



Activity and deactivation nature of Ru/MnCO₃ catalysts for Fischer–Tropsch reaction

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ABSTRACT

The catalytic activities and different behaviors for catalyst deactivation by forming surface hydrocarbon deposits were investigated on the Cl-free Ru/MnCO₃ Fischer–Tropsch synthesis (FTS) catalysts in a low pressure fixed-bed reactor. Catalytic activity of LT-Ru(NO) was found to be a little higher than that of Ru(NO). The differences seem to stem mainly from ruthenium particle sizes and reduction behavior of adsorbed CO on the catalysts, which would be consistent with the results of CH₄ formation from temperature-programmed reduction (TPR) of pre-adsorbed CO, as well as Ru particle sizes, as ascertained by H₂ and CO adsorptions and TEM measurements. The Ru particle sizes of used catalysts obtained after 120 h-reaction were approximately close to those of fresh catalysts and no ruthenium aggregation occurred. The origin of catalyst deactivation was investigated in terms of the extent of hydrocarbon deposition. The adsorbed atomic carbon at the peak temperature around 250–350 °C was eliminated by H₂ treatment, but the more heavy hydrocarbons at peak temperature over 400 °C such as polymeric and graphitic carbons were not removed by any treatment. The nature of hydrocarbon deposition would be suggested by measuring the deposited carbon with the help of the characterizations, such as thermo-gravimetric analysis, temperature-programmed reduction and diffuse reflectance infrared Fourier transform (FT-IR) measurements.

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1. Introduction

Biomass has recently received increased attention as one potential source of renewable energy [1]. Among all biomass conversion processes, the BTL (biomass to liquid) process is one of the most promising ways to utilize biomass in remote and/or local areas to form sulfur-free jet fuels [2]. The development of high-performance catalysts for the Fischer–Tropsch synthesis is one of the key technologies required for the small-scale BTL process of ca. 10 t/d of biomass resources, which are approximately 1/1000-scale of gas-to-liquid (GTL) process. Ruthenium is known to be the most active metal for this reaction. Indeed, higher CO/H₂ conversion levels, hydrocarbon productivities, and chain growth probabilities can be achieved when using Ru-based catalysts [3–5].

Industrial output of ruthenium is ca. 1/2000 of that of cobalt and the metal cost of Ru is approximately four to five times that of Co metal [6], while space–time–yield in FT reaction catalyzed by Ru is, at least, three to five times higher than that of Co

catalyst [7,8]. Thus, hydrocarbon productivity per Ru or Co metal cost could be almost the same. As opposed to iron, ruthenium catalysts have been found not to be negatively affected by product water [9–12] or oxygenate-containing atmosphere, which is an important requisite to successfully convert biomass-derived syngas into hydrocarbons [12,13], since no formation of inactive ruthenium oxides would occur [9]. So, we believe, taking catalyst regeneration into account, Ru-based small-scale BTL process is of interest.

Ruthenium catalysts have been first found to be active for “poly-methylene synthesis” [14] and, thereafter, it has been reported that rather typical Fischer–Tropsch (FT) product distributions can be yielded on both unsupported and supported ruthenium [9,15–17], when tested at moderate reaction conditions (i.e. pressures ca. 0.1–2 MPa, temperature: 200–250 °C). Anatase-supported Ru clusters were found to be more active than when deposited on rutile [18]. Iglesia et al. [19] showed that the catalytic performance of supported Ru in FTS is moderately affected by the support (silica, alumina, titania) or metal dispersion. Pérez-Zurita et al. [20] studied the production of higher alcohols from syngas with Ru clusters deposited on different reducible supports, concluding that the catalytic performance depends on their reducibility. They found that

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