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ZrO_2-impregnated red mud as a novel catalyst for steam catalytic cracking of vacuum residue

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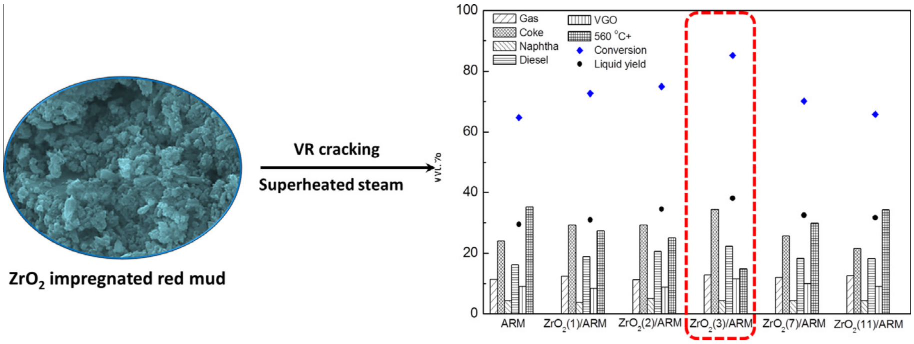
HIGHLIGHTS

- ZrO_2-impregnated red mud were used for steam catalytic cracking of vacuum residue.
- 3 wt% ZrO_2-impregnated red mud exhibited the best performance.
- 3 wt% ZrO_2-impregnated red mud shows a high surface area and good catalyst stability.
- 3 wt% ZrO_2-impregnated red mud improves hydrogenation activity.
- ZrO_2-impregnated red mud has good durability for steam catalytic cracking.

GRAPHICAL ABSTRACT



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ABSTRACT

ZrO_2-impregnated red mud catalysts were employed as a novel catalyst for catalytic cracking of vacuum residue with steam. Under the batch reaction condition at 470 °C for 2 h with superheated steam, 3 wt% ZrO_2-impregnated red mud exhibited the best performance for catalytic cracking of vacuum residue. Furthermore, under the same reaction conditions, the conversion and liquid yield of 3 wt% ZrO_2-impregnated red mud were higher than those of 3 wt% ZrO_2-supporting Al–FeOx, a well-known catalyst for catalytic cracking of heavy oil with steam. 3 wt% ZrO_2-impregnated red mud also showed better catalytic performance than 3 wt% ZrO_2-supporting Al–FeOx under the fixed-bed reaction conditions at 500 °C for 2 h with steam atmosphere, resulting in higher conversion as well as liquid yield. The better catalytic performance of 3 wt% ZrO_2-impregnated red mud was due to large surface area and high catalyst stability. The large surface area of 3 wt% ZrO_2-impregnated red mud could generate more active sites for hydrogenation, which induced higher H/C ratio in liquid product. X-ray diffraction data of the spent catalysts showed that iron oxide phase in 3 wt% ZrO_2-impregnated red mud maintained a hematite structure while it in 3 wt% ZrO_2-supporting Al–FeOx was transformed to magnetite, inactive phase for catalytic cracking.

1. Introduction

Refineries face the problem of increasing production of heavier cuts such as vacuum gas oil (VGO) and vacuum residue (VR) [1,2]. New technology that converts the heavy hydrocarbon feedstock of VR into more valuable products with lower boiling points is highly sought after. Among several processes including coking, visbreaking, and catalytic cracking, catalytic cracking with steam has attracted attention since it uses steam as an alternative, inexpensive hydrogen source [3–10]. Several studies have been reported that provide water as an alternative hydrogen source for heavy oil upgrading including aquaconversion [7,8] and supercritical water treatment [9,10]. The catalytic cracking of

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heavy oil in a steam atmosphere has been developed with iron oxide supporting ZrO_2 catalysts (ZrO_2–FeOx), and this process succeeded in production of lighter fuels from atmospheric-distilled residual oil and vacuum-residual oil [3–6].

Red mud (RM), a solid waste product of the Bayer process, is composed of a mixture of iron, aluminum and titanium oxides, with significant silicon, calcium and sodium oxide contents. RM has been applied as a catalyst for liquefaction of coal [11,12], biomass [13] and hydrogenating anthracene oil [14]. In our previous studies, we developed and used RM as a catalyst for slurry-phase hydrocracking of [15–17]. Its main components are iron oxides and it is a potential catalyst for catalytic cracking of VR with steam by impregnation of ZrO_2. In this work, ZrO_2-impregnated RM was prepared and applied as a novel catalyst for catalytic cracking of VR with steam. To our knowledge, there are no reports in the literature on the catalytic cracking of VR with steam in the presence of ZrO_2-impregnated RM. Our results demonstrated that ZrO_2-impregnated RM is a good catalyst for steam catalytic cracking of VR.

2. Experimental

2.1. Catalysts and materials

RM was supplied by the KC Corporation (Seoul, South Korea) and activated with the Pratt and Christoverson method [18]. The activated RM was denoted as ARM. ZrO_2 was impregnated into the ARM by a conventional impregnation technique using an aqueous excess solution of ZrO_2 precursor. Certain amounts of $ZrO(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich, 99%) salt was dissolved in a beaker and then 5 g of ARM was added to the solution. The solution was stirred at 30 °C for 1 h and slowly heated to 50 °C while stirring constantly to evaporate water. The paste samples were dried at 100 °C in an oven for 12 h and then calcined at 550 °C for 2 h with a ramp of 1.5 °C/min. The catalysts obtained are referred to as $ZrO_2(x)$/ARM where x is the nominal weight percentage of ZrO_2 (x = 1, 2, 3, 7, 11). A ZrO_2-supporting complex metal oxide of Fe and Al catalyst was also synthesized for comparison, following to the procedure in literature [4]. The support was prepared by a coprecipitation method using aqueous iron (III) chloride and aluminum sulfate (concentration of $FeCl_3{\cdot}6H_2O$ = 4.8 wt%; $Al_2(SO_4)_3.14–18H_2O$ = 4.8 wt%), and then treated with steam at 550 °C for 1 h (denoted as Al–FeOx). ZrO_2 was impregnated into the Al–FeOx by a conventional impregnation technique using an aqueous excess solution of $ZrO(NO_3)_2{\cdot}6H_2O$. The final powder product was designated as ZrO_2/Al–FeOx. The ZrO_2 contents in each catalyst were measured by EDX analysis and provided in Table 1. A commercial VR was used as a feedstock for the reaction tests and its properties was described in Table S1 (see the supplementary material).

2.2. Catalyst characterization

The structures of the catalysts were analyzed using an X-ray diffractometer (Rigaku RAD-3C, Japan) with Cu Ka radiation (l = 1.5418 Å) at a scan rate of 2° (2θ)/min, operated at 35 kV and 20 mA. The composition of catalysts was determined by an energy-dispersive X-ray spectrometer (FE-SEM–EDX, JEOL, JSM-600F, Japan). The surface area of the catalysts was evaluated from nitrogen adsorption isotherms measured at −195.6 °C (Micromeritics ASAP 2020 apparatus, USA).

2.3. Catalytic cracking of VR with steam

Experiments were performed in a 100 ml batch type autoclave fitted with a stirrer. The reactor was loaded with 20 g of VR, 1 g of catalyst and 20 g of deionized water. The pressure of the system was approximately 3 MPa when the system was heated to 470 °C. Water exists as steam under these conditions. Before heating, the reactor was purged with N_2 to ensure an oxygen-free atmosphere. After 2 h reaction time, the reactor was cooled to room temperature using a water cooler and a fan. The gas products were released to the air. Reactor contents were centrifuged to separate the liquid products from the solid–liquid mixture. Conversion of VR and the yield of each product were calculated by balancing the content of the desired boiling point products in the following equations:

$$\text{Gas yield (wt\%)} = \frac{[\text{input VR weight}] - [\text{weight of all of the products}]}{\text{Feed VR weight}} \times 100$$

$$\text{Liquid yield (wt\%)} = \frac{[\text{weight of naphtha} + \text{diesel} + \text{VGO products}]}{\text{Feed VR weight}} \times 100$$

$$\text{Coke yield (wt\%)} = \frac{[\text{weight of coke produced during the reaction}]}{\text{Feed VR weight}} \times 100$$

$$\text{Each desired product yield (wt\%)} = \frac{[\text{products weight of desired boiling point}]}{\text{Feed VR weight}} \times 100$$

$$\text{Conversion (wt\%)} = [\text{Gas yield}] + [\text{liquid yield}] + [\text{Coke yield}]$$

The distribution of desired liquid products – naphtha (<150 °C), diesel (<350 °C), VGO (<560 °C) and 560 °C+ fraction (>560 °C) – was measured by GC-SIMDIS (AC Analytical Controls, Agilent 7890). The analysis conditions were based on ASTM D-2887 (simulated distillation) and ASTM D-5307 methods [19,20]. The hydrogen and carbon contents in liquid products were analyzed by Thermo Scientific™ FLASH 2000 CHNS/O Analyzers. To evaluate the reproducibility of the experiments, each experiment was repeated several times. The remaining product in solid form was extracted with toluene to remove soluble deposits, oil, and remaining feed [21]. The toluene-insoluble fraction consisted of coke, catalyst, and inorganic matter. After washing, the solids were dried in an oven at 120 °C for 4 h, and then ground using an agate mortar. The coke yield was determined by TGA analysis (Fig. S1 in the supplementary material).

For further understanding the reaction mechanism and evaluating the catalytic activity of ZrO_2-impregnated red mud, $ZrO_2(3)$/ARM and $ZrO_2(3)$/Al–FeOx were applied for steam catalytic cracking of VR in a fixed-bed reactor (Fig. S2 in the supplementary material). The fixed-bed reactor was loaded with 0.5 g of catalyst; reaction temperature was 500 °C and reaction pressure was 0.1 MPa. We diluted the VR with toluene to reduce its viscosity and used the resulting solution at 10 wt% of VR as feedstock. All of catalysts were confirmed to be inactive to toluene in a preliminary experiment. The time factor W/F_R was 0.6 h, where F_R is the flow rate of VR without toluene and W is the amount of catalyst. A mixture of steam and nitrogen was introduced into the reactor as a carrier gas. The flow rate of nitrogen was 75 cm^3/min and the flow rate of steam was defined by vaporization of 0.3 ml/min