Synthesis of SSZ-13 zeolite in the presence of dimethylethylcyclohexyl ammonium (DMECHA) ion and application of SSZ-13 in direct conversion of ethylene to propylene

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Highlights

- SSZ-13 could be obtained with very small amount of inexpensive DMECHA.
- Anions such as hydroxide, chloride and bromide were not important in the synthesis.
- Some silica sources were required in the synthesis when aluminuous Y was applied.
- ETP reaction was carried out with synthesized SSZ-13, and showed very good performances.

1. Introduction

Direct conversion of ethylene to propylene (ETP) is very important considering the possible unbalance in near future between ethylene and propylene since the production of ethylene relies partly (and the contribution increases with time) on ethane cracking and shale gas (do not produce propylene). The ETP can be carried out with various catalysts. Zeolites such as SSZ-13, ZSM-5, UZM-35 and SAPO-34 were actively applied for this reaction [1-3]. In this study, SSZ-13 zeolites prepared in wide conditions with inexpensive structure-directing agent (SDA, here DMECHA) were applied in the ETP in order to estimate the possible reduction of the production cost of SSZ-13. Even though the syntheses of SSZ-13 under DMECHA were reported two times [4, 5] recently, further work is required not only to understand the syntheses themselves but also to estimate the possible applications including ETP.

2. Methods

The syntheses of SSZ-13 were done from Y zeolites (with different silica/alumina ratios or SARs), NaOH, H_2O, sodium silicate (different amounts) in the presence of dimethylethylcyclohexyl ammonium (DMECHA) ions (OH^-, Cl^- and Br^-), similar to a reported method [2]. The physicochemical properties of SSZ-13 zeolites were analyzed with XRD, nitrogen adsorption, ^{27}Al NMR, NH_3-TPD, ICP and SEM. The ETP reaction was carried out at atmospheric pressure at 300-450 ℃ with a conventional fixed-bed reactor made of a stainless-steel tube. Pure ethylene, diluted with nitrogen, was fed by using a MFC and heated before reaction. FID-GC was applied to analyze the products and fed ethylene.

3. Results and discussion

Fig. 1 show the XRD patterns of synthesized in wide conditions, suggesting the importance of extra silica sources especially when aluminous Y zeolites were applied as one of precursors for the syntheses. Interestingly, zeolites with analcime (ANA structure) were obtained in the absence of sodium silicate. Moreover, very small amount of DMECHA was enough for the syntheses and anions do not have any effect on the syntheses (therefore, it is not required to convert DMECHA-Br or –Cl into hydroxide form). The obtained SSZ-13s were analyzed and showed that the material is highly porous and composed of tetrahedral Al (that are helpful for acid catalyses, after ion-exchange into proton). The representative SSZ-13 were applied in ETP and showed remarkable performances in the production from ethylene (as illustrated in Fig. 2).

4. Conclusions

In this study, SSZ-13 zeolites were synthesized from Y zeolite, sodium silicate, and NaOH in the presence of DMECHA as SDA. Moreover, the SSZ-13s were applied in direct conversion of ethylene to propylene. It was found that very small amount of DMECHA was enough for the synthesis and anions do not have any

role in the synthesis. The SSZ-13, obtained in this study in cost-effective way, was very effective in the ETP, suggesting the possible applications of the material in various acid catalyses.

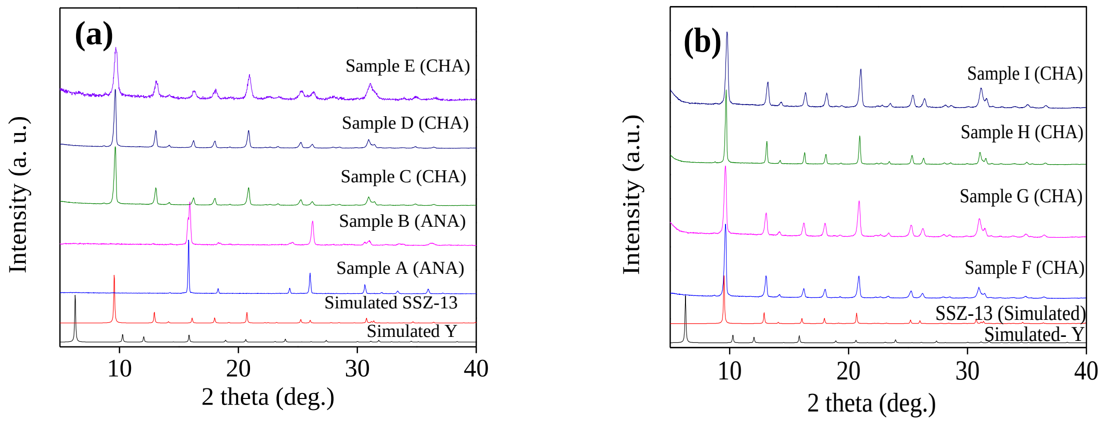

Figure 1. XRD patterns of synthesized zeolites from the conversion of Y with various SARs in the DMECHABr template: (a) without Na_2SiO_3 and (b) with additional Na_2SiO_3.

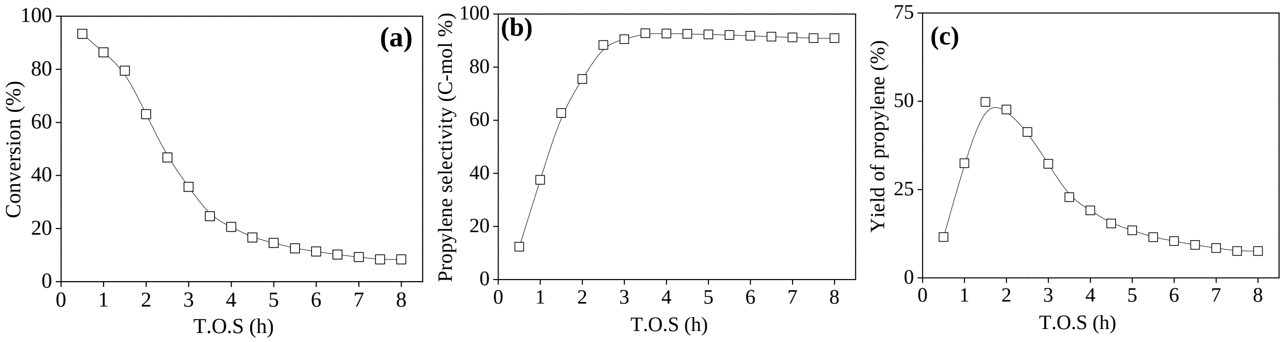

Figure 2. Effect of time-on-stream on the (a) ethylene conversion, (b) propylene selectivity, and (c) propylene yield from ETP reactions over SSZ-13 zeolite synthesized in the presence of DMECHABr.

References

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Keywords

Ethylene-to-propylene; DMECHA; SSZ-13; Y zeolite.