Single-step hydroconversion of triglycerides into biojet fuel using CO-tolerant PtRe catalyst supported on USY

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ABSTRACT

The direct hydroconversion of triglycerides into biojet fuel (i.e., cascade reactions including hydrogenation, deoxygenation, and hydrocracking) is challenging, even though it is beneficial in terms of process intensification. This is because the minute amount of CO produced during deoxygenation can poison the metal component of various metal–acid bifunctional catalysts, causing undesired overcracking and rapid catalyst deactivation through coke formation. To overcome this problem, we synthesized a CO-tolerant catalyst by supporting bimetallic PtRe on ultra-stable Y (USY) zeolite as acidic support. Compared to conventional catalyst (e.g., Pt/USY), PtRe/USY showed markedly enhanced tolerance to CO because it had weakened interaction with CO and also could rapidly convert the chemisorbed CO into less harmful methane and H_2O through methanation. Consequently, overcracking and catalyst deactivation were greatly suppressed during the direct triglyceride hydroconversion. It is remarkable that PtRe/USY is intrinsically a much poorer hydrocracking catalyst than Pt/USY under pure H_2 atmosphere because of its high hydrogenolysis activity. However, H_2O and CO produced in situ during the deoxygenation of triglycerides selectively poisoned the active sites for undesired hydrogenolysis, thereby making PtRe/USY a highly stable and selective catalyst for producing biojet fuel. Under the optimum condition, 41 wt% of biojet fuel with respect to palm oil could be produced through direct hydroconversion, which satisfied all the required fuel specifications.

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1. Introduction

The International Air Transport Association (IATA) announced that fuel consumption in the aviation sector will increase by 5% annually [1]. To reduce anthropogenic CO_2 emissions, IATA decided to achieve carbon-neutral growth by 2020 and 50% reduction by 2050 as compared to 2005 [2]. Biomass-derived jet fuel (or biojet fuel) has been considered one of the most promising solutions in the aviation industry for reducing the operating cost and the environmental impact. Four major catalytic processes have been investigated for producing biojet fuel [3]: (a) oil-to-jet (deoxygenation and hydrocracking of triglycerides) [4–9], (b) gas-to-jet (gasification and Fischer–Tropsch synthesis) [10–12], (c) alcohol-to-jet (alcohol dehydration and oligomerization) [13–17], and (d) sugar-to-jet (biological/catalytic upgrading of sugars) [18,19]. Among these technologies, the oil-to-jet technology is already commercially available, and the produced biojet fuel has been tested for commercial and military flights [20–22]. The resultant biojet fuel is known to contain even lower aromatic and sulfur contents than those in petroleum-derived jet fuel [23–25], and it is currently allowed for blending into conventional jet fuel up to 50% [25].

Commercial oil-to-jet processes generally include multiple reaction steps and require at least two sequentially connected reactors (Scheme 1) [3–5]. In the first reactor, three major reactions occur over supported metal (e.g., Pt, Pd, or Ni) [5,6,26–28] or MoS_2-type [29,30] catalysts: (1) hydrogenation of the C=C bonds in the unsaturated fatty acid units of triglycerides (reaction *i* in Scheme 1a), (2) hydrogenolysis of triglycerides into fatty acids (reaction *ii*), and (3) deoxygenation of the fatty acids into linear paraffins (reaction *iii*). After the reactions in the first reactor are complete, inorganic gas products (CO, CO_2, and H_2O) are removed, and the liquid paraffin products are injected into the second reactor for hydrocracking (reaction *iv*) over metal–acid bifunctional catalysts (Scheme 1b) [5,31,32]. The final hydrocarbon products are fractionated by distillation to collect *iso*-rich C_8-C_{16} paraffins,