Continuous zeolite membrane reactor for esterification of ethanol and acetic acid

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Abstract

Inert membrane reactors have been a subject of interest during the last decade, the two main applications consist of distributing a reactant to increase selectivity and remove a product to enhance conversion in equilibrium-limited reactions. This paper is related to the second option. Inorganic zeolite membranes have been selected due to its ability to withstand harsh conditions, and its high separation performance of water over alcohols in pervaporation. Two different zeolite membranes, mordenite and zeolite A have been tested in the esterification of acetic acid with ethanol in a continuous membrane reactor packed with catalyst Amberlyst[TM] 15. Both membranes are capable of shifting the equilibrium in less than 1 day of experiment. Mordenite membranes showed a great resistance to acidic reaction medium, with conversions of about 90% maintained for 5 days of experiment, with very high separation factors $H_2O/EtOH$ and H_2O/HAc.
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Keywords: Membrane reactor; Esterification; Zeolite membrane; Mordenite

1. Introduction

Esterification of carboxylic acids with alcohols is a typical example of an equilibrium-limited reaction. Traditionally, two main methods have been carried out for equilibrium displacement: (i) either using an excess of alcohol [1], the limiting step of the reaction results in the attack of the carboxylic group by the alcohol [2]; (ii) or trying to separate the formed water from the reaction medium by means of reactive distillation [3]. The use of a large amount of reactant causes an increase of operation costs because it is necessary to separate the excess of alcohol, while reactive distillation is only effective when the difference between volatilities of reactants and products is high enough.

In esterification reactions the function of the catalyst is to donate protons for the autoprotolysis of the carboxylic acid. For this purpose, either inorganic acids, such as H_2SO_4, HCl, HI or $ClSO_3OH$ [4] or organic acids as *p*-toluenesulphonic acid [5,6] have been used. In spite of their lower cost, the interest for homogeneous catalysts in the chemical industry has decreased because of their miscibility with reaction medium, which gives rise to problems such as their separation or the corrosion of

devices in contact with the acid. As a result there is an increasing attention for heterogeneous catalysts, such as ionic exchange resins [5,7–9], or zeolites [10–15]. Among zeolites, H-ZSM-5, zeolite β and zeolite Y are the most employed for esterification reactions. Their performance depends on their acidity and pore size structure for the accessibility of the reactants. In a recent study [15], which compares the catalytic activity, per gram of catalyst, for the esterification of acetic acid with butanol, the ion-exchange resins showed the highest activity, followed by sulphated zirconia and finally zeolites; among them the zeolite H-USY (with a Si/Al = 20) was the most active.

Membrane reactors operating in pervaporation conditions are an attractive alternative for equilibrium-limited esterifications because of the following features: (1) separation efficiency is not limited by relative volatility as in distillation; (2) in pervaporation conditions only permeate experiments a phase change so that the energy consumption is lower than for distillation; (3) with a suitable membrane, pervaporation could be carried out at reaction temperature.

In the literature, the most frequent configuration to carry out esterification reactions coupled with pervaporation consist of a batch reactor, where the reaction takes place, with a homogeneous or heterogeneous catalyst, followed by a polymeric membrane for pervaporation, and refluxing the retentate to the reactor. This configuration has been used for the esterification of

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acetic acid with methanol [16,17] or borneol [18], oleic acid with different alcohols [19,20], or propanoic acid with propanol [21]. Some authors have accomplished modifications to this configuration, such as placing the membrane inside the batch reactor [22–24], or using an adsorbent material in the permeate side in order to enhance the separation of water [25]. There are only a few works carrying out esterification in a continuous reactor. Waldburger et al. [26] studied the esterification of acetic acid with ethanol using a heterogeneous catalyst, and proposed a set of PVA membrane reactors to operate in continuous. Zhu et al. [27] studied the production of ethyl acetate with a membrane reactor of a polymeric–ceramic composite membrane, using sulphuric acid as catalyst. While polymeric membranes may have the desired selectivity, they often lack the ability to withstand reaction conditions (in terms of temperature, concentrations, pH, etc.). This is why inorganic membranes are presented as an alternative, mainly of silica and zeolites.

Zeolite membranes have pores in the range of molecular sizes, which implies that they are capable of very specific interactions (e.g., selective adsorption, molecular sieving) with the target molecules, and their characteristics make them ideal candidates to integrate reaction and separation [28]. The number of references existing about zeolite membrane reactors in esterification reactions is limited, most of the works used a discontinuous configuration similar to that described for polymeric membranes. Gao et al. [29] and Tanaka et al. [30] studied the esterification of acetic acid with ethanol, catalyzed by an exchange resin, using a zeolite A-PVA composite membrane, and a zeolite T membrane, respectively. Jafar et al. [6] developed the esterification of lactic acid and ethanol, homogeneously catalyzed, using a zeolite A membrane for water separation, but working in vapour permeation conditions and not in pervaporation as in above-mentioned cases. The unique work in which an esterification reaction is carried out with a zeolitic membrane reactor operating in continuous is that of Bernal et al. [31], that treated the synthesis of ethyl acetate with a H-ZSM-5 membrane that actuated as catalyst and water separator simultaneously.

Recently, Peters et al. [32,33] prepared silica membranes coated with previously available zeolite crystals, with the aim of integrating the catalytic activity of the zeolite and the high performance of silica for water separation. Zeolite Y was selected as the most active based on previous studies [15]. The performance of the reactor is mainly limited by the reaction kinetics and, starting with an equilibrium mixture (68% conversion), they reach a 73% conversion after 7 h.

To conclude with this brief overview: (i) the coupled system reaction/pervaporation is an effective way to overcome the equilibrium limitations; (ii) a continuous system will be preferred from the industrial point of view; (iii) the ratio of water production over water removal is a key factor, being the selectivity of the membrane and activity of the catalyst the parameters for optimization. It is also important to preserve the stability of the membrane and the catalyst under reaction conditions. In this work we have studied the esterification reaction of acetic acid with ethanol to produce ethyl acetate, in a continuous system, with a zeolitic membrane reactor using mordenite [34,35] and zeolite A membranes [36], as high selective membranes for

water permeation, and Amberlyst^{TM} 15 ion-exchange resin as heterogeneous catalyst with high activity [29,30], packed inside the membrane tube.

2. Experimental

2.1. Synthesis and characterization of zeolite membranes

Mordenite and zeolite A membranes were prepared onto symmetric, tubular α-Al$_2$O$_3$ supports with 1900 nm of pore size (7 mm i.d., 10 mm o.d.). The ends of the supports were enamelled to give a total permeation length of 5 cm. The synthesis of zeolite membranes was carried out by means of secondary growth over the outer surface of the alumina support. The seeding technique employed was rubbing using Mordenite (0.1 μm $\times$ 0.5 μm, Tosoh Company, Japan) and zeolite A (1 μm, IQE, Spain) commercial crystals. Hydrothermal treatment for mordenite membranes was carried out at 453 K for 8 h using a gel with the following molar composition: 1SiO$_2$:0.38Na$_2$O:80H$_2$O:0.025Al$_2$O$_3$ [34]. In the case of zeolite A, the synthesis step was carried out in a semi-continuous system, recently developed in our laboratory [36], where fresh gel was periodically supplied to the synthesis vessel at 363 K for 5 h. The precursor gel molar composition for this synthesis was: 1.8SiO$_2$:3.9Na$_2$O:1Al$_2$O$_3$:273H$_2$O. After synthesis, mordenite membranes were post-treated with a NaOH solution of pH 10, at 180 °C for 8 h [37] to improve their PV performance.

The characterization techniques employed were N$_2$ permeation measurements and X-ray diffraction (XRD) analysis (Rigaku/Max diffractometer Cu Kα radiation and graphite monochromator).

2.2. Reaction experimental set-up

The membrane was sealed inside a stainless steel module which was placed in a thermostatic bath to maintain the membrane at a temperature of 358 K. The temperature was controlled by means of a thermocouple placed inside the membrane reactor. In the permeate side vacuum was maintained at 2 mbar.

The feed for esterification experiments consisted of an equimolar mixture of acetic acid and ethanol, with a feed flow of 5×10^{-3} mL/min, 1 g of Amberlyst^{TM} 15 was placed inside the zeolite membrane. The pressure in the retentate side was 1.3 bar. Conversion was calculated from the analysis of samples taken at the exit of both membrane sides with a GC (HP 5890 SERIES II) equipped with a capillary column Rt-QPLOT (Restek) and TCD and FID detectors.

In the pervaporation experiments, also carried out at 358 K, the feed was an ethanol/water mixture with a 90% of ethanol in weight, with a feed flow of 5 mL/min. The pressure in the retentate side was 2 bar. Feed and permeate samples were analyzed in the GC described above.

Batch reactor used for some reaction experiments consisted of a stirred flask working under reflux. 3.6 g of catalyst were placed inside the reactor with 100 mL of an equimolar acetic acid/ethanol mixture. The temperature was controlled at 358 K by means of a type K thermocouple. Conversions reached at

different reaction times were obtained from samples of 1–2 cm^3 taken from the flask and analyzed by gas chromatography.

3. Results and discussion

3.1. Synthesis and characterization of zeolite membranes

Table 1 summarizes the properties of the membranes synthesized in this work and the results of preliminary pervaporation experiments. The weight gain after the synthesis and post-treatment in a basic solution is similar in mordenite membranes. In the case of zeolite A, the weight gain is higher since no post-treatment was applied to this membrane. Nitrogen permeance is measured after conventional drying overnight of the membrane in a stove at 105 °C. This value should be considered as a preliminary test for the assessment of the quality of the membrane, in terms of cracks and defects. Nitrogen permeances above 10^{-6} mol/m^2 s Pa could be indicative of cracks and defects, which is not the case for the studied membranes. The standard test for the quality of the membranes is the evaluation of the pervaporation performance, all the membranes tested exhibited high selectivity towards water separation. The water flux is similar in the mordenite membranes, which implies the reproducibility of the preparation method, while the flux is higher in the case of zeolite A membranes. This difference could be attributed to the higher water adsorption capacity and affinity of zeolite A versus mordenite, since zeolite A is highly hydrophilic due to its low Si/Al ratio.

3.2. Batch experiments, catalytic activity

To know the catalytic activity of Amberlyst^{TM} 15 for the esterification reaction studied, an experiment in a batch reactor was carried out; the results are presented in Fig. 1. After 2 h of experiment a 66.7% conversion was reached, this is close to the theoretical equilibrium conversion at 358 K (72.4%, calculated with ASPEN PLUS®). The same experiment was accomplished without catalyst and with commercial H-MOR crystals (Tosoh Corporation, HSZ-640HOA) with a Si/Al ratio of 19. In this case after 1 day of experiment only a 27% conversion was reached, the same as in the blank experiment without catalyst, thus indicating that there was no relevant catalytic activity for the mordenite crystals. The catalytic activity of Amberlyst^{TM} 15 is high enough to carry out the experiments in a continuous membrane reactor, besides, mordenite crystals have a negligible catalytic activity, which implies that the membrane reactor studied in this work could be classified as an inert membrane reactor.

Table 1
Membranes synthesized properties and pervaporation performance

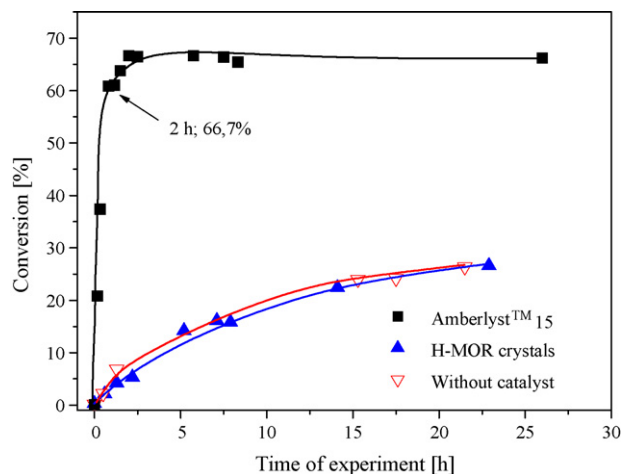| Membrane	Weight gain (mg/g)	N$_2$ permeation (mol/(m^2 s Pa))	H$_2$O/ EtOH S.F.	H$_2$O flux (kg/(m^2 h))
MOR-1	4.2	2.70×10^{-7}	164	0.075
MOR-2	4.0	9.50×10^{-9}	36	0.078
ZA-1	8.6	1.40×10^{-9}	92	0.150

Temperature = 358 K.

Fig. 1. Conversion vs. time, esterification of acetic acid with ethanol. Batch reactor, volume = 100 mL, catalyst weight = 3.6 g. Operation temperature: 358 K.

3.3. Continuous inert membrane reactor results

Continuous esterification experiments in membrane reactors and in a fixed bed reactor (FBR) were carried out in the experimental set-up previously described, the experimental results are presented in Fig. 2. After 2 days of experiment the fixed bed reactor, containing Amberlyst, reaches steady state conversion around 67%, slightly lower than equilibrium. The time needed to reach steady state conversion is higher than in the case of batch reactor due to the low feed flow 5×10^{-3} mL/min, employed for the experiment, which is the same as in the membrane reactor. The reasons for this low feed flow are related to the membrane permeability (presented in Table 1), the water flux through the 5 cm length mordenite membranes is around 2×10^{-3} mL/min. The time needed to fill up the reactor and the piping is around 10 h, and the samples are collected every 12 h, to get an enough sample, for this reason the first representative sample is after 24 h from the beginning of the experiment. In the FBR the catalyst is active; nevertheless equilibrium conversion could not
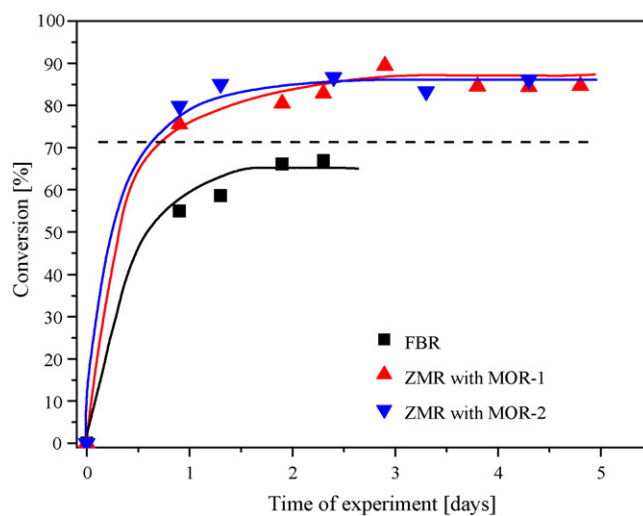

Fig. 2. Conversion vs. time, esterification of acetic acid with ethanol. Zeolite membrane reactor (ZMR) and fixed bed reactor (FBR). Space time: 4 h; operation conditions—temperature: 358 K; feed pressure: 1.3 bar.

be overcome. On the other hand, the zeolite membrane reactor after 1 day of experiment exceeds equilibrium conversion. The mordenite membranes show a good reproducibility, with similar conversions for both mordenite membrane reactors. Using membrane MOR-1 an 89% maximum conversion was reached, while 87% was obtained with MOR-2, in both membranes the conversion was notably higher than the corresponding equilibrium value at the experiment temperature (72.4%), shifting equilibrium at a time of experiment shorter than 1 day. As far as we concern these high conversion values were not previously reported using a continuous membrane reactor for esterification reaction. The ability to separate water of mordenite membranes shifts equilibrium conversion towards the esterification product. Besides, high conversions were maintained without perceptive loss after almost 5 days, indicating the remarkable stability of mordenite membranes under acidic conditions, even with their relatively high Al content that provides their hydrophilic character.

Zeolite A membranes are highly hydrophilic membranes, well known for its ability to separate water [28]. Fig. 3 compares the results for the continuous esterification experiments using mordenite membranes and zeolite A membrane. In the case of membrane ZA-1 the equilibrium was shifted in less than 1 day of experiment, reaching a conversion of 73.3%, similarly to that of the mordenite membranes. However, after that point conversion declines, while using mordenite membranes conversion increased. This behaviour could be explained because of the larger amount of Al in zeolite A compared to mordenite, that makes zeolite A more hydrophilic but at the same time more unstable under acidic conditions. The separation factors H_2O/EtOH and H_2O/HAc during esterification experiments with MOR-1 and ZA-1 are depicted in Fig. 4. It could be observed that in the case of MOR-1 there was an increase on separation factors H_2O/EtOH and H_2O/HAc up to the third day of experiment, reaching values of 200 and 95, respectively, and these values were maintained until the end of the experiment. These increases could be related with the increasing production of water in the catalyst side. The initial separation factors

Fig. 4. Separation factors H_2O/EtOH and H_2O/HAc for esterification experiments with mordenite and zeolite A membrane reactors. Same conditions as in Fig. 3.

Table 2
Esterification results, after 2 days of experiment, for mordenite and zeolite A membrane reactors and fixed bed reactor (FBR), catalyst Amberlyst™ 15

Membrane	Space time (h)	Conversion (%)	S.F. H_2O/react.	
			EtOH	HAc
FBR	4.09	66.9	–	–
MOR-1	4.07	89.4	192	98
MOR-2	4.29	86.7	59	170
ZA-1	4.04	53.1	32	18

Temperature = 358 K.

observed for zeolite A were 315 for H_2O/EtOH and 89 for H_2O/HAc, even higher than for mordenite membrane, however these separation factors decrease up to 32 and 18, respectively, resulting in a loss of reactants trough permeate side that causes the drop of conversion for zeolite A membrane reactor (Table 2).
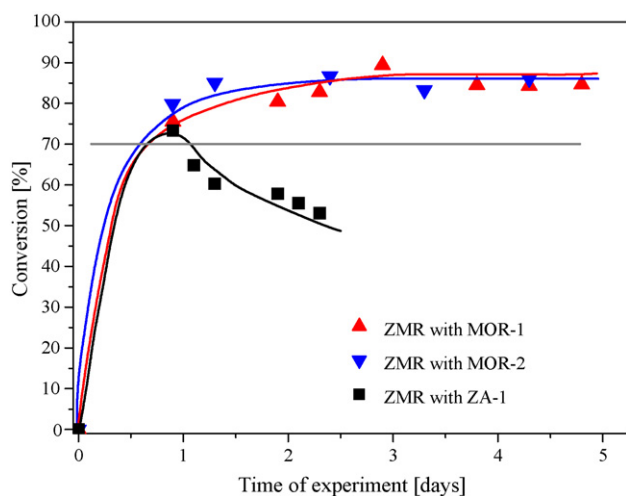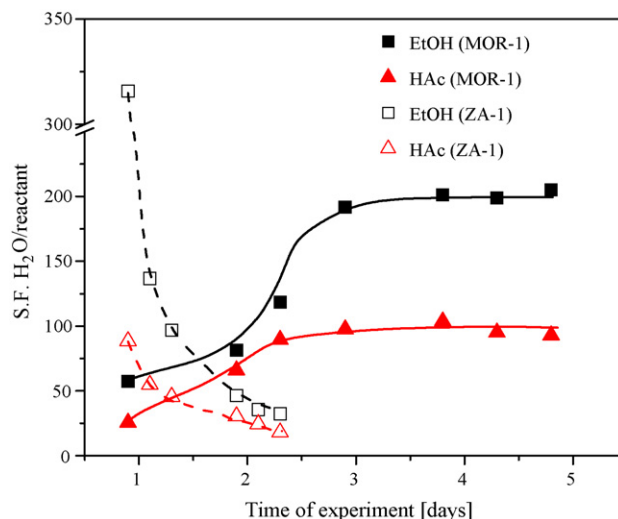

Fig. 3. Conversion vs. time, esterification of acetic acid with ethanol. Mordenite and zeolite A membrane reactors. Same conditions as in Fig. 2.
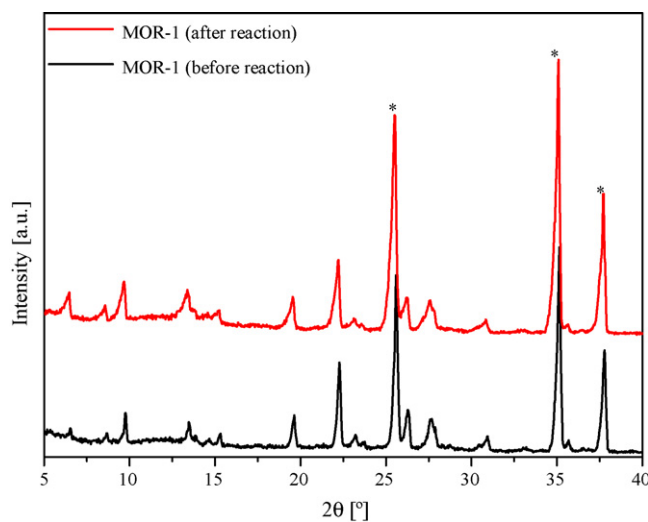

Fig. 5. XRD patterns for membrane MOR-1 before (bottom graph) and after (top graph) esterification reaction experiments. Peaks marked with * correspond to alumina support.
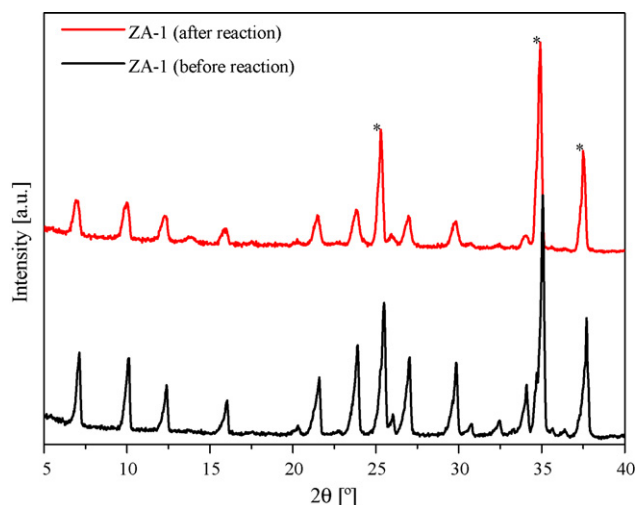
Fig. 6. XRD patterns for membrane ZA-1 before (bottom graph) and after (top graph) esterification reaction experiments. Peaks marked with * correspond to alumina support.

The membranes MOR-1 and ZA-1 were characterized, using XRD technique, before and after reaction experiments. In the case of mordenite membrane, Fig. 5, either before and after reaction, the diffraction peaks are well defined and correspond to the mordenite pattern, indicating that the membrane remained crystalline after 120 h of operation. For zeolite A membrane diffraction patterns, Fig. 6, correspond to zeolite A, before reaction peaks are well defined while those after reaction have a lower intensity and sharpness, which could imply a deterioration of zeolite A during the reaction experiments in acidic medium, meanwhile mordenite membranes are resistant to the acidic conditions occurred in the esterification reaction.

4. Conclusions

Esterification of acetic acid with ethanol can be successfully carried out in continuous zeolitic tubular membrane reactors of mordenite and zeolite A, with Amberlyst™ 15 as the catalyst. Both mordenite and zeolite A membranes are capable of shifting the equilibrium in less than 1 day of experiment. Mordenite membranes showed a great resistance to acidic reaction medium, with conversions of about 90% maintained for 5 days of experiment, with very high separation factors $H_2O/EtOH$ and H_2O/HAc. In the case of zeolite A membrane conversion dropped dramatically because of the instability of this zeolite to the reaction acidic conditions.

Acknowledgement

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