

Study on tricyclopentadiene hydrogenation using pellet-type Ru catalyst

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Abstract: Tetrahydrotricyclopentadiene has been used as a fuel having a high energy density. THTCPD can be prepared through hydrogenation of tricyclopentadiene. In this study, tricyclopentadiene hydrogenation was carried out over pellet-type Ru/KIT-6 catalysts in a batch reactor equipped with catalyst basket. The physical and chemical properties of the catalysts were analyzed by N₂ adsorption, H₂-TPR, TEM and XRD. The activity of TCPD hydrogenation over the Ru/KIT-6 catalyst was higher than that over the Ru/Al₂O₃ and Ru/Kieselguhr catalyst, which could be attributed to the larger pore diameters of the Ru/KIT-6 catalyst. The optimal loading of Ru was determined to be 1.5 wt%.

Keywords: Tricyclopentadiene, Tetrahydrotricyclopentadiene, Hydrogenation, Ru/KIT catalyst

1. Introduction

As the energy problems emerging in the world, research on high-performance liquid fuels has become necessary¹. Exo-tetrahydrotricyclopentadiene (exo-THTCPD) is one of high-energy-density fuel because of its high density resulted from multiple bonds of hydrocarbons². Exo-THTCPD can be prepared from decyclopentadiene (DCPD) through oligomerization, isomerization and hydrogenation.³ Tetrahydrotricyclopentadiene (TCPD) has two unsaturated bonds, with one in the norbornene ring and the other in the cyclopentene ring. Compared with single-ring or non-ring compounds, the hydrogenation of multi-ring compounds is more difficult because of the steric hindrance of multi-ring structures. It has been shown that nickel catalysts have very low activity for TCPD hydrogenation. Pt and Pd catalysts can catalyze the reaction, but the activities still need to be improved.⁴ In this study, hydrogenation was conducted using pellet type Ru/KIT-6 catalysts in a batch reactor equipped with mechanical stirrer.

2. Experimental

The KIT-6 material was prepared with an aqueous solution of amphiphilic polymer P123 (Aldrich) mixed with 1-butanol (Aldrich) as a template. Tetraethyl orthosilicate (TEOS, Aldrich,) was used as a silicon source.⁵ Ru/KIT-6 was prepared by incipient wetness method. The prepared catalyst was extruded using an extruder and then calcined at 650 °C for 3 h to remove the organic binder. Reduction of the catalysts was carried out in H₂ flow at 450 °C. The activated catalyst was passivated using 5% O₂ / inert gas (N₂ or He). The hydrogenation reaction of TCPD was conducted in a 200 ml batch reactor equipped with a mechanical stirrer. 40 g of TCPD and 4 g of catalyst were charged into the reactor. The reaction was conducted at 120 °C under 10 bar of hydrogen. Then the products were analyzed by gas chromatography.

3. Results and discussion

With regard to the XRD patterns of the Ru/KIT-6 catalysts, peaks that appeared in the (211), (220) and (332) reflections showed a bicontinuous cubic $Ia\bar{3}d$ symmetrical structure (Fig. 1). This indicates no changes of the basic mesoporous structure of siliceous KIT-6 after Ru loading. Although the loading of Ru over KIT-6 was expected to decrease the specific surface area and the pore diameter, a relatively high surface area and large pore size (~ 8 nm) was observed. As a result, an Ru/KIT-6 material synthesized through Ru

grafting over siliceous KIT-6 was shown to have a well-ordered mesoporous structure and a large pore size. Hydrogenation of TCPD was carried over pellet-type Ru/KIT-6 catalysts in a batch reactor in order to compare their activity with that of the Ru/Al₂O₃ and Ru/Kieselguhr catalyst. As shown in Fig. 2, the activity of TCPD hydrogenation over the Ru/KIT-6 catalyst was higher than that over the Ru/Al₂O₃ and Ru/Kieselguhr catalyst, which could be attributed to the larger pore diameters of the Ru/KIT-6 catalyst. The optimal loading of Ru was determined to be 1.5 wt%. Calcination in an air atmosphere at 550 °C was found to be effective for the regeneration of the used Ru/KIT-6 catalyst for TCPD hydrogenation.

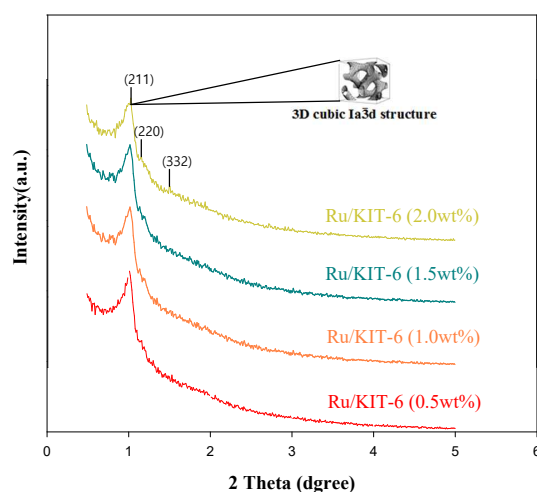


Figure 1. Low angle XRD patterns of Ru/KIT-6 catalysts.

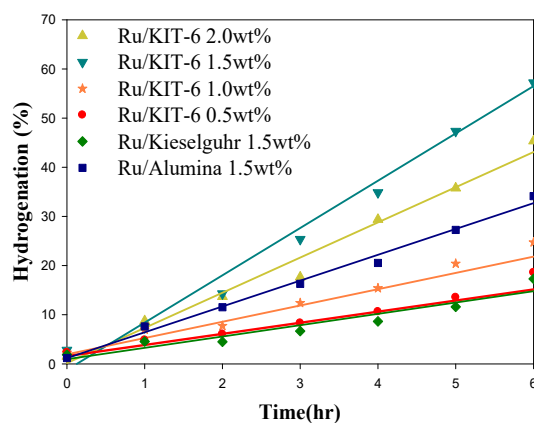


Figure 2. Comparison of catalytic activity of various catalyst (catalyst concentration: 10 wt%, reaction temperature: 120 °C, stirring speed: 150 rpm, pressure: 10 bar, reaction time : 6 h).

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