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Application of a mordenite membrane to the esterification of acetic acid and alcohol using sulfuric acid catalyst[☆]

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ABSTRACT

The well acid-stable and hydrophilic mordenite membrane is applied as a “membrane extractor reactor” for the esterification of acetic acid and alcohol with the H_2SO_4 as catalyst. The mordenite membrane reactors are placed into the reaction mixtures and continuously remove water from the esterification mixture by pervaporation, which could greatly improve the alcohol conversions of esterification. Besides, the effects of the reaction conditions (such as temperature, molar ratio of acetic acid/alcohol, and catalyst loading) on the ethanol conversion are investigated in details. As the reactional temperature, the molar ratio of acetic acid/alcohol, the catalyst loading, and the ratio of effective membrane surface area to esterification mixture volume are 85 °C, 1.5, 0.05 wt% (0.005 mol/L), and 0.31 cm^2/cm^3, the ethanol and *n*-butanol conversions of esterifications are up to 98.13% and 98.73%, respectively. Even if the mordenite membrane is applied to pervaporation-esterification for 8 times (96 h), the mordenite membranes are still kept the typical diffraction peaks and morphology by XRD and SEM characterization, and the dehydration performance of the membrane for 90 wt% HAc/H_2O mixture at 75 °C is almost the same as the as-synthesized mordenite membranes, and the flux and separation factor of the mordenite membrane after 8 times PV-esterification are 0.44 kg m^{-2} h^{-1} and 627.

1. Introduction

Esterification of acetic acid and alcohol is a classic reaction controlled by the thermodynamic equilibrium, and the excess of one reactant or removing by-product water can be used to overcome the equilibrium [1]. Generally, the by-product water can be continuously removed by distillation or co-distillation with the entrainers, which are energy consumption and harmful for environment [2,3]. As compared to the traditional distillation, the membrane reactor is more compact, less capital intensive, giving higher conversion and selectivity separation process for the thermodynamically and kinetically controlled esterification [4,5]. Therefore, the combination of the esterification of alcohol and carboxylic acid with inorganic and polymeric membranes membrane separation by pervaporation or vapor permeation arrangements have been drawn much attention in last decades [6–19]. For example, Rathod et al. used for pervaporation-assisted esterification of lactic acid and iso-propanol by polyvinyl alcohol-polyether sulfone (PVA-PES) composite hydrophilic membrane, and the conversion of lactic acid was increased from its equilibrium value of 51%–86% [15].

Owing to the high permeability, chemical stability and thermodynamic stability, the zeolite membranes are often used for membrane-assisted esterification and leaded to a high ester yield. Tanaka et al. coupled the zeolite T membranes with esterification of acetic acid and ethanol using Amberlyst-15 as catalyst, the

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conversion of acetic acid was almost 100% after 8 h by continuously removing water from the esterification [11]. The mordenite and LTA type membranes have been tested in the esterification of acetic acid with ethanol in a continuous membrane reactor packed with catalyst Amberlyst TM-15 [12]. Both the membranes are capable of shifting the equilibrium in less than 1 day of experiment. The mordenite membranes showed a great resistance to acidic reaction medium, and the acetic acid conversions were about 90% even after 5 days experiment. Khajavi et al. reported on the esterification in the sodalite membrane reactor of acetic acid with ethanol/n-butanol to produce ethyl acetate/butyl acetate using Amberlyst-15 as catalyst [14]. The conversions of acetic acid to ethyl acetate and butyl acetate were enhanced from 67% to 62%–98% and 92%, respectively. Hasegawa et al. applied the CHA membrane to the esterification of adipic acid with isopropyl alcohol using sulfuric acid as the catalyst, and the membrane was placed in the vapor phase to avoid direct contact with sulfuric acid [15]. The yield of diisopropyladipate is increased from 56% to 98% by membrane assistance.

Generally, the catalyst of esterification is the concentrated H_2SO_4 in industry, it is important that the membrane reactor could keep its structural integrity during the reaction. As far as we know, there are hardly any references about that the zeolite membrane reactor could be placed into the esterification mixtures with the concentrated H_2SO_4 as catalyst and remove water from the mixture on-line by pervaporation (PV) or vapor permeation (VP). In our pervious study, the mordenite membranes had well dehydration performance and acid-stability for long-term dehydrating high acetic acid content aqueous mixtures and quaternary esterification products [20]. Therefore, the acid-stable mordenite membrane is applied to separation water from the esterification of alcohol and acetic acid on-line by PV in this study, and the membrane reactor is placed into the reaction mixture containing H_2SO_4. Moreover, the effects of reaction conditions (temperature, molar ratio of acetic acid and ethanol, catalyst loading) on alcohol conversions of the esterification are discussed in details, and the stability of the mordenite membrane for the PV-esterification are characterized by PV, SEM, EDX and XRD results.

2. Experimental

2.1. Preparation and characterization of mordenite membrane

The hydrophilic and acid-stable mordenite membranes are prepared on the mullite supports (Noritake, outer diameter = 12 mm, inner diameter = 9, pore size = 1.3 μm, length = 100 mm) [21,22]. The synthesis gels have a molar composition of $SiO_2:0.08Al_2O_3:0.2Na_2O:0.1NaF:35H_2O$ and are prepared as our previous study [20]. NaOH (sodium hydroxide, 97 wt%, Wako) and $NaAlO_2$ (sodium aluminate, Al/NaOH = 0.79, Wako) are dissolved in deionized water, and colloidal silica (AS-40, 40 wt%, Aldrich) is subsequently added and formed a white gel under continuously stirring. Thereafter, an amount of NaF (sodium fluoride, 99 wt%, Wako) is added to the white gel, and the resulting mixture is stirred at room temperature for 6 h. Then, the precursor synthesis gel is transferred into a stainless steel autoclave, where the two pieces of the seeded support are immersed in the synthesis gel vertically. The autoclave is placed into an air oven for 6 h, which are heated to 170 °C beforehand. Finally, the samples are rinsed thoroughly in boiling water after crystallization and dried in an 80 °C oven for several hours.

The structures of the mordenite membranes are characterized by X-ray diffraction (XRD, Rigaku, Smartlab, Cu-$K\alpha$ radiation), and the XRD patterns are obtained in the range of $2\theta = 5$–$45°$ at a scanning rate of $4° \min^{-1}$. The morphologies and element composition of the mordenite membranes are characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi Su 8020) and Energy Dispersive X-ray (EDX, Hitachi Su 8020).

2.2. PV-esterification

The apparatus of PV-esterification is showed in Fig. 1. Amounts of alcohol, acetic acid and 18.4 mol/L H_2SO_4 are added to the 200 ml 3-neck flask fitted with a reflux condenser, and the flask is heated to a certain temperature (80–95 °C) by oil bath. Simultaneously, the mordenite membrane is placed into the reaction mixture and separated water from the mixtures by vacuum pump, and the time is noted the starting time of the experiment. It is noted that the time of conventional esterification is started parallel to the starting time of the PV-esterification experiment. The permeates are collected in the cold trap by liquid nitrogen. Both the reaction mixtures and permeates are by the gas chromatograph (GC-2014C, SHIMADZU, Threshold detection level < 0.01 wt%) per hour. It is noted that the H_2O content in the permeations are above 99 wt% without explanation. The pH values of the different concentration acetic acid aqueous mixtures are measured using a pH meter (Aohaosi Instruments Co., Ltd., STARTER 3C).

In this work, the initial molar ratio of acetic acid/alcohol (R), catalyst loading (C), and the ratio of effective membrane surface area to initial esterification mixture volume (S/V) are 1/1.5–2, 0–0.5wt%, and 0–0.5 cm^2/cm^3, respectively. The effects of reaction conditions on the reactant conversion of PV-esterification are summarized in Table 1. The conversion of the alcohol can be calculated by the molar content of ethanol according to following equations:

$$C_{EtOH}[\%] = M_{ethyl\ acetate} \Big/ \left(M_{ethanol} + M_{ethyl\ acetate}\right) \times 100\%$$

where $M_{ethyl\ acetate}$ and $M_{ethanol}$ are the molar contents of ethyl acetate and ethanol of the reaction mixtures. Besides, the PV performances of the mordenite membranes are evaluated by the total flux (J) and separation factor ($\alpha_{w/o}$) of water over organics. The effective surface area of the membrane (A), J and $\alpha_{w/o}$ of the membranes are determined as:

$$A = \pi dl$$

$$J = m/(A \cdot t)$$

$$\alpha_{w/o} = (Y_w/Y_o)/(X_w/X_o)$$

where d, l, t, m, Xw, Xo, Yw, and Yo denote the outside diameter of the support, the length of the membrane immersed in 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.

3. Result and discussion

3.1. Comparison of esterification with or without mordenite membrane by PV

Fig. 2a displays the ethanol conversions of the esterification of ethanol and acetic acid coupled with or without the mordenite membrane by PV. As the values of R, C, T, and S/V are 1.5/1, 0.05 wt%, 85 °C, and 0.31 cm^2/cm^3, the EtOH conversion is gradually increased with the PV-esterification process, and the value is improved to 98.13% after 10 h. While the traditional esterification is