The Effect of Rare Earth on the Activity of Methanol Synthesis Catalyst

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Abstract: In this paper several rare earth oxides were added into methanol synthesis catalyst by solid-mixing method to improve the activity of methanol synthesis catalyst. Nd_2O_3, CeO_2, La_2O_3 and Sm_2O_3 decrease the catalyst activity, while Pr_2O_3, Gd_2O_3 and Eu_2O_3 increase the methanol yield.

Keywords: Rare earth, methanol synthesis catalyst.

Although the $CuO/ZnO/Al_2O_3$ catalyst has been used as a successful methanol synthesis catalyst from CO hydrogenation for many years, its catalytic activity is not high enough for methanol synthesis from pure CO_2 hydrogenation. Many new synthesis methods, including sol-gel co-precipitation method and ultrasonic synthesis method, were used to prepare the methanol synthesis catalyst[1,2]. In the literature, many metal oxides such as ZrO_2, Cr_2O_3, Ga_2O_3, Al_2O_3, SiO_2 and TiO_2 *etc*. were added into catalyst to improve its catalytic activity and methanol selectivity[3~7]. However, among the rare earth oxides, only La_2O_3 and CeO_2 were used[8,9]. In our laboratory we added 7 types of rare earth oxides to conventional $CuO/ZnO/Al_2O_3$ catalyst, and some good results were obtained.

The $CuO/ZnO/Al_2O_3$ catalyst was prepared by conventional co-precipitation method. A mixed aqueous solution of metal nitrates and an aqueous solution of Na_2CO_3 were added dropwise to distilled water under stirring. The resulted precipitate was aged for 24 hours and filtered out, washed with distilled water and dried in air at 393K overnight. The catalysts modified with rare earth oxides were prepared by mixing the rare earth oxides with this catalyst precursor. All catalysts were calcined in air at 673K for 5h. Before reaction, the catalyst was reduced in a pure hydrogen flow at 523K.

The hydrogenation reaction of CO_2 was conducted at 523K with a total pressure of 4MPa in a fixed bed flow reactor by feeding a gas mixture of H_2 and CO_2 with a H_2/CO_2 molar ratio of 3. The results are shown in **Table 1**. The CO_2 conversion of the catalyst containing Pr_2O_3 is lower than that of the catalyst without rare earth oxide, but its higher methanol selectivity leads to the same methanol yield with the base catalyst ($CuO/ZnO/Al_2O_3$). The activities of the catalysts containing optimum amounts of Nd_2O_3, CeO_2, La_2O_3 and Sm_2O_3 are all lower than that of the base catalyst. The catalyst containing Gd_2O_3 gives the best methanol yield of 7.24%, and the highest methanol selectivity. The catalyst containing Eu_2O_3 gives the highest CO_2 conversion and higher methanol yield than the base catalyst. The above results indicate that Pr_2O_3 and Gd_2O_3 can increase the methanol selectivity, and Eu_2O_3 can increase the conversion of CO_2. Among all the catalysts, the one modified with Gd_2O_3 gives the best catalytic performance. The characterization of these catalysts is in progress.

Table 1. Effect of rare earth oxides as additives on catalytic performance

Catalyst	Rare earth oxides content in catalyst (wt) ‰	Conversion of CO_2 (%)	Selectivity of methanol (%)	Yield of methanol (%)
1	—	19.4	32.6	6.32
2	6.4Pr_2O_3	17.8	35.4	6.32
3	6.4Nd_2O_3	18.5	32.9	6.07
4	6.4CeO_2	18.5	32.4	6.01
5	6.4La_2O_3	18.7	30.5	5.72
6	6.4Sm_2O_3	18.3	31.6	5.80
7	6.4Eu_2O_3	20.2	32.3	6.52
8	6.4Gd_2O_3	19.6	36.9	7.24

The base catalyst component：$CuO/ZnO/Al_2O_3$=40:40:20(wt/wt/wt).
Reaction condition: 4MPa，523K, H_2/CO_2=3, SV=10000ml/g.h.

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