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Construction of HZSM-5 Zeolite in Medium Containing Fluoride Ion and Its Performance in the Conversion of Methanol to Propylene

Somayeh Ahmadpour[1], Fereydoon Yaripour[2]* and Farhad Khorasheh[1]

1. Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

2. Catalysis Research Group, Petrochemical Research and Technology Company, National Iranian Petrochemical Company, Tehran, Iran

f.yaripour@npc-rt.ir

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Abstract

In this research, HZSM-5 zeolite was made in medium containing fluoride ions, and its performance in the process of methanol to propylene conversion was investigated. Potassium fluoride was used as the supplying material for this ion. Physical-chemical properties of catalysts were determined by using XRD, FESEM, N2 adsorption/desorption and NH3-TPD analysis. The XRD pattern confirmed the formation of crystalline structure associated with zeolite HZSM-5 in potassium fluoride-synthesized zeolite (F-HZSM-5 specimen). FESEM images of F-HZSM-5 zeolite showed a change in morphology and an increase in particles size compared to the reference sample HZSM-5. Results of the NH3-TPD analysis showed a reduction in the concentration of total acid sites in the F-HZSM-5 zeolite. The activity of the samples in a fixed-bed reactor and in the same operating conditions was investigated. The F-HZSM-5 catalyst showed less lifetime in comparison with the reference sample. However, this catalyst over a period of 10 days had an average selectivity of propylene and a propylene/ethylene ratio of 41.8 and 10.9, respectively.

Keywords: HZSM-5 Zeolite, Conversion of Methanol to Propylene, Potassium Fluoride, Mineralizer.

INTRODUCTION

Propylene is an important bulk chemical used for the production of polypropylene, acrylonitrile and propylene oxide. Due to the growing demand for propylene and anticipated shortages of petroleum resources, developing alternative methods has attracted much attention in recent years. MTP (methanol-to-propylene) process is a promising way to replace petroleum in propylene production. HZSM-5 is known as an efficient catalyst for the MTP process because of its well-defined, three-dimensional 10-ring microporous channel structure [1].

In the MTP process, among the properties of H-ZSM-5, acidity and morphology of the crystals can significantly influence the catalytic activity and product selectivity. Various methods have been suggested to improve the H-ZSM 5 catalyst lifetime in the MTP reaction. One of the important modifications of the original synthesis was the improvement of the control of the particle size of the final zeolite [2].

A significant development in the field of zeolite synthesis emerged when fluorides anions were used, making the synthesis possible in neutral, alkaline and even in acidic media. This synthesis way presents several advantages, fewer metastable phases formation, the implication of a certain ease of preparation of any desired zeolite, neutral medium (or acidic) enabling the incorporation of elements sparingly soluble in alkaline media such as Co_2^+, Fe_3^+, Ti_4^+ [3].

The purpose of this study is to synthesize an HZSM-5 in a fluoride medium and investigate its performance in the MTP reaction. The principal aim is to raise a high selectivity toward propylene, and therefore develop a simple strategy to design a new generation of MTP (methanol-to-propene) catalyst exhibiting the MFI structure.

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METHODOLOGY

The HZSM-5 and F-HZSM-5 zeolites were prepared by hydrothermal synthesis according to the following procedure. The calculated amounts of sodium aluminate, silicic acid, sodium hydroxide, tetrapropyl ammonium bromide, potassium fluoride, and deionized water were mixed well to form a gel under fast stirring for 3 h. Concentrated sulfuric acid was applied to adjust the gel pH. Also, crystallization was carried out at 180°C under autogenous pressure for 48 h with stirring in a stainless-steel Teflon-lined autoclave. The resultant solid was recovered by filtration, washed several times with deionized water until the pH value of the decanted water reached 7, and then dried 12 h at 110°C. The catalyst samples were calcined to remove the organic template in a muffle furnace under an air flow at 540°C for 12 h. Finally, the solid powder was ion-exchanged with 1 mol/L NH_4NO_3 solution at 90°C for 10 h under continuous agitation, followed by filtration and washing. After drying, the NH_4ZSM-5 zeolite was calcined at 540°C for 12 h to obtain the H-form of zeolite.

The samples were characterized by XRD, FESEM, Brunauer–Emmett–Teller (BET) and NH_3-TPD analysis. The catalytic performances of HZSM-5 catalysts were evaluated in a continuous-flow fixed-bed reactor under the same operation conditions (T = 460°C, P = 1 atm, and WHSV = 1.44 h^{-1}).

DISCUSSION AND RESULTS

Figure 1 shows the FESEM images of the HZSM-5 and F-HZSM-5 catalysts. In the HZSM-5 sample, the cubic particles with a size smaller than 1 µm and their agglomeration are observable. The F-HZSM-5 sample, however, exhibited a quite different crystal shape and size. The FESEM images of F-HZSM-5 sample exhibited the large prismatic crystals having ~10µm in size [2, 4].

CONCLUSIONS

In this research, HZSM-5 zeolite was made in a medium containing fluoride ions, and its performance was investigated in the process of methanol to propylene conversion. Physical-chemical properties of the catalysts were determined by using XRD, FESEM, N2 adsorption/desorption and NH_3-TPD analysis. FESEM images of F-HZSM-5 zeolite showed a change in morphology and particles size increase compared with reference sample HZSM-5. The activity of the samples in a fixed-bed reactor and in the same operating conditions was investigated. The F-HZSM-5 catalyst showed less lifetime compared to the reference sample. However, this catalyst over a period of 10 days had an average selectivity of propylene and a propylene/ethylene ratio of 41.8, and 10.9 respectively.

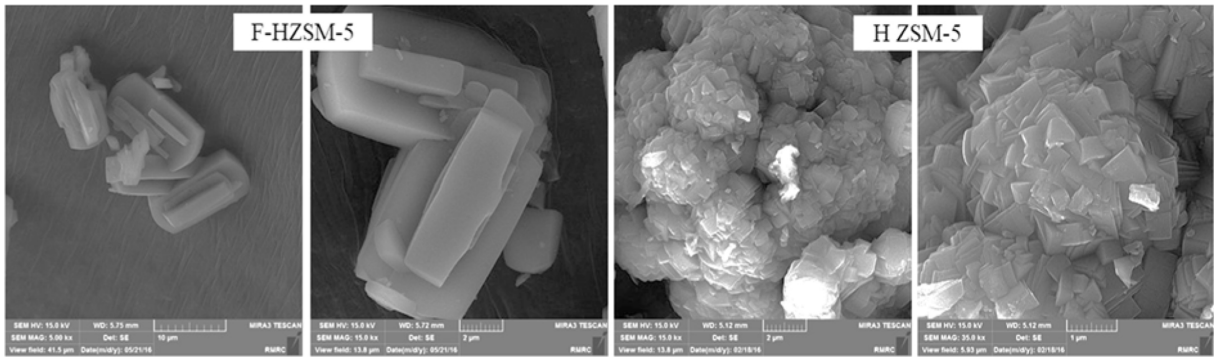

Figure 1: FESEM images of HZSM-5 and F-HZSM-5 zeolites.

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