



# Article Article Ammonia Decomposition over Ru/SiO<sub>2</sub> Catalysts

Ho Jin Lee<sup>1</sup> and Eun Duck Park <sup>1,2,\*</sup>

- <sup>1</sup> Department of Energy Systems Research, Ajou University, Suwon 16499, Korea
- <sup>2</sup> Department of Chemical Engineering, Ajou University, Suwon 16499, Korea
- \* Correspondence: edpark@ajou.ac.kr; Tel.: +82-31-219-2384; Fax: +82-31-219-1612

**Abstract:** Ammonia decomposition is a key step in hydrogen production and is considered a promising practical intercontinental hydrogen carrier. In this study, 1 wt.% Ru/SiO<sub>2</sub> catalysts were prepared via wet impregnation and subjected to calcination in air at different temperatures to control the particle size of Ru. Furthermore, silica supports with different surface areas were prepared after calcination at different temperatures and utilized to support a change in the Ru particle size distribution of Ru/SiO<sub>2</sub>. N<sub>2</sub> physisorption and transmission electron microscopy were used to probe the textural properties and Ru particle size distribution of the catalysts, respectively. These results show that the Ru/SiO<sub>2</sub> catalyst with a high-surface area achieved the highest ammonia conversion among catalysts at 400 °C. Notably, this is closely related to the Ru particle sizes ranging between 5 and 6 nm, which supports the notion that ammonia decomposition is a structure-sensitive reaction.

Keywords: ammonia decomposition; hydrogen production; Ru/SiO<sub>2</sub>; calcination temperature

## 1. Introduction

Climate change caused by increasing CO<sub>2</sub> concentrations in the atmosphere is a serious threat to human survival on Earth. This is directly related to the current carbon-based energy systems, in which coal and petroleum are the primary energy sources. Recently, renewable energy sources, including solar and wind power, have been considered as potential solutions. However, intermittent power generation, which is a typical characteristic of solar and wind energy, requires an energy-storage system. Along with battery systems, power-to-gas (PtG) systems are also regarded as effective methods. In the PtG system, H<sub>2</sub> is first produced through water electrolysis with renewable electricity, stored, transported, and finally used to produce heat and electricity. Various routes have been proposed for hydrogen transportation, including high-pressure H<sub>2</sub> gas, liquefied H<sub>2</sub>, liquid organic H<sub>2</sub> carriers, and ammonia. For intercontinental hydrogen transportation, ammonia has an advantage, especially from a practical perspective, owing to its commercial use.

Ammonia is a promising hydrogen carrier because of its high gravimetric (17.8 wt.%  $H_2$ ) and volumetric (121 kg m<sup>-3</sup> in the liquid form)  $H_2$  density. [1–5]. Hydrogen production through ammonia decomposition can meet the near-zero carbon  $H_2$  production requirement, resulting in a very low carbon footprint [6–10]. Hydrogen can be produced from ammonia via the following reaction (Equation (1)):

$$2NH_3 (g) \leftrightarrow N_2 (g) + 3H_2 (g) \Delta H^{\circ} = 46.22 \text{ kJ/mol}$$
(1)

The generally accepted reaction mechanism for ammonia decomposition is as follows: (1) the adsorption of ammonia on the catalyst surface, (2) the successive cleavage of N–H bonds on adsorbed ammonia to release hydrogen atoms, and (3) the recombinative desorption of N and H atoms to form gaseous nitrogen and hydrogen molecules [11]:



Citation: Lee, H.J.; Park, E.D. Ammonia Decomposition over Ru/SiO<sub>2</sub> Catalysts. *Catalysts* **2022**, *12*, 1203. https://doi.org/10.3390/ catal12101203

Academic Editor: José Antonio Calles

Received: 15 September 2022 Accepted: 3 October 2022 Published: 9 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 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/).

$NH_3 + * \rightarrow NH_3 *$	(i)
$NH_3 * + * \rightarrow NH_2 * + H *$	(ii)
$NH_2 * + * \rightarrow NH * + H *$	(iii)
$\mathrm{NH}$ * + * $\rightarrow$ $\mathrm{N}$ * + $\mathrm{H}$ *	(iv)
$N * + N * \rightarrow N_2$	(v)
$H^* + H^* \rightarrow H_2$	(vi)

where \* represents the number of active sites on the catalyst surface.

In general, the recombinative desorption of N is the rate-determining step in ammonia decomposition [5,12–14]. A broad range of metals have been tested for ammonia decomposition, such as Ru [15–24], Ni [15,24–28], Rh [15,29], Co [30–32], Fe [15,31,33], Pt [15,34,35], and Pd [15,36]. Among them, Ru has been the most studied metal as it is the most active catalyst. Ammonia decomposition over Ru-based catalysts is recognized as a structure-sensitive reaction [37,38]. Sensitivity is induced by active B5-type surface sites. These B5 sites have been recognized as being highly active for both the dissociation of N<sub>2</sub> and the association of N because of their unique geometric configuration and electronic properties [7,39,40].

In addition to active metals, the selection of support is important for supported metal catalysts, as its surface acidity or basicity, surface oxygen vacancies, redox properties, and metalsupport interaction can enhance catalytic performance. To date, the catalytic performance of Ru has been reported to be dependent on supports such as activated carbon [23,41], carbon nanotubes [15,19–22,42], Al<sub>2</sub>O<sub>3</sub> [16–18,20,28,43], SiO<sub>2</sub> [24,25,39,40,44–46], MgO [16,18,20,47,48], ZrO<sub>2</sub> [22,49,50], TiO<sub>2</sub> [50], and CeO<sub>2</sub> [16,47,51]. Unlike other supports [52], SiO<sub>2</sub> is an inert support, and the role of the active metal can be clearly discussed in the case of SiO<sub>2</sub>-supported metal catalysts. The effect of the surface area of SiO<sub>2</sub> and pretreatment conditions on the catalytic performance can be interpreted in terms of the distribution and sizes of the Ru particles.

In this study, ammonia decomposition was performed on Ru catalysts (Ru/SiO<sub>2</sub>(SC)) supported on SiO<sub>2</sub> supports of different surface areas obtained by varying the calcination temperature. The effect of Ru particle size on the catalytic activity for ammonia decomposition was also examined over Ru/SiO<sub>2</sub> catalysts (Ru/SiO<sub>2</sub>(C)) calcined at different temperatures. Characterization techniques such as N<sub>2</sub> physisorption and transmission electron microscopy (TEM) were used to relate the catalytic performance to the textural properties of the catalysts and the Ru particle size distribution.

#### 2. Results and Discussion

## 2.1. Physicochemical Properties of Ru/SiO<sub>2</sub>

The textural properties of the various Ru/SiO<sub>2</sub> catalysts were probed via N<sub>2</sub> physisorption. The N<sub>2</sub> adsorption and desorption isotherms of Ru/SiO<sub>2</sub>(SC) and Ru/SiO<sub>2</sub>(C) are shown in Figure S1. All Ru/SiO<sub>2</sub>(C) and Ru/SiO<sub>2</sub>(SC) catalysts showed Type IV(a) physisorption isotherms and type H<sub>2</sub>(b) hysteresis loops, except for Ru/SiO<sub>2</sub>(SC950). The pore size distributions of the Ru/SiO<sub>2</sub>(SC) catalysts in Figure S2a reveal that a single main peak appears in the pore size distribution for all the catalysts, except for Ru/SiO<sub>2</sub>(SC950). Ru/SiO<sub>2</sub>(SC950) appears to have very small amounts of N<sub>2</sub> adsorption; therefore, there is no noticeable peak in the pore size distribution. The physical properties of these catalysts are listed in Table 1. The BET surface areas and pore volumes of the Ru/SiO<sub>2</sub>(SC) catalysts decreased with increasing calcination temperatures from 700 to 950 °C. There were no noticeable changes in the BET surface area and pore volume of Ru/SiO<sub>2</sub>(C100), Ru/SiO<sub>2</sub>(C300), and Ru/SiO<sub>2</sub>(C500). These values appeared to decrease when the SiO<sub>2</sub> support was calcined at 700 °C or higher. The average pore diameter of Ru/SiO<sub>2</sub> catalysts is approximately 6 nm as long as the calcination temperature does not exceed 900 °C. However, its value increases when further increasing the calcination temperature above 900 °C.

To measure the particle size of Ru metal in the Ru/SiO<sub>2</sub> catalysts, TEM images were obtained for Ru/SiO<sub>2</sub>(C) and Ru/SiO<sub>2</sub>(SC) catalysts after reduction with H<sub>2</sub> at 350 °C. The average Ru particle size can be calculated for Ru/SiO<sub>2</sub>(C) catalysts, which have relatively well-dispersed Ru nanoparticles. The average particle size of Ru metal in Ru/SiO<sub>2</sub>(C100), Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(C500), and Ru/SiO<sub>2</sub>(C700) were determined

as  $2.3 \pm 0.72$ ,  $6.0 \pm 1.9$ ,  $5.4 \pm 1.4$ , and  $5.6 \pm 2.2$  nm, respectively (Figure 1 and Table 1). Ru/SiO<sub>2</sub>(SC700) and Ru/SiO<sub>2</sub>(SC800) also have well-dispersed Ru nanoparticles, and their average sizes were 2.0  $\pm$  0.51 and 2.1  $\pm$  0.39, respectively (Figure 2 and Table 1). On the other hand, Ru catalysts supported on  $SiO_2$  calcined at temperatures higher than 800 °C possess irregular, extremely large Ru agglomerates. Therefore, the average particle size of Ru metal could not be estimated for Ru/SiO<sub>2</sub>(SC900), Ru/SiO<sub>2</sub>(SC930), and Ru/SiO<sub>2</sub>(SC950). However, they still had some Ru nanoparticles, and their average particle sizes were calculated to be 3.8  $\pm$  1.0, 3.7  $\pm$  2.0, and 3.4  $\pm$  2.0, respectively (Figure 2 and Table 1). These results imply that the SiO<sub>2</sub> support with a small surface area is not beneficial for obtaining well-dispersed Ru nanoparticles. However, it can be said that the oxidation of Ru catalysts supported on  $SiO_2$  with a large surface area has the potential to increase the Ru particle size to a certain degree without severe agglomeration. It is worth mentioning that large, irregular Ru lumps were observed even in the 1 wt.% Ru/SiO<sub>2</sub>(SC900) with a BET surface area of  $102 \text{ m}^2/\text{g}$ . More Ru lumps with extremely large sizes can be found in the  $Ru/SiO_2$  catalysts with smaller BET surface areas than in  $Ru/SiO_2$ (SC900). Note that relatively well-dispersed Ru nanoparticles with an average Ru particle size of approximately 6 nm were obtained for Ru/SiO<sub>2</sub> catalysts calcined at 300, 500, and 700 °C. This was related to the high surface area of the SiO<sub>2</sub> support.

**Table 1.** The physicochemical properties of the Ru/SiO<sub>2</sub> catalysts.

Catalyst	Surface Area <sup>a</sup> (m <sup>2</sup> /g)	Pore Volume <sup>a</sup> (cm <sup>3</sup> /g)	Average Pore Size <sup>a</sup> (nm)	Average Ru Particle Size <sup>b</sup> (nm)
Ru/SiO <sub>2</sub> (C100)	428	0.67	6.2	2.3
Ru/SiO <sub>2</sub> (SC700)	339	0.48	5.7	2.0
Ru/SiO <sub>2</sub> (SC800)	283	0.46	6.5	2.1
Ru/SiO <sub>2</sub> (SC900)	102	0.16	6.3	3.8 <sup>c</sup>
Ru/SiO <sub>2</sub> (SC930)	51	0.094	7.4	3.7 <sup>c</sup>
Ru/SiO <sub>2</sub> (SC950)	10	0.036	12	3.4 <sup>c</sup>
Ru/SiO <sub>2</sub> (C300)	425	0.62	5.9	6.0
Ru/SiO <sub>2</sub> (C500)	436	0.65	6.0	5.4
Ru/SiO <sub>2</sub> (C700)	328	0.50	5.8	5.6

 $^{a}$  Surface area, pore volume, and average pore diameter were calculated based on the N<sub>2</sub> physisorption data.  $^{b}$  The particle size is the result of analysis via transmission electron microscopy.  $^{c}$  The particle size was calculated excluding large agglomerated Ru lumps.



**Figure 1.** TEM images and particle size distributions of Ru metal for (a)  $Ru/SiO_2(C100)$ , (b)  $Ru/SiO_2(C300)$ , (c)  $Ru/SiO_2(C500)$ , and (d)  $Ru/SiO_2(C700)$ . All catalysts were calcined in air at different temperatures and subsequently reduced in H<sub>2</sub> at 350 °C.



**Figure 2.** TEM images and particle size distributions of Ru metal for (a)  $Ru/SiO_2(SC700)$ , (b)  $Ru/SiO_2(SC800)$ , (c)  $Ru/SiO_2(SC900)$ , (d)  $Ru/SiO_2(SC930)$ , and (e)  $Ru/SiO_2(SC950)$ . All catalysts were reduced in H<sub>2</sub> at 350 °C. The large Ru agglomerates were excluded in the particle size distribution.

The temperature-programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR) revealed that all Ru oxides in Ru/SiO<sub>2</sub> samples calcined at 300, 500, and 700 °C could be reduced below 200 °C (Figure S3). Doublet peaks were observed in temperatures ranging from 100 and 200 °C for all samples. The H<sub>2</sub>-TPR peak at 110 °C strengthened, but the other H<sub>2</sub>-TPR peak at 135 °C weakened when increasing the calcination temperature from 300 to 700 °C.

The X-ray diffraction (XRD) patterns were obtained for Ru/SiO<sub>2</sub>(C) catalysts and are displayed in Figure S4. The presence of RuO<sub>2</sub> was confirmed in all catalysts except for the Ru/SiO<sub>2</sub>(C100) catalyst (Figure S4a). The crystallite sizes of RuO<sub>2</sub> in Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(C500), and Ru/SiO<sub>2</sub>(C700) were determined to be ~12 nm. All these XRD peaks due to RuO<sub>2</sub> disappeared after reduction with H<sub>2</sub> at 350 °C, but new XRD peaks owing to Ru appeared in all catalysts except for the Ru/SiO<sub>2</sub>(C100) catalyst (Figure S4b). The crystallite sizes of Ru in Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(C500), and Ru/SiO<sub>2</sub>(C700) were determined to be ~8 nm. This implies that RuO<sub>2</sub> in the calcined catalyst can be reduced into Ru after reduction with H<sub>2</sub> at 350 °C, which is in line with the results of H<sub>2</sub>-TPR.

## 2.2. Catalytic Performance for Ammonia Decomposition

The catalytic activity for ammonia decomposition was evaluated for Ru/SiO<sub>2</sub> catalysts. Ammonia conversion as a function of the reaction temperature over different catalysts is shown in Figure 3. In the case of the Ru/SiO<sub>2</sub>(SC) catalysts (Figure 3a), Ru/SiO<sub>2</sub>(SC700), Ru/SiO<sub>2</sub>(SC800), and Ru/SiO<sub>2</sub>(SC900) showed similar ammonia conversions with Ru/SiO<sub>2</sub>(C100) at the same temperature. This can be attributed to the similar Ru particle sizes of Ru/SiO<sub>2</sub>(SC700), Ru/SiO<sub>2</sub>(SC800), and Ru/SiO<sub>2</sub>(SC800), and Ru/SiO<sub>2</sub>(C100). Notably, Ru/SiO<sub>2</sub>(SC900) had both Ru nanoparticles with an average particle size of 3.8 nm and large Ru lumps. Ru/SiO<sub>2</sub>(SC930) had similar catalytic activity with Ru/SiO<sub>2</sub>(C100) at low temperatures but became inferior to Ru/SiO<sub>2</sub>(C100) at high temperatures. Note that Ru/SiO<sub>2</sub>(SC950) was also vastly inferior to Ru/SiO<sub>2</sub>(C100) at 450 °C and higher. As these catalysts have both Ru nanoparticles and extremely large Ru lumps, it was difficult to establish any correlation between the catalytic activity and Ru particle size. However, it was clear that extremely large Ru agglomerates, which can easily form on a SiO<sub>2</sub> support with a small surface area, are not plausible for ammonia decomposition.



**Figure 3.** Ammonia conversion for ammonia decomposition over Ru/SiO<sub>2</sub> catalysts. (**a**) Ru/SiO<sub>2</sub>(C100) (black), Ru/SiO<sub>2</sub>(SC700) (red), Ru/SiO<sub>2</sub>(SC800) (blue), Ru/SiO<sub>2</sub>(SC900) (green), Ru/SiO<sub>2</sub>(SC930) (pink), and Ru/SiO<sub>2</sub>(SC950) (brown). (**b**) Ru/SiO<sub>2</sub>(C100) (black), Ru/SiO<sub>2</sub>(C300) (dark green), Ru/SiO<sub>2</sub>(C500) (dark blue), and Ru/SiO<sub>2</sub>(C700) (dark pink). Reaction conditions: feed composition (25 mol% NH<sub>3</sub>, 70 mol% He, and 5 mol% CH<sub>4</sub>), WHSV = 60,000 mL g<sub>cat</sub>.<sup>-1</sup> h<sup>-1</sup>.

Figure 3b shows Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(C500), and Ru/SiO<sub>2</sub>(C700) demonstrating similar catalytic activities, and their superiority to Ru/SiO<sub>2</sub>(C100) at all reaction temperatures. These catalysts had relatively well-dispersed Ru nanoparticles with an average particle size of 6 nm, larger than those of Ru/SiO<sub>2</sub>(C100). This implies that Ru particle size is an important factor that affects the catalytic activity for ammonia decomposition. As ammonia decomposition is a structure-sensitive reaction, the larger 6 nm-sized Ru particles performed better than the smaller 2 nm-sized ones, which is consistent with previous claims [53,54].

The H<sub>2</sub> formation rates based on the amount of Ru metal were obtained at 400 °C over Ru/SiO<sub>2</sub>(C) and Ru/SiO<sub>2</sub>(SC) catalysts. Figure 4a shows that the initial catalytic activities were maintained over all the Ru/SiO<sub>2</sub>(SC) catalysts, and their rates decreased in the following order: Ru/SiO<sub>2</sub>(SC900) > Ru/SiO<sub>2</sub>(SC700) > Ru/SiO<sub>2</sub>(SC800) > Ru/SiO<sub>2</sub>(SC930) > Ru/SiO<sub>2</sub>(SC950)~Ru/SiO<sub>2</sub>(C100). The H<sub>2</sub> formation rates over the Ru/SiO<sub>2</sub>(C) catalysts decreased in the following order: Ru/SiO<sub>2</sub>(C100). Note that the H<sub>2</sub> formation rates decreased slowly with time on stream over Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(500), and Ru/SiO<sub>2</sub>(700), even though their H<sub>2</sub> formation rates were much higher than that of Ru/SiO<sub>2</sub>(C100).

Kinetic data at different temperatures were obtained over Ru/SiO<sub>2</sub>(C500) and Ru/SiO<sub>2</sub> (C100), as shown in Figure S5. The apparent activation energies were determined as 108 and 146 kJ/mol, respectively. The kinetic data were compared to those reported previously (Table 2). The H<sub>2</sub> formation rate over Ru/SiO<sub>2</sub>(C100) at 400 °C was similar to that over Ru/SiO<sub>2</sub> [46,55]. The apparent activation energies over Ru/SiO<sub>2</sub>(C100) were much higher than those over Ru/ $\kappa$ -Al<sub>2</sub>O<sub>3</sub> and Ru/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalysts, even though the average Ru particle size ranged from 2 nm to 3 nm for all catalysts. However, Ru nanoparticles of approximately 5 nm can be formed in Ru/SiO<sub>2</sub>(C500), which has similar apparent activation energy as the Ru/ $\kappa$ -Al<sub>2</sub>O<sub>3</sub> and Ru/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>, and Ru/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. However, its H<sub>2</sub> formation rate was lower than that of Ru/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> (C300). Notably, the average Ru particle size increased from 2.6 to 9.8 nm when Ru/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> calcined in air at 300 °C. This implies that Ru particle size is critical to catalytic activity for ammonia decomposition, as supported by previous studies [43,55].



**Figure 4.** Stability test over Ru/SiO<sub>2</sub> catalysts at 400 °C. (**a**) Ru/SiO<sub>2</sub>(C100) (black), Ru/SiO<sub>2</sub>(SC700) (red), Ru/SiO<sub>2</sub>(SC800) (blue), Ru/SiO<sub>2</sub>(SC900) (green), Ru/SiO<sub>2</sub>(SC930) (pink), Ru/SiO<sub>2</sub>(SC950) (brown). (**b**) Ru/SiO<sub>2</sub>(C100) (black), Ru/SiO<sub>2</sub>(C300) (dark green), Ru/SiO<sub>2</sub>(C500) (dark blue), and Ru/SiO<sub>2</sub>(C700) (dark pink). Reaction conditions: feed composition (25 mol% NH<sub>3</sub>, 70 mol% He, and 5 mol% CH<sub>4</sub>).

**Table 2.** Comparison of catalytic performance of  $Ru/Al_2O_3$  and  $Ru/SiO_2$  catalysts for ammonia decomposition.

Catalyst	Average Ru Particle Size <sup>a</sup> (nm)	WHSV (mL/g <sub>cat</sub> /h)	r <sub>H2</sub> b (mol <sub>H2</sub> /mol <sub>Ru</sub> /min)	Ea <sup>c</sup> (kJ/mol)	Ref.	
Ru/CNT	4.3	60,000	13	71	[42]	
$Ru/\alpha$ -Al <sub>2</sub> O <sub>3</sub>	4.2	60,000	39	83	[43]	
Ru/κ-Al <sub>2</sub> O <sub>3</sub>	3.0	60,000	23	103	[43]	
Ru/θ-Al <sub>2</sub> O <sub>3</sub>	2.6	60,000	15	106	[43]	
$Ru/\theta$ -Al <sub>2</sub> O <sub>3</sub> (C300)	9.8	60,000	70	98	[43]	
Ru/SiO <sub>2</sub>	2.3	30,000	9.3	108	[46]	
Ru/K <sub>2</sub> SiO <sub>3</sub>	2.0	30,000	43	73	[46]	
Ru/c-MgO	12	38,710	87	76	[48]	
Ru/TiO <sub>2</sub>	-	6000	8.8	63	[50]	
Ru/ZrO <sub>2</sub>	-	6000	7.4	66	[50]	
Ru/CeO <sub>2</sub>	<2	6000	7.1	83	[51]	
Ru/SiO <sub>2</sub>	2.8	360,000	8.5	-	[55]	
Ru/SiO <sub>2</sub> (C100)	2.3	60,000	5.2	146	– This work	
Ru/SiO <sub>2</sub> (C500)	5.4	60,000	56	108		

<sup>a</sup> The particle size is the result of analysis via TEM. <sup>b</sup> The hydrogen formation rate was measured at 400 °C. <sup>c</sup> Activation energy was determined based on the kinetic data at different temperatures.

## 3. Experiment

#### 3.1. Catalyst Preparation

All Ru catalysts were prepared via a wet impregnation method using an aqueous solution of ruthenium nitrosyl nitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Sigma-Aldrich Co. Llc., St. Louis, MO, USA) and SiO<sub>2</sub> (ZEOprep 60, Zeochem Co. Ltd., Uetikon, Switzerland). Before the Ru precursor was impregnated onto the support, silica was calcined in air at different temperatures to obtain different surface areas. The prepared catalysts were dried in an oven at 100 °C for 12 h. The calcination temperature of SiO<sub>2</sub> is denoted by the sample name.

For example,  $Ru/SiO_2(SC700)$  indicates that  $SiO_2$  was calcined in air at 700 °C before the impregnation step.

The dried Ru/SiO<sub>2</sub>(C100) catalyst was calcined in air at different temperatures before the reduction step. These samples were denoted as Ru/SiO<sub>2</sub>(C100), Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(C500), and Ru/SiO<sub>2</sub>(C700), where the numbers in parentheses indicate the calcination temperature in °C. We refer to these catalysts as Ru/SiO<sub>2</sub>(C). All the catalysts were reduced using H<sub>2</sub> at 350 °C for 3 h before the activity test. The Ru contents for all catalysts were intended to be 1 wt.%.

#### 3.2. Catalytic Performance

The activity of the ammonia decomposition reaction was evaluated in a packed-bed reactor at atmospheric pressure. In general, catalyst powder of 100 mg was loaded in the middle of a quartz reactor (O.D. = 9.525 mm, I.D. = 7.745 mm) and retained by quartz wool. Before the activity test, the prepared catalyst sample was first reduced with pure H<sub>2</sub> gas at a flow rate of 30 mL/min at 350 °C, if not specified, for 1 h, followed by cooling to 25 °C. H<sub>2</sub> gas was then switched with He gas to purge the residual hydrogen at a flow rate of 30 mL/min for 30 min. Then, the feed gas, which was composed of 25 mol% NH<sub>3</sub>, 70 mol% He, and 5 mol% CH<sub>4</sub>, was fed into the reactor at a total flow rate of 100 mL/min. CH<sub>4</sub> was used as an internal standard. The catalytic activity for ammonia decomposition was monitored by increasing the temperature from 300 to 600 °C under atmospheric pressure. The reactants and products were separated using a Porapak Q column and analyzed using a thermal conductivity detector (TCD) in a gas chromatograph (GC, ChroZen, YOUNGIN chromass, Anyang, South Korea). The conversion of NH<sub>3</sub> ( $X_{NH_3}$ ) and the H<sub>2</sub> formation rate ( $r_{H_2}$ ) were calculated using the following equations:

$$X_{NH_3}(\%) = \frac{F_{NH_3,in} - F_{NH_3,out}}{F_{NH_3,in}} \times 100$$
(2)

$$r_{H_2}(mol_{H_2}/mol_{R_u}/min) = \frac{F_{NH_3,in} \times X_{NH_3} \times 0.015 \times 101.07}{m_{cat.} \times 0.01}$$
(3)

where  $F_{NH_3,in}$ ,  $F_{NH_3,out}$ , and  $m_{cat.}$  are the molar flow rates of NH<sub>3</sub> ( $mol_{NH_3}/min$ ) in the feed and outlet gases and the mass of catalyst (g), respectively.

To obtain the kinetic data for ammonia decomposition, separate experiments were performed by mixing small amounts of the catalyst and a diluent SiO<sub>2</sub> (ZEOprep 60, Zeochem Co. Ltd., Uetikon, Switzerland) in order to keep the NH<sub>3</sub> conversion below 20%. The apparent activation energy (Ea) of each catalyst was calculated using the following equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where *k* is the reaction rate constant, *A* is the pre-exponential factor, *R* is the gas constant, and *T* is the absolute temperature.

#### 3.3. Characterization

The Ru content of each catalyst was confirmed to be 1 wt.% with an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Fisher scientific, Waltham, MA, USA) performed with an OPTIMA 5300 DV instrument. N<sub>2</sub> physisorption was analyzed using a Micromeritics ASAP 2020 system in which the supports and catalysts were degassed under vacuum at 200 °C for 4 h. The specific surface areas (S<sub>BET</sub>) of the samples were calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions of the catalysts were obtained using the Barrett–Joyner–Halenda (BJH) method. High-resolution transmission electron microscopy (HRTEM, TitanTM 80–300, FEI, Hillsboro, OR, USA) and HRTEM (JEM-2100F, JEOL Ltd., Tokyo, Japan) were used to characterize the average particle size of Ru in the catalysts. These samples were deposited on a Cu grid covered with a holey carbon film. Temperature-programmed reduction with  $H_2$  (H<sub>2</sub>-TPR) was performed using a Autochem 2920 instrument (Micromeritics Instrument Corp., Norcross, GA, USA). After loading 0.10 g of the sample, the temperature was increased from 30 to 800 °C while feeding 10 mol% H<sub>2</sub>/Ar at a flow rate of 30 mL min<sup>-1</sup> monitoring the TCD signal. X-ray diffraction (XRD, Rigaku Smartlab, Tokyo, Japan) patterns were obtained using a Rigaku D/Max instrument with a Cu K $\alpha$  source to assess the bulk crystalline structure of the samples. The primary crystallite size of RuO<sub>2</sub> and Ru in the samples was determined using the Scherrer equation [56]:

$$L = \frac{0.9\lambda_{K_{\alpha 1}}}{\beta_{2\theta}cos\theta_{max}}$$
(5)

where L is the average particle size,  $\beta_{2\theta}$  is the full width at half maximum (FWHM) of the peak,  $\lambda_{K_{\alpha 1}}$  is the wavelength of the X-ray radiation (0.15406 nm), and  $\theta_{max}$  is the angular position of the (211) peak maximum of RuO<sub>2</sub> or the (101) peak maximum of Ru.

# 4. Conclusions

Various Ru/SiO<sub>2</sub> catalysts were prepared via calcination at different temperatures to obtain supports with different surface areas or via calcination of the dried Ru/SiO<sub>2</sub> catalyst at different temperatures to determine the effect of the Ru particle size on the catalytic activity for ammonia decomposition. Many Ru lumps were obtained, with supports having a small surface area, resulting in a slight change in the catalytic activity for ammonia decomposition of large Ru agglomerates observed in the Ru catalyst supported on supports with very small surface areas is not favorable for catalytic activity, especially at high temperatures. On the other hand, well-dispersed and relatively large Ru nanoparticles could be obtained after calcining Ru/SiO<sub>2</sub> at temperatures from 300 to 700 °C, which might be due to the high surface area of SiO<sub>2</sub>. Catalytic activity was enhanced when the Ru particle size increased from 2.3 to 5.4 nm in Ru/SiO<sub>2</sub>. This finding supports the notion that ammonia decomposition is a structure-sensitive reaction.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal12101203/s1, Figure S1: (a) N<sub>2</sub> adsorption (filled points) and desorption (unfilled points) isotherms of Ru/SiO<sub>2</sub>(C100) ( $\bigcirc$ ), Ru/SiO<sub>2</sub>(SC700) ( $\triangle$ ), Ru/SiO<sub>2</sub>(SC800) ( $\bigtriangledown$ ), Ru/SiO<sub>2</sub>(SC900) ( $\Leftrightarrow$ ), Ru/SiO<sub>2</sub>(SC930) ( $\Box$ ), and Ru/SiO<sub>2</sub>(SC950) ( $\diamond$ ) and (b) N2 adsorption (filled points) and desorption (unfilled points) isotherms of Ru/SiO<sub>2</sub>(C100) ( $\bigcirc$ ), Ru/SiO<sub>2</sub>(C300) ( $\triangle$ ), Ru/SiO<sub>2</sub>(C500) ( $\bigtriangledown$ ), Ru/SiO<sub>2</sub>(C700) ( $\Leftrightarrow$ ); Figure S2: (a) Pore size distribution of Ru/SiO<sub>2</sub>(C100) ( $\bigcirc$ ), Ru/SiO<sub>2</sub>(SC700) ( $\triangle$ ), Ru/SiO<sub>2</sub>(SC800) ( $\bigtriangledown$ ), Ru/SiO<sub>2</sub>(SC900) ( $\Leftrightarrow$ ), Ru/SiO<sub>2</sub>(SC930) ( $\Box$ ), and Ru/SiO<sub>2</sub>(SC950) ( $\diamond$ ) and (b) pore size distribution of Ru/SiO<sub>2</sub>(C100) ( $\bigcirc$ ), Ru/SiO<sub>2</sub>(C300) ( $\triangle$ ), Ru/SiO<sub>2</sub>(C500) ( $\bigtriangledown$ ), Ru/SiO<sub>2</sub>(C700) ( $\Leftrightarrow$ ); Figure S3: Temperature-programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR) patterns of Ru/SiO<sub>2</sub> calcined at different temperatures, such as Ru/SiO<sub>2</sub>(C300), Ru/SiO<sub>2</sub>(C500), and Ru/SiO<sub>2</sub>(C700); Figure S4: X-ray diffraction (XRD) patterns for Ru/SiO<sub>2</sub> catalysts calcined at different temperatures (a) and Ru/SiO<sub>2</sub> catalysts calcined at different temperatures and then reduced with H<sub>2</sub> at 350 °C (b); Figure S5: Arrhenius plots for ammonia decomposition over Ru/SiO<sub>2</sub>(C100) and Ru/SiO<sub>2</sub>(C500).

**Author Contributions:** Experimental investigation and data analysis, writing—original draft preparation, investigation, H.J.L.; supervision, writing—review and editing, project administration, funding acquisition, E.D.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the C1 Gas Refinery Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT (2015M3D3A1A01064899). This research was also supported by the H2KOREA, funded by the Ministry of Education (2022).

Data Availability Statement: Not applicable.

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

## References

- 1. Bell, T.E.; Torrente-Murciano, L. H<sub>2</sub> Production via Ammonia Decomposition Using Non-Noble Metal Catalysts: A Review. *Top. Catal.* **2016**, *59*, 1438–1457. [CrossRef]
- David, W.I.; Makepeace, J.W.; Callear, S.K.; Hunter, H.M.; Taylor, J.D.; Wood, T.J.; Jones, M.O. Hydrogen production from ammonia using sodium amide. J. Am. Chem. Soc. 2014, 136, 13082–13085. [CrossRef] [PubMed]
- Le, T.A.; Do, Q.C.; Kim, Y.; Kim, T.-W.; Chae, H.-J. A review on the recent developments of ruthenium and nickel catalysts for CO<sub>x</sub>-free H<sub>2</sub> generation by ammonia decomposition. *Korean J. Chem. Eng.* 2021, *38*, 1087–1103. [CrossRef]
- 4. Lucentini, I.; Garcia, X.; Vendrell, X.; Llorca, J. Review of the Decomposition of Ammonia to Generate Hydrogen. *Ind. Eng. Chem. Res.* **2021**, *60*, 18560–18611. [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* 2018, 226, 162–181. [CrossRef]
- 6. Andersson, J.; Grönkvist, S. Large-scale storage of hydrogen. Int. J. Hydrogen Energy 2019, 44, 11901–11919. [CrossRef]
- Lamb, K.E.; Dolan, M.D.; Kennedy, D.F. Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification. *Int. J. Hydrogen Energy* 2019, 44, 3580–3593. [CrossRef]
- 8. He, F.; Li, Y. Advances on Theory and Experiments of the Energy Applications in Graphdiyne. CCS Chem. 2022, 1–23. [CrossRef]
- 9. Yu, H.; Xue, Y.; Hui, L.; Zhang, C.; Fang, Y.; Liu, Y.; Chen, X.; Zhang, D.; Huang, B.; Li, Y. Graphdiyne-based metal atomic catalysts for synthesizing ammonia. *Natl. Sci. Rev.* 2021, *8*, nwaa213. [CrossRef]
- Liu, Y.; Xue, Y.; Hui, L.; Yu, H.; Fang, Y.; He, F.; Li, Y. Porous graphdiyne loading CoO<sub>x</sub> quantum dots for fixation nitrogen reaction. *Nano Energy* 2021, *89*, 106333. [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]
- Yin, S.F.; Xu, B.Q.; Zhou, X.P.; Au, C.T. A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications. *Appl. Catal. A* 2004, 277, 1–9. [CrossRef]
- Duan, X.; Qian, G.; Fan, C.; Zhu, Y.; Zhou, X.; Chen, D.; Yuan, W. First-principles calculations of ammonia decomposition on Ni(110) surface. Surf. Sci. 2012, 606, 549–553. [CrossRef]
- 14. Rathore, S.S.; Biswas, S.; Fini, D.; Kulkarni, A.P.; Giddey, S. Direct ammonia solid-oxide fuel cells: A review of progress and prospects. *Int. J. Hydrogen Energy* **2021**, *46*, 35365–35384. [CrossRef]
- Yin, S.-F.; Zhang, Q.-H.; Xu, B.-Q.; Zhu, W.-X.; Ng, C.-F.; Au, C.-T. Investigation on the catalysis of CO<sub>x</sub>-free hydrogen generation from ammonia. J. Catal. 2004, 224, 384–396. [CrossRef]
- 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. *Appl. Catal. B* 2020, 268, 118424. [CrossRef]
- 17. Zheng, W.; Zhang, J.; Xu, H.; Li, W. NH<sub>3</sub> Decomposition Kinetics on Supported Ru Clusters: Morphology and Particle Size Effect. *Catal. Lett.* **2007**, *119*, 311–318. [CrossRef]
- 18. Hayashi, F.; Toda, Y.; Kanie, Y.; Kitano, M.; Inoue, Y.; Yokoyama, T.; Hara, M.; Hosono, H. Ammonia decomposition by ruthenium nanoparticles loaded on inorganic electride C12A7:e<sup>-</sup>. *Chem. Sci.* **2013**, *4*, 3124. [CrossRef]
- 19. Chen, J.; Zhu, Z.H.; Wang, S.; Ma, Q.; Rudolph, V.; Lu, G.Q. Effects of nitrogen doping on the structure of carbon nanotubes (CNTs) and activity of Ru/CNTs in ammonia decomposition. *Chem. Eng. J.* **2010**, *156*, 404–410. [CrossRef]
- Wang, Z.; Cai, Z.; Wei, Z. Highly Active Ruthenium Catalyst Supported on Barium Hexaaluminate for Ammonia Decomposition to CO<sub>x</sub>-Free Hydrogen. ACS Sustain. Chem. Eng. 2019, 7, 8226–8235. [CrossRef]
- 21. Hill, A.K.; Torrente-Murciano, L. Low temperature H<sub>2</sub> production from ammonia using ruthenium-based catalysts: Synergetic effect of promoter and support. *Appl. Catal. B* 2015, 172–173, 129–135. [CrossRef]
- Yin, S.-F.; Xu, B.-Q.; Ng, C.-F.; Au, C.-T. Nano Ru/CNTs: A highly active and stable catalyst for the generation of CO<sub>x</sub>-free hydrogen in ammonia decomposition. *Appl. Catal. B* 2004, *48*, 237–241. [CrossRef]
- García-García, F.R.; Gallegos-Suarez, E.; Fernández-García, M.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. Understanding the role of oxygen surface groups: The key for a smart ruthenium-based carbon-supported heterogeneous catalyst design and synthesis. *Appl. Catal. A* 2017, 544, 66–76. [CrossRef]
- Choudhary, T.V.; Sivadinarayana, C.; Goodman, D.W. Catalytic ammonia decomposition: CO<sub>x</sub>-free hydrogen production for fuel cell applications. *Catal. Lett.* 2001, 72, 197–201. [CrossRef]
- Atsumi, R.; Noda, R.; Takagi, H.; Vecchione, L.; Di Carlo, A.; Del Prete, Z.; Kuramoto, K. Ammonia decomposition activity over Ni/SiO<sub>2</sub> catalysts with different pore diameters. *Int. J. Hydrogen Energy* 2014, 39, 13954–13961. [CrossRef]
- 26. Inokawa, H.; Ichikawa, T.; Miyaoka, H. Catalysis of nickel nanoparticles with high thermal stability for ammonia decomposition. *Appl. Catal. A* **2015**, *491*, 184–188. [CrossRef]
- Muroyama, H.; Saburi, C.; Matsui, T.; Eguchi, K. Ammonia decomposition over Ni/La<sub>2</sub>O<sub>3</sub> catalyst for on-site generation of hydrogen. *Appl. Catal. A* 2012, 443–444, 119–124. [CrossRef]
- Zheng, W.; Zhang, J.; Ge, Q.; Xu, H.; Li, W. Effects of CeO<sub>2</sub> addition on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for the reaction of ammonia decomposition to hydrogen. *Appl. Catal. B* 2008, *80*, 98–105. [CrossRef]
- 29. Maeda, A.; Hu, Z.; Kunimori, K.; Uchijima, T. Effect of high-temperature reduction on ammonia decomposition over niobiasupported and niobia-promoted rhodium catalysts. *Catal. Lett.* **1988**, *1*, 155–157. [CrossRef]

- 30. Lendzion-Bielun, Z.; Narkiewicz, U.; Arabczyk, W. Cobalt-based Catalysts for Ammonia Decomposition. *Materials* **2013**, *6*, 2400–2409. [CrossRef] [PubMed]
- Lendzion-Bieluń, Z.; Pelka, R.; Arabczyk, W. Study of the Kinetics of Ammonia Synthesis and Decomposition on Iron and Cobalt Catalysts. *Catal. Lett.* 2008, 129, 119–123. [CrossRef]
- 32. Torrente-Murciano, L.; Hill, A.K.; Bell, T.E. Ammonia decomposition over cobalt/carbon catalysts—Effect of carbon support and electron donating promoter on activity. *Catal. Today* 2017, 286, 131–140. [CrossRef]
- Hu, Z.-P.; Chen, L.; Chen, C.; Yuan, Z.-Y. Fe/ZSM-5 catalysts for ammonia decomposition to CO<sub>x</sub>-free hydrogen: Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. *Mol. Catal.* 2018, 455, 14–22. [CrossRef]
- 34. Antunes, R.; Steiner, R.; Marot, L.; Meyer, E. Decomposition studies of NH<sub>3</sub> and ND<sub>3</sub> in presence of H<sub>2</sub> and D<sub>2</sub> with Pt/Al<sub>2</sub>O<sub>3</sub> and Ru/Al2O<sub>3</sub> catalysts. *Int. J. Hydrogen Energy* **2022**, *47*, 14130–14140. [CrossRef]
- 35. Varisli, D.; Rona, T. CO<sub>x</sub> Free Hydrogen Production from Ammonia Decomposition Over Platinum Based Siliceous Materials. *Int. J. Chem. React. Eng.* **2012**, 10. [CrossRef]
- Polanski, J.; Bartczak, P.; Ambrozkiewicz, W.; Sitko, R.; Siudyga, T.; Mianowski, A.; Szade, J.; Balin, K.; Lelatko, J. Ni-Supported Pd Nanoparticles with Ca Promoter: A New Catalyst for Low-Temperature Ammonia Cracking. *PLoS ONE* 2015, 10, e0136805. [CrossRef]
- García-Bordejé, E.; Armenise, S.; Roldán, L. Toward Practical Application Of H<sub>2</sub> Generation From Ammonia Decomposition Guided by Rational Catalyst Design. *Catal. Rev.* 2014, 56, 220–237. [CrossRef]
- Karim, A.M.; Prasad, V.; Mpourmpakis, G.; Lonergan, W.W.; Frenkel, A.I.; Chen, J.G.; Vlachos, D.G. Correlating Particle Size and Shape of Supported Ru/γ-Al<sub>2</sub>O<sub>3</sub> Catalysts with NH<sub>3</sub> Decomposition Activity. J. Am. Chem. Soc. 2009, 131, 12230–12239. [CrossRef]
- 39. Wang, F.; Deng, L.-D.; Wu, Z.-w.; Ji, K.; Chen, Q.; Jiang, X.-M. The dispersed SiO<sub>2</sub> microspheres supported Ru catalyst with enhanced activity for ammonia decomposition. *Int. J. Hydrogen Energy* **2021**, *46*, 20815–20824. [CrossRef]
- Li, L.; Chen, F.; Shao, J.; Dai, Y.; Ding, J.; Tang, Z. Attapulgite clay supported Ni nanoparticles encapsulated by porous silica: Thermally stable catalysts for ammonia decomposition to CO<sub>x</sub> free hydrogen. *Int. J. Hydrogen Energy* 2016, 41, 21157–21165. [CrossRef]
- Yin, S.F.; Xu, B.Q.; Zhu, W.X.; Ng, C.F.; Zhou, X.P.; Au, C.T. Carbon nanotubes-supported Ru catalyst for the generation of CO<sub>x</sub>-free hydrogen from ammonia. *Catal. Today* 2004, 93–95, 27–38. [CrossRef]
- Wang, S.J.; Yin, S.F.; Li, L.; Xu, B.Q.; Ng, C.F.; Au, C.T. Investigation on modification of Ru/CNTs catalyst for the generation of CO<sub>x</sub>-free hydrogen from ammonia. *Appl. Catal. B* 2004, *52*, 287–299. [CrossRef]
- 43. Kim, H.B.; Park, E.D. Ammonia decomposition over Ru catalysts supported on alumina with different crystalline phases. *Catal. Today* **2022**, *in press*. [CrossRef]
- Li, Y.; Yao, L.; Song, Y.; Liu, S.; Zhao, J.; Ji, W.; Au, C.T. Core-shell structured microcapsular-like Ru@SiO<sub>2</sub> reactor for efficient generation of CO<sub>x</sub>-free hydrogen through ammonia decomposition. *Chem. Commun.* 2010, 46, 5298–5300. [CrossRef]
- 45. Yao, L.; Shi, T.; Li, Y.; Zhao, J.; Ji, W.; Au, C.-T. Core–shell structured nickel and ruthenium nanoparticles: Very active and stable catalysts for the generation of CO<sub>x</sub>-free hydrogen via ammonia decomposition. *Catal. Today* **2011**, *164*, 112–118. [CrossRef]
- Zhiqiang, F.; Ziqing, W.; Dexing, L.; Jianxin, L.; Lingzhi, Y.; Qin, W.; Zhong, W. Catalytic ammonia decomposition to CO<sub>x</sub>-free hydrogen over ruthenium catalyst supported on alkali silicates. *Fuel* 2022, *326*, 125094. [CrossRef]
- Nakamura, I.; Fujitani, T. Role of metal oxide supports in NH<sub>3</sub> decomposition over Ni catalysts. *Appl. Catal. A* 2016, 524, 45–49. [CrossRef]
- 48. Fujitani, T.; Nakamura, I.; Hashiguchi, Y.; Kanazawa, S.; Takahashi, A. Effect of Catalyst Preparation Method on Ammonia Decomposition Reaction over Ru/MgO Catalyst. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1186–1192. [CrossRef]
- 49. Lorenzut, B.; Montini, T.; Pavel, C.C.; Comotti, M.; Vizza, F.; Bianchini, C.; Fornasiero, P. Embedded Ru@ZrO<sub>2</sub> Catalysts for H<sub>2</sub> Production by Ammonia Decomposition. *ChemCatChem* **2010**, *2*, 1096–1106. [CrossRef]
- 50. Hu, Z.; Mahin, J.; Torrente-Murciano, L. A MOF-templated approach for designing ruthenium–cesium catalysts for hydrogen generation from ammonia. *Int. J. Hydrogen Energy* **2019**, *44*, 30108–30118. [CrossRef]
- Hu, Z.; Mahin, J.; Datta, S.; Bell, T.E.; Torrente-Murciano, L. Ru-Based Catalysts for H<sub>2</sub> Production from Ammonia: Effect of 1D Support. *Top. Catal.* 2018, 62, 1169–1177. [CrossRef]
- Chen, C.; Wu, K.; Ren, H.; Zhou, C.; Luo, Y.; Lin, L.; Au, C.; Jiang, L. Ru-Based Catalysts for Ammonia Decomposition: A Mini-Review. *Energy Fuels* 2021, 35, 11693–11706. [CrossRef]
- 53. García-García, F.R.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. Role of B5-Type Sites in Ru Catalysts used for the NH<sub>3</sub> Decomposition Reaction. *Top. Catal.* **2009**, *52*, 758–764. [CrossRef]
- 54. Zheng, W.; Zhang, J.; Zhu, B.; Blume, R.; Zhang, Y.; Schlichte, K.; Schlogl, R.; Schuth, F.; Su, D.S. Structure-function correlations for Ru/CNT in the catalytic decomposition of ammonia. *ChemSusChem* **2010**, *3*, 226–230. [CrossRef]
- 55. Varisli, D.; Elverisli, E.E. Synthesizing hydrogen from ammonia over Ru incorporated SiO<sub>2</sub> type nanocomposite catalysts. *Int. J. Hydrogen Energy* **2014**, *39*, 10399–10408. [CrossRef]
- 56. Patterson, A.L. The Scherrer formula for X-ray particle size determination. Phys. Rev. 1939, 56, 978–982. [CrossRef]