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Dehydration of 1-butanol over γ-Al_2O_3 catalytic membrane

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Abstract

Dehydration of 1-butanol over the catalytic membrane was carried out in a tubular membrane reactor. The main products were 1-butene and *trans*- and *cis*-2-butene. From experiments it can be found that operating conditions had an obvious influence on conversion of 1-butanol and the active sites on the membrane surface had a remarkable effect on the selectivity of 1-butene.

1. Introduction

The use of inorganic membrane reactors to enhance the productivity of chemical and biochemical processes is one of the most promising aspects of current membrane technology [1]. In most studies [2–8] concerning porous inorganic membrane reactors the membrane is used only for its separate function, but more interesting is the case that the membrane and the catalyst are integrated in a one unit operation, i.e., an active membrane with simultaneously catalytic and separate activities [9–13]. The key benefits of the integrated concept may include lower reagent requirements, higher conversion efficiency and lower cost.

Both the operating conditions and the surface properties of membrane can affect the reaction taking place in a catalytic membrane reactor. The catalytic membrane used was a γ-Al_2O_3 top layer supported on a tubular α-Al_2O_3 membrane. We chose dehydration of 1-butanol as a probe reaction to test the performance of the membrane reactor. There are four main reasons (1) γ-Al_2O_3 is a typical acidic catalyst and dehydration of 1-butanol is one of the model reactions testing its acidity [14], (2) distribution of the relative acid strength can be partially displayed by the distribution of the product isomers, (3) the products are not complex and easily to analyze and (4) sealing of the reactor is easy because dehydration takes place at a lower temperature.

2. Experimental

γ-Al_2O_3 top layer with a thickness of 5–10 μm was made through a dipping process and then calcining at a certain temperature (723–1023 K). The dipping sol was synthesized by peptizing Pural SB powders (Condea, Germany). Pore diameter and pore size distribution of the membrane were characterized by N_2 adsorption at low temperature using unsupported membrane

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[15,16]. The membrane reactor was shown in Fig. 1. 1-butanol was introduced to the reaction zone via a saturator at 273 K; both carrier gas and purging gas were N_2. In the reaction zone both the feeding side and the purging side were maintained at one atmosphere. Analysis of 1-butanol and butene isomers was carried out with two gas chromatographs at the same time. Conversion of 1-butanol and the selectivity of 1-butene were calculated by the following formulas:

Conversion of 1-butanol:

$$C\% = \frac{[\text{1-butanol}]_{r1+r2} - [\text{1-butanol}]_{p1+p2}}{[\text{1-butanol}]_{r1+r2}}$$

Selectivity of 1-butene:

$$S\% = \frac{[\text{1-butene}]_{p1+p2}}{[\text{1-butene}]_{p1+p2} + [\text{2-butene}]_{p1+p2}}$$

1 and 2 represent the molecular amount of the feeding side and purging side, respectively, 'r' is reactant and 'p' is product.

3. Results and discussion

3.1. The influence of reaction temperature on dehydration of 1-butanol

The reaction temperature was an important factor in membrane reaction which affected conversion and selectivity of the reaction. In experiments, the feeding rate and purging rate were unchanged, the reaction temperature was varied from 473 K to 623 K. For the membranes calcined at different temperature, the results were shown in Fig. 2 and Fig. 3. The overall conversion of 1-butanol increased with increasing reaction temperature, but the selectivity of 1-butene only slightly decreased. Three main reasons may

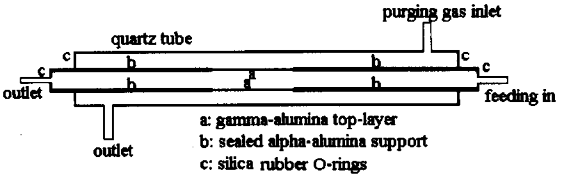

Fig. 1. Double-pipe configuration membrane reactor.

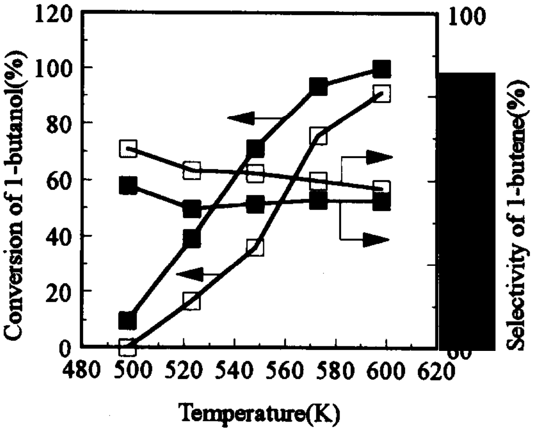

Fig. 2. The influence of temperature on dehydration of 1-butanol, purging rate and feeding rate are 30 ml/min; N_2:C_4H_9OH = 759:1 (molecular ratio). ■ Membrane calcined at 723 K; □ membrane calcined at 823 K.

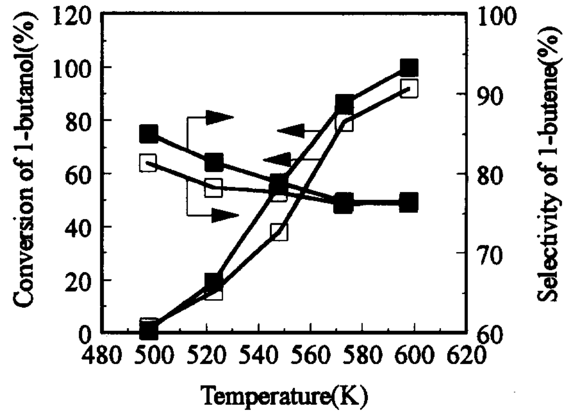

Fig. 3. The influence of temperature on dehydration of 1-butanol, purging rate and feeding rate are all 30 ml/min; N_2:C_4H_9OH = 759:1 (molecular ratio). ■ Membrane calcined at 923 K; □ membrane calcined at 1023 K.

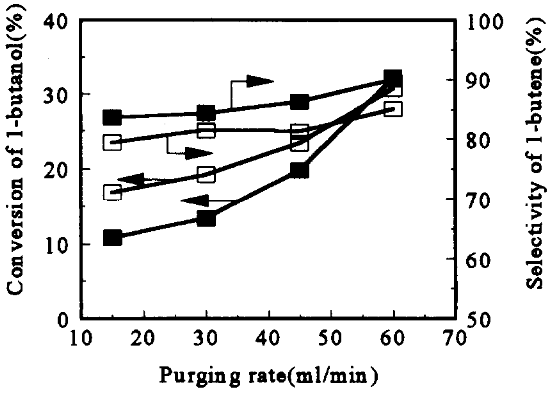

Fig. 4. The influence of purging rate on dehydration of 1-butanol, the feeding rate is 30 ml/min, the reaction temperature is 523 K; N_2:C_4H_9OH = 759:1 (molecular ratio). ■ membrane calcined at 1023 K; □ Membrane calcined at 923 K.

lead to these results, (1) with increasing reaction temperature the amount of active reactant molecules increased, then reaction rate enhanced, thus an increase in overall conversion and 1-butene isomerization may occur, (2) in a catalytic membrane reactor, the catalyst is supported on top layer. When feeding gas flowed in the inner tube, reactant molecules could not only adsorb on the active sites of the top layer, but also adsorb on the inner surface of the pore while reactant diffused through the pore to the supported side. The speed of reactant molecules increased with increasing reaction temperature, then contact probability between reactant molecules and catalyst increased, thus more molecules could adsorb on active sites in unit time to enhance conversion and isomerization and (3) activity of the catalytic membrane increased with increasing temperature.

3.2. *The influence of purging rate on dehydration of 1-butanol*

One advantage of the catalytic membrane reactor is that products can be quickly removed from reaction zone. It can enhance selectivity and reduce by-product. The experimental results were displayed in Fig. 4. Reaction temperature and feeding rate were remained unchanged during the reaction. It can be found that both conversion of 1-butanol and the selectivity of 1-butene increased with increasing purging rate. These phenomena may be caused by the following facts. At high purging rate, products are immediately swept away, desorption of products is prompted but its adsorption is difficult, the concentration of available active sites on the pore surface of catalytic membrane increased, consequently, purging rate increasing results in a higher conversion and a lower isomerization.

3.3. *The influence of feeding rate on dehydration of 1-butanol*

The amount of reactant entering the reaction zone was changed with the variation of feeding rate. From Fig. 5 it can be found that conversion

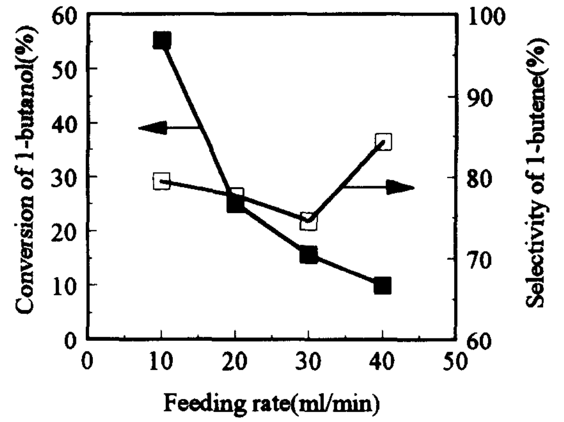

Fig. 5. The influence of feeding rate on dehydration of 1-butanol, the purging rate is the same as the feeding rate. N_2:C_4H_9OH = 759:1 (molecular ratio), the membrane was calcined at 1023 K, the reaction temperature is 523 K.

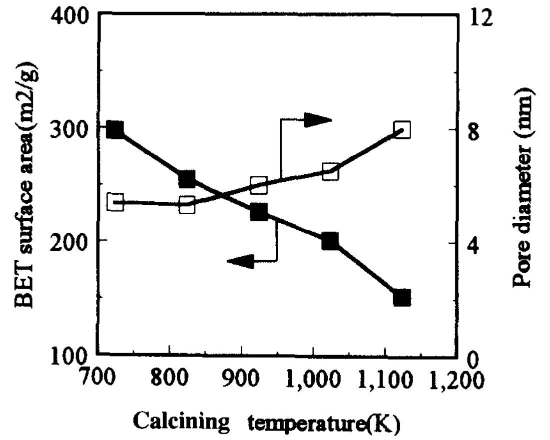

Fig. 6. The influence of calcining temperature on BET area and pore diamter.

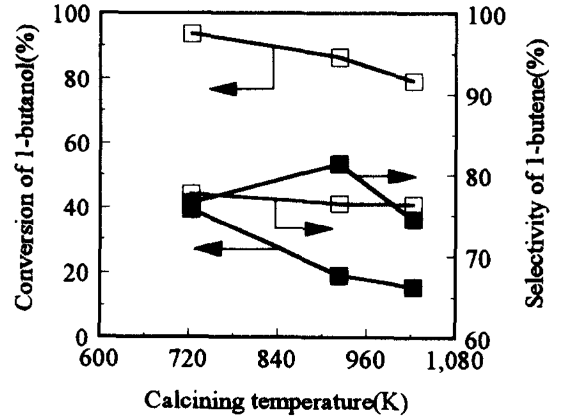

Fig. 7. The influence of membrane calcining temperature on dehydration of 1-butanol, purging rate and feeding rate are 30 ml/min; N_2:C_4H_9OH = 759:1 (molecular ratio). ■ Reaction at 523 K, □ reaction at 573 K.

Table 1
Influence of active sites on conversion and selectivity (NH_3-treated)

Membrane calcining temperature (K)	NH_3-treated	Conversion of 1-butanol (%)	Selectivity of butene (%)		
			1-butene	*trans*-2-butene	*cis*-2-butene
823	No	39.2	70.1	15.8	14.1
	Yes	34.6	90.5	9.5	–
923	No	19.2	81.4	18.1	0.5
	Yes	15.9	86.5	11.4	2.1

The reaction temperature is 523 K. Both feeding rate and purging rate are 30 ml/min.

Table 2
Influence of active sites on conversion and selectivity (NaOH-treated)

Reaction temperature (K)	NaOH-treated	Conversion of 1-butanol (%)	Selectivity of butene (%)		
			1-butene	*trans*-2-butene	*cis*-2-butene
523	No	25.0	77.6	18.8	3.4
	Yes	11.8	95.7	3.9	0.4
573	No*	79.2	76.4	14.8	8.8
	Yes	77.9	90.7	6.2	3.1

The membrane was calcined at 1023 K. All gas flow rates were 20 ml/min except * which was 30 ml/min.

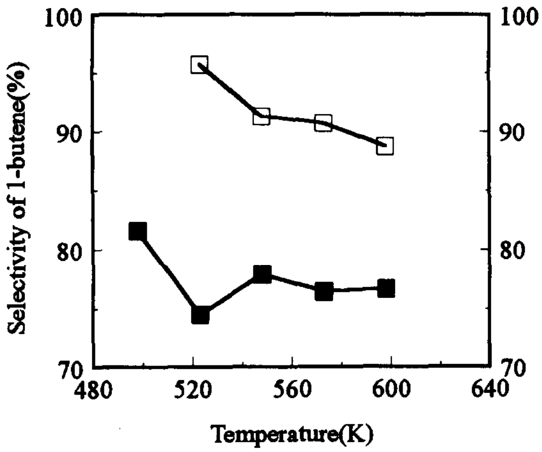

Fig. 8. The selectivity of 1-butene over membrane before and after Na treatment, purging rate and feeding rate are 20 ml/min. N_2:C_4H_9OH = 759:1 (molecular ratio); the membrane was calcined at 1023 K. ■ before Na treatment; □ after Na treatment.

of 1-butanol decreased when the feeding rate increased, the selectivity of 1-butene was around 80%. Selectivity of 1-butene was not greatly changed because the factors, such as active sites and reaction temperature, that affected selectivity of 1-butene were not changed. Space time rate increasing may lead to increasing of reactant amount for unit catalyst in unit time, the amount of 1-butanol that passed the reactor without contacting catalytic membrane increased, as a result conversion of 1-butanol and the space time yield decreased.

3.4. The influence of membrane calcining temperature on dehydration of 1-butanol

According to the results obtained from unsupported membrane (Fig. 6), BET surface area decreased while pore diameter increased with membrane calcining temperature increasing. For the same reaction conditions but different calcining temperatures of the membrane, experimental results were shown in Fig. 7. It can be found that conversion of 1-butanol decreased when membrane calcining temperature increased, the selectivity of 1-butene was not changed. The pore diameter range of γ-Al_2O_3 membrane is 4–7 nm, reactant and products diffused in pore as Knudsen diffuse. Gas permeability increased with increasing average pore diameter, but active sites in a unit area decreased when BET area decreased, this led to a cutting down in the activity of the catalytic membrane, therefore, conversion of 1-butanol was reduced.

The supported γ-Al_2O_3 membrane is so thin (only 5–10 μm) that products were quickly removed. It is difficult for 1-butene to adsorb again on the membrane to isomerize to 2-butene. Consequently, the control factors of selectivity of 1-butene would be the distribution of acid strength of the membrane. According to the results of pyridine adsorbed FTIR study, the distribution of acid strength was not greatly changed when calcining temperature was changed [17], these might explain the unchanged selectivity of 1-butene.

The membrane calcined at 823 K was not in good agreement with the three other membranes reported above. It had a relatively lower conversion and higher selectivity. One possible reason was that decomposing of the organic binder and plasticizer might poison the active sites on the membranes.

3.5. The influence of active sites on dehydration of 1-butanol

The active sites on catalytic membranes were one of the important factors which affected reaction properties of the membrane reaction. From previous experiments it can be found that operating conditions affected mainly on conversion of 1-butanol. In this experiment, we used alkali treated methods to test how active sites affected the reaction. The catalytic activity of membrane was tested before and after exposure of the membrane to an atmosphere of ammonia, while ammonia had no effect on weak acid centers, it strongly deactivated relatively strong acid centers. Although overall conversion of 1-butanol was only partially reduced, the selectivity of 1-butene was greatly increased (Table 1). Dehydration of alcohol only needs weak acid centers but double-bond isomerization of olefin needs relatively stronger acid centers. The relatively stronger acid centers were deactivated previously after membrane exposure to ammonia, therefore, the selectivity of 1-butene increased and 1-butanol conversion decreased. The experimental results of sodium hydroxide treated were the same as that of ammonia (Table 2, Fig. 8), from these results it may be concluded that active sites on catalytic membrane can be varied by pre-modification methods.

4. Conclusions

1. Conversion of 1-butanol increased with increasing reaction temperatures.
2. Conversion of 1-butanol and the selectivity of 1-butene increased with increasing purging rates.
3. Conversion of 1-butanol decreased with increasing feeding rates.
4. Under the same reaction conditions, conversion of 1-butanol decreased with membrane calcining temperature increasing, but the selectivity of 1-butene remained unchanged.
5. After ammonia or sodium treatment, selectivity of 1-butene greatly increased while conversion of 1-butanol slightly decreased.

It seems that the operating conditions had an obvious influence on conversion of 1-butanol and the active sites had a remarkable effect on selectivity of 1-butene, this was determined by the characteristics of the catalytic membrane reactor.

Acknowledgements

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