

Novel Ru - K/Carbon Nanotubes Catalyst for Ammonia Synthesis

Yun CAI, Jing Dong LIN, Hong Bo CHEN, Hong Bin ZHANG, Guo Dong LIN,
Dai Wei LIAO*

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

Abstract: A novel ammonia synthesis catalyst, potassium-promoted ruthenium supported on carbon nanotubes, was developed. It was found that the Ru-K/carbon nanotubes catalyst had higher activity for ammonia synthesis (20.85 ml NH₃/h/g-cat) than the Ru-K/fullerenes (13.3 ml NH₃/h/g-cat) at atmospheric pressure and 623 K. The catalyst had activity even at 473 K, and had the highest activity (23.46 ml NH₃/h/g-cat) at 643 K. It was suggested that the multi-walled structure favored the electron transfer, the hydrogen-storage and the hydrogen-spill which were favorable to ammonia synthesis.

Keywords: Ammonia synthesis, ruthenium, carbon nanotubes.

Since 1970s alkali metal-promoted ruthenium was found to be an active catalyst for ammonia synthesis under atmospheric pressure, ruthenium catalysts come to be considered as a second-generation-catalyst for ammonia synthesis after the iron-based catalyst¹⁻². We have reported the activity of ammonia synthesis of ruthenium-based catalysts on various supports previously and found that fullerene was the best support³. Recently, we used the carbon nanotubes, which have metallic or semiconducting properties due to their fiber geometry and the curvature of graphitic planes⁴, as a support of ruthenium-based catalyst for ammonia synthesis and it was found that this catalyst has the even higher activity than that supported on fullerene in the similar conditions.

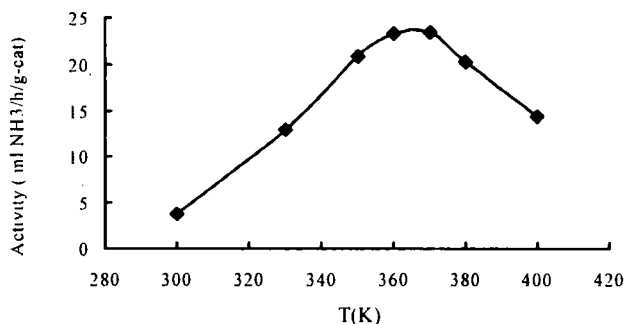
The KNO₃ solution was injected into a bottle, which was vacuumed beforehand, filled with carbon nanotubes, then disturbed and impregnated overnight. The solution was vaporized to dry. The aqueous ruthenium trichloride solution was dealt with K/carbon nanotubes in the same way. The eventual solids were then dried at 383K for 5 h. The precursor was reduced in a micro-reactor with flowing hydrogen at a temperature-program up to 673 K.

Ammonia synthesis was carried out with N₂/3H₂ mixing gas at rate of 1700 ml/h which was 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 catalyst K-Ru/carbon nanotubes exhibited the highest activity (23.46 ml NH₃/h/g-cat) at 643 K, which is higher than the highest activity of K-Ru/C_{60/70} (13.3 ml NH₃/h/g-cat , 623 K). 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 based ammonia catalysts. For carbon nanotubes, theoretical calculations showed that, depending upon the fiber geometry and the curvature of graphitic planes, the nanotubes have metallic or semiconducting properties. Therefore, when carbon nanotubes were used as a support, the electron transfer from K to Ru could be greatly promoted and the activation energy of reaction could be enormously decreased. Moreover, the high hydrogen-uptake capacity of the K-doped carbon nanotubes⁵ should be favorable to ammonia synthesis.

Figure 1 Ammonia synthesis activity of Ru-K/carbon nanotubes



For the catalyst, Ru-K/carbon nanotubes, the yield of NH₃ was 12.92, 20.85, 23.29, 23.46, 20.27, 14.45 ml NH₃/h/g-cat at 603 K, 623 K, 633 K, 643 K, 653 K and 673 K, respectively. The optimal reaction temperature is 643 K. We also found that the catalyst has activity even at 473 K.

Acknowledgments

This work was supported by the NSF of China (#29773037), the NSF of Fujian province (#E9910001) and the opening project grant from the State Key Lab of Phys. Chem. on Solid Surf.

References

1. K. Aika, H. Hori, A. Ozaki, *J. Catal.*, **1972**, 27, 424.
2. Y. Niwa, K. Aika, *J. Catal.*, **1996**, 162, 138.
3. G. Wei, L. H. Wang, Y. J. Lin, J. Yi, H. B. Chen, D. W. Liao, *Chi. Chem. Lett.*, **1999**, 10, 433.
4. J. W. Mintmire, B. I. Dunlap, C. T. White., *Phys. Rev. Lett.* **1992**, 68, 631.
5. P. Chen, X. Wu, J. Lin, K. L. Tan, *Science.*, **1999**, 285, 91.

Received 22 October 1999

Revised 3 January 2000