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Effect of MgO promoter on Ru/γ-Al_2O_3 catalysts for tricyclopentadiene hydrogenation

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ABSTRACT

The objective of this study is to elucidate the effects of MgO promotors on the catalytic physico-chemical properties of Ru/γ-Al_2O_3 catalysts and the activity during the tricyclopentadiene (TCPD) hydrogenation reaction. Ru/γ-Al_2O_3 and Ru-MgO/γ-Al_2O_3 catalysts were produced by means of a coprecipitation method and formed in a bead type. The specific surface area of the regenerated Ru-MgO/γ-Al_2O_3 catalyst is much larger than that of the regenerated Ru/γ-Al_2O_3 catalyst. It was confirmed that the addition of MgO has the effect of alleviating the decrease of the specific surface area during the repetitive regeneration procedure. The addition of MgO had no significant effect on the reducibility of the Ru/γ-Al_2O_3 catalyst. The results of XRD, CO chemisorption and TEM imagery show that the addition of MgO to the Ru/γ-Al_2O_3 catalyst has the effect of decreasing the mobility of Ru atoms during repetitive regeneration at 650 °C. It was confirmed that the degree of catalyst deactivation during four repetitive regeneration trials was much lower than that with an unpromoted catalyst, likely because the addition of MgO prevented the sintering of Ru at the regeneration temperature of 650 °C. The Ru-MgO/γ-Al_2O_3 catalyst is a possible candidate as a reusable catalyst for use during the TCPD hydrogenation reaction.

1. Introduction

Exo-tetrahydrotricyclopentadiene (exo-THTCPD) has drawn keen interest as a type of high-energy-density fuel (HEDF) that features a high density (1.04 g/ml) and high heating value (40 ~ 42 MJ/L) [1–4]. Exo-tetrahydrotricyclopentadiene (exo-THTCPD) goes through the following three steps of production [5–10]: First, as by-products of the naphtha cracking process, cyclopentadiene (CPD) and endo-dicyclopentadiene (endo-DCPD) are produced. In the endo-DCPD and CPD oligomerization step, endo-tricyclopentadiene (endo-TCPD) is produced. Second, endo-tetrahydrotricyclopentadiene (endo-THTCPD) is produced from the hydrogenation reaction of endo-TCPD. Third, isomerization converts endo-THTCPD into exo-THTCPD.

There have been some research findings on catalysts for the DCPD hydrogenation reaction. In contrast, there have been very few studies of heterogeneous catalysts for the TCPD hydrogenation reaction [11]. As a TCPD hydrogenation catalyst, Pd-B/γ-Al_2O_3 prepared through an impregnation approach has been studied [12]. γ-Alumina has been widely used as a catalyst support for high-temperature hydrogenation reactions owing to its good thermal stability. In addition, catalysts containing Pd, Pt, and Rh metals are known for their outstanding activity during hydrogenation reactions of multicyclic hydrocarbons [13–19]. This study applies catalysts where Ru, which is less expensive than the precious metals discussed above, is deposited onto γ-alumina to realize the TCPD hydrogenation reaction.

During the hydrogenation reaction of multicyclic hydrocarbons, the catalysts are supposed to be regenerated for reuse. One major cause of catalyst deactivation is coke, and combustion of coke deposited at temperatures as high as 600 °C is necessary for catalyst regeneration. Metallic sintering is likely to occur as precious metallic catalysts are regenerated at a high temperature, which is a major cause of catalyst deactivation [20–24]. Although Ru catalysts are known to have higher thermal stability than Pt and Pd catalysts, Ru metals as well often involve sintering at temperatures as high as 600 °C [20].

In order to prevent metallic particle sintering on a catalyst surface, the reaction temperature and regeneration temperature are decreased or a textural promotor is deposited along with the metal. It is known that oxides such as Ba, Zn, La, Si, and Mn serve as a textural promotor in catalysts where a precious metal is deposited onto an alumina support [25,26]. MgO can also be utilized as a textural promotor because it can

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