Methanol-to-Olefins Catalysis with Dealuminated Template-free SSZ-13 Zeolites

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Abstract: Template-free SSZ-13 (TF-SSZ-13) zeolite is evaluated for catalyzing the methanol-to-olefins (MTO) reaction. By calcination or steaming NH_4-TF-SSZ-13, Al atoms can be removed from framework positions, resulting in an increase in framework Si/Al ratio. The acid amount and strength can be controlled by calcination or steaming at different temperatures. TF-SSZ-13 catalyst steamed at 600 °C, with preserved structure, showed high, stable olefins selectivities and long catalytic lifetime, due to the suitable acid amount and strength.

Keywords: Methanol-to-olefins, Zeolite catalysis, Dealumianted template-free CHA.

1. Introduction

CHA-type aluminosilicate zeolite, SSZ-13 has been described as a very efficient catalyst for the methanol-to-olefins (MTO) reaction [1-3]. However, the conventional synthesis of SSZ-13 zeolite uses a large amount of organic templates, which significantly increases the cost of catalyst and also brings some pollutions from calcination of organic templates. Here, Al-rich template-free SSZ-13 (TF-SSZ-13) zeolite was synthesized and dealuminated. Thus prepared dealuminated TF-SSZ-13 catalyst shows excellent performance in MTO reaction, compared with the commercial high-silica H-CHA catalyst.

2. Experimental

TF-SSZ-13 zeolite was synthesized according to our previous work [4]. The as-synthesized product was ion-exchanged with NH_4NO_3 aqueous solution to obtain the NH_4-form one. Then, the NH_4-TF-SSZ-13 samples were calcined under air at 500-700 °C for 5 h. Thus obtained products were denoted as “H-TF-SSZ-13-xCal”, where x means the calcination temperature. On the other hand, the NH_4-TF-SSZ-13 samples were steaming-treated under 50% H_2O/N_2 at 500-700 °C for 1 h. Thus obtained products were denoted as “H-TF-SSZ-13-yST”, where y means the steaming treatment temperature. For comparison, high-silica H-CHA zeolite with Si/Al ratio of 15 was provided by BASF SE, Germany.

The MTO reaction was carried out at 350 °C under atmospheric pressure. The pressure of methanol was set at 5 kPa. Helium was used as a carrier gas. W/F for methanol was set at 33.7 g-cat h mol^{-1}. The catalyst was activated in flowing He at 500 °C for 1 h prior to the reaction and then cooled to the desired reaction temperature. The reaction products were analyzed by an online gas chromatograph (GC-2014, Shimadzu) equipped with HP-PLOT/Q capillary column and an FID detector. The selectivities of the products were calculated on the basis of carbon number.

3. Results and discussion

From the XRD and N_2 adsorption results, both the crystallinity and micropore volume for the calcined TF-SSZ-13 gradually decreased with increasing the calcination temperature, meaning that the structure was partially destroyed after calcination at high temperature. In contrast, the CHA structure almost remained for steam-treated TF-SSZ-13, regardless of the steaming temperature. The micropore volume of the steam-treated TF-SSZ-13 varied from 0.18 to 0.22 cm^3/g. Although the bulky Si/Al ratio remained at ca. 3.7 after calcination or steaming, the framework Si/Al ratio was increased, which can be calculated according to the ^{29}Si MAS NMR results. For example, the framework Si/Al ratios for H-TF-SSZ-13-600Cal and H-TF-SSZ-13-600ST were 5.5 and 6.4, respectively. This fact means more Al atoms were removed from the framework after the steaming treatment. From the NH_3-TPD results, the acid amount gradually decreased with increasing the calcination or steaming temperature. Moreover, the strong acid sites were preferentially removed after steaming treatment compared to calcination, which can be proved by CO adsorption FTIR results.

Figure 1 shows the MTO performances for the different catalysts. All the catalysts showed 100% initial methanol conversion. However the catalytic lifetime was drastically different. Among the calcined TF-SSZ-13, H-TF-SSZ-13-600Cal showed slightly short lifetime compared to commercial high-silica H-CHA. H-TF-SSZ-13-500Cal showed very short catalytic lifetime, which was due to the high amount of strong acid sites. Although the strong acid amount was low for H-TF-SSZ-13-700Cal, the catalytic stability was not good, which was related to the destroyed structure. In contrast, the steam-treated TF-SSZ-13 showed longer lifetime than calcined ones at the same treatment temperature. Especially, H-TF-SSZ-13-600ST showed long lifetime compared to the high-silica H-CHA, although it had high acid amount and low framework Si/Al ratio. On the other hand, the H-TF-SSZ-13-600ST also showed high, stable olefins selectivities.

These results indicate that steaming treatment was a good method for the dealumiantion of TF-SSZ-13 to preserve the structure. The dealuminated TF-SSZ-13 obtained by steaming at medium temperature showed good MTO performance. This may be due to the suitable acid amount and strength, proved by NH_3-TPD and CO adsorption FTIR results.

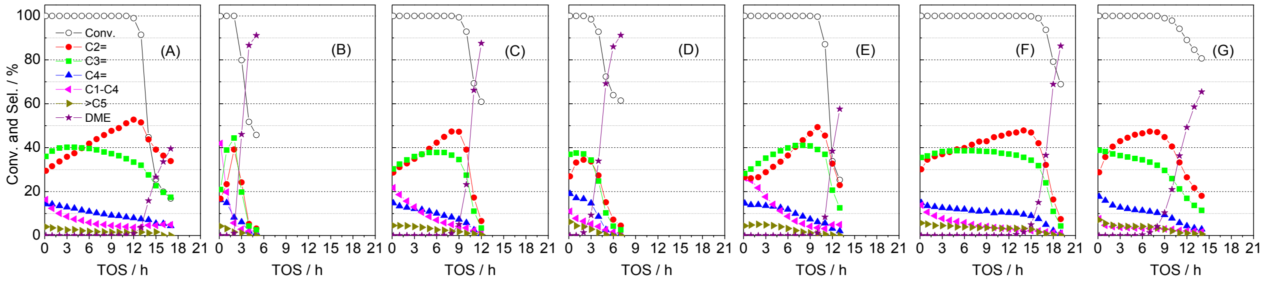

Figure 1. Change of methanol conversion and products selectivities with time-on-stream (TOS) over H-CHA(Si/Al=15) (A), H-TF-SSZ-13-500Cal (B), H-TF-SSZ-13-600Cal (C), H-TF-SSZ-13-700Cal (D), H-TF-SSZ-13-500ST (E), H-TF-SSZ-13-600ST(F), and H-TF-SSZ-13-700ST (G).

4. Conclusions

By calcination or steaming NH_4-TF-SSZ-13, Al can be removed from framework positions, resulting in an increase in framework Si/Al ratio and thus a lowered active acid site density. After the steaming treatment, more Al atoms were removed from the framework; meanwhile the strong acid sites were preferentially removed. TF-SSZ-13 catalyst steamed at 600 ℃, with preserved structure, showed high, stable olefins selectivities and long catalytic lifetime due to the suitable acid amount and strength.

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