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Research article

Catalytic cracking of n-hexane over HEU-1 zeolite for selective propylene production: Optimizing the SiO_2/Al_2O_3 ratio by in-situ synthesis

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ABSTRACT

HEU-1 zeolites with different SiO_2/Al_2O_3 ratios (60–530) were in-situ synthesized and systematically evaluated in n-hexane catalytic cracking reaction. The influencing factors including SiO_2/Al_2O_3 ratio, weight hourly space velocity and reaction temperature were investigated to optimize the light olefin yield, especially propylene. Compared to HZSM-48 and HZSM-5 zeolites with similar SiO_2/Al_2O_3 ratios, HEU-1-300 (SiO_2/Al_2O_3 = ca. 300), for example, displays much higher yield of ethylene plus propylene than HZSM-48 and comparable with HZSM-5. Furthermore, the propylene yield (35.6%) on it is higher than HZSM-5 by 9.0 percentage points, thus leading to higher propylene/ethylene ratio of 2.1. This excellent cracking performance of HEU-1-300 is ascribed to the combination of its moderate Brönsted acidity, due to the optimal SiO_2/Al_2O_3 ratio, and unique framework topology. Moreover, both HEU-1 and HZSM-48 zeolites present much lower aromatics selectivity in the gas effluent than HZSM-5. For HEU-1 zeolite, it displays significant product shape selectivity due to its confined channel system, even though the large void space favors the formation of large intermediate species or aromatics precursors, while there is transition state shape selectivity for HZSM-48 structure which possesses no enough void space available to accommodate the large and complex hydrocarbons. HEU-1 topological structure also has pronounced effect on the formation and oxidation of coke deposition.

1. Introduction

Worldwide demand for propylene has been steadily increasing in recent years due to its potential application in the fields such as polypropylene, chloropropylene, acrylonitrile and others. At present, propylene is produced primarily as a by-product of petroleum refining processes, such as fluid catalytic cracking (FCC) (28%) and naphtha steam cracking (70%) [1,2]. However, the latter is a particularly energy-consuming (>1073 K) process, and produces lower propylene selectivity than ethylene (propylene/ethylene ratio < 0.6) [3,4]. Therefore, naphtha catalytic cracking based on various catalysts has been proposed in order to circumvent the problems in the conventional processes and treated as an attractive alternative way to make up the insufficiency of propylene supply in the future [5,6]. Among the cracking catalysts, acidic zeolites are recognized as the best candidates due to their tailoring acidities, uniform pore channels and favorable regeneration properties. In particular, ZSM-5 zeolite with three-dimensional pore channels has attracted considerable attention due to its long activity stability and relatively high propylene selectivity and also been used as catalyst to elucidate the cracking reaction mechanism and coke formation [7–10].

Meanwhile, some of the other zeolites with intriguing structures have been also investigated for the conversion of light hydrocarbons, such as MCM-22 [11,12], MCM-68 [13], ITQ-21 [14], and so on [15,16], and they have presented extraordinary properties of diffusion and shape selectivity. ZSM-48 zeolite, for example, having one-dimensional (1D) 10-membered-ring (10-MR) channels displayed higher propylene selectivity than ZSM-5 in C_4-olefins catalytic cracking reaction [17].

EU-1 zeolite (EUO) possesses a monodimensional 10-MR (0.58 nm × 0.41 nm) medium pore channel system, though periodically interrupted by 12-MR "side-pockets" (0.68 nm × 0.58 nm in diameter and 0.81 nm in depth) [18]. It is usually prepared from aluminosilicate gels using linear hexamethonium (HM) or large dibenzyl-dimethyl ammonium (DBDMA) ions as structure directing agents (SDAs). Furthermore, the active sites of HEU-1 obtained from HM ions are located both in the main 10-MR channels and the bottom of 12-MR side-pockets as well, comparing to those from DBDMA located only in the 12-MR side lobes [19,20]. More and more promising results, concerning the use of EU-1 zeolite as catalyst, were obtained in the reactions of C_8 aromatics isomerization [21,22], n-heptane hydrogen isomerization [23] and dimethyl ether to olefins [24,25]. Research works that tune acidity of EU-1 zeolite combined with its original pore architecture to enhance control over the product distribution are available [26,27], in

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Nomenclature

FCC	fluid catalytic cracking
1D	one-dimensional
10-MR	10-membered-ring
HM	hexamethonium
DBDMA	dibenzyl-dimethyl ammonium
SDAs	structure directing agents
P/E ratio	propylene/ethylene ratio
$HMBr_2$	hexamethonium bromide
XRD	X-ray diffraction
BET	Brunauer-Emmett-Teller
XRF	X-ray fluorescence
NH_3-TPD	temperature-programmed desorption of ammonia
TPO	temperature-programmed oxidation
WHSV	weight hourly space velocity
FID	flame ionization detector
B/L	Brönsted/Lewis
TOS	time on stream
BTX	benzene, toluene, and xylenes

which the sequential treatment for as-synthesized EU-1 zeolite with alkaline or acid solution was applied to adjust the acidity and/or introduce mesoporous. However, the process of demetalization results in the decrease of the microporosity and even crystal destruction, which will lessen the effect of EU-1 structure on the catalytic performance, because the acidity and shape selectivity vary simultaneously with the pore structure and crystallinity. On the other side, this widely used post-processing method for EU-1 zeolite is partly because of the difficulty for in situ synthesis of pure EU-1 zeolite with relatively high SiO_2/Al_2O_3 ratio directly. When the SiO_2/Al_2O_3 ratio in synthetic gel got higher than 120, only mixed phases of EU-1 and ZSM-48 were obtained in HM system [28]. Fortunately, an effective seeds-assistant method was developed in our lab for synthesizing purely high-silica EU-1 zeolite with SiO_2/Al_2O_3 ratio higher than 120 and even up to 1800 [29]. Afterwards, we also demonstrated that as-synthesized high-silica EU-1 zeolite (SiO_2/Al_2O_3 = ca. 400) exhibited superior propylene selectivity (52%) and higher propylene/ethylene (P/E) ratio (15) compared to ZSM-5, ZSM-48 and beta zeolites in methanol to propylene reaction [30]. This excellent result was mainly ascribed to the special topological structure and moderate acid density, due to the optimal SiO_2/Al_2O_3 ratio. Before this, the rich aluminum EU-1 zeolite presented low propylene yield but primary paraffin and aromatic species in methanol to hydrocarbons reaction [31,32]. For catalytic cracking reaction, the transformation of long-chain alkanes to short-chain alkenes occurs at least partly via the carbenium ion/β-scission mechanism, i.e. classical bimolecular cracking mechanism [33]. Since EU-1 zeolite has active sites located in the cross section similar to that of beta (0.66 × 0.67 nm, 0.56 × 0.56 nm) and the more confined 10-MR channel than ZSM-5, this pore structure would be appropriate for naphtha catalytic cracking to light olefins [19]. However, the low selectivity to propylene (20%) accompanied with large amounts of propane and aromatic was obtained over Al-rich EU-1 zeolite and it should be ascribed to the excessive acid content, which accelerated the secondary reactions in the cracking reaction [34]. Therefore, further elucidation of the relationship between EU-1 structure (acidity/pore size) and the activity/selectivity would be very necessary.

Herein, EU-1 zeolites with SiO_2/Al_2O_3 ratios ranging from 60 to 530 were synthesized in HM system and the influence of SiO_2/Al_2O_3 ratio on activity, selectivity and stability for n-hexane cracking was systematically investigated. Concurrently, the changes of product distribution at different weight hourly space velocities and temperatures were also discussed. Furthermore, the catalytic performance and coke deposition behaviors over three different topological zeolites of EU-1 (EUO), ZSM-5 (MFI) and ZSM-48 (*MRE) with similar SiO_2/Al_2O_3 ratios of ca. 300 were also compared in the process of n-hexane catalytic cracking. Thereupon, we envisage that high-silica EU-1 zeolite would be treated as an alternative catalyst for enhancing propylene selectivity and P/E ratio in light hydrocarbon cracking reaction.

2. Experimental

2.1. Zeolites synthesis

EU-1 zeolites with different SiO_2/Al_2O_3 ratios were synthesized in the presence of hexamethonium bromide ($HMBr_2$, 99%) purchased from Aldrich based on the approach reported in our previous work [29]. The SiO_2/Al_2O_3 ratios of the initial preparation gel were 60, 90, 160, 300 and 530, respectively. ZSM-5 and ZSM-48 zeolites were also synthesized according to the literatures [29,35], meanwhile the SiO_2/Al_2O_3 ratios in synthesis gels were both 300. In order to obtain the protonated zeolites, all of the as-synthesized materials were firstly calcined in air at 823 K for 5 h to remove the template. After that, the obtained samples were ion-exchanged twice with 1 $mol \cdot L^{-1}$ NH_4NO_3 solution at 363 K for 2 h, followed by calcination in air again at 823 K for 3 h. Before conducting catalytic tests, the protonated zeolites were tableted, crushed, and sieved to 20–40 mesh. The samples denoted as HEU-1-α, HZSM-48-β and HZSM-5-γ referred to the initial gels SiO_2/Al_2O_3 ratios were α, β, and γ, respectively.

2.2. Zeolites characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) using Cu Kα radiation and these XRD patterns were also used to calculate the relative crystallinity according to our previous work [29]. Followed by nitrogen adsorption-desorption experiments measured on a Micromeritics ASAP 2020 M instrument at 77 K, the powder zeolites were evacuated at 823 K for 6 h and degassed at 573 K under vacuum for 5 h. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) equation with the adsorption data obtained at relative pressures (P/P_0) between 0.05 and 0.25. The external surface area was calculated using t-plot method and the total pore volume was derived from the nitrogen amount adsorbed at P/P_0 of 0.99.

A Rigaku ZSX-100 X-ray fluorescence (XRF) analyzer was used to investigate the element compositions of the prepared zeolites. Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out to evaluate the acidity of the samples on a TP-5076 adsorption instrument and the detailed process can be found in the literature [30]. The Brönsted and Lewis acid amounts of the samples were investigated

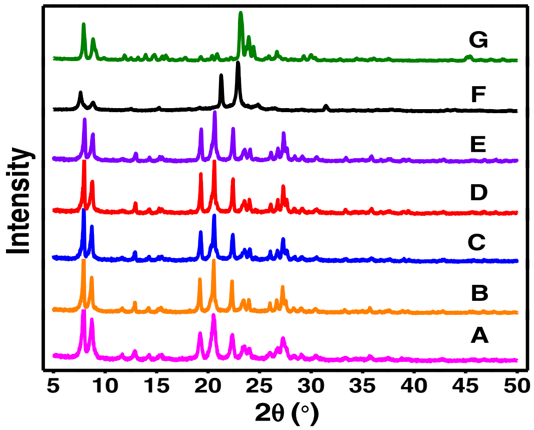

Fig. 1. XRD patterns of zeolites EU-1 with initial gel SiO_2/Al_2O_3 ratios of 60, 90, 160, 300 and 530 (A–E), ZSM-48 (F) and ZSM-5 (G).

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