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Ru/RScSi intermetallics for ammonia synthesis in mild conditions

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Introduction

For a century now, ammonia synthesis is carried out using the Haber-Bosch (HB) process ($N_2 + 3H_2 \rightleftharpoons 2NH_3$), which requires severe operating conditions ($T=400-600\text{ }^\circ\text{C}$; $P=150-200\text{ bars}$). It is currently responsible for 1.6% of the world CO_2 emissions, mainly due to fossil hydrogen sources^[1]. Ammonia, mainly used for soil fertilization, is one of the most synthesized chemical compounds in the world (180 Mt/year) with a high growth projection due to its potential as a decarbonized alternative energy carrier. To support ammonia synthesis from alternative non-continuous green hydrogen production, the NH_3 synthesis should be performed in milder conditions, according to an increase in the performance of HB catalysts. With this aim, new families of solids are developed and electride and/or hydride supported materials received particular attention. In this study, ruthenium supported intermetallic-electrides, whose electron-donating effect is expected to stimulate N_2 conversion, were investigated and compared to a Ru/MgO reference catalyst. More precisely, the influence of rare earth in the Ru/RScSi intermetallic catalyst (R =rare earth: La, Ce, Pr, Gd, Nd, Sm) was studied for ammonia synthesis under mild temperature and pressure conditions ($T=300-400\text{ }^\circ\text{C}$; $P=1-5\text{ bars}$). Transient experiments were also carried out on promising formulations to highlight the determining steps in the reaction mechanism.

Materials and Methods

Catalysts were prepared according to [2]. The ammonia synthesis activity measurement ($300-400\text{ }^\circ\text{C}$; $1-5\text{ bars}$) was carried out in a home-made pressure reactor ($H_2:N_2$ (3:1), 60 mL min^{-1} , $0.1\text{ g}_{\text{cata}}$). The compositions of the feed gas and effluent stream were monitored continuously (1 Hz) using online MKS 2030 Multigas infrared analyzer with high NH_3 sensitivity (2-3 ppm). Transient experiments were studied with pulses of N_2 or H_2 in the secondary gas atmosphere (H_2/N_2) or with alternating H_2-N_2 flows.

Results and Discussion

First, the influence of rare-earth (R) element in Ru/RScSi electride-like intermetallic catalysts for ammonia synthesis under mild conditions ($300-450\text{ }^\circ\text{C}$; $1-5\text{ bar}$) was investigated. At $400\text{ }^\circ\text{C}$, the catalytic performances in ammonia synthesis (Table 1) follow the La to Gd lanthanides series ($Ru_{1.7}/LaScSi = Ru_{1.7}/CeScSi = Ru_{1.7}/PrScSi > Ru_{1.7}/NdScSi > Ru_{1.5}/SmScSi > Ru_{1.3}/GdScSi$) and appear correlated with the formation of the hydride phase. Hydride phase formation and stabilization was studied by means of XRD and H_2 -TPD experiments.

N_2 isotopic exchange (Table 1) evidenced that the RScSi supports generally help for the dissociation of the N_2 molecule, and transient flow experiments (Figure 1B) indicated the

possible N- species storage and that hydrogen in the formed NH_3 molecule comes mainly from the gas-phase H_2 and not primarily from the hydride phase.

Table 1. N_2 isotopic exchange behaviors and NH_3 production rate of Ru/RScSi catalysts.

	$Ru_{1.7}/LaScSi$	$Ru_{1.7}/CeScSi$	$Ru_{1.7}/PrScSi$	$Ru_{1.7}/NdScSi$	$Ru_{1.5}/SmScSi$	$Ru_{1.3}/GdScSi$	$Ru_{2.1}/MgO$
Initial $^{14}N_2 + ^{15}N_2 \rightarrow 2^{14}N^{15}N$ exchange rate @ $450\text{ }^\circ\text{C}$ (10^{22} at/g/min)	55.4	50.1	13.9	1.5	0.4	4.4	0.0
NH ₃ production rate @ 1 bar (mmol/h/g)							
NH ₃ /400°C	2.56	2.40	2.33	2.05	1.30	0.63	0.66
NH ₃ /300°C	0.14	0.58	0.04	0.02	0.13	0.01	0.01

In addition, $Ru_{1.7}/CeScSi$ catalyst showed remarkable catalytic activity at low temperature ($300\text{ }^\circ\text{C}$) with $0.58\text{ mmol}_{NH_3}/h/g$ at 1 bar (Table 1). Transient experiments (Figure 1A) combined with H_2 -RTP hydride stability measurements suggest that NH_3 formation at $300\text{ }^\circ\text{C}$ is impacted by (i) reversible hydrogen storage–release properties and (ii) the suspected formation/desorption of NH_x -like species.

Furthermore, the substitution of Sc (transition metal) and Si (p-block element) elements on Ru supported cerium-based intermetallics (R , rare earth) highlighted that ammonia synthesis at $300\text{ }^\circ\text{C}$ could respect either rather associative or dissociative mechanism depending on the catalyst formulation.

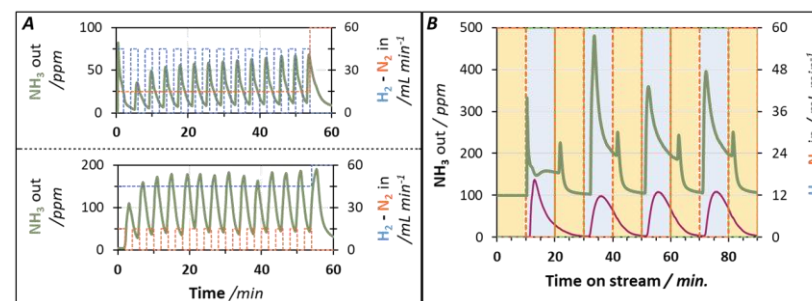


Figure 1. $Ru_{1.7}/CeScSi$ catalytic performances in (A): N_2/H_2 pulses in H_2/N_2 atmosphere at $300\text{ }^\circ\text{C}$; (B): Alternative H_2-N_2 flows at $450\text{ }^\circ\text{C}$.

Significance

This work is of major industrial significance because of the expected growth in ammonia production, while fundamental aspects are developed about ammonia synthesis mechanisms at low temperature.

References

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2. C. Croisé *et al.*, ChemCatChem, **2023**, *15*, e202201172