

Direct Synthesis of a Fluidizable SAPO-34 Catalyst for a Fluidized Dimethyl Ether-to-Olefins Process

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Abstract The dimethyl ether to olefins process is very important for converting coal to chemicals. A SAPO-34 molecular sieve with a particle size up to 50 μm has been synthesized with morpholine as the template. The cold model fluidization experiment indicates that the SAPO-34 catalyst with average size of 45–50 μm is of good fluidization properties. After high temperature steam treatment at 1073 K for 8 h, this large fluidizable catalyst showed good reactivity and selectivity for the dimethyl ether to olefins (DTO) reaction in a micro-reactor. X-ray diffraction characterization showed that the structure of the catalyst was maintained well. A fluidized reactor of 50 mm inner diameter was used to carry out the DTO reaction, which showed that the fluidizable SAPO-34 is a selective catalyst for light olefin production.

Keywords SAPO-34 · Dimethyl ether-to-olefins · Propene · Ethene · Fluidization

1 Introduction

The oil shortage worldwide has resulted in a need for alternative non-oil routes to produce light olefins especially propene, the production of which has received much attention in recent years due to the increasing demand. The methanol to olefins (MTO) process has provided such an additional route to light olefins including propene and there

have been many molecular sieve catalysts examined for this process such as ZSM-5 [1–3]. Among the different types of catalysts, SAPO-34 is believed to be the best for its high selectivity to ethene and propene due to its moderate acid strength and relatively small pore opening [4–8]. Compared to the fixed-bed process, the fluidized-bed process has major advantages in heat transfer and continuous regeneration of the catalyst [9], which is of great importance for the MTO process due to its strong exothermicity and rapid deactivation of SAPO-34 catalyst. Bos [10] also found that the fluidized-bed reactor is more promising than the fixed-bed reactor for MTO in the ethene mode by developing a kinetic model. Thus investigation on the catalytic performance of SAPO-34 molecular sieve in the fluidized-bed would be important and beneficial.

During the MTO process, it is generally accepted that methanol has to be converted to dimethyl ether (DME) first, and followed by the conversion of DME to light olefins [11, 12]. Thus, the DME-to-olefins (DTO) reaction should be closely related to the MTO process because there is a fast conversion equilibrium between methanol, DME and water. This paper selects DME as the feedstock and aims to provide information about the catalytic performance of a SAPO-34 catalyst which can be directly fluidized for use in a Fluidized-Dimethyl ether-To-Olefins (FDTO) process.

At present, the size of the SAPO-34 molecular sieve obtained with tetraethylammonium hydroxide (TEAOH) or triethylamine (TEA) as the template and applied in the MTO process is about 1–5 μm [13–15], which cannot be used directly under the condition of industrial fluid catalytic cracking. Thus, it must be treated by spraying and granulation, and the resulting catalyst has poorer abrasion resistance and more complicated process for fluidization as compared with the single crystal. There have been some

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literatures on the direct synthesis of zeolites with large particle size, such as zeolite Y [16]. However, study on the synthesis of single crystals of SAPO-34 with size suitable for fluidized-bed applications is still limited. In the present study, we prepared a large SAPO-34 molecular sieve catalyst with morpholine as the template to achieve the suitable particle size for fluidization, and tested its stability, activity and selectivity to light olefins.

2 Experimental

2.1 Synthesis

SAPO-34 was prepared by the method described in the reference [17] using the starting materials of pseudoboehmite (73 wt% Al_2O_3), orthophosphoric acid (85 wt% H_3PO_4), colloidal silica (40 wt% SiO_2), with morpholine (Peking Masutoshi Fine Chemical Co., Ltd.) as the template while adopting TEA as the template for the control group. For the morpholine-template catalyst, the chemical composition of the starting gel was $1.0\text{Al}_2\text{O}_3 : 1.0\text{P}_2\text{O}_5 : 0.5\text{SiO}_2 : 2.0\text{Mor} : 30\text{H}_2\text{O}$ and for the control group, the chemical composition was $1.0\text{Al}_2\text{O}_3 : 1.0\text{P}_2\text{O}_5 : 0.5\text{SiO}_2 : 3.0\text{TEA} : 30\text{H}_2\text{O}$. The synthesis procedure followed for gel preparation in this experiment is described as given below.

First, 11.5 g of pseudoboehmite was dissolved in 15 g of deionized water to form alumina sol, and then mixture of 19.24 g of phosphoric acid and 15 g of water was added to the alumina sol under stirring. Mixture of 6.26 g of colloidal silica and 5 g of water was further added and finally 14.5 g of morpholine was added and the resulting mixture was stirred for 2 h at room temperature. The resulting gel mass was transferred into autoclave and crystallized for 36 h at 473 K. The solid product was then washed several time and dried overnight at 393 K. As-synthesized product was then calcined in air at 873 K for 4.5 h.

2.2 Characterization of Samples

The crystallinity and the phase purity of the as-synthesized samples were characterized by a Japan Science D/max-RB powder diffractometer with Cu K_α radiation. The size distribution was analyzed by a Malvern Mastersizer and scanning electron microscope (SEM) images obtained on a JSM 7401 instrument operated at 3.0 kV. The BET surface area was measured by nitrogen adsorption at 77 K on the ASAP2010 volumetric adsorption analyzer.

2.3 Hydrothermal Treatment and Reactor Performance

High-temperature steam treatment (100% steam, 622 N mL/min gas flow under standard state) was carried out in order

to investigate the hydrothermal stability of as-synthesized SAPO-34 sample with morpholine as the template. The sample was divided into 3 groups that were subjected to hydrothermal treatment of different severity, namely, 973 K–2 h, 973 K–6 h and 1073 K–8 h. Then, the three groups of samples were characterized by XRD and examined for the conversion of DME (99.7 vol%) by pulse input in a micro-reactor, which was a fixed bed reactor at atmosphere pressure. Catalyst samples (0.012 g SAPO-34 and 0.028 g SiO_2) were loaded into a quartz reactor with an inner diameter of 5.0 mm. The temperature of the reaction was 723 K and the weight hourly space velocity (WHSV) was 218 h^{-1} . The reaction products were analyzed online by an Agilent GC1790 gas chromatograph equipped with a FID detector.

2.4 Cold Model Fluidization Experiment

The as-synthesized SAPO-34 samples were tested in a cold model fluidization experiment with a reactor that was a 1 m long and 23 mm inner diameter plexiglas pipe with top hatched and bottom carrying gas distributors.

2.5 Reactive Fluidization Experiment

47 g of SAPO-34 catalyst without hydrothermal treatment was examined in a reactive fluidization experiment which was carried out in a fluidized bed with inner diameter 50 mm and height 1 m. DME with a gas flow rate was 1.08 mL/min and argon was used as an inert diluent gas and co-fed with DME into the reactor at a flow rate of 2.16 mL/min. Space velocity in WHSV was kept to 2.85 h^{-1} . The reaction products were analyzed online by the Agilent GC1790.

3 Results and Discussion

3.1 Crystallinity and Size Distribution of SPAO-34 Crystals

The XRD data of the samples studied showed the diffractions of the SAPO-34 crystal structure. Figure 1 shows X-ray diffraction patterns of the as-synthesized SAPO-34 samples prepared by the different templates. The position and the intensity of the diffraction peaks of both samples are similar to those of SAPO-34 materials reported in the literature [18] without any impurity phase. The absence of a baseline drift and high peak intensity with no line broadening indicated good crystallinity for the sample that used morpholine as the template. Based on the XRD data of the three highest peaks area, the crystallinity of the sample with TEA as the template was calculated to be 67.9% of that of the sample with

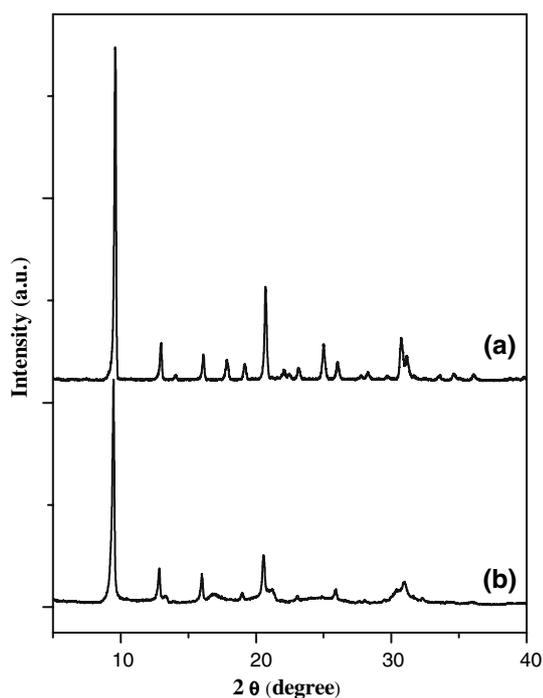


Fig. 1 XRD patterns of as-synthesized SAPO-34 samples: (a) morpholine as the template, (b) TEA as the template

morpholine as the template. Both samples had a cubic morphology seen in SEM photos (Fig. 2), which also showed that the size of crystals with morpholine as the template was much larger, with the average particle size of 46.5 μm , than the crystals of the sample with TEA as a template agent which was only 4.17 μm . The results from the Malvern Mastersizer (Fig. 3) confirmed that the particle size of the final product was determined by the nature of template used during synthesis. However, as shown in Figs. 2 and 3, the samples with morpholine and TEA as template agents both showed a wide distribution in the particle size, which depended on the crystallization conditions, for example, whether agitated.

The samples that used the different templates had a similar pore size distribution measured by nitrogen adsorption-desorption, which indicated that the as-synthesized SAPO-34

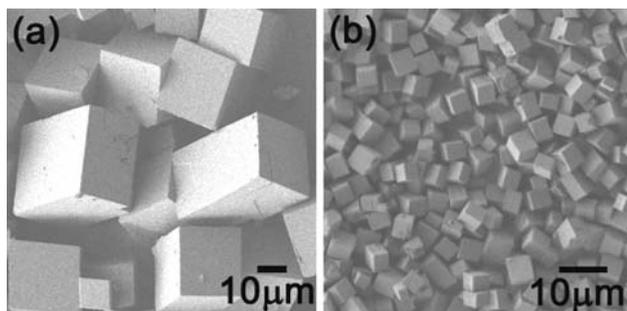


Fig. 2 SEM images of as-synthesized SAPO-34 samples: (a) morpholine as the template, (b) TEA as the template

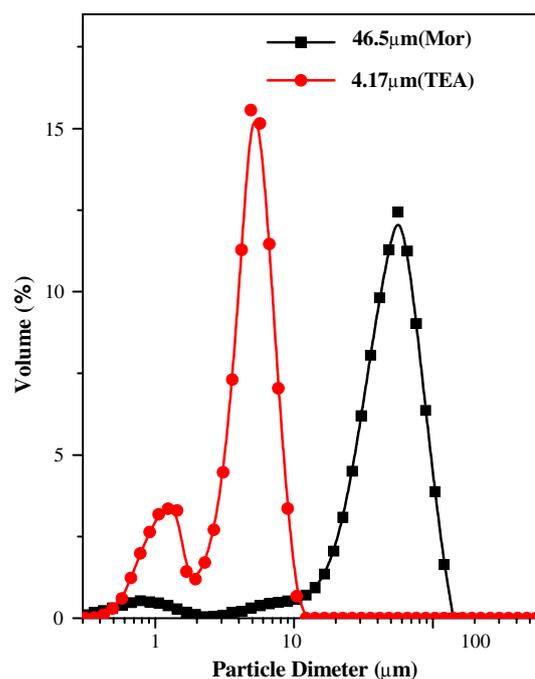


Fig. 3 Size distribution of as-synthesized SAPO-34 samples

molecular sieve was mainly of a microporous structure. The BET surface area of sample with morpholine is 488 m^2/g while that of sample with TEA is 560 m^2/g . The results are similar to that of the sample that used TEOH as the template reported in the literatures [19, 20].

3.2 The Hydrothermal Stability of Fluidizable SPAO-34 Catalyst

The hydrothermal stability of a SAPO-34 molecular sieve has been studied by a steaming treatment of different severity. Results of the XRD characterization for the three groups of samples treated by steam compared with that of untreated sample are shown in Fig. 4, which indicated little difference for the position of the diffraction peaks of all the samples. Crystallinity of samples after hydrothermal treatment at 973 K–2 h, 973 K–12 h and 1073 K–8 h are 100%, 90.2% and 73.1% of that of sample without hydrothermal treatment, respectively. This indicated the hydrothermal treatment used in the experiment extent did not destroy the structure of the catalyst severely, or in other words, a SAPO-34 molecular sieve with morpholine as the template was of good hydrothermal stability. This is consistent with the experimental data of previous work [21].

The catalytic testing of DME conversion was carried out over the samples above and the results showed the severity of the hydrothermal treatment had little influence on the conversion of DME. Taking the result of the sample with the 1073 K–8 h hydrothermal treatment (Fig. 5) as the example of the behavior of DME conversion, it can be seen

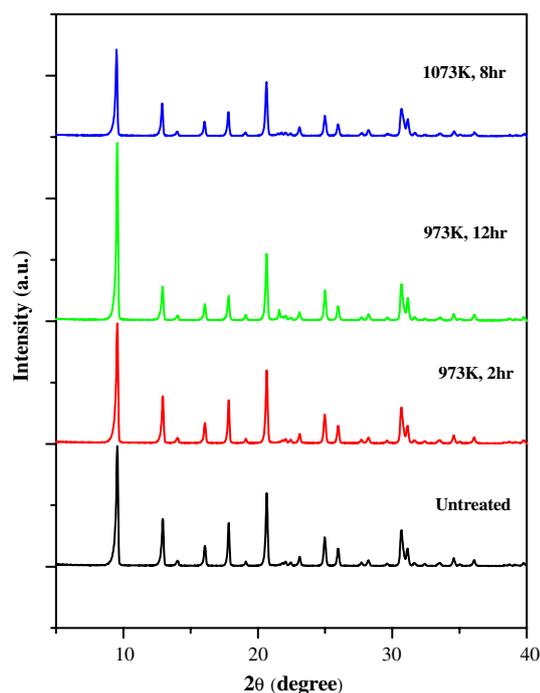


Fig. 4 XRD patterns of as-synthesized SAPO-34 samples after hydrothermal treatments of different severity

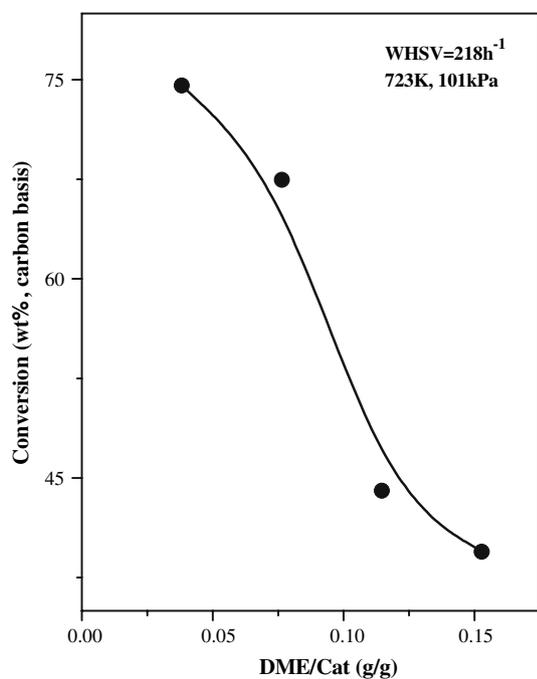


Fig. 5 DME conversion in the microreactor over the SAPO-34 sample after hydrothermal treatment at 1073 K–8 h

that the conversion of DME decreased very fast with reaction time due to coke formation. It was difficult to maintain the reactions on the acid sites of the catalyst because of occupied acid sites and blockage of the pore structure [22]. Marchi and Froment [23] suggested that the

deactivation by coke and its effect on product distribution depend on the way the coke is deposited on the catalyst. SAPO-34 with an interconnecting three-dimensional network of pores with supercages provides room for accommodating some coke without the immediate blocking of the pores. Aromatics and branched isomers form inside the cavities and adsorb irreversibly on the strong acid sites, which resulted in a decrease in the concentration of strong acid sites. With increasing coke deposition on the catalyst, the pores are blocked and the concentration of acid sites drops abruptly, and so does the DME conversion. Obviously the investigation of coke deposits is still a severe task in DTO process [24].

Here, we mainly focus on the difference in the selectivity to propene and ethene among the three groups of samples (Figs. 6 and 7). The experimental results showed that a hydrothermal treatment of proper severity can help to improve the selectivity to propene. This is mainly because a milder steam treatment will modify the acid sites of the catalyst in favor of the production of propene, but as the conditions become more severe, the structure of the catalyst is partially destroyed, which will adversely affect propene production as shown in Fig. 7. For ethene, the results from the hydrothermal treatment with different conditions showed a strong trend that the selectivity to ethene increased as the hydrothermal treatment got more severe, also because of the modification of the acid sites, which helped to decrease the hydrogen transfer reaction that led to alkanes [25]. There was little difference in the

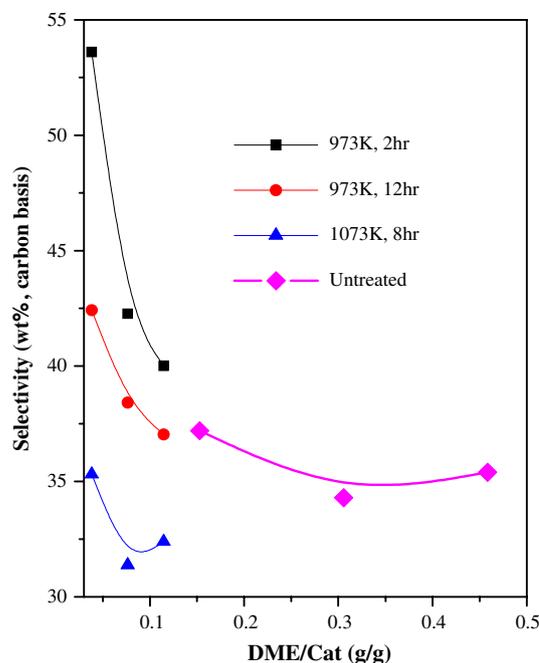


Fig. 6 Selectivity to propene over SAPO-34 samples after hydrothermal treatments of different severity

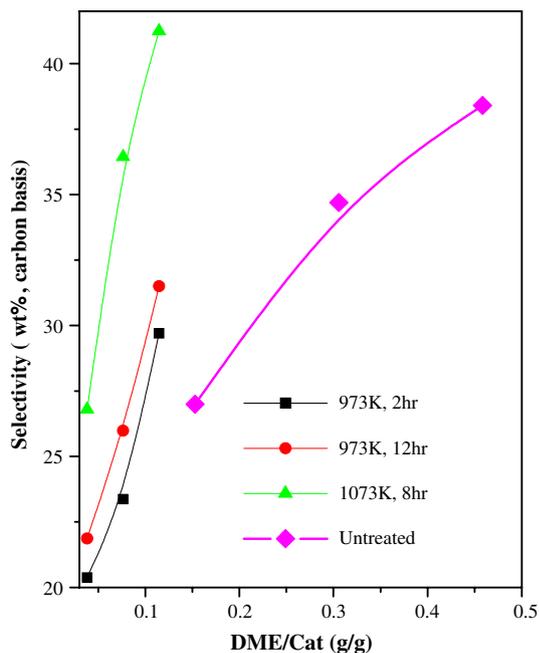


Fig. 7 Selectivity to propene over SAPO-34 samples after hydrothermal treatments of different severity

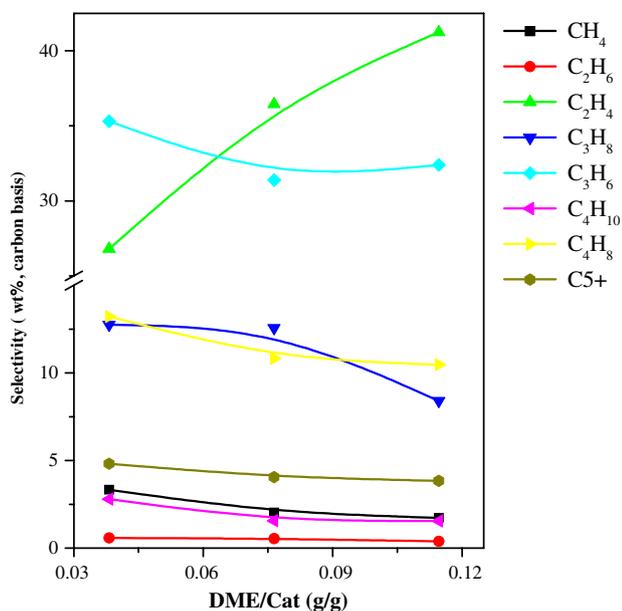


Fig. 8 Selectivity to light olefins over the SAPO-34 samples after hydrothermal treatment at 1073 K-8 h

selectivity to the other products, thus, we also use the results of the sample with the 1073 K-8 h steam treatment as the example to show the product distribution (Fig. 8). The product distribution showed that even after the catalyst was treated by steam at 1073 K for 8 h, the selectivity to propene and ethene was 60–70%, which is close to that of a SAPO-34 catalyst without any hydrothermal treatment. Thus, this confirmed the XRD results above, that is, the

SAPO-34 molecular sieve that used morpholine as the template agent has good hydrothermal stability.

3.3 The Fluidization Property of SPAO-34 Catalyst

The Geldart particle classification system divides solid particles into four groups designated A, B, C, D, which is based on the relationship between the particle average size and density difference between particles and gas. Among the four kinds of particles, Group A powders are regarded as fine particles especially for operation of an FCC (fluidized cracking catalyst) in fluidized beds. The SAPO-34 molecular sieve with a size of 46.5 μm is a Geldart-A particle, that is, it should have good fluidization characteristics such as small minimum fluidizing velocity u_{mf} . From Fig. 9, we can see that the pressure drop increased with flow rate at first. When the fluid rate reached about 0.025 m/s (u_{mf}), fluidization began and the particles inside the layer started to rearrange. Then, as the gas velocity increased further, the pressure drop stabilized and remained constant. The pressure-drop-velocity variation corresponded well to the characteristic described by Davidson [26].

3.4 Reactive Fluidization Experiment

The reactive fluidized bed results showed a similar rapid deactivation (Fig. 10) and selectivity to different gaseous products (Fig. 11) as those in the micro-scale fixed bed reactor. Considering the average selectivity to propene and ethene, the lower space velocity in the fluidized bed resulted in the further crack of propene and decreased its

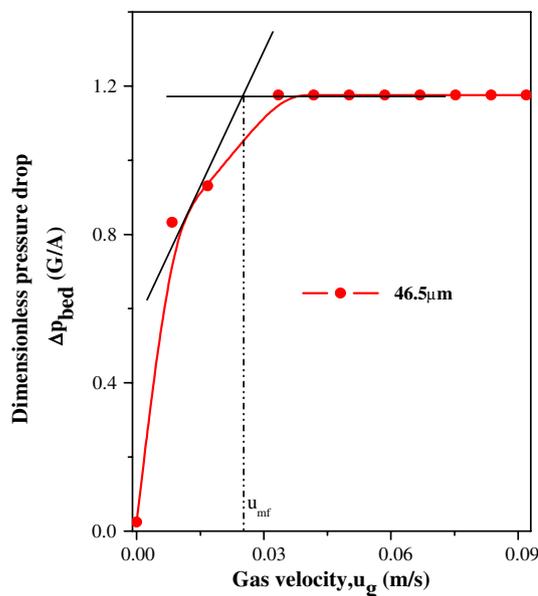


Fig. 9 Cold model fluidization result over as-synthesized SAPO-34 samples

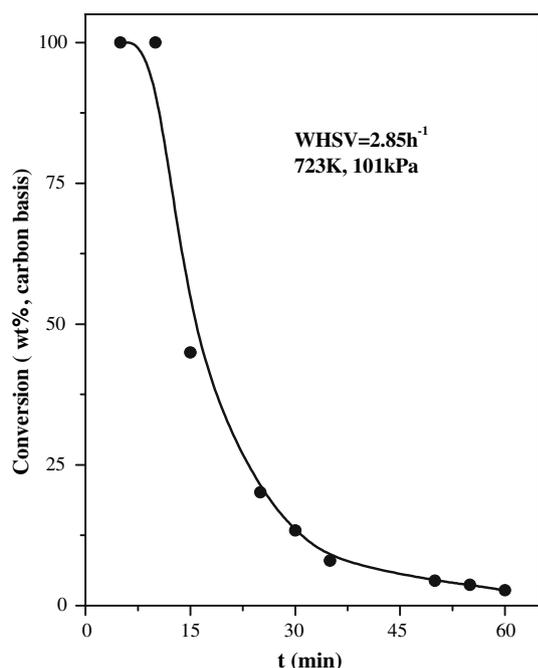


Fig. 10 DME conversion in the fluidized bed over as-synthesized SAPO-34 samples

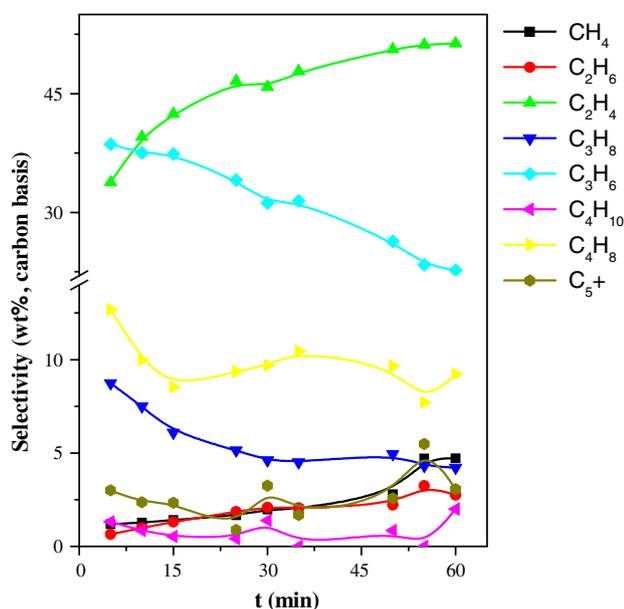


Fig. 11 Product distribution over as-synthesized SAPO-34 samples

selectivity, but it slightly increased the selectivity to ethene (difficult to decompose further), when compared with those in the microreactor. It was observed that the selectivity to ethene and propene approached 70–80%, which was even higher than that in the micro-scale fixed bed reactor. This is due to the low space velocity in the fluidized bed. In addition, the cubic particles keep good especially for the larger ones after the reactive fluidization experiment,

which indicates the as-synthesized fluidizable SAPO-34 sample has good mechanical strength. The results are useful and should be further investigated in order to increase the yield and the selectivity of light olefins especially propene.

4 Conclusion

Large SAPO-34 molecular sieve crystals have been synthesized by the use of morpholine as the template. XRD characterization showed that the catalysts treated by hydrothermal methods of different severity had a similar structure. This together with the catalytic activity of the catalysts for the conversion of DME in a microreactor showed that the severe hydrothermal treatment had little negative effect on the activity, but to some extent, improved the selectivity to ethene. The catalyst is of good hydrothermal stability. Cold model fluidization experiments indicated that the SAPO-34 catalyst with an average size of 45–50 μm , that used morpholine as the template, had good fluidization properties. Reactive fluidized bed results showed that the catalytic performance was similar to that in the micro-scale fixed bed reactor and indicated that the fluidizable SAPO-34 is a very selective catalyst for light olefin production.

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