Enhanced Ammonia Synthesis Activity of Ceria-Supported Ruthenium Catalysts Induced by CO Activation

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Abstract

Metal-support interactions strongly affect the catalytic performances of ceria-supported metal catalysts, and hydrogen treatment at high temperature is important for the preparation of catalysts that show strong metal-support interaction (SMSI). With SMSI, the proportion of metal species existed in the form of metallic state is lowered, consequently hindering the performance of a metal catalyst for a reaction that requires metallic sites. Here we show that CO activation of a Ru/CeO2 catalyst not only enhances the reduction degree and exposure of Ru species, but also increases Ce3+ concentration, oxygen vacancy (OV) and active oxygen, resulting in the formation of electron-enriched Ruô- species and Ruô--OV-Ce3+ sites. As a result, a Ru/CeO2 catalyst after CO activation shows high ammonia synthesis activity, and the ill effect of hydrogen poisoning is effectively alleviated. These findings are important for the design of supported metal catalysts that afford metallic species as active sites.

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Abstract: Metal–support interactions strongly affect the catalytic performances of ceria-supported metal catalysts, and hydrogen treatment at high temperature is important for the preparation of catalysts that show strong metal-support interaction (SMSI). With SMSI, the proportion of metal species existed in the form of metallic state is lowered, consequently hindering the performance of a metal catalyst for a reaction that requires metallic sites. Here we show that CO activation of a Ru/CeO₂ catalyst not only enhances the reduction degree and exposure of Ru species, but also increases Ce³⁺ concentration, oxygen vacancy (O_V) and active oxygen, resulting in the formation of electron-enriched Ru^{δ -} species and Ru^{δ -}O_V-Ce³⁺ sites. As a result, a Ru/CeO₂ catalyst after CO activation shows high ammonia synthesis activity, and the ill effect of hydrogen poisoning is effectively alleviated. These findings are important for the design of supported metal catalysts that afford metallic species as active sites.

Keywords: Ammonia synthesis, CO activation, Metal–support interaction, Ru/CeO₂

1. Introduction

Ammonia (NH₃) is not only an important chemical for the synthesis of N-containing compounds,¹ but also a carrier of hydrogen energy.²⁻³ The process of catalytic ammonia synthesis from hydrogen and nitrogen consumed 1-2% of the world's energy every year;⁴⁻⁶ thus it is urgent to develop an efficient catalyst and sustainable process for ammonia production. Recently, ceria-supported Ru catalysts have attracted much interest in ammonia synthesis due to the unique electronic property, Ce^{4+}/Ce^{3+} redox ability and hydrogen adsorption capacity of ceria.⁷⁻¹¹

In general, the interaction between reducible oxides and metal species has a strong effect on catalytic performance.¹²⁻¹⁴Strong metal-support interaction (SMSI), electronic metal-support interaction (EMSI), and nature of interfacial perimeter are known factors that would cause such an effect. SMSI is due to the coverage of metal particles by suboxides, which could enhance catalytic activities by inducing Lewis acidity and/or changing the electronic structure of metal species.¹⁵⁻¹⁹ Furthermore, as a result of charge transfer or EMSI between metal species and reducible oxide support, there is electronic perturbation and electron rearrangement of metal species, leading to enhancement of catalytic performance as a result of changes in adsorption and/or dissociation properties of reactant gases.^{12, 20-21} On the other hand, the accumulation of excess charges or close contact between support and metal species at the interfacial perimeter sites would affect the adsorption, reaction and spillover of reactants or products, consequently exerting a strong influence on the activities of oxides-supported metal catalysts.²²⁻²⁵

Ammonia synthesis consists of several reaction steps, including the adsorption and dissociation of N_2 and H_2 molecules, the reaction of N and H atoms, and the desorption of unreacted gases (N₂ and H₂) and NH_x species.²⁶⁻²⁷ It is envisioned that any change in Ru-ceria interaction of a Ru/ceria catalyst would strongly affect the catalytic activity for ammonia synthesis due to alteration of adsorption properties of reactant gases. Through the decrease of metal loading, one can enhance metal-support interaction and increase atom economy by maximizing the number of interfacial sites. Guo et al. observed that SMSI was the strongest for Ru/CeO₂ with single Ru atoms, and hydrogen spillover was more pronounced for catalyst samples with larger Ru particles. Moreover, Ru in the form of Ru clusters showed high activities in CO_2 methanation because there was a balance between SMSI and H-spillover effect.²⁸ Ganzler et al. proposed that large Pt particles lowered the reducibility of ceria, and the activity for CO oxidation decreased as a result of the decrease of interfacial sites between ceria and Pt particles.²⁹ Lykhach et al. showed that the charge transfer between Pt species and ceria was governed by the size of Pt particles.¹⁴ It was observed that a higher reduction temperature is required for the preparation of a catalyst with SMSI, especially for catalysts with metal clusters of small size.³⁰⁻³¹ Unfortunately, there was sintering of metal clusters during high temperature reduction, 31 and the decoration or encapsulation of metal species by suboxides from the reducible support would lower the proportion of metal species that exist in metallic state. The detrimental effect of the diminution of metallic sites on catalytic performance would be pronounced for catalytic reactions that require metallic species as active sites, such as the reactions for ammonia synthesis.

In the present work, we demonstrate that for Ru/CeO₂ catalyst the reduction degree and the exposed proportion of Ru species could be enhanced by CO activation, leading to significant enhancement of Ce³⁺, oxygen vacancy (O_V) and active oxygen concentration that are beneficial for the formation of electron-enriched Ru^{δ -} species, Ru^{δ -}-O_V-Ce³⁺ sites and surface active oxygen. As a result, there is significant change of hydrogen adsorption property, and the Ru/CeO₂ catalyst after CO activation shows higher ammonia synthesis activity, with the ill effect of hydrogen poisoning significantly alleviated.

2. Experimental Section

2.1. Catalyst Preparation

CeO₂ was prepared according to the process described elsewhere.^{10, 32} The RuNO₃/CeO₂ was obtained by incipient wetness impregnation of ceria with ruthenium(III) nitrosyl nitrate solution (1.5% w/v, Aldrich), and the nominal Ru-to-ceria weight ratio was 1%. A portion of the obtained RuNO₃/CeO₂ was reduced in hydrogen at 550 °C for 6 h and is herein denoted as Ru/CeO₂-H. The rest of RuNO₃/CeO₂ was treated in CO gas at 250 or 500 °C for 2 h to obtain Ru/CeO₂-Cx, where x is the CO treatment temperature.

Afterwards, Ru/CeO_2 -Cx was reduced in hydrogen at 550 °C for 6 h, and the as-obtained catalysts are denoted as Ru/CeO_2 -Cx H.

2.2. Catalyst Characterization

D/H exchange reaction was conducted on a Micromeritics AutoChem II 2920 equipment. First, 100 mg of a sample was treated at 550 °C for 6 h in hydrogen, then purged with Ar and cooled down to 400 °C. Afterwards, the sample was exposed to D_2 and held at 400 °C for 1 h. After cooling to 50 °C in D_2 and purged with Ar for 1 h, the sample was exposed to a $3.3\%N_2$ -10%H₂-Ar mixture, and the mass signals were recorded by a Hiden Analytical HPR-20 spectrometer.

Temperature-programmed surface reaction (TPSR) measurement was carried out on the same AutoChem II 2920 instrument. The fresh sample was exposed to D_2 , Ar, or N_2 at 400 degC for 1 h, and then cooled to 50 degC in the gas selected for exposure. Finally, the feed gas was switched to a $3.3\%N_2$ -10%H₂-Ar mixture, and the catalyst sample was heated to 600 degC.

Other characterizations including N_2 physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), hydrogen temperature-programmed reduction (H₂-TPR), X-ray phototoelectron spectroscopy (XPS), H₂chemisorption, are given in Supporting Information.

2.3. Catalyst Evaluation

Ammonia synthesis was carried out in a continuous flow fixed-bed stainless steel reactor (inner diameter = 12 mm). Prior to reaction, the catalyst (0.20 g, 32–60 mesh) was diluted with quartz sand of similar size and reduced in a stoichiometric H_2-N_2 gas mixture at 550 degC for 6 h. There were no external and internal diffusion limitations under the conditions adopted in this work.³³⁻³⁴ Catalyst evaluation was conducted after the reaction was maintained for more than 3 h under a selected condition. The produced ammonia was trapped by sulfuric acid solution and then analyzed by ion chromatography (Thermo Scientific, ICS-600); subsequently, the reaction rates and TOF values could be obtained.

3. Results and Discussion

3.1 Structure Characterization

The BET areas of prepared Ru catalysts are in the range of $81-86 \text{ m}^2 \text{ g}^{-1}$ (Table S1), indicating that the adopted treatment conditions have only a slight effect on the specific surface area of Ru catalysts. XRD patterns of cubic fluorite CeO₂ phase (JCPDS 34-0394) can be observed for all samples (Figure S1), suggesting that the treatments do not alter the crystal phase of ceria support. There is no detection of diffraction peaks ascribable to Ru species, indicating well dispersion of Ru species on ceria, which is in consistent with the aberration-corrected HAADF-STEM images (Figure S2). The as-prepared RuNO₃/CeO₂ catalyst shows two Ru $3d_{5/2}$ peaks at 281.4 eV and 282.8 eV that are characteristic of Ru⁴⁺ and Ru⁶⁺, respectively (Figure S3).^{10, 35-38} Strong hydrogen reduction peak at 128 degC and a weak shoulder peak at 200 degC in the H₂-TPR profile of RuNO₃/CeO₂ can be assigned to the reduction of RuO_x and CeO₂, respectively (Figure S4). However, only a broad and weak hydrogen consumption peak in the temperature range of 70 to 400 degC can be observed over the Ru/CeO₂-C250 and Ru/CeO₂-C500 catalysts, indicating that most of the Ru species has been reduced during CO activation.

The distinct bands corresponding to reduced Ru^{0} species can be observed in the DRIFTS spectra taken over $\mathrm{RuNO_3/CeO_2}$ exposed to CO at 150 degC (Figure S5), indicating that Ru oxides on the ceria surface can be activated by CO at 150 degC. A further increase of activation temperature would lead to the dissociation of CO molecules on the Ru surface, and the produced oxygen could oxidize metallic Ru species and spillover to ceria, a phenomenon similar to that observed over ceria-supported Co catalyst as reported by Parastaev et al.³¹ As a result, the presence of ruthenium oxide can be detected in the DRIFTS (Figure S5) or XPS investigations of Ru/CeO₂-C500 (Figure S6). There are three distinct CO bands at 1985, 2063 and 2125 cm⁻¹ in the DRIFTS spectra of the Ru/CeO₂-H, Ru/CeO₂-C250H and Ru/CeO₂-C500H catalysts (Figure

S7), which are assignable to bridge-type CO species bonded to Ru metal, linearly adsorbed CO species on reduced Ru particles, and carbonyl species on partially oxidized Ru (Ruⁿ⁺), respectively,^{37, 39-40} indicating the coexistence of ruthenium oxide and ruthenium metal for all samples.

Presented in Figures 1a–c are the XPS Ce 3d, Ru 3d and O 1s spectra of the as-prepared ceria-supported Ru catalysts. The Ce 3d profiles can be deconvoluted into ten peaks, two pairs of $3d_{5/2}$ (880.4 eV and 884.8 eV) and their $3d_{3/2}$ features are assigned to Ce^{3+} species, and the other six Ce 3d peaks are ascribed to Ce^{4+} species. The O 1s spectra can be deconvoluted into two peaks at 529.0 eV and 531.2 eV, which are characteristic of lattice oxygen and oxygen vacancies (O_V), respectively.^{35-36, 41} Compared to the use of H₂ as reducing agent, the use of CO can lead to pronounced ceria reducibility of ceria-supported metal catalysts.^{29, 42} Thus the Ce^{3+} and O_V concentrations of the CO activated samples, as evaluated by the ratios of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ and O_{β}/O_{α} ,^{35, 41} are higher than those of Ru/CeO₂-H (Figure 1d).

Figure 1 XPS spectra of as-prepared Ru catalysts (a) Ce 3d, (b) Ru 3d, and (c) O 1s; (d) $Ce^{3+}/(Ce^{3+}+Ce^{4+}), O_{\beta}/O_{\alpha}$ and $(Ru^0+Ru^{\delta-})/(Ru^0+Ru^{\delta-}+Ru^{n+})$ intensity ratios.

Besides the Ru $3d_{5/2}$ peaks of ruthenium oxides (Ru⁴⁺ and Ru⁶⁺), there is a new Ru $3d_{5/2}$ peak at 279.8 eV for the Ru/CeO₂-H, Ru/CeO₂-C250H and Ru/CeO₂-C500H catalysts (Figure 1b), which is characteristic of metallic Ru^{0,10, 35-38} Because some Ru species is covered by suboxides originated form ceria, the $Ru^0/(Ru^0+Ru^{n+})$ ratio of Ru/CeO_2 -H is much smaller, only11.7%, which can be related to SMSI. During hydrogen treatment of ceria-supported Ru catalysts, reverse oxygen spillover from ceria to ruthenium oxides leads to the formation of oxygen vacancies as well as the encapsulation of Ru metal by suboxides (Figure S8).^{31, 43-44} As a result, the proportion of exposed Ru species would decrease, and the Ru 3d to Ce 3d intensity ratio (I_{Ru 3d}/I_{Ce3d}) is 0.0056 for Ru/CeO₂-H, which is lower than that of the corresponding sample without heat treatment (0.0075). The suboxides would hinder the reduction of Ru oxide, thus a high proportion of Ru species in the form of ruthenium oxide still exists after hydrogen reduction. On the other hand, the oxygen vacancies and partially reduced ceria can provide electrons to Ru metal,^{8, 45} leading to the formation of electron-enriched Ru species (Ru^{δ -}), in line with the observation over Au catalyst.⁴⁵ In such a case, the presence of a larger amount of Ce³⁺ and oxygen vacancy over the Ru/CeO₂-C250H and Ru/CeO₂-C500H samples would result in increase of Ru^{δ -}, causing a shift of Ru 3d_{5/2} peak to lower binding energy. The dissociation of CO on Ru surface and the spillover of oxygen that follows would hinder Ru species from being covered by ceria,³¹ and the presence of Ru metal causes the reduction of ceria preferentially following the hydrogen spillover mechanism during the subsequent hydrogen treatment of the CO-activated samples (Figure S8). Then the $(Ru^0 + Ru^{\delta-})/(Ru^0 + Ru^{\delta-} + Ru^{n+})$ ratio increases up to 71.6% and 60.6% for Ru/CeO₂-C250H and Ru/CeO₂-C500H, respectively, and the I_{Ru3d}/I_{Ce3d} ratio also increases for Ru/CeO_2 -C250H (0.01) and Ru/CeO_2 -C500H (0.0095).

Raman experiment was conducted to study the defects of samples, and the results are shown in Figure 2. Four peaks can be found in the Raman spectrum of CeO₂: a strong peak at 460 cm⁻¹ (fluorite F2g mode) and three weak peaks at 250, 587 and 1180 cm⁻¹, corresponding to second-order transverse acoustic mode (2TA), defect-induced mode (D), and second-order longitudinal optical mode (2LO), respectively.^{28, 35, 41, 46-48} The Raman peaks at 250 cm⁻¹ and 460 cm⁻¹ shift to lower wavenumber after the introduction of Ru species into ceria for Ru/CeO₂-H, suggesting that there is electron transfer from Ru species to CeO₂ for the hydrogen reduced Ru/CeO₂.⁴⁹ The I₍₅₈₇₊₁₁₈₀₎/I₄₆₀ ratio that reflects defect concentration such as oxygen vacancies,^{41, 46, 50-51} was calculated by means of peak fitting. It is obvious that the presence of Ru species results in an increase of ceria defects, in agreement with previous results.^{10, 35} The two peaks at 695 cm⁻¹ and 970 cm⁻¹ are assignable to the Ru⁵-O_V-Ce³⁺ bond of Ru/CeO₂-H arising from metal–support interaction.^{28, 35, 51} The number of ceria defects and Ru⁵-O_V-Ce³⁺ bonds significantly increase for Ru/CeO₂-C250H and Ru/CeO₂-C500H. It is especially so in the case of CO activation at 500 °C. Among the three prepared catalysts, Ru/CeO₂-C500H is the highest in the amount of ceria defects and Ru⁵-O_V-Ce³⁺ bonds. Referring to pure ceria, the peak of fluorite F2g mode remains unchanged in the Ru/CeO₂-C250H and Ru/CeO₂-C500H cases, indicating that the transfer of electron from Ru species to CeO₂ is inhibited, which is consistent with the XPS result that electron transfer is from ceria to Ru species.

Figure 2 (Left) Raman spectra of various samples and (Right) $I_{695+970}/I_{460}$ and $I_{587+1180}/I_{460}$ intensity ratios.

Overall, combining the DRIFTS, XPS and Raman results, it can be deduced that the reducibility and exposure of Ru species would significantly increase after CO activation of Ru/CeO₂ catalyst, resulting in significant enhancement of Ce^{3+} , oxygen vacancy and $Ru^{\delta-}O_V$ - Ce^{3+} concentrations.

3.2 Ammonia synthesis performance

Figure 3 reveals the temperature dependence of ammonia synthesis rate and the reaction orders over the prepared catalysts. The increase of reaction temperature leads to enhancement of catalytic activities for all samples, and the Ru/CeO_2 catalysts subjected to CO activation show higher ammonia synthesis rates than that subjected to hydrogen reduction only. The rates of Ru/CeO_2 -C250H and Ru/CeO_2 -C500H are 8.03 mmol g_{cat}⁻¹ h⁻¹ and 9.24 mmol g_{cat}⁻¹ h⁻¹ at 400 °C and 1.0 MPa, which are roughly two-fold that of Ru/CeO₂-H (4.06 mmol $g_{cat}^{-1} h^{-1}$) under the same reaction conditions. The turnover frequencies for Ru catalysts with CO activation are comparable to those of Ru catalysts reported in literatures (Table S2).^{7, 9, 52-57} As shown in Figure S9, Ru/CeO₂-C250H and Ru/CeO₂-C500H show stability better than that of Ru/CeO₂-H. The estimated activation energies are 60, 67 and 72 kJ mol⁻¹ for Ru/CeO₂-H, Ru/CeO₂-C250H and Ru/CeO₂-C500H, respectively, suggesting that the significant discrepancy in ammonia synthesis activity among the three cannot be directly attributed to the change of activation energy. The reaction orders of N_2 are 1.0, 1.2 and 1.3 for Ru/CeO₂-H, Ru/CeO₂-C250H and Ru/CeO₂-C500H, respectively, and the corresponding reaction orders of NH_3 are -0.72, -0.75 and -0.79. On the other hand, the estimated H_2 reaction order is negative (-0.53) for Ru/CeO₂-H, but changes to 0.3 and 0.36 for Ru/CeO₂-C250H and Ru/CeO₂-C500H, respectively, suggesting that CO activation can alleviate the problem of hydrogen poisoning for Ru catalysts. Hence the increase of reaction pressure form 1 to 7 MPa leads to a more significant enhancement of the activity for the CO-activated Ru catalysts (Ru/CeO₂-C250H and Ru/CeO₂-C500H) in comparison with the Ru/CeO₂-H catalyst (Figure S10). It can also be deduced that CO activation mainly affects the performance of Ru/CeO_2 catalysts by changing the hydrogen adsorption/desorption property.

Figure 3 (a) Temperature dependence of ammonia synthesis rate (0.2 g, 1.0 MPa, 120 mL min⁻¹) and (b) N_2 , H_2 and NH_3 reaction orders.

3.3 Adsorption property of Ru catalysts

To better understand why CO activation enhances the performance of Ru/CeO_2 catalysts, various characterization techniques were employed to investigate the activation of the catalysts as well as the adsorption and desorption of reactants. H_2 molecules can dissociate on Ru^0 metallic sites to form hydrides, and then the H atoms can spillover to the support to generate hydroxyl groups.⁵⁸⁻⁶⁰ Molecular H₂ also dissociate on ceria to form heterolytic products (Ce-H and OH) and homolytic products (two OH groups).⁶¹⁻⁶² The presence of Ru species facilitates the desorption of hydrogen species at a raised temperature either in the form of water or hydrogen molecule (Figure S11). A D/H exchange reaction was designed to explore the adsorption nature of hydrogen on the Ru catalysts. After D₂adsorption at 400 degC and Ar purging at 50 degC for 60 min, a 3.3%N₂-10%H₂-Ar mixture was introduced to the catalysts (Figure 4). Although a large amount of hydrogen species would adsorb on ceria (Figure S11), there is little production of D-containing species during D/H exchange reaction at 50 degC, which might be due to the strong adsorption of D species. Compared to CeO_2 , the production of HD, D_2 , HDO and D_2O is significantly higher over the Ru catalysts, confirming that the presence of Ru species facilitates desorption of D species. Because the concentrations of HD and HDO are much larger than those of D_2 and D_2O , it can be concluded that there is dynamic exchange of deuterium species adsorbed on Ru and the hydrogen species from gaseous phase. Furthermore, the signals of HDO and D_2O evolution over Ru/CeO_2 -C500H are stronger than those over Ru/CeO_2 -H, revealing that there is a larger amount of D species on the former that would desorb from Ru sites by reacting with neighboring oxygen atoms. The presence of active oxygen on the Ru catalysts is confirmed by CO-TPR analysis; and the amount of active oxygen on the CO activated catalysts are higher than that on the hydrogen-treated one (Figure S12). Moreover, two CO_2 evolution peaks at 190 degC and 363 degC can be found over the CO activated Ru catalysts, proving that there are surface lattice oxygen species which would much more easily react with $CO.^{63-64}$ The CO_2 evolution peaks at 190 degC and 363 degC are absent in the case of Ru/CeO₂-H. The discrepancy in the property of surface lattice oxygen might be attributed to the pathways of oxygen spillover during the thermal treatment process as a result of using different agents for the reduction of the Ru catalysts (Figure S8).

Figure 4 Evolution profiles of HD, D_2 , HDO, and D_2O with time at 50 degC detected by mass spectrometry during the D/H exchange reaction.

In comparison with the Ru/CeO₂-H and Ru/CeO₂-C500H catalysts, much stronger HD, D₂, HDO and D₂O signals are observed over ceria with the rise of temperature during TPSR study in 3.3%N₂-10%H₂-Ar mixture over the samples pre-adsorbed with D₂ (Figure S13), further confirming that the presence of Ru species facilitates the desorption of deuterium species. Despite significantly weaker, there are HD and D₂ desorption over the ceria-supported Ru catalysts below 300 degC, suggesting that most of the deuterium species adsorbed on ceria could be removed during TPSR study. It can be concluded that the hydrogen species from the gaseous phase is responsible for ammonia synthesis, which is in line with the observation of Kammert et al. over Ru/C12A7 electride catalyst. It was report that hydrogen species adsorbed on Ru species, rather than the hydride encaged in the C12A7 electride contributed to ammonia synthesis.⁶⁵ Despite most of the deuterium species pre-adsorbed on Ru or ceria in the Ru catalysts has been removed, a series of reaction steps, such as the dissociative adsorption of H₂ and N₂, the reaction of hydrogen atoms and nitrogen atoms, the formation of water and desorption of NH_x intermediate species, would continue on the active sites of Ru catalysts. As a result, the difference in the nature of active sites would exert a strong influence on the reaction pathways of ammonia synthesis.

A possible mechanism for ammonia synthesis over the ceria-supported Ru catalysts is proposed in Figure 5. There is EMSI between Ru metal and ceria, and CO activation leads to significant enhancement of Ru species exposure, Ce^{3+} concentration, and number of oxygen vacancy. The oxygen vacancies and partially reduced ceria would provide electrons to Ru metal, leading to the generation of electron-enriched Ru^{δ-} species and Ru^{δ} -O_V-Ce³⁺ sites. There is electron donation from Ru^{δ} to the antibonding orbital of adsorbed N_2 , resulting in weakening of N[?]N bond.⁵⁶ The H₂molecules can dissociate on Ru metal sites to form hydrides, and some of the H atoms migrate to the ceria support and are stabilized by oxygen species. However, too much hydrogen species would hinder nitrogen dissociation and hence the reactions of ammonia synthesis; thus the pre-adsorption of D_2 leads to notable decrease of NH_x mass signals (m/z=15, 16 and 17) over Ru/CeO_2 -C500H (Figure S14). Nonetheless, with CO activation, there is ample active oxygen in the Ru catalysts to remove the surplus hydrogen species on Ru sites, releasing the active sites for N_2 dissociation and ammonia synthesis. An overall outcome is the alleviation of hydrogen poisoning effect. Wu et al. reported that the increase of hydrogen species mobility using polar MgO(111) instead of nonpolar MgO could lead to lessening of hydrogen poisoning for Ru/MgO catalyst.⁶⁶ Meantime, there are stronger NH and NH₂ signals over Ru/CeO₂-C500H as compared to those over Ru/CeO₂-H during TPSR study (Figure S15). There is water evolution during TPSR study for all Ru catalysts, indicating that the hydrogen species located on surface oxygen participate not only in ammonia formation by reverse spillover, but also in water generation/desoprtion that leads to replenishment of oxygen vacancies. On the other hand, it is envisioned that the spillover effects would be weakened for Ru/CeO_2 catalyst with large Ru particles, and the result shows that the positive effect of CO activation on ammonia synthesis decreases with the increase of Ru loading (Figure S16).

Figure 5 Possible ammonia synthesis pathways over a ceria-supported Ru catalyst. (a) Electron transfer from partially reduced ceria and oxygen vacancies to Ru metal on ceria surface, (b) N[?]N bond weakening as a result of electron donation from the electron-enriched Ru^{δ} species to the antibonding orbital of N₂, together with H₂dissociative adsorption on Ru surface, and H atom migration and stabilization by oxygen species. (c) N atoms on Ru surface react with the neighboring H atoms for form ammonia. Also, H atoms in ceria desorb via water generation.

4. Conclusions

We have successfully prepared ceria-supported Ru catalysts with high degree of reduction and high exposure of Ru species by CO activation. The CO treatment also leads to significant increase of Ce^{3+} , oxygen vacancy and active oxygen concentration. A combination of DRIFTS, XPS and Raman investigations reveals that the evolution of partially reduced ceria and oxygen vacancies would lead to the formation of electronenriched Ru^{$\delta-$} species and Ru^{$\delta-$}-O_V-Ce³⁺ sites, which would facilitate the dissociation of dinitrogen. The D/H exchange and TPSR experiments show that there is dynamic exchange of hydrogen species adsorbed on Ru catalysts with that from the gaseous phase. The presence of a larger amount of active oxygen on the CO activated Ru catalysts can help remove the surplus hydrogen species on the Ru sites, releasing the active sites for N₂adsorption/dissociation and ammonia synthesis. As a result, CO activation of Ru/CeO₂ catalyst significantly enhances the ammonia synthesis activity, showing roughly a two-fold increase, and the ill effect of hydrogen poisoning for Ru catalysts is alleviated. These findings are important for the design of supported metal catalysts for reactions that are based on metallic active sites.

Supporting Information

The calculation results of mass transport and heat transfer, reaction orders, temperature dependence of ammonia synthesis rates, Arrhenius plots, time dependence of ammonia synthesis rates, HAADF-STEM image and the corresponding element mappings, TEM images, DRIFTS spectra, XPS Ce3d spectra, O1s spectra, mass signals obtained from H_2 -TPD measurement, Time-resolved D/H exchange reaction and TPSR, D₂-TPD of ceria, textural property of samples, Catalytic performance of various Ru catalysts reported elsewhere and related references.

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