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Oxidative dehydrogenation of butane using inert membrane reactor with a non-uniform permeation pattern

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Abstract

Inert ceramic membrane reactors have been investigated for the oxidative dehydrogenation of butane to butadiene and butene. The partially coated porous ceramic membranes have been used as an air distributor to a fixed-bed of V–Mg–O catalyst. The catalyst characterization was carried out by BET, X-ray diffraction (XRD). The performance of inert membrane reactors (IMRs) has been compared to that obtained in a conventional fixed-bed reactor (FBR). The IMRs are more efficient than the FBR. The moderate non-uniform inert membrane reactor (NIMR1) slightly outperforms the uniform inert membrane reactor (UIMR) in most operation conditions investigated. A feeding mode with 10% of air mixing with butane in the NIMR1 (10NIMR1) was found to be more efficient than the feeding mode with all air permeating through ceramic membrane. Selectivity of up to 61.1% and a yield of 42.2% were obtained in the 10NIMR1.

Keywords: Butane; Oxidative dehydrogenation; Magnesium *ortho*-vanadate; Ceramic membrane; Membrane reactor

1. Introduction

A membrane reactor has tremendous potential for several reaction types, including dehydrogenation and partial oxidation reactions. In the last decade, most of the applications of membrane reactors made use of the membrane to separate a product as it forms. This was the case of dehydrogenation reactions. If hydrogen is selectively removed from the reactor, the yield can be improved by reducing thermodynamic equilibrium limitations [1,2]. Another important field of application for membrane reactors involves their use as distributors of one or more reactants. In this case, distributing a reactant to reduce local partial pressures and favor desired reaction pathways can increase the selectivity to the desired product. Either a permselective or non-permselective membrane is used to distribute the feed. This mode of operation has application for series-parallel reactions where high partial pressure of one reactant promotes undesired reaction pathways.

For many partial oxidation reactions, the oxygen partial pressure determines the product selectivity. Oxygen fed in stoichiometric proportions with other reactants promotes deep oxidation to carbon oxides (CO and CO_2). Distributing the oxygen along the length of the reactor lowers the oxygen partial pressure and thus, increases the selectivity to desired products. Reactor configurations using dense membranes to transport anionic oxygen have been reported [3,4]. Due to the slow transport of oxygen through the PbO/MgO film or silver membrane, the hydrocarbon yields are very low. The low permeability of solid electrolyte membrane also leads to low hydrogenation yields. Porous membrane was described for nonselective oxygen transport and high permeability was obtained. It was reported that relatively high yields or selectivities to desired products in methane oxidative coupling, oxidative dehydrogenation of lower alkanes and partial oxidation reaction [5–11].

The oxidative dehydrogenation of butane over V–Mg–O catalysts using the fixed-bed reactor (FBR) was reported [12–19]. The performance of V–Mg–O catalyst was affected by oxygen partial pressure [7,14]. In this work, a reactor is developed in which a partially coated tubular porous ceramic membrane is used as an air distributor to the V–Mg–O catalytic bed. Butane is fed to the reaction (tube) side and air is fed to the shell side. The permeation flux is controlled by the applied pressure differential. Two kind of membrane has been used: membrane with uniform permeation distribution and membrane with non-uniform permeation distribution. The oxygen partial pressure in the outlet of the reactor is higher than that in the inlet of the reactor using uniform membrane as distributor. The concentrations of desired products (butene and butadiene) are highest in the outlet of the reactor. In this case, the selectivity to C_4

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Nomenclature

F	flux (m^3/s)
L	length (m)
n	molar ratio
p	pressure (Pa)
S	selectivity
T	temperature (K)
W	catalyst weight (kg)
X	conversion
Y	yield

Subscripts

C_4	butene and butadiene
r	tube side
t	total flux

dehydrogenation products can decrease for the deep oxidation of butene and butadiene to carbon oxides. It is necessary to decrease the oxygen partial pressure in the whole reactor especially in the outlet of it. Two kind of ways are put forward: (i) using membrane with non-uniform permeation pattern to decrease the permeation rate in the outlet of the reactor; (ii) part of air is cofed with butane and the rest permeates through the membrane into the tube side. It was found that, for the oxidation of butane to maleic anhydride (MA) in a membrane reactor, when part of the oxygen was shifted moderately from the shell to the tube side, the MA yield increased [10]. Combination of non-uniform membrane with correct cofeeding mode leads to low oxygen partial pressure in the whole reaction regions.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst preparation procedure was similar to one previously described [14]. The aqueous solution of magnesium nitrate was added to the aqueous solution of ammonium carbonate. The white precipitate was filtered, washed, dried and calcined. The resultant MgO was added to an aqueous solution containing 0.3 mol/l ammonium hydroxide and 0.4 mol/l ammonium vanadate at 343 K. The suspension was stirred and evaporated to dryness for 48 h. The resulting solid was calcined at 823 K for 6 h. Then it was mixed with 1.0 mol/l HNO_3 to make block. Then the block was calcined again at 823 K to disperse HNO_3. It was crushed and sieved to obtain a particle size between 0.25 and 0.42 mm. The catalyst contained 24% V_2O_5 and was termed 24-V–Mg–O.

The catalyst surface area measured by BET technique is 52 m^2/g. X-ray diffraction (XRD) was performed on a Rijaku D/MAX2400 diffractometer equipped with Cu Kα radiation. Fig. 1 showed the XRD pattern of 24-V–Mg–O catalyst. Two crystal phases clearly identified were MgO and $Mg_3(VO_4)_2$. In addition, a trace of vanadium oxide (V_2O_5) was identified. Other possible compounds of V–Mg–O such as MgV_2O_6 and $Mg_2V_2O_7$ were not detected.

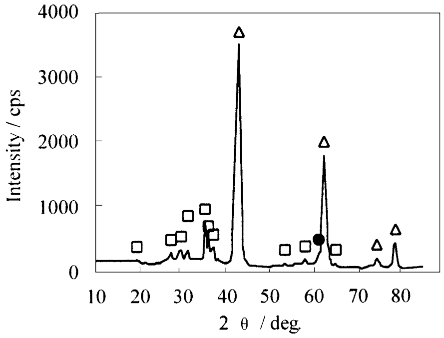

Fig. 1. XRD pattern of 24-V–Mg–O catalyst (X-ray: Cu Kα1/40 kV/100 mA; scan speed: 4°/min; scan step 0.2°). (△) MgO; (□) $Mg_3(VO_4)_2$; (●) V_2O_5.

2.2. Preparation of membrane and permeation flux

The original α-Al_2O_3 membrane has a mean pore diameter of 1 μm, an approximate porosity of 40% and a thickness of 2 mm. Each tube is 250 mm in length and has an o.d. of 12 mm. The both ends of the tube are externally coated with glaze. The glaze extends 75 mm down the tube to prevent air permeation outside of the reaction zone. The original permeability is too high to control air permeation by pressure differential. The remaining 100 mm of the membrane was partially coated with glaze. The preparation procedure was slightly different to Tonkovich described [8]. Glaze power was added to water to make into pulp. The glaze pulp was uniformly applied to the external membrane surface area. The tube was dried at 353 K for 2 h and calcined at 1023 K for 1 h. Part of pore was coated by glaze. The procedure was repeated several times to obtain required permeation.

When the pressure differential exceeds 5×10^3 Pa, the back permeation of butane can be prevented completely. In this work, three different membranes were used: membrane with a uniform permeability and two membranes with non-uniform permeability. The non-uniform membrane was divided four sections. Each section was 25 mm long. The permeability at each of the four membrane sections varied because the times of partially coating were different. The uniform membrane was partially coated four times. In order to obtain non-uniform membrane, 75% of the permeation area was again partially coated with glaze, dried and calcined. Then the same procedure was repeated for 50% of the membrane, and finally for the 25% of the membrane. Table 1 showed the air permeation flux at the four membrane sections.

Table 1
Air permeation flux at the four membrane sections[a]

Membrane	F_t (10^{-7} m^3/s)	F (10^{-7} m^3/s)			
		Section 1	Section 2	Section 3	Section 4
Uniform	20.0	5.0	5.0	5.0	5.0
Non-uniform 1	12.6	5.0	3.6	2.5	1.5
Non-uniform 2	9.4	5.0	2.5	1.4	0.5

[a] $T = 873$ K, $\Delta p = 1.0 \times 10^4$ Pa

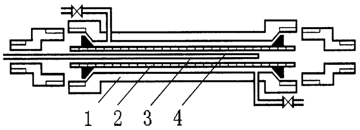

Fig. 2. The configuration of the membrane reactor. (1) Stainless steel shell; (2) ceramic tube; (3) catalytic bed; (4) thermocouple well.

2.3. Test station and membrane reactor configuration

All the flow rates of reactants were measured using flow gauge. Water was removed from the reactor effluents using ice trap. The incondensable gases were analyzed by gas chromatography. Fig. 2 showed the configuration of the membrane reactor. A ceramic tube was enclosed in an outer stainless steel shell. A thermocouple well located along the catalytic bed to measure the temperature profiles in the reactor. The 24-V–Mg–O catalyst and inert quartz chips were packed in the annular space between membrane wall and thermocouple well. The other space in the ceramic tube was packed with inert quartz chips. An electric furnace maintained a constant and equal temperature at the catalytic bed. Unless otherwise indicated, the temperature values reported below referred to the set point of the furnace.

3. Result and discussion

3.1. Blank experiments

The blank experiments showed that under typical operating conditions ($T = 873$ K, $F_t = 5 \times 10^{-6}$ m^3/s, $n_{C_4H_{10}}/n_{O_2}/n_{N_2} = 4/8/88$), butane conversion in an empty membrane reactor or in a membrane reactor packed with quartz chips was <1%. The reactions on the surface of ceramic membrane and the homogeneous reactions can be neglected.

3.2. Temperature profiles in the reactors

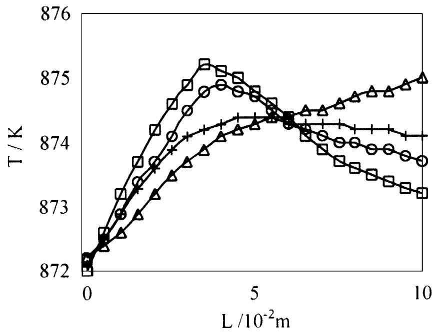

Fig. 3. Temperature profiles obtained in different reactors ($W = 1.0 \times 10^{-3}$ kg, $F_t = 5.0 \times 10^{-6}$ m^3/s, $n_{C_4H_{10}}/n_{O_2}/n_{N_2} = 4/8/88$). (□) FBR; (△) UIMR; (+) NIMR1; (○) NINR2.

The oxidative dehydrogenation of butane to butadiene and butene is an exothermic process. The deep oxidation to carbon oxides is also an exothermic process. It is, therefore, important to measure the magnitude of the temperature gradients in the bed when high conversions of butane are reached. The reactor used in this work is neither isothermal nor adiabatic. In the experimental system used in this work, the temperature is controlled only at the center of the stainless shell. Fig. 3 showed the temperature profiles obtained in different reactors. The temperature of set point was 833 K. The total flow rate was 5×10^{-6} m^3/s. All the gas including air, butane and nitrogen was fed to the tube side in the FBR. In the uniform inert membrane reactor (UIMR), non-uniform inert membrane reactor (NIMR1) and NIMR2, butane and nitrogen was fed to the tube side and air was fed to the shell side. The temperature profile in the FBR was the most abrupt. The highest temperature in the reaction zone was about 2 K higher than the inlet temperature in the NIMR1. But in other reactors investigated, the temperature increased approximately 3 K. The temperature increased along the length of the catalytic bed in the UIMR. The reaction rates were accelerated because oxygen partial pressure was high in the outlet of the UIMR. Approximately 68% of air permeated through the membrane in the first half of the NIMR1. Air (80%) was fed to catalytic bed in the first half of the NIMR2. Therefore, the temperature in the first half of the NIMR1 was lower than that in the first half of the NIMR2. The effect of temperature difference along the catalytic bed was small and could be neglected.

3.3. The performance of the reactors

3.3.1. The effect of contact time (W/F_t)

The effect of contact time (W/F_t) on conversion, selectivity and yield was showed in Fig. 4. The feed rates of butane, air and nitrogen were kept constant. The total flux (F_t) was 5×10^{-6} m^3/s for every type of reactors. The weight of catalyst (W) was varied. As the contact time increased, the conversions of butane and oxygen increased, the yield to C_4 dehydrogenation products (C_4) increased, but the selectivity to C_4 dehydrogenation products decreased. The carbon balance was satisfied to within ±5%.

There are several reasons that may contribute to the lower selectivity to C_4 dehydrogenation products at higher value of W/F_t. The effect of W/F_t on the performance of V–Mg–O

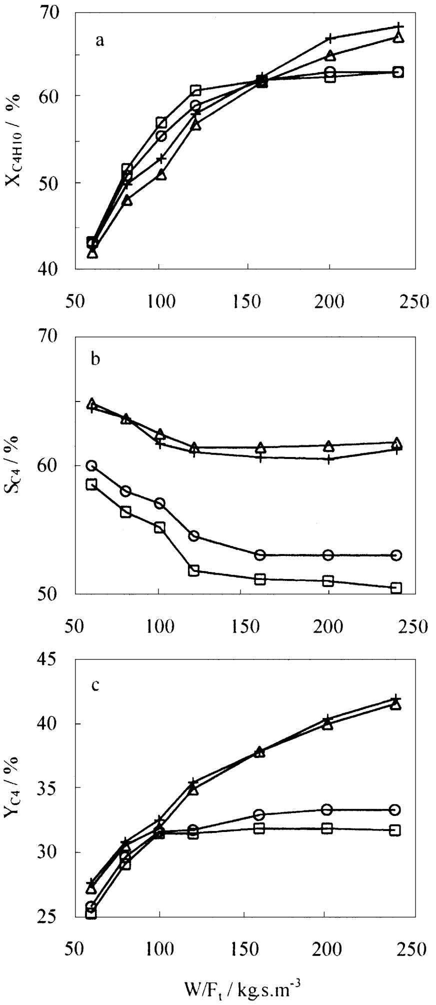

Fig. 4. Effect of W/F_t on conversion (a), selectivity (b) and yield (c) ($T = 873\,K$, $F_t = 5.0 \times 10^{-6}\,m^3/s$, $n_{C_4H_{10}}/n_{O_2}/n_{N_2} = 4/8/88$). Symbols are the same as in Fig. 3.

catalyst indicates that at very short contact time, the C_4 dehydrogenation products and carbon oxides are formed from butane via parallel reactions. With increasing butane conversion, the selectivity to carbon oxides increases, implying the existence of consecutive reactions of these products at longer residence times. The oxidative dehydrogenation of butane is a complex parallel consecutive reaction network. Butane reacts with lattice oxygen to create butene and butadiene. At the same time, butane, butene and butadiene all can be deep oxidized to CO_x. The intermediate products (butene and butadiene) are easier to be deep oxidized than butane. In addition, the C_4 dehydrogenation products are easy to desorb form the surface of catalyst at low butane conversion. Therefore, higher selectivity to C_4 dehydrogenation products is obtained at low butane conversion.

3.3.2. The effect of oxygen partial pressure

Oxygen partial pressure plays important role in the oxidative dehydrogenation of butane to butene and butadiene. The lattice oxygen is consumed by dehydrogenation reaction, and then the reduced V–Mg–O catalyst is reoxidized by gas-phase oxygen. The rates of catalyst reduction with butane and reoxidization with oxygen show strong dependant on the extent of catalyst reduction. The rates of these two processes are equal and should coincide with the rate of steady-state catalytic reaction if the latter occurs through a redox mechanism. With increasing the extent of catalyst reduction, the selectivity to C_4 dehydrogenation products increases while the activity of the catalyst decreases [20]. While all the gases are fed to the tube side in the FBR. The oxygen partial pressure is high in the inlet of the reactor. The selectivity to CO_x will be high in that zone of the FBR. Though the pressure drop along the catalytic bed can be neglected and air permeation rate is equal along the bed in the UIMR, the oxygen permeated through the membrane is not used up. Therefore, the oxygen partial pressure is very low in the inlet of the UIMR but high in the outlet of it. There are some disadvantages in this case. Firstly, the extent of reduction of catalyst in the inlet of the UIMR increases. Coke may occur and the catalyst cannot provide enough lattice oxygen to react with butane. Secondly, the oxygen partial pressure is high in the outlet of reaction zone with the highest partial pressure of desired C_4 dehydrogenation products. The deep oxidation of C_4 dehydrogenation products increases. Obviously, this will reduce the selectivity to C_4 dehydrogenation products. While non-uniform membrane with correct permeation along the membrane is used, the oxygen partial pressure can be maintained lower in the whole reaction zone. It can be concluded from Fig. 4 that the feeding mode of the NIMR1 is the most favorable. It is difficult to obtain the optimal distribution of permeation rate along the membrane.

Fig. 5 showed the effect of molar ratio of $n_{O_2}/n_{C_4H_{10}}$ on conversion, selectivity and yield. Butane flux and the total flux were kept constant. With the value of $n_{O_2}/n_{C_4H_{10}}$ increased, butane conversion increased, oxygen conversion and the selectivity to C_4 dehydrogenation products decreased. The NIMR1 gave the highest yield to C_4 dehydrogenation products in all molar ratio of $n_{O_2}/n_{C_4H_{10}}$. The FBR gave the lowest selectivity and yield to C_4 dehydrogenation products. The feeding mode has a strong influence on the performance of reactors. The key to the performance of FBR and IMR lies in the variation of the θ/λ ratio (ratio of the degrees of oxidation of selective and non-selective sites) alone the reactor. The θ/λ profiles is better in the IMR, resulting in a high selectivity to C_4 dehydrogenation products [11]. The selectivity to C_4 dehydrogenation products varied from 66.6 (for $n_{O_2}/n_{C_4H_{10}} = 1.0$) to 46.6% (for $n_{O_2}/n_{C_4H_{10}} = 3.0$) in the FBR. In the NIMR1 with moderate non-uniform permeation pattern, the selectivity varied from 71.0 (for $n_{O_2}/n_{C_4H_{10}} = 1.0$) to 50.5% (for $n_{O_2}/n_{C_4H_{10}} = 3.0$). Therefore, it is very important to lower the oxygen partial pressure in the whole reaction zone. Decreasing the permeability moderately along the membrane can cater for this necessity.

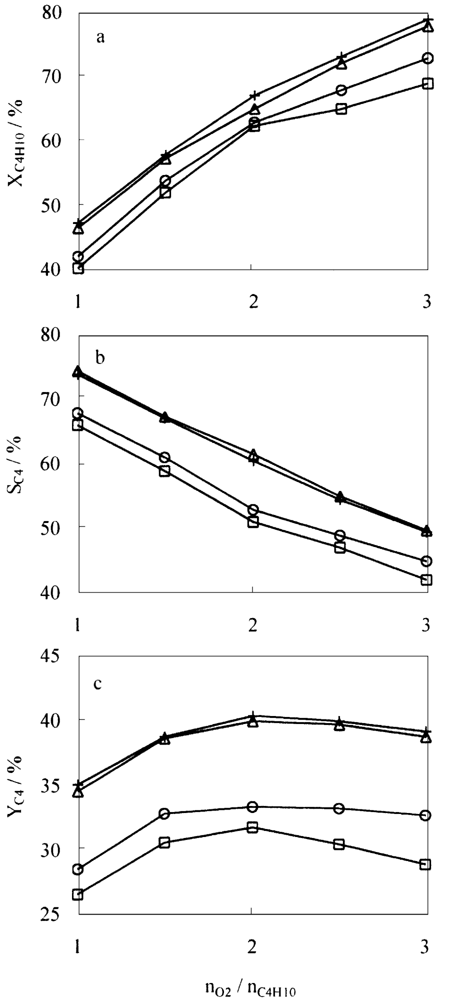

Fig. 5. Effect of $n_{O_2}/n_{C_4H_{10}}$ on conversion (a), selectivity (b) and yield (c) (T = 873 K, W = 1.0 × 10^{-3} kg, $F_{C_4H_{10}}$ = 2.0 × 10^{-7} m^3/s, $n_{C_4H_{10}}$ = 4%). Symbols are the same as in Fig. 3.

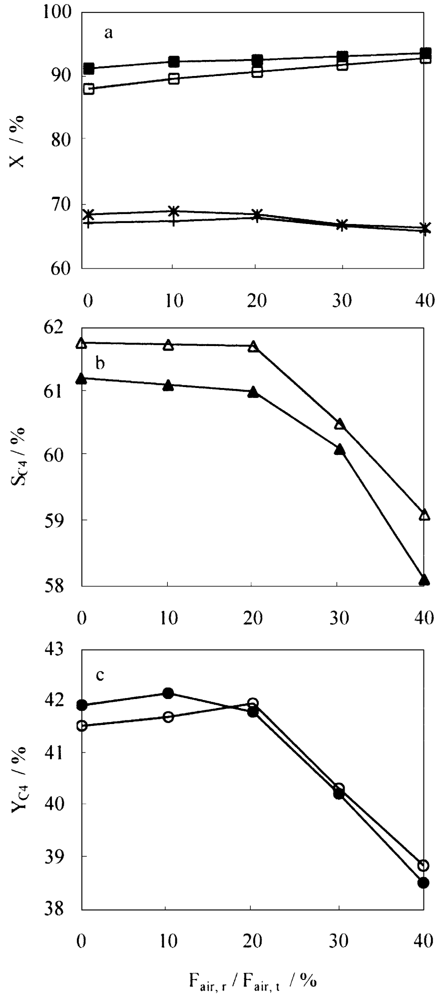

Fig. 6. Effect of partially cofeeding on the performance of the UIMR and NIMR1 (T = 873 K, W = 1.0 × 10^{-3} kg, F_t = 5.0 × 10^{-6} m^3/s, $n_{C_4H_{10}}/n_{O_2}/n_{N_2}$ = 4/8/88). (+) $X_{C_4H_{10}}$ – UIMR; (□) X_{O_2} – UIMR; (△) S_{C_4} – UIMR; (○) Y_{C_4} – UIMR; (∗) $X_{C_4H_{10}}$ – NIMR1; (■) X_{O_2} – NIMR1; (▲) S_{C_4} – NIMR1; (●) Y_{C_4} – NIMR1.

3.3.3. The effect of partially cofeeding

As mentioned above, the performance of V–Mg–O catalyst was reference with the extent of reduction. Relatively higher selectivity to C_4 dehydrogenation products was obtained in the NIMR1 and UIMR. While part of air is cofed with butane and the rest of air is fed to shell side, the extent of mixing will be promoted. In addition, the catalyst can provide enough lattice oxygen and the coke reaction can decrease in the inlet region. Furthermore, partially cofeeding air decreases the permeation rate and decreases the oxygen partial pressure in the outlet region with the highest concentration of C_4 dehydrogenation products in the reactor. Fig. 6 showed the effect of partially cofeeding on the performance of the UIMR and NIMR1. The uniform membrane reactor with 20% of air cofeeding with butane was termed as 20UIMR. The yield to C_4 dehydrogenation products obtained in the 20UIMR was higher than that obtained in the UIMR. The yield to C_4 dehydrogenation products obtained in the 10NIMR1 was higher than that obtained in the NIMR1. The non-uniform membrane 1 was used as air distributor in the NIMR1. The 10NIMR1 gave the highest selectivity and yield to C_4 dehydrogenation products. The selectivity of up to 61.1% and the yield of 42.2% were obtained in the 10NIMR1 under correct operation conditions. The selectivity and yield obtained are higher than that reported in the literature (S_{C_4} = 50.1%, Y_{C_4} = 28.2%) [14].

4. Conclusions

The oxidative dehydrogenation of butane to butadiene and butene over 24-V–Mg–O catalyst is a complex reaction network. The selectivity to C_4 dehydrogenation products decreases with the increasing oxygen partial pressure. The selectivity decreases with the increasing butane conversion. It is very important to lower the oxygen partial pressure in the whole reaction zone. The porous inert ceramic membrane partially coated with glaze was used as air distributor to obtain low oxygen partial pressure. The creation of a pattern of moderately decreasing permeability in the direction of flow along the membrane length lowers the oxygen partial pressure and increases the selectivity and yield to C_4 dehydrogenation products. Cofeeding part of air with butane can increase the yield to C_4 dehydrogenation products due to low oxygen partial pressure in the outlet of reactor. 10NIMR1 gaves the highest yield to C_4 dehydrogenation products.

Acknowledgements

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