Effect of controlled silylation deposition of SSZ-13 catalyst for ethylene-to-propylene reaction

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Propylene is an important raw material for polypropylene, propylene oxide, and acrylonitrile, and is usually produced from naphtha cracking. However, the supply of propylene might be deficient relative to demand in near future considering the rapidly increasing ethylene supply from ethane cracker and shale gas [1,2]. In this light, the co-production of ethylene and propylene via an ethylene-to-propylene (ETP) process as a post-process of the above ethylene production process have attracted much attention recently. Usually, the price spread between ethylene and propylene is under $ 300. A highly selective catalyst is thus required for application to the ETP process. SSZ-13 catalyst has been recognized as a good candidate for ETP reaction. However, the issues of low propylene yield and high deactivation should be resolved to allow its practical use.

In order to develop a highly selective ETP catalyst by passivating the unselective acid sites and narrowing the pore mouth openings of SSZ-13, the surface of SSZ-13 catalysts (Si/Al_2=27.8) has been modified by a chemical liquid deposition (CLD) technique using different silicon alkoxides as silylation agent such as TEOS (tetraethyl orthosilicate), TMOS (tetramethyl orthosilicate), and TBOS (tetrabutyl orthosilicate).

The ETP reaction has been evaluated in a fixed-bed reactor for the ETP reaction. The modified catalysts were characterized by pyridine/NH_3-TPD, BET, SEM, XRD and ICP analyses.

Table 1 shows the effect of the type of silylation agent on the maximum propylene yield of ETP reaction over silylated SSZ-13 catalysts at 400 ^oC. The kinds of silicone alkoxide that were applied affected the maximum propylene yield of the ETP reaction. From this result, the preferred silylation agent was TEOS irrespective of silylation cycle due to the difference in the silylation reaction between TEOS and the surface hydroxyl groups of SSZ-13.

Silylation cycle	Maximum propylene yield (wt%)		
	TMOS	TEOS	TBOS
1cycle	37.5	54.2	51.5
2cycle	12.3	59.8	53.2

Table 1 Effects of the types of silylation agent on the maximum propylene yield of ETP reaction over silylated SSZ-13 catalysts at 400 ^oC.

Fig. 1 shows the effects of silylation cycle and the reaction temperature on the maximum propylene yield of ETP reaction over silylated SSZ-13 catalysts using TEOS. It was found that the reaction temperature and silylation cycle affected the ETP reactivity, and the highest propylene yield of 64.4% was obtained at conditions of 330 ^oC and 1 cycle silylation.

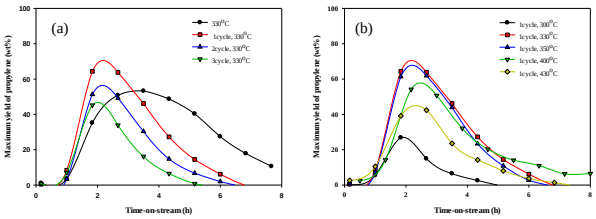

Fig.1 Effects of silylation cycle (a) and reaction temperature (b) on the maximum propylene yield of ETP reaction over silylated SSZ-13 catalysts using TEOS.

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