Preparation of Isoamyl Acetate by High Performance ZSM-5 Zeolite Membrane

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A high performance ZSM-5 zeolite membrane is applied to remove H\textsubscript{2}O from the esterification of acetic acid and isopentanol by pervaporation. The influences of reaction conditions on the isoamyl acetate yield are studied in detail. Compared with the traditional esterification of acetic acid and isopentanol, the esterification with “membrane extractor” has a high isoamyl acetate yield at low reaction temperature. The reaction temperature, acetic acid/isopentanol molar ratio and effective membrane surface area to esterification mixture ratio volume of 100°C, 3.0/1.0, 2.0 wt% NaHSO\textsubscript{4}, and 0.26 cm\textsuperscript{2}/cm\textsuperscript{3}, respectively, the isoamyl acetate yields were 98.39%, the membrane flux and separation factor (H\textsubscript{2}O to organic) were 0.21 kg·m\textsuperscript{–2}·h\textsuperscript{–1} and 1040, respectively. Further, the ZSM-5 zeolite membrane shows good long-term stability and reproducibility for the pervaporation-esterification, the isoamyl acetate yields of the esterification-pervaporation for intermittent 8 times or continuous 160 h still remained at 97.73% and 98.30%, respectively. In addition, the ZSM-5 zeolite membrane still retained the typical MFI diffraction peaks and morphology by XRD and SEM characterization after long-term PV–esterification.

Introduction

Isoamyl acetate is one of the most significant esters, which has been extensively applied in the field of food industries, medicine, printing and dyeing (Eisenmenger and Reyes-De-Corcuera, 2010). Esters are produced by esterification with concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) as catalyst in general, which could lead to many problems, such as corrosion of the reactors and pipes, as well as difficulty in product separation and catalyst recovery (Osorio-Viana et al., 2014; Romero et al., 2015; Santos et al., 2017). Besides, esterification is a traditional reversible and equilibrium-limited reaction, which could be improved by continuous in-situ removal of one or more products.

The pervaporation membrane reactor (PVMR) has many superior functions, such as simple equipment, conversion-improving and energy-savings, which has attracted constant and widespread attention over the recent years (Romero et al., 2015). Esterification integrated with PVMR could shift the chemical equilibrium and improve the conversion of reversible esterification by removing product H\textsubscript{2}O (Romero et al., 2007). Tanaka et al. (2001) successfully prepared ethyl acetate and ethyl lactate with T zeolite membrane intermit-
a novel catalyst for esterification and has several advantages, such as attractive price, convenient operation and high yield in esterification (Ning et al., 2009).

In this study, acid-resistant ZSM-5 zeolite membranes were applied to on-line dehydration of the esterification of acetic acid and isopentanol by PV, and the membrane was immersed into the reaction mixture with NaHSO4 catalyst. In order to optimize the reaction conditions and reduce the energy consumption of pervaporation–esterification (PV–esterification), the effects of reaction conditions (temperature, acetic acid/isopentanol molar ratio and catalyst type) on isoamyl acetate yield of esterification are discussed in detail. Further, the long-term stability and reproducibility of ZSM-5 zeolite membrane for the PV–esterification are discussed.

1. Experimental

The hydrophilic and acid-stable ZSM-5 membranes were prepared on mullite supports (Noritake, outer diameter = 12 mm, inner diameter = 9, pore size = 1.3 mm, length = 100 mm). The synthesis gels have a molar composition of \( \text{SiO}_2 : 0.067\text{Al}_2\text{O}_3 : 0.2\text{Na}_2\text{O} : 0.1\text{NaF} : 50\text{H}_2\text{O} \) and were prepared as in our previous study (Zhu et al., 2016a). NaOH (sodium hydroxide, 96 wt%, Yongda Tianjin) and Al\(_2\)(SO\(_4\))\(_3\)·18H\(_2\)O (aluminum sulfate, 99 wt%, Sinopharm) were dissolved in deionized water, then an amount of NaF (sodium fluoride, 99 wt%, Aladdin) was added to the white gel. Thereafter, colloidal silica (Ludox HS-40, Sigma-Aldrich) was subsequently added to form a white gel under continuous stirring, and the resulting mixture was stirred at room temperature for 2 h. Then, the precursor synthesis gel was transferred into a stainless steel autoclave, where the three pieces of the seeded support were immersed in the synthesis gel vertically. The autoclave was placed into an air oven for 24 h, which had been heated to 185°C beforehand. Finally, the samples were rinsed thoroughly in boiling water after crystallization and dried in an 80°C oven for several hours.

The PV–esterification apparatus was identical with our previous work (Zhu et al., 2016b). A certain amount of acetic acid, isopentanol and catalyst were added to a 150-mL three-necked flask equipped with a condensing tube, and the flask was heated to a certain temperature (80–110°C) by an oil bath. Except for discussing the effect of the catalyst, the catalyst for other reactions was NaHSO4, and the catalyst loadings were 2.0 wt%. Simultaneously, the ZSM-5 zeolite membrane was immersed into the reaction mixtures and separated H\(_2\)O from the mixtures by PV, and the time was noted for the start time of the experiment. It is worth noting that the conventional esterification and the PV–esterification experiment had to start at the same time. The permeates were collected in a cold trap that used liquid nitrogen. Both the reaction mixtures and permeates were analyzed by gas chromatograph (GC-2014C, SHIMADZU, Threshold detection level < 0.01 wt%) every hour.

For the present work, the effects of reaction conditions on the isoamyl acetate yield of PV–esterification are summarized in Table 1. The isoamyl acetate yield (Y) was calculated by the molar content of isopentanol according to the following equation.

\[
Y \text{[%]} = \frac{n_{\text{isoamyl acetate}}}{n_{\text{isopentanol}}} \times 100\%
\]

Herein, \( n_{\text{isopentanol}} \) was the initial molar content of isopentanol in the reaction mixture, and \( n_{\text{isoamyl acetate}} \) was the molar content of isoamyl acetate in the reaction mixture at a certain time. Further, the PV performance of ZSM-5 zeolite membranes were evaluated by the total flux (\( J \)) and separation factor (\( \alpha_{\text{w/o}} \)) of water over organics. The effective surface area of the membrane (A), \( J \) and \( \alpha_{\text{w/o}} \) of the membranes were determined as follows.

\[
A = \pi dl
\]

\[
f = \frac{m}{(At)}
\]

\[
\alpha_{\text{w/o}} = \frac{Y_w}{Y_o} / \left( \frac{X_w}{X_o} \right)
\]

Herein, \( d \), \( l \), \( t \), \( m \), \( X_w \), \( X_o \), \( Y_w \), and \( Y_o \) denote the outside diameter of the support, the length of the membrane immersed

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<th>Table 1 Effects of reaction conditions on isoamyl acetate yield of PV–esterification</th>
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* \( \text{H}_3\text{O}_4\text{PW}_{12}\cdot\text{xH}_2\text{O} \).
into the feed mixture, the test time, the mass of permeate condensed in the cooled trap over a known test time, and the mass fractions of the water and organic components at the feed and permeate sides, respectively.

2. Results and Discussion

2.1 Esterification with or without PV

Figure 1 shows isoamyl acetate yield of esterification (isopentanol and acetic acid) coupled with and without ZSM-5 zeolite membrane by PV \( (T = 100°C, R = 3.0/1.0, 2.0 \text{ wt% NaHSO}_4) \). As shown in Figure 1, the esterification without PV reached chemical equilibrium after 4h, and the isoamyl acetate yield was 85.81%. Because the ZSM-5 zeolite membrane could continuously remove \( \text{H}_2\text{O} \) from the reaction mixtures on-line, it could break up the chemical equilibrium of the esterification. The isoamyl acetate yield was improved and achieved 98.39% after 10h with ZSM-5 zeolite membrane by PV. As a consequence, the ZSM-5 zeolite membrane was a favorable extractor for dehydrating esterification on-line with the NaHSO\(_4\) as catalyst in this study. Further, the reaction conditions had a significant influence on the product yields of esterification and pervaporation performance of the ZSM-5 zeolite membrane, and the influences of reaction conditions on the PV–esterification were investigated as follows.

2.2 Effect of catalyst

Usually, the catalyst of esterification (acetic acid and isopentanol) was concentrated \( \text{H}_2\text{SO}_4 \) in industry, and the expensive alloy materials had to strengthen the acid-stability of the esterification apparatus, which would increase the production costs of ester greatly. Over the past few years, sulfamic acid, heteropoly acid and rare-earth solid superacid were desired as replacements for concentrated \( \text{H}_2\text{SO}_4 \) as the catalysts in esterification, but most of them have tedious preparation procedures, low esterification yields and complicated post-processing (Kiss and Keglevich, 2016; Tejero et al., 2016; Yu et al., 2016). \( \text{NaHSO}_4 \) is a novel and green catalyst for esterification, for example, esterification of the chloroacetic acid and isooamyl alcohol with \( \text{NaHSO}_4 \) the yield of isoamyl chloroacetate was up to 98.45% (Li et al., 2009). As shown in Figure 2 and Table 1, NaHSO\(_4\) was selected as the catalyst in preparation of isoamyl acetate by high performance ZSM-5 zeolite membrane in this study, and the final isoamyl acetate yield was 98.39% in PV–esterification. Further, concentrated \( \text{H}_2\text{SO}_4 \), PHA, NaHSO\(_4\)-\( \text{H}_2\text{O} \), NaHSO\(_4\) (catalyst loading, 2.0 wt%) were used as catalyst for the PV–esterification in this work, and the isoamyl acetate yields were 98.29%, 98.37%, and 97.47%, respectively. Hence, NaHSO\(_4\) had good, comparable catalytic performance for the PV–esterification in this study, and the as-synthesized ZSM-5 zeolite membrane had good hydrophilicity and acid-resistance with different acidic catalyst.

2.3 Effect of initial molar ratio of acetic acid and isopentanol

As a typical reversible reaction, the esterification equilibrium of acetic acid and isopentanol could be shifted by excessive reactant, and an excess of isopentanol was used to improve the yield of isoamyl acetate in the past (Eisemenger and Reyes-De-Corcuera, 2010; Osorio-Viana et al., 2014; Santos et al., 2017). In fact, the price of isopentanol is currently about four times that of acetic acid. (Acetic acid: 310USD/t, http://cn.made-in-china.com/gongying/yingqing01-MqHxTsWCnNYU.html, 2017/7/17, Isoamyl alcohol: 1255 USD/t, http://cn.made-in-china.com/gongying/yingqing01-QqlmOEBVnypZ.html, 2017/7/17). Further, the ZSM-5 zeolite membrane could allow for selectively permeation of water from high acetic acid concentrated aqueous mixture by pervaporation in our previous studies (Zhu et al., 2016b). In order to raise the production efficiency and economize the production cost, the excess of acetic acid could be supposed to enhance the isoamyl acetate yield of the esterification in this work. As presented in Figure 3, the effect of the initial molar ratio of acetic acid and isopentanol \( (R) \) on isoamyl acetate yields of PV–esterification were investigated in this study. When the values of \( R \) were 1.0/1.2, 1.2/1.0, 2.0/1.0, 3.0/1.0, the isoamyl acetate yields of
PV–esterification were 82.93%, 88.15%, 90.32%, and 95.75%, respectively. Apparently, an excessive amount of acetic acid in reaction mixtures improved the equilibrium conversion of PV–esterification.

2.4 Effect of temperature
The traditional reaction temperature of acetic acid and isopentanol was 110–140°C, which required much energy in the chemical process (Schildhauer et al., 2005). Meanwhile, the acidic reaction mixtures were extremely corrosive to the apparatus at high temperature, and expensive alloy materials were needed for the apparatus. In addition, temperature was a considerable factor on PV performance of zeolite membrane and the reactant conversion of esterification. In order to make a balance between energy-saving and dehydration performance of ZSM-5 zeolite membrane, the effects of temperature on the PV–esterification were carried out at 80°C, 90°C, 100°C, and 110°C in this study, respectively. Figure 4 shows the isooamy acetate yield of PV–esterification at different temperature. Both the chemical reaction rate and the dehydration performance of ZSM-5 zeolite membrane were improved with rising reaction temperature, and the isooamy acetate yields of the PV–esterification were 79.16%, 90.32%, and 94.23% at 80°C, 90°C, and 100°C, respectively. While the thermodynamic properties of esterification (Zhang et al., 2006), the isooamy acetate yield was slightly lower at 110°C than that values at 100°C in this work.

Due to the esterification is an endothermic reaction, the high temperature is favorable. Moreover, the reaction equilibrium constant is increased along with the temperature, and the water flux of ZSM-5 membrane is gradually increased with the temperature. The ZSM-5 zeolite membrane could continuously remove H2O from the reaction mixtures on-line, which could break up the chemical equilibrium of the esterification and enhance the isooamy acetate yield.

2.5 Stability of ZSM-5 zeolite membrane for PV–esterification
The stability of the zeolite membrane reactor is essential in industrial application. The ZSM-5 zeolite membrane had good dehydration performance for the PV–esterification of isooamy acetate with NaHSO4 and it is necessary to investigate the stability of the ZSM-5 zeolite membrane for PV–esterification in this study. Figure 5 shows the effect of ZSM-5 zeolite membrane usage times on isooamy acetate yield of PV–esterification (R = 3.0/1.0, NaHSO4, T = 100°C).
in Figure 6, the isoamyl acetate yield still remained 98.30% after 160 h by continuously removing water from the reaction mixtures. These results obviously prove that the ZSM-5 zeolite membrane has good stability and dehydration performance for PV–esterification with NaHSO₄.

Further, the XRD patterns and surface SEM images of the ZSM-5 zeolite membranes before and after 8 times PV–esterification at the optimum reaction condition (the value of R, T and t are 3.0/1.0, 100°C, 10 h) are shown in Figures 7 and 8. It could be clearly seen that the membrane still kept the typical and high intensity MFI diffraction peaks, and the aggregated ZSM-5 layer was fully covered on the support surface after 8 times PV–esterification.

**Conclusion**

The hydrophilic and acid-resistant ZSM-5 zeolite membrane showed good dehydration performance for the esterification of acetic acid and isoamyl alcohol by PV, and the isoamyl acetate yield was greatly enhanced by continuously removing water on-line. When the reaction temperature, acetic acid/isoamyl alcohol molar ratio, the catalyst type and loading, and the ratio of effective membrane surface area to esterification mixture volume were 100°C, 3.0/1.0, 2.0 wt%NaHSO₄ and 0.26 cm²/cm³, the isoamyl acetate yield was up to 98.39%. Further, the ZSM-5 zeolite membrane showed good long-term stability and reproducibility for the PV–esterification, the isoamyl alcohol conversions for 8 times PV–esterification and a 160 h long-term test still remained 97.73% and 98.30%, respectively.

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**Nomenclature**

\[ A = \text{the effective surface area of the membrane [m}^2\text{]} \]
\[ J = \text{the total flux of the total flux [kg·m}^{-1}·\text{h}^{-1}\text{]} \]
\[ \beta_{\text{isopentanol}} = \text{the initial molar of isopentanol in the reaction mixture [mol]} \]
\[ \beta_{\text{isoamyl acetate}} = \text{the molar of isoamyl acetate in the reaction mixture [mol]} \]
\[ PV = \text{pervaporation [---]} \]
\[ PVMR = \text{pervaporation membrane reactor [---]} \]
\[ R = \text{the initial molar ratio of acetic acid and isopentanol [---]} \]
\[ T = \text{the temperature of PV–esterification [°C]} \]
\[ Y = \text{the yield of isoamyl acetate [---]} \]
\[ \alpha_{\text{w/o}} = \text{separation factor of water over organics [---]} \]

**Literature Cited**


