A Process for DME and butene to Propylene over Ca/MFI/SiO$_2$ catalyst

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Propylene is an important chemical base material for polypropylene. Now, most of propylene is mainly produced from petroleum refining and the naphtha steam-cracking. Due to the growing demand for propylene and the shortage of petroleum resource in the future, new processes with high yield of propylene are required[1].

The catalytic process of methanol or DME to propylene has attracted interesting[2,3]. Recently, we have successfully developed a MFI zeolite catalyst for the DME to propylene process. Over this catalyst, the DME conversion is 100% and the propylene selectivity is about 40%, but the selectivity of C$_4$-C$_6$ olefins is about 45%. For getting highest propylene yield, C$_4$-C$_6$ olefins must be recycled.

In this study, we report the development of a new process for DME and recycle olefins to produce propylene over a calcium modified MFI catalyst.

1. Experimental

MFI (ZSM-5) type zeolites were synthesized hydro thermally. H-form MFI was prepared by ammonia exchange, Ca/MFI, were prepared by ion exchange of the parent zeolites in H-MFI, using aqueous solution of NO$_3$. After exchange the catalysts were filtered, washed and slowly dried at room temperature for about 48 h, and then at 723 K for 10 h. The Ca/MFI zeolite mix with SiO$_2$ powder and binder, then extrusion dry, calcinations, crack and sieve. Finally, the 1.18-0.71 mm size of catalyst was used for DTP reaction.

DTP reaction was carried out in a fix-bed reactor at atmospheric pressure, taking 0.4 g zeolite catalyst diluted with 2 g inert silica (0.075-0.5 mm in size). Nitrogen was used as diluent. The products were analyzed on-line with two gas chromatographs: CO, CO$_2$ and CH$_4$ were analyzed by using an activated charcoal column with a thermal conductivity detector (TCD) and hydrocarbons were analyzed by using a 30 m long Al$_2$O$_3$-KCl capillary column with a flame ionization detector (FID).

2. Result and discussion

2.1. Reactivity of different olefins with or without DME

The conversion of C$_2$-C$_6$ olefins on Ca/MFI/SiO$_2$ catalyst under the same reaction conditions with only DME to propylene process shows that the olefin conversion increases as the olefin carbon number increases. The ethylene almost not convert, and 90% of C$_6$ olefin has cracked. This is due to the cracking rate of olefin increases as the hydrocarbon chain increases. Another reason is the weak acidity of Ca/MFI/SiO$_2$ catalyst.

However, the conversions of C$_2$-C$_6$ olefins are strongly changed when feed with DME, even ethylene conversion has been increased to 20%. It is also interesting that their products distribution are same
with only DME conversion. This means C2+ olefins are intermediate products. Firstly DME dehydrate into carbium CH2*, CH2* polymerizes to format ethylene, another carbium will react with ethylene to produce propylene. And so on logger olefins are produced. On the contrary, higher olefins will crack at high temperature. This point is important for DME-to-propylene project, because the by-products can be recycled to make more propylene.

**Fig. 1** conversion of DME with olefins over Ca/MFI/SiO2 zeolites.

### 2.2 Ratio of butene to DME

**Fig. 2** shows as the ratio of butene to DME in feed increases, propylene selectivity decreases, C5 and C6 olefins selectivities increase, and butene selectivity is not change obviously. This is due to much C5 and C6 olefins have been produced from butene, and then can not crack at once. Another reason is the acidity of this catalyst is very weak, not favourable for olefin crack reaction. The by-products is about 45Wt.% in the DME-to-propylene process, so that, the reaction results will not change even all the by-product olefins recycling.

**Fig. 2** products distribution with different ratio of butane to DME.

DME

2.3. Ratio of (DME+C4)/N2

The effect of ratio of (DME+ butene)/N2 on the conversion and products distribution were shown on **Fig. 3**. **Fig. 3** shows DME conversion is 100% even 35% of (DME+ butene)/(DME+butane+N2), but the conversion butane decreases from 50% to 25%. Propylene selectivity decreases from 48% to 28%, aromatics selectivity increases. This is due to higher hydrocarbon content result in aromatization reaction take place easily. The crack reaction is suppressed.

Although propylene yields are higher under lower ratio, the reactor handle capacity decreases, higher ratio is suitable.

**Fig. 3**. conversion and products distribution with different ratio of (DME+C4)/((DME+C4=+N2) (mol/mol)

Reaction results shown that reaction rate of butene to propylene were promoted with DME addition in the feed. Propylene selectivity decreases as the ratio of butene/DME or the ratio of hydrocarbons/N2 increase. High temperature is beneficial to butene conversion, but ethylene and aromatics selectivities increase. The reaction mechanism of DME and butene to propylene has been proposed on this catalyst.

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### References