

Microwave-assisted ammonia synthesis over Cs-Ru/CeO₂ catalyst at ambient pressure: effects of metal loading and support particle size

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Abstract

Industrially, ammonia is produced by Haber-Bosch process under high temperatures and pressures, consuming more than 2% of the world's energy production. This paper presents microwave-assisted catalytic synthesis of ammonia operated at atmospheric pressure and temperatures from 260-360 °C. A Cs-promoted Ru catalyst supported on cerium oxide with different metal loading (4-24 wt.% Ru) and support particle size (25 nm, 50 nm and 5µm) was investigated. The small size cerium oxide support resulted in the highest activity while the large cerium oxide support was less favorable, leading to lower activity associated to large Ru particle size and lower dispersion.

Keywords: Ammonia synthesis; Microwave irradiation; Cs-Ru/CeO₂ catalyst; Ru particle size and dispersion; Oxygen vacancy

1. Introduction

Ammonia is a highly produced and consumed chemical in the world. It is widely used as a raw material for nitrogen containing chemicals and fertilizers, commonly used for the production of polymers, fibers, explosives, nitric acid and intermediates for pharmaceutical and dyes [1]. Ammonia is emerging as an energy source of choice for fueling the shipping industry to transition away from conventional fuels and reduce GHG emission [2]. Industrially, ammonia is produced by Haber-Bosch process under high temperatures (400–500 °C) and high pressures (150–300 bar) over Iron-based catalyst. This process is capital intensive and consumes more than 2% of world energy production as it operates at high temperatures and pressures. Many efforts have been made to minimize the energy consumption and reduce the capital and operating cost. For the past years the energy consumption for the Haber-Bosch process has been reduced by 30%, but it is still too high to meet the minimum energy requirement [3]. Immense capital investment and high operating pressure, limits the deployment of the Haber Bosch process for intermittent renewable energy source. The current Haber Bosch process is too vast to be arrayed for renewable energy and the scale down of the conventional Haber Bosch process to satisfy the capacity of renewable energy source may double or triple the cost of ammonia production. As a result, an alternative process is required to produce ammonia at small scale to meet the intermittent renewable energy requirement. Microwave technology can be an alternative process for the energy and cost intensive Haber Bosch process to produce ammonia at small scale with the supply of renewable energy source to mitigate the high production cost. Microwave technology can produce ammonia at low temperature and pressure with the use of an electromagnetic sensitive catalyst and are best suited for intermittent renewable energy source due to their swift response time [4,5]. Microwave reactor can be started and shutdown within minutes. It can handle small scale ammonia synthesis that requires large turndown ratio if intermittent nature of energy is supplied.

Microwaves offer instantaneous and volumetric heating via interaction with electromagnetic radiation, which is fundamentally different from conventional thermal heat conductive or convective transfer through direct heating [6,7]. Microwave irradiation selectively heats active sites on the surface of heterogeneous catalyst, facilitating the transfer of electrons between catalyst and reaction intermediates. Microwaves selective heating of the heterogeneous catalyst significantly reduces temperature, pressure, reaction time, and activation energy [5,8]. This selective heating of the catalyst is due to dielectric loss or Debye-type loss [7,8]. In microwave-assisted ammonia synthesis, the adsorbed nitrogen and hydrogen are polar and can couple through a Debye-type loss process that results in their selective heating. This causes the dissociation of N_2 and H_2 species into activated N_2 and H_2 species. These activated nitrogen species combine with hydrogen species to form the desired ammonia product on the catalyst surface [5,7].

A catalyst with high activity under microwave condition is much desired to further improve the energy efficiency and ammonia production. The cleavage of the strong $N\equiv N$ bond (945 KJ/mol) is the rate determining step for ammonia synthesis [9]. Electron donation from d-orbitals of active transition metal into π^* orbital of N_2 weakens the N_2 bond, facilitating the ammonia synthesis [10]. Transition metals such as Ru and Fe are very active for N_2 dissociation and Ru catalyst is a promising one for ammonia synthesis [11]. Various studies have shown that Ru-based catalyst exhibited higher activity than Fe-based catalyst [3]. At the same temperature and at half of the pressure, Ru-based catalyst showed five times higher activity than Fe-based catalyst [3]. Ru

species contains special geometrical structures known as B5-type sites which are one of the main factors that can affect ammonia synthesis. B5-type sites are very active and their activities depend on Ru crystal size and morphology [12,13]. These sites exist on the surfaces of Ru metal and are responsible for nitrogen adsorption [14]. They can be increased with decreasing Ru particle size [3,7]. In conventional heating, many researchers have investigated the role of support and promoter on Ru metal catalyst and how it affects the catalytic activity to produce ammonia at milder conditions, minimizing the energy and capital cost. The geometric and electronic properties of Ru catalyst are highly affected by the support and promoter, resulting in different ammonia production rates [7,15]. The use of cerium oxide support and Cs promoter exhibited high performance for microwave-assisted ammonia synthesis.

Our previous studies indicated that CeO₂ is a promising support for Ru catalyst in microwave-assisted ammonia synthesis [7]. The reversible transformation of CeO₂ support between Ce⁴⁺/Ce³⁺ and abundant oxygen vacancies, causes an increase in Ru metal surface electron density, resulting in higher ammonia synthesis [16,17]. Moreover, over CeO₂ support, Ru shows high dispersion with small particle size, increasing the catalytic activity [7]. The oxygen vacancies of CeO₂ act as a nest to form strong interaction between transition metals (Fe and Ru) and cerium oxide support through SMSI (Strong Metal Support Interaction) [18]. Oxygen vacancies on cerium oxide are also responsible for N₂ and H₂ adsorption and their concentration is highly affected by cerium oxide particle size. Zhang et al. [19] investigated the effect of reducing cerium oxide particle size. In his study lowering cerium oxide particle size was found to increase oxygen vacancies, improving oxygen mobility on the surface of cerium oxide [19]. The increase in oxygen vacancies enhances the adsorption of N₂ and H₂ species, increasing the ammonia production. Based on several investigations cerium oxide support can easily form metal-Ce-O bonds (Pt, Ag and Ru) [20]. The formation of this bond results in small and highly dispersed metal particles. The use of alkali metals such as Cs acts as an electron promoter and promote through the transfer of electrons from the alkali to the metal surface (Ru) boosting the catalytic activity towards ammonia synthesis. The promoting effect of Cs is stronger when reduced [21]. Beside promotion effect, Cs can reduce Ru particle size and prevents Ru metal sintering [7,22].

Increasing the Ru loading usually results in enhanced activity, as it supplies more activity sites. However, at higher loading, Ru particles agglomerates forming large Ru species lowering Ru dispersion and resulting in B5-type active sites reduction.

In this work, the effects of CeO₂ support size and Ru loading on ammonia synthesis under microwave reactor at low temperatures (260-360 °C) and atmospheric pressure are systematically investigated. Moreover, the Cs has been selected as a promoter to improve the ammonia synthesis activity based on our previous studies [7]. Three CeO₂ with different particle size (25 nm, 50 nm, and 5 μm) were selected as support, meanwhile, the Ru loading ranging from 4 wt.% to 24 wt.% were investigated for their activity towards ammonia synthesis.

2. Experimental Section

2.1. Catalyst preparation

All chemicals were purchased from Sigma Aldrich: Ruthenium (III) Nitrosyl nitrate (Ru [NO][NO₃]₃, Ru 31.3% min), Cesium Nitrate (CsNO₃, 99.8% metals basis) and Cerium oxide (CeO₂<25 nm nanoparticle, 50 nm nano-powder,>99.95% purity and <5 μm, 99.9% trace metals). All catalysts are prepared using incipient wetness impregnation method. For Cs-Ru/CeO₂ (2-4 wt.%, with 50 nm CeO₂ as support) catalyst, 1.2g CeO₂ (50 nm) was impregnated with 2 wt.% CsNO₃ and 4 wt.% Ru [NO][NO₃]₃, stirred for 6 hours, dried in drying oven for 12 hours and finally calcinated at 550 °C for 6 hours. All other catalysts with metal loading (Cs-Ru) 2-4 wt.%, 4-8 wt.%, 6-12wt.%, 8-16 wt.%, 10-20 wt.% and 12-24 wt.% were prepared similarly. The different sized cerium oxide support was prepared with the same procedure (25 nm, 50 nm and 5μm CeO₂), impregnated with 2 wt.% Cs and 4 wt.% Ru.

Table 1. List of catalyst studied with different support particle size and metal loading

Catalyst	Ru loading (wt.%)	Cs loading (wt.%)	CeO ₂ particle size
Cs-Ru/CeO ₂ 25 nm	4%	2%	25 nm
Cs-Ru/CeO ₂ 50 nm	4%	2%	50 nm
Cs-Ru/CeO ₂ 5 μm	4%	2%	5 μm
Cs-Ru/CeO ₂ (4-8%)	8%	4%	50 nm
Cs-Ru/CeO ₂ (6-12%)	12%	6%	50 nm
Cs-Ru/CeO ₂ (8-16%)	16%	8 %	50 nm
Cs-Ru/CeO ₂ (10-20%)	20%	10 %	50 nm
Cs-Ru/CeO ₂ (12-24%)	24%	12%	50 nm

2.2. Catalyst Testing

The catalytic activity for ammonia synthesis was tested in a fixed-bed reactor made of 8 mm-ID and 12 mm-OD quartz tube and loaded with 1.2g 60-100 mesh catalyst. The reactor tube was placed in a variable frequency microwave reactor system (Lambda MC1330-200). The microwave reactor has two IR sensors, one is used to measure reactor tube temperature, and the other is used to measure catalyst surface temperature. The CeO₂ supported catalysts (1.2g) was tested in a flowing gas mixture of 75 vol. % H₂ and 25% vol. N₂ under 6000 mL/g_{cat}·hr Gas Hourly Space Velocity (GHSV). The inlet gases N₂ and H₂ were ultra-high purity grade (UHP, 99.999%) supplied from Airgas, Inc.

The catalyst bed was first heated up to the reaction temperature of 260 °C for two hours, then the temperature was increased to 300 °C, 340 °C and 360 °C at 30 minutes interval under a microwave frequency of 5.850 GHz. The final product was analyzed using a four-channel Micro-GC (Inficon 3000).

The catalytic activity for ammonia synthesis was also studied under thermal heating. 1.2 g of 60-100 mesh catalyst was tested in a flowing gas mixture of 75 vol. % H₂ and 25% vol. N₂ under 6000 mL/g_{cat}·hr Gas Hourly Space Velocity (GHSV). The same gas purity of UHP, 99.999% was used, supplied from Airgas, Inc. The temperature was measured by thermal couple. The final ammonia concentration in the effluent was analyzed using a four-channel Micro-GC (Inficon 3000).

2.3. Catalyst Characterization

2.3.1 XRD

X-ray diffraction (XRD) of the powder samples were analyzed in a PANalytical X'Pert Pro (PW3040) set to 45 kV and 40 mA that utilize Cu K α radiation. The scans were taken from 10° to 100° at a scan rate of 5°/min. The peaks were identified with the help of Highscore plus Analyses software supplied by PANalytical.

2.3.2 CO Chemisorption

The average Ru particles size and metal dispersion was estimated through chemisorption technique with carbon monoxide (CO) as the adsorbate. The measurements were performed in Micromeritics Autochem HP 2950 instrument at 35°C. The samples were reduced with H₂ at 400°C for 30 minutes prior to measurements. The chemisorption data were used for calculating the Ru particles size and dispersions.

2.3.3 H₂-TPR

Hydrogen temperature-programmed reduction (H₂-TPR) was carried out in a Micromeritics Autochem HP 2950 instrument. In the TPR measurement, 0.3 g sample was first pretreated at 150 °C for 60 min in a flow of N₂ (30 mL/min) followed by cooling down to 100 °C. Then, the sample was heated up to 900 °C at a heating rate of 10 °C /min in a flow of 10% H₂ in argon (30 mL/min). Hydrogen consumption was measured using calibration of the signal obtained using a TCD.

2.3.4 Raman Spectroscopy

Raman spectroscopy was utilized to analyze the oxygen vacancies of cerium oxide support having different particle. Raman Spectroscopy was carried out in Renishaw InVia Raman spectrometer with a 532nm green excitation line.

3. Results and Discussion

3.1. Catalytic Performance Comparison

Ammonia synthesis is significantly affected by the properties of the catalyst such as active metal loading, and support particle size. Based on various studies, as the size of the cerium oxide is decreased, it promotes reducibility and oxygen vacancies [19]. The increase in oxygen vacancy enhances the movement of oxygen through the crystal lattice, assisting cerium oxide particles to undergo reduction-oxidation cycles [19,23]. In this study, the effect of support particle size over Cs-Ru/CeO₂ (2-4 wt.%) catalysts with different CeO₂ support particle size was investigated. All the catalyst contains the same Ru and Cs loading. As shown in Figure 1a, the small sized cerium oxide support displayed the highest ammonia production rate at all reaction temperatures. The Cs-Ru/CeO₂ (2-4 wt.%, 25 nm) catalyst exhibited the highest ammonia production rate, reaching 938 μmol_{NH₃}/g_{cat} hr. At the same reaction temperature of 260 °C, the ammonia synthesis rate over Cs-Ru/CeO₂ (2-4 wt.%, 50 nm) catalyst was slightly lower of 884 μmol_{NH₃}/g_{cat} hr as compared to the 25 nm CeO₂ support catalyst. The largest cerium oxide support, Cs-Ru/CeO₂ (2-4 wt.%, 5 μm), exhibited the lowest ammonia synthesis rate of 737 μmol_{NH₃}/g_{cat} hr at 260 °C. The highest ammonia production for the small (25 nm) CeO₂ support is mostly associated to small sized Ru species, and Ru is highly dispersed over the small sized cerium oxide support (25 nm CeO₂), as compared to the 50 nm and 5 μm cerium oxide support. The thermal ammonia synthesis over Cs-Ru/CeO₂ catalyst having different cerium oxide support particle size is shown in Figure 1b. Microwave reactor can synthesize ammonia at lower temperature as compared to conventional fixed bed reactor. The same conversion of ammonia is obtained at lower temperature of 260 °C when microwave reactor is used as compared to 400 °C when fixed bed reactor is used. Based on this contrast, microwave reactor lowered the ammonia synthesis temperature. The low temperature ammonia synthesis in microwave reactor is highly associated to selective heating of the microwave's irradiation as compared to conventional bulk heating through conduction or convection [5,8,24]. The durability test for Cs-Ru/CeO₂ (CeO₂ 50 nm) is also presented in Figure

1c. The catalyst was stable at all reaction temperatures with no loss in activity. However, the increase in reaction temperature resulted in a decrease in ammonia synthesis in all three supported catalyst both in thermal and microwave heating, related to exothermic nature of the ammonia synthesis reaction, not favorable to high temperature [25].

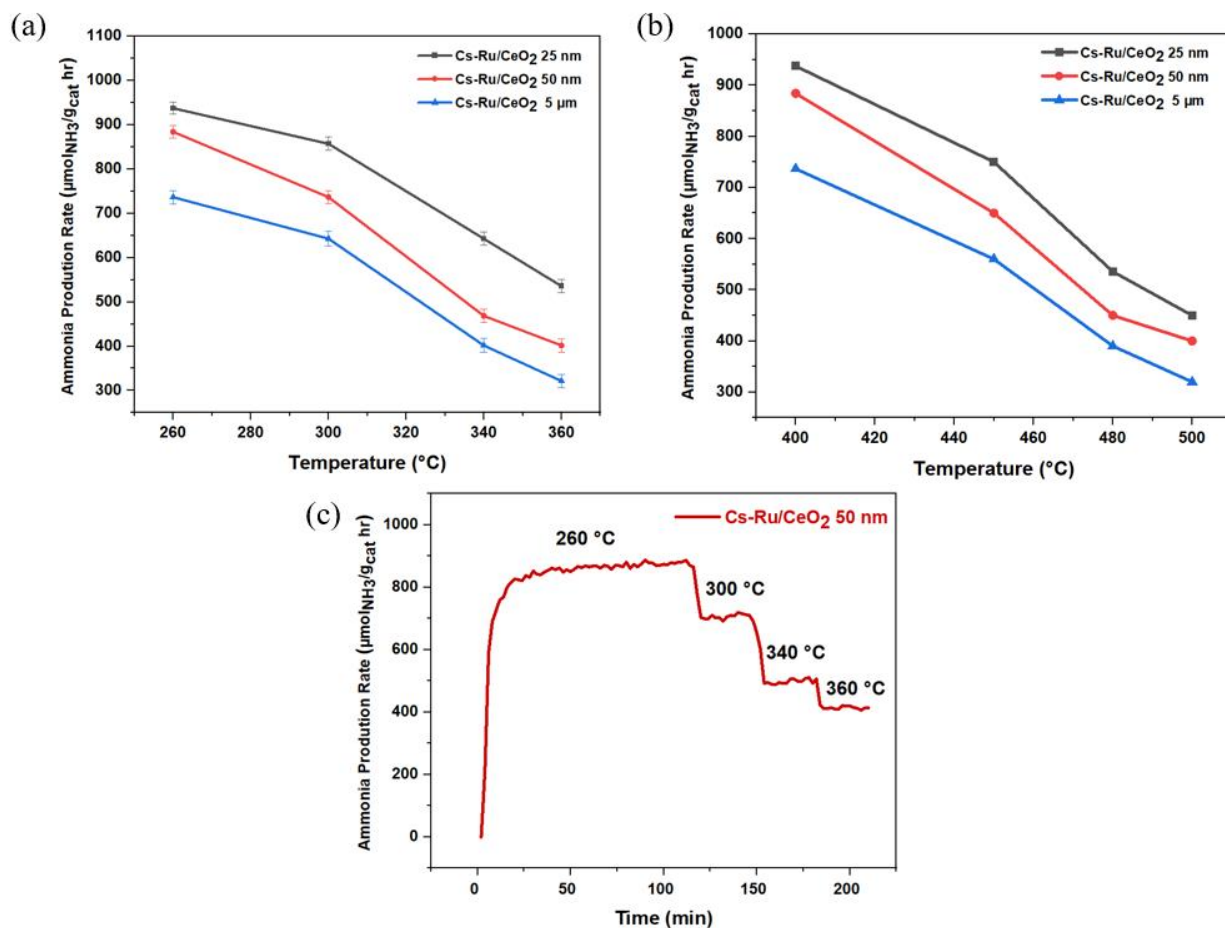


Figure 1. Ammonia production rate ($\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{cat}}\cdot\text{hr}$) for different sized cerium oxide support (a). Microwave heating (b). Thermal heating (c). Durability test for Cs-Ru/CeO₂ catalyst

As shown in Figure 2, a significant increase in ammonia production can be noticed on going from 4 wt.% Ru loading to 20 wt.% Ru loading, while for higher than 20 wt.% Ru loading activity seems to attain a plateau at 260 °C. Liang et al. [26] reported similar finding in his study on K promoted Ru catalyst supported on activated carbon for ammonia synthesis, attaining a plateau at 4-8 wt.% Ru loading. To investigate Ru utilization and productivity, the ammonia production per mass of active Ru metal ($\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{Ru}}\cdot\text{hr}$) is calculated. As shown in Figure 2, the ammonia productivity per mass of Ru decreased with increase in Ru loading. The ammonia production per gram of Ru at 2-4 wt.% loading is 21764 $\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{Ru}}\cdot\text{hr}$ as compared to 5588 $\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{Ru}}\cdot\text{hr}$ at 12-24 wt.% loading, showing the usage of Ru catalyst to produce a known mass of ammonia. This suggests

the utilization of Ru metal catalyst towards ammonia synthesis. Higher Ru loading exhibits lower ammonia production per mass of Ru, suggesting Ru catalyst is not fully utilized. This low utilization of Ru species at higher loading is associated to large size of Ru species, reducing the number of B5-type active sites for N₂ adsorption, thus lowering the ammonia production.

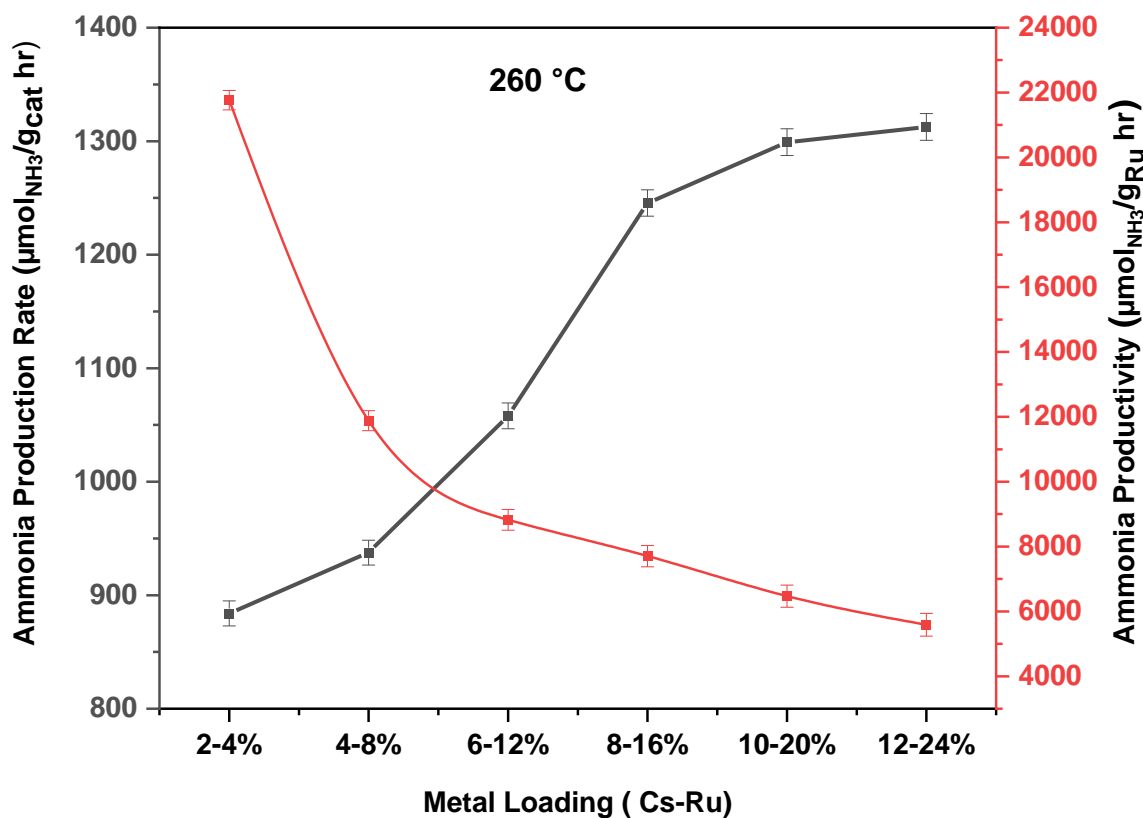


Figure 2. Cs-Ru/CeO₂ catalyst activity with different metal loading (CeO₂ 50 nm)

3.2 Catalyst Characterization

3.2.1 XRD Measurement

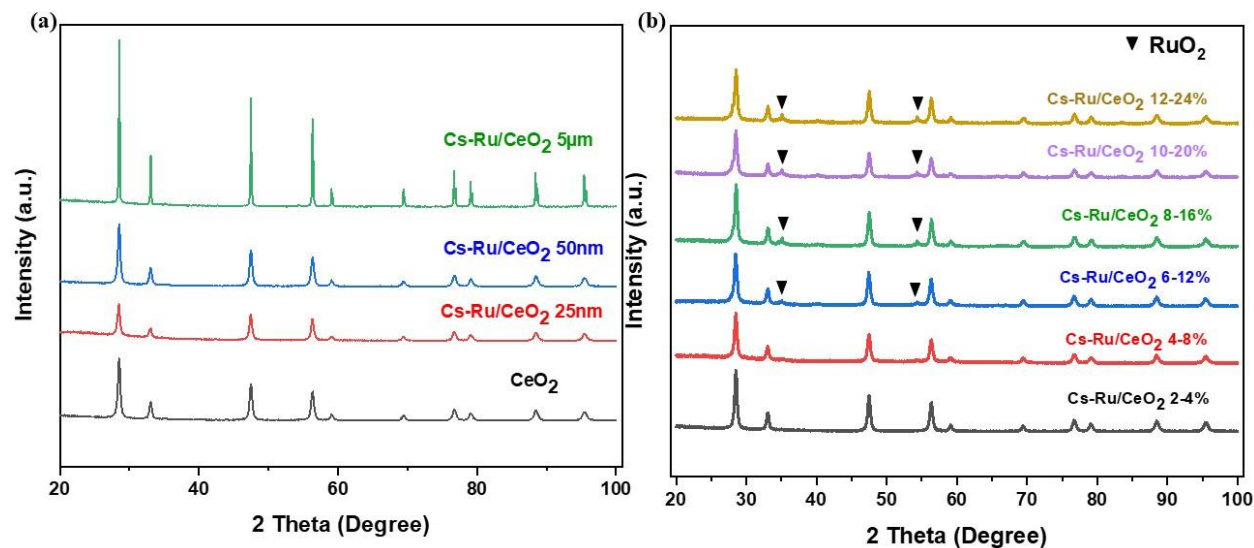


Figure 3. XRD of Cs-Ru/CeO₂ catalysts with (a). different CeO₂ particle size, (b). different metal loading of Cs-Ru

Figure 3 shows the XRD patterns of the Cs-Ru/CeO₂ catalyst with different support particle size and metal loading, respectively. Typical diffraction peaks of ceria fluorite structure (JCPDS 34-0394) are observed for all the samples. It is difficult to find any characteristic diffraction peaks that are attributed to Ru and Cs for all the three different sized cerium oxide support as shown in Figure 3a. These indicate the formation of small and highly dispersed Ru and Cs species over the cerium oxide support. As shown in Figure 3b, for the different metal loading, it is difficult to detect any characteristic Ru and Cs diffraction peaks at lower loading, e.g., 2-4 wt. % and 4-8 wt. % Cs-Ru loading. As the metal loading is increased to 6-12 wt.%, Ru diffraction peak is detected and no Cs peak is detected at all the loadings related to small size and high dispersion. As the metal loading is further increased, Ru diffraction peaks can be seen more clearly. The increase in Ru diffraction peak intensity as Ru loading increased, suggests an increase in Ru particle size and Ru is not highly dispersed over cerium oxide support as compared to lower Ru loading.

3.2.2 CO Chemisorption

CO chemisorption was conducted to study Ru particle size and dispersion over cerium oxide support. As presented in Table 2, in the 25 nm cerium oxide support, low crystalline and highly dispersed Ru species are observed as compared to the 5 μm cerium oxide support which exhibited large Ru species with the lowest dispersion. The interaction between Ru and CeO₂ support significantly affects Ru particle size and dispersion over the cerium oxide support [27]. The low

crystalline Ru species over the small sized cerium oxide support is linked to the reversible oxidation state of ceria from Ce^{4+} to Ce^{3+} , causing the Ru particles to be highly absorbed into the oxygen vacancy of CeO_2 crystal lattice to form a Ru-O-Ce phase [19]. The formation of this bond strength the interaction between ceria and Ru, and limits Ru mobility, promoting small sized Ru species with high dispersion [27,28]. The size of Ru particle alters the number of B5-type active sites on Ru surface, which are responsible for strong physical adsorption of nitrogen. This active sites can be increased with the decrease in Ru particle size [12,13]. In our comprehensive study of Cs-Ru/ CeO_2 catalyst, Ru dispersion is correlated to Ru particle size. With a decrease in cerium oxide support particle size, Ru particle size is reduced, and Ru is highly dispersed over the cerium oxide support, increasing the number of B5-type active sites, thus enhancing the ammonia production [13]. As cerium oxide support size increased, Ru particle size enlarged and Ru dispersion reduced, resulting in lower catalytic activity. Many researchers have reported the size of Ru particle analyzed using TEM to be smaller as compared to CO chemisorption [14,22]. Similar Ru particle size analyzed by CO chemisorption is reported by Wang et al [7] over CeO_2 support loaded with Ru and Cs. In his finding Ru species could not be spotted under high-resolution TEM (HRTEM) and suggested to small size of the Ru particles or some of the Ru species are embedded in the ceria lattice [7,27].

Table 2. CO chemisorption for the different sized cerium oxide support (Cs: 2 wt.%, Ru: 4 wt.%) and metal loading

Catalyst	Ru dispersion (%)	Ru particle size diameter (nm)	NH_3 production rate ($\mu mol_{NH_3}/g_{cat} \text{ hr}$) at 260 °C
Cs-Ru/ CeO_2 25 nm	18.3%	7.2 nm	938
Cs-Ru/ CeO_2 50 nm	13.3%	9.9 nm	884
Cs-Ru/ CeO_2 5 μm	3.9%	33.5 nm	737
Cs-Ru/ CeO_2 2-4 wt.%	13.3%	9.9 nm	884
Cs-Ru/ CeO_2 4-8 wt.%	8.8%	15 nm	945
Cs-Ru/ CeO_2 6-12 wt.%	7.9%	16.8 nm	1058
Cs-Ru/ CeO_2 8-16 wt.%	5.6%	23.5 nm	1246
Cs-Ru/ CeO_2 10-20 wt.%	3.7%	36 nm	1299
Cs-Ru/ CeO_2 12-24 wt.%	3.1%	42 nm	1313

CO chemisorption was also conducted to study Ru dispersion and particle size for the different metal loadings. As shown in Table 2, as metal loading increased from 2-4 wt.% to 12-24 wt.%(Cs-Ru), Ru particle size increased causing a decrease in Ru dispersion. This is largely related to increased Ru metal content in the catalyst system, causing Ru particles to sinter, forming large Ru particles with low dispersion. The price of Ru metal is expensive, high Ru loading may not be beneficial to ammonia synthesis as large quantity of Ru species are under-utilized related to low dispersion and large particle size.

3.2.3 H₂-TPR measurement

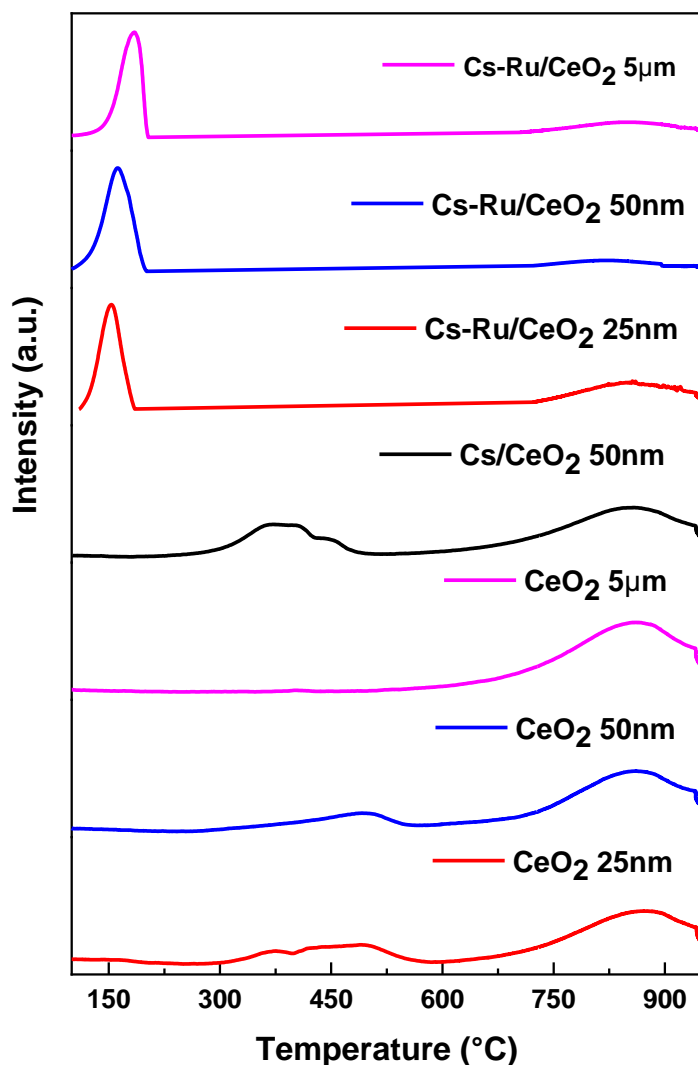


Figure 4. H₂-TPR of Cs-Ru/CeO₂ catalyst with different cerium oxide support particle size

Hydrogen temperature-programmed reduction (H₂-TPR) was utilized to investigate the effects of support particle size and active metal loading amount on the reducibility of Ru catalyst. The reducibility of Ru is affected by the particle size and metal-support interaction. The interaction between Ru and CeO₂ support forms Ru-Ce-O bonds. The formation of this bond gives path to the formation of radical oxygen anion species, which is very active and easy to lose electrons resulting in the formation of oxygen vacancies and change in the oxidation state of ceria between Ce⁴⁺ and Ce³⁺ [18]. Figure 4 shows H₂-TPR profile of the Cs-Ru/CeO₂ catalyst with different support particle size. H₂-TPR profiles for Cs/CeO₂ and CeO₂ are added for reference purposes. All the Cs-Ru/CeO₂ samples are loaded with the same amount of Cs (2 wt.%) and Ru (4 wt.%) and exhibit a broad reduction peak at 150–200 °C. It is generally accepted that the low temperature reduction is due to the removal of surface oxygen and the reduction of Ru from Ru⁴⁺ to Ru⁰ [29,30]. The

intense low temperature reduction peak in the 25 nm cerium oxide support shows Ru particle size is small and can easily be reduced at lower temperature of 150 °C. As the support size increased to 50 nm and 5 μm, Ru reduction temperature increased to 160 °C and 190 °C, respectively. A decrease in the size of cerium oxide is correlated with an expansion of the crystal lattice, enhancing the oxygen vacancies on the surface of cerium oxide [31]. The increase in crystal lattice with decreasing particle size provides more oxygen mobility on the cerium oxide surface, increasing the ionic conductivity and enhancing the ammonia production [19]. Moreover, the reduction peak of Cs in Cs/CeO₂ vanished in all Cs-Ru/CeO₂ catalyst. This is mostly due to Cs and Ru atoms were closely associated as first neighboring atoms and affected Ru and Cs reduction behavior. Ru has higher dissociation capability; Cs can easily be reduced from hydrogen spillover[22].

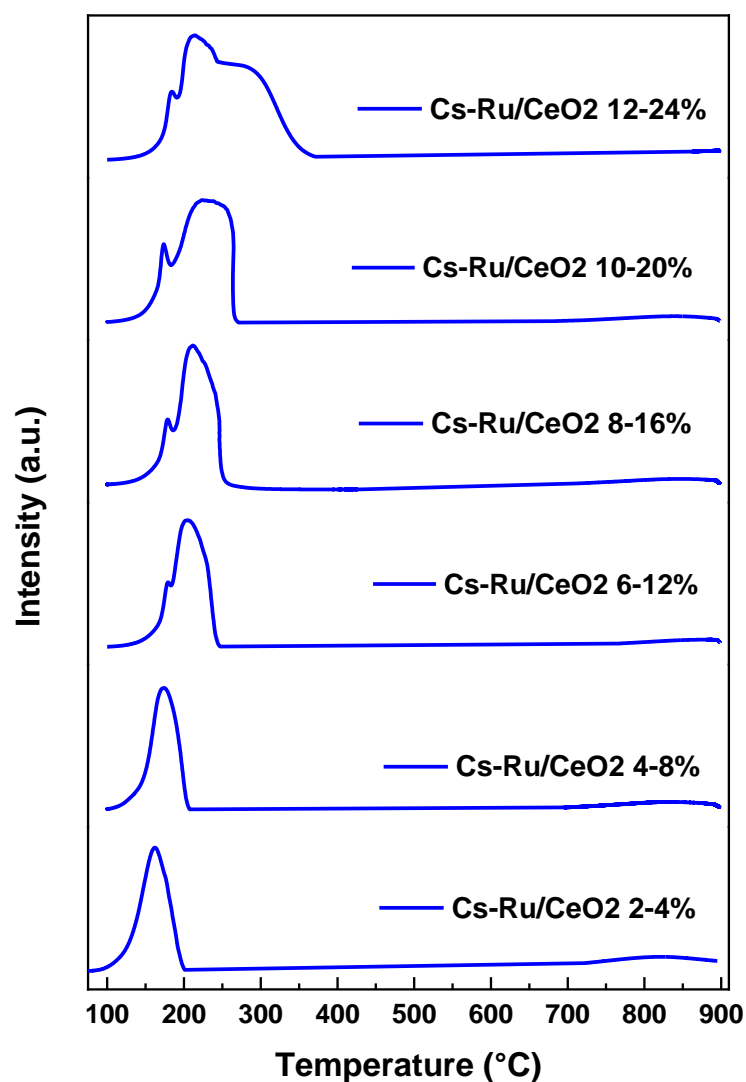


Figure 5. H₂-TPR of Cs-Ru/CeO₂ catalyst with different metal loading

Figure 5 shows the H₂-TPR profiles of the Cs-Ru/CeO₂ catalyst with different metal loading. In all of them the same support particle size (50 nm) was used with different metal loading. The 2-4% (Cs-Ru) metal loading shows the lowest reduction temperature of 160 °C, and the 12-24 wt.% loading shows the highest reduction temperature of 230 °C. The increase in reduction temperature is mainly due to high content of Ru metal, increasing Ru particle size as confirmed using CO chemisorption, thus, requiring more energy to reduce Ru.

The main peak shown in Figure 5 is attributed to the complete reduction of Ru⁴⁺ to Ru⁰ and the interaction of Ru species with CeO₂ support [7]. When Ru loading is increased to 6-12 wt.%, the main Ru reduction peak shifts to 200 °C. This is mainly because of the increase in Ru particle size with the increase in metal loading. At low Cs and Ru loading (2-4 wt.% and 4-8 wt.%), one reduction peaks at 160 °C and 175 °C is observed which is attributed to Ru.

When Cs and Ru loadings are further increased, a shoulder peak and main peak are observed. The low temperature shoulder reduction peak is attributed to highly dispersed Ru species that have strong interaction with ceria and main peak is attributed to the reduction of slightly larger Ru particles. Based on our finding, increasing the metal loading increases the reduction temperature due to high Ru metal content and large Ru particle size.

3.2.4 Raman Spectroscopy

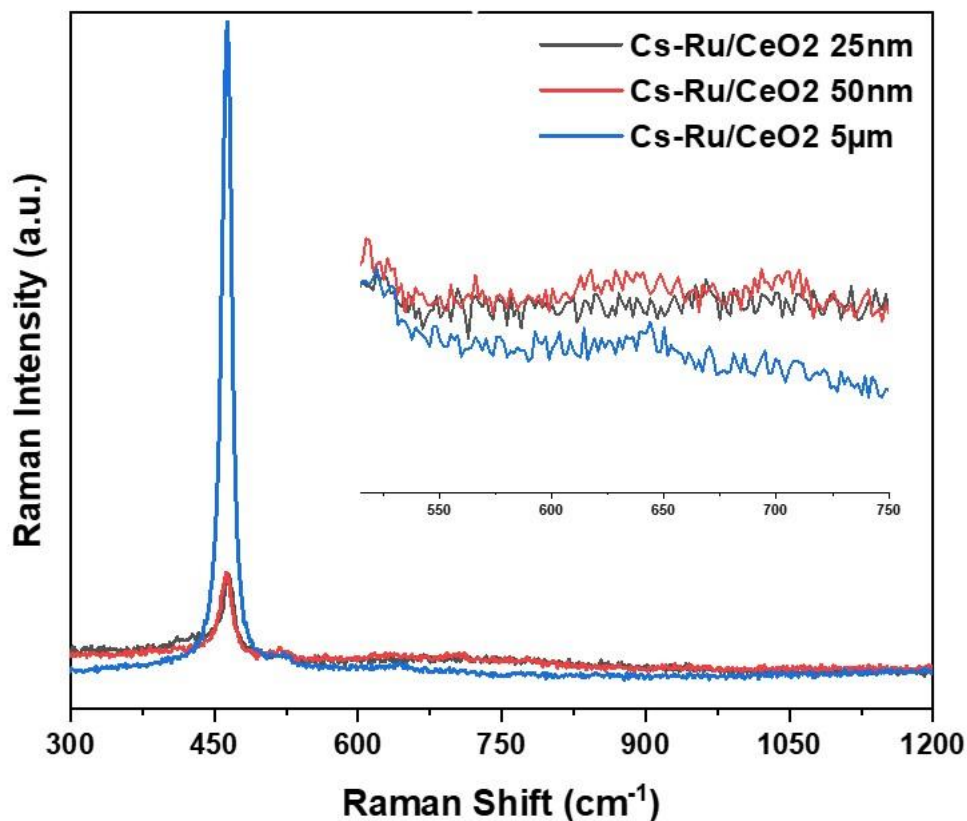


Figure 6. Raman Spectroscopy for different sized cerium oxide support

Raman spectroscopy is an analytical instrument that can provide information regarding oxygen vacancy in cerium oxide. Raman was performed to study oxygen vacancy on three different sized cerium oxide support (25 nm, 50 nm, 5 μm) loaded with 2% Cs and 4% Ru as shown in Figure 6. For all different sized cerium oxide support, there is a strong peak at 463 cm^{-1} which broadens with a decrease in cerium oxide particle size. This peak is attributed to the symmetrical vibration modes (F_{2g}) and a second peak at 650 cm^{-1} is attributed to defect-induced modes (D) [32]. The ratios of the integrated peak area of the D and F_{2g} modes ($I_D/I_{F_{2g}}$) was calculated to determine the oxygen vacancy for the three different sized CeO_2 support [32]. $I_D/I_{F_{2g}}$ ratio is a common technique used to calculate the oxygen vacancies for cerium oxide [27]. The 25 nm cerium oxide support showed the highest $I_D/I_{F_{2g}}$ ratio (4.026×10^{-1}) as compared to the 50 nm (3.2×10^{-1}) and 5 μm (0.49×10^{-1}) cerium oxide support, indicating the 25 nm cerium oxide support has more oxygen vacancy as shown in Table 3. High oxygen vacancies over ceria fluorite structure strengthen the SMSI, enhancing the catalytic activity towards ammonia synthesis. The increase in oxygen vacancies and low crystallinity of Ru species, enhance the adsorption of H_2 and N_2 species, facilitating the ammonia production [18,33,34].

Table 3. Oxygen vacancy for the different sized cerium oxide support loaded with 2% Cs and 4% Ru

Catalyst	F_{2g}	D	$I_D/I_{F_{2g}}$
Cs-Ru/ CeO_2 25nm	9.2×10^4	3.7×10^4	0.40
Cs-Ru/ CeO_2 50nm	7.2×10^4	2.3×10^4	0.32
Cs-Ru/ CeO_2 5 μm	1.2×10^4	6.3×10^3	0.049

4. Mechanistic Discussion

In the present study we investigated the effect of support particle size and metal loading on the catalytic performance of Cs-Ru/ CeO_2 catalyst in microwave-assisted ammonia synthesis. Microwave irradiation can produce ammonia at lower temperature as compared to thermal heating. Based on our study of Cs-Ru/ CeO_2 catalyst for ammonia synthesis, the same concentration of ammonia is produced at 260 $^\circ\text{C}$ when microwave reactor is utilized and at 400 $^\circ\text{C}$ when conventional fixed bed reactor was used. Microwave reactor produced the desired ammonia product at lower temperature, related to selective heating of the microwave's irradiation [5,8,24]. Similar discovery is also reported by Wang et al. [7]. In microwave selective heating, electromagnetic waves instigate electron donation and electric and magnetic fields between metal sites [24]. The active sites of the catalyst along with the electromagnetic field lowers the activation energy of the reaction, facilitating N_2 cleavage to produce ammonia at low temperature and pressure[5]. During the microwave-assisted ammonia synthesis process, the heat is generated at the catalyst surface through dielectric loss or Debye-type loss heating which leads to surface heating, without primarily heating the reaction gases (N_2 and H_2) [8]. Additionally, the adsorbed species on the surface (N_2 , H_2 , and NH_3) are necessarily polar and can couple through a Debye-

type loss process [5]. Based on our previous studies Cs-Ru/CeO₂ catalyst is a good microwave sensitive catalyst that can operate efficiently under microwave for ammonia synthesis. The interaction between Ru metal and support is vital for the creation of electron-rich Ru. Since the reaction is mainly activated at the Ru site, Ru species must be reduced from Ru⁴⁺ to Ru⁰ [24]. The formation of small sized Ru species is significant as they can be reduced easily at lower temperature and promote N₂ dissociation. The size of Ru species highly depends on the size and type of support [7]. The use of cerium oxide as support plays a significant role by creating abundant oxygen vacancies as it changes its oxidation state from Ce⁴⁺ to Ce³⁺, enhancing the adsorption of hydrogen and nitrogen [16].

The rate determining step for ammonia synthesis is N₂ dissociation [9]. The activation barrier for H₂ is much lower than N₂, hence, H₂ molecules can easily be absorbed and dissociated over the catalyst surface as compared to N₂ [5,10]. Cs as a promoter has high electron donation ability and electron transfer is crucial to weaken the N≡N bond [7,22]. The transfer of electrons from promoter and support to Ru surface, increases electron density into π* orbital of N₂, facilitating N₂ cleavage, thus enhancing the ammonia production [26]. Under microwave irradiation the electron transfer process could be accelerated even more, facilitating activation of nitrogen atoms to react with hydrogen atoms to produce the desired ammonia.

Stability is a key for catalyst development. In our study, Cs-Ru/CeO₂ catalyst durability was tested at temperatures ranging from 260-360 °C. Cs-Ru/CeO₂ catalyst is stable at all reaction temperatures. Durability test on Cs-Ru/CeO₂ catalyst under microwave was also conducted by Wang et al.[35] for Seven days with multiple startup-shutdowns and reported no catalyst deactivation or loss in activity towards ammonia synthesis for total of 80 hrs. on stream [35]. From the different characterization techniques and ammonia synthesis experimental data, cerium oxide support particle size significantly affects the dispersion and size of Ru species, modifying Ru reduction temperature and ammonia production. Lowering cerium oxide support particle size(25nm CeO₂) improves Ru dispersion and forms low crystalline Ru species, thus increasing the number of B5- type active sites that are responsible for strong N₂ adsorption for enhanced ammonia production [7,13]. The high oxygen vacancies on the 25nm cerium oxide support also causes an increase in electron donation to Ru metal due to strong bonding between Ru and ceria and the reversible Ce⁴⁺ and Ce³⁺ redox, facilitating the adsorption of H₂ and N₂ species, enhancing the ammonia production [33]. As cerium oxide support size increases to 50 nm and 5 μm large sized Ru species with low dispersion are observed lowering the ammonia production. Besides support particle size, metal loading affects ammonia synthesis. The lower metal loading exhibited small sized Ru species as compared to higher loading. As the metal loading increased ammonia concentration was improved, however ammonia productivity per mass of Ru decreased, suggesting Ru catalyst is not fully utilized and some Ru elements are not in the active phase in the cerium oxide support. The increase in ammonia production at a higher loading does not guarantee the total usage of all active sites. Based on our study, microwave irradiation reduces the reaction temperature, however other critical variables such as Ru particle size, dispersion, and cerium oxide oxygen vacancy affects the ammonia production. The optimum support particle size and metal loading for enhanced ammonia synthesis over Cs-Ru/CeO₂ catalyst is 25 and 50 nm cerium oxide support loaded with 2 wt.% Cs and 4 wt.% Ru.

5. Conclusion

In this study, the effect of Ru loading and cerium oxide support size in microwave-assisted ammonia synthesis at low temperatures and atmospheric pressure has been comprehensively investigated. Microwave technology can accommodate small scale production to produce ammonia at mild conditions with the supply of intermittent renewable energy source. Based on our investigation of different sized cerium oxide support for microwave assisted ammonia synthesis the small sized cerium oxide support (25nm CeO₂) exhibited the highest activity towards ammonia synthesis. This is mostly due to small Ru particle size and higher dispersion over the small sized cerium oxide support. High oxygen vacancy on the small sized support also enhanced the SMSI and the adsorption of H₂ and N₂ species, facilitating the catalytic activity towards ammonia synthesis. Moreover, the 5 μm cerium oxide support was less favorable due to large size of Ru species with low dispersion. The effect of metal loading was also studied where high ammonia concentration was obtained as metal loading increased, however Ru catalyst utilization decreased as metal loading increased. Since the cost of Ru is expensive, high metal loading with low utilization is economically not feasible.

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