

Insights into Ru Crystal Phase Regulated by Reducing Agent for the Catalytic Activity of Ammonia Synthesis

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Abstract: Ru nanoparticles with fcc and hcp crystal phases were obtained by chemical reduction method using different precursors and reducing agents, and their catalytic properties in ammonia synthesis were compared. The catalytic reaction rate ($666.4 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) of fcc Ru catalyst is higher than that of hcp Ru ($378.9 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) at the reaction temperature (400°C) and pressure (1 MPa). The results indicate that the exposed crystal faces have a certain impact on the catalytic activity. The dissociation ability to N_2 of fcc Ru exposed (111) and (200) is better than that of hcp Ru exposed (100). When the ruthenium catalyst was loaded on rod-like CeO_2 support, the ammonia synthesis activity was further improved. The ammonia synthesis activity of fcc Ru/ CeO_2 is 1.4 times higher than that of hcp Ru/ CeO_2 under the test conditions.

Key words: Ru nanocatalyst; crystal phase control; ammonia synthesis

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With the increasing global greenhouse effect and increasingly serious global warming phenomenon, ammonia has attracted wide attention as a green energy source, because it does not produce carbon dioxide during combustion. In the meanwhile, ammonia is one of the important basic chemicals and an important fertilizer raw material, which is widely used in the manufacture of textiles, plastics and fertilizers^[1]. At present, the conventional Haber-Bosch process continues to be employed for industrial ammonia synthesis, which uses Fe-based catalysts and requires harsh reaction conditions ($300\sim 500^\circ\text{C}$, $10\sim 30\text{ MPa}$)^[2]. Due to the high energy required for ammonia synthesis, 2% of global energy is used to produce ammonia each year^[3]. Therefore, it is very important to develop efficient ammonia synthesis catalysts under mild conditions. At low temperature and low pressure, the ammonia synthesis activity of Ru catalyst is better than that of Fe catalyst^[4-5]. However, as a precious metal, the concentration of Ru in the Earth's crust is 1.0×10^{-9} , so its high price impedes its further application in industry^[6]. Therefore, it is necessary to improve the catalytic performance of Ru. Thus, the economical and sustainable utilization of Ru as a precious metal in ammonia synthesis can be realized.

DFT calculation and experiments show that the synthesis of ammonia on Ru-based catalyst is a structure-sensitive reaction, where in the particle size, morphology and exposed facets of Ru nanoparticles significantly influence their catalytic activity^[7-10]. The B5 site is a collection of 5 Ru atoms on Ru nanoparticles and is the most active center for N_2 dissociation. The small-size particles of 1.8~3.5 nm are more conducive to

the formation of the B5 sites^[11]. The performance of Ru based catalyst is related to the electronic structure of Ru nanoparticles. A series of studies have proved that the catalytic performance of the catalyst can be achieved by adjusting the electronic state of the Ru-based catalyst. Wei *et al.*^[12] found that Ru loaded on CeO_2 and MgO-CeO_2 have different electronic states and thus exhibit different catalytic activities. Nagaoka *et al.*^[13] modified the Ru electronic structure through the strong interaction between metal and the reduction support, thereby improving the ammonia synthesis activity.

In addition, most metals have bcc, hcp and fcc three crystalline phase structures. The coordination environment and spatial distribution of metal atoms vary greatly in different crystal phases^[14]. Therefore, it is significant to regulate the crystal phase of the metal in improving the catalytic performance. In recent years, regulating crystal phase structure of Ru has gradually attracted the attention of researchers. Bulk Ru has hcp crystal structure in all temperature ranges^[15]. With the development of nanotechnology, Ru with fcc crystal phase can be stabilized under both synthetic and reaction conditions. Kitagawa *et al.*^[15] synthesized uniform sized Ru nanoparticles with different crystal phases using chemical reduction methods with different metal precursors. Recently, researches have been conducted on improving the catalytic activity by adjusting the crystal phase of Ru. Chen *et al.*^[16] investigated the effect of Ru crystal on hydrolytic dehydrogenation of ammonia borane. The results indicated that the catalytic performance of fcc Ru is mainly affected by surface oxidation, while the activity of hcp Ru is predominantly affected by the size effect. Ma *et al.*^[17]

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synthesized the water-dispersed fcc Ru catalyst with abundant open surfaces and improved its catalytic activity in Fischer-Tropsch synthesis. This is mainly because in the process of CO dissociation, fcc Ru exposed more active sites on the crystal surface than hcp Ru. Decomposing $\text{N}\equiv\text{N}$ requires a high energy barrier ($945 \text{ kJ}\cdot\text{mol}^{-1}$), so it is generally believed that N_2 dissociation is the rate determining step in ammonia synthesis^[18–19]. Xia's group^[20–23] reported the preparation of fcc Ru nanocages with different surface structures and evaluated the activity of fcc Ru for N_2 reduction synthesis of ammonia through DFT calculations. The results showed that N_2 molecules were more strongly binding to fcc-(111) than hcp-(0001). At the same time, the activation energy barrier of fcc-(111) for $\text{N}-\text{N}$ dissociation is decreased, indicating that fcc-(111) has a stronger effect on N_2 dissociation. In addition, although the (100) surface preferentially exposed by fcc Ru has a slightly weaker binding to N, its activation energy barrier is further reduced. These results indicate that Ru nanoparticles with fcc crystal phase are potential catalysts in ammonia synthesis. However, up to now, the study of Ru crystal phase in ammonia synthesis catalyst has been confined to theoretical calculation, and the experimental part has not been confirmed.

In this study, Ru nanoparticles with fcc and hcp crystal phases were obtained *via* chemical reduction method by controlling the precursor and reducing agent, and the catalytic properties in ammonia synthesis were compared. The fcc Ru catalyst shows higher catalytic reaction rate ($666.4 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) by comparing with the hcp Ru ($378.9 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) at the reaction temperature (400°C) and pressure (1 MPa). This is mainly because the exposed crystal faces of fcc Ru and hcp Ru nanoparticles are different, and the dissociation ability of fcc-(111) to N_2 is stronger, so it has higher ammonia synthesis activity, which is consistent with the theoretical research findings of predecessors. On this basis, the obtained Ru-based catalyst was loaded on rod-like CeO_2 support to further improve its ammonia synthesis activity. At 400°C , the activity of fcc Ru/ CeO_2 is $3\,309.1 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is 1.4 times higher than that of hcp Ru/ CeO_2 ($2\,314.5 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). The physical and chemical properties of the catalyst were characterized by TEM, XRD, XPS, TPR and TPD.

1 Experimental

1.1 Chemicals

All the reagents used in the experiment are commercially available. They can be directly used without any further purification or treatment. The purity of the gases used in the experiment was 99.999%.

1.2 Preparation of catalysts and support

For the synthesis of fcc Ru, 83.7 mg $\text{Ru}(\text{acac})_3$ and 55.5 mg PVP(k29-32) were dissolved in 10 mL triethylene glycol (TEG), and then heated in an oil bath at 200°C for 3 h. After cooling the reaction to room temperature, the products were washed and centrifuged with acetone. The volume ratio of acetone to the solvent used was 3. The preparation method of hcp Ru is similar to fcc Ru, except that 66.24 mg RuCl_3 as precursor and 10 mL glycol (EG) as solvent.

For the synthesis of CeO_2 , 6.96 g $\text{Ce}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 19.6 g NaOH were dissolved in 5 and 35 mL deionized water respectively, and then the two solutions were mixed, and finally, the obtained mixture transferred to a 50 mL

hydrothermal reactor at a height of 4/5, and stored in a vacuum oven at 100°C for 24 h. The precipitate obtained after hydrothermal reaction is washed with deionized water to neutral and dried in the oven at 60°C . After drying, the product was placed in a crucible and roasted in a muffle furnace at 450°C for 4 h at a heating rate of $2.5^\circ\text{C}\cdot\text{min}^{-1}$. After roasting, the sample was taken out and CeO_2 was obtained.

For the preparation of fcc Ru/ CeO_2 , 15 mg fcc Ru was dissolved in 15 mL deionized water, 0.5 g of prepared CeO_2 was added, impregnated and stirred at room temperature for 24 h, then centrifuged and washed with deionized water. The obtained product was fcc Ru/ CeO_2 after drying in a 60°C oven. The loading mass fraction of Ru is 3%. The preparation method of hcp Ru/ CeO_2 (Ru mass fraction, 3%) is similar to fcc Ru/ CeO_2 , except that the active metal used is 15 mg hcp Ru.

1.3 Catalyst evaluation

The catalyst activity was evaluated by ammonia synthesis. The experiment was conducted in a fixed bed, and the catalyst packed in a $\Phi 6$ mm stainless steel reaction tube at a dosage of 200 mg each time. The total flow rate of N_2 and H_2 is $60 \text{ mL}\cdot\text{min}^{-1}$ ($\text{N}_2/\text{H}_2=3$), and the reaction pressure is 1 MPa. After the catalyst stabilizes at the testing temperature, the outlet ammonia concentration was determined by chemical titration (Congo red as an indicator, the concentration of H_2SO_4 used was $0.05 \text{ mol}\cdot\text{L}^{-1}$).

1.4 Catalyst characterization

The crystal structure of the catalyst was characterized by X-ray powder diffraction (XRD) (X'Pert PANalytical, Dutch), using Cu-K α radiation ($\lambda=0.154\,050 \text{ nm}$), 2θ ranges were $5^\circ\sim 80^\circ$. The morphology and structure of the samples were analyzed by JEM-2010 transmission electron microscope (TEM) under 200 kV acceleration voltage. The elemental composition of the sample was detected by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), and the electron binding energy of all spectra was calibrated by C 1s at 284.8 eV. The TP-5080 instrument of Tianjin first right company was used for temperature programmed reduction (H_2 -TPR) and temperature programmed desorption (NH_3 -TPD, CO_2 -TPD, N_2 -TPD) experiments.

2 Results and discussion

We synthesized Ru nanoparticles with different crystal phases by chemical reduction method. By adjusting the precursors and reducing agents, Ru nanoparticles with different crystal phases were prepared. The morphology and particle size distribution of fcc Ru and hcp Ru were studied using TEM. Ru nanoparticles prepared by $\text{Ru}(\text{acac})_3$ and TEG exhibited fcc crystal phase, while those prepared by RuCl_3 and EG had hcp structure. As shown in Fig. 1(a) and (c), the diameter of fcc Ru nanoparticles is mostly 2.8 nm, while hcp Ru is 2.0 nm, which are consistent with the size distribution of B5 site of Ru catalyst in ammonia synthesis. The lattice fringes in HRTEM further confirm the difference between the two crystal phases. As displayed in Fig. 1(b) and (d), the lattice fringe of fcc Ru is 0.20 and 0.22 nm, corresponding to its (200) and (111) crystal planes, respectively. The lattice fringe of 0.23 nm in hcp Ru is the (100) crystal plane.

The structure of the prepared Ru nanoparticles was characterized using high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). As shown in Fig. 2, it can be observed that the hcp Ru

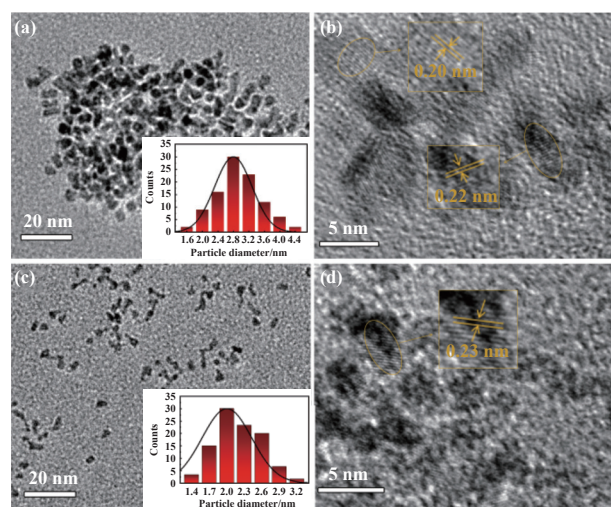


Fig.1 TEM images, particle size distribution and HRTEM images of fcc Ru (a, b) and hcp Ru (c, d)

nanoparticles (Fig. 2(a)) display the lamination sequence of hcp ABABAB... along the direction [100]. However, the fcc Ru nanoparticles showed the stacking order of ABCABC... (Fig. 2(c)), which shows the representing fcc [111] plane of Ru nanoparticles. In the SAED results, (111), (200), (220) and (311) planes of fcc Ru were observed, while hcp Ru showed (100) and (110) planes. Therefore, there are significant differences in the exposed crystal faces of Ru nanoparticles with different crystal phases.

XRD analysis further confirmed the difference of crystal phase between the two Ru nanoparticles. From Fig. 3, it can be seen that fcc Ru and hcp Ru exhibited different crystal faces, consistent with those previously reported^[22]. The diffraction peaks around 40.8°, 47.4° and 69.3° can be corresponded to (111), (200) and (220) planes of the fcc Ru, and the peaks at 38.4°, 42.2°, 44.0°, 58.3° and 69.4° can correspond to the (100), (002), (101), (102) and (110) diffractions of hcp Ru.

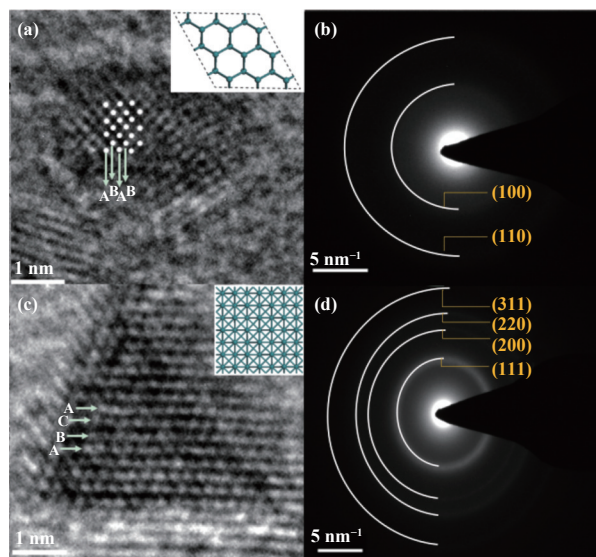


Fig.2 HRTEM and SAED images of hcp Ru (a, b) and fcc Ru (c, d)

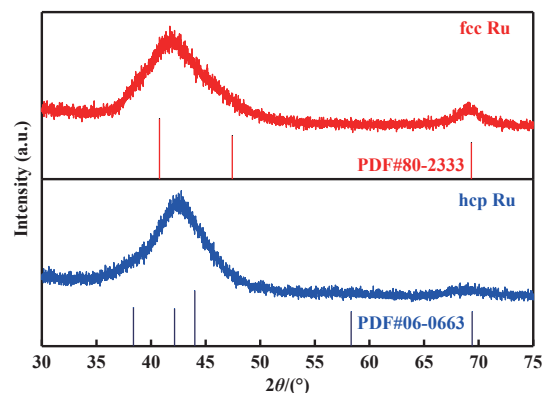


Fig.3 XRD patterns of fcc Ru and hcp Ru

Using ammonia synthesis as a model reaction, the influence of Ru crystal phase on catalytic reactions was investigated (Fig. 4). It was observed that the reaction rate (r) over fcc Ru ($666.4 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) is about 1.76 times than that of hcp Ru ($378.9 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) at the condition of 400 °C and 1 MPa (Fig. 4 (a)). The result clearly demonstrated that the crystal phase of Ru significantly affects the performance of ammonia synthesis. This is mainly because the exposed crystal surfaces of Ru nanoparticles with two crystal phases have different degrees of N₂ dissociation, which leads to the difference in catalytic ammonia synthesis performance. Combined with our experimental results and the theoretical calculation of Xia *et al.*^[18-21], the dissociation ability to N₂ of fcc Ru exposed (111) and (200) is stronger than that of hcp Ru exposed (100), so the catalytic performance of fcc Ru in ammonia synthesis is superior to that of hcp Ru.

To evaluate the support impact, CeO₂ was selected as support for Ru nanoparticles with two crystal phases. CeO₂ with nanorod morphology was synthesized (Fig. 4(d)) and fcc Ru/CeO₂ and hcp Ru/CeO₂ were obtained by loading Ru of two crystal phases. Fig. 4(c) shows the XRD patterns of the two catalysts. Interestingly, both samples showed typical characteristic peaks of CeO₂, and no diffraction peaks were observed for fcc Ru or hcp Ru species. This may be attributed to the low loading of Ru or the uniform distribution of active metal on the support. Fig. 4(b) showed that the catalytic activity of both fcc Ru/CeO₂ and hcp Ru/CeO₂ catalysts for ammonia synthesis reaction increased with the rise of temperature in the range of 340 to 400 °C. In addition, because of the strong interaction between the metal and the support, it was observed that the catalytic activity of the Ru-based catalyst supported on CeO₂ is higher than that of the unsupported Ru catalyst. Within in the testing temperature range, the ammonia synthesis activity of fcc Ru/CeO₂ was superior than that of hcp Ru/CeO₂. The activity of fcc Ru/CeO₂ at 400 °C is $3\,309.1 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is 1.4 times higher than that of hcp Ru/CeO₂ ($2\,314.5 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). This indicates that the crystal phase of Ru remains an important factor affecting the ammonia synthesis activity even when it is loaded on the support.

The elemental composition and electronic structure of Ru-based catalyst samples were further analyzed by XPS. Fig. 5 (a) and (b) show the Ru 3p_{3/2} orbital spectra of fcc Ru, hcp Ru, fcc Ru/CeO₂ and hcp Ru/CeO₂. Three Ru deconvolution peaks were observed at 461.5, 462.5 and 464.8 eV, corresponding to Ru⁰, Ru⁴⁺ (RuO₂) and Ru^{x+} (RuO_x, 4<x<8)^[24]. In all of these samples, the proportion of Ru⁰ is more than 50%, indicating

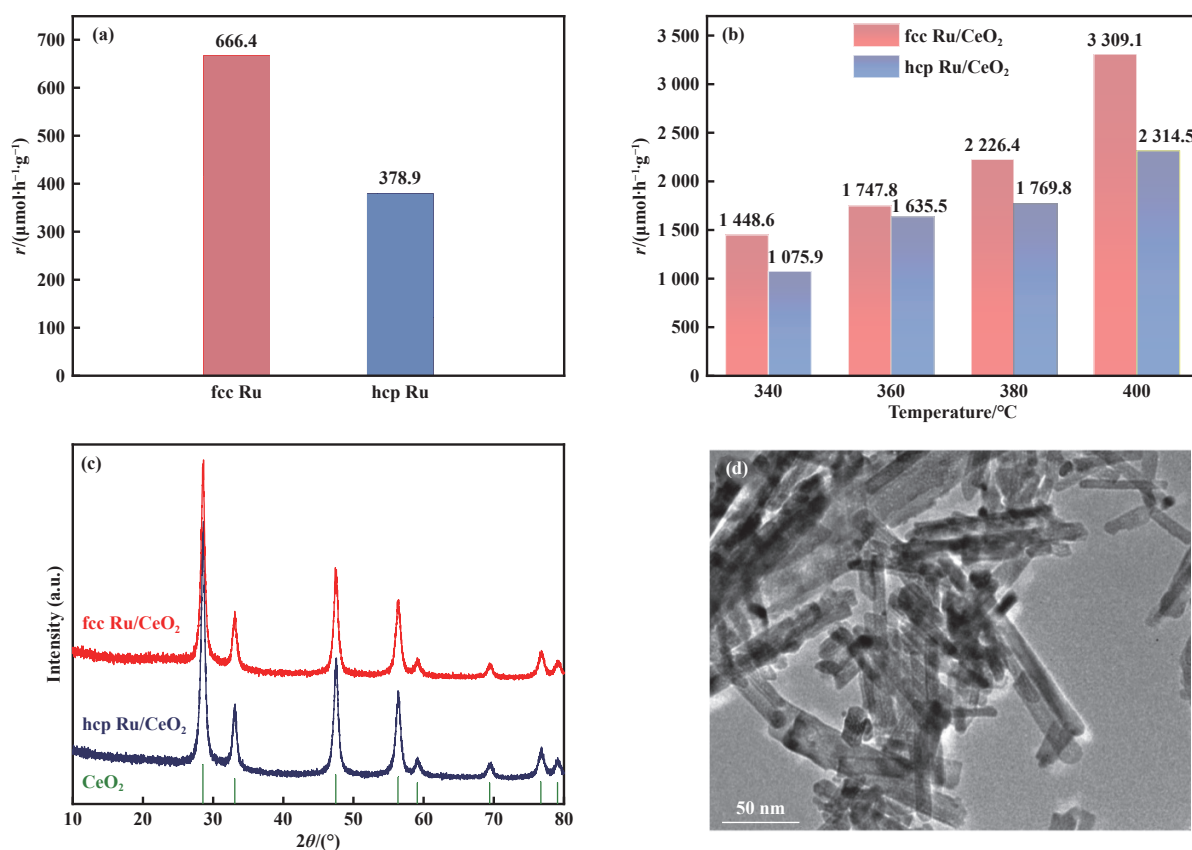


Fig.4 Ammonia synthesis activities of (a) fcc Ru and hcp Ru (400 °C, 1 MPa), (b) fcc Ru/CeO₂ and hcp Ru/CeO₂ (340–400 °C, 1 MPa); XRD patterns of fcc Ru/CeO₂ and hcp Ru/CeO₂ (c), TEM image of CeO₂ (d)

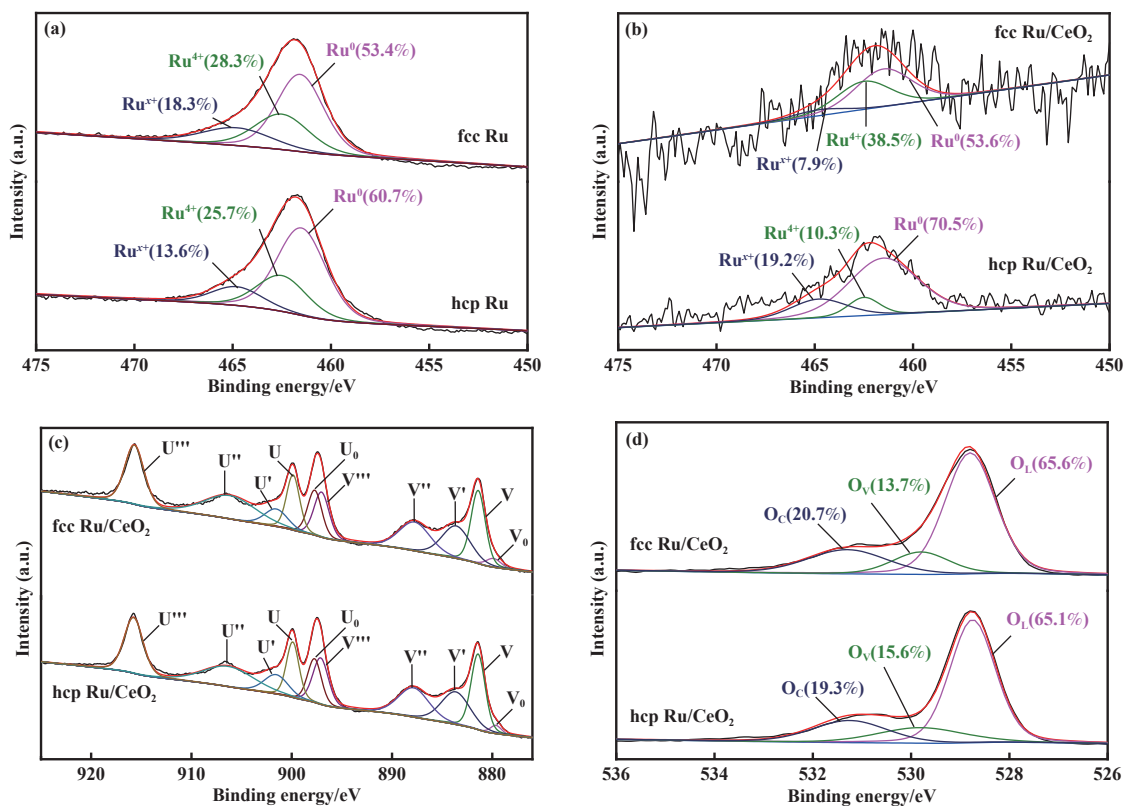


Fig.5 XPS spectra of Ru 3p (a, b), Ce 3d (c) and O 1s (d)

that it is more dominant than the positively charged Ru. This indicates that there are much Ru nanoparticles or clusters present on the catalyst surface. When Ru nanoparticles with different crystal phases are loaded onto CeO_2 support, the content of Ru^0 in fcc crystalline Ru was almost unchanged, the proportion of Ru^{4+} increased from 28.3% to 38.5%, and the proportion of Ru^{3+} decreased from 18.3% to 7.9%. The increase of Ru^{4+} content indicates the binding of $\text{Ce}-\text{O}$ bond to Ru nanoparticles and there is an interaction between metal and support. For Ru with hcp phase, the content of Ru^0 increases from 60.7% to 70.5%, the proportion of Ru^{4+} decreases from 25.7% to 10.3%, and the proportion of Ru^{3+} increases from 13.6% to 19.2%. This result shows that the content of Ru^0 is the most among the three Ru types, regardless of whether the Ru nanoparticles are loaded on the support or not. Metal Ru will promote the formation of weak basic sites^[25], which facilitates the dissociation of $\text{N}\equiv\text{N}$. The Ce 3d spectra is shown in Fig. 5(c), fitted to ten components. It can be seen that among the ten peaks, Ce^{3+} and Ce^{4+} exist simultaneously, and the four peaks labeled V_0 , V' , U_0 and U' belong to Ce^{3+} , while the six peaks V , V'' , V''' , U , U'' and U''' correspond to Ce^{4+} ^[26-27]. For the two samples, hcp Ru/ CeO_2 has a higher $\text{Ce}^{3+}/\text{Ce}^{4+}$ (0.43) compared to fcc Ru/ CeO_2 (0.36). The oxygen vacancies in hcp Ru/ CeO_2 are higher than those in fcc Ru/ CeO_2 because the existence of Ce^{3+} is related to oxygen vacancies. Fig. 5(d) shows the spectra of O 1s. O_L , O_V and O_C correspond to lattice oxygen bound with metal cations, O^{2-} in the oxygen-deficient region, and chemically absorbed and dissociated oxygen, respectively. The oxygen vacancy can be roughly calculated by O_V/O_L , and the result obtained is that hcp Ru/ CeO_2 (0.24) is higher than fcc Ru/ CeO_2 (0.21). In general, the presence of oxygen vacancies can increase the electron density on the Ru metal surface, thus enhancing ammonia synthesis activity^[28-29]. However, our results show that the fcc Ru/ CeO_2 with lower oxygen vacancy concentration exhibit higher ammonia synthesis activity, which indicates that the ammonia synthesis performance is more affected by the Ru crystal phase.

In order to investigate the reducibility of oxygen on the catalyst surface, H_2 -TPR test was conducted on the prepared catalyst. As shown in Fig. 6, there are two peaks were observed at 347 and 420 °C for fcc Ru, and at 391 and 477 °C for hcp Ru. These two peaks can be attributed to RuO_x species. When Ru of different crystal phases is loaded onto CeO_2 support, the reduction peaks of RuO_2 was observed below 300 °C (109 and 268 °C for fcc Ru/ CeO_2 , 117 and 266 °C for hcp Ru/ CeO_2),

suggesting that there is an interaction between Ru and the support that is conducive to H_2 reduction^[30]. The peaks around 800 °C correspond to the reduction of the bulk of CeO_2 ^[31]. In addition, the hcp Ru/ CeO_2 exhibits two reduction peaks at 363 and 588 °C, mainly due to the reduction of oxygen on the surface of CeO_2 ^[28]. Therefore, there is an interaction between the metal and the support, so that the catalyst supported on CeO_2 has a higher ammonia synthesis activity.

The electronegativity of the support has a significant impact on the performance of ammonia synthesis catalysts. The CO_2 -TPD profiles of different catalysts are shown in Fig. 7(a) and (b). The CO_2 desorption temperatures of fcc Ru and hcp Ru occurred at 220, 510 °C and 220, 530 °C, respectively. However, there are three desorption peaks of fcc Ru/ CeO_2 (137, 354 and 550 °C), while hcp Ru/ CeO_2 has only two peaks (147 and 332 °C). Generally speaking, the desorption temperature and number of desorption peaks of CO_2 are related to the intensity and quantity of basic sites, respectively^[14]. The CO_2 -TPD shows that fcc Ru/ CeO_2 is the strongest among the four catalysts, which is conducive to the electron transfer to Ru, thereby promoting N_2 activation and $\text{N}\equiv\text{N}$ dissociation, so fcc Ru/ CeO_2 has a higher ammonia synthesis activity.

Further understanding of the effect of Ru exposed crystal faces on ammonia synthesis activity was obtained through N_2 -TPD. As shown in Fig. 7(c) and (d), N_2 desorption occurred at 240, 502 °C (fcc Ru) and 229, 534 °C (hcp Ru), respectively, which indicating that fcc Ru has a strong adsorption capacity for N_2 . When loaded on CeO_2 , the number of N_2 desorption peaks increased, and the desorption of N_2 at fcc Ru/ CeO_2 and hcp Ru/ CeO_2 both occur at 150, 350 and 550 °C. These results indicate that the interaction between the metal and the support can promote the adsorption of N_2 .

The adsorption and desorption of NH_3 are also important factors in evaluating the activity of ammonia synthesis. The NH_3 -TPD profiles of different catalysts are presented in Fig. 7 (e) and (f). The desorption of NH_3 by fcc Ru and hcp Ru occurs between 230 and 450 °C. After loading on CeO_2 , the desorption temperature is advanced, and the first peak of NH_3 desorption is observed at 155 and 140 °C, respectively. There are five NH_3 desorption peaks in fcc Ru/ CeO_2 , while hcp Ru/ CeO_2 only has two peaks. The dissociation adsorption energy of N_2 is linearly related to the adsorption energy of NH_x ^[32]. The stronger the dissociation ability of the metal to N_2 , the more difficulty of subsequent hydrogenation to ammonia, and the weaker the adsorption energy of the metal, the more difficult it is for the

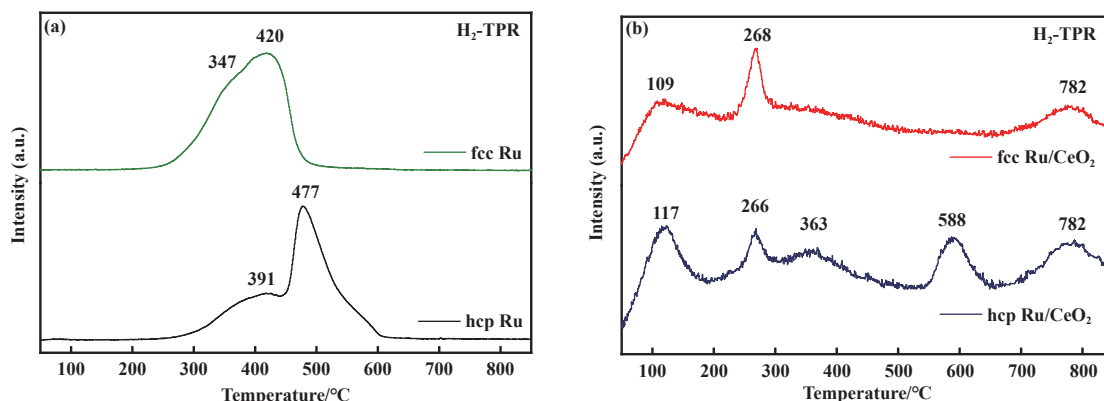


Fig.6 H_2 -TPR profiles of fcc Ru and hcp Ru (a), fcc Ru/ CeO_2 and hcp Ru/ CeO_2 (b)

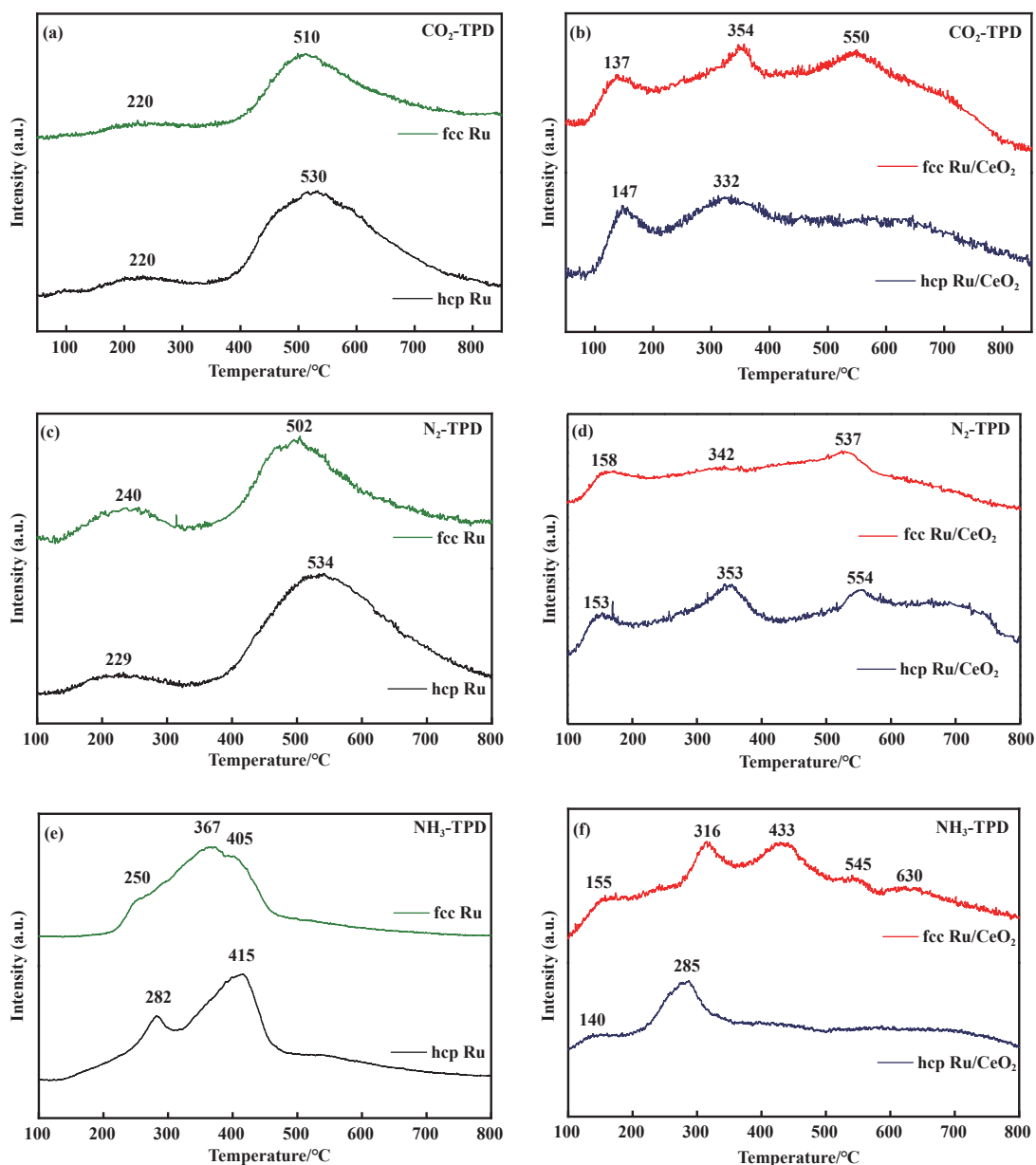


Fig.7 CO₂-TPD (a, b), N₂-TPD (c, d) and NH₃-TPD (e, f) profiles of fcc Ru and hcp Ru (a, c, e), fcc Ru/CeO₂ and hcp Ru/CeO₂ (b, d, f)

dissociation of N₂, and the lower the ammonia synthesis activity. Only when N₂ dissociation and NH_x desorption reach a relative equilibrium state, can higher ammonia synthesis activity be obtained. The Ru-based catalyst with fcc crystal phase has strong desorption of N₂, so the desorption of NH₃ is relatively weak. For Ru-based catalysts with hcp crystal phase, the activation capacity of N₂ is poor, but the desorption capacity of NH₃ is stronger. Therefore, the dissociation of N₂ and desorption of NH₃ of Ru-based catalysts with fcc crystal phase may be closer to the equilibrium state, and thus have higher ammonia synthesis activity.

3 Conclusions

In conclusion, Ru nanoparticles with fcc and hcp crystal phases were prepared by chemical reduction method by regulating metal precursors and reducing agents. The research results indicate that exposed crystal planes have a certain

impact on catalytic activity. The dissociation ability to N₂ of fcc Ru exposed plane (111) and (200) is better than that of hcp Ru exposed plane (100). The fcc Ru catalyst shows a higher ammonia synthesis rate (666.4 μmol·h⁻¹·g⁻¹) comparing with the hcp Ru (378.9 μmol·h⁻¹·g⁻¹) at the reaction temperature (400 °C) and pressure (1 MPa). On this basis, the obtained Ru-based catalyst was loaded on rod-like CeO₂ support to further improve its ammonia synthesis activity. The catalytic activity of fcc Ru/CeO₂ was higher than that of hcp Ru/CeO₂ in the test temperature range. At 400 °C, the activity of fcc Ru/CeO₂ is 3 309.1 μmol·h⁻¹·g⁻¹, which is 1.4 times higher than that of hcp Ru/CeO₂ (2 314.5 μmol·h⁻¹·g⁻¹). This indicates that the crystal phase of Ru metal is still an important factor affecting the ammonia synthesis activity even when it is loaded on the support. This work will help us to further understand the influence of the crystal phase effect of Ru-based catalysts on ammonia synthesis.

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还原剂调控的不同晶相纳米 Ru 催化剂对氨合成活性的影响

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摘要: 通过调控前驱体和还原剂, 采用化学还原法制备了具有不同晶相的 Ru 纳米颗粒, 分别为 fcc Ru 和 hcp Ru。研究了 Ru 晶相对氨合成反应活性的影响, 发现 fcc Ru 主要暴露的 (200) 和 (111) 晶面对 N₂ 的解离要优于传统 hcp Ru 的 (100) 晶面, 具有较高的氨合成活性。在 400 °C, 1 MPa 的测试条件下, fcc Ru 催化剂的反应速率为 666.4 μmol·h⁻¹·g⁻¹, 是 hcp Ru(378.9 μmol·h⁻¹·g⁻¹) 的 1.76 倍。进一步将两种晶相的 Ru 负载在 CeO₂ 载体上, 所得氨合成活性进一步提高, fcc Ru/CeO₂ 的氨合成活性仍高于 hcp Ru/CeO₂, 说明 Ru 的晶相对氨合成活性的影响占主导因素。

关键词: Ru 纳米催化剂; 晶相调控; 氨合成