

Effect of zeolite type on the production of ethylene from propylene

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Abstract: This study is the first to examine the selective production of ethylene from propylene (propylene-to-ethylene, PTE) with using various structural types of zeolites. The catalytic performances of these zeolite catalysts were tested in a continuous fixed-bed reactor. Among these zeolite catalysts, ten-membered ring zeolites with three-dimensional pore structures (ZSM-5 and ZSM-11) exhibited stable catalytic performances with considerable ethylene selectivity compared to other zeolite catalysts. The phosphorous-modified ZSM-5 catalyst exhibited the highest ethylene selectivity of more than 70% with moderate propylene conversion of 36.3% at a low propylene space velocity and a partial pressure condition.

Keywords: Propylene-to-ethylene, Ethylene production, Olefin interconversion.

1. Introduction

Light olefins are used as the main petrochemical building blocks to manufacture not only plastic goods but also various industrial products such as packaging, rubber, construction materials, textiles, and furnishings. To create these common applications, ethylene and propylene globally use more than 155 and 94.2 million tons per year, respectively. The worldwide market for light olefins is predicted to increase steadily at about 4% and 5% for ethylene and propylene, respectively [1]. At present, the dominant technology for the production of light olefins is the petroleum-derived naphtha cracking process. While a high yield of ethylene (32%) exists compared to propylene (16%) in the naphtha cracking process, the price spread between these two light olefins depends on regional supply and demand levels. This can be caused by the type of hydrocarbon feed and the cracker used as well as the chemical manufacturing industry that uses light olefins. Therefore, olefin interconversion technology is needed to manage the supply-demand balance of light olefins between propylene and ethylene.

Herein, the selective production of ethylene from propylene is explored for the first time with various types of zeolites in a continuous fixed-bed reactor. The effects of the reaction conditions, silica-alumina ratios (Si/Al₂, SARs), and surface P modification in the ZSM-5 zeolites was also systematically studied in relation to the relationship between the PTE results and properties of the zeolites.

2. Experimental (or Theoretical)

SAPO-34, SSZ-13, and ZSM-11 zeolites were prepared in the laboratory following previously reported methods [2,3]. The other zeolite materials (ZSM-5, Y zeolite, Beta, ZSM-22, and ZSM-35) were obtained from Zeolyst. ZSM-5 zeolites with different Si/Al₂ ratios were denoted as ZSM-5-X (X represents Si/Al₂). All zeolites were converted to H-form zeolites by an ion-exchange with an ammonium nitrate and calcination at 550 °C. The phosphorous-modified ZSM-5 zeolites were prepared via the simple wet impregnation method. The P-loaded zeolites were termed P-ZSM-5-50(Y) (where Y denotes the P loading amount). The prepared zeolites were characterized by various analytic techniques such as NH₃-TPD, TGA, EDS, STEM, and ²⁷Al MAS NMR et. al.

3. Results and discussion

In total, eight zeolite materials were prepared to evaluate the effects of the zeolite pore structure during the propylene-to-ethylene process, obtaining them from a commercial zeolite supplier and by synthesis in the laboratory. Zeolite materials with various structures were applied to the propylene-to-ethylene reaction as catalysts under the following fixed reaction condition: 550 °C, 0.1 MPa, 1.09 h⁻¹ WHSV, 0.0065 MPa C₃₌ partial pressure and a total flow rate of 70.6 ml/min (C₃₌ + N₂). Figure 1 shows the propylene conversion and ethylene yield as a function of time for 12 h, and the major product selectivities at 1 h. In Figure 1, only two zeolites, ZSM-5 and ZSM-11, exhibited fairly constant C₃₌ conversion rates and C₂₌ yields over the entire

reaction time in comparison with the other zeolites. This indicates that medium-pore zeolites (10-MR) having a 3-D pore channel structure could provide superior catalytic stability with high catalytic activity in the PTE reaction compared with the 10-MR zeolites with the 1-D (ZSM-22) and 2-D (ZSM-35) structures. Among the 10-MR zeolites, at the initial reaction period of 1 h, the ethylene selectivities of ZSM-22 (44.4%) and ZSM-35 (46.6%) were similar to those of ZSM-11 (46.6%) and ZSM-5 (50.8%), but the propylene conversion increased in the order of ZSM-22 (1-D, 10.7%) < ZSM-35 (2-D, 23.6%) < ZSM-11(3-D, 47.3%) < ZSM-5 (3-D, 80.5%). This ordering also showed the same trend in the reaction time of 12 h, but the values for the C₃₌ conversion for the 1-D and 2-D 10-MR zeolites were decreased to 1.8% and 8.6% (8.9–15.0% change), respectively, whereas those of the 3-D 10-MR zeolites slightly only changed (0.6–1.4% change). From the coke amounts of the spent catalysts processed by thermogravimetric analyses (TGAs), the deactivation of the 10-MR zeolites may have resulted from the easier pore blocking due to coke formation in the 10-MR pores with the 1-D and 2-D channels compared to the 10-MR pores with 3-D bidirectional channels in the ZSM-5 and ZSM-11 samples.

One of the 8-MR zeolites with the 3-D CHA structure, SSZ-13, showed the steepest decrease in the propylene conversion rate during the initial reaction period (< 2 h). The other 8-MR zeolite, SAPO-34, also showed relatively gradual deactivation of the catalyst from a low C₃₌ conversion rate (22.1% at 1 h) in the initial reaction period, and the propylene conversion reached a plateau (~6.5%) after 7.5 h. However, the ethylene selectivity levels of these 8-MR zeolites exceeded 62% for the entire reaction time. From these PTE results and from coke analyses of the 8-MR zeolites, SAPO-34 and SSZ-13 catalysts may not be favorable for the mass transfer of reactants and products, with pores more easily blocked due to the formation of coke from the smallest pore channels (cage windows) compared to 10-MR zeolites.

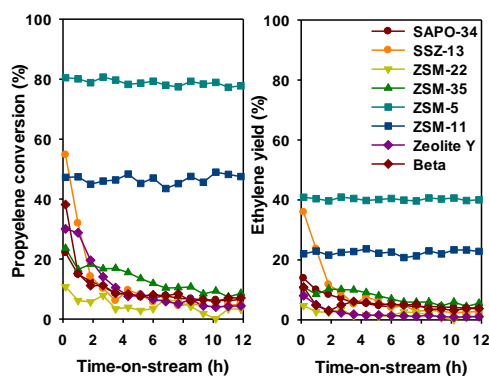


Figure 1. Propylene conversion and ethylene yield over the zeolites with time-on-stream.

4. Conclusions

For the purpose of the selective and stable production of ethylene from propylene in a fixed-bed reactor system, zeolite materials with various channel systems and pore sizes were applied to a PTE reaction. In particular, the medium-pore ten-membered ring zeolites ZSM-5 and ZSM-11 exhibited higher ethylene selectivity and stable catalytic activity levels compared to the zeolites with smaller and larger pores.

According to the catalytic results of the PTE reactions over ZSM-5 zeolites with changes in the Si/Al₂ ratios and phosphorus amounts, propylene conversion was largely dependent on the number of strong acid sites, and the optimum acidity level and phosphorus loading amount were required to obtain high ethylene and low byproduct selectivities.

References

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