

Catalytic Cracking of C₄-olefin to Produce Propylene over H-ZSM-5

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Introduction

Propylene is one of the most important basic organic products, and the annual growth rates for propylene exceeds that of ethylene as a result of the huge growth in the propylene derivatives, e.g., polypropylene. Accordingly, olefin manufacturers are seeking cost effective options to increase the propylene production. One of the effective approaches for this purpose is to integrate the propylene production process into refinery or petrochemical plants, starting from a less valuable feedstock, such as C₄-olefins or higher carbon olefin from crackers and refineries [1-3]. In this work, a series of unique modified HZSM-5 samples with high Si/Al ratio (above 150) and different crystal sizes were prepared, and their catalytic performance for olefins catalytic cracking reaction that allows high selective production of propylene and ethylene by conversion of C₄-olefin from crackers and refineries was investigated. The catalyst developed by SINOPEC features the utilization of a tailor made ZSM-5 zeolite with high Si/Al ratio and small crystal size, which is smaller than 0.5 μm. Unique post-synthetic method was used to enhance the adsorption performance of the zeolite samples. Without requiring an inert diluent stream, the catalyst exhibited unordinary stability and high activity, typically the catalyst cycle length is over 1000 h, and ~30 wt% propylene and ~9 wt% ethylene are obtained in the pilot plant for per pass. So the reactor size and operating costs can be minimized as a result of long catalyst cycle time, high yield of propylene and no diluent addition.

Materials and Methods

ZSM-5 zeolite was synthesized hydrothermally at 100-150 °C for 1-3 d. The zeolite material was mixed with binder, the binder content ranges from 15-50 by weight, then the mixture was extruded into cylindrical extrudates. The extrudates were dried and calcined to remove the template at 550 °C. Activation of zeolite samples were performed by repeated ion exchange with 5 wt.% NH₄NO₃ solutions, followed by calcining at 550 °C for 4 h. C₄-olefin cracking reactions were carried out in a continuous flow fixed-bed system, with a stainless-steel tubular reactor containing 3-5 g of catalyst. The pilot-plant operations were carried out in a fixed bed adiabatic reactor containing 1-1.5 kg of catalyst. The reactions were conducted at 500-600 °C under atmospheric pressure.

Results and Discussion

A series of HZSM-5 samples with high Si/Al ratio (ranges from 20-800) and different crystal sizes were prepared, and their catalytic performances in C₄-olefin cracking reactions were investigated. HZSM-5 sample with high Si/Al ratio (above 150) shows higher yield of propylene in C₄-olefin cracking reactions, at the same time, less C₁-C₃ paraffines were produced. Three kinds of ZSM-5 samples with different crystal sizes were synthesized. SEM images show that the crystal sizes of the three samples are about 20-30 μm, 1-2 μm and

0.2-0.3 μm, respectively. Sample characteristic results show that three samples have almost the same BET surface area (~380 m²/g) and acid sites (~0.27 × 10⁻³ mol/g). The cracking of C₄-olefin test showed that the catalytic stabilities of the three samples are closely related to the crystal sizes of the samples, H-ZSM-5 with small crystal size exhibited higher stability in the reaction than H-ZSM-5 with large crystal size. Unique post-synthetic method was used to enhance the adsorption performance of the zeolite samples. Adsorption isotherms of n-hexane showed that the adsorption volume on the zeolite samples can be improved from ~0.14 cm³/g to ~0.18 cm³/g (25 °C, P/P₀=0.2) by the post-synthetic method, at the same time, the BET surface areas can be improved from ~280 cm²/g to ~360 cm²/g. The long term performance of the tailor made HZSM-5 catalyst for cracking of C₄-olefin was carried out in a fixed bed adiabatic reactor containing 1.5 kg of catalyst, and the results are shown in Figure 1. Pilot-plant results showed that even no any inert diluent stream was added into the system, the catalyst exhibited unordinary stability and high activity, typically the catalyst cycle length is over 1000 h, and ~30 wt% propylene and ~9 wt% ethylene are obtained.

Significance

Currently, more than 8000 hours of pilot-plant operations have been completed, and an industrial technology demonstration plant is under designing in China.

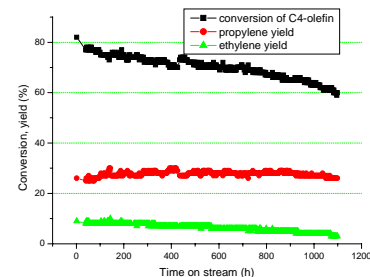


Figure 1. Long term performance of the tailor made HZSM-5 catalyst for cracking of C₄-olefin

Acknowledgments

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