Ammonia Synthesis over Cs- or Ba-Promoted Ruthenium Catalyst Supported on Strontium Niobate

Minxuan Chen[ab], Mingwei Yuan[ab], Jinjun Li[a], Zhixiong You[*ab]

[a] *School of Resources and Environmental Sciences, Wuhan University, Wuhan 430079, P.R. China.*

[b] *International Cooperation Base for Sustainable Utilization of Resources and Energy in Hubei Province, Wuhan 430072, P.R. China*

** Zhixiong You: +86 27-68778893, zyou@whu.edu.cn*

Abstract: Strontium niobates with different crystalline structure and morphology have been prepared via a hydrothermal method and applied as a support for ruthenium catalyst in ammonia synthesis. The sample synthesized with a nominal Sr/Nb = 2.0, have a pure $Sr_2Nb_2O_7$ crystalline phase and specific surface area of 87 $m^2\ g^{-1}$. The highest ammonia synthesis rate over 8Cs- or 4Ba-2wt%Ru/$Sr_2Nb_2O_7$ was 4986 and 2317 (μmol $g^{-1}_{cat}\ h^{-1}$) at 0.1 MPa and 673 K, respectively, suggesting $Sr_2Nb_2O_7$ is a promising support for Ru catalysts.

Keywords: Ammonia synthesis, Ruthenium catalysts, Strontium niobate.

1. Introduction

Ruthenium-based catalysts have been extensively investigated as the second-generation ammonia synthesis catalysts and Ru catalysts supported on high surface area graphite (HSAG) have been industrially applied in the KBR advanced ammonia synthesis process (KAAP) since 1992 [1-4]. However, methanation causes gradual degradation of the carbon support, limiting the lifetime of Ru/C catalyst [5-7]. It is thus still of importance to find a suitable oxide support for ruthenium catalyst.

2. Experimental

The $Sr_2Nb_2O_7$ support was synthesized via a hydrothermal method. First, a precursor of niobium ($Nb_2O_5 \cdot nH_2O$) was synthesized from $NbCl_5$ and 4 wt% NH_4OH aqueous solution via a hydrothermal method [8]. Second, the resultant $Nb_2O_5 \cdot nH_2O$ and $Sr(OH)_2 \cdot 8H_2O$ with different molar ratio were mixed in 45 ml distilled water and heated at 473 K for 24 h.

Ruthenium catalysts were prepared by impregnation method. The activity and stability of the catalysts were evaluated at 673 K and 0.1 MPa. The high catalytic performance of the catalyst was investigated with XRD, TEM, SEM, NH_3-TPD and etc.

3. Results and discussion

Fig.1 shows the XRD patterns of the synthesized strontium niobate samples. When equal amount of $Sr(OH)_2$ and Nb_2O_5 (Sr/Nb = 0.5) was mixed and hydrothermally treated, $SrNb_2O_6$, Nb_2O_5 and $Sr_2Nb_2O_7$ phases (Fig.1a) were observed in the sample. Raising the Sr/Nb to 1.0, we obtained a sample containing mainly orthorhombic $Sr_2Nb_2O_7$ phase (PDF#70-0114). Further increasing the Sr/Nb to a value above 1.0, no obvious change in the crystalline structure of the samples was observed (Fig.1c-f). This result appears to demonstrate that the added $Sr(OH)_2$ exceeding the stoichiometry of $Sr_2Nb_2O_7$ has little effect on the crystalline structure of the resultant strontium niobates.

Fig.2 shows the ammonia synthesis rate over Ru/$Sr_2Nb_2O_7$ catalysts promoted by different amount of Ba or Cs. For both Ba- or Cs-Ru/$Sr_2Nb_2O_7$ catalysts, the ammonia synthesis rate increased first and then decreased with increasing in the addition amount of promoters. The optimal molar ratio of Ba or Cs promoter to Ru was 4 or 8, respectively. The highest activity over 4Ba- or 8Cs-2wt%Ru/$Sr_2Nb_2O_7$ at 673 K and 0.1 MPa was 1279 or 4170 μmol $g^{-1}_{cat}\ h^{-1}$, which was 5 or 17 times larger than that of the unpromoted catalyst.

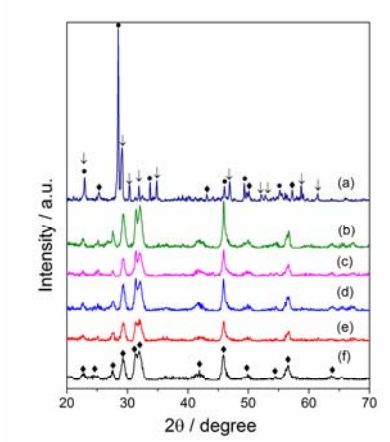

Figure 1. XRD patterns of strontium niobate samples prepared by a hydrothermal reaction at 473 K for 24 h with different molar ratio of Sr/Nb: (a) Sr/Nb = 0.5, (b) Sr/Nb = 1.0, (c) Sr/Nb = 1.5, (d) Sr/Nb = 2.0, (e) Sr/Nb = 2.5, and (f) Sr/Nb = 3.0. ♦: $Sr_2Nb_2O_7$, ↓:$SrNb_2O_6$, ●:Nb_2O_5.

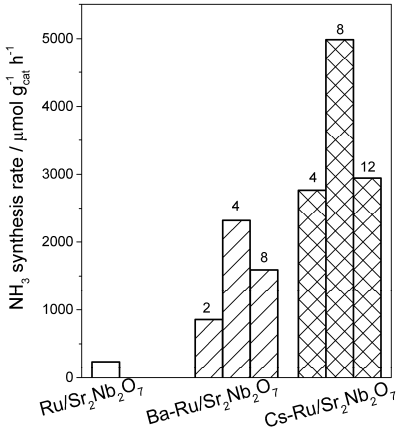

Figure 2. Ammonia synthesis rate over $Ru/Sr_2Nb_2O_7$ catalysts promoted by different amount of Ba or Cs at 673 K and 0.1 MPa, the catalysts were activated at the optimized temperature 673 and 773 K, respectively. Reaction conditions: 100.0 mg catalyst, 60 mL (STP)/min synthesis gas ($3H_2 + N_2$).

4. Conclusions

Strontium niobates with a large surface area was prepared using hydrothermal method and examined as support for Ru catalyst for ammonia synthesis. The Ba- or Cs-promoted Ru catalyst supported on $Sr_2Nb_2O_7$ synthesized with nominal Sr/Nb = 2.0 showed superior catalytic activity and stability for ammonia synthesis than Cs-Ru/MgO, which was considered as one of the most ative oxide support at present. Thus, strontium niobate can be a practically promising potential candidate for Ru ammonia synthesis catalysts.

References

1. D. Szmigiel, H. Bielawa, M. Kurtz, J. Catal. 205 (2002) 205.
2. Z. You, K. Inazu, K. Aika, T. Baba, J. Catal. 251 (2007) 321.
3. X. Yanga, W. Zhanga, C. Xiaa, X. Xionga, X. Mua, B. Hu, Cat Comm. 11 (2010) 867.
4. L. Forni, D. Molinari, I. Rossetti, N. Pernicone, Appl. Catal. A. 185 (1999) 269.
5. Z. Kowalczyk, S. Jodzis, W. Raróg, J. Zieli´nski, J. Pielaszek, Appl. Catal. A. 173 (1998) 153.
6. P.J. Goethel, P.T. Yang, J. Catal. 111 (1988) 220.
7. Z. Kowalczyk, J. Sentek, S. Jodzis, R. Diduszko, A. Presz, A. Terzyk, Z. Kucharski, J. Suwalski, Carbon. 34 (1996) 403.
8. W. Fan, Q. Zhang, W. Deng, Y. Wang, Chem. Mater. 25 (2013) 3277.