

Article



Efficient Hydrogen Production from Ammonia Using Ru Nanoparticles on Ce-Based Metal–Organic Framework (MOF)-Derived CeO₂ with Oxygen Vacancies

Wenying Wu, Wenhao Yao, Yitong Liu, Senliang Xi * and Teng Zhang *

Key Laboratory of Cluster Science Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Advanced Research Institute of Multidisciplinary Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China; wwy15933833065@163.com (W.W.); ywh200012@163.com (W.Y.); m18735721812_1@163.com (Y.L.) * Correspondence: 3220215207@bit.edu.cn (S.X.); 7520180073@bit.edu.cn (T.Z.)

Abstract: Ammonia is a promising hydrogen storage material because it is easy to store and decompose into CO_X -free hydrogen. A Ru-based catalyst exhibits good catalytic performance in ammonia decomposition, and enhancing the interaction between the Ru atoms and the support is an important way to further improve its catalytic activity. In this study, CeO₂ was prepared by calcination using a cerium-based metal–organic framework (MOF) as the precursor, and the number of oxygen vacancies on the surface of CeO₂ was regulated by hydrogen reduction. The XPS and Raman results showed that abundant oxygen vacancies were formed on the surface of these CeO₂, and their number increased with an increase in the reduction time. The Ru/CeO₂-4 h catalyst, using CeO₂ reduced for 4 h as the support, exhibited good catalytic activity in ammonia decomposition, reaching 98.9% ammonia conversion and 39.74 mmol g_{cat}^{-1} min⁻¹ hydrogen yield under the condition of GHSV = 36,000 mL g_{cat}^{-1} h⁻¹ at 500 °C. The XAFS results demonstrated that Ru was stably anchored with oxygen vacancies on the surface of CeO₂ via Ru-O-Ce bonds. Density functional theory calculations further showed that these bondings lower the reaction energy barrier for N-H bond cleavage, thereby significantly enhancing the catalytic activity.

Keywords: Ru catalyst; ammonia decomposition; oxygen vacancy; metal–organic frameworks

1. Introduction

Hydrogen energy storage and transportation is an important link restricting the development of hydrogen energy. The flammable and explosive characteristics of hydrogen make its transportation a difficult problem [1,2]. Ammonia is considered to be a promising hydrogen storage medium, which has the advantages of easy liquefaction ($25 \,^{\circ}$ C, 8.6 bar), high-volume hydrogen density ($120 \,\text{kg cm}^{-3}$), low manufacturing cost, and itself being a carbon free fuel [1,3]. The properties of ammonia are conducive to the overall improvement of production, storage, and transportation infrastructure [4–6].

The decomposition reaction of ammonia is an endothermic process, manifested as follows:

$$2NH_3 (g) \rightarrow N_2 (g) + 3H_2 (g) \quad \Delta H = 91.2 \text{ kJ mol}^{-1}$$
 (1)

To achieve the complete conversion of ammonia, the decomposition temperature usually needs to be maintained over 800 $^{\circ}$ C, which would consume a large amount of energy. Thus, developing novelly efficient catalysts to reduce the energy consumption is



Academic Editors: Luca Gonsalvi and Eun Duck Park

Received: 20 March 2025 Revised: 20 May 2025 Accepted: 21 May 2025 Published: 23 May 2025

Citation: Wu, W.; Yao, W.; Liu, Y.; Xi, S.; Zhang, T. Efficient Hydrogen Production from Ammonia Using Ru Nanoparticles on Ce-Based Metal-Organic Framework (MOF)-Derived CeO₂ with Oxygen Vacancies. *Molecules* **2025**, *30*, 2301. https://doi.org/10.3390/ molecules30112301

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). very important for the industrial application of ammonia decomposition to hydrogen [7]. In recent years, the development of ammonia decomposition catalysts has made great progress [8–11]. Fe, Co, Ni, Ru, and other metal catalysts have been widely researched, providing a variety of options for the development of ammonia decomposition technology. Among these metals, Ru is the most effective active center due to its excellent catalytic activity at low and medium temperatures [12–15]. Meanwhile, the selection of the carrier is also very important. As reported in previous work, the strong metal–support interaction (SMSI) between Ru and the carrier could further enhance the catalytic activity of the Ru catalyst for NH₃ decomposition [16–22].

Metal oxides, such as CeO₂ [23–25], MgO [26,27], La₂O₃ [28], Al₂O₃ [29–31], ZrO₂ [32,33], are widely used as carriers for Ru catalysts in the ammonia decomposition process due to their surface acidity/basicity, surface oxygen vacancy, reoxidation properties, and the interaction between metal and support. Among these carriers, CeO₂ showed higher NH₃ decomposition catalytic activity than Ru/Al₂O₃ due to the strong SMSI and electronic modification of Ru active sites by CeO₂ [34]. Hu et al. [35] loaded Ru single atoms onto cerium oxide nanospheres (CeO₂-Nss) prepared by an improved colloidal deposition method and cerium oxide nanorods (CeO₂-NRs) prepared by the hydrothermal method. N₂ and H₂ on CeO₂-Ns and CeO₂-NR catalysts are more easily desorbed than MgO-supported catalysts prepared by other methods. According to the research, Ru/CeO₂ has great potential as the ammonia decomposition catalyst.

For the last few years, the application of the metal-organic framework (MOF) in catalyst preparation has been widely studied [36]. The MOF structure combines inorganic metals and organic linkers with a high surface area, diversity of assemblies, and uniform porosity. These advantages give the MOF the potential to be the catalyst, catalyst support, or precursor in many chemical reactions [37]. There have been numerous reports on the preparation of CeO₂ using MOF structures. Sivan et al. [38] reported a Ce-BTC-derived Ru/CeO₂ catalyst with highly dispersed Ru, and it shows excellent and more stable performance in NH_3 synthesis. He et al. [39] reported that the high-porosity Ru/CeO_2 catalyst prepared with Ce-UiO-66 improved the catalytic performance of CO₂ methanation compared with the CeO₂-supported Ru catalyst prepared by the traditional method. Chen et al. [40] used CeO₂ obtained by pyrolysis of Ce-MOF for toluene combustion; when compared with CeO₂ prepared by the precipitation method, MOF-CeO₂ exhibits a better catalytic activity due to its structure and abundant oxygen vacancy. According to the research, CeO₂ derived from Ce-MOF could exhibit superior surface properties to support the Ru metal, and this strategy is a potential path to prepare high-performance ammonia decomposition catalysts.

In this study, the Ce-BPDC was synthesized as the precursor, followed by calcination in air and reduction in hydrogen atmosphere to obtain CeO_2 with abundant oxygen vacancies. The number of oxygen vacancies on the surface of CeO_2 were adjusted by controlling the reduction time. Then, the Ru catalysts supported on these CeO_2 were prepared by impregnation, and their catalytic performances on ammonia decomposition were evaluated. Furthermore, these catalysts were comprehensively characterized to explore the relationship between the structure and catalytic properties, as well as the reaction mechanism.

2. Results and Discussion

2.1. Structural Characterization of Carrier and Catalyst

The characterization results of Ce-BPDC are consistent with the results in the literature (see Supporting Information for detailed description). The PXRD results of CeO₂-t obtained by calcining Ce-BPDC at 500 °C and then reducing in the H_2 /Ar atmosphere for different times (t = 0, 0.5, 1, 1.5, 2, 3, 4 h) are given in Figure S4. The pattern of the CeO₂ standard

sample showed diffraction peaks at 28.5, 33.1, 47.5, 56.3, 59.1, 69.4, 76.7, 79.1, and 87.4, corresponding with a face-centered cubic phase of the CeO₂ fluorite structure. Compared with that of CeO₂, the diffraction peaks of CeO₂-t shifted toward a higher angle, which could be attributed to the transformation of Ce⁴⁺ to Ce³⁺ during the calcination process of Ce-BPDC [41]. The N₂ adsorption/desorption isotherms of CeO₂-t are given in Figure S5. The specific surface area of cerium oxide obtained by the calcination of Ce-BPDC decreased significantly from 1502 m² g⁻¹ to about 45 m² g⁻¹. After loading Ru, the specific surface area of the catalyst did not change significantly. The morphology of CeO₂-t was characterized by SEM and TEM (Figures S6 and S7). The results show that the morphology of CeO₂-t after calcination was basically similar to that of the Ce-BPDC precursor, while its crystal particle size decreases.

The Ru/CeO₂-t catalysts were prepared by the impregnation method with RuCl₃, and their PXRD patterns are shown in Figure 1. It was found that the face-centered cubic phase of CeO₂ fluorite structure was retained, and no characteristic diffraction peak of Ru was observed, indicating that Ru was highly dispersed on the surface of the support [42]. The Ru content in these catalysts was characterized through Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The results show that the Ru loading of Ru/CeO₂-t (t = 0, 0.5, 1, 1.5, 2, 3, 4 h) was 4.29, 4.42, 4.34, 4.46, 4.20, 4.32, and 4.19 wt%, respectively. In order to have a deeper understanding of the catalyst microstructure and the dispersion of Ru on the CeO₂ support, detailed observations were made using HRTEM. The lattice stripes of Ru and CeO₂ can be observed in Figure S8. The spacing of 0.31 nm corresponds to the (111) face of CeO₂, and its lattice spacing was about 0.21 nm, corresponding to the (101) face of Ru substance. The EDS (Figure S8) results show that Ru was evenly dispersed on the surface of CeO₂-t. The particle size of Ru in the catalyst Ru/CeO₂-t (t = 0, 0.5, 1, 1.5, 2, 3, 4 h) was mainly concentrated between 1.5 and 4 nm (Figure S9).



Figure 1. The PXRD profile of the Ru/CeO₂-t.

2.2. Comparison of Catalytic Performance of Ammonia Decomposition to Hydrogen

The ammonia decomposition performance of the catalyst was tested in a self-built fixed-bed reactor (Figure S10), where 0.05 g catalyst was mixed with 2.95 g quartz sand and then transferred to a reactor equipped with quartz cotton. By injecting 50% NH_3/Ar gas, the system temperature was adjusted to the corresponding reaction temperature. The

catalyst was evaluated at a certain gas hourly space velocity (GHSV) in the temperature range of 375–500 $^{\circ}$ C. The detailed procedures are listed in the Supporting Information.

Under the GHSV condition of 12,000 mL g_{cat}^{-1} h⁻¹, the catalytic activities of Ru/CeO₂-t and Ru/CeO₂-C (Ru supported on the commercial CeO₂) catalysts in NH₃ decomposition were compared and analyzed, as presented in Table 1. It was found that, compared with Ru/CeO₂-C, the catalytic performance of the MOF-derived CeO₂-supported Ru catalyst significantly improved. In addition, the ammonia decomposition performance increased significantly with the increase in the reaction temperature. Meanwhile, the catalytic activity also increased on increasing the reduction time, during which the catalytic activity of Ru/CeO₂-4 h is the highest. The ammonia conversion rate of Ru/CeO₂-4 h reached 98.38% at 475 °C and 100% at 500 °C, respectively. In order to evaluate the practical application potential of Ru/CeO₂-4 h catalyst, the ammonia decomposition performance at high GHSV $(36,000 \text{ mL g}_{cat}^{-1} \text{ h}^{-1})$ was evaluated. And the results are shown in Figure S11. It can be seen that Ru/CeO₂-4 h still maintained a high catalytic activity, and the ammonia conversion rate was up to 97.04% at 475 °C and 98.9% at 500 °C, respectively. The hydrogen production rate was calculated according to the ammonia conversion of the catalyst (described in Section 3.3). Under the condition of GHSV = 36,000 mL $g_{cat}^{-1} h^{-1}$, the hydrogen production rate of Ru/CeO₂-4 h was 38.99 mmol g_{cat}^{-1} min⁻¹ at 475 °C and 39.74 mmol g_{cat}^{-1} min⁻¹ at 500 °C, respectively. Under similar conditions, the synthesized Ru/CeO₂-t catalyst was compared with the reported Ru catalysts, as shown in Table S2. It is worth noting that the catalytic activity of Ru/CeO₂-4 h remained in the first echelon.

Table 1. NH₃ conversion of Ru/CeO₂-t catalyst at GHSV = 12,000 mL $g_{cat}^{-1} h^{-1}$.

	T °C					
	375	400	425	450	475	500
NH ₃ Conv./% ^a						
Ru/CeO ₂ -C	7.87	16.86	33.47	52.66	73.75	85.16
Ru/CeO ₂ -0 h	23.41	45.26	64.44	78.95	91.88	95.95
Ru/CeO ₂ -0.5 h	30.24	55.79	73.53	86.24	92.95	96.99
Ru/CeO ₂ -1 h	34.92	57.94	75.56	87.79	95.7	97.72
Ru/CeO ₂ -1.5 h	38.85	61.37	78.57	89.77	97.11	99.01
Ru/CeO ₂ -2 h	37.98	58.97	76	87.84	96.63	98.13
Ru/CeO ₂ -3 h	42.86	64.91	81.04	92.19	98.22	99.90
Ru/CeO ₂ -4 h	43.58	65.10	81.74	92.39	98.38	100.00

^a The calculation formula of NH₃ conv./% is $X_{NH_3}(\%) = \frac{[NH_3]_{int} - [NH_3]_{out}}{[NH_3]_{out}} \times 100\%$, which is described in detail in Section 3.3.

In order to evaluate the long-term stability of the catalyst, the Ru/CeO₂-4 h catalyst was subjected to a 50 h stability test under GHSV = 36,000 mL g_{cat}^{-1} h⁻¹. The results are shown in Figure S12. No catalytic performance attenuation was observed after the 50 h test, which demonstrated that Ru/CeO₂-4 h had excellent catalytic stability in the ammonia decomposition reaction.

2.3. Surface Chemical State of the Carrier and the Catalyst

It has been reported that hydrogen can react with lattice oxygen (O_L) in CeO₂ to form H₂O, while inducing the reduction of Ce⁴⁺ to Ce³⁺ and generating oxygen vacancies (O_V) [43]. The existence of O_V can enhance the SMSI between Ru and CeO₂ support, and perhaps, this is the reason that Ru/CeO₂-4 h exhibits excellent catalytic activity and stability. To systematically investigate the existence of O_V on the surface of CeO₂-t, Raman spectroscopy and the XPS test were performed.

 O_V can cause lattice distortions that create new characteristic peaks in the Raman spectrum or change the position and intensity of existing peaks [44]. Thus, Raman spec-

troscopy was used to reveal the defect location of the samples in this work, and the results are shown in Figure 2. The Raman peaks of CeO₂-t and Ru/CeO₂-t at 456 and 605 cm⁻¹ can be attributed to the octahedral symmetric tensile vibration mode (F_{2g}) and the defect induction mode (D) [45]. Since the D-mode peak is caused by the presence of Ce³⁺, the intensity ratio of the D-peak to the F_{2g} peak (I_D/I_{F2g}) can be used to reflect the relative concentration of O_V in CeO₂ and Ru/CeO₂ [46]. The results are given in Table S3. The I_D/I_{F2g} value increased on increasing the reduction time, indicating that more O_V were formed on the surface of CeO₂. The Raman spectrum of CeO₂-C is shown in Figure S13. It was found that CeO₂ prepared from the Ce-BPDC precursor had greater reducibility in a H_2/Ar atmosphere than commercial CeO₂, resulting in more O_V generation during the reduction process.



Figure 2. Raman spectra of various supports (a) and catalysts (b).

In addition, the surface electronic states and chemical compositions of Ru/CeO₂-t and the carrier CeO_2 were studied by XPS. Ru 3p XPS measurements were performed to study the Ru valence states (Figure S14), which exhibited characteristic peaks of Ru^0 (462.2 eV) and Ru^{4+} (465.2 eV). The different chemical valence states of Ru on these samples may be due to the charge transfer between CeO_2 carriers and Ru nanoparticles. In order to verify this, the Ce 3d spectra were recorded. The Ce 3d spectra of CeO₂-t are shown in Figure S15, and the Ce 3d spectra of Ru/CeO₂-t are shown in Figure 3a, which were divided into 10 groups due to the hybridization of Ce 4f orbitals with O 2p valence bands [47]. The six peaks at 882.4, 889.4, 898.4, 901, 907.3, and 916.9 eV are attributed to the Ce⁴⁺ species, while the other four peaks at 881.4, 885.4, 899, and 903.6 eV are attributed to the Ce^{3+} species [48]. Each cerium cation is coordinated by eight oxygen anions, and due to the electronic structure of cerium, charge is reversibly transferred between Ce⁴⁺ and Ce^{3+} [49]. Thus, the emergence of Ce^{3+} species is usually accompanied by the formation of O_V on the CeO₂ surface [50]. The concentration of O_V can be inferred from the relative atomic ratio of $Ce^{3+}/(Ce^{4+} + Ce^{3+})$, as shown in Table S4. It can be observed that the concentration of O_V on the surface of CeO₂-t and Ru/CeO₂-t increased with an increase in the reduction time, which is consistent with the Raman results. Among these catalysts, the $Ce^{3+}/(Ce^{4+} + Ce^{3+})$ ratio of Ru/CeO₂-4 h was the highest, indicating that the most O_V was generated in Ru/CeO_2 -4 h, which accorded with the test results of the catalyst performance.



Figure 3. The (a) Ce 3d and (b) O 1s XPS profiles of Ru/CeO₂-t.

To further confirm the variation law of O_V , the O 1s XPS spectra of Ru/CeO₂-t catalysts were collected (Figure 3b). The peak at 529.1–529.6 eV corresponds to the O_L , the peak at 531.1 eV corresponds to O_V , and the peak observed at 533.4 eV is attributed to chemisorbed oxygen (O_C) in CeO₂ [51]. The number of O_V can be quantified according to the ratio of $O_V/(O_L + O_C + O_V)$ [52]. The results are shown in Table S4. It decreased in the order of Ru/CeO₂-4 h > Ru/CeO₂-3 h > Ru/CeO₂-2 h > Ru/CeO₂-1.5 h > Ru/CeO₂-1 h > Ru/CeO₂-0.5 h, indicating that the number of O_V at Ru/CeO₂-4 h was the highest. The concentration of O_V on the CeO₂-t surface showed the same trend. The results were consistent with the Raman results and the Ce 3d XPS spectra.

Figure S16 presents the Ce 3d and O 1s XPS spectra of hydrogen-reduced commercial CeO₂, with the quantified Ce³⁺/(Ce³⁺ + Ce⁴⁺) and O_V/(O_V + O_L + O_C) ratios summarized in Table S5. The results (Tables S4 and S5) demonstrate that CeO₂ derived from Ce-BPDC displayed a superior reducibility. This result is consistent with the Raman result.

According to the literature, the surface basicity of the catalyst is conducive to ammonia decomposition; usually, the stronger the surface basicity, the higher the activity [53]. CO₂-TPD was used to characterize the distribution of the surface basicity of the catalyst, and the results are shown in Figure S17. The number and intensity of basic sites can be determined according to the area and location of the desorption peaks. A certain number of weakly basic sites, moderately strong basic sites, and strong basic sites appeared in these catalysts. The area above 500 °C was a strong basicity site; the basicity strength increased with the increase in the reduction time. The desorption amount of CO₂ on the surface of Ru/CeO₂-4 h was the largest. From the above analysis, it can be concluded that the density of strong basic sites of Ru/CeO₂-4 h was the largest, which is also in good agreement with the ammonia decomposition activity of the catalyst. As an electron donor, O_V increases the electron density of the adjacent metal site and enhances the Lewis basic site. On the surface of CeO₂, oxygen ions near the O_V can act as Lewis base sites. The increase in O_V could increase the basicity sites on the surface of CeO₂ to a certain extent [54]. Therefore, the concentration of O_V on the surface of Ru/CeO₂-4 h catalyst is the highest. This was consistent with the Raman and XPS results.

To further clarify the electronic states and coordination environment evolution of Ru species, we conducted Ru K-edge X-ray absorption fine structure (XAFS) tests on the Ru/CeO₂-t (t = 0, 0.5, 1, 2, 3, 4 h) catalysts and used Ru foil (Ru⁰) and RuO₂ (Ru⁴⁺) as reference standards. As shown in Figure S18a, the absorption edge positions of all the

Ru/CeO₂-t samples were similar to those of the RuO₂ standard samples, confirming that Ru mainly existed in the +4 valence state (Ru⁴⁺). Figure S18b shows the Fourier transform Ru K-edge extended X-ray absorption fine structure (EXAFS) curves of all the samples. The figure shows two different peaks, 1.41 Å (the first shell) and 2.43 Å (the second shell), corresponding to Ru-O and Ru-Ru coordination, respectively. Then, a wavelet transform (WT) analysis was conducted on the EXAFS data, thereby further exploring in detail the contributions of different coordination shells to the Ru/CeO₂-t EXAFS signal. In Figure 4, two main maximum intensities can be observed, which belong to the first coordination shell of Ru-O-Ce and the second coordination shell of Ru-Ru, respectively. The results show that Ru was stably anchored on the carrier surface through the Ru-O-Ce bond, and it was found that, with the increase in the reduction time, Ru-Ru gradually weakened, while the strength of the Ru-O-Ce bond increased. This further indicates that the interaction between Ru and the carrier increases with an increase in the reduction time.



Figure 4. The WT-EXAFS of the Ru K-edge of Ru/CeO₂-t, (**a**) Ru foil, (**b**) RuO₂, (**c**–**h**) Ru/CeO₂-t (t = 0, 0.5, 1, 2, 3, 4 h).

2.4. Reaction Mechanism

To gain a deeper understanding of the O_V impact on ammonia decomposition, we conducted density functional theory (DFT) calculations and developed three reaction models: CeO₂, Ru/CeO₂, and Ru/CeO₂-O_V (Figure S19). Figures S21 and S22 illustrate the reaction process of ammonia on the catalyst surface. The NH₃ decomposition reaction follows a well-defined pathway: initially, NH₃ is adsorbed onto the catalyst surface; subsequently, it undergoes a gradual dehydrogenation process; finally, N₂ and H₂ are generated and released from the surface.

As shown in Figure 5, the dehydrogenation potential energy of Ru/CeO_2-O_V was lower than that of CeO_2 and Ru/CeO_2 , which is due to the stronger adsorption of NH_3 by this catalyst. It can be seen from the figure that the breaking of the N-H bond is the ratedetermining step of the reaction. The reaction energy barrier required for the N-H cleavage of the Ru/CeO_2-O_V system is lower than that of Ru/CeO_2 and CeO_2 , thereby significantly improving the catalytic activity. Furthermore, Figure S20 compares the adsorption energy data of NH_3 on the three models. The results show that the Ru/CeO_2-O_V model had the highest adsorption intensity for NH_3 , reaching 1.021 eV, while the adsorption energies of the Ru/CeO_2 and CeO_2 models were 0.813 eV and 0.605 eV, respectively. This discovery clearly indicates that the presence of oxygen vacancies can reduce the reaction energy barrier for N-H bond breaking and significantly enhance the adsorption capacity of the catalyst for NH₃. This phenomenon is due to the strong interaction between the metal and the carrier, which helps to improve the catalytic performance.



Figure 5. Potential energy diagram of NH_3 dehydrogenation on the surface of CeO_2 , Ru/CeO_2 , and Ru/CeO_2 - O_V models.

3. Experimental Section

3.1. Materials

Ammonium cerium nitrate (Ce(NH₄)₂(NO₃)₆, \geq 98%), 4-4' diphenyl dicarboxylic acid (H₂BPDC, 99%), N, N-dimethylformamide (C₃H₇NO, DMF, \geq 99.5%), acetone (C₃H₆O, \geq 99.5%), anhydrous ethanol (C₂H₅OH, \geq 99.7%), ruthenium trichloride (RuCl₃, \geq 99.9%) purchased from Aladdin Co., Ltd., and deionized water for laboratory use.

3.2. Catalyst Preparation

Ce-BPDC was synthesized by an improved hydrothermal method. The detailed preparation process is in the Supporting Information. After the successful synthesis of Ce-BPDC, it was calcined at 500 °C for 5 h to obtain CeO₂. The CeO₂ was reduced in the H₂/Ar atmosphere for different durations (t = 0, 0.5, 1, 1.5, 2, 3, 4 h; 0 means the CeO₂ sample was not reduced) at 500 °C, and the obtained samples were recorded as CeO₂-t. The detailed preparation process of the carrier can be found in the Supporting Information. Briefly, 1 g of CeO₂-t (t = 0, 0.5, 1, 1.5, 2, 3, 4 h) and 0.108 g (0.52 mmol) of RuCl₃, respectively, were weighed and mixed in different glass bottles. Subsequently, 15 mL of deionized water was added to each vial and stirred on a mixing table for 8 h to obtain a gray solution. The solution was washed three times with deionized water, and the resulting precipitate was dried overnight in an 80 °C oven and finally allowed to yield the Ru catalyst. The experimental amount of Ru for each catalyst was 5 wt%. The resulting sample was named as the Ru/CeO₂-t (t = 0, 0.5, 1, 1.5, 2, 3, 4 h) catalyst.

3.3. Catalyst Activity Evaluation

The hydrogen production evaluation process of ammonia decomposition catalyst was carried out in a fixed-bed reactor. Typically, 0.05 g of catalyst (40–60 mesh) was fully mixed

with 2.95 g of quartz sand (40–60 mesh) and then transferred to a reactor equipped with quartz cotton. Before the activity test, the catalyst was heated to 200 °C with a ramp rate of 5 °C/min in 5% H₂/Ar (50 mL/min) and reduced at 200 °C for 2 h. After switching to 50% NH₃/Ar, the system temperature was adjusted to the corresponding reaction temperature. The catalyst was evaluated at a certain gas hourly space velocity (GHSV) in the temperature range of 325–600 °C at atmospheric pressure. The feed gas and the yield were analyzed by online gas chromatography (GC) equipped with a thermal conductivity detector (TCD). The conversion rate of NH₃ (X_{NH₃}) and the generation rate of H₂ (r_{H₂}) were calculated using the following formula:

$$X_{\rm NH_3}(\%) = \frac{[V_{\rm N_2}]_{\rm out}/[V_{\rm NH_3}]_{\rm out}}{[V_{\rm N_2}]_{\rm out}/[V_{\rm NH_3}]_{\rm out} + 0.5} \times 100\%$$
$$r_{\rm H_2}(\rm mmol/g_{\rm cat}/\rm min) = \frac{\frac{V_{\rm NH_3}}{22.4} \times X_{\rm NH_3} \times 1.5}{m_{\rm cat}}$$

where $[V_{N2}]_{out}$, and $[V_{NH3}]_{out}$ are the volume percentage of N_2 and NH_3 in the effluent, respectively. V_{NH3} is the NH_3 flow rate (mL/min), and m_{cat} is the mass of the catalyst (g).

4. Conclusions

In this study, Ce-MOF-derived CeO₂ carriers were prepared by calcining Ce-BPDC, and then the obtained CeO₂ was reduced in a H_2/Ar atmosphere for different times (t = 0, 0.5, 1, 1.5, 2, 3, 4 h). Finally, a series of Ru-based catalysts were prepared by the impregnation method. The ammonia decomposition results showed that the performance of the Ru/CeO₂-t was superior to that of the commercial CeO₂-supported Ru catalyst. Under the condition of GHSV = 36,000 mL g_{cat}^{-1} h⁻¹, the ammonia conversion rate and hydrogen production rate of Ru/CeO₂-4 h at 500 $^{\circ}$ C were 98.9% and 39.74 mmol g_{cat}⁻¹ min⁻¹, respectively. Furthermore, the catalytic activity remained stable after continuous testing for 50 h. The XRD, SEM, and TEM results showed that Ru was well dispersed on the surface of CeO₂-t. The Raman and XPS characterization results showed that, with the extension of the reduction time, the number of oxygen vacancies in these samples increased. This phenomenon can be attributed to the valence state transformation from Ce^{4+} to Ce^{3+} on the surface of CeO_2 during the hydrogen reduction process, thereby inducing the generation of more O_V. The results of the synchrotron radiation showed that an increase in oxygen vacancy concentration can enhance the interaction between the metal and the carrier. The DFT calculation determined that the rate-determining step of ammonia decomposition was the cleavage of the N-H bond, and the existence of oxygen vacancies can significantly reduce the reaction energy barrier of N-H cleavage, thereby improving the ammonia decomposition performance. These findings highlight a new idea for the design of ammonia decomposition catalysts and might open up new possibilities for the development of MOF-based catalysts in industrial application.

Supplementary Materials: The following Supporting Information can be downloaded at https: //www.mdpi.com/article/10.3390/molecules30112301/s1: Table S1: NH₃ conversion of Ru/CeO₂-C catalyst at GHSV = 12,000 mL g_{cat}⁻¹ h⁻¹. Table S2: Comparison of the synthesized catalysts with Ru-based catalysts reported in the literature. Table S3: The Raman quantification results. Table S4: XPS quantitative results of CeO₂-t and Ru/CeO₂-t. Table S5: XPS quantitative results of CeO₂-C and Ru/CeO₂-C. Figure S1: The XRD profile of the Ce-BPDC (a) and the SEM images of the Ce-BPDC (b). Figure S2: N₂ adsorption/desorption isotherms (a) and aperture distribution curve (b) of Ce-BPDC. Figure S3: The TGA curve of the Ce-BPDC. Figure S4: The XRD profile of the CeO₂-t. Figure S5: The N₂ adsorption isotherm of the derivative cerium oxide (a) and its corresponding catalyst (b). Figure S6: The SEM of the CeO₂-0 h (a), CeO₂-0.5 h (b), CeO₂-1 h (c), CeO₂-1.5 h (d), CeO₂-2 h (e), CeO₂-3 h (f). Figure S7: The TEM of the CeO₂-t. Figure S8: The TEM and the corresponding EDS of Ru/CeO₂-t. Figure S9: The AC-STEM of Ru/CeO₂-0 h (a), Ru/CeO₂-0.5 h (b), Ru/CeO₂-1 h (c), Ru/CeO₂-1.5 h (d), Ru/CeO₂-2 h (e), Ru/CeO₂-3 h(f), Ru/CeO₂-4 h(g). Figure S10: Schematic diagram of a fixed-bed reactor. Figure S11: NH₃ conversion diagram of Ru/CeO₂-4 h catalyst, GHSV = 36,000 mL g_{cat}⁻¹ h⁻¹. Figure S12. Stability test of Ru/CeO₂-4 h catalyst, GHSV = 36,000 mL g_{cat}⁻¹ h⁻¹. Figure S13: Raman spectra of CeO₂-C (a) and Ru/CeO₂-C (b). Figure S14: The Ru 3p_{3/2} XPS of Ru/CeO₂-t. Figure S15: The (a) Ce 3d and (b) O 1s XPS of CeO₂-t. Figure S16: The (a) Ce 3d and (b) O 1s XPS of CeO₂-C. Figure S17: CO₂-TPD curves for catalyst. Figure S18: XAS characterization results: (a) Ru K-edge XANES spectra of Ru/CeO₂-t and (b) Fourier transform K3-weighted EXAFS spectra. Figure S19: Adsorption energy of NH₃ on surfaces of CeO₂, Ru/CeO₂, and Ru/CeO₂-Ov models. Figure S20: The reaction process of ammonia on Ru/CeO₂ catalyst surface. Figure S21: The reaction process of ammonia on Ru/CeO₂ catalyst surface. Figure S22: The reaction process of ammonia on Ru/CeO₂-O_V catalyst surface. Figure S22: Ce 3d (a) and O 1s (b) spectra of catalyst Ru/CeO₂-2 h before and after pretreatment. References [55–76] are cited in the supplementary materials.

Author Contributions: Literature search, writing, and creation of figures and tables, W.W., W.Y., and Y.L.; review, editing, and supervision, S.X. and T.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, Grant No. 22102008.

Data Availability Statement: The data presented in this study are available upon request from the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- 1. Sun, S.; Jiang, Q.; Zhao, D.; Cao, T.; Sha, H.; Zhang, C.; Song, H.; Da, Z. Ammonia as hydrogen carrier: Advances in ammonia decomposition catalysts for promising hydrogen production. *Renew. Sustain. Energy Rev.* **2022**, *169*, 112918. [CrossRef]
- Mukherjee, S.; Devaguptapu, S.V.; Sviripa, A.; Lund, C.R.F.; Wu, G. Low-temperature ammonia decomposition catalysts for hydrogen generation. *Appl. Catal. B Environ.* 2018, 226, 162–181. [CrossRef]
- 3. Andersson, J.; Grönkvist, S. Large-scale storage of hydrogen. Int. J. Hydrogen Energy 2019, 44, 11901–11919. [CrossRef]
- 4. Feng, J.; Zhang, X.; Wang, J.; Ju, X.; Chen, P. Applications of rare earth oxides in catalytic ammonia synthesis and decomposition. *Catal. Sci. Technol.* **2021**, *11*, 6330–6343. [CrossRef]
- Morlane, N.; Katikaneni, S.P.; Paglieri, S.N.; Harale, A.; Solami, B.; Sarathy, S.M.; Gascon, J. A technological roadmap to the ammonia energy economy: Current state and missing technologies. *Chem. Eng. J.* 2021, 408, 127310. [CrossRef]
- Wan, Z.; Tao, Y.; Shao, J.; Zhang, Y.; You, H. Ammonia as an effective hydrogen carrier and a clean fuel for solid oxide fuel cells. Energy Convers. Manag. 2021, 228, 113729. [CrossRef]
- Bell, T.E.; Torrente-Murciano, L. H₂ production via ammonia decomposition using non-noble metal catalysts: A review. *Top. Catal.* 2016, 59, 1438–1457. [CrossRef]
- Dongil, A.B. Recent progress on transition metal nitrides nanoparticles as heterogeneous catalysts. *Nanomaterials* 2019, 9, 1111. [CrossRef]
- Cha, J.; Lee, T.; Lee, Y.-J.; Jeong, H.; Jo, Y.S.; Kim, Y.; Nam, S.W.; Han, J.; Lee, K.B.; Yoon, C.W.; et al. Highly monodisperse sub-nanometer and nanometer Ru particles confined in alkali-exchanged zeolite Y for ammonia decomposition. *Appl. Catal. B Environ.* 2021, 283, 119627. [CrossRef]
- Wu, Z.-W.; Li, X.; Qin, Y.-H.; Deng, L.; Wang, C.-W.; Jiang, X. Ammonia decomposition over SiO₂-supported Ni-Co bimetallic catalyst for CO_x-free hydrogen generation. *Int. J. Hydrogen Energy* 2020, 45, 15263–15269. [CrossRef]
- Hu, Z.P.; Chen, L.; Chen, C. Fe/ZSM-5 catalysts for ammonia decomposition to CO_x-free hydrogen: Effect of SiO₂/Al₂O₃ ratio. *Mol. Catal.* 2018, 455, 14–22. [CrossRef]
- 12. Cao, C.F.; Wu, K.; Zhou, C.; Yao, Y.H. Electronic metal-support interaction enhanced ammonia decomposition efficiency of perovskite oxide supported ruthenium. *Chem. Eng. Sci.* **2022**, 257, 117719–117726. [CrossRef]
- 13. Antunes, R.; Steiner, R.; Marot, L. Decomposition studies of NH₃ and ND₃ in presence of H₂ and D₂ with Pt/Al₂O₃ and Ru/Al₂O₃ catalysts. *Int. J. Hydrogen Energy* **2022**, *47*, 14130–14140. [CrossRef]

- 14. Pinzón, M.; Avilés-García, O.; Osa, A.R. New catalysts based on reduced graphene oxide for hydrogen production from ammonia decomposition. *Sustain. Chem. Pharm.* 2022, 25, 100615–100625. [CrossRef]
- 15. Mazzone, S.; Goklany, T.; Zhang, G. Ruthenium-based catalysts supported on carbon xerogels for hydrogen production via ammonia decomposition. *Appl. Catal. A Gen.* **2022**, *632*, 118484–118499. [CrossRef]
- 16. Yin, S.F.; Xu, B.Q.; Wang, S.J.; Ng, C.F.; Au, C.T. Magnesia-Carbon Nanotubes (MgO-CNTs) Nanocomposite: Novel Support of Ru Catalyst for the Generation of COx-Free Hydrogen from Ammonia. *Catal. Lett.* **2004**, *96*, 113–116. [CrossRef]
- 17. Choudhary, T.V.; Sivadinarayana, C.; Goodman, D.W. Catalytic ammonia decomposition: CO_X-free hydrogen production for fuel cell applications. *Catal. Lett.* **2001**, *72*, 197–201. [CrossRef]
- 18. Fang, H.; Wu, S.; Ayvali, T.; Zheng, J.; Fellowes, J.; Ho, P.-L.; Leung, K.C.; Large, A.; Held, G.; Kato, R.; et al. Dispersed surface Ru ensembles on MgO(111) for catalytic ammonia decomposition. *Nat. Commun.* **2023**, *14*, 647. [CrossRef]
- 19. Yin, S.F.; Zhang, Q.H.; Xu, B.Q.; Zhu, W.X.; Ng, C.F.; Zhou, X.P.; Au, C.T. Carbon nanotubes-supported Ru catalyst for the generation of COx-free hydrogen from ammonia. *Catal. Today* **2004**, *93*, 27–38. [CrossRef]
- Ju, X.; Liu, L.; Xu, X.; Wang, J.; He, T.; Chen, P. Strong metal-support interaction modulatescatalytic activity of Ru nanoparticles on Gd₂O₃ forefficient ammonia decomposition. *iScience* 2024, 27, 110931. [CrossRef]
- Wang, Z.; Luo, H.; Wang, L.; Li, T.; Li, S.; Liu, Y.Q. Promotion of Low-Temperature Catalytic Activity of Ru-Based Catalysts for Ammonia Decomposition via Lanthanum and Cesium Codoping. ACS Sustainable Chem. Eng. 2024, 12, 5620–5631. [CrossRef]
- 22. Im, Y.; Muroyama, H.; Matsui, T.; Eguchi, K. Investigation on catalytic performance and desorption behaviors of ruthenium catalysts supported on rare-earth oxides for NH₃ decomposition. *Int. J. Hydrogen Energy* **2022**, *47*, 32543–32551. [CrossRef]
- Furusawa, T.; Kuribara, H.; Kimura, K.; Sato, T.; Itoh, N. Development of a Cs-Ru/CeO₂ Spherical Catalyst Prepared by Impregnation and Washing Processes for Low-Temperature Decomposition of NH₃: Characterization and Kinetic Analysis Results. *Ind. Eng. Chem. Res.* 2020, 59, 18460–18470. [CrossRef]
- 24. Huang, C.; Yu, Y.; Tang, X.; Liu, Z.; Zhang, J.; Ye, C.; Ye, Y.; Zhang, R. Hydrogen generation by ammonia decomposition over Co/CeO₂ catalyst: Influence of support morphologies. *Appl. Surf. Sci.* **2020**, *532*, 147335. [CrossRef]
- Lucentini, I.; Serrano, I.; Soler, L.; Divins, N.J.; Llorca, J. Ammonia decomposition over 3D-printed CeO₂ structures loaded with Ni. *Appl. Catal. A Gen.* 2020, 591, 117382. [CrossRef]
- Ju, X.; Liu, L.; Yu, P.; Guo, J.; Zhang, X.; He, T.; Wu, G.; Chen, P. Mesoporous Ru/MgO prepared by a deposition-precipitation method as highly active catalyst for producing CO_x-free hydrogen from ammonia decomposition. *Appl. Catal. B Environ.* 2017, 211, 167–175. [CrossRef]
- 27. Ju, X.; Liu, L.; Zhang, X.; Feng, J.; He, T.; Chen, P. Highly Efficient Ru/MgO Catalyst with Surface-Enriched Basic Sites for Production of Hydrogen from Ammonia Decomposition. *ChemCatChem* **2019**, *11*, 4161–4170. [CrossRef]
- Muroyama, H.; Saburi, C.; Matsui, T.; Eguchi, K. Ammonia decomposition over Ni/La₂O₃ catalyst for on-site generation of hydrogen. *Appl. Catal. A Gen.* 2012, 443–444, 119–124. [CrossRef]
- 29. Gu, Y.; Ma, Y.; Long, Z.; Zhao, S.; Wang, Y.; Zhang, W. One-pot synthesis of supported Ni@Al₂O₃ catalysts with uniform small-sized Ni for hydrogen generation via ammonia decomposition. *Int. J. Hydrogen Energy* **2021**, *46*, 4045–4054. [CrossRef]
- Bell, T.E.; Ménard, H.; González Carballo, J.M.; Tooze, R.; Torrente-Murciano, L. Hydrogen production from ammonia decomposition using Co/γ-Al₂O₃ catalysts—Insights into the effect of synthetic method. *Int. J. Hydrogen Energy* 2020, 45, 27210–27220. [CrossRef]
- 31. Zhang, Z.S.; Fu, X.P.; Wang, W.W.; Jin, Z.; Song, Q.S.; Jia, C.J. Promoted porous Co₃O₄-Al₂O₃ catalysts for ammonia decomposition. *Sci. China Chem.* **2018**, *61*, 1389–1398. [CrossRef]
- 32. Yin, S.F.; Zhang, Q.H.; Xu, B.Q.; Zhu, W.X.; Ng, C.F.; Au, C.T. Investigation on the catalysis of CO_x-free hydrogen generation from ammonia. *J. Catal.* **2004**, 224, 384–396. [CrossRef]
- Lorenzut, B.; Montini, T.; Pavel, C.C.; Comotti, M.; Vizza, F.; Bianchini, C.; Fornasiero, P. Embedded Ru@ZrO₂ Catalysts for H₂ Production by Ammonia Decomposition. *ChemCatChem* 2010, *2*, 1096–1106. [CrossRef]
- 34. Thien, A.L.; Youngmin, K.; Hyun, W.K. Ru-supported lanthania-ceria composite as an efficient catalyst for COx-free H₂ production from ammonia decomposition. *Appl. Catal. B Environ.* **2021**, *285*, 119831.
- 35. Hu, X.-C.; Fu, X.-P.; Wang, W.-W.; Wang, X.; Wu, K.; Si, R.; Ma, C.; Jia, C.-J.; Yan, C.-H. Ceria-supported ruthenium clusters transforming from isolated single atoms for hydrogen production via decomposition of ammonia-ScienceDirect. *Appl. Catal. B Environ.* **2020**, *268*, 118424. [CrossRef]
- 36. Chaouiki, A.; Fatimah, S.; Chafiq, M.; Ryu, J.; Ko, Y.G. State-of-the-art advancements in metal-organic framework nanoarchitectures for catalytic applications. *Appl. Mater. Today* **2024**, *38*, 102224. [CrossRef]
- 37. Khalil, I.E.; Fonseca, J.; Reithofer, M.R. Tackling orientation of metal-organic frameworks (MOFs): The quest to enhance MOF performance. *Coordin. Chem. Rev.* 2023, *481*, 21503. [CrossRef]
- 38. Sivan, S.E.; Kang, K.H.; Han, S.J. Facile MOF-derived one-pot synthetic approach toward Ru single atoms, nanoclusters, and nanoparticles dispersed on CeO₂ supports for enhanced ammonia synthesis. *J. Catal.* **2022**, *408*, 316–328. [CrossRef]

- He, Y.; Zheng, X.; Mao, D.; Meng, T.; Mao, H.; Yu, J. Promoting catalytic CO₂ methanation using Ru catalyst supported on Ce-MOF-derived CeO₂. *Renew. Energy* 2025, 245, 122834. [CrossRef]
- 40. Chen, X.; Yu, E.; Cai, S.; Jia, H.; Chen, J.; Liang, P. In situ pyrolysis of Ce-MOF to prepare CeO₂ catalyst with obviously improved catalytic performance for toluene combustion. *Chem. Eng. J.* **2018**, *344*, 469–479. [CrossRef]
- Khan, M.E.; Khan, M.M.; Cho, M.H. Ce³⁺-ion, Surface Oxygen Vacancy, and Visible Light-induced Photocatalytic Dye Degradation and Photocapacitive Performance of CeO₂-Graphene Nanostructures. *Sci. Rep.* 2017, *7*, 5928. [CrossRef] [PubMed]
- 42. Li, J.; Liu, Z.; Cullen, D.A. Distribution and Valence State of Ru Species on CeO₂ Supports: Support Shape Effect and Its Influence on CO Oxidation. *ACS Catal.* **2019**, *9*, 11088–11103. [CrossRef]
- 43. Liu, P.; Zheng, C.; Liu, W.; Wu, X.; Liu, S. Oxidative Redispersion-Derived Single-Site Ru/CeO₂ Catalysts with Mobile Ru Complexes Trapped by Surface Hydroxyls Instead of Oxygen Vacancies. *ACS Catal.* **2024**, *14*, 6028–6044. [CrossRef]
- 44. Wang, X.; Yin, Y.; Wang, H. Precision tailoring strategy of oxygen vacancies for electromagnetic pollution regulation. *Appl. Surf. Sci.* **2025**, *681*, 20–25. [CrossRef]
- Pu, Z.Y.; Lu, J.Q.; Luo, M.F. Study of oxygen vacancies in Ce_{0.9}Pr_{0.1}O_{2-δ} solid solution by in situ X-ray diffraction and in situ Raman spectro-scopy. J. Phys. Chem. C 2007, 111, 18695–18702. [CrossRef]
- Wang, F.; He, S.; Chen, H. Active site dependent reaction mechanism over Ru/CeO₂ catalyst toward CO₂ methanation. *J. Am. Chem. Soc.* 2016, 138, 6298–6305. [CrossRef]
- Yoo, C.J.; Lee, D.W.; Kim, M.S. The synthesis of methanol from CO/CO₂/H₂ gas over Cu/Ce_{1-x}Zr_xO₂ catalysts. *J. Mol. Catal. A Chem.* 2013, *378*, 255–262. [CrossRef]
- Sakpal, T.L.L. Structure-dependent activity of CeO₂ supported Ru catalysts for CO₂ methanation. J. Catal. 2018, 367, 171–180. [CrossRef]
- 49. Huang, X.; Zhang, K.; Peng, B. Ceria-Based Materials for Thermocatalytic and Photocatalytic Organic Synthesis. *ACS Catal.* **2021**, *11*, 9618–9678. [CrossRef]
- 50. Wang, Z.; Huang, Z.; Brosnahan, J.T. Ru/CeO₂ Catalyst with Optimized CeO₂ Support Morphology and Surface Facet for Propane Combustion. *Environ. Sci. Technol.* **2019**, *53*, 5349–5358. [CrossRef]
- 51. Huang, H.; Dai, Q.; Wang, X. Morphology effect of Ru/CeO₂ catalysts for the catalytic combustion of chlorobenzene. *Appl. Catal. B Environ.* **2014**, *158–159*, 96–105. [CrossRef]
- 52. Hu, Z.; Liu, X.; Meng, D. Effect of Ceria Crystal Plane on the Physicochemical and Catalytic Properties of Pd/Ceria for CO and Propane Oxidation. *ACS Catal.* **2016**, *6*, 2265–2279. [CrossRef]
- 53. Le, T.A.; Kim, Y.; Han, S.J.; Do, Q.C.; Kim, G.J.; Im, Y.; Chae, H.-J. Ru dispersed on CeO₂{100} facets boosting the catalytic NH₃ decomposition for green H₂ generation. *Chem. Eng. J.* **2024**, *493*, 152503. [CrossRef]
- 54. Ren, X.; Zhang, Z.; Wang, Y. Capping experiments reveal multiple surface activesites in CeO₂ and their cooperative catalysis. *RSC Adv.* **2019**, *9*, 15229–15237. [CrossRef]
- 55. Luo, L.; Huang, L.; Liu, X. Mixed-Valence Ce-BPyDC Metal-Organic Framework with Dual Enzyme-like Activities for Colorimetric Biosensing. *Inorg. Chem.* 2019, *58*, 11382–11388. [CrossRef]
- 56. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169. [CrossRef]
- 57. Blöchl, P.E. Projector augmented-wave method. Phys. Rev. B 1994, 50, 17953. [CrossRef]
- Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865.
 [CrossRef]
- Montini, T.; Melchionna, M.; Monai, M. Fundamentals and Catalytic Applications of CeO₂-Based Materials. *Chem. Rev.* 2016, 116, 5987–6041. [CrossRef]
- 60. Li, X.; Ji, W.; Zhao, J.; Wang, S.; Au, C. Ammonia decomposition over Ru and Ni catalysts supported on fumed SiO₂, MCM-41, and SBA-15. *J. Catal.* **2005**, *236*, 181–189. [CrossRef]
- 61. Wang, Z.; Qu, Y.; Shen, X.; Cai, Z. Ruthenium catalyst supported on Ba modified ZrO₂ for ammonia decomposition to COx-free hydrogen. *Int. J. Hydrogen Energy* **2019**, *44*, 7300–7307. [CrossRef]
- 62. Feng, J.; Liu, L.; Ju, X.; Wang, J.; Zhang, X.; He, T. Highly dispersed ruthenium nanoparticles on Y₂O₃ as superior catalyst for ammonia decomposition. *ChemCatChem* **2021**, *13*, 1552–1558. [CrossRef]
- 63. Jeon, N.; Kim, S.; Tayal, A.; Oh, J.; Yoon, W.; Kim, W.B. Y-doped BaCeO₃ perovskite-supported Ru catalysts for COx-free hydrogen production from ammonia: Effect of strong metal–support interactions. *ACS Sustain. Chem. Eng.* **2022**, *10*, 15564–15573. [CrossRef]
- 64. Li, Y.; Yao, L.; Song, Y.; Liu, S.; Zhao, J.; Ji, W.; Au, C.T. Core-Shell Structured Microcapsular-like Ru@SiO₂ Reactor for Efficient Generation of COx-Free Hydrogen through Ammonia Decomposition. *Chem. Commun.* **2010**, *46*, 5298–5300. [CrossRef]
- 65. Wang, Z.; Cai, Z.; Wei, Z. Highly active ruthenium catalyst supported on barium hexaaluminate for ammonia decomposition to COx-free hydrogen. *ACS Sustain. Chem. Eng.* **2019**, *7*, 8226–8235. [CrossRef]
- Meng, Q.; Liu, H.; Xu, K.; Wang, W.; Jia, C. CeO₂ modified Ru/γ-Al₂O₃ catalysts for ammonia decomposition reaction. *J. Rare Earths* 2023, *41*, 801–809. [CrossRef]

- Li, L.; Wang, Y.; Xu, Z.P.; Zhu, Z. Catalytic ammonia decomposition for CO-free hydrogen generation over Ru/Cr₂O₃ catalysts. *Appl. Catal. A* 2013, 467, 246–252. [CrossRef]
- 68. Lucentini, I.; Casanovas, A.; Llorca, J. Catalytic ammonia decomposition for hydrogen production on Ni, Ru and NiRu supported on CeO₂. *Int. J. Hydrogen Energy* **2019**, *44*, 12693–12707. [CrossRef]
- Lucentini, I.; Colli, G.G.; Luzi, C.D.; Serrano, I.; Martínez, O.M.; Llorca, J. Catalytic ammonia decomposition over Ni-Ru supported on CeO₂ for hydrogen production: Effect of metal loading and kinetic analysis. *Appl. Catal. B Environ.* 2021, 286, 119896. [CrossRef]
- 70. Kim, A.; Cha, J.; Kim, J.S.; Ahn, C.; Kim, Y.; Jeong, H. Hydrogen production from ammonia decomposition over Ru-rich surface on La₂O₂CO₃-Al₂O₃ catalyst beads. *Catal. Today* **2023**, *411*, 113867. [CrossRef]
- Huang, C.; Yu, Y.; Yang, J.; Yan, Y.; Wang, D.; Hu, F. Ru/La₂O₃ catalyst for ammonia decomposition to hydrogen. *Appl. Surf. Sci.* 2019, 476, 928–936. [CrossRef]
- 72. Yin, S.; Xu, B.; Ng, C.; Au, C. Nano Ru/CNTs: A highly active and stable catalyst for the generation of COx-free hydrogen in ammonia decomposition. *Appl. Catal. B Environ.* **2004**, *48*, 237–241. [CrossRef]
- Chung, D.B.; Kim, H.Y.; Jeon, M.; Lee, D.H.; Park, H.S.; Choi, S.H. Enhanced ammonia dehydrogenation over Ru/LaxAl₂O₃ (x = 0-50 mol%): Structural and electronic effects of La doping. *Int. J. Hydrogen Energy* 2017, 42, 1639–1647. [CrossRef]
- Hu, Z.; Mahin, J.; Datta, S.; Bell, T.E.; Torrente-Murciano, L. Ru-based catalysts for H₂ production from ammonia: Effect of 1D support. *Top. Catal.* 2019, 62, 1169–1177. [CrossRef]
- 75. Li, L.; Zhu, Z.H.; Yan, Z.F.; Lu, G.Q.; Rintoul, L. Catalytic ammonia decomposition over Ru/carbon catalysts: The importance of the structure of carbon support. *Appl. Catal. A* **2007**, *320*, 166–172. [CrossRef]
- 76. Kocer, T.; Oztuna, F.E.S.; Kurtoğlu, S.F.; Unal, U.; Uzun, A. Graphene aerogel-supported ruthenium nanoparticles for COx-free hydrogen production from ammonia. *Appl. Catal. A* **2021**, *610*, 117969. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.