

Combinatorial Supports for Ru-based Ammonia Synthesis Catalysts

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Abstract: The support materials of ruthenium-based catalysts for ammonia synthesis were prepared using mixed solutions composed of magnesium nitrate, aluminum nitrate and calcium nitrate with a certain ratio. The catalysts supported on complex oxides were more active and the optimal activity temperatures were lower than that supported on single oxide under the same conditions. The catalyst with Mg-Al complex oxide as support prepared by calcinating hydrotalcite-like compound had significantly higher activity, 38.42 mL NH₃·h⁻¹·g⁻¹ at 673 K. The BET determination showed that the Mg-Al complex oxide possessed large surface area, 140.95 m²·g⁻¹, similar to γ-Al₂O₃.

Keywords: Hydrotalcite, magnesium aluminum oxide, ammonia synthesis, ruthenium.

The support plays an important role in controlling the Ru crystal morphology and the abundance of B₅-type sites¹. The hydrotalcite-like compounds were found as a novel support material for the preparation of alkaline catalysts². We prepared complex supports and investigated their effect on the activity of the Ru-based ammonia catalyst.

The 30.6 g of Mg(NO₃)₂·6H₂O and 15.0 g of Al(NO₃)₃·9H₂O were dissolved in 80 mL of distilled water. The second solution was prepared with 6.16 mL of NH₃·H₂O and 7.68 g of (NH₄)₂CO₃ in 100 mL of H₂O. The mixed solution was prepared by dropwise addition of the two solutions under stirring and the pH = 8-9 at room temperature, and then aged for 3 h. The precipitate was filtrated and washed with distilled water, and finally dried overnight at 353 K to obtain the hydrotalcite-like compound. The Mg-Al complex oxide was prepared by calcinating the compound at 1073 K for 6 h, and then impregnated with Ca(NO₃)₂ solution with the molar ratio of Mg/Al/Ca = 3/1/2 for 30 h, dried overnight, then calcinated at 1073 K, and marked as Mg-Al-Ca (1). The sample Mg-Al-Ca (2) was prepared by same method but from the mixing solution of Mg(NO₃)₂/Al(NO₃)₃/Ca(NO₃)₂.

Ru-based supported catalysts were prepared by incipient wetness method. The catalyst support was impregnated with acetone solution of RuCl₃·nH₂O up to ruthenium content of 4 w%, under stirring for 6 h. After concentration in a rotary evaporator, the obtained material was dried in air at 383 K overnight and subjected to preliminary reduction with a 1N₂/3H₂ stream at 698 K, and then cooled in 1N₂/3H₂ atmosphere. The

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potassium promoter was introduced by incipient wet impregnation with KNO_3 solution at room temperature with molar ratio of $\text{K}^+/\text{Ru} = 5/1$. After stirring for 6 h and infusing for 24 h, the samples were dried in a rotary evaporator at 343K and then dried in the air at 383 K for 12 h. The ammonia synthesis activities of the catalysts with about 35-60 meshes were evaluated by $1\text{N}_2/3\text{H}_2$ flow of 2100 mL/h at 0.2 MPa from 623 K to 773 K. The amount of effluent ammonia was determined by titration method.

As we can see from the **Table 1**, under the same reaction conditions, the catalyst K-Ru/Mg(Al)O exhibited the highest activity, $38.42 \text{ mL NH}_3 \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ at 673K, 3 times more active than K-Ru/MgO, $12.88 \text{ mL NH}_3 \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ at 748K. This means that selection of supports takes great effects on the activity of catalysts. The ammonia synthesis activity of different supports are $\text{K-Ru/Mg(Al)O} > \text{K-Ru/Mg-Al-Ca(1)} > \text{K-Ru/Mg-Al-Ca(2)} > \text{K-Ru/Al}_2\text{O}_3 > \text{K-Ru/CaO} > \text{K-Ru/MgO}$. The combinatorial supports showed higher activity than single supports. However, the sequence of temperature corresponding to the highest activity is just opposite to that of the activity. The optimal temperature for K-Ru/Mg(Al)O, 673K, is the lowest of all, on the contrary, that of K-Ru/MgO is the highest, 748K. The Mg(Al)O has a larger surface area of $140.95 \text{ m}^2 \cdot \text{g}^{-1}$, similar to $\gamma\text{-Al}_2\text{O}_3$, $110\text{-}180 \text{ m}^2 \cdot \text{g}^{-1}$. The other two combinational supports have little surface areas but higher activities than Al_2O_3 . It suggested that the activity of the catalyst is influenced not only by the dispersion of Ru crystals but also by the crystal structure of the supports.

Table 1 Ammonia synthesis activities and BET surface areas

| Catalyst | Optimal activity temperature(K) | Highest activity ($\text{NH}_3/\text{mL} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$) | Surface area of support ($\text{m}^2 \cdot \text{g}^{-1}$) |
|-------------------------------|---------------------------------|--|--|
| K-Ru/MgO | 748 | 12.88 | |
| K-Ru/ Al_2O_3 | 698 | 23.79 | |
| K-Ru/CaO | 723 | 23.22 | |
| K-Ru/Mg(Al)O | 673 | 38.42 | 140.95 |
| K-Ru/Mg-Al-Ca(1) | 698 | 30.75 | 29.10 |
| K-Ru/Mg-Al-Ca(2) | 698 | 26.12 | 14.69 |

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