



Effect of desilication of H-ZSM-5 by alkali treatment on catalytic performance in hexane cracking

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ABSTRACT

The effects of external surface and acid properties of desilicated H-type ZSM-5 zeolites (H-ZSM-5) on their catalytic performance in hexane cracking were investigated. H-ZSM-5 with two different crystallite sizes of 100 nm and 1 μm were treated with NaOH solution of different concentrations. The external surface area (S_{EXT}) was increased with an increase in the NaOH concentration, because of the formation of mesopores inside the H-ZSM-5 crystallites as a result of desilication. The increase in the S_{EXT} of the H-ZSM-5 catalysts contributed to mitigating the catalyst deactivation during the hexane cracking. Although the amount of coke deposited on the alkali-treated H-ZSM-5 was larger than that on the parent H-ZSM-5, the micropore volume of the alkali-treated H-ZSM-5 decreased less due to coke deposition than that of the parent. The deactivation rate and the decrease in the micropore volume of the small-sized H-ZSM-5 catalysts were smaller than those of the large-sized catalysts, because they had shorter average diffusion path lengths. Thus the activity of the alkali-treated H-ZSM-5, especially small-sized one is less sensitive to coke deposition. Lewis acid sites (LASs) were generated by treating with NaOH of high concentrations. The selectivities to benzene, toluene and xylene (BTX) in the hexane cracking were increased with an increase in the LASs amount at high reaction temperatures (≥ 873 K). The LASs on the alkali-treated H-ZSM-5 were selectively removed by acid treatment. The resultant H-ZSM-5 exhibited a slightly lower hexane conversion and a lower selectivity to BTX but a small amount of coke compared to the parent and alkali-treated H-ZSM-5 catalysts, suggesting that LASs on alkali-treated H-ZSM-5 accelerated the dehydrogenation including hydride transfer and aromatization, forming BTX, which would be precursors of coke.

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1. Introduction

Light olefins such as ethylene and propylene have been mainly produced by thermal cracking of naphtha. The thermal cracking process needs a high reaction temperature (>1073 K) and gives a low propylene/ethylene ratio (<0.6), whereas the demand for propylene is growing faster than that for ethylene [1,2]. Therefore, there is an increasing demand for processes capable of controlling the composition of olefins under energy-saving and environmentally benign mild reaction conditions.

The catalytic cracking of naphtha over acidic zeolite catalysts gives a high propylene/ethylene ratio at lower temperatures [2,3], since the transformation of long-chain paraffins to short-chain olefins occurs at least partly via the carbenium ion/ β -scission mechanism [4]. Therefore, this process may be a promising alternative to produce the light olefins. Among various zeolites, ZSM-5

with the **MFI** structure has been recognized as a prime candidate for the practical catalytic cracking, because of its high thermal and hydrothermal stabilities and its considerably high resistance to deactivation by coking as well as its strong acidity [2,3,5–8]. However, zeolites are generally subject to deactivation mainly due to pore blocking by coke formed during the cracking. Recently, we have reported that reduction in the crystallite size of ZSM-5 is highly effective in improving the catalytic lifetime in the hexane cracking owing to large external surface area and short diffusion path lengths [9]. Therefore, it is expected that the enlargement of external surfaces of H-ZSM-5 makes the catalyst life longer.

It has been reported that mesoporous zeolites can be prepared by various direct synthesis methods using carbon [10–12], organosilane surfactants [13] and cationic polymers [14]. Moreover, the desilication to form mesopores inside zeolite crystallites by the post treatment with NaOH solution have been reported [15,16]. Ogura et al. have reported that the NaOH treatment improves the conversion and activity per Al in the cumene cracking over alkali treated H-ZSM-5 [15]. They have claimed that alkali post-treatment does not lead to stronger acidity but leads to a

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