Applied Catalysis A: General 447–448 (2012) 186–192

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Slurry-phase hydrocracking of vacuum residue with a disposable red mud catalyst

Chinh Nguyen-Huy[a], Hyukmin Kweon[a], Hanna Kim[a], Do Kyoung Kim[b], Do-Woan Kim[b], Seung Hoon Oh[b], Eun Woo Shin[a,*]

[a] School of Chemical Engineering and Bioengineering, University of Ulsan, Daehakro 93, Nam-gu, Ulsan 680-749, South Korea
[b] Catalyst Lab, SK Innovation, Exporo 325, Yuseong-gu, Daejon 305-712, South Korea

ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form 1 June 2012
Accepted 15 September 2012
Available online 8 October 2012

Keywords:
Red mud
Vacuum residue
Slurry-phase
Hydrocracking

ABSTRACT

In this study, red mud (RM) was used as a catalyst in slurry-phase hydrocracking of vacuum residue (VR) in batch system. Without RM, thermal cracking occurred and a lighter fraction and higher conversion was achieved than in the presence of catalyst. However, the catalytic cracking obviously inhibited both the coke formation and residue cracking reaction. We investigated the influence of reaction temperature, reaction time and RM concentration on VR conversion. Reaction temperature and time significantly improved the yield of naphtha, diesel and vacuum gas oil; unfortunately, they also increased the gas fraction, which is an undesirable product. Catalyst concentration negligibly affected the VR conversion while vacuum gas oil fraction in product distribution increased with catalyst concentration, indicating that the cracking reaction was suppressed in the presence of catalyst. Through the characterization of fresh and spent catalysts by diverse techniques, it has been determined that the crystalline iron oxide of RM transforms into pyrrhotite ($Fe_{(x-1)}S_x$), an active phase for the hydrocracking reaction, due to presence of sulfur in VR. Our results show that RM is possibly self-activated during the reaction and the pretreatment step can be eliminated.

1. Introduction

Crude oil still plays a leading role in the global supply of fuels and energy even though there is controversy related to its impact on the environment, including climate change. Vacuum residue (VR) is the heaviest fraction obtained from the vacuum distillation of atmospheric residue (AR). The use of VR as a heavy furnace oil fraction is limited due to its considerable contribution to environmental pollution. These heavy hydrocarbon feedstocks must be converted into more valuable products with lower boiling points. The efficiency of refineries is highly dependent on the availability of processes that convert VR into low-boiling products.

VR can be converted into low-boiling fractions through coking, visbreaking, catalytic cracking and hydrocracking processes. Nowadays, many researchers are striving to improve the catalytic hydrocracking process [1–3]. Hydrocracking with a fixed-bed or ebullated-bed reactor has been performed commercially, but there is often a critical problem with catalytic deactivation caused by coking and the deposition of heavy metals, particularly when an increase in the conversion of residue is intended or a heavier feedstock is processed. Slurry-phase residue hydrocracking is a newly developed technique for processing heavy oils [4–6]. It is favorable to achieve high conversion because of the enhancement in the mass-transfer rate, which is beneficial not only to the catalytic reaction, but also for temperature control within the reactor. In today's world, research on the slurry-phase hydrocracking processes is very active. There are now more than 10 such technologies in pilot stages and some of them have already been used in industrialized applications [4].

Catalysts for the slurry-phase hydrocracking of heavy oil have undergone two development phases, i.e., heterogeneous solid powder catalysts and homogeneous dispersed catalysts. Although the homogeneous dispersed catalysts show a better catalytic performance than solid powder catalysts, this does not mean that the solid powder catalysts are not attractive to researchers. There is an ongoing search for a low cost catalyst with good catalytic performance for industrialized applications. Red mud (RM) is a by-product from the manufacturing of alumina by the Bayer process, specifically the solid residue of the caustic leaching of bauxite. The main constituents of RM are iron, titanium and aluminum oxides, with significant silicon, calcium and sodium oxide content. RM has been studied as a hydrogenation catalyst for coal [7,8], biomass [9], oil shale [10], and certain organic compounds [11]. Although RM has less activity than the noble metals and metal oxides, it has a lower

* Corresponding author. Tel.: +82 52 259 2253; fax: +82 52 259 1689.
E-mail address: ewshin@mail.ulsan.ac.kr (E.W. Shin).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.09.043