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Catalytic cracking of 1-butene to propene and ethene on MCM-22 zeolite

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Abstract

Catalytic cracking of butene to propene and ethene was investigated over HMCM-22 zeolite. The performance of HMCM-22 zeolite was markedly influenced by time-on-stream (TOS) and reaction conditions. A rapid deactivation during the first 1 h reaction, followed by a quasi-plateau in activity, was observed in the process along with significant changes in product distributions, which can be attributed to the fast coking process occurring in the large supercages of MCM-22.

Properly selected reaction conditions can suppress the secondary reactions and enhance the production of propene and ethene. According to the product distribution under different butene conversion, we propose a simple reaction pathway for forming the propene, ethene and by-products from butene cracking.

HMCM-22 exhibited similar product distribution with the mostly used high silica ZSM-5 zeolite under the same conversion levels. High selectivities of propene and ethene were obtained, indicating that the 10-member ring of MCM-22 zeolite played the dominant role after 1 h of TOS. However, MCM-22 exhibited lower activity and stability than that on high silica ZSM-5 zeolite with longer time-on-stream.

Keywords: Butene; Catalytic cracking; Propene; Ethene; HMCM-22 zeolite

1. Introduction

One of the fastest growing petrochemical markets is that for propene, driven primarily by the high growth rate of polypropene [1]. Traditional methods to produce propene cannot satisfy the propene demand [2]. For example, co-product propene production from steam cracking is determined largely by the feed state; yet much of the new steam cracking capacity is based on ethane feed, which produces little propene [3]. Indeed in FCC units propene is obtained at a relatively low yield and enhancement of the yield has proven expensive and limited [1–5]. Another two on-purpose propene technologies are also available: propane dehydrogenation and metathesis, but these have seen only limited applicability [1,2,6]. Propane dehydrogenation requires high investment and both technologies require opportunistic feedstock economics. A newly emerging technology is catalytic cracking of C_4+ alkenes to propene and ethene, of which the feed can be any hydrocarbons containing sufficient amounts of C_4+ alkenes, such as steam cracker by-products, FCC low value refinery streams, catalytic cracked naphtha and light gasoline [7–11].

Several patents have been granted on the technology of catalytic cracking of C_4+ alkenes; most such processes were carried out on high-silica ZSM-5 zeolite [1–9]. Due to the low acidity and particular pore topology of the high-silica ZSM-5 zeolite, high selectivity of propene plus ethene was obtained. Similar to ZSM-5, MCM-22 zeolite possesses one pore system that includes two-dimensional sinusoidal intersecting 10-member ring channels. Besides that, MCM-22 zeolite also possesses another pore system, which contains large supercages defined by 12-member ring of 0.71 nm inner diameter and 1.82 nm height [12]. However, the use of MCM-22 as the catalyst in the process of C_4+ alkenes catalytic cracking to propene/ethene has not been

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reported so far. Also, whether both pore systems of MCM-22 or only one of them play the major role in butene catalytic cracking is not known and needs to be investigated.

Asensi et al. [13] have studied isomerization of 1-butene to isobutene on MCM-22 zeolite under various operating conditions; they discussed the mechanisms of formation of isobutene and by-products from 1-butene on MCM-22 zeolite. In this work, we investigated the performance of MCM-22 zeolite in catalytic cracking of 1-butene to propene plus ethene under a wide range of operating conditions, i.e. temperature, 1-butene space velocity, 1-butene partial pressure in the feed, and time on stream. Moreover, the performance of MCM-22 and that of high silica ZSM-5 zeolite in the catalytic cracking of 1-butene were compared under similar conditions. On the basis of these results, a mechanism of formation of propene, ethene and by-products from 1-butene is proposed.

2. Experimental

2.1. Synthesis of zeolite MCM-22 and catalyst preparation

A sample of zeolite MCM-22 with Si/Al_2 ratio of 30 was synthesized following the procedure described in Ref. [13] and using hexamethylene imine (HMI) as template. The molar composition of the gel: SiO_2:Al_2O_3:Na_2O:HMI:H_2O is equal to 1:0.033:0.11:0.35:0.45. Crystallization of the gels was carried out in 100 ml stainless steel autoclaves rotated at 60 rpm at a temperature of 138 °C. After the autoclave was cooled to room temperature, the product was filtered, washed with deionized water, and dried at 100 °C overnight. Finally, the MCM-22 zeolite was calcined at 550 °C for 5 h under static air to remove the organic template from their channels. Then the calcined sample was ion-exchanged with 0.8 mol/l ammonium nitrate solution at 90 °C repeatedly (for three times) so as to convert the zeolite into its NH_4-form. After that, the zeolite crystals were washed with deionized water, dried at 120 °C and then pressed binder-free; the material was crushed to 20–35 mesh size particles and then calcined under static air at 550 °C for 3 h to convert the zeolite to its H-form. As reference catalyst, high silica ZSM-5 zeolite (Si/Al_2 ratio of 350, from Shanghai Fuxu Zeolite Corporation, China) was selected and the HZSM-5 catalyst was prepared using the method stated above.

2.2. Catalyst characterization

The component phases and the degree of crystallinity of the samples were determined by the powder XRD technique. The XRD pattern of the sample was recorded on a Rigaku D/Max RB diffractometer using Cu Kα radiation, operating at 40 kV and 40 mA, with a scanning speed of 10°/min.

The acidity of the sample was determined by the NH_3-TPD technique. The sample (0.14 g) was loaded into a U-shaped stainless steel microreactor and pretreated at 500 °C for 0.5 h in flowing He. After the pretreatment, the sample was cooled to 150 °C and saturated with NH_3 gas. Then the NH_3-TPD was carried out under a constant flow of He (20 ml/min) from 150 to 700 °C at a heating rate of 18 °C/min. The desorbed ammonia was monitored continuously with a gas chromatograph equipped with a thermal conductivity detector.

Room-temperature IR spectra were recorded with a Nicolet 710 FT-IR spectrometer from zeolite wafers (10 mg cm^{-2}) mounted in a vacuum cell. Pretreatment of zeolites was performed in the cell at 500 °C under vacuum for 1 h. For the adsorption/desorption studies, pyridine vapor was adsorbed onto the zeolite. The excess of pyridine was removed under vacuum over three consecutive periods (1 h each) under the heating at 150, 350, and 450 °C, followed by IR measurements.

TG profiles were recorded on a Perkin-Elmer TG 1700 instrument. The catalyst loading was about 0.01 g and the flow rate of N_2 was 30 ml/min. The catalyst was heated from 50 to 850 °C in a 20% O_2/N_2 stream at a heating rate of 10 °C/min.

2.3. Catalytic experiments

Catalytic cracking of 1-butene over the zeolite catalysts was carried out in a continuous stainless steel reactor (7 mm diameter) with a thermocouple in the center of the catalyst bed, using 1-butene (>99.5% pure) as feed. The catalyst was activated at 550 °C for 1 h under a nitrogen flow before starting a reaction run. Then the 1-butene and/or nitrogen was passed through the reactor at various temperatures and different 1-butene partial pressures. The 1-butene space velocity (WHSV) was changed between 0.8 and 50 h^{-1} to obtain different conversion levels. The reaction products were analyzed by an on-line Varian 3800 gas chromatograph equipped with a flame ionic detector, using a PONA column.

3. Results and discussion

3.1. Physicochemical characteristics of MCM-22 catalyst

The XRD pattern of the calcined sample is presented in Fig. 1. It fits the typical crystalline MCM-22 phase similar to the diffraction peaks reported previously [12,13].

The acidity of the H-form MCM-22 determined by NH_3-TPD technique is shown in Fig. 2. The curve-fitting results are also presented in Fig. 2. As seen, there are three NH_3-desorption peaks located at 250, 350 and 520 °C on the MCM-22 zeolite, consistent with the results of the HMCM-22 reported previously [14,15]. The slight difference in the peak temperatures may result from the samples with different Si/Al_2 ratio and from the different experimental conditions. As claimed [14,15], the peak at 250 °C is