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Research article

Catalytic cracking of vacuum gasoil over -SVR, ITH, and MFI zeolites as FCC catalyst additives

Abdelrahman I. Hussain [a,c], Arudra Palani [a], Abdullah M. Aitani [a], Jiří Čejka [a,b], Mariya Shamzhy [b], Martin Kubů [b], Sulaiman S. Al-Khattaf [a,c,*]

[a] Center of Research Excellence in Petroleum Refining & Petrochemicals, King Fahd University of Petroleum & Minerals, Dhahran, 31261, Saudi Arabia
[b] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, CZ-182 23 Prague 8, Czech Republic
[c] Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

The cracking behaviour of three medium-pore zeolites -SVR, ITH, and MFI, with varying Si/Al molar ratio, was evaluated using an equilibrium FCC catalyst (E-Cat) and a hydrotreated vacuum gasoil (VGO) in a microactivity test unit (MAT). The increase in the yield of light olefins (21–29 wt% over E-Cat/additive vs. 16 wt% over E-Cat) was accompanied by a drop in the yield of gasoline (26–39 wt% over E-Cat/additive vs. 43 wt% over E-Cat) due to the cracking of reactive species in gasoline fraction (mainly olefins and isoparaffins). With increasing Si/Al ratio in zeolites MFI-280 and –SVR-120, propylene yield passed through maxima reaching 13.5 wt% and 12.8 wt%, respectively, compared with 7.0 wt% over E-Cat. Maximum propylene yield occurred partially due to gasoline over-cracking to light olefins (inverse relation with Si/Al ratio). The effect of MFI crystal size showed that large size crystals enhanced the yield of light olefins as compared to small size crystals due to secondary cracking of gasoline molecules. Results of kinetic study based on 4-lump model showed proportional relation between MFI Si/Al ratio and activation energy for the conversion of gasoline to gases. Activation energy increased from 14.2 kcal/mol to 16.3 kcal/mol as Si/Al ratio increased from 30 to 2000.

1. Introduction

The primary objective of the fluidized catalytic cracking (FCC) process is to increase the production of gasoline by processing vacuum gasoil (VGO) and other low-value feeds such as atmospheric residues [1,2]. FCC gasoline continues to be a major component in the total gasoline pool produced in an integrated refinery. As the market conditions evolve, FCC units are being optimized to produce light olefins along with transportation fuels [1,3]. Conventional FCC units produce approximately 4–6 wt% propylene. Revamping operating conditions and catalyst system enabled over 20–25 wt% propylene production [1,2]. High propylene yield from FCC units is a result of high VGO conversion and selective cracking which maximizes monomolecular reactions and minimizes secondary reactions [3,4]. The most cost effective route to enhance light olefins yield from FCC units is the use of medium-pore zeolite additives [5–7]. MFI additive cracks reactive species in gasoline fraction to LPG olefins. Other zeolite structures such as SSZ-74, SSZ-33, MFI, TNU-9, IM-5 MCM-36, MCM-22 and ferrierite were evaluated to increase the yield of light olefins in VGO catalytic cracking [5]. Maximum yield of propylene of 11 wt% was reported over MCM-36 and ferrierite compared to 7 wt% over the base catalyst [5].

Adewuyi et al. [8] investigated blending of various amounts of MFI additive to USY FCC catalyst in VGO cracking. Maximum enhancement in propylene yield of 11.8 wt% compared to 5.4 wt% over the base catalyst was found at 25 wt% additive level. After further increase in MFI addition, reactive species in gasoline fraction were completely converted and significant decrease in the conversion was observed due to the dilution effect [8]. The reason is a poor ability of bulkier molecules of gas oil to diffuse through the small pore of MFI to reach the active sites. Li et al. compared the catalytic conversion of VGO using MFI and USY based catalysts [9]. The authors reported that at temperature of 560 °C and high C/O ratio equal to 8 g/g the conversion over MFI as base catalyst can reach comparable levels to USY catalyst. Catalytic cracking processes such as deep catalytic cracking (DCC) utilized MFI based catalyst under more severe conditions to enhance propylene yield [1,4].

The successful zeolite additive in enhancing propylene yield must be active to for cracking of gasoline fraction selectively to light olefins. Zeolites activity and selectivity are greatly influenced by their acidic properties such as, acid sites type (Brønsted or Lewis), concentration,

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* Corresponding author at: Center of Research Excellence in Petroleum Refining & Petrochemicals, P.O. Box 5040, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.
E-mail addresses: arupalya@kfupm.edu.sa (A. Palani), maitani@kfupm.edu.sa (A.M. Aitani), jiri.cejka@jh-inst.cas.cz (J. Čejka), mariya.shamzhy@jh-inst.cas.cz (M. Shamzhy), martin.kubu@jh-inst.cas.cz (M. Kubů), skhattaf@kfupm.edu.sa (S.S. Al-Khattaf).

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Nomenclature

k_{ij}	reaction rate constant for reaction of lump *i* to lump *j*
$k_{o\text{-}ij}$	pre-exponential factor for the reaction of lump *i* to lump *j*
E_{ij}	apparent activation energy for reaction of lump *i* to lump *j*
t	contact time
t_{os}	time on stream
α	deactivation constant
φ	deactivation function
Y_i	weight fraction of lump *i*
T	reaction temperature
T_o	average temperature of the experiment
R	universal gas constant

strength and location [10–12]. Several studies investigated the effect of the number of acid sites on MFI catalytic behaviour in hydrocarbons cracking [13,14]. Direct correlation exists between the number of acid sites and product yields. Framework tetrahedral aluminum is the source of zeolite acidity. Therefore, zeolite Si/Al molar ratio has major impact on its performance as catalysts [14]. Lu et al. investigated the effect of MFI Si/Al molar ratio as FCC catalyst additive in the cracking of C4 alkanes [10]. They found that high Si/Al molar ratio (>80) was more effective in producing light olefins. The hydrogen transfer reactions were minimized due to a lower number of acid sites. Other studies described elevated hydrothermal stability correlated to high Si/Al molar ratio [15, 16]. Low aluminum content reduces the level of Al extraction from the framework. This increases framework stability and improves the efficiency in light olefins production [16].

High silica –SVR zeolite is characterized by 3-dimensional 10-ring channel system with pore openings at 5.5 × 5.7, 5.2 × 5.9 and 5.2 × 5.6 Å [17]. Zeolite ITH possesses interconnecting 9 − (4.0 × 4.9 Å), 10 − (4.8 × 5.7 Å) and 10 − (4.7 × 5.1 Å) ring channels. It has been prepared by Corma and coworkers in germanosilicate reaction mixture [18]. The incorporation of Al into ITH framework, accompanied with a formation of strong acid sites, was achieved either by applying direct template-assisted hydrothermal synthesis (Si/Al = 30–65) [19] or by post-synthesis alumination (Si/Al = 34–70) [20]. It was shown, that small pore dimensions and strong acidity in directly synthesized Al-containing ITH zeolite (Si/Al = 30) increased propylene production in VGO cracking compared with MFI [19].

In this work, three medium-pore aluminosilicate zeolites of -SVR (10 × 10 × 10-ring channels), MFI (10 × 10 × 10-ring channels) and ITH (10 × 10 × 9-ring channels) topology with varying Si/Al molar ratio were investigated for their catalytic performance as FCC additives in the cracking of hydrotreated VGO derived from Arabian Light crude oil. Zeolite additives were compared by VGO conversion and products yields. In addition, effect of crystal size using MFI zeolites, catalytic parameters such as $C_3^{=}$/gasoline ratio, C_3 olefinicity and hydrogen transfer coefficient were also investigated.

2. Experimental section

2.1. Materials

The E-Cat was a commercial equilibrium zeolite catalyst acquired from a local refinery. It has a Si/Al molar ratio of 3.3, BET area of 158 m^2/g and pore volume of 0.14 cm^3/g. The E-Cat was calcined for 5 h at 550 °C in air to have the sample free of coke according to ASTM test method D3907 [21]. The zeolites MFI, -SVR and ITH additives were activated for 5 h at 550 °C to get the H-form. The zeolites were pelletized, crushed and 80–90 μ size of the material was sieved out. The E-Cat containing additive was prepared by blending 75 wt% of E-Cat and 25 wt% of sieved additive. Catalysts are hereafter named by the additive used in the form of framework type-Si/Al ratio. For example, MFI-80 corresponds to a catalyst contains 75 wt% E-Cat and 25 wt% MFI zeolite with Si/Al ratio of 80. The gasoil feed used in all experiments was hydrotreated Arabian Light VGO obtained from a local refinery (Table 1).

MFI-23 (CBV2314), MFI-30 (CBV3024E), MFI-55 (CBV5524G), MFI-80 (CBV8014) and MFI-280 (CBV28014) were acquired from Zeolyst in NH_4-form. MFI-500, MFI-1200 and MFI-2000 samples were synthesized using a molar gel composition of 36 TPAOH: x Al_2O_3:150 SiO_2: 2300 H_2O where x varies with Si/Al ratio. Required amount of aluminum nitrate and deionized water were added to tetrapropylammonium hydroxide (40 wt%, TPAOH). The mixture was stirred at 0 °C for 30 min and tetraethylorthosilicate (TEOS) was added drop wise under stirring at room temperature. The solution was stirred at room temperature for overnight and crystallized in a Teflon-lined stainless-steel autoclave at 170 °C for 48 h. After crystallization, the product was washed with deionized water, dried overnight at 100 °C and calcined at 550 °C for 6 h. The obtained MFI was ion exchanged with aqueous 1 M NH_4NO_3 at 90 °C for 3 h and calcined at 550 °C for 6 h.

Large crystal size MFI-2000 was synthesized using molar gel composition of 1 SiO_2: 0.08 TPABr: 0.0005 Al_2O_3: 0.10 NH_4F: 20 H_2O. The gel was subjected to hydrothermal crystallization process at 200 °C for 2 days. The solid products obtained were washed with water and dried at 100 °C overnight. The template was removed by calcination in air at 550 °C for 6 h. Nano (small) crystal size MFI-2000 was synthesized using molar gel composition of 1.0SiO_2: 0.0005 Al_2O_3: 0.085 TPAOH: 3.72H_2O. In a typical synthesis, 6 g of fumed silica was mixed with tetrapropylammonium hydroxide (40% TPAOH) and water. The resulting gel was crystallized for 4 days at 90 °C. After crystallization, the product was washed with water, dried at 100 °C overnight and calcined in air at 550 °C for 6 h.

SSZ-74 (-SVR-40, SVR-80) were synthesized according to Strohmaier and Weston [22]. The gel was prepared by mixing 0.5 g water, 1.4 g Ludox LS-30, 1.5 g 25.8% 1,6-bis(*N*-methyl-pyrrolidinium) hexane solution, 1.4 g 20% KBr solution and 0.3 g 15% $Al(NO_3)_3$ solution. The mixture was stirred until homogeneous and then put into the Teflon-lined stainless steel 25 ml autoclaves and heated at 160 °C for 7 days under agitation. SSZ-74 (-SVR-120, SVR-silica) was synthesized in a fluoride medium in the presence of 1,6-bis (*N*-methylpyrrolidinium) hexane hydroxide as structure-directing agent (SDA) [17]. 64 g SDA-OH was mixed with 12.6 g TEOS and kept to dry in a hood for 5 days. LZ-210 zeolite (0.2 g) as a source of Al, seeds of -SVR (0.1 g), distilled water (3.7 g) and 40% HF (1.3 g) were added and stirred with plastic spatula until the thick gel was formed. Crystallization proceeded in Teflon-lined stainless steel 25 ml autoclaves at 170 °C for 6 days under agitation. Solid product was separated by filtration, washed with distilled water and dried at 65 °C. Calcination of all –SVR zeolites was done at 120 °C for 2 h, 540 °C for 5 h and at 580 °C for

Table 1
Properties of hydrotreated vacuum gas oil feed.

Density (g/cm^3) (15 °C)	0.896
Sulfur (ppm)	300
Nitrogen (ppm)	170
Saturates (wt%)	59
Aromatics (wt%)	40
Residue (wt%)	0.8
Simulated distillation (°C)	
Initial boiling point	308
5%	348
25%	376
50%	420
90%	507
Final boiling point	568