

Construction of Co/CeO₂ catalyst and study on catalytic performance

Long Li, Lifang Zhao, Yunyan Li, Weiwen Wang*

(School of Chemical Engineering, Qindao University of Science and Technology, Shandong Qingdao 266042, China)

Abstract. High-temperature ammonia decomposition is a promising method for hydrogen production, but high temperatures and low conversion rates limit its wide application. In order to solve this problem, the development of nano-materials is essential to achieve high performance ammonia oxidation decomposition. In this paper, ordered mesoporous Co/CeO₂ catalyst was synthesized by codeposition method and a new process of ammonia hydrogen production was developed and designed without the need for external heating. The catalyst was characterized by XRD, BET and TEM. The results show that the catalyst activity is the highest when Co content is 10wt%. When the molar ratio of NH₃/O₂ is 4:1, the bed temperature increases from 165°C to 405°C, the conversion rate of NH₃ and O₂ is 72% and 81%, respectively, and the productivity of H₂ is 45%. The catalyst also showed good stability and reusability.

1. Introduction

Hydrogen energy is recognized as a clean energy with great potential. Hydrogen energy has the advantages of high calorific value, high density, wide source, abundant yield, high energy utilization rate, and pollution-free products, so it is considered as one of the most promising clean energy. The energy density of hydrogen (140 MJ/kg) is three times that of petroleum and 4.5 times that of coal. Applications of hydrogen energy are leading the way in the field of transport, including cars and other means of transport and as an energy carrier for storing excess electricity generated off-peak. However, hydrogen energy is still facing the problems of poor safety performance, storage and transportation difficulties, and high storage material requirements, which make it difficult to apply on a large scale. Ammonia is a high-quality hydrogen carrier, easier to liquefy and transport. It has high combustion value, green environmental protection, mature synthesis technology and safe and convenient storage and transportation mode. In the context of the increasingly severe environmental protection situation, especially in the context of China actively advocating the realization of "carbon peak" and "carbon neutrality", it is of great significance to explore the use of ammonia fuel as a new energy source to reduce carbon emissions. The development of the process of ammonia decomposition to hydrogen is not synchronized. The production capacity of hydrogen and ammonia is not a significant barrier to meeting the high demand, and current ammonia decomposition systems are not capable of producing enough pure hydrogen in large quantities at low temperatures. Therefore, ammonia decomposition becomes the bottleneck of hydrogen chain, and the

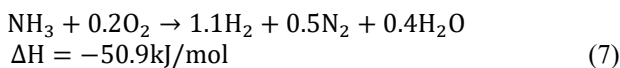
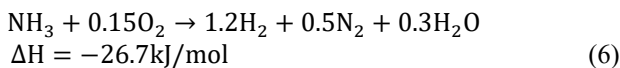
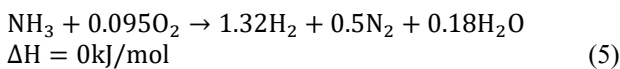
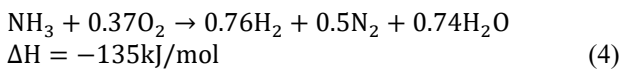
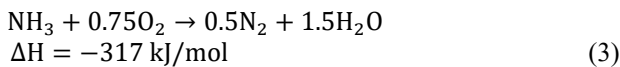
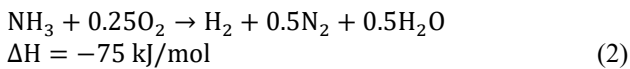
current research focus on the process of NH₃ decomposition. Ammonia decomposition for hydrogen production as a green and environmentally friendly technology has received widespread attention^[1-3]. Currently, there are many types of catalysts used for ammonia decomposition hydrogen production, including Ru-based, Fe-based, Ni-based, Co-based, and copper-based single metal catalysts, as well as combinations of multiple metals^[4-6]. In addition to these metal combinations, materials such as metal nitrides and carbides are also used as catalysts. Although traditional ammonia decomposition hydrogen production catalysts show high efficiency in laboratory conditions, they face a series of challenges in large-scale production. The equilibrium calculation shows that the NH₃ conversion rate can reach 99%. However, it takes a lot of time and energy to reach reaction condition. Therefore, developing catalysts that can quickly initiate and have high H₂ production rates has become a hot research topic. This catalyst will help overcome the application difficulties of traditional catalysts in large-scale production^[7-8].

In this paper, we discussed a new method of NH₃ oxidative decomposition for H₂ production. We studied the simultaneous occurrence of ammonia oxidation decomposition reactions, and compared the performance of different catalysts to reveal the reaction mechanism of the catalysts. By studying a new type of catalyst, we have made a contribution to the field. These results provide a direction for the preparation and improvement of efficient catalysts.

* Corresponding author: wwwang@qust.edu.cn

2. Triggering Tests

The catalyst fixed bed evaluation system was used to evaluate the performance of the catalyst (Fig. 1). N₂ gas leakage test was carried out before the experiment to ensure no gas leakage during the whole experiment. Before the experiment, the catalyst was pretreated at 500°C H₂/Ar. Stop heating and wrap the reactor in glass wool to reduce heat loss. The experiment was carried out under the condition of insulation. When the bed temperature drops to 165 °C, gas mixture is introduced into the reactor in a certain proportion. The reduction carrier and the supported metal oxide release heat, thus activating the ammonia oxidation decomposition reaction. The reaction temperature rises rapidly and reaches stability after a period of time. After a period of reaction, O₂ stops and the reaction terminates. After the reaction stops, in the absence of oxygen, when the temperature rises above 165 °C, O₂ is reintroduced to restart the reaction. In subsequent cycles, the ammoxidation decomposition reaction is repeatedly triggered several times. A routine sample was taken from the outlet gas and the gas components were detected. The gas composition was analyzed using gas chromatography. The following formula is used to calculate conversion (Eq. 8-9) and the hydrogen production rate via Eq. 10.



$$X_{\text{NH}_3} = \frac{(M_{\text{NH}_3,\text{in}} - M_{\text{NH}_3,\text{out}})}{M_{\text{NH}_3,\text{in}}} \times 100\% \quad (8)$$

$$X_{\text{O}_2} = \frac{(M_{\text{O}_2,\text{in}} - M_{\text{O}_2,\text{out}})}{M_{\text{O}_2,\text{in}}} \times 100\% \quad (9)$$

$$Y_{\text{H}_2} = \frac{M_{\text{H}_2,\text{out}} \times 2}{M_{\text{NH}_3,\text{in}} \times 3} \times 100\% \quad (10)$$

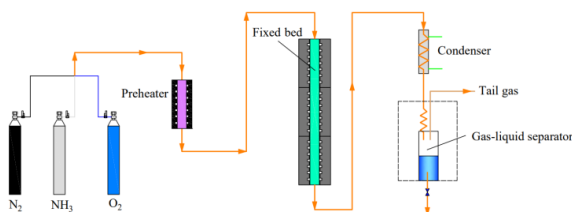


Fig. 1. Standard experimental protocol for the triggering test

3. Results

3.1 Activity Tests

First, the catalyst activity was tested by placing 0.25g of catalyst in a reactor. Before the reaction, N₂ (30mL · min⁻¹) was introduced for 30 min to flush out the air in the device. Then the catalyst was heated to 500°C in an H₂/Ar to remove water and carbon dioxide from the catalyst surface. Turn off the heat, the bed temperature dropped to 165°C. At this point, the gas was switched to supply an ammonia-oxygen mixture (NH₃:O₂=100:25 mL · min⁻¹) as shown in Fig. 2. Sampling bags were used to collect gas samples every 20 s to detect the gas composition. This indicates that ammonia first undergoes oxidation to produce N₂, and then undergoes ammonia oxidation decomposition to produce H₂. Furthermore, the experimental results show that the NH₃ oxidation decomposition is fast, and NO_x and N₂O are not detected. Until 150 s, the formation rate of the gas is almost stable, indicating that the reaction has reached equilibrium. Throughout the reaction process, the heat required for ammonia decomposition comes from the oxidation of NH₃, and the generation speed of hydrogen is faster due to the ammonia's internal heat.

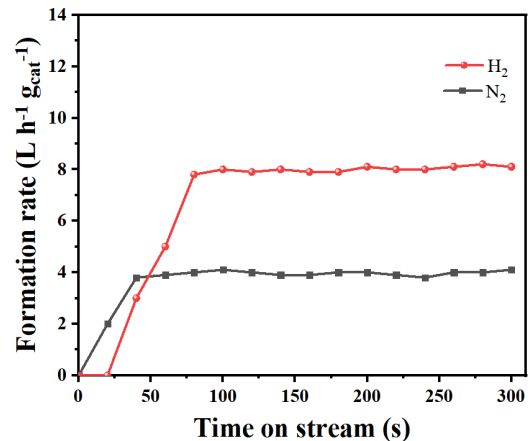


Fig. 2 The formation rate of H₂ and N₂

As shown in Fig. 3, when the reaction gas was fed to the 10wt% Co/CeO₂ catalyst reactor, the catalytic bed temperature remained basically unchanged, and the bed temperature decreased with the passage of time, indicating that no reaction occurred. However, under the same experimental operation described above, when the temperature is reduced to 165 °C, the bed temperature rises rapidly, indicating that the reaction is occur at 165 °C. The spontaneous combustion temperature of 10wt% Co/CeO₂ was determined at 165°C. With the increase of Co load from 1wt % to 10wt%, the spontaneous combustion temperature of catalyst decreased gradually. When Co content exceeds 10%, the spontaneous combustion temperature does not change.

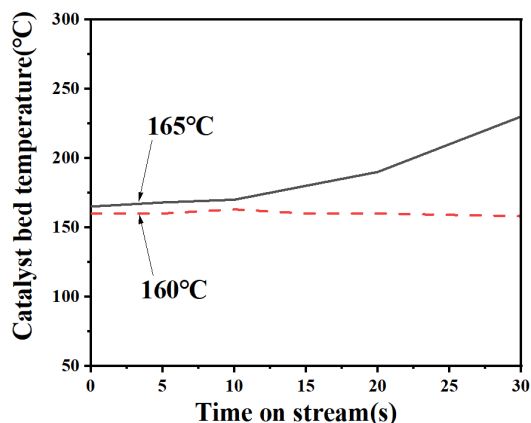


Fig. 3. The bed temperature of 10wt% Co/CeO₂

3.2 Catalysts Characterization

The Co/CeO₂ catalyst was studied by SEM and HRTEM, as shown in Fig. 4. The results show the lattice spacing is between $d=0.236 \sim 0.238\text{nm}$, and the structure is orderly porous. The particles are evenly dispersed, the lattice spacing is obvious, and there is no agglomeration. The active metal can be found successfully attached to the catalyst surface, indicating that we have prepared the Co/CeO₂ catalyst, and the active metal is uniformly distributed on the catalyst surface.

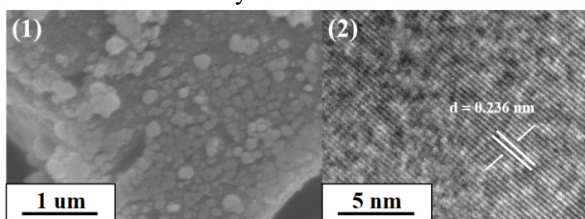


Fig. 4. (1)TEM, (2) HRTEM images of 10wt%Co/CeO₂

The XRD pattern of Co/CeO₂ catalyst particles was analyzed, as shown in Fig 5a. $2\theta = 28.6^\circ, 32.9^\circ, 47.5^\circ, 56.3^\circ, 59.1^\circ, 69.4^\circ, 76.7^\circ, 79.1^\circ$ respectively corresponding to the peak (111), (200), (220), (311), (222), (400), (331) and (420) plane, This indicates that fluorite structure exists in all catalysts. After loading Co, the characteristic peak of CeO₂ remained unchanged and the structure was intact, indicating that the structure of CeO₂ remained intact. However, no diffraction peaks were observed for Co, which may be due to their small grain size or high dispersion. In addition, the XRD patterns of the catalysts were similar before and after 100 h of reaction, indicating that the catalyst did not undergo obvious sintering before and after reaction, and the structure remained stable. At the same time, the content of Co remained basically unchanged during the reaction, which indicates that the catalyst has excellent stability.

The N₂ physical adsorption isotherm is exhibited in Fig.5b. BET was 42.5 m²/g and a hysteresis loop of H3, indicating that Co/CeO₂ catalyst has a larger specific surface area and a wider channel pore structure. $P/P_0 = 0.4\sim 1$, indicating high porosity of the catalyst. It can be seen providing a larger reaction space and exposing more active sites.

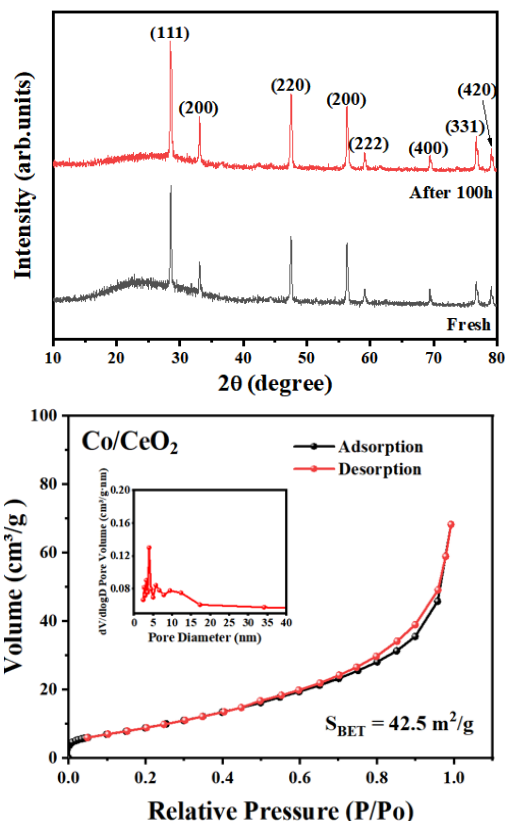


Fig. 5. (a) XRD before and after reaction. (b) BET

3.3 Cyclic Experiment and Stability

We conducted an ammonia oxidation decomposition cycle experiment at 165°C to test the stability of the catalyst (Fig. 6a). The specific process of the experiment was as follows: When the temperature dropped to 165°C, the feed was switched to an ammonia-oxygen mixture, and the reaction started. The reaction was stopped after 120 min of oxygen supply, and the reaction was completed. At this time, the bed temperature began to drop rapidly to 165°C, O₂ was supplied again, the reaction was restarted. This process was repeated five times (Fig. 6b). We took five samples at each sampling point and took the average value as the experimental result. The ammonia conversion rate was 70.1% ($\pm 2.1\%$), the oxygen conversion rate was 80% ($\pm 1.6\%$), the hydrogen yield was 43.5% ($\pm 1.8\%$), and the conversion rate and hydrogen yield were not reduced during the experiment. The experimental results show that the Co/CeO₂ catalyst exhibits significant stability and repeatability. We conducted 100 h stability test (Fig. 6c). This indicates that the catalyst has good stability, which is beneficial for practical production and reducing costs (Table 1). The XRD analysis compared the catalyst before and after the reaction, confirming the catalyst's stability. It is very important in commercial application.

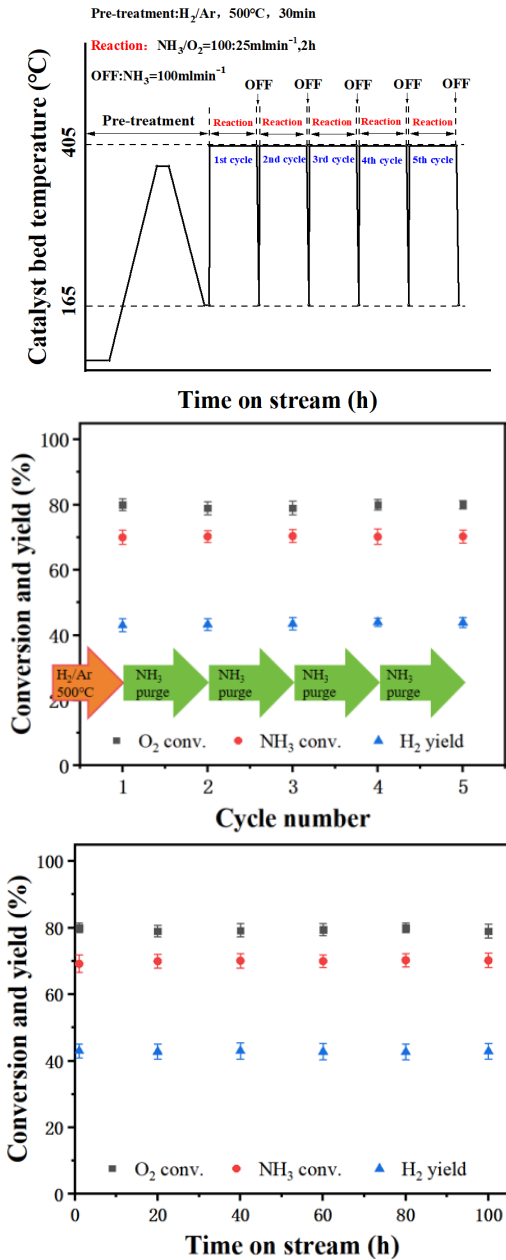


Fig. 6. (a) Cycle tests, (b) Catalytic activity (c) Catalyst stability

Table 1. Amount of Co in Co/CeO₂ before and after 5 cycles and stability tests

Treatment	Mass % of Co
Fresh	10
After 5 cycles	9.88
After 100 h	9.82

4. Conclusion

This study discovered a new process for oxidizing ammonia into hydrogen without the need for external heating, which can be initiated immediately upon the addition of ammonia and oxygen without complex processes. The Co/CeO₂ catalyst showed excellent catalytic performance, with NH₃ and O₂ conversion rates of 72% and 81%, respectively, and a hydrogen yield of 45% when the NH₃/O₂ ratio was 4:1. The catalyst also showed good stability and reusability, and the method

for preparing the catalyst was simple and cost-effective, significantly reducing production costs. The hydrogen production process has the advantages of low start-up, fast heating, high energy utilization rate and high hydrogen production rate. We expect that the process can be widely used in commercial applications.

References

- Awad O I, Zhou B, Harrath K, et al. Characteristics of NH₃/H₂ blend as carbon-free fuels: A review [J]. International Journal of Hydrogen Energy, 2023, 48(96): 38077-100.
- Wan Z, Tao Y, Shao J, et al. Ammonia as an effective hydrogen carrier and a clean fuel for solid oxide fuel cells [J]. Energy Conversion and Management, 2021, 228: 113729.
- G. Chehade, I. Dincer, Progress in green ammonia production as potential carbonfree fuel, Fuel 299 (2021) 120845.
- Selvakumaran D, Pan A, Liang S, et al. A review on recent developments and challenges of cathode materials for rechargeable aqueous Zn-ion batteries [J]. Journal of Materials Chemistry A, 2019, 7(31): 18209-36.
- York R, Bell S E. Energy transitions or additions? Why a transition from fossil fuels requires more than the growth of renewable energy [J]. Energy Research & Social Science, 2019, 51: 40-3.
- Braff W A, Mueller J M, Trancik J E. Value of storage technologies for wind and solar energy [J]. Nature Climate Change, 2016, 6(10): 964.
- Markard J. The next phase of the energy transition and its implications for research and policy [J]. Nature Energy, 2018, 3(8): 628-33.
- Bockris J O M. The hydrogen economy: Its history [J]. International Journal of Hydrogen Energy, 2013, 38(6): 2579-88.