# Preparation and catalytic distillation testing of an acidic zeolite film catalytic packing for synthesis of ETBE

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A novel type of zeolite film catalytic packing for synthesis of ETBE from ethanol and $C_4$-cut olefin was developed, characterized and evaluated in a catalytic distillation column. The experimental results show that the zeolite film composed of acidic BEA crystals, of a size of about 500 nm, is essentially continuous and free of cracks, and that the packing has better characteristics in both catalysis and the separation of products from reactants that is comparable to that of resin catalysts used in industrial distillation towers.

**KEY WORDS:** zeolite film catalytic packing; catalytic distillation; ETBE.

## 1. Introduction

ETBE (ethyl *tert*-butyl ether) may become a better option as an automotive fuel octane booster since it can be produced from bio-ethanol that can be obtained from renewable resources. In addition, ETBE has superior qualities since its low blending Reid vapor pressure, less than 55 kPa, is required in some places during summer. This makes ETBE an interesting alternative to MTBE [1].

Currently, a strong acidic macroporous ion-exchange resin is a common catalyst for etherification. Despite the resin's good catalytic activity for the etherification, its thermo-stability and selectivity are poor. Acidic zeolites have been identified as good substitutes for the resin because of their good activity, perfect selectivity, thermo-stability and reproducible response [2–5].

The application of reactive distillation with heterogeneous catalysts (so-called catalytic distillation) is quite attractive for the production of fuel ether because the heat of reaction can be utilized efficiently for vaporization of the liquid phase and the chemical equilibrium can be influenced positively by removal of products [6,7]. Nowadays, zeolites are commonly used in the configuration of extrudates or beads. Due to the size of the catalysts, there are some problems related to their use in a catalytic distillation column such as difficulty in removing products out of the reaction zone promptly and a higher pressure drop in the catalytic distillation column than that in a conventional distillation column so as to increase energy consumption. Therefore, an operation configuration involving a thin active zeolite film on a structured packing, with a large contact surface between reactants and the catalyst combined with a short diffusion length, in the reaction zone of the catalytic distillation column is expected to ensure good mass transfer and heat transfer [8,9]. A few methods for the preparation of supported zeolite film or zeolite film packing have been developed so far [8–16], but the performance of zeolite film packing when used in a catalytic distillation column has not been addressed.

The aim of the present study is to develop a novel type of zeolite film packing for synthesis of ETBE and to exploit its unique advantages in a catalytic distillation column.

## 2. Experimental

### 2.1. Materials

TEABr (tetraethyl ammonium bromide; Xingfu Chemical Factory, Beijing, China) was used as a template agent for the preparation of zeolite film. $SiO_2$ particles (0.254–0.318 mm; Haiyang Chemical Factory, Qingdao, China), $NaAlO_2$ solution (3.73 M) and NaOH solution (5.74 M) were used as silica, aluminum and sodium sources, respectively. The seeds of zeolite BEA (about 200 nm) were made by *in situ* hydrothermal synthesis accompanied by churning. A saddle ceramic with pyramids (5 mm × 5 mm, $SO_2/Al_2O_3 = 3.13$; Yulong Ceramics Corporation, Zhuzhou, China) was used as a support.

Resin D005 (average diameter of 0.5 mm, exchange content of above 4.7 mmol/g; Dandong Chemical Factory, Shenyang, China) was used in comparative experiments.

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Ethanol (99.9% pure, <0.1% water; Reagent Corporation, Tianjin, China) and $C_4$-cut olefin (31.4% isobutene; Yanshan Chemical Corporation, Beijing, China) were used for synthesis of ETBE.

### 2.2. Preparation of the acidic zeolite film packing

The zeolite film packing was prepared using secondary hydrothermal growth on a precursor seed layer of BEA crystals over a pretreated ceramic support. A chemical composition of the precursor solution of $Al_2O_3$:30 $SiO_2$:6 TEABr:10.5 NaOH:240 $H_2O$ (in molar ratio) was employed for the formation of the zeolite film at a temperature of 145 °C for 40 h (autogenous pressure) in a 150 $cm^3$ Teflon-lined autoclave. After hydrothermal treatment twice, the sample was calcined at 450 °C for 4 h at 1 °C/min, modified by ion exchanging with an aqueous solution of 0.5 M $NH_4Cl$ and steamed at 350 °C for 3 h at 1 °C/min to form the acidic zeolite film packing.

### 2.3. Catalytic distillation

The catalytic distillation experiments were carried out in a laboratory-scale stainless steel column (diameter of 30 mm). The column consisted of a total condenser with circulating alcohol at a temperature of 273 K as a coolant, a reboiler with a mantle heater, and a column body composed of three sections: (1) a rectifying section of 200 mm in height below the condenser, (2) a stripping section of 400 mm in height above the reboiler (both sections were packed with triangle stainless steel gauze packings), and (3) a reaction–separation section of 1200 mm in height packed with the acidic zeolite film catalytic packings located at the middle of the column. (The same amount of ion-exchange resin D005 particles as that of the zeolite, packed within small pockets wrapped with stainless steel corrugated gauze, was used instead of the zeolite film packings while comparative experiments were being conducted.) There were 15 theoretical plates per meter of the stainless steel gauze packing, 12 theoretical plates per meter of the zeolite film packings and 7 theoretical plates per meter of the resin pocket packings, as determined by total reflux distillation with benzene and tetrachloromethane.

When the catalytic distillation was carried out, ethanol and $C_4$-cut olefin were introduced, with positive displacement pumps, into the column body at the higher part and the lower part of the reaction–separation section after being preheated, respectively (figure 1). The reflux ratio was controlled with a solenoid valve with a timer. The liquid level in the reboiler was maintained by adjusting the valve of the withdrawing pipe connected to a tank. The pressure was controlled with compressed nitrogen at the top of the column. After the experiment had been conducted for 4 h, the liquid streams were sampled from the top of the column and from the reboiler, simultaneously, every half an hour. The compositions of the samples were analyzed with SQ-206 gas chromatography. The experiment would not be finished until the compositions of the samples did not vary with time any more.

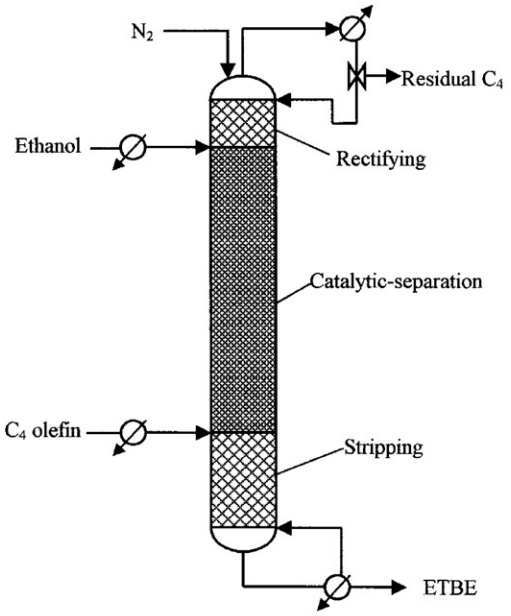


Figure 1. Experimental set-up for the catalytic distillation.

## 3. Results and discussion

### 3.1. Characterization of the zeolite film catalytic packing

The acidic zeolite film packing was characterized by several techniques such as XRD (X-ray diffraction), SEM (scanning electron microscopy), and pyridine-IR (infrared spectrum of pyridine adsorbed on the zeolite film).

Figure 2 shows the X-ray diffraction pattern of crystals of the zeolite film. The peaks at $2\theta = 7.4°$ and

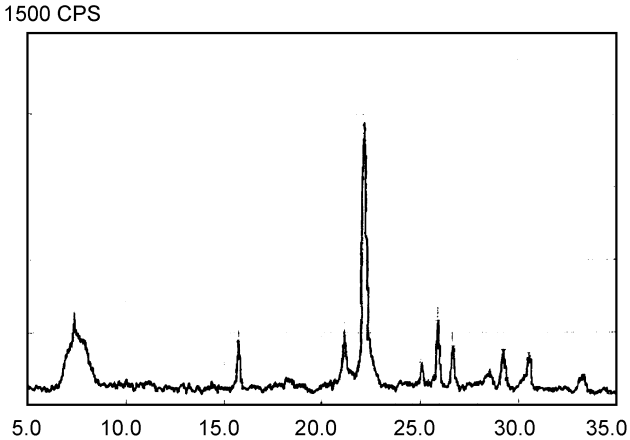


Figure 2. X-ray diffraction pattern of crystals of the zeolite film.

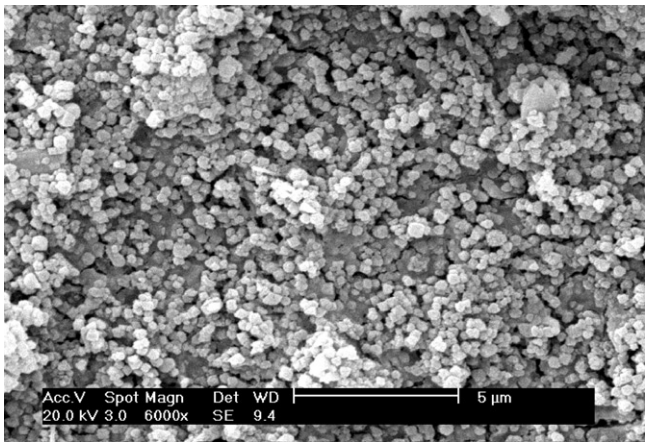


Figure 3. SEM image of the external surface of the zeolite film packing.

$2\theta = 22.2^\circ$ represent zeolite BEA film. The relative crystallinity remained at about 99% evaluated from the ratio of intensity of the most intense reflection peak at $2\theta = 22.2^\circ$ of the zeolite film to that of zeolite particles in the final solution.

Figure 3 shows an SEM image of the external surface of the zeolite film packing. The sizes of crystals are about 500 nm. The film is essentially continuous and free of cracks with a thickness of about 3 $\mu$m.

Figure 4 shows the IR spectra of pyridine adsorbed on the zeolite film at 200 and at 350 °C compared to that of non-adsorbate on the zeolite film. Brønsted acidic center is expressed with the band at about 1540 $cm^{-1}$ and Lewis acidic center is expressed with the band at about 1450 $cm^{-1}$. The spectrum at 350 °C shows a distribution of stronger acidic centers and that at 200 °C shows a distribution of the total acidic centers. IR spectra show

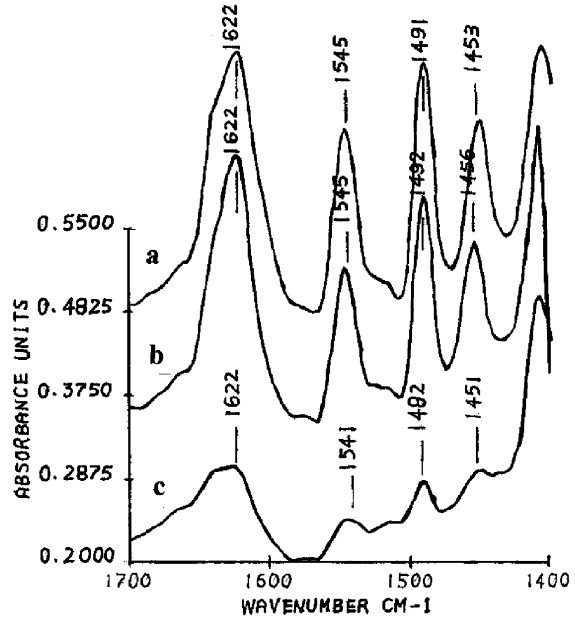


Figure 4. IR spectra of pyridine adsorbed on the zeolite film: (a) at 200 °C, (b) at 350 °C, (c) non-adsorbate on zeolite film.

that there are many Brønsted acidic centers and Lewis acidic centers over the zeolite film and that most of them are stronger ones.

### 3.2. Catalytic distillation testing of the zeolite film packing for synthesis of ETBE

Synthesis of ETBE from ethanol and isobutene is an exothermic reaction and the temperature greatly influences the reaction rate. In the reaction–separation section, the exotherm causes some of the liquid to be vaporized so that the compositions of the liquid phase and the vapor phase in this section are influenced by both the reaction and the amount of exotherm. In addition, the effect of pressure on the boiling point temperature of the liquid in the column can result in a variation in the temperature of the reaction–separation section. Consequently, the operating pressure influences the reaction rate. According to previous work [4], the temperature for synthesis of ETBE over the zeolite BEA catalyst should be 85 °C, which can be obtained in the reaction–separation section of the column at an operating pressure ($P$) of about 500 kPa. Therefore, the investigations of the catalytic distillation were conducted at 500 kPa.

It is necessary to optimize the period when reactants flow through the reaction–separation section in order to ensure sufficient contact between liquid reactants and the catalytic film. There are three factors that can influence it: reflux ratio, reboil rate and space velocity. In this work, the effects of reflux ratio and reboil rate on the conversion of isobutene were investigated at a fixed space velocity of 1/h. Also, the influence of the feed ratio of ethanol/isobutene on conversion of isobutene was considered. The experiments were conducted by varying one of the operating conditions while the others were fixed.

Ranges of feed molar ratio of ethanol/isobutene ($F$) corresponding to different conversions of isobutene ($X$) were investigated and are shown in figure 5. As can be seen, higher conversions of isobutene were obtained at a feed molar ratio between 1 and 2 where the conversion increases with increasing feed ratio. It is noticeable that conversion of isobutene increases considerably with

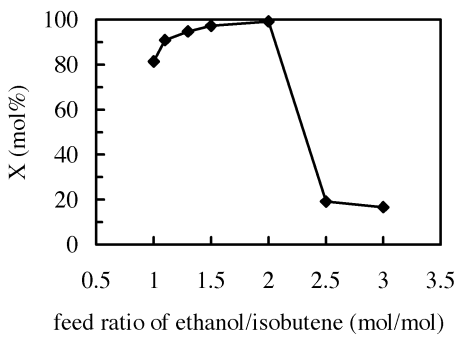


Figure 5. Conversion of isobutene as a function of feed molar ratio of ethanol/isobutene; $P = 500$ kPa, $R = 7$, $B = 0.11\ m^3/h$.

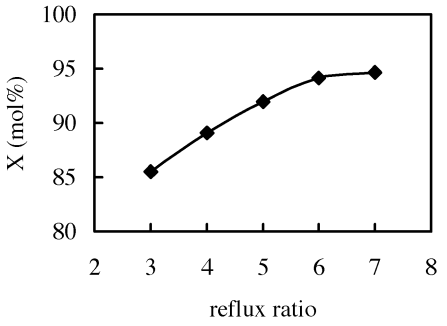


Figure 6. Conversion of isobutene as a function of reflux ratio; $P = 500$ kPa, $F = 1.3$, $B = 0.11\ m^3/h$.

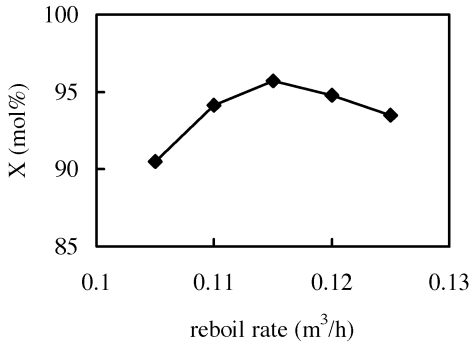


Figure 7. Conversion of isobutene as a function of reboil rate; $P = 500$ kPa, $F = 1.3$, $R = 6$.

feed molar ratio of 1 to 1.1. On the other hand, lower conversions of isobutene were obtained for the range where the conversion decreases with increasing the feed molar ratio from 2.5 to 3. This result indicates that increasing the feed ratio, in catalytic distillation, does not always increase the conversion of isobutene, which is different from the situation in a reactor.

There is a distillation boundary in the system of ethanol/$C_4$-cut/ETBE because of the non-ideal mixture behavior. In non-reaction distillation, the compositions of distillate and liquid in the reboiler are limited within some regions [17]. According to the results of this experiment, there is an upper limited value in the feed ratio of ethanol/isobutene for ETBE synthesis in a catalytic distillation process. As long as the value of feed molar ratio is less than 2, an ordinary distillation boundary can be removed by conducting the reaction and separation simultaneously and a higher conversion of isobutene can be obtained.

In addition, the composition of the liquid in the reboiler should be taken into account. Since most extra ethanol may run down into the reboiler, there is a demand for the feed ratio of ethanol/isobutene to be as low as possible. Therefore, the optimal value of the feed molar ratio, considering both conversion of isobutene and purity of the product in the reboiler, should be 1.1.

The effect of reflux ratio ($R$) on conversion of isobutene is shown in figure 6. As an increase of reflux ratio can both prolong the time for the contact between reactants and the catalysts and improve the separation of the product from the reactants, there is always an increase in conversion of isobutene with increasing reflux ratio. Figure 6 also shows that the conversion does not vary much by changing the reflux ratio from 6 to 7. To achieve minimum consumption of energy, the optimal reflux ratio should be 6.

Finally, the variation of conversion of isobutene with respect to reboiler heat duty is shown in figure 7. The conversions are more than 90% for a range of reboil rate ($B$) from 0.105 to 0.125 $m^3/h$. The maximum conversion of isobutene appears at a reboil rate of 0.115 $m^3/h$. Further increase of reboil rate can cause some of the product in the reboiler to be vaporized and to run up into the reaction zone, which is disadvantageous to conversion of isobutene. Therefore, the optimal value of reboil rate is 0.115 $m^3/h$.

In order to evaluate the capacity of the acidic zeolite film packing in a catalytic distillation column, comparative experiments were carried out. The pockets of ion-exchange resin catalyst used in industrial distillation towers were chosen for comparative experiments. The results are shown in figure 8.

As can be seen in figure 8, higher conversions of isobutene can be obtained by using the zeolite film packing than by using the resin pockets, which is mainly attributed to the active sites spread all over the surfaces of the zeolite film packing, where the separation of the products from the reactants can take place. In this case, the products can be removed out of the reaction centers as soon as they are formed so that there are few products in the centers and so a positive reaction is accelerated. On the other hand, the exotherm of the reaction is consumed by evaporation of the liquid immediately, as reaction and separation can take place at the same sites. In contrast, it is unable to disperse the active centers of the resin over the surfaces of the pockets or the places where the liquid contacts with the vapor. Therefore, reaction and separation of products are in different places. Conversion of isobutene will be restrained as the products and exotherm in the middle of the pockets are hardly removed out of the active sites.

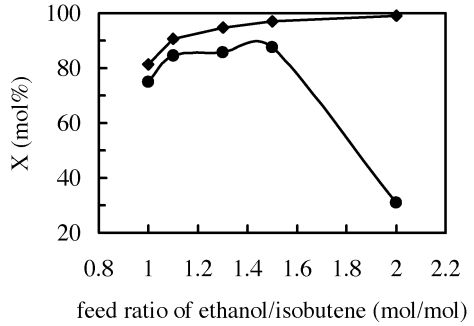


Figure 8. Comparison of zeolite film packing (◆) to resin catalyst (●); $P = 500$ kPa, $R = 7$, $B = 0.11\ m^3/h$.

Furthermore, there are more theoretical trays per meter of the zeolite film packing than of the resin pockets, which can provide more efficient separation of the products and the reactants in the reaction–separation section of the column.

The upper limit of the feed ratio of ethanol/isobutene for a higher conversion of isobutene was also observed in the catalytic distillation using the resin as a catalyst. The limiting value of that using the resin is lower than that using the zeolite film packing.

## 4. Conclusions

A zeolite film catalytic packing was prepared by secondary growth, using a cheaper template, on a structured ceramic support and modified by ion exchange and steaming. The zeolite film composed of BEA crystals, of a size of about 500 nm, covers the surfaces of the support compactly, as characterized using XRD and SEM. IR spectra show that there are many stronger Brønsted acidic centers and stronger Lewis acidic centers on the zeolite film.

The zeolite film packing was evaluated in the synthesis of ETBE from ethanol and $C_4$-cut olefin in a continuous catalytic distillation column. It has better characteristics in both catalysis and the separation of products from reactants that is comparable to that of resin catalysts used in industrial distillation towers. The optimal conditions, at a pressure of 500 kPa, were found to be an ethanol/isobutene feed molar ratio of 1.1, a reflux ratio of 6 and a reboil rate of 0.115 $m^3$/h.

There is an upper limit value of 2 for the feed molar ratio of ethanol/isobutene for ETBE synthesis in the catalytic distillation column using the zeolite film packing. As long as the values of the feed molar ratio are less than this, an ordinary distillation boundary can be removed by conducting the reaction and separation simultaneously and a higher conversion of isobutene can be obtained.

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