

## Novel Ruthenium Catalyst ( K-Ru/C<sub>60/70</sub> ) for Ammonia Synthesis

Guang WEI\*, Li Hua WANG, Yi Ji LIN, Jun YI, Hong Bo CHEN, Dai Wei LIAO

Department of Chemistry, State Key Lab of Physical Chemistry on Solid Surfaces,  
Institute of Physical Chemistry, Xiamen University, Xiamen 361005

**Abstract:** A novel ammonia-synthesis catalyst, potassium-promoted ruthenium supported on fullerene ( K-Ru/C<sub>60/70</sub> ), was prepared and evaluated. It was found that K-Ru/C<sub>60/70</sub> was the most active catalyst for ammonia synthesis at atmospheric pressure and 623 K compared with other support materials such as silica, activated carbon, zeolite,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and rare earth metal oxide.

**Keywords:** Ammonia synthesis; ruthenium; fullerene.

Commercial doubly or triply-promoted fused iron catalysts have been widely used still up to now. The industrial ammonia catalytic process on promoted iron catalysts under high pressure and at high temperature has not undergone essential changes up to the present day. Alkali metal-promoted ruthenium was found to be an active catalyst for ammonia synthesis under atmospheric pressure in 1970s. Ruthenium catalyst can be considered as a second-generation-catalyst for ammonia synthesis after the iron-based catalyst<sup>1-4</sup>. Recently, we investigated activity of ammonia synthesis of ruthenium-based catalysts on various supports. It was found that fullerene was the best support.

Various supports including silica (SiO<sub>2</sub>), activated carbon (AC), zeolite (NaX),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, respectively, were impregnated with aqueous ruthenium trichloride solution for 18 h. Support C<sub>60</sub>/C<sub>70</sub>, however, was impregnated with ruthenium trichloride acetone solution for 18 h. Solid KNO<sub>3</sub> was added then. The solution was vaporized to dry. The solids were then dried at 383 K for 6 h. The precursor was reduced in micro-reactor with flowing hydrogen at a temperature-program up to 773 K.

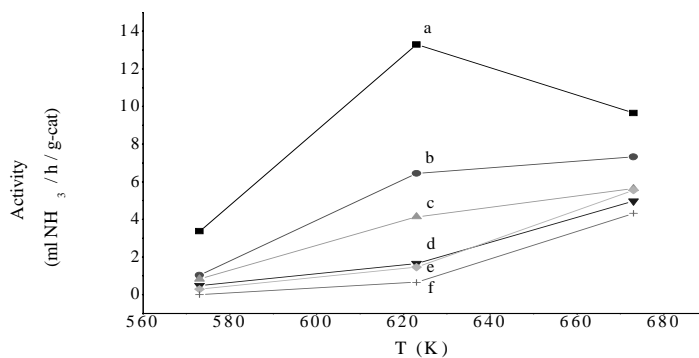
Ammonia synthesis was carried out with N<sub>2</sub>/3H<sub>2</sub> mixing gas at rate of 3600 ml/h which was first purified through 402 deoxidizer and 4A zeolite. The reaction temperature was controlled with AL-708 type temperature-programmed controller.

As we can see from **Figure 1**, the order of catalytic activity at 623 K is SiO<sub>2</sub> < NaX < AC <  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < CeO<sub>2</sub> < C<sub>60/70</sub> as supports. The catalyst K-Ru/C<sub>60/70</sub> exhibited the highest activity ( 13.3 ml NH<sub>3</sub>/h/g-cat ). The electronic promotion effect is the most important effect for ruthenium based ammonia catalysts. The promotion effect of alkali metal is well understood to be due to the electron donation from the alkali metal to ruthenium. The fullerene ( C<sub>60</sub> and C<sub>70</sub> ), namely Buckyball, is said to have many novel properties such as superconductivity, magnetism and conductivity. Therefore, when fullerene was used as a support, the electron transfer from K to Ru could be greatly

promoted. The activation energy of reaction was enormously decreased. Moreover, the fullerene has the biggest specific surface. It is favorable to the dispersion of ruthenium and protection from agglomeration of ruthenium on the surface.

The catalysts with rare earth metal oxides as a support material also exhibited higher activity (6.44 ml NH<sub>3</sub>/h/g-cat). It may be due to the *f* orbitals of Ce promoted the electron transfer to ruthenium.

**Figure 1.** Ammonia synthesis activity of ruthenium catalysts



a. K-Ru/C<sub>60-70</sub> b. K-Ru/CeO<sub>2</sub> c. K-Ru/γ-Al<sub>2</sub>O<sub>3</sub> d. K-Ru/AC e. K-Ru/NaX f. K-Ru/SiO<sub>2</sub>

For the catalyst, K-Ru/C<sub>60/70</sub>, the yield of NH<sub>3</sub> was 3.37, 13.3 and 9.66 ml NH<sub>3</sub>/h/g-cat at 573 K, 623 K and 673 K, respectively. The optimal reaction temperature is 623 K rather than 673 K. This could be due to that the loss of potassium increased at higher temperature. We also found the optimal content of Ru was 4 % rather than 2 % for the ruthenium catalyst. It was due to that the special geometrical structure of fullerene allowed higher dispersion of ruthenium.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China under Grant No. 29773037 and the opening project grant from the State Key Lab of Physical Chemistry on Solid Surfaces.

### References and notes

1. K. Aika, H. Hori, A. Ozaki, *J. Catal.*, **1972**, 27, 424.
2. K. Aika, K. Shimazaki, Y. Hattori, A. Ohya, S. Ohshima, A. Ozaki, *J. Catal.*, **1985**, 92, 296.
3. S. Murata, K. Aika, *J. Catal.*, **1992**, 136, 110.
4. Y. Niwa, K. Aika, *J. Catal.*, **1996**, 162, 138.

Received 4 December 1998