Minerals Engineering 127 (2018) 1–5

Contents lists available at ScienceDirect

Minerals Engineering

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

Short communication

Towards efficient extraction of La(III) from spent FCC catalysts by alkaline pre-treatment

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ARTICLE INFO

Keywords:
Spent FCC catalysts
Rare earth metal
Leaching
Measured crystallinity
Alkaline treatment

ABSTRACT

In Vietnam, Dzung Quat Refinery disposes about 7300 tonnes of spent fluid catalytic cracking (SFCC) catalysts per year. The recovery of rare earth metals (La(III), Ce(III),…) contained in SFCC catalysts using acid leaching process has attracted much attention of scientific community. In this study, the effect of alkaline pre-treatment of spent catalysts prior to the acid leaching process on the leaching yield of La(III) was investigated. The results showed that alkaline pre-treatment caused zeolite destruction, which had a positive effect on the leaching of La (III). High leaching yields of La(III), 80% and 86%, were achieved when the SFCC catalysts were pre-treated with NaOH and NH_3, respectively, before leaching with 2 M HNO_3 solution at 50 °C. These results were comparable with the one obtained from the sample that was leached by 7 M HNO_3 at 50 °C without the initial alkaline pre-treatment. NH_3 pre-treatment significantly enhanced the zeolite destruction in the SFCC catalysts and increased La(III) leaching yield compared to the NaOH pre-treatment. It is likely due to NH_3 interactions with contaminant metals (e.g. Ni, V, and Fe), which were deposited on catalysts during cracking process.

1. Introduction

Fluid catalytic cracking (FCC) is an important process in the refining industry to convert high boiling hydrocarbon fractions (FCC feedstock) to valuable commercial products such as light olefins, gasoline, diesel (Chiranjeevi et al., 2014). Besides hydrocarbons, FCC feedstock also contains unwanted contaminant metals including vanadium (V), nickel (Ni), iron (Fe), calcium (Ca) and sodium (Na) (Topete, 2011). These metals tend to deposit on the FCC catalysts, decreasing cracking performance and promoting coke formation. To maintain the catalytic activity at an acceptable level, it is necessary to regenerate the catalysts by burning off the coke with air at high temperature (Sadeghbeigi, 2012). However, FCC catalysts are progressively deactivated irreversibly due to the high temperature of the process and the presence of metal contaminants (Ferella et al., 2016). Therefore, during the operation, part of the FCC catalysts is removed from the cracking unit and replaced with fresh catalysts in order to keep the overall catalytic activity. The removed catalysts become spent FCC (SFCC) catalysts and most of them have been disposed in landfills. The amount of SFCC catalysts is increasing very fast each year, up to 700,000 tonnes/year, and such amount cannot be simply treated by landfills (Ferella et al., 2016). Moreover, there are still some concerns about the leachability of the metals, which reside within the SFCC catalysts, such as nickel, vanadium and iron (Furimsky, 1996).

A very interesting way for the treatment of SFCC catalysts is the extraction of rare earth (RE) metals. Typically, SFCC catalysts contain from 0.5 wt% to more than 3 wt% of rare earth oxides (such as oxides of lanthanum, cerium, praseodymium, neodymium,…) (Gao and Owens, 2012; Innocenzi et al., 2015). The extraction of RE metals from SFCC catalysts has attracted many researchers and investors since rare earths supply chains are fully controlled by the Chinese government that could influence the availability as well as the price of rare earth elements (Ferella et al., 2016; Ilankoon et al., 2018). Consequently, recovery of RE from SFCC catalysts is not only a good option for a sustainable supply of RE metals but also an excellent way to reduce environmental concerns.

FCC catalysts, having zeolite Y as the main component, operate under severe conditions, especially during the regeneration step with the presence of steam, air and high temperature (Sousa-Aguiar et al., 2013). As consequences, FCC catalysts undergo dealumination which

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https://doi.org/10.1016/j.mineng.2018.07.020
Received 9 November 2017; Received in revised form 20 July 2018; Accepted 21 July 2018
0892-6875/

increases Si/Al ratio, and influences the activity and the selectivity of the catalysts (Aaron, 2017). RE oxides (mainly La_2O_3 and CeO_2) have been reported to limit the extent to which zeolite dealumination occurs (Sishi et al., 2017; Vierheilig, 2014). These oxides have been widely investigated as promoters to improve the activity, selectivity and thermal stability of FCC catalysts (Jinyu et al., 2017b; Trigueiro et al., 2002; Roelofsen et al., 1986). During reaction and regeneration steps, RE elements are known to form bridges with framework oxygen atom of zeolite (Roelofsen et al., 1986; de la Puente el al., 2000; Du et al., 2013). Yang et al. (2003) proposed that the positive electric field of RE induces an increase in negative charge on the oxygen atom. This, in turn, causes the neighbor Al atom to become more positively charged. As a consequence, electrostatic attraction between Al and O atoms is stronger and the Al—O bond rupture is much more difficult. The incorporation of RE enhances the hydrothermal stability of the Al—O bond and thus, of the zeolite framework. The results of several studies also indicate that there is positive correlation between the hydrothermal stability and the concentration of RE metals in the FCC catalysts (Jinyu et al., 2017b; Sishi et al., 2017; Vierheilig, 2014).

Vierheilig (2014) employed a leaching process to recover RE metals from SFCC catalysts. About 83% of RE metals (including lanthanum – the most abundant element, cerium, praseodymium, and neodymium) were recovered with a small amount of Al contaminant (7%) when using 16 M nitric acid at a temperature of 80 °C in 3.5 h. Similar to Veirheilig, Gao and Owens (2012), in their patent, also used HNO_3 or HCl to leach RE oxides out of SFCC catalysts. The leaching conditions were 5 wt% of HCl or 68 wt% of HNO_3, 70–82 °C and the duration of digestion varied from 5 min to 3 h. More than 65% of RE oxides were leached out from the SFCC catalysts, and the final product showed a high purity (96.46 wt% La_2O_3 and 1.14 wt% CeO_2). Innocenzi et al. (2015) carried out the leaching step with 2 M H_2SO_4 at either 25 or 80 °C in 3 h. Better leaching yields of RE metals (89% of La and 82% of Ce) were obtained at a higher temperature (80 °C). Wenzel et al. (2016) also studied the recovery of RE metals from the SFCC catalysts. The study focused on investigating factors that possibly affect the leaching step such as types of acid, acid concentration, temperature, time, and solid-to-liquid ratio. The results showed that more than 90% of the La (III) amount in SFCC catalysts were dissolved in HNO_3 after 1 h at 80 °C. In general, the leaching step usually takes place at high concentration of acid or at high temperature to facilitate the leaching yields of RE metals (Gao et al., 2012; Innocenzi et al., 2015; Jinyu et al., 2017a; Vierheilig, 2014; Wenzel et al., 2016). However, doing that also promotes the leaching yields of other metals in SFCC catalysts such as Al, Fe, Ni, and V. Moreover, utilization of high acid concentration and high temperature in leaching step will increase the cost of the process.

According to Briend-Faure (1988), the treatment of zeolite with alkaline solutions leads to pronounced structural damage of zeolite Y. It is expected that the decrease in structural stability of zeolite could facilitate the leaching of RE elements. Thus, the aim of the present work is to examine the effect of SFCC catalysts pre-treatment with ammonia or sodium hydroxide on the damage of zeolite structure and on the leaching efficiency.

2. Experimental

2.1. Materials

The SFCC and fresh FCC (FFCC) catalysts samples were provided by Dzung Quat Refinery (June 2016). The received samples were dried at 140 °C for 48 h. Ammonia solution (28 wt%) and sodium hydroxide (≥96 wt%) were used for the pre-treatment of the SFCC catalysts prior to the leaching step. Nitric acid (68 wt%) was used as the leaching agent.

2.2. Experimental procedure

Alkaline pre-treatment: 10 g of SFCC catalysts were added to 30 mL of base solution, prepared at desired pH using NH_3 or NaOH. The mixture was then stirred with a speed of 200 rpm at 30 °C for 60 min. The solid was filtered through PTFE-filters and dried at 100 °C in 24 h.

Leaching: The solid was leached by HNO_3 (from 2 M to 7 M) at 50–80 °C for 60 min with a stirring speed of 200 rpm. The ratio of "solid (g)/solution (ml)" was kept constant at 1/3 (10 g of SFCC catalysts and 30 mL of HNO_3). The leachate solution was analyzed by an inductively coupled plasma (ICP-OES) spectrometer OPTIMA 2000 DV (PerkinElmer).

Nickel impregnation onto FFCC catalysts procedure: The fresh catalysts were pre-treated at 540 °C for 3 h in air. FFCC catalysts were then impregnated with nickel naphthenate dissolved in i-octane according to Mitchell method (Mitchell, 1980). The Ni loading added to FFCC catalysts is 1 wt%. Ni impregnated sample was dried at 110 °C for 12 h, calcined in air at 550 °C for 6 h and subsequently steamed at 800 °C for 4 h. This sample is noted FCC-Ni.

2.3. Analysis

The metal quantities presented in fresh and SFCC catalysts were determined by X-ray fluorescence (XRF) using S4 Pioneer instrument (Bruker) based on the standard ASTM D 7085 (2010). The metal contents in the catalysts were also determined by ICP-OES method. Firstly, a complete chemical digestion of the catalysts were performed in a microwave MARS 5E (CEM) with a $HNO_3/HF/H_2O_2/H_3BO_3$ mixture (Wenzel et al., 2016). Then the metal concentrations in the obtained solution were analyzed using an ICP-OES spectrometer OPTIMA 2000 DV. These concentrations are utilized to calculate the corresponding metal contents in the initial catalysts. The RE and Al contents in the leachate solution were evaluated by ICP-OES method in order to calculate leaching yield. Each elemental analysis experiment was conducted three times. The average is considered as the final composition.

XRD patterns were recorded in the $5^\circ \leq 2\theta \leq 40^\circ$ range on a Bruker D8 Advance diffractometer using CuKα radiation generated at 40 kV and 40 mA. The percentage of crystallinity was measured using ASTM D3906-03 standard method (2013). The standard deviations of repetition for the measurement of crystallinity of FCC catalysts do not exceed 0.04.

N_2 physisorption was performed on all samples on a TRISTAR 3020 Micromeritics unit. Prior to analysis, the samples were degassed in situ at 400 °C for 4 h under vacuum. The zeolite and total surface areas were calculated by the t-plot method following the standard test in the ASTM D4365 (2013).

3. Results and discussion

Table 1 shows the compositions of the SFCC catalysts. Silica and alumina had highest concentrations (45.4 wt% Al_2O_3; 46.8 wt% SiO_2). Lanthanum oxide and cerium oxide contents were 2.52 wt% and 0.18 wt%, respectively. Other metal oxides (TiO_2, Fe_2O_3, NiO, V_2O_5, MgO, CaO, Na_2O) had concentrations lower than 2 wt%.

3.1. Effect of alkaline pre-treatment on the FCC catalysts structure

Table 2 summarizes the measured crystallinity, the zeolite unit cell size and the surface areas of the studied samples. Apparently, the crystallinity of SFCC catalyst decreased after alkaline pre-treatment. When pH value of NH_3 solution was increased from 7 to 10, the measured crystallinity dropped significantly from 56.4% to 36.2%. The unit cell size and zeolite surface area also reduced corresponding to the decrease in crystallinity, whereas the total surface area variation was rather insignificant. NaOH solution, when used as the alkaline, resulted in similar effects on these parameters. These results indicate that the