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Synthesis of cerium-substituted MFI type metallosilicate catalyst for selective formation of propylene from methanol

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ABSTRACT

The conventional H-ZSM-5 and the cerium (Ce)-substituted MFI type metallosilicate catalysts with Si/Al ratio of 220 and Si/Ce ratio of 50 were successfully synthesized by hydrothermal method. Tetra propyl ammonium bromide (TPABr) was utilized as the template material for the synthesis of catalyst samples. The prepared catalysts were properly characterized by XRD and FE-SEM analysis. The catalytic conversion of methanol to propylene (MTP) was conducted over the prepared catalysts. The MTP reaction was carried out in a plug flow and fixed-bed reactor under atmospheric pressure. The operating conditions were as follow: reaction temperature of 500 °C and weight hourly space velocity (WHSV) of 2.51 h^{-1}. Both of the catalyst samples demonstrated high catalytic activity in the MTP reaction. In comparison with the conventional H-ZSM-5 catalyst, the propylene selectivity was improved significantly over the Ce-substituted MFI metallosilicate. The propylene selectivity obtained over the conventional H-ZSM-5 and the Ce-substituted MFI metallosilicate were 33.16% and 41.03%, respectively.

Keywords: Methanol to propylene; propylene selectivity; Ce-substituted MFI metallosilicate; hydrothermal synthesis

1. Introduction

The methanol to propylene (MTP) process which is initiated from the methanol to olefins (MTO) process has launched as a new technology for selective production of propylene from methanol [1, 2]. Methanol is the feedstock of the MTP and it is usually produced from natural gas, coal and biomass in large scale. Therefore, the MTP has been known as a prospective process for production propylene [3].
Nowadays, the investigations in the MTP process are carried out to provide the modified catalysts with higher activity and higher selectivity to propylene. For an attempt to improve the MTP catalysts, addition of different promoters to the zeolites has been carried out to moderate the strength of the acidic sites. The most investigations in this field belong to the modification by the impregnation method [4-9]. For instance, Liu et al. [6] enhanced the propylene selectivity to 55.6% over phosphorous impregnated H-ZSM-5 and also added some promoters such as W, Ce, Mn, Fe, Cr, Mo, Ga, V and Ni to H-ZSM-5; concluded that the activity of the catalysts impregnated by P, W, Ce, Mn, Fe and Cr were the best in propylene selectivity, respectively. Hadi et al. [10] modified the activity of H-ZSM-5 by impregnation of Ca, Mn, Cr, Fe, Ni, Ag, Ce and P. The best selectivity to propylene was acquired over the Mn/H-ZSM-5 catalyst.
In the present work, the high silica conventional H-ZSM-5 and the Ce-substituted MFI metallosilicate zeolite (H-CeAlMFI) with Si/Al ratio of 220 and Si/Ce ratio of 50 were synthesized hydrothermally and then were used in the MTP reaction.

2. Experimental

2.1. Catalyst synthesis

The Ce-substituted MFI metallosilicate (H-CeAlMFI) was synthesized by the hydrothermal technique. The synthetic gel was provided with the molar composition of 100 SiO_2: 0.2273 Al_2O_3: 1 Ce_2O_3: 18.9 Na_2O: 12.5 TPAB: 3200 H_2O. The composition was adjusted to reach the Ce-substituted MFI metallosilicate with Si/Al ratio of 220 and Si/Ce ratio of 50. For carrying out the hydrothermal synthesis, the gel was transferred to the Teflon-lined stainless-steel autoclave at 170 °C for 72 h. After that, the product was washed with distilled water. The resulting paste was dried at 100 °C for 12 h and subsequently calcined at 550 °C for 4 h in the air atmosphere.