Influence of reaction conditions on catalytic ammonia synthesis using Ru/MgO-CeO_2 prepared by different methods

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Abstract: MgO-CeO_2 mixed support was fabricated by three different methods, i.e., impregnation, co-deposition and physical mixing. 1 wt-% Ru was loaded by impregnation method. Dispersion of Ru, CeO_2, and MgO was determined by TEM analysis. The activity of Ru/MgO-CeO_2 catalysts prepared by different methods for ammonia synthesis was determined using H_2 and N_2 as reactants. Effect of reaction conditions was studied in terms of temperature, H_2/N_2 ratio, and pressure. Below 400 ºC, higher rate for ammonia synthesis was obtained at $H_2/N_2 < 3$.

Keywords: Ammonia synthesis, Ru catalyst, MgO-CeO_2 mixed oxide support.

1. Introduction

Ammonia synthesis is one of the important catalytic processes in the chemical industry. It is not only useful as a source of fertilizers but also as a promising H_2 storage, and is thought to be a clean fuel as only water and N_2 are produced by direct combustion. At industrial level catalytic ammonia synthesis is carried by Haber-Bosch process which requires high temperature/pressure (500-600 °C, 20-30 MPa) installations [1]. For the development of small-scale ammonia plants for storage of H_2 from renewable energy sources, optimization at relatively mild reaction conditions is of great importance. Ru catalysts have been studied as highly active catalysts for ammonia synthesis [2,3]. Constant supply of H_2 produced from renewable energy is very hard because of its fluctuating behavior so that we should confirm catalytic activities under various operating situations. In the present work, Ru catalyst supported on MgO-CeO_2 mixed oxide was synthesized by three different methods and applied for ammonia synthesis. The aim of the present work is to evaluate the effect of preparation method and reaction conditions on performance and stability of the catalyst during ammonia synthesis.

2. Experimental

MgO-CeO_2 (Mg/Ce = 5/1) mixed support was fabricated by three different methods, i.e., impregnation, co-deposition and physical mixing. 1 wt-% Ru was loaded on mixed support by impregnation method using $Ru(NO_3)_3$ as a metal precursor. After the impregnation of Ru, the catalyst was dried at 100 ºC, overnight, followed by H_2 treatment at 300 ºC for 1 h.

The catalyst activity for ammonia synthesis was measured in a fixed bed flow-reactor system. Before testing, the catalyst (2.0 mL) was activated in a flowing gas mixture of 75% H_2 and 25% N_2 at 600 ºC and ambient pressure for 30 min. Ammonia synthesis was carried out at a temperature range of 325-425 °C, 0.1-2.5 MPa gauge pressure keeping the space velocity (SV) constant as 3000 h^{-1}. The ammonia concentration in product gas was analyzed by the decrease of electron conductivity in the H_2SO_4 solution.

3. Results and discussion

The dispersion of Ru, Ce and Mg among the prepared catalysts was determined by TEM analysis. According to the TEM images, the dispersion of all the three elements depended on the method of preparation. The order for high dispersion of Ru and Ce among the catalysts synthesized by different methods is as co-deposition > impregnation > physical mixing. The activity of the catalysts was evaluated for ammonia synthesis in terms of space-time yield (STY). Figure 1 shows the mapping of the results obtained at various temperature, H_2/N_2 ratio and gauge pressure conditions using Ru/MgO-CeO_2 catalysts

prepared by different methods. According to the Figure 1, as temperature increased from 325 ºC up to 425 ºC, the suitable value of the H_2/N_2 ratio to attain higher catalytic activity increased for all three catalysts. A detailed analysis of the results showed that the highest activity for catalyst prepared by impregnation method was obtained at the highest experimental temperature and gauge pressure conditions of 425 ºC and 2.5 MPa for H_2/N_2 ratio 1 (Fig. 1a). Whereas, catalyst prepared by co-deposition method showed the highest rate for ammonia synthesis at relatively lower temperature of 375 ºC for H_2/N_2 ratio 1 (Fig. 1b). On the other hand, the highest rate for ammonia synthesis among the catalysts prepared by three different methods was realized for the one prepared by physical mixing showing the highest activity at 375 ºC for H_2/N_2 ratio 1.5 (Fig. 1c).

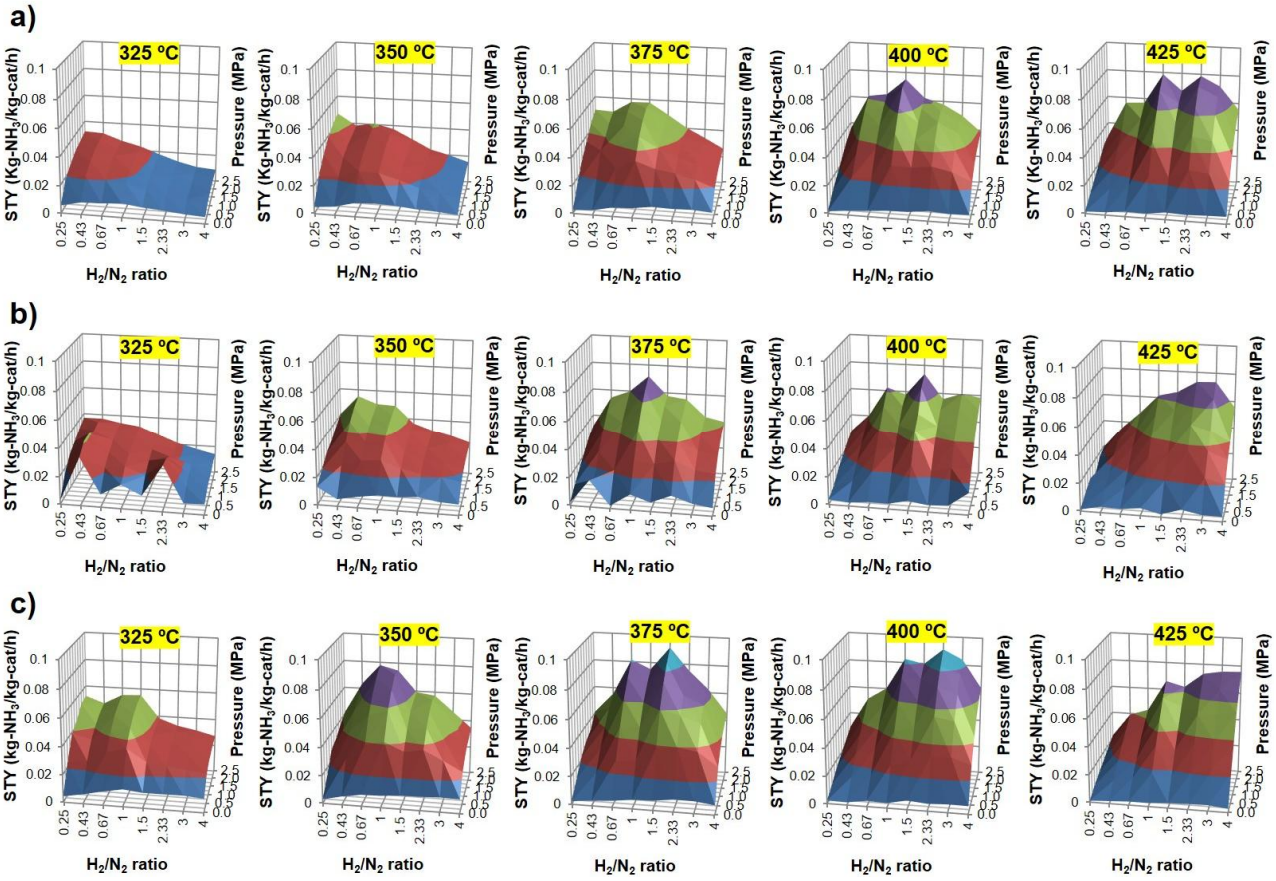

Figure 1. Mapping of experimental results obtained at various temperature, H_2/N_2 ratio, and pressure conditions using Ru/MgO-CeO_2 catalysts prepared by different methods: a) impregnation, b) co-deposition, c) physical mixing.

4. Conclusions

The activity of the catalyst depends on the method of preparation. The suitable H_2/N_2 ratio and temperature conditions to attain the highest activity are different for the catalysts prepared by different methods. Below 400 ºC temperature, higher STY for ammonia can be obtained by decreasing H_2/N_2 ratio. Such detailed study to evaluate the effect of preparation method of catalyst and reaction optimization is necessary for the development of small scale ammonia plants required for storage of H_2 from renewable energy sources.

References

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