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Catalytic cracking of crude oil to light olefins and naphtha: Experimental and kinetic modeling

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ABSTRACT

The direct catalytic cracking of three light crude oils have been evaluated over an equilibrated FCC catalyst (E-Cat) blended with MFI zeolite in a microactivity test unit at 550 °C and catalyst/oil ratio between 1 to 4. At 60% conversion, the Super Light (ASL) crude oil yielded about 10 wt.% C₂–C₄ olefins and 60 wt.% naphtha over E-Cat, Extra Light (AXL) crude oil yielded 13 wt.% light olefins and 52 wt.% naphtha, while for Arab Light (AL) crude oil, light olefins and naphtha produced were 12 and 51 wt.%, respectively. The addition of MFI with varying Si/Al molar ratio (Z30, Z280 and Z1500) to E-Cat increased the yield of light olefins with a maximum at 21.3 wt.% for AXL over E-Cat/Z280. PIONA analysis of co-produced naphtha showed an increase in aromatics content over all additives with a maximum obtained from the cracking of AL over Z30 (91 wt.%). Steam treatment of Z280 led to a slight change in the yield of light olefins and reduction of naphtha aromatics for the three types of crude oils. A four-lump kinetic model accurately predicted experimental yields of AL cracking over E-Cat and E-Cat/Z280 between 500 °C and 550 °C. From the kinetic model, the apparent activation energy for the conversion of naphtha to gases decreased from 21.2 kcal/mol over E-Cat to 16.2 kcal/mol over E-Cat/Z280 which indicates that Z280 facilitated the increased cracking of naphtha-range species to light olefins

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1. Introduction

While thermal cracking of various hydrocarbons remains the main source of light olefins, intense research is ongoing to develop cost-effective catalytic routes that are less energy intensive and that emit less carbon emissions (Rahimi and Karimzadeh, 2011). The major source of ethylene and propylene is the traditional steam naphtha cracker that supplies about 57% of global propylene as a by-product to ethylene production. The fluid catalytic cracking (FCC) unit is also an important source of propylene producing about 35% of world propylene as a by-product to gasoline production (Chau et al., 2016; Sadrameli, 2016). The remaining 8% of world propylene is produced

by 'on-purpose' processes such as propane dehydrogenation, olefin metathesis and methanol-to-propylene.

The FCC process is known for its flexibility to crack a wide range of low-value heavy hydrocarbons as well as new potential feedstocks such as straight-run shale oils and bio-oils (vegetable and pyrolysis) through modifications to catalyst and operating conditions (Bryden et al., 2014; Vogt and Weckhuysen, 2015). However, light paraffinic oils contain lower molecular weight components boiling below 343 °C that are more difficult to crack especially the components below 221 °C with low coke production (Letzsch and Ashton, 1993). Corma et al. (2017) reviewed the direct catalytic cracking of crude oil to produce basic chemicals, mainly light olefins, using technologies derived from FCC. Several oil

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Nomenclature

E_{ij}	Apparent activation energy for reaction of lump I to lump j
k_{ij}	Reaction rate constant for reaction of lump I to lump j
$k_{o,ij}$	Pre-exponential factor for the reaction of lump I to lump j
R	Universal gas constant
t	Contact time
T	Reaction temperature
T_o	Average temperature of the experiment
t_{os}	Time on stream
Y_i	Weight fraction of lump i
α	Deactivation constant
φ	Deactivation function

and chemical companies have patented various catalytic methods for the conversion of whole crude oil to light olefins and naphtha by integrating FCC unit with other processes (Powers, 2006; Long et al., 2014). Chen et al. (2015) suggested a two-stage FCC riser for the cracking of a mixture of shale oil and 30% vacuum residue to enhance the production of propylene.

Maximizing propylene yield in FCC unit requires specific catalysts or additives and the operation at high severity and short contact time (Buchanan, 2000). MFI additives can increase propylene yield from about 5 wt.% in conventional FCC unit to about 15 wt.% depending on the type of feedstock (Aitani et al., 2000). MFI additives crack C_7 – C_{10} gasoline range components to light olefins, mainly propylene and butenes (Arandes et al., 2000). The amount of MFI crystal added to USY-based FCC catalysts has increased with values as high as 25–30 wt.% are reported in some FCC units. High propylene yields in FCC result from naphtha over-cracking and low hydrogen transfer reactions as a function of the strength of additive acid sites and fast diffusion of desired light olefins (Awayssa et al., 2014).

Various methods have been developed for testing FCC catalysts and diverse feeds ranging from light hydrotreated vacuum gas oil (VGO) to blends containing atmospheric and vacuum residues (Corma and Sauvanaud, 2013; Bryden et al., 2015; Vogt and Weckhuysen, 2015). The early method was the Micro Activity Test (MAT) which uses a fixed-bed reactor to measure conversion by changing the catalyst-to-oil (C/O) ratio. Despite its various drawbacks related to operation mode and reactant–catalyst contact, the MAT method is still used. Other laboratory fluidized-bed techniques have been developed to overcome the above drawbacks and provide more realistic laboratory testing taking into consideration FCC process short residence time and fast catalyst deactivation. These techniques include the GREC Riser Simulator reactor (Arandes et al., 2000; Passamonti et al., 2012), ACE Advanced Cracking Evaluation (Kayser, 2000), micro-downer (Corma and Sauvanaud, 2013) and circulating riser pilot plant unit (Lappas et al., 2015; Bryden et al., 2015).

In this work, we have studied the direct catalytic cracking of three light crude oils in a MAT unit at FCC operating conditions using commercial E-Cat blended with MFI additive. The effect of MFI Si/Al molar ratio (30, 280 and 1500) and post modification by steaming on light olefins yield were evaluated. Kinetic modeling of crude oil cracking was conducted using a 4-lump model to determine the kinetic constants and the activation energies between 500 °C to 550 °C and catalyst/oil ratios of 2 to 4.

2. Experimental

2.1. Feedstocks and base catalyst

The crude oils used in this study, Arab Super Light (ASL), Arab Extra Light (AXL) and Arab Light (AL), were procured from a

domestic oil company. The properties of ASL, AXL and AL are listed in Table 1. ASL feed is a low-sulfur crude oil with an API gravity of 51° while AXL has an API of 39° and higher sulfur content was about 1.2 wt.%. Arab Light crude oil with an API gravity of 34 has the highest sulfur content (1.8 wt.%) of the three feeds. The naphtha fraction (C_5 – 221 °C) in ASL, AXL and AL crude oils was 42, 34 and 31 wt.% respectively. Based on PIONA analysis, the composition of naphtha fraction in three crude oils was highly paraffinic (~65 wt.%) while aromatic content was 15 wt.% in ASL and 27 wt.% in both AXL and AL. Naphthenes were 19, 8 and 9 wt.% in the naphtha fraction of ASL, AXL and AL, respectively.

The equilibrium FCC catalyst (E-Cat) was obtained from a domestic refinery. The textural and acid properties of the E-Cat are presented in Table 2. The E-Cat was calcined at 550 °C for 3 h prior to its use. The temperature was increased at 5 °C/min during calcination.

2.2. MFI additives and modification

Three MFI zeolites with different Si/Al molar ratios of 30, 280 and 1500 (Z30, Z280, Z1500) were procured from Zeolyst. The zeolites were in ammonium form and were calcined at 550 °C in air for 3 h before use. Z280 was subsequently modified by steaming (St-Z280).

The steaming of Z280 (St-Z280) was done in a fixed-bed steamer. The sample was heated slowly at 5 °C/min up to 600 °C in nitrogen flow. Steam flow was started at 600 °C and continued for 6 h.

The parent and modified MFI additives were pelletized, crushed and 80–90 μ size of the material was sieved out. The E-Cat containing additives used in MAT testing were prepared by physically blending 75 wt.% of E-Cat and 25 wt.% of sieved additives. It has been reported that the maximum enhancement in light olefins yield occurs at 25 wt.% of additive level (Adewuyi et al., 1995). Above 25 wt.% of additive level in the E-Cat/additive blend, significant decrease in the conversion was observed due to dilution effect.

2.3. Catalyst characterization

The crystallinity of the zeolite additives was determined by X-ray powder diffraction (XRD) using a Rigaku Miniflex desktop diffractometer with a graphite monochromator. The textural properties of the additives were determined by N_2 adsorption measurements at 77 K, using Micromeritics ASAP 2020 analyzer. Samples were out-gassed at 350 °C under 10^{-5} Torr vacuum for 3 h before adsorption measurements. The Brunauer-Emmett-Teller (BET) surface area was calculated from the desorption data in the relative pressure (P/Po) range of 0.06–0.2. The shape of the zeolite crystals was determined by scanning electron microscopy (SEM Jeol, JSM-5500LV). Temperature programmed desorption (TPD) technique was used to measure the acidic properties. The TPD measurement was carried out using Mettler Toledo Star instrument.

2.4. Catalytic cracking tests

A fixed-bed microactivity test (MAT) unit was used to assess the catalytic cracking performance of the crude oils. The MAT tests were performed according to the ASTM D-3907 test method. The feed injection system was modified to inject crude oil feeds. For each MAT test, a full mass balance was obtained.

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