Selective and stable production of ethylene from propylene over surface modified ZSM-5 zeolites

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Olefin interconversion technology is needed to meet the supply-demand balance of light olefins between propylene and ethylene. Up to now, ethylene-to-propylene (ETP) process has been extensively studied due to higher price of propylene and the expectation of an increase of the propylene demand. Moreover, plenty of ethylene is supplied from newly constructed many ethane crackers in order to use shale gas in U.S. However, in the region of Asia, the price of propylene is cheaper than ethylene price because there are many propylene sources such as naphtha cracker and PDH. Therefore, propylene-to-ethylene (PTE) process is desired to selectively convert propylene to ethylene in the Asia area.

Regarding the techniques of for the PTE process, Philips disclosed and commercialized tri-olefin process by using olefin metathesis reaction in 1960s. This process was composed with series of the metathesis reactors (ethylene and butene) and a hydrocarbon cracker to maximize ethylene yield since ethylene self-metathesis showed less than 46% of propylene one-pass selectivity [1]. Herein, the selective production of ethylene from propylene was firstly explored with various types of zeolites in the continuous fixed-bed reactor. The effect of silica-alumina ratio (Si/Al_2, SAR) and surface modification in the ZSM-5 zeolites also systematically studied with concerning the relationship between the PTE results and physicochemical properties of the zeolites characterized by various analytical methods.

Fig. 1 shows the catalytic results of PTE reaction over various types of zeolite catalysts. Except ZSM-5 zeolite, most zeolites exhibited distinct catalytic deactivation over the reaction time. Especially, deactivation within a short period of time in the small pore zeolites (SSZ-13, SAPO-34, etc.), or cage-like zeolites (HY, Beta, etc.). Stable propylene conversion is only shown in the ZSM-5 catalyst due to 3-D bidirectional 10-MR pores, which prevents the formation of cokes.

This catalytically stable ZSM-5 zeolite was selected and modified surface properties for the development of selective and stable PTE reaction. Fig. 2 shows the catalytic results of ZSM-5 catalysts with different SARs and phosphorous amounts. From these results, the PTE reaction is highly depended on the SAR and surface P modification in ZSM-5 zeolite. 1 wt% P modified ZSM-5 with SAR = 50 exhibited the highest ethylene selectivity 67% with moderate propylene conversion 60% in PTE reaction.

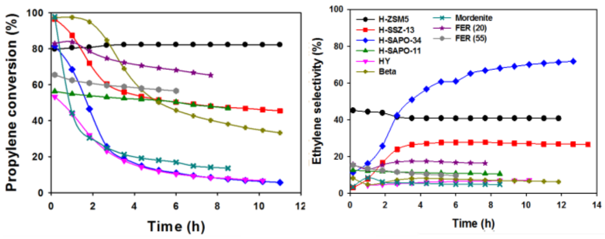

Fig. 1 Propylene conversion (left) and ethylene selectivity (right) with various zeolites.

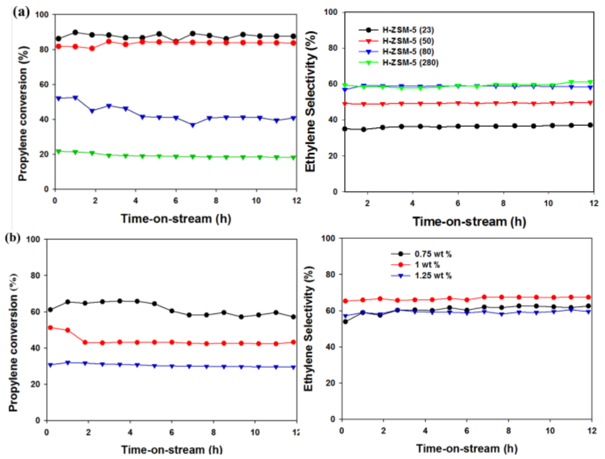

Fig. 2 Propylene conversion and ethylene selectivity over ZSM-5 zeolites with (a) different SARs, and (b) different P amounts

REFERENCES

[1] US3485890DA, Phillips Petroleum Co., 1969