

Synthesis of iso-C₄ Hydrocarbons from CO/H₂ over CeO₂-TiO₂ Oxides

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Introduction

The hydrogenation of CO to branched C₄ hydrocarbons (isobutene and isobutane) is referred to as isosynthesis reaction. Some metal oxides, such as ThO₂, La₂O₃, Y₂O₃, CeO₂, HfO₂ and ZrO₂ etc, have been used as catalysts in the isosynthesis. Recently, CeO₂ has been receiving enormous attention due to its high oxygen storage capacity (OSC), and it has been widely used as a catalyst or a support in catalytic reactions, such as CO oxidation, and automobile exhaust treatment [1]. It has been reported that Ce-Ti-O solid solution showed high redox performance [2]. Li et al. reported that redox properties have a significant effect on the selective formation of iso-C₄ hydrocarbons from CO/H₂ [3]. Therefore, the catalytic performance of CeO₂-TiO₂ binary oxides in the isosynthesis could be expected. In this paper, we report our recent results of CeO₂-TiO₂ as a catalyst tested in the isosynthesis.

Materials and Methods

The CeO₂-TiO₂ binary oxides with different Ce/Ti ratios were prepared by a sol-gel method. Ti[(CH₂)₃CH₃]₄ and Ce(NO₃)₃·6H₂O were used as raw materials and dissolved in ethanol and deionized water, respectively. The two solutions were mixed together under vigorous stirring to get a sol. The sol was gelled and dried at 110°C, and then calcined at 500°C for 3h to get the CeO₂-TiO₂ catalysts. The crystal phases and texture properties of the catalysts were characterized by XRD, TEM and N₂ adsorption-desorption isotherms. The hydrogenation of CO was carried out in a high-pressure fixed-bed flow type stainless steel tube reactor (i.d. 8 mm). Reaction conditions: CO/H₂=1:1; Volume of catalysts (20-40 mesh) =1mL; T=698K; P=5.0MPa; GHSV=720h⁻¹. The products were analyzed by two on-line gas chromatographs.

Results and Discussion

Pure CeO₂ showed a typical cubic fluorite structure at peaks 2θ ~ 28.6 and 33.1°, while Pure TiO₂ showed an anatase structure (2θ ~25.4°) with a part of rutile phase (2θ ~ 27.6°). There were no obvious changes in the structure of CeO₂ when small amount of TiO₂ was incorporated into CeO₂, and no TiO₂ phase was detected at a TiO₂ content of 10-50% in CeO₂-TiO₂. For 80%CeO₂-20%TiO₂ sample (Figure 1, d), the peak at 2θ ~ 30.6° was attributed to the crystalline of Ce₂O₃. The N₂ BET surface areas of the catalysts are shown in Table 1. All the CeO₂-TiO₂ oxides exhibited larger surface areas than pure CeO₂ and TiO₂.

The catalytic activity and selectivity over the CeO₂-TiO₂ catalysts are also listed in Table 1. The main products of CO hydrogenation over CeO₂-TiO₂ catalysts were C₁-C₃ hydrocarbons and CO₂. The selectivities to the hydrocarbons were in the range of 50-64%. TiO₂ showed relatively high CO conversion but lower iso-C₄ selectivity, while CeO₂ showed relatively high iso-C₄ selectivity. When Ti component was incorporated into CeO₂, the activity of CeO₂-TiO₂ increased compared with pure CeO₂. The CO conversion and i-C₄ selectivity achieved maximum (22.9 % and 44.4%) over 80%CeO₂-20%TiO₂ catalyst.

Table 1 Catalytic performance of CeO₂-TiO₂ in CO hydrogenation

No	Content of CeO ₂ (mol %)	Surface area (m ² g ⁻¹ cat.)	CO Conv. (%)	Distribution of hydrocarbons / (C mol %)		
				C ₁ -C ₃	C ₄	i-C ₄
1	0	33	24.3	79.3	14.3	5.1
2	20	87	17.8	52.8	39.7	27.4
3	50	63	17.1	47.1	46.1	35.4
4	80	67	22.9	38.0	55.3	44.4
5	85	97	21.2	41.4	52.0	44.2
6	90	79	20.0	40.2	53.1	45.2
7	100	54	15.0	56.2	36.8	31.5

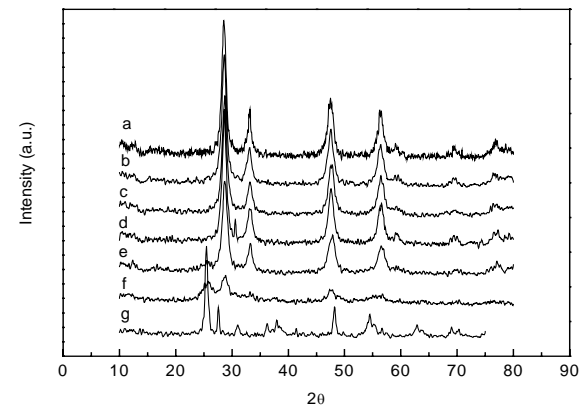


Figure 1. XRD patterns of CeO₂-TiO₂. Content of CeO₂ in CeO₂-TiO₂ (mol %): (a) 100; (b) 90; (c) 85; (d) 80; (e) 50; (f) 20; (g) 0.

Significance

The isosynthesis is a promising process to meet the urgent demand of i-C₄ hydrocarbons since the amount of i-C₄ extracted from C₄ stream of petroleum cracking process is far less to meet the expected demand. CeO₂-TiO₂ binary oxides showed comparatively high catalytic activity and i-C₄ selectivity at moderate reaction conditions.

References

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