

Enhancing Brønsted and Lewis Acid Sites of the Utilized Spent RFCC Catalyst Waste for the Continuous Cracking Process of Palm Oil to Biofuels

I. Istadi,* Teguh Riyanto, Luqman Buchori, Didi Dwi Anggoro, G. Gilbert, Kania Adelia Meiranti, and Elok Khofiyanda

Cite This: *Ind. Eng. Chem. Res.* 2020, 59, 9459–9468

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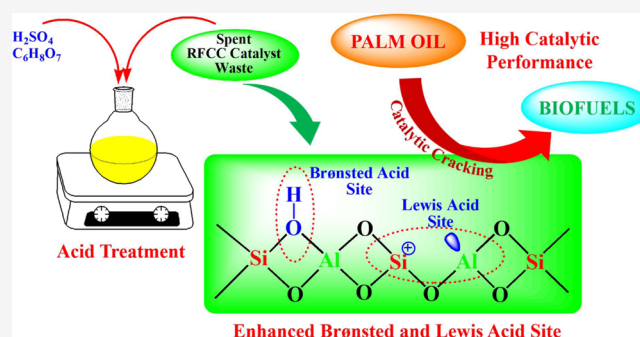
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ABSTRACT: Catalyst waste from the residue fluid catalytic cracking (RFCC) plant process can still be utilized to catalyze the catalytic cracking of palm oil to fuels. However, we should regenerate the active sites of the catalyst waste. This paper focuses on enhancement of Brønsted and Lewis acid sites on the spent RFCC catalyst waste through various acid treatments in order to regenerate its catalyst active sites. In order to regenerate the Brønsted and the Lewis acid sites as active sites in the palm oil catalytic cracking, the spent RFCC catalyst was treated by citric acid, sulfuric acid, and mixture of both acids. The catalysts were characterized by X-ray fluorescence, X-ray diffraction, Brunauer–Emmett–Teller–Barrett–Joyner–Halenda, and pyridine-FTIR analysis. The modified catalyst performance was tested over a fixed bed reactor for the catalytic cracking process of palm oil to liquid fuels. It was found that the acid treatment on the spent RFCC catalyst can increase surface area, pore volume, and Brønsted to Lewis acid site ratio of catalysts. The Brønsted acid sites of the spent RFCC catalyst strongly increase by the treatment using sulfuric acid, which is because of the proton transfer from acid to catalyst and because of the formation of sulfate groups (HOSO_3^-) in the catalysts. It was found that the Brønsted acid site leads to the formation of long-chain hydrocarbon, while the Lewis acid site pronounces the formation of short-chain hydrocarbon and coke. Moreover, the total acidity and the Lewis acid site amount on the catalyst have roles in the formation of hydrocarbon fraction in the liquid product.



1. INTRODUCTION

Biofuel appears as a promising alternative as a renewable energy because of the increase in energy demand and the decrease in fossil fuel reserves. Biofuels, such as biodiesel (FAME, fatty acid methyl ester), green gasoline (bio-gasoline), green kerosene, and green diesel (fossil diesel-like), can be produced from vegetable oils. Biodiesel production from vegetable oils was widely studied by researchers, in which the most developed process of biodiesel production was transesterification.^{1–3} However, biodiesel needs to be mixed with fossil diesel, and its hygroscopicity caused the clogging in the engine filter.⁴ Furthermore, the engine needs to be modified for the use in mixtures with fossil diesel at levels above 20%.⁴ The other processes for biofuel (bio-gasoline, green kerosene, and green diesel) production are thermal cracking,⁵ catalytic cracking,^{6–8} and hydrodeoxygenation⁹ and deoxygenation^{10–12} reaction. The catalytic cracking was widely developed by researchers because of low energy requirement, low operational cost, and high flexibility to utilize many vegetable oil types rather than thermal cracking.¹³ Palm oil is the most favorable vegetable oil as the feedstock for biofuel production,^{14,15} which is because of the high content of long-

chain hydrocarbon, the relatively equal ratio of saturated and unsaturated oil content,¹⁶ giving significant contribution on aromatic compounds in the liquid product,⁵ and abundant availability in the world especially in Indonesia and Malaysia regions.

The catalytic cracking reaction of palm oil follows the chain reaction mechanism involving initiation, propagation, and termination.¹⁷ The main step is the initiation step, which is the attack of one Brønsted acid site or Lewis acid site from the catalyst to the reactant molecule to form a carbenium ion as a carbocation.¹⁷ However, until now, the role of each acid site (Brønsted or Lewis acid site) was still not clear, although many researchers suggested in this case. For this reason, many researchers have developed the heterogeneous acid catalysts

Received: March 3, 2020

Revised: April 26, 2020

Accepted: April 29, 2020

Published: April 29, 2020

