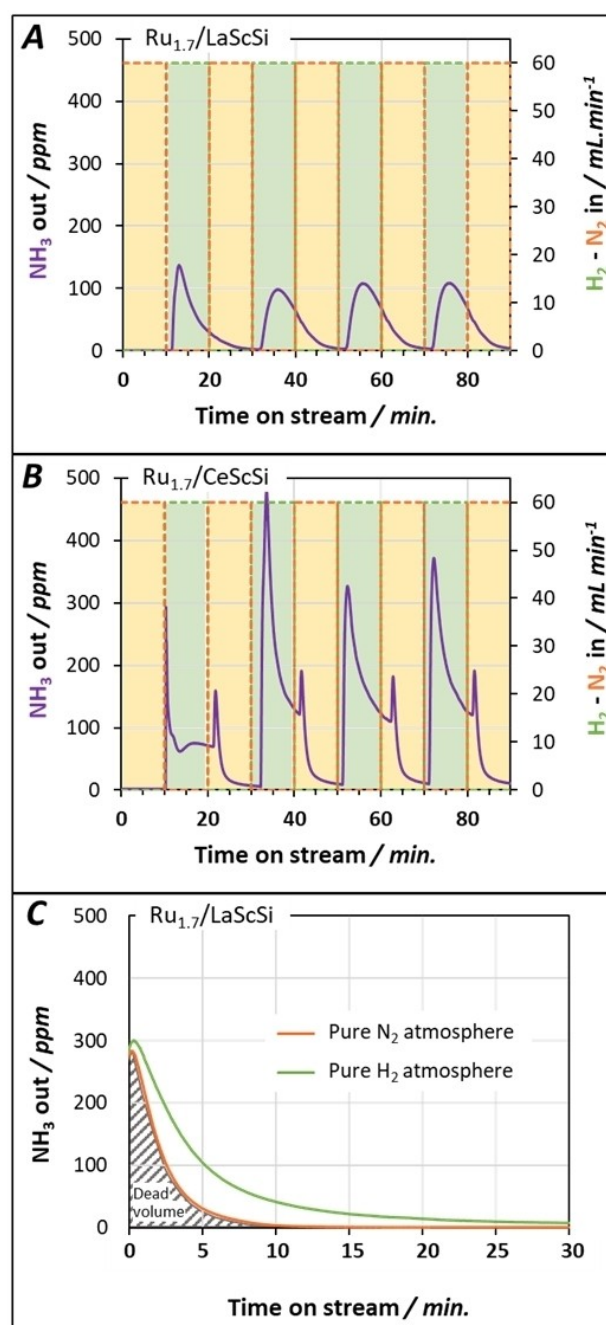
(*a* = 4.319 Å and *c* = 16.400 Å), evidencing the formation of a partial hydride.

In addition, the difference of activity observed between the two catalysts at 300 °C might be strongly linked to the difference hydride stability observed by H<sub>2</sub>-TPD (Figure 8B).

Finally, it appears that the N<sub>2</sub> adsorption/dissociation properties of ruthenium, shown by dinitrogen isotopic exchange experiments (Figure 6), might not be the limiting step in ammonia synthesis for Ru/RScSi samples, and that the H<sub>2</sub> adsorption-desorption properties must be considered as well. In fact, Gong *et al.*<sup>[10b]</sup> recently proposed a dual-site action mode to explain the activities observed on Ru-loaded La-TM-Si like samples (TM = Co, Fe and Mn) because the rate-determining step was then found to be NH<sub>2</sub> formation. To highlight the mechanisms encountered in NH<sub>3</sub> synthesis over Ru supported LaScSi and CeScSi intermetallic materials, transient catalytic experiments were also carried out.

Two selected Ru/RScSi materials (Ru<sub>1.7</sub>/LaScSi and Ru<sub>1.7</sub>/CeScSi) were evaluated under alternating H<sub>2</sub> (60 mL·min<sup>-1</sup>) or N<sub>2</sub> (60 mL·min<sup>-1</sup>) flow at 450 °C. Results of transient catalytic tests are presented in Figure 10.

Over Ru<sub>1.7</sub>/LaScSi, it is clearly evidenced that NH<sub>3</sub> is only emitted under gaseous H<sub>2</sub> flow in absence of N<sub>2</sub> in the gas phase (marked by the green phases), whereas no ammonia is detected under N<sub>2</sub> atmosphere only (marked by the orange phases). These results are consistent with the H<sub>2</sub>-TPD profile (Figure 8B) that show rather high stability of the hydride at this temperature, compared to Ru<sub>1.7</sub>/CeScSi. It also shows that N<sub>2</sub> is adsorbed and probably dissociated on the catalyst surface, and that the resulting N species reacted with dissociated H<sub>2</sub> and/or molecular H<sub>2</sub> during the step under pure hydrogen flow. It also emphasizes that NH<sub>3</sub> cannot be emitted without gaseous H<sub>2</sub>, meaning that stored H<sup>-</sup> species are not able to react with N-



**Figure 10.** Transient flow experiments with alternative flow of N<sub>2</sub> or H<sub>2</sub> on Ru<sub>1.7</sub>/LaScSi (A) and Ru<sub>1.7</sub>/CeScSi (B) at 450 °C. NH<sub>3</sub> emissions (ppm) at 450 °C under pure N<sub>2</sub> or H<sub>2</sub> purge after NH<sub>3</sub> synthesis on Ru<sub>1.7</sub>/LaScSi (C).

species at this temperature. Concerning the Ru<sub>1.7</sub>/CeScSi catalyst, an ammonia slip is observed during the switch under pure N<sub>2</sub> flow. It is suggested that either (i) adsorbed NH<sub>x</sub>-like species remaining on the surface of the material are desorbed during subsequent switch to N<sub>2</sub> or (ii) that cerium-based materials destabilizes hydrogen more efficiently than lanthanum-based ones as indicated by the H<sub>2</sub>-TPD results (Figure 8B). The better catalytic performances of the Ce-based compound at 300 °C, while being slightly less efficient at 400 °C compared

with its La-based counterpart, could be then explained by the lower temperature of H desorption of CeScSiH<sub>x</sub> hydride. It reveals that hydrogen species as H<sup>-</sup> ions may also be involved in NH<sub>3</sub> formation.

Electride-like materials present nanocages containing electrons which can capture hydrogen species as H<sup>-</sup> ions. Kitano *et al.*<sup>[9]</sup> reported that, in [Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup>(e<sup>-</sup>)<sub>4</sub>, H<sup>-</sup> ions react with nitrogen species formed from N<sub>2</sub> dissociation, which results in ammonia formation. Note that similar behaviors were also encountered over Ca<sub>2</sub>N:e<sup>-</sup> supported Ru catalysts were both electrons and hydride ions likewise play a crucial role in effective ammonia synthesis.<sup>[24]</sup> The electron-hydride ion exchange reaction by H desorption through a cage wall composed of a rigid monolayer of materials require high temperature to achieve surface metal hydrides. Besides, Wang *et al.*<sup>[25]</sup> reported that some hydride materials such as the ternary ruthenium complexes Li<sub>4</sub>RuH<sub>6</sub> and Ba<sub>2</sub>RuH<sub>6</sub> allow the non-dissociative reduction of N<sub>2</sub>. It was reported also that hydridic hydrogen transports electrons and proton to stabilize N<sub>x</sub>H<sub>y</sub> intermediates. Consequently, hydride desorption temperature impacts the NH<sub>3</sub> production, as illustrated in [11]. Our experiments support that hydride character formed by hydrogen sorption promotes to NH<sub>3</sub> synthesis but ammonia is still mainly formed by reduction of N<sub>2</sub> with hydrogen from the gas phase. Overall, it also supports the dual-site catalytic mechanism concept where the NH<sub>x</sub> formation may be considered as the rate-determining step for some kind of catalysts, instead of the generally admitted N<sub>2</sub> adsorption/dissociation step.

These results are confirmed in Figure 10C where the Ru<sub>1.7</sub>/LaScSi catalyst was exposed to pure N<sub>2</sub> or H<sub>2</sub> atmosphere after ammonia synthesis at 450 °C. This experiment confirmed a significant ammonia formation under H<sub>2</sub> while no ammonia emission was observed under N<sub>2</sub> (starting from 400 ppm NH<sub>3</sub>, same ammonia purge profiles are obtained without catalyst under N<sub>2</sub> or H<sub>2</sub> flow, denoted as dead volume in Figure 10C). This test highlights again that Ru-supported intermetallic samples can store N-containing species under pure N<sub>2</sub>, able to react with gaseous H<sub>2</sub> to produce NH<sub>3</sub>. It appears also from Figure 10C that 26 μmol g<sup>-1</sup> of stored N<sub>ad</sub> atom are used at 450 °C over Ru<sub>1.7</sub>/LaScSi sample, compared to 50 μmol g<sup>-1</sup> for Ru<sub>1.7</sub>/CeScSi material (curves not shown).

Note that this phenomenon was not observed over Ru<sub>2.1</sub>/MgO catalyst although Szmigel *et al.*<sup>[26]</sup> revealed by temperature-programmed surface reaction experiments that atomic nitrogen with a surface stoichiometry of N<sub>ads</sub>/Ru<sub>s</sub> = 1/3 can be preadsorbed over promoted (Ba, Cs) ruthenium catalysts supported on magnesia.

## Conclusion

We have investigated the effect of various rare earth elements on the catalytic activity of Ru supported RScSi silicides (R=La, Ce, Pr, Nd, Sm, Gd) for ammonia synthesis under mild temperature and pressure conditions. A tendency towards a decrease in the catalytic performances is observed when moving from La to Gd, which appears to be related to a lesser ability of the

RScSi phases to absorb hydrogen, according to XRD measurements. This could be ascribed to the prevention of hydrogen poisoning of the Ru surface when the hydride phase is formed during ammonia synthesis from H<sub>2</sub> and N<sub>2</sub> gases. In addition, the hydrogen desorption temperature seems to play a role as well in the catalytic activities at low temperature (300 °C). It suggests that the electride character and thus the electron-donor effect can be tuned through partial hydrogenation of the RScSi materials. Further hydrogenation experiments coupled to neutron diffraction study and DFT calculations are under way to better answer this question. Finally, isotopic exchange and transient flow experiments offer a better understanding of the mechanism of ammonia formation. They evidence that the RScSi support helps for the dissociation of the N<sub>2</sub> molecule with possible N- species storage and that hydrogen in the formed NH<sub>3</sub> molecule comes mainly from the gas-phase H<sub>2</sub> and not primarily from the hydride phase. This challenges the involvement of Ru as the only active site and seems to suggest that the formation/desorption of NH<sub>x</sub> species could be determinant for NH<sub>3</sub> synthesis performances.

## Experimental Section

### Materials

The studied RTX intermetallic samples are RScSi with R=La, Ce, Pr, Nd, Sm, Gd. They were synthesized from melting the pure elements, starting from rare earth ingots (La 99.9% Sigma-Aldrich, Ce 99.8% Alfa Aesar, Pr 99.9% Smart-elements, Nd 99.9% Smart-elements, Sm 99.9% Alfa Aesar, Gd 99.95% Smart-elements), Sc pieces (99.9% Neyco) and Si lumps (99.9999% Alfa Aesar). Rare earth metals were pre-melted in a high-frequency furnace to evaporate volatile oxides. The molar ratio of 1:1.05:1 with an excess of scandium was used to compensate for residual ScO present in the Sc precursor. The pure metals were cut and weighted to synthesize samples of about 5 g. Then they were arc-melted 5 times under an atmosphere of pure argon (≈700 mbar), returning the button upside down in between each melting to ensure homogeneity. The weight loss of the resulting silvery buttons after melting were less than 0.3 wt%. The as-cast samples (i.e. after melting) were later wrapped in tantalum foil, sealed in evacuated quartz ampoules, and annealed at 900 °C for 4 weeks. The method described previously was not used to synthesize SmScSi, as samarium has a high vapor pressure at elevated temperature. Instead, the elements were cut into small pieces and sealed inside a tantalum crucible under argon atmosphere, then they were melted inside a high-frequency induction furnace, and eventually annealed for 10 days at 1000 °C inside a quartz ampoule. As the quality of the samples are comparable, we do not expect any influence of the sample preparation on the catalytic activities.

The resulting pristine buttons were crushed in an agate mortar and sieved in the ranges 250–100, 100–40 and <40 μm for the subsequent deposition of Ru nanoparticles. A theoretical amount of 2.5 wt% Ru was used for chemical vapor deposition on the pristine phases using Ru<sub>3</sub>(CO)<sub>12</sub> as Ru precursor in an evacuated quartz tube at 250 °C. This deposition method described in details in ref [9] remains the common technique for intermetallic materials. The starting amount of Ru was chosen after testing of different Ru content (1 to 7.5 wt% Ru).



A reference Ru/MgO sample was also prepared for comparison with Ru-supported intermetallic materials. Various processes can be undertaken to prepare conventional ruthenium samples and impregnation is the most commonly used method to obtain Ru-based ammonia synthesis catalysts. MgO support (99.99%, Acros Organic) was first calcinated under air at 500 °C during 2 h (5 °C.min<sup>-1</sup>). 2.5 wt%. Ru was added by impregnation of the corresponding amount of ruthenium nitrosyl nitrate solution (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, Alfa Aesar) in excess of water. The preparation was stirred during 12 h, then dried at 80 °C using a sand bed and placed in an oven at 100 °C during a night. The solid was then treated 2 h at 300 °C under a flow of H<sub>2</sub> (60 mL.min<sup>-1</sup>, heating ramp rate: 5 °C.min<sup>-1</sup>). Finally, the sample was sieved between 100 and 40 μm for the catalytic testing. Other sieved ranges have been tested and mentioned when appropriate. The effect of the carbonyl precursor on ruthenium deposition on MgO was also investigated. The results are presented in the supplementary information file.

## Characterization

**X-ray diffraction.** The samples were analyzed after melting, annealing, and catalytic activity test by powder X-ray diffraction (XRD). The data were collected at room temperature (RT) on a PANalytical X'pert PRO MPD diffractometer in Bragg-Brentano θ-θ geometry equipped with a secondary monochromator and X'Celerator multi-strip detector. Each measurement was made within an angular range of 2θ = 8–80° and lasted for 87 minutes. The Cu-Kα radiation was generated at 45 kV and 40 mA (λ = 1.5418 Å). Powder XRD patterns were analyzed using the Fullprof Suite program and the unit cell parameters were determined through full-pattern matching.<sup>[27]</sup> Rietveld method was also used to estimate the relative proportion of each phase when both pristine and hydride phases were present in the sample.

**Elemental analyses.** They were carried out to assess the ruthenium loadings. After solubilisation of the samples in acid media, analyses were performed with an ICP-OES apparatus (Agilent 5110S).

**Transmission Electron Microscopy (TEM).** Micrographs were recorded on JEOL 2100 instrument operated at 200 kV with a LaB<sub>6</sub> source and equipped with a Gatan Ultra scan camera. EDX spectroscopy was carried out with a Hyperline (Premium) detector (active area: 30 mm<sup>2</sup>) using the software SM-JED 2300T for data acquisition and treatment. EDX analysis zone was defined on the particle, and it was generally ranging from 5 to 15 nm. Ru dispersion was averaged over both spherical metal particles and hexagonal close packed particles (*hcp*) model to cover a wide range of particle sizes.<sup>[28]</sup>

**Surface Area and Porosimetry.** Nitrogen adsorption-desorption isotherms were recorded at -196 °C, using a Tristar 3000 Micromeritics apparatus. Prior to the measurement, the samples were pretreated at 250 °C under vacuum for 8 h. The surface area was calculated using the BET model. Note that intermetallic-based catalysts present very low specific area of around 1 m<sup>2</sup> g<sup>-1</sup> compared to 21 m<sup>2</sup> g<sup>-1</sup> for Ru<sub>2.1</sub>/MgO reference sample.

**Nitrogen isotopic exchange.** Experiments were performed in a setup described in [29]. The sample was placed in a U-form quartz reactor and the reaction was carried out in a closed recycle system which was connected to (i) a mass spectrometer (Pfeiffer Vacuum, QMS 200) for the monitoring of the gas phase composition and (ii) to a vacuum pump. The recycling pump placed in the system removes limitations due to gas-phase diffusion. The isothermal nitrogen homomolecular isotopic exchange experiments (INHIE, also called equilibration reaction) were undertaken on 100 mg of catalysts. The sample was treated under pure hydrogen at 350 °C (10 °C.min<sup>-1</sup>, 1 h) followed by a vacuum step from 350 °C to 450 °C

(10 °C.min<sup>-1</sup>) for 30 min. After the purge, the isotopic mixture was charged (200 mbar of <sup>14</sup>N<sub>2</sub> and 200 mbar of <sup>15</sup>N<sub>2</sub>, 98% + purity, supplied by Cambridge Isotope Laboratories, Inc.). The 28, 29, and 30 m/z signals were monitored as a function of time to follow the exchange. The m/z values of 2, 17, 18 and 32 were also recorded to determine the possible releasing of H<sub>2</sub> from the material after hydrogenation, the possible formation of NH<sub>3</sub> during the reaction and the eventual possible leakage causing air entrance in the system. The initial rate of homomolecular exchange (rate of equilibration) is given by Eq.1:

$$R_q(t=0) = \frac{2N_g}{P_0} \left( \frac{dP_{29}}{dt} \right)_{t=0} \quad (1)$$

Where  $N_g$  is the number of <sup>15</sup>N and <sup>14</sup>N in the gas phase;  $P_0$  the total pressure;  $P_{29}$  the partial pressure of <sup>14</sup>N<sup>15</sup>N and  $t$  the time of equilibration.

**H<sub>2</sub>-TPD (temperature programmed desorption).** The experiments were performed on a Micromeritics Autochem 2920 apparatus equipped with a thermal conductivity detector (TCD). Catalyst (50 mg) was placed in a U-shape quartz reactor. Before the measurement, catalysts were first treated under pure hydrogen from RT to 350 °C (5 °C.min<sup>-1</sup>) and cooled down to RT under H<sub>2</sub>, followed by purging step under argon for 1 hour. Note that similar TPD results are obtained with a purge step at 100 °C. Next, temperature programmed desorption is carried out up to 1000 °C (5 °C.min<sup>-1</sup>) under 30 mL.min<sup>-1</sup> of Ar.

## Catalytic tests

The ammonia synthesis activity measurement was carried out in a fixed-bed reactor under a flow of H<sub>2</sub>:N<sub>2</sub> (3:1) (N<sub>2</sub> > 99.9999% and H<sub>2</sub> > 99.9999%). The catalyst (100 mg) was placed in a home-made pressure reactor and the total flow rate was fixed at 60 mL.min<sup>-1</sup>. The gas mixture was imposed by electronic mass-flow controllers.

The compositions of the feed gas and effluent stream were monitored continuously (1 Hz) using online MKS 2030 Multigas infrared analyzer with high NH<sub>3</sub> sensitivity (2-3 ppm). Ammonia synthesis was recorded from RT to the desired temperature (heating ramp of 5 °C.min<sup>-1</sup>). Isotherm experiments were carried out to evaluate the stability of catalysts and the pressure effect up to 5 bar, using a back-pressure regulator. Results are expressed directly in term of emitted ammonia (ppm), synthesis rate (mmol/h/g) or turn over frequency (TOF, min<sup>-1</sup>) estimated from the average Ru particle sizes measured by TEM.

Transient experiments were performed at stabilized temperature after an increase to the desired temperature under N<sub>2</sub> flow. The catalyst was then submitted to an alternating atmosphere of pure hydrogen or nitrogen every 10 min with a total flow of 60 mL.min<sup>-1</sup>.

## Acknowledgements

*The authors gratefully acknowledge the French National Agency for Research (ANR, Intermetallist Project, ref. ANR-19-CE07-0023), the Regional Council of Nouvelle Aquitaine, the French Ministry of Research and the European Regional Development Fund (ERDF) for financial supports.*

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** intermetallic · hydride · NH<sub>3</sub> · ruthenium · transient experiments

- [1] H. Liu, *Chin. J. Catal.* **2014**, *35*, 1619–1640.
- [2] A. Afif, N. Radenahmad, Q. Cheok, S. Shams, J. H. Kim, A. K. Azad, *Renewable Sustainable Energy Rev.* **2016**, *60*, 822–835.
- [3] R. Javaid, H. Matsumoto, T. Nanba, *ChemistrySelect* **2019**, *4*(7), 2218–2224.
- [4] G. Ertl, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1219–1227.
- [5] a) B. C. McClaine, R. J. Davis, *J. Catal.* **2002**, *211*, 379–386; b) Y. V. Larichev, B. L. Moroz, V. I. Zaikovskii, S. M. Yunusov, E. S. Kalyuzhnaya, V. B. Shur, *J. Phys. Chem. C* **2007**, *111*, 9427–9436; c) N. Saadatjou, A. Jafari, S. Sahebdelfar, *Chem. Eng. Commun.* **2015**, *202*, 420–448.
- [6] a) J. S. J. Hargreaves, *Appl. Petrochem. Res.* **2014**, *4*, 3–10; b) N. Bion, F. Can, J. Cook, J. S. J. Hargreaves, A. L. Hector, W. Levason, A. R. McFarlane, M. Richard, K. Sardar, *Appl. Catal. A* **2015**, *504*, 44–50; c) P. Wang, F. Chang, W. Gao, J. Guo, G. Wu, T. He, P. Chen, *Nat. Chem.* **2017**, *9*, 64–70; d) Y. Inoue, M. Kitano, K. Kishida, H. Abe, Y. Niwa, M. Sasase, Y. Fujita, H. Ishikawa, T. Yokoyama, M. Hara, H. Hosono, *ACS Catal.* **2016**, *6*, 7577–7584; e) V. S. Marakatti, E. M. Gaigneaux, *ChemCatChem* **2020**, *12*(23), 5838–5857.
- [7] J. L. Dye, *Acc. Chem. Res.* **2009**, *42*, 1564–1572.
- [8] S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, H. Hosono, *Science* **2003**, *301*, 626–629.
- [9] M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S.-W. Kim, M. Hara, H. Hosono, *Nat. Chem.* **2012**, *4*, 934–940.
- [10] a) Y. Gong, J. Wu, M. Kitano, J. Wang, T.-N. Ye, J. Li, Y. Kobayashi, K. Kishida, H. Abe, Y. Niwa, H. Yang, T. Tada, H. Hosono, *Nat. Catal.* **2018**, *1*, 178–185; b) Y. Gong, H. Li, J. Wu, X. Song, X. Yang, X. Bao, X. Han, M. Kitano, J. Wang, H. Hosono, *J. Am. Chem. Soc.* **2022**, *144*, 8683–8692.
- [11] Y. Gong, H. Li, C. Li, X. Yang, J. Wang, H. Hosono, *Chem. Mater.* **2022**, *34*(4), 1677–1685.
- [12] H. Mizoguchi, S.-W. Park, K. Kishida, M. Kitano, J. Kim, M. Sasase, T. Honda, K. Ikeda, T. Otomo, H. Hosono, *J. Am. Chem. Soc.* **2019**, *141*(8), 3376–3379.
- [13] Y. Lu, T. Tada, Y. Toda, S. Ueda, T. Yokoyama, M. Kitano, H. Hosono, *J. Am. Chem. Soc.* **2016**, *138*(12), 3970–3973.
- [14] J. Wu, Y. Gong, T. Inoshia, D. C. Fredrickson, J. Wang, Y. Lu, M. Kitano, H. Hosono, *Adv. Mater.* **2017**, *29*, 1700924.
- [15] a) S. Gupta, K. G. Suresh, *J. Alloys Compd.* **2015**, *618*, 562–606; b) A. V. Morozkin, L. M. Viting, I. A. Sviridov, I. A. Tskhadadze, *J. Alloys Compd.* **2000**, *297*, 168–175.
- [16] a) K. Ooya, J. Li, K. Fukui, S. Iimura, T. Nakao, K. Ogasawara, M. Sasase, H. Abe, Y. Niwa, M. Kitano, H. Hosono, *Adv. Energy Mater.* **2021**, *11*, 2003723; b) J. Kammert, J. Moon, Y. Cheng, L. Daemen, S. Irle, V. Fung, J. Liu, K. Page, X. Ma, V. Phaneuf, J. Tong, A. J. Ramirez-Cuesta, Z. Wu, *J. Am. Chem. Soc.* **2020**, *142*(16), 7655–7667.
- [17] a) E. Gaudin, S. F. Matar, R. Pöttgen, M. Eul, B. Chevalier, *Inorg. Chem.* **2011**, *50*(21), 11046–11054; b) S. Tencé, T. Mahon, E. Gaudin, B. Chevalier, J. L. Bobet, R. Flacau, B. Heying, U. C. Rodewald, R. Pöttgen, *J. Solid State Chem.* **2016**, *242*, 168–174; c) B. Chevalier, W. Hermes, B. Heying, U. C. Rodewald, A. Hammerschmidt, S. F. Matar, E. Gaudin, R. Pöttgen, *Chem. Mater.* **2010**, *22*, 5013–5021; d) T. Mahon, E. Gaudin, A. Villesuzanne, R. Decourt, J.-L. Bobet, O. Isnard, B. Chevalier, S. Tencé, *Inorg. Chem.* **2018**, *57*, 14230–14239.
- [18] Y. Gong, H. Li, C. Li, X. Bao, H. Hosono, J. Wang, *J. Adv. Ceram.* **2022**, *11*(9), doi.org/10.1007/s40145-022-0633-z.
- [19] J. Wu, J. Li, Y. Gong, M. Kitano, T. Inoshita, H. Hosono, *Angew. Chem. Int. Ed.* **2019**, *58*, 825–829; *Angew. Chem.* **2019**, *131*, 835–839.
- [20] N. Saadatjou, A. Jafari, S. Sahebdelfar, *Chem. Eng. Commun.* **2014**, 420–448.
- [21] C. J. H. Jacobsen, S. Dahl, P. L. Hansen, E. Törnqvist, L. Jensen, H. Topsøe, D. V. Prip, P. B. Møenshaug, I. Chorkendorff, *J. Mol. Catal.* **2000**, *163*, 19–26.
- [22] F. R. García-García, A. Guerrero-Ruiz, *Top. Catal.* **2009**, *52*, 758–764.
- [23] T. Mahon, E. Gaudin, A. Villesuzanne, B. Chevalier, S. Tencé, *Inorg. Chem.* **2019**, *58*, 15255–15268.
- [24] M. Kitano, Y. Inoue, H. Ishikawa, K. Yamagata, T. Nakao, T. Tada, S. Matsuishi, T. Yokoyama, M. Hara, H. Hosono, *Chem. Sci.* **2016**, *7*, 4036–4043.
- [25] Q. Wang, J. Pan, J. Guo, H. A. Hansen, H. Xie, L. Jiang, L. Hua, H. Li, Y. Guan, P. Wang, W. Gao, L. Liu, H. Cao, Z. Xiong, T. Vegge, P. Chen, *Nat. Catal.* **2021**, *4*, 959–967.
- [26] D. Szmigielski, H. Bielawa, M. Kurtz, O. Hinrichsen, M. Muler, W. Raróg, S. Jodzis, Z. Kowalczyk, L. Znak, J. Zieliński, *J. Catal.* **2002**, *205*, 205–212.
- [27] J. Rodríguez-Carvajal, *Phys. B. Condens. Matter.* **1993**, *192*(1–2), 55–69.
- [28] a) Y. Zhou, Y. Ma, G. Lan, H. Tang, W. Han, H. Li, Y. Li, *Chin. J. Catal.* **2019**, *40*, 114–123; b) A. Comas-Vives, K. Furman, D. Gajan, M. C. Akatay, A. Lesage, F. H. Ribeiro, C. Copéret, *Phys. Chem. Chem. Phys.* **2016**, *18*, 1969–1979.
- [29] S. M. Hunter, D. H. Gregory, J. S. J. Hargreaves, M. Richard, D. Duprez, N. Bion, *ACS Catal.* **2013**, *3*, 1719–1725.

Manuscript received: September 28, 2022  
Revised manuscript received: December 8, 2022  
Accepted manuscript online: December 16, 2022  
Version of record online: January 9, 2023