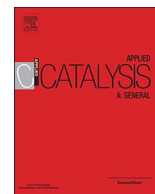




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## Deactivation study of carbon-supported ruthenium catalyst with potassium promoter

Bingyu Lin<sup>a</sup>, Yunjie Guo<sup>a</sup>, Jingdong Lin<sup>b,c</sup>, Jun Ni<sup>a</sup>, Jianxin Lin<sup>a</sup>, Lilong Jiang<sup>a,\*</sup>, Yong Wang<sup>b,c,d</sup><sup>a</sup> National Engineering Research Center of Chemical Fertilizer Catalyst, School of Chemical Engineering, Fuzhou University, Fujian, 350002, China<sup>b</sup> Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China<sup>c</sup> National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, Xiamen University, Xiamen, 361005, China<sup>d</sup> Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, United States

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## ABSTRACT

Carbon-supported Ru catalyst with alkali promoter is arguably the most significant advancement in ammonia synthesis. However, the insufficient stability of this type of catalysts greatly limits their applications, and carbon methanation is often considered as the reason for deactivation. Here we report that there is no clear correlation between carbon methanation and the loss of activity. Rather, carbon oxidation at high temperature, especially via the formation of carbon monoxide, was found to have a strong influence on the activity and stability of Ru catalysts. As a result, there is a significant increase in carbon loss, leading to the sintering of Ru particles and thereby altered hydrogen adsorption. Consequently, catalytic activity and stability of Ru/C catalysts are reduced. This finding contributes to the development of strategies to design carbon-supported metal catalysts with high activity and stability.

## 1. Introduction

Carbon materials have been widely used in heterogeneous catalysis either as catalyst supports or directly as catalysts [1–3]. Increased attention has been paid to the utilization of carbon in the catalysis field with the development of new carbon materials such as carbon nano tubes (CNTs), nanofibers, graphene, fullerenes, nanodiamonds and the ordered mesoporous carbon materials. However, poor stability and lack of understanding of carbon materials' properties on the catalytic performances are the major obstacles to the wide application of these new carbon materials in heterogeneous catalysis, and only a few types of carbons have been successfully applied as catalyst supports or directly as catalysts for industrial application.

The ammonia synthesis is the most important invention of the twentieth century [4]. The application of Ru catalyst supported on high surface area graphite promoted with alkali metal in ammonia plant is arguably the most significant advancement following the work of Haber and Bosch [5]. However, the industrial application of carbon-supported ruthenium catalysts for ammonia synthesis is very limited due to poor stability. The methanation of carbon is suggested to be a major deactivation reason because ruthenium metals have high catalytic activities in hydrogenation of carbons [6,7]. Several strategies, which focused on decreasing the methanation of carbon, have been applied to

improve the stability of carbon-supported ruthenium catalysts in the presence of hydrogen. The graphitization of carbon has been reported as one of the widely used strategies for the preparation of carbon-supported Ru catalysts with high stability [5,8–12]. Forni et al. [9,13,14] found the onset temperature of methane formation increased significantly with the increase of the graphitization temperature of carbon for Ru/C catalyst. Brown et al. [5] reported that BP had successfully prepared high surface area graphitic carbon from a natural carbon. Ru catalyst supported on the as-prepared carbon was stable against methanation of carbon and therefore can be used in ammonia plant. The rational use of promoters is also helpful to improve the stability of carbon-supported metal catalysts [15–18]. Kowalczyk et al. [15] found that K promoter and Ru metal could increase the methanation reaction rates, while the presence of barium inhibited the formation of methane for Ru/C catalysts. Rossetti et al. [16] also confirmed that promoters (Ba, Cs or K) and their loading had a strong impact on the starting temperature of methane formation. The simultaneous application of carbon graphitization and rational usage of promoters can further enhance the stability of carbon-supported ruthenium catalyst. The use of these strategies could decrease the amount of the formed methane, but the stability of Ru/C catalysts is still far below what is required for the industrial application. Therefore, it is critical to provide understanding of the underlying deactivation mechanisms of

\* Corresponding author.

E-mail address: [jl@fzu.edu.cn](mailto:jl@fzu.edu.cn) (L. Jiang).<http://dx.doi.org/10.1016/j.apcata.2017.04.020>

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Ru/C catalysts in order to develop strategies to improve carbon-supported ruthenium catalyst activity and stability for its industrial applications.

It is well known that a large amount of oxygen-containing functional groups exist in carbon material [19]. Moreover, the addition of Ru metal and promoters would also introduce oxygen sources. Our previous work [20] reported that the formation of CO was unavoidable for carbon-supported Ru catalysts with potassium promoter at above 500 °C. Not only carbon methanation, but also carbon oxidation to form carbon monoxide or carbon dioxide could lead to the carbon loss [21,22]. Consequently, besides carbon methanation, carbon oxidation would significantly affect the performances of Ru/C catalysts, which may be another critical issue for the deactivation of carbon-supported Ru catalysts for ammonia synthesis.

In this work, K-Ru/C and Ba-K-Ru/C catalysts were prepared. The physicochemical properties of Ru catalysts before and after reaction were characterized. The relationship between the catalyst performances and the deactivation mechanism of Ru catalysts was systematically investigated. We believe that our study not only will provide direction to improve the Ru/C catalyst stability, but also will be useful for the design of other carbon-supported metal catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

The high surface area and partially graphitic carbon was prepared according to the following procedures [12,23]: commercial activated carbon (1035 m<sup>2</sup>/g, Shanghai Carbon Ltd.) was heated in nitrogen at 1950 °C for 2 h, and then oxidized in steam at 430 °C for 30 h. The surface area and total pore volume of the as-obtained carbon were 854 m<sup>2</sup>/g and 0.5 cm<sup>3</sup>/g, respectively. Ru (0.10 g Ru metal per gram of carbon) was introduced into carbon (32–60 mesh) by incipient wetness impregnation with RuCl<sub>3</sub> solution. The as-obtained samples were reduced in hydrogen at 450 °C for 6 h. Finally, K or Ba promoter was introduced by the impregnation method using Ba(NO<sub>3</sub>)<sub>2</sub> and KOH as promoter precursor, the theoretical weight ratio of promoter to carbon was 9 wt.% and 12 wt.% for Ba and K promoter, respectively. The catalysts were named as K-Ru/C and Ba-K-Ru/C.

### 2.2. Catalyst characterizations

Transmission electron microscopy (TEM) was carried out using a FEI Tecnai G2 F20 microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific ESCALAB 250 photoelectron spectroscopy with monochromatized Al Kα X-rays (1486.6 eV). Thermogravimetric curves (TG) were obtained using a Seteram Setsys Evolution Thermomechanical Analyser. The measurements were carried out in 2.5%N<sub>2</sub>–7.5%H<sub>2</sub>–90%Ar gas mixture or argon with a heating rate of 10 °C/min. Raman spectra of the samples were obtained from an InVia Reflex Raman microscope equipped with a 532 nm laser. Temperature-programmed reduction (TPR), Temperature-programmed desorption of hydrogen (H<sub>2</sub>-TPD) and Temperature-programmed surface reaction (TPSR) studies were carried out in a Micromeritics AutoChem 2920 instrument with mass spectrometry (Hidden Analytical HPR-20). For TPR, the catalyst (100 mg, sieve fraction 0.30–0.56 mm) was heated with a rate of 10 °C/min in a flow of 10% H<sub>2</sub>/Ar mixture (30 mL min<sup>-1</sup>). For H<sub>2</sub>-TPD, the catalyst (100 mg) was reduced in hydrogen at 430 °C for 2 h, flushed in Ar at 430 °C for 1 h and then cooled down to 400 °C. The sample adsorbed hydrogen at 400 °C for 1 h and then cooled down to 50 °C. After flushed with Ar for 1 h, the catalyst was heated up to 900 °C at 10 °C min<sup>-1</sup> and then held at 900 °C for 30 min. For TPSR, the reduced catalyst (100 mg) was heated up to 900 °C at 10 °C min<sup>-1</sup> in flowing of 2.5%N<sub>2</sub>–7.5% H<sub>2</sub>–90%Ar gas mixture, the signals were recorded by a mass spectrometry (Hidden Analytical HPR-20), where the signals of *m/z* = 2 (H<sub>2</sub>),

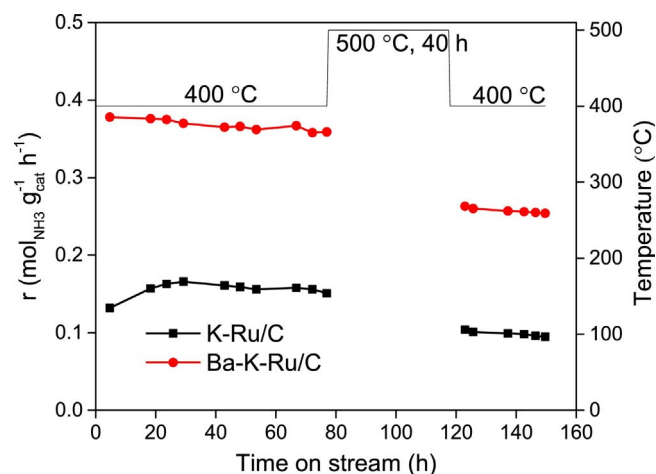


Fig. 1. Ammonia synthesis rates as a function of time (reaction condition: 400 °C, 10 MPa, H<sub>2</sub>/N<sub>2</sub> = 75/25, 70 dm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>; heat treatment condition: 500 °C, 10 MPa, H<sub>2</sub>/N<sub>2</sub> = 75/25, 70 dm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>).

15 (CH<sub>4</sub>), 28 (CO), 44 (CO<sub>2</sub>) were monitored.

### 2.3. Activity measurements

Ammonia synthesis activity was measured in a stainless steel reactor with the type-K thermocouples. The catalysts (0.30 g, 32–60 meshes, diluted with quartz powder in a 1:30 volumetric ratio) were reduced in the mixture gas (H<sub>2</sub>/N<sub>2</sub> = 3.0 v/v) at different temperatures (200, 300, 400 and 430 °C) and held for 2 h at each temperature. Under steady-state conditions of pressure (10 MPa), temperature (400 °C) and gas flow rate (70 dm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), the ammonia concentration in the gas flow after the reactor was calculated based on a known amount of diluted H<sub>2</sub>SO<sub>4</sub> solution (0.015 mol L<sup>-1</sup>), and then the ammonia synthesis rate was measured. The detail calculation equations can be found in our previous paper [20].

## 3. Results and discussion

### 3.1. Ammonia synthesis activity

Fig. 1 shows the ammonia synthesis rates as a function of time on stream. The catalytic activities initially increased with time on stream until a plateau was reached for K-Ru/C catalysts. Whereas the ammonia synthesis rates of the Ba-K-Ru/C catalyst decreased slightly with time on stream. Since the treatment of the catalysts under severe condition is helpful for estimating the stability of carbon-supported Ru catalysts, a high temperature treatment process at 500 °C for 40 h was carried out. As shown in Fig. 1, the high temperature treatment led to the significantly decrease in the ammonia synthesis rates for Ru catalysts. The activities decreased by about 37% and 29% for K-Ru/C and Ba-K-Ru/C, respectively. The surface areas of the fresh K-Ru/C and Ba-K-Ru/C catalysts were 468 and 341 m<sup>2</sup>/g, respectively. The surface areas of the spent catalysts slightly decreased to 443 and 305 m<sup>2</sup>/g for K-Ru/C and Ba-K-Ru/C, respectively. This result suggests that the significant differences in the catalytic performances are not likely due to the change in carbon surface area change between the fresh and spent catalysts.

### 3.2. TEM study

No distinct diffraction reflections corresponding to potassium, barium or ruthenium compounds were observed in the XRD patterns of the fresh catalysts (Fig. S1), which may be due to the high dispersion of these species on carbon support. The reflections of Ru metal could be observed in the spent catalysts, indicating the increased Ru particle size

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