Catalytic cracking of heavy naphtha-range hydrocarbons over different zeolites structures

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ABSTRACT

The effects of textural, structural, morphological, and acidic properties of HZSM-5, H-mordenite and (MFI/MOR) composite zeolite on the catalytic cracking of heavy naphtha-range hydrocarbons (dodecane, iso-octane, and ethylbenzene) as well as heavy naphtha were studied. XRD and SEM results revealed the presence of (MFI/MOR) overgrowth composite zeolite upon recrystallization of H-mordenite in the presence of tetrapropylammonium bromide. Significant cracking of dodecane occurred over different zeolites, however, very low cracking of iso-octane was observed over HZSM-5. The conversion of ethylbenzene, iso-octane and dodecane at 400 °C was 69.6, 74.5 and 86.4 wt.%, respectively, over H-mordenite, compared with 69.8, 11.2 and 83.8 wt.%, respectively, over HZSM-5. (MFI/MOR) overgrowth zeolite exhibited an intermediate level of cracking. Catalytic cracking of hydrocarbon mixtures followed similar trends as those for pure model compounds. Catalytic cracking of heavy naphtha was higher over HZSM-5, compared to H-mordenite (94.4 wt.% vs. 76.5 wt.%). The kinetic modeling studies indicated that the rate of hydrocarbon cracking varies with the nature of model compounds and zeolite structure. The apparent activation energies (E_a) for the three model compounds increased in the following order; HZSM-5 > (MFI/MOR) > H-mordenite, whereas the difference in E_a over various zeolites was much larger for iso-octane and ethylbenzene.

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1. Introduction

The steam cracking of naphtha has been the workhorse of the petro-chemical industry for the production of ethylene and for co-production of propylene and benzene. However, the increasing demand for propylene and the search for less energy-intensive processes have renewed interest in the catalytic cracking of naphtha as an important route for the production of light olefins [1–3]. Most of the studies on catalytic cracking of naphtha were conducted using straight-run paraffinic naphtha and, to a lesser extent, cracked naphtha (such as FCC, visbreaker and coker) over a wide range of zeolites, mainly modified HZSM-5 [4,5].

Various techniques were employed to modify zeolite acidity and pore size to maximize the selectivity to light olefins and to minimize by-product and coke formation. In general, strong acid sites are needed to initiate cracking reaction while specific pore structures are needed to suppress the formation of coke and large hydrocarbons. Among various zeolites, modified HZSM-5 has shown the most favorable results for naphtha cracking [4,6]. Compared with MOR, BEA, and SAPO-11, HZSM-5 showed the highest cracking activity for heavy naphtha containing mixture of *n*-paraffins, *i*-paraffins, naphthenes, olefins, and aromatics [6]. The

yield of light olefins was strongly influenced by the concentration and strength of acid sites with maximum yield being obtained over HZSM-5 at the lowest Si/Al ratio of 20. HZSM-5 was reported to be more active than USY zeolite in the transformation of Fischer Tropsch (FT) naphtha fraction at 450 °C under commercial FCC conditions [7]. Increasing HZSM-5 loadings, from 0.5 to 20 wt.% in a silica/kaolin matrix increased LPG yield, accompanied with an increase in the products of hydrogen transfer reactions.
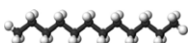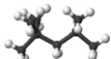
HZSM-5 zeolites with various acid site densities exhibited almost the same selectivity at the same *n*-heptane conversion [8]. Using HZSM-5 (Si/Al molar ratio = 31), the highest ethylene and propylene yield of 60 wt.% and 99.6% conversion was obtained at 650 °C [9,10]. It has been shown that Henry's equilibrium constant, enthalpy of *n*-hexane adsorption at 150 °C and its protolytic cracking activity increased as the pore size of various zeolites in the following order: HZSM-5 > MOR > BEA > Y zeolite [9,10]. Reyniers and co-workers [11–13] investigated the catalytic cracking of naphtha range model compounds such as methylcyclohexane and iso-octane over HZSM-5 and Y zeolites. In the cracking of iso-octane, acid properties of HZSM-5 determined its activity while its framework topology controlled the selectivity to light olefins. A single-event microkinetic modeling including acidity descriptors was applied to catalytic cracking of iso-octane over a series of Y zeolites with Si/Al molar ratio ranging from 2.6 to 30 [13].

Nano-sized HZSM-5 zeolites with sizes less than 150 nm showed better catalytic and adsorptive properties than micro-sized zeolites in

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Table 1
Some properties of naphtha-range model compounds.

Model compound	3-D structure	Critical diameter (nm)	Molecular weight (g/mol)	Boiling point (°C)	Specific gravity (at 15.6 °C)
Dodecane		0.49	170.3	216.3	0.7524
Iso-octane		0.56	114.2	99.2	0.6988
Ethylbenzene		0.66	106.2	136.2	0.8737

the cracking of n-hexane [14]. The result was attributed to the rapid diffusion of light olefins out of the intracrystalline pores due to low diffusion resistance. The Si/Al ratio affected n-hexane conversion, and the major light olefin component was propylene at low conversion. In another study [15], it was concluded that the activity of n-hexane cracking and selectivity to olefins were related to the crystal size and the ratio of surface acid sites to total acid sites. La and P exhibited the best catalytic performance for the cracking of C_5 raffinate to light olefins [16].

Few studies on the utilization of composite or co-crystalline zeolites for the cracking of naphtha-range hydrocarbons have been reported. In some applications, the composite zeolites obtained by co-crystallization or overgrowth can be effective in improving their catalytic performance compared with the individual pure phases [17]. A HZSM-5/MOR co-crystalline zeolite synthesized with and without using a template showed excellent catalytic performance in naphtha cracking with total yield of ethylene and propylene reaching 55 wt.% at a H-mordenite content of 5% [18]. Chen and co-workers [19] investigated the catalytic cracking of n-heptane over fresh and steamed HZSM-5/MOR zeolites and found that the steamed sample has much higher initial activity and faster deactivation rate. It was concluded that the enhanced activity with low propylene selectivity was caused by the decreased diffusion limitation due to the generation of mesopores during hydrothermal treatment. In another study [20], a hierarchical composite zeolite of HZSM-5 and ZRP-1 showed higher selectivity to ethylene and propylene in the cracking of n-heptane. The results were attributed to the mesopores and the optimum amount of Brönsted (B) and Lewis (L) acid sites as well as higher L/B ratio compared with HZSM-5 or ZRP-1 [20]. Xie et al. [21] carried out a series of investigations on MCM-49/ZSM-35 and observed a notable synergistic effect during the FCC gasoline upgrading process [22]. This was mainly attributed to MCM-49 and ZSM-35 analogs in the co-crystallized zeolites may be stacked much closer than those in the physical mixture and some parts of the intergrowth may be formed because of the partially similar basic structure of MCM-49 and ZSM-35. Francesconi et al. [23] synthesized a series of intergrowths of zeolite MFI/MEL structures with various Si/Al ratios and degree of intergrowth. They have observed that n-decane cracking over the intergrowth (MFI/MEL) zeolite was intermediate between the corresponding parent MFI and MEL zeolites.

From this review, it is clear that the application of composite zeolites in the cracking of naphtha-range hydrocarbons needs further investigation. The aim of this study is to investigate the effects of physicochemical properties, viz. textural, structural, diffusion, and acidic properties, of zeolites with different structure and Si/Al molar ratio (i.e. HZSM-5 (Si/Al = 30, 80), H-mordenite (Si/Al = 24.8, 180), and (MFI/MOR) overgrowth composite zeolite (Si/Al = 19.4)) on the cracking of heavy-naphtha range hydrocarbons (i.e. iso-octane, n-dodecane and ethylbenzene), mixtures of hydrocarbons, and heavy naphtha.

2. Experimental

2.1. Preparation of zeolites

2.1.1. Parent zeolites

The commercial zeolites used in this study were procured from Zeolyst; ZSM-5 (CBV3024E, nominal Si/Al = 30, NH_4-form, and CBV8014, nominal Si/Al = 80, NH_4-form), and H-mordenite (CBV21A, nominal Si/Al = 21, NH_4-form). H-mordenite of high Si/Al ratio was procured from Tosoh Chemicals (HSZ-690HOA, nominal Si/Al = 180, H-form). Prior to testing, the as-received NH_4-form zeolites were calcined in standing air at 550 °C for 5 h (ramping rate of 3 °C/min). These zeolites are hereafter referred as HZ30, HZ80, MOR21 and MOR180, respectively.

2.1.2. HZSM-5-mordenite overgrowth composite zeolite

HZSM-5-mordenite composite material was synthesized by the recrystallization of MOR21 under hydrothermal conditions. A predetermined amount of H-mordenite was mixed with sodium hydroxide (Sigma Aldrich), tetrapropylammonium bromide (TPABr, Aldrich, 98%) and de-ionized (DI) water according to the gel composition: $6Na_2O$: $0.84 Al_2O_3$: $16.8 SiO_2$: 8 TPABr: $1000H_2O$. The mixture was then heated under rotation in a Teflon-lined Parr autoclave at 170 °C for two days. The product is filtered, washed with deionized water and dried at 80 °C. The as-synthesized zeolite was slowly heated to 200 °C, kept at this temperature for 2 h, and then calcined at 550 °C for 7 h to remove the structure directing agent. The H-form of ZSM-5/mordenite composite was obtained by ion-exchanged with 0.1 M of NH_4NO_3 (Riedel-deHaën) at 80 °C for 16 h. The catalyst was then calcined following similar procedures as for the Na-form composite zeolite. The HZSM-5-mordenite composite is hereafter referred as (MFI/MOR). Physical mixture of HZ30 and MOR21 in 1:1 weight ratio is referred to as HZ30 + MOR21.

2.2. Catalyst characterization

The Si/Al ratio of zeolites was determined by inductively coupled plasma spectrometer (ULTIMA 2, ICP-OES) from Horiba Scientific Co. The textural properties were characterized by N_2 adsorption measurements at 77 K, using Quantachrome Autosorb 1-C adsorption analyzer. Samples were outgassed at 220 °C under vacuum (10^{-5} Torr) for 3 h before N_2 physisorption. The BET specific surface area was determined from the adsorption data in the relative pressure (P/P_0) range from

Table 2
PIONA analysis of heavy naphtha feedstock.

Composition (wt.%)	n-Paraffins	i-Paraffins	Olefins	Naphthenes	Aromatics	Total
C-6	4.47	1.39	–	2.05	0.34	8.25
C-7	10.92	8.21	–	5.26	2.36	26.75
C-8	9.60	9.17	1.37	3.24	6.20	29.58
C-9	6.72	8.33	0.72	2.66	4.86	23.29
C-10	2.66	3.54	1.51	0.61	1.43	9.75
C-11	0.86	1.11	–	0.14	0.10	2.21
C-12	0.17	–	–	–	–	0.17
Total (wt.%)	35.40	31.75	3.60	13.96	15.29	100.00