

氯化钌氨作前驱体制备高活性的氨合成催化剂

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摘要: 以氯化钌和水合肼反应制备了新型的氯化钌氨前驱体 $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ 。透射电镜和 CO 化学吸附结果表明, 由 $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ 前驱体制备的活性炭(AC)负载的 RuN/AC 催化剂中, 钌纳米粒子分散度高, 粒径分布均匀。与以氯化钌为前驱体制备的 Ru/AC 催化剂相比, RuN/AC 催化剂具有更高的氨合成活性, 在 10 MPa 和 $10\,000\text{ h}^{-1}$ 条件下活性增幅超过 10%。

关键词: 氯化钌氨; 前驱体; 钌; 负载型催化剂; 氨合成

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Ruthenium Ammonium Chloride as a Precursor for the Preparation of High Activity Catalysts for Ammonia Synthesis

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Abstract: Ruthenium ammonium chloride, $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$, was prepared by the chemical reaction of ruthenium chloride with hydrazine hydrate and used as a novel ruthenium precursor for the preparation of activated carbon (AC)-supported Ru catalysts for ammonia synthesis. The results from TEM and CO chemisorption show that the Ru nanoparticles on the RuN/AC catalyst prepared from the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor have much higher dispersion and more uniform size distribution than that on the Ru/AC catalyst from the RuCl_3 precursor. The activity of the RuN/AC catalyst for ammonia synthesis was increased by more than 10% compared with the Ru/AC catalyst under the reaction conditions of 10 MPa and $10\,000\text{ h}^{-1}$.

Key words: ruthenium ammonium chloride; precursor; ruthenium; supported catalyst; ammonia synthesis

Ruthenium catalysts have been considered the second-generation catalysts for ammonia synthesis [1–3]. They show some unparalleled advantages in reduction of power consumption and increase of ammonia production at low temperature and low pressure [4–6]. However, the high cost of the precious metal obstructs the broad application of Ru catalysts in ammonia synthesis. One of the focuses for Ru-based catalysts is how to increase B_5 sites of Ru and improve the utilization ratio of Ru in the support [7–10].

The main precursors of Ru catalysts are $\text{Ru}_5(\text{CO})_{12}$, RuCl_3 , $\text{Ru}(\text{acac})_3$, $\text{RuNO}(\text{NO}_3)_3$, etc. The prices of different precursors vary significantly, and the low-cost precursors have high performance price ratio. Therefore, the relatively cheap precursor of RuCl_3 is widely adopted in the preparation of Ru catalysts. However, the Ru dispersion is relatively low,

and the particle size of the Ru/AC (AC = activated carbon) catalyst is nonuniform, which is not favourable for the full use of Ru [8–14].

Some researchers have investigated the pre-reduction of RuCl_3 and the modification of support in order to increase the effective utilization ratio of Ru. Recently, a sol-gel process of RuCl_3 for preparing well-defined Ru nanoparticles was focused [14,15]. However, the troublesome and time-consuming preparation procedures are the main obstacles for their extensive application.

In this paper, RuN/AC catalysts were prepared with the ruthenium ammonium chloride precursor, and this complex precursor was obtained by the reaction of ruthenium chloride with hydrazine hydrate. The Ru nanoparticles obtained were uniform and highly dispersed. The preparation method

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for Ru catalysts is simple, rapid, and suitable for large-scale preparation.

1 Experimental

1.1 Preparation of the ruthenium ammonium chloride precursor

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ($n = 1-3$, 37% of Ru content) and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ were used as starting materials. All chemicals used were analytical reagent grade and used without further treatment. The hydrazine hydrate was added dropwise into the aqueous solution of ruthenium chloride at ambient temperature. Subsequently, the black turbid solution turned into transparent pink by heating to boiling. Ruthenium ammonium chloride, $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$, was obtained by drying the transparent solution under an infrared lamp.

1.2 Preparation of the catalysts

Graphited activated carbon (AC) was sieved to 12–16 mesh and impregnated with $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ or RuCl_3 aqueous solution. The pH of the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ solution was adjusted with HNO_3 . The nominal Ru loading was 4.0% against the support. After drying under an infrared lamp, the samples were reduced in a flowing gas mixture of 75% H_2 in N_2 for 5 h at a certain temperature and then cooled to ambient temperature in the same flow. The Ba and K promoters were introduced by impregnation with $\text{Ba}(\text{NO}_3)_2$ solution followed by KOH, and the samples were dried under an infrared lamp. The content of Ba was 4.0% against the support. The catalysts obtained from RuCl_3 and $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursors were denoted Ru/AC and RuN/AC, respectively. The Ru/AC and RuN/AC catalysts promoted by $\text{Ba}(\text{NO}_3)_2$ and KOH were denoted 4%Ru-4%Ba-K/AC and 4%RuN-4%Ba-K/AC, respectively.

1.3 Characterization of the catalysts

Crystal structure of the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor was determined by powder X-ray diffraction (XRD) on an X'Pert PRO diffractometer using $\text{Co } K_\alpha$ radiation. The morphologies of Ru nanoparticles were studied using transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). The samples for the TEM test were treated with ultrasonic for 30 min in ethanol. CO chemisorption was carried out using a Micromeritics AutoChem 2910 instrument. Prior to the measurements, the catalyst (ca. 250 mg) was reduced in a H_2 stream at 723 K for 1.5 h and then flushed with a helium stream for 1.5 h to remove H_2 adsorbed on the catalyst surface. The sample was finally cooled in a helium stream to

323 K. CO chemisorption was measured by the pulse method by introducing CO flowing over the sample maintained at 298 K. Ru dispersion was calculated from the cumulative volume of CO adsorbed during pulse, assuming a chemisorption stoichiometry $n(\text{CO})/n(\text{Ru}) = 1$.

1.4 Measurements of catalytic activity

The catalyst activity for ammonia synthesis was measured in a stainless steel reactor. Before testing, the catalysts (2 ml) were activated in a flowing gas mixture of 75% H_2 in N_2 from ambient temperature to 773 K at 1 K/min (kept at 473, 573, 673, 723, and 773 K for 2 h, respectively) and then stabilized under the reaction conditions (i.e., 10 MPa, 673 K, $10\,000\text{ h}^{-1}$, and H_2/N_2 volume ratio of 3) for more than 2 h. The ammonia concentration in the effluent was determined by a chemical titration method [5].

2 Results and discussion

2.1 Effect of hydrazine hydrate to Ru molar ratio on the precursor structure

Fig. 1 shows the XRD patterns of the Ru precursor prepared at various molar ratios of hydrazine hydrate to Ru. The components included unreacted RuCl_3 when the molar ratio was 5. The main crystal phase was $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ (JCPDS 77-2443) at molar ratios of 5–20. When the molar ratio increased from 20 to 30, the $\text{Ru}(\text{NH}_3)_6\text{Cl}_2$ (JCPDS 73-

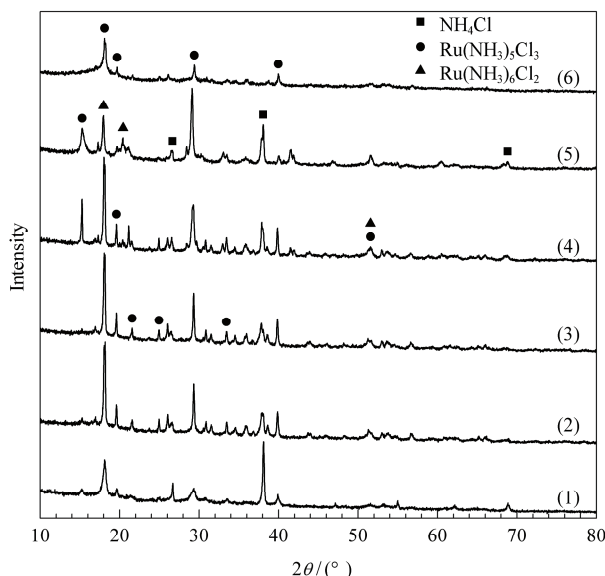


Fig. 1. XRD patterns of the Ru precursor prepared at different molar ratios of hydrazine hydrate to Ru. (1) 5; (2) 10; (3) 15; (4) 20; (5) 30; (6) After washing precursor (2) with ethanol to remove the NH_4Cl by-product.

1010) phase began to appear, which is a result of the reduction of $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ by hydrazine hydrate. The by-product was NH_4Cl (JCPDS 73-0365). In view of the above results, we prepared the precursor of ruthenium ammonium chloride with the molar ratio of hydrazine hydrate to Ru being 10. The precursors containing NH_4Cl were used directly without further treatment because NH_4Cl can sublimate to NH_3 and HCl at above 623 K [16]. For comparison, pure $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ was used to investigate the effect of K content on activity.

2.2 Effect of different precursors on the size distribution of Ru particles

Fig. 2 shows the TEM images of the Ru/AC catalyst from the RuCl_3 precursor and the RuN/AC catalyst from $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$. The reduction temperature of the two precursors was 723 K. It can be seen that Ru particles were highly dispersed on the AC surface for the Ru/AC catalyst, but the particle size distribution was not uniform. Some particles were ca. 1 nm, and the largest particle diameter was ca. 8 nm. A majority of particles had diameters from 3 to 5 nm [17]. For the RuN/AC catalyst, Ru particles were also highly dispersed on the surface of AC. The largest particle was ca. 8 nm, but very few large particles were detected. Most of the Ru particles were 2.5–3.0 nm in size, which afforded Ru particles having large specific surface area (Table 1) and more active sites according to the optimum scale of crystal sizes [7].

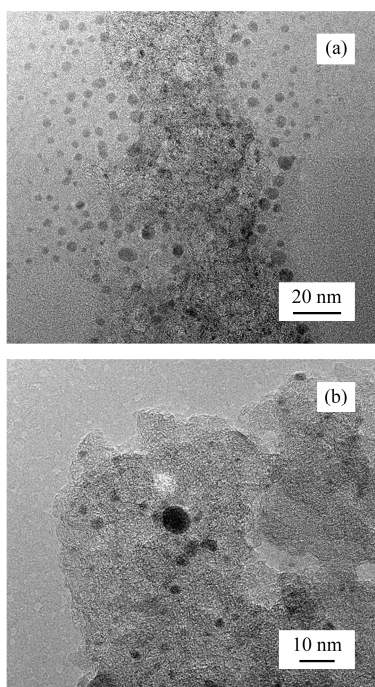


Fig. 2. TEM images of Ru/AC from the RuCl_3 precursor (a) and RuN/AC from the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor (b).

Table 1 Effect of the pH value of impregnating solution on Ru dispersion measured by CO chemisorption

Catalyst	pH	Ru dispersion ^a (%)	A_{BET} of Ru (m^2/g)	Ru size (nm)
Ru/AC	1.0	33.15	121.10	4.0
RuN/AC	1.0	48.99	178.96	2.6
	3.0	46.21	168.81	2.8
	5.0	44.03	160.85	2.9
	7.0	44.40	162.57	2.9

^aReduction temperature: 723 K.

The TEM results show that different precursors significantly influenced the size of Ru nanoparticles. The particles in RuN/AC were more uniform than those in Ru/AC. It is known that there exist many groups on the surface of AC, such as carbonyls and lactones [18–21], and the amount and variety of these functional groups determine the Ru dispersion [22]. The interaction between different precursors and the functional groups is dissimilar, and strong interaction leads to high dispersion [11]. $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ has more available adsorption sites than RuCl_3 , which led to a much stronger interaction between the precursor and support. The TEM results corroborated this speculation. From Fig. 2, most of Ru particles on Ru/AC were on the carbon film of the copper TEM grid, but most of Ru particles on the RuN/AC were on the AC support. This phenomenon indicated that the Ru particles from $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ were anchored on the surface of AC.

B_5 sites are only present on crystals larger than 1.5 nm. The maximum probability for B_5 sites is found for particle sizes of 1.8–2.5 nm, and the probability monotonically decreases for particles larger than 2.5 nm [7]. In the Ru/AC catalyst, some particles were between 1 and 8 nm, but most of particles were 3–5 nm. This wide range is disadvantageous for the formation of B_5 -type sites. However, for the RuN/AC catalyst, the addition of hydrazine hydrate resulted in the Ru particle size distribution in the range of 2.5–3.0 nm, which suggested that more active sites existed in the RuN/AC catalyst from the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor [7].

It can be seen from Table 1 that the size of Ru particles determined from CO chemisorption was closely related with the precursors, but the influence of pH value of the impregnation solution was not remarkable. Comparing the data from CO chemisorption with the TEM results, it is clear that the Ru dispersion was consistent. The Ru size for the Ru/AC catalyst from CO chemisorption was 4.0 nm, in agreement with the TEM result. The Ru dispersion on the RuN/AC catalyst was significantly increased compared with that on the Ru/AC catalyst. The increase in Ru dispersion led to an increase in Ru surface area and therefore significantly influenced the catalyst activity. The use of the

$\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor was more favorable for dispersing Ru particles on the AC surface and increasing the utilization ratio of Ru.

2.3 Effect of preparation conditions on catalytic activity for ammonia synthesis

Fig. 3 shows the effect of catalyst reduction temperature on their activity for ammonia synthesis. The optimal reduction temperatures of $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ was 673 K, 50 K lower than that of Ru/AC [17]. Lower or higher reduction temperature resulted in a lower activity for ammonia synthesis.

This may be because chlorine ions could not be removed completely at lower reduction temperature, and residual chloride as a poison decreased the catalyst activity for ammonia synthesis. However, higher reduction temperature led to agglomeration of Ru nanoparticles, which decreased the number of B_5 active sites and also the catalyst activity.

Fig. 4 represents the effect of pH value of impregnating solution on activity of the RuN/AC catalyst reduced at 673 K. Ruthenium ammonium chloride is a complex with excellent water solubility, and its aqueous solution is neutral. The pH was adjusted by adding nitric acid without changing the physical state of the solution, which was different from RuCl_3 . Therefore, Ru loading at different pH with the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor was favorable. The activity varied in a very small range with increasing pH, which showed that the pH of the impregnating solution has little effect on the activity. This result indicated that the $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursor can be used by adjusting the pH of the impregnating solution or direct loading on the oxide support before reduction with hydrogen, which is different from the RuCl_3 precursor [14,15,23,24].

Fig. 5 shows the effect of K content on activity of 4%RuN-4%Ba-K/AC catalyst. In the tests, the $\text{Ru}(\text{NH}_3)_5\text{-}$

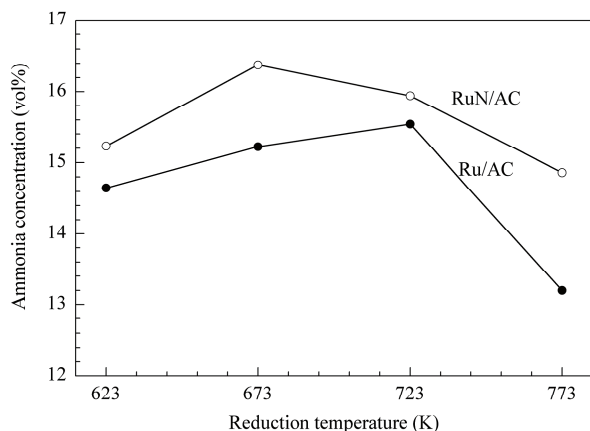


Fig. 3. Effect of reduction temperature on the catalyst activity for ammonia synthesis. Reaction conditions: 698 K, 10 MPa, 10000 h^{-1} , H_2/N_2 volume ratio of 3.

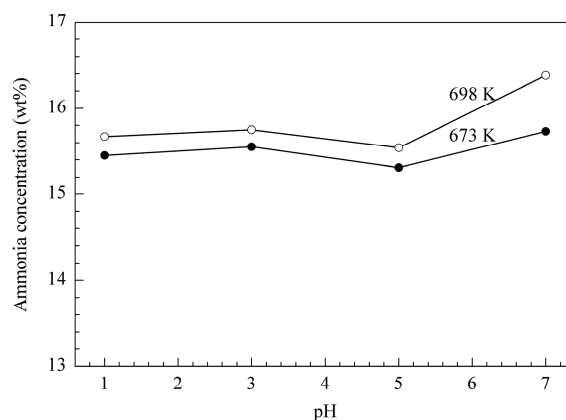


Fig. 4. Effect of pH value of impregnating solution on activity of the RuN/AC catalyst for ammonia synthesis at different reaction temperatures. Reaction conditions: 10 MPa, 10000 h^{-1} , H_2/N_2 volume ratio of 3.

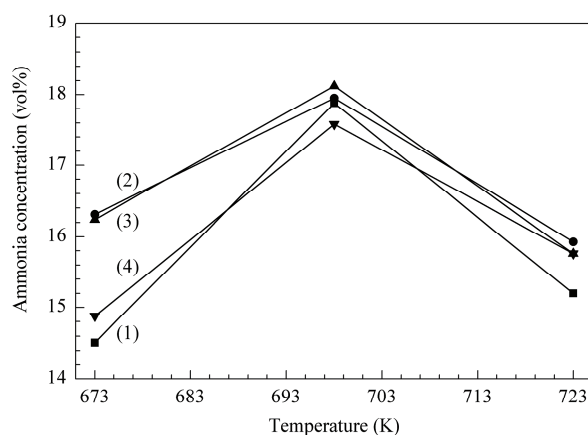


Fig. 5. Effect of K content on ammonia synthesis activity of the 4%RuN-4%Ba-K/AC catalyst. (1) 8%; (2) 10%; (3) 12%; (4) 14%.

Cl_3 precursor was purified with ethanol to remove the NH_4Cl by-product. The results indicated that K content remarkably influences the catalyst activity at low reaction temperature, and the suitable K content was 10%–12%.

Ammonia synthesis is a strongly structure sensitive reaction on ruthenium. Unprompted Ru/AC catalysts are almost inactive for ammonia synthesis. Ba is known as a structural promoter [25–29] or electronic promoter [30–33] in the literature. Generally, Ba and K promoters are known as a structural promoter and an electronic promoter, respectively. The K promoter is introduced to significantly improve the ammonia synthesis activity at low temperature by eliminating the effect of electron withdrawing groups such as chloride ion and acidic groups.

Table 2 shows the ammonia concentration and turnover frequency (TOF) over the catalysts from RuCl_3 and $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ precursors reduced at 723 and 673 K, respectively. It is obvious that the activity for ammonia synthesis of the catalyst prepared with $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ was much higher

Table 2 Effect of different precursors on the activity for ammonia synthesis

Catalyst	Ammonia concentration ^a (vol %)			TOF (s ⁻¹)		
	673 K	698 K	723 K	673 K	698 K	723 K
4%Ru-4%Ba-12%K/AC	14.25	15.54	13.62	0.09	0.10	0.09
4%RuN-4%Ba-12%K/AC	15.73	16.89	14.67	0.10	0.12	0.10

Reaction conditions: 10 MPa, 10000 h⁻¹. ^a Experimental error was ca. 0.2 vol %.

than that with RuCl₃. The difference in the activity and TOF between the two catalysts at low temperature was much higher than that at high temperature. These results clearly indicate that the Ru(NH₃)₅Cl₃ precursor produces a significant improvement in the catalyst activity in comparison with RuCl₃ precursor. The activity increase at 673 K was ca. 10% for the Ru(NH₃)₅Cl₃ without purification. These results are obviously correlated with the high dispersion and full utilization of Ru for the Ru(NH₃)₅Cl₃ precursor. The maximum increase in catalyst activity was 16.6% at 698 K for the purified Ru(NH₃)₅Cl₃ (Fig. 5), which could be related to the reduced content of chlorine in the catalyst.

3 Conclusions

Ruthenium ammonium chloride can be obtained when the molar ratio of hydrazine hydrate to ruthenium chloride is 5–20. The size distribution of Ru is uniform, and the utilization ratio of Ru is higher for the RuN/AC catalyst than for the Ru/AC catalyst. The optimal reduction temperature of the Ru(NH₃)₅Cl₃ precursor is lower than that of the RuCl₃ precursor. The pH of impregnating solution of the Ru(NH₃)₅Cl₃ precursor has little effect on the catalyst activity. Ruthenium ammonium chloride as a novel Ru precursor has advantages such as low reduction temperature, wide adjustable pH range of solution, high Ru dispersion, better size distribution of Ru after reduction, and high activity at low temperature. These suggest that the Ru(NH₃)₅Cl₃ precursor can be used as a novel Ru precursor.

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更正说明

因编辑工作失误, 本刊 2009, **30**(2): 92~94 发表的文章“还原温度对 Co-La-Zr/AC 催化剂合成气制高碳混合醇性能的影响”(作者: 焦桂萍, 丁云杰, 朱何俊, 李显明, 董文达, 李经伟, 吕元) 中图 1(a) 有误, 正确的图 1(a) 应是○代表 Cubic Co, ●代表 CoC. 特此更正及致歉.

(《催化学报》编辑部)