

Low-Temperature Ammonia Decomposition using Cs-Ru/CeO₂ Catalyst

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Highlights

- Ru-Cs/CeO₂ catalyst was successfully synthesized via polyol reduction method.
- This catalytic formulation allowed an NH₃ conversion of about 99% at 400 °C and 1 bar.
- High activity at relatively low temperatures thanks to the synergistic effect of caesium and ruthenium.

1. Introduction

In the pursuit of more sustainable energy solutions, hydrogen is considered the ultimate clean energy carrier, as it is possible to produce it from electrolysis employing renewable energy and only water is emitted from its conversion to power. However, transport and storage of hydrogen are challenging due to the risks related to its handling and due to the low volumetric energy density. A more viable way to store hydrogen is to convert it to ammonia as the infrastructures involved in its production, storage and distribution are already fully operational [1]. The effective utilization of ammonia as a hydrogen storage media involves also the step of ammonia decomposition through an endothermic equilibrium reaction and the separation and purification of the resulting hydrogen. This reaction is typically conducted in a temperature range of 450 – 550 °C and a pressure range of 1 – 3 bar. Therefore, a promising route for process intensification is the development of a membrane reactor technology to simultaneously decompose ammonia and separate hydrogen in a single unit, enabling lower temperature conversion due to Le Chatelier's principle [2]. More specifically, the focus of this research is to investigate the catalytic activity at lower temperature compared with conventional technologies through highly active ruthenium catalysts synthesized via polyol reduction method.

2. Methods

1%_{wt} Cs-5%_{wt} Ru/CeO₂ catalyst was prepared via polyol reduction method. A solution composed by all the metal precursor salts was prepared using ethylene glycol as solvent. This solution was placed in a three-neck round bottom flask connected to a Graham condenser used to cool down and condense the reactive vapours, and recycle them as liquids back into the synthesis vessel. The system was heated up to 110 °C then kept at this temperature for 2 hours to obtain a homogeneous colloidal solution, after which the mixture was cooled down naturally. Then, a potassium hydroxide solution was added to the mixture and the resulting gel was aged and then washed with ultrapure water. Finally, the catalyst was dried and then calcined at 550 °C for 4 hours. The catalyst was characterized through nitrogen physisorption, Powder X-Ray Diffractometry and X-ray Photoelectron Spectroscopy. Activity tests for ammonia decomposition were carried out in a custom-made experimental setup in a temperature range of 250 – 400 °C and a pressure range of 1 – 5 bar, feeding 100 Nml·min⁻¹ of ammonia in a stainless-steel reactor (I.D. 10 mm).

3. Results and discussion

The results of the nitrogen physisorption analysis in terms of specific surface area and pore dimensions show surface area about 82 m²·g⁻¹, pore size about 5.3 nm and pore volume about 0.140 cm³·g⁻¹. Furthermore, as reported in the Figure 1a, the XRD pattern of the catalyst revealed the characteristic peaks of cubic lattice of CeO₂, with the main peaks located at 28.5°, 33.1°, 47.5°, 56.4°, 58.2°, 69.5°, 76.0° and 77.9° [3]. No additional peaks assignable to ruthenium or caesium have been detected. This might be related to both the low amount of ruthenium and caesium and the small size of ruthenium clusters. The Ce 3d XPS deconvoluted spectrum showed ten peaks, as reported in the Figure 1b, of

which six peaks can be attributed to Ce^{4+} and four peaks can be assigned to Ce^{3+} . The Ce^{3+} concentration in the sample is related to the formation of oxygen vacancies and it can be estimated by the ratio of the sum of peak areas of Ce^{3+} to the area of all other peaks [4]. It resulted that the Ce^{3+} concentration for the catalyst is approximately 44%. Moreover, the abundance of Ce^{3+} species could cause charge imbalance and hence the promotion of unsaturated chemical bonds on the catalyst surface.

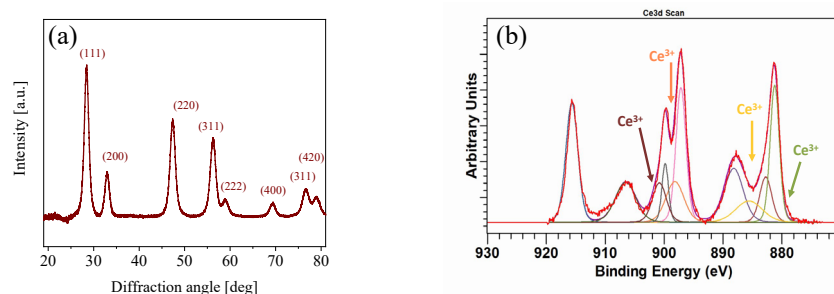


Figure 1. (a) XRD pattern of fresh catalyst material, (b) Ce 3d XPS deconvoluted spectrum.

The results of the activity tests are showed in the figure below (Figure 2).

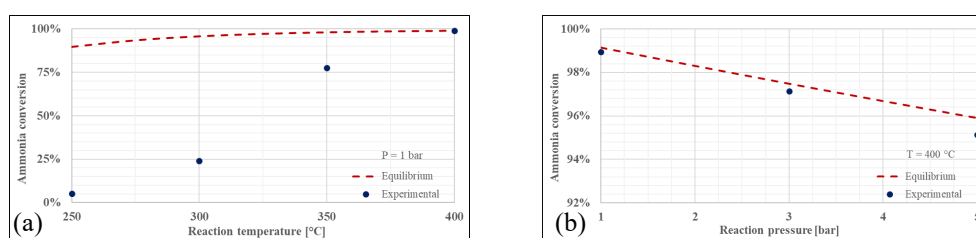


Figure 2. NH_3 conversion in function of (a) reaction temperature at 1 bar and (b) reaction pressure at 400 °C.

These results show an extremely high catalytic activity at relatively low temperature reaching an ammonia conversion of 99% at 400 °C and 1 bar. Furthermore, at this temperature, the achieved conversion is approaching the equilibrium conversion and, to the best of our knowledge, it is the highest value achieved so far in NH_3 decomposition under similar reaction conditions. This can be ascribed to the beneficial electron donation mechanism to ruthenium clusters due to the caesium promoter together with the high surface area and surface oxygen vacancies of the ceria support [5]. Similar results in literature can be found only for reaction systems employing very diluted feeding streams [6].

4. Conclusions

The Ru-Cs/ CeO_2 synthesized in this work is a promising catalyst in the NH_3 decomposition reaction. The synergetic effect of promoter and support enhances low temperature activity and opens new routes for NH_3 decomposition process at lower temperature. Furthermore, we aim at combining the catalyst with a tailored H_2 -selective membrane to investigate further increase of NH_3 conversion at $T < 400$ °C and to simplify the downstream separation train for H_2 purification. This will ultimately lead to a significant reduction of the process costs, while reaching high H_2 separation efficiency.

References

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Keywords

Ammonia decomposition; hydrogen separation; process intensification; ruthenium catalyst.