

Combination and interaction of ammonia synthesis ruthenium catalysts

Qing-Chi Xu^{a,*}, Jing-Dong Lin^a, Jun Li^a, Xian-Zhu Fu^a, Zhen-Wei Yang^a,
Wei-Ming Guo^b, Dai-Wei Liao^{a,c,d,**}

^a Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

^b Department of Chemical Engineering and Bioengineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

^c Institute of Physical Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

^d The State Key Laboratory of Physical Chemistry on Solid Surfaces, Xiamen University, Xiamen 361005, People's Republic of China

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Abstract

Based on combination advantages of both supports MgO and carbon nanotubes (CNTs), a novel combination-type catalyst for ammonia synthesis has been developed, in which two catalysts, K-Ru/MgO and K-Ru/CNTs, are combined with the optimal weight ratio of 1/1. The results show that the highest catalytic activity of the combination-type ruthenium catalyst, K-Ru/CNTs + K-Ru/MgO, for ammonia synthesis reaches $4453 \mu\text{mol NH}_3 \text{ h}^{-1} \text{ g}_{\text{-cat}}^{-1}$ at 673 K under 0.2 MPa, which is about two times higher than the average activity of the two catalysts under the same operating conditions. It is suggested that there is a complementary interaction between the two supports (CISS), MgO and CNTs, and the combination of both K-MgO and K-CNTs promotes electron transfer from alkali metallic atoms to the B₅-sites of ruthenium. © 2006 Elsevier B.V. All rights reserved.

Keywords: Combination-type ruthenium catalyst; Support–support interaction; Ammonia synthesis; Magnesia; Carbon nanotubes

1. Introduction

Catalytic synthesis of ammonia is a never-ending story [1]. It is due to not only the controversy of mechanism but also the development of catalysts. As we known, it spends about 80 years from the first-generation fused iron catalyst to the second-generation active-carbon-supported ruthenium catalyst. The promoted Ru/AC catalyst is an attractive ammonia synthesis catalyst which operating condition is much milder and activity is higher than that of the promoted iron catalyst [2,3]. Recently, Liao and co-workers [4] indicate that carbon nanotubes (CNTs) is a support better than active carbon for the ruthenium catalysts. However, the carbon-type supports have considerable disadvantages including high cost and methanation under operating conditions [5]. Therefore, now more and more attentions

are paid to the irreducible oxide supports to develop catalysts with high stabilization and high catalytic activity [6].

The MgO-supported ruthenium-based catalyst exhibits higher stabilization than the CNTs-supported ruthenium-based catalyst under operating conditions [7]. However, the ammonia synthesis activity of the promoted Ru/MgO is still much lower than that of the promoted Ru/CNTs [7–9]. Hence, it is important and urgent to develop a ruthenium catalyst with both high catalytic activity and stabilization under operating conditions.

For this aim, MgO-Al₂O₃-supported and barium-promoted ruthenium catalyst was prepared but its catalytic activity was even lower than that of MgO-supported and barium-promoted ruthenium catalyst [10]. Yin et al. [5] prepared MgO-CNTs-supported and potassium-promoted ruthenium catalyst for ammonia decomposition, which exhibited higher catalytic activity and stabilization than that of CNTs-supported and potassium-promoted ruthenium catalysts under the same operating conditions. However, using binary support, the dispersion of Ru particles on different supports is not uniform since the quite different surface properties between the CNTs and MgO.

In this paper, we prepared K-Ru/CNTs and K-Ru/MgO separately and then combined them at different weight ratio to obtain

* Corresponding author. Tel.: +86 592 218 3045; fax: +86 592 218 3043.

** Corresponding author at: Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China. Tel.: +86 592 218 3045; fax: +86 592 218 3043.

E-mail addresses: xuqingchi@yeah.net (Q.-C. Xu), dwliao@xmu.edu.cn (D.-W. Liao).

a combination-type catalyst. The results show that the ammonia synthesis activity of this type ruthenium catalyst increases greatly. A strong interaction between support (MgO) and support (CNTs) (SISS) is suggested.

2. Experimental

2.1. Preparation of supports

The magnesia with high surface area was prepared according to the procedure described by Choudhary et al. [11]. Ammonia water was dropped into a solution of magnesium nitrate (analytical purity) at room temperature until the pH value reached about 11. The Mg(OH)₂ suspension was filtered and washed with distilled water and then dried at 373 K, followed by calcining at 873 K, first in air for 1 h and then in nitrogen for 5 h [11]. The sizes of the prepared MgO particles are about 14 nm and the well-developed and moderately strained crystallites are formed. The CNTs was prepared by catalytic decomposition of methane over a Ni/MgO catalyst [12], and purified in nitric acid solution at 453 K for about 24 h and washed with distilled water for several times and then dried at 373 K. The textural parameters of magnesia and CNTs used in the ruthenium catalysts were measured by BET experiments.

2.2. Preparation of the combination-type ruthenium catalysts

Ru/MgO and Ru/CNTs catalysts were prepared by impregnation separately. During the impregnation process, the prepared MgO and the purified CNTs, respectively, were soaked in an organic solution, such as acetone, containing RuCl₃, and the weight ratio of Ru to support was about 5%. After impregnating over 6 h, the organic solvent was removed to obtain dry solids and then they were dried at 373 K overnight in air. The obtained RuCl₃/CNTs and RuCl₃/MgO were reduced in hydrogen flow (99.999% purity, 30 ml/min) at 698 K for 24 h to eliminate Cl⁻ and then cooled down to room temperature. The reduced Ru/CNTs catalyst was impregnated with an aqueous solution of potassium nitrate (mol ratio of K to Ru was 1/1) for about 6 h and then evaporated to obtain a dry solid. The K-Ru/MgO catalyst was also prepared by the same impregnation process and the mol ratio of K to Ru was 3/1. The prepared K-Ru/CNTs and K-Ru/MgO were mixed with different weight ratios (K-Ru/CNTs:K-Ru/MgO = 1/5–3/1) in acetone solvent and stirred for 6 h, then acetone solvent was removed and subsequently the combined ruthenium catalysts were dried at 373 K overnight in air. Finally the combined ruthenium catalysts were heated at 698 K for 6 h in a protect air, the obtained combination-type ruthenium catalysts were marked as K-Ru/CNTs + K-Ru/MgO.

CNTs-MgO-supported (weight ratio of CNTs to MgO was 1/1) and potassium-promoted ruthenium catalyst was also prepared by impregnation (abbreviated as K-Ru/MgO-CNTs). The ammonia synthesis activity of the K-Ru/MgO-CNTs catalyst was also evaluated under the same operating conditions for comparison. All catalysts were crushed and sieved between 250 and 425 μm.

2.3. Catalytic activity measurements

Ammonia synthesis activities of the ruthenium catalysts were evaluated over 0.20 g of the catalyst powders in a fixed bed flow reactor (i.d. = 8 mm) made of stainless steel and with a stoichiometric mixture of purified 3H₂ and N₂ at a pressure of 0.2 MPa and constant flow rate of 2100 ml/h at the standard conditions of the temperature and pressure—according to a common practice in all experiments. The ammonia synthesis activity was measured after the catalyst was stabilized at the reaction temperature for 30 min and the catalytic activity was expressed as μmol NH₃ h⁻¹ g_{-cat}⁻¹. The produced ammonia was determined by a chemical titration method using fixed amount of diluted sulfuric acid solution containing methyl red as indicator.

2.4. Catalyst characterization

The surface areas of the support materials were determined by using a Micromeritics Tristar nitrogen adsorption analyzer.

X-ray powder diffraction analysis (XRD) is carried out by a Philips PW1010 X-ray diffractometer, by employing the Cu Kα radiation. The XRD pattern is recorded with a scan step of 0.016° (2θ) for 10 s in the range from 10° to 90°.

Surface images and sizes of ruthenium nanoparticle were investigated by a TECNAL F30 High-resolution transmission electron microscopy (HRTEM).

3. Results and discussions

The surface areas of the support materials determined by the BET-method are shown in Table 1. Both MgO and CNTs have high surface areas, and the pore volume of MgO is higher than that of CNTs.

The XRD pattern of the combination-type ruthenium catalyst is shown in Fig. 1. According to the XRD analysis, there are characteristic peaks related to the CNTs (2θ: 26.07°, 43.98° and 84.75°) and the MgO (2θ: 36.89°, 42.86°, 62.24°, 74.61° and 78.54°). In addition, the ruthenium catalyst shows clear characteristic diffraction lines of ruthenium crystallites, revealing that the ruthenium particles size lies above the detection limit of the diffractometer, which may because of the negative effect of MgO on ruthenium dispersion [5].

TEM results (Fig. 2) reveal that the size of ruthenium particles on CNTs is 2–6 nm. Otherwise, the size of ruthenium particles on MgO is 2–16 nm, which is much larger than the optimal crystal size (2 nm). Herein, the catalytic activity of individual K-Ru/MgO catalyst is much lower than the catalytic activity of K-Ru/CNTs. In addition, from Fig. 2 we can see that the ruthenium particles disperse on both CNTs and MgO uniformly. Fig. 3

Table 1
BET, N₂ adsorption/desorption

Support material	Surface area (m ² /g)	Pore volume (cm ³ /g)	Mean pore radius (nm)
MgO	101	0.37	14.55
CNTs	119	0.21	10.00

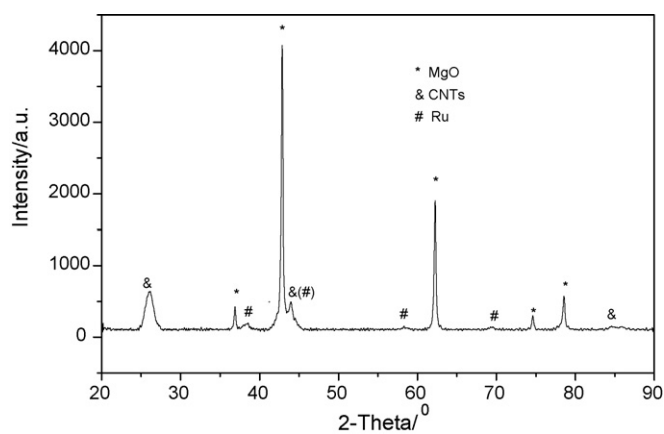


Fig. 1. XRD pattern of the composite ruthenium catalyst.

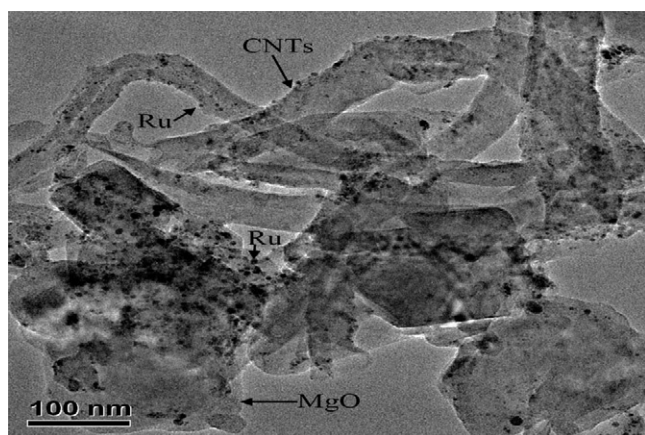


Fig. 2. TEM image of K-Ru/MgO + K-Ru/CNTs.

shows a TEM picture of the K-Ru/MgO-CNTs catalyst, revealing that most of the ruthenium particles locate on the surface of MgO and only a small part of the ruthenium particles locate on the surface of CNTs. From the TEM images of K-Ru/MgO-CNTs, it is clear that the use of binary supports with different surface properties will lead to severe nonuniformity of ruthenium particles dispersing on the surfaces of CNTs and MgO. On the other hand, by impregnated separately, the phenomena

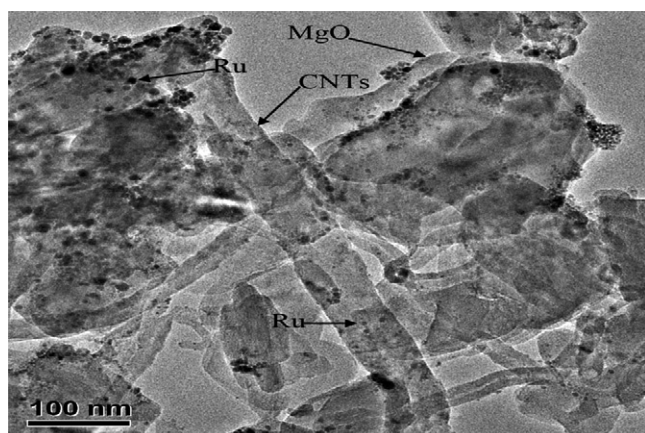


Fig. 3. TEM image of K-Ru/CNTs-MgO.

of preferential absorb of Ru on the surfaces of MgO will not happen.

It has been reported that, for CNTs-supported ruthenium catalysts, the optimal weight ratio of Ru to CNTs is about 4–5 wt% [4]. However, from the comparison between Figs. 2 and 3, it is evident that for the as-prepared K-Ru/MgO-CNTs only a small part of Ru particles can be found on the surfaces of CNTs. In this case, the weight ratio of Ru particles on the surfaces of CNTs to the CNTs is small and it may depart from the optimal weight ratio of Ru to CNTs. Therefore, the nonuniformity of Ru particles dispersing on the surface of CNTs and MgO leads to a great drop of ammonia synthesis activity, even though there is a great advantage of the combination of MgO and CNTs. However, for the combination-type ruthenium catalyst, weight ratios of Ru particles on the surface of CNTs to CNTs and Ru particles on surface of MgO to MgO both approach the optimal weight ratio. In this instance, K-Ru/MgO and K-Ru/CNTs catalysts in the combination-type catalyst exhibit the optimal catalytic activities for ammonia synthesis, respectively.

Results of many research works disclose that activation of N_2 is believed to be a rate-limiting step of ammonia synthesis over ruthenium surface [13–15]. It has been reported that basic supports are effective supports for ruthenium catalysts, because those basic supports can transfer electrons to the ruthenium surface atoms easily, which bring about a higher electron density in the ruthenium and lower the ionization potential [16,17]. It has been speculated that the lower the electronegativity of a support or a promoter, the greater the catalytic activity of ruthenium catalyst for ammonia synthesis [18]. MgO is found to be one of the most effective oxide supports for its basicity and high surface area. However, it has been suggested that a role of supports is the medium of electron transfer from alkali to ruthenium surfaces, but in the case of MgO the electrons cannot transfer to the surfaces of ruthenium particles easily because MgO is insulator [19,20]. CNTs is supported to be a good medium of electrons transfer from alkali to ruthenium surfaces for its high graphitization [4,21]. Whereas, due to the electron withdrawing nature of active carbon and CNTs, carbon-supported ruthenium catalysts show poorly active for ammonia synthesis without alkali metal [20,22]. Based on above discussions, both MgO-supported ruthenium catalyst and CNTs-supported ruthenium catalyst still have deficiency, and the catalytic activities for ammonia synthesis are not high enough.

Fig. 4 shows that the catalytic activity of the combination-type ruthenium catalyst is much higher than that of K-Ru/CNTs and K-Ru/MgO, which may due to the combination of both the basicity of MgO and the high graphitization of CNTs [5]. In the combination-type catalyst, MgO can enhance the basicity of K-Ru/CNTs catalyst and solve the electron withdrawing nature of CNTs, which improve the ammonia synthesis activity of K-Ru/CNTs, and, at the same time, K-CNTs can make the transfer of electron from alkali to ruthenium surface more easily for K-Ru/MgO catalyst. For the combination-type ruthenium catalysts both K-Ru/MgO and K-Ru/CNTs remain their instinctive high ammonia synthesis activities. Moreover, the interaction of K-Ru/MgO and K-Ru/CNTs can resolve the limitation of individual catalysts in some extent. Therefore, the combination-type

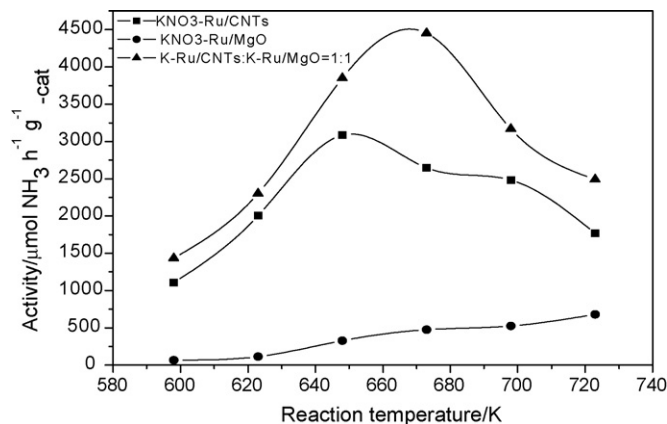


Fig. 4. Integral reaction rate for ammonia synthesis over different ruthenium catalysts vs. temperature: 0.2 MPa, 2100 ml/h of $N_2/3H_2$ at the standard conditions, 0.20 g sample.

ruthenium catalyst exhibits much higher catalytic activity than the average catalytic activity of K-Ru/CNTs and K-Ru/MgO. Besides, it also has been reported that MgO-CNTs supported ruthenium catalyst is more stable than CNTs-supported ruthenium under operating conditions [5].

Fig. 5 shows that the ammonia synthesis activity of the K-Ru/MgO-CNTs catalyst is much lower than that of the combination-type ruthenium catalyst (K-Ru/MgO:K-Ru/CNTs = 1:1), even though the combination of MgO and CNTs also occurs. That is because both MgO and $RuCl_3$ are polarized and the $RuCl_3$ is easy to be absorbed on the surfaces of MgO relatively. However, CNTs is unpolarized molecule and the $RuCl_3$ is hard to be absorbed on the surfaces of CNTs, even though the surface area of CNTs is a little larger than that of MgO. During the process of impregnating $RuCl_3$ on the surfaces of MgO and CNTs separately, we can find that almost all of $RuCl_3$ could be absorbed on the surfaces of MgO in 0.5 h under continually stirring, but just a small part of $RuCl_3$ is absorbed on the surfaces of CNTs even after 6 h under continually stirring. Herein, during the preparation of Ru/MgO-CNTs, most part of $RuCl_3$ is absorbed on the surfaces of MgO and only a small part of $RuCl_3$ is absorbed on the surfaces of CNTs, which

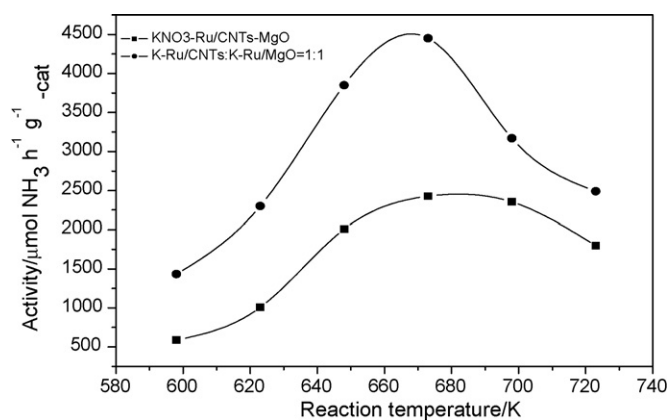


Fig. 5. Integral reaction rate for ammonia synthesis over different prepared ruthenium catalysts vs. temperature: 0.2 MPa, 2100 ml/h of $N_2/3H_2$ at the standard conditions, 0.20 g sample.

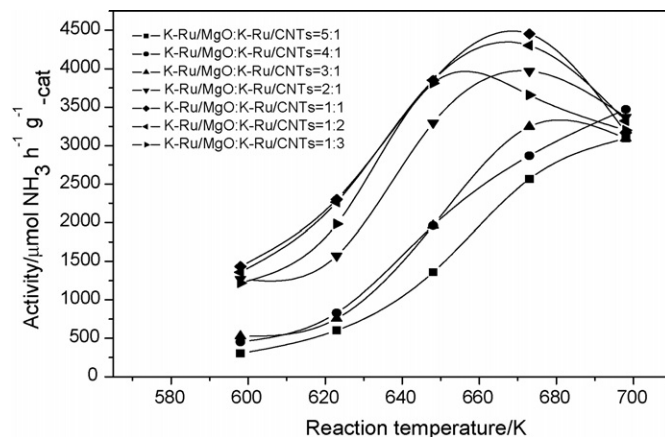


Fig. 6. Integral reaction rate for ammonia synthesis over the composite ruthenium catalysts with different weight ratios of K-Ru/MgO to K-Ru/CNTs vs. temperature: 0.2 MPa, 2100 ml/h of $N_2/3H_2$ at the standard conditions, 0.20 g sample.

leads to the dispersion of ruthenium on the surfaces of MgO and CNTs is not uniform and the weight ratio of Ru particles to support depart from the optimal ratio, which is substantiated by the TEM picture of K-Ru/MgO-CNTs catalyst (Fig. 3). In this circumstance, the individual catalytic activity of K-Ru/CNTs and K-Ru/MgO in K-Ru/MgO-CNTs is low, and the catalytic activity of K-Ru/MgO-CNTs is not high, even though there is the great advantage of the combination of MgO and CNTs.

The weight ratio of K-Ru/MgO to K-Ru/CNTs has great influence on the catalytic activity for ammonia synthesis. Fig. 6 shows the catalytic activities of the combination-type ruthenium catalysts with different weight ratios of K-Ru/MgO to K-Ru/CNTs. As we can see from Fig. 6, the best weight ratio of K-Ru/MgO to K-Ru/CNTs is 1/1. That may be because the combination between MgO and CNTs is strong and the interactional effects are prominent at this weight ratio, and thus the catalytic activity can be greatly improved. From Table 2 we also can see that the highest activity of the optimal combination-type ruthenium catalyst is $4453 \mu\text{mol NH}_3 \text{ h}^{-1} \text{ g}^{-1} \text{ cat}$, which is about two times higher than the average ammonia synthesis activity of K-Ru/CNTs and K-Ru/MgO at the same operating conditions.

It is very surprise and important why the catalytic activity of the optimal combination-type ruthenium catalyst is higher than that of every individual catalyst. It is suggested that there may be a complementary interaction between two supports (CISS), MgO and CNTs. The combination of both K/MgO and K/CNTs

Table 2
Ammonia synthesis activities of the prepared ruthenium catalysts ($\mu\text{mol h}^{-1} \text{ g}^{-1} \text{ cat}$)^a

Catalyst	Reaction temperature (K)					
	598	623	648	673	698	723
KNO ₃ -Ru/CNTs	1106	2005	3085	2647	2482	1768
KNO ₃ -Ru/MgO	66	115	328	476	525	681
Average activities	586	1060	1707	1562	1054	1224
K-Ru/CNTs:K-Ru/MgO = 1:1	1434	2302	3849	4453	3170	2491

^a The Ru/supports (w/w) of the catalysts is 5/100. The ammonia synthesis was carried out at 0.2 MPa pressure and $N_2/3H_2$ flow rate of 2100 ml/h.

promotes electron transfer from alkali metallic atoms to the B₅-sites of ruthenium. The further study on the combination effect is on going.

4. Conclusions

For the as-prepared combination-type ruthenium catalysts, ruthenium particles well disperse on the surfaces of MgO and CNTs relatively. The optimal weight ratio of K-Ru/MgO to K-Ru/CNTs for the preparation of the combination-type ruthenium catalysts is 1/1, that is because the combination between MgO and CNTs is strong and the interactional effects are prominent at this weight ratio. The catalytic activity for ammonia synthesis can reach about $4453 \mu\text{mol NH}_3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ at 673 K under 0.2 MPa, which is much higher than the activity of K-Ru/MgO and K-Ru/CNTs under the same operating conditions.

A complementary interaction between two supports (CISS) is suggested, which promotes electron transfer from alkali metallic atoms to the B₅-sites of ruthenium more easily.

Due to the high catalytic activity and high thermal stability under operating conditions, the combination-type ruthenium catalyst of K-Ru/MgO and K-Ru/CNTs may be a good catalyst for ammonia synthesis. For the favorable interaction of different catalysts or supports, the combination-type ruthenium catalysts require further theoretical research.

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