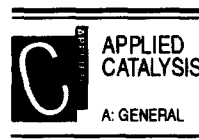




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Applied Catalysis A: General 154 (1997) 129–138



Catalytic dehydrogenation of ethanol in Pd–M/ γ -Al₂O₃ composite membrane reactors

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Received 22 May 1996; received in revised form 23 September 1996; accepted 4 October 1996

Abstract

Alumina membranes modified by Pd–M (M=Ru, Rh, Ni, Ag) and Pd were prepared by the sol–gel method, and characterized by SEM, XRD and N₂ adsorption. The single or binary metals were highly dispersed in alumina. The average pore diameters of binary metals modified membranes were 4–7 nm, which was a bit smaller than that for Pd single metal modified alumina membrane. The H₂/N₂ gas separation tests showed that the separation factor of the gaseous mixture exceeded the Knudsen value (3.74). The dehydrogenation of ethanol to acetaldehyde was carried out in membrane reactors incorporating Pd–M and Pd modification. The yield of acetaldehyde in Pd–Ru, Pd–Ag, Pd–Rh modified membrane reactors was higher than that in single metal Pd modified membrane reactor, while the yield in the Pd–Ni/ γ -Al₂O₃ membrane reactor was lower than that in Pd/ γ -Al₂O₃ membrane reactor. At moderate reaction conditions, the yield increased by 15% in Pd–Ru modified membrane reactor compared with the thermodynamic equilibrium value. The properties and characteristics of all modified membranes were compared and discussed in this paper.

Keywords: Alumina membrane; Ethanol dehydrogenation; Modification with binary metals; Membrane reactor; Gas permeation

1. Introduction

Acetaldehyde is one of the most important intermediate aliphatic chemicals serving as the raw material for the production of acetic acid, acetic anhydride, ethyl acetate, butylaldehyde, penta-erythritol and many other products. The product of two commercial processes is always a highly diluted aqueous acetaldehyde

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solution. It is difficult to get acetaldehyde in high concentration, which is sometimes required [1]. In contrast, the direct dehydrogenation of ethanol results in simpler products with a high concentration of acetaldehyde. However, the conversion of the direct dehydrogenation process is relatively low due to thermodynamic equilibrium limitations. Using the membrane reactors can significantly improve the conversion of ethanol [2], which may have a potential for the direct dehydrogenation of ethanol to acetaldehyde in industrial process.

There are several possibilities for the incorporation of the membranes in catalytic reactions. Dense metallic membranes, such as palladium and palladium alloy membranes always offer absolute selectivity to hydrogen. Gryaznov et al. demonstrated [3,4] a number of examples for membrane catalysis using palladium membrane reactors. The field of metal membrane reactors was also reviewed recently by Armor [5], but some limitations still exist: As the palladium metal membrane permeates only H_2 by solution–diffusion mechanism the permeated hydrogen flux is too slow, and easily suffering from hydrogen embrittlement due to phase transition between α and β forms of palladium. These limitations were partly overcome for palladium alloy membranes such as Pd–M (1–30 wt% Ag, Rh, Ru) alloy membrane [6], which exhibit much higher flux and avoid hydrogen embrittlement. In spite of the relatively numerous applications of these dense metallic membranes in laboratory catalysis process, dense metallic membrane's high price, low flux, easily suffering from metal sintering or fatigue and even some technology limitations have restricted their industrial application.

Despite the lower perm-selectivity for H_2 , porous membranes, such as metal modified alumina membranes, are more attractive for industrial operation, because they offer much higher fluxes than dense ones at a small portion of the cost. Saracco et al. [8] summarized the studies conducted on porous membranes used to enhance certain equilibrium-limited reactions in an recent review. Ross et al. [9] discussed the application of inorganic membranes in conjunction with catalysis in another review. Many recent works focused on the modification of the alumina membrane attempting to combine some advantages of both dense metallic membranes and porous alumina membranes. Liu et al. [10] used the solution impregnation method followed by heat treatment, which may lead to large reductions in permeability due to pore plugging. Uhlhorn et al. [11] had studied alumina membrane impregnated with silver. There was significant surface diffusion of oxygen and hydrogen, and the separation factor for H_2/N_2 improved from 3.8 to 8.8. Chai et al. [12] had prepared noble metal modified alumina membranes by mixing the metal salts with the Boehmite sol. The separation factor of H_2/N_2 for these membranes exceeds the limitation of the Knudsen value (3.74). Deng et al. [2], also prepared Pd, Pt modified alumina membrane by the sol–gel method, and the separation factor of H_2/Ar was better than Knudsen value (4.46). Considering the improvement of the Pd–M alloy membranes upon Pd dense membrane, in the present work, a series Pd–M and Pd modified alumina membranes were prepared by the sol–gel method. The effect of the induced metals on the pore size

distribution and on the separation of H_2/N_2 was investigated. Ethanol dehydrogenation was performed in the membrane reactors.

2. Experimental

2.1. Membrane preparation and membrane reactor

The solutions of $Pd(NH_3)_2(NO_3)_2-M(NO_3)_x$ were added to the Boehmite sol ($\gamma-AlOOH$), which was obtained following the procedure of Yoldas [13]. The outer surface of the porous ceramic tube (o.d. 12 mm, i.d. 10 mm, average pore size 1.1 μm) were dipped into metal ions dispersed sols, dried at room temperature for 24 h, then heated and calcined at 823 K for 16 h. Repetition of this procedure was required. About 35 mm of the middle part of the ceramic tube was permeable, the other enamelled part of the ceramic tube was impervious. The metal oxides in γ -alumina membrane were reduced to metallic state under flowing hydrogen (80 ml/min) at 673 K for 2 h with a slow heating rate of 1 $K \cdot min^{-1}$, then cooled down in flowing argon. The compositions of $Pd-M/\gamma-Al_2O_3$ membranes were as follows: $Pd-M/Al=4/1000$ and $Pd/M=3/1$ (mole ratio).

The membrane reactor was a two-tube reactor, the schematic diagram of which was shown in our previous work [14]. The membrane reactor consists of a glass and a membrane tube as the outer (i.d. 18 mm) and the inner (o.d. 12 mm) tubes, respectively. O-ring packing was used to seal the stainless-steel body of the reactor to the glass and the membrane tube at the two sides. Ethanol vapor carried by argon through the outer path encountered the packed catalyst bed ($Cu-P/SiO_2$, 40–60 mesh, $h=35$ mm) in the middle of the outer path. The ethanol vapor was continuously pumped to the catalyst bed at a W/F of 700–3000 g-cat-min/mol, and at a pressure of 120–125 KPa. There is a ΔP of 20 KPa between the retentate side (outer path) and permeate side (inner path) of the membrane reactor. The hydrogen produced in reaction permeate through the membrane into the inner tube, and was carried away by sweeping argon gas in concurrent way.

2.2. Characterization of membranes

Micromeritics ASAP 2000 apparatus employing nitrogen adsorption at 77 K was used to measure the pore size distribution of the membranes. The specific areas were determined by BET methods. Scanning electron microscopy (SEM) was carried out using a Hitachi-S-520 instrument. The X-ray diffraction (XRD) was performed using a Regaku Dmax-ra with nickel filtered $Cu K\alpha$ radiation. The gas permeation tests for H_2/N_2 gaseous mixtures were carried out in pressure (10 KPa)-over the outer and inner tube. The permeability was measured by a soap bubble flow meter. The mole ratio of the permeated or retained gas was determined by gas chromatography. The separation factor for equi-molar gaseous mixture of H_2 and

N₂ was defined as:

$$\alpha_{ij} = \frac{y_i x_j}{y_j x_i}$$

[15] where X_i, X_j, Y_i, Y_j were the mole ratio of the retained and permeated gas for i and j species, respectively.

2.3. Dehydrogenation of ethanol

The catalytic dehydrogenation of ethanol to acetaldehyde was performed in both conventional and the membrane reactors. The Cu–P/SiO₂ catalyst (Cu–2.6 wt%, Cu/P=5/1, mole ratio, 40–60 mesh) prepared by an ion-exchange method was reduced in hydrogen flow (80cm³/min) at 623 K for 2 h before being used in the reaction. An on-line gas chromatography with a thermal conductivity was used to analyze the products. A 4-meter-long Porapak P column was used to separate CH₃CHO, CH₃CH₂OH, CH₃CH₂OCH₂CH₃ and CH₃CH₂COOC₂H₅. The carrier gas is argon and the temperature of the column was 150°C. Products from both the outer and inner tubes were analyzed and then collected by two cold traps of liquid nitrogen–ethanol separately. The yield of acetaldehyde was calculated as:

$$y\% = \frac{(w_i y_i\% + w_o y_o\%)}{w_i + w_o}$$

[14] where y_i, y_o, w_i, w_o were the yield and weight of acetaldehyde in the inner and outer tube respectively.

3. Results and discussion

3.1. Characterization of membranes

The pore size distributions for Pd–M/γ–Al₂O₃ membranes were shown in Fig. 1. There are two peaks at 3–4 nm and 8–9 nm respectively for all five membranes. The first peak is larger than the second for all four Pd–M/γ–Al₂O₃ membranes, while for Pd/γ–Al₂O₃ membrane the second peak is the larger one. The portion of the larger peak increases with the following series: Pd–Ag/γ–Al₂O₃ < Pd–Ru/γ–Al₂O₃ < Pd–Rh/γ–Al₂O₃ < Pd–Ni/γ–Al₂O₃ < Pd/γ–Al₂O₃. The pore size of modified membranes is larger than that of a pure alumina membrane (3–4 nm), which was caused by the enlarged particle size in the sol when the metal salts was introduced [2]. The data of the average pore size, pore volume and specific surface area for the membranes were listed in Table 1. The pore size of the binary metal modified membrane is a little smaller than that of single Pd metal modified membrane, which was obviously caused by the addition of a second metal. The pore volumes of modified membranes also changed with the addition of different second metal

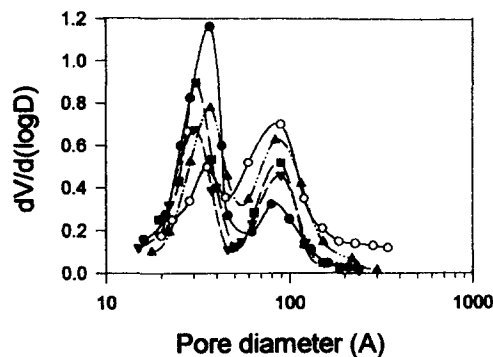


Fig. 1. Pore size distribution of different membranes. (●) Pd–Ag/ γ -Al₂O₃, (■) Pd–Ru/ γ -Al₂O₃, (▲) Pd–Rh/ γ -Al₂O₃, (▼) Pd–Ni/ γ -Al₂O₃, (○) Pd/ γ -Al₂O₃.

Table 1
Pore size and pore volume of different membranes

Membrane	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Pd–Ru/ γ -Al ₂ O ₃	237.64	0.32	4.68
Pd–Rh/ γ -Al ₂ O ₃	266.45	0.37	4.76
Pd–Ag/ γ -Al ₂ O ₃	258.16	0.40	5.35
Pd–Ni/ γ -Al ₂ O ₃	295.67	0.47	6.28
Pd/ γ -Al ₂ O ₃	280.10	0.50	6.65

M, so that the addition of metal ions into Boehmite sol had an important effect on the γ -alumina membranes, which caused the change of the textural properties of alumina membrane.

The fracture section of various Pd–M/ γ -Al₂O₃ membranes observed by SEM was shown in Fig. 2. It could be observed that the small pore layer was on the outside of the tube, and the thickness of membrane is 6–8 μ m. SEM provides clues to prove that the structure of the obtained membranes should be asymmetry.

The XRD patterns for various modified membranes were shown in Fig. 3. The major diffraction peaks in the XRD patterns for different modified membranes are mainly the four typical γ -Al₂O₃ diffraction peaks at 2θ angles of 37.6°, 39.5°, 45.9° and 66.8°. Dotted lines were given to identify these five γ -Al₂O₃ diffraction peaks. The diffraction peaks of palladium should be at the 2θ angles of 40.1°, 46.7° and 68.1°, which are the peaks of Pd(111), Pd(200) and Pd(220), respectively. The broadened peak at these angles showed that the metal particles are very small. So we can say that the metals introduced here are highly dispersed in the membrane.

The separation factor represents the efficiency of separation for a membrane, which quantitatively represents the perm-selectivity of the membrane. Fig. 4 showed the effect of the temperature on the separation factor of H₂/N₂ gaseous mixture. The pressure difference ($P-P'$) of the retentate and permeate sides was 1.5×10^4 Pa, and the molar ratio of the H₂ to N₂ was 1.0. It could be seen that the

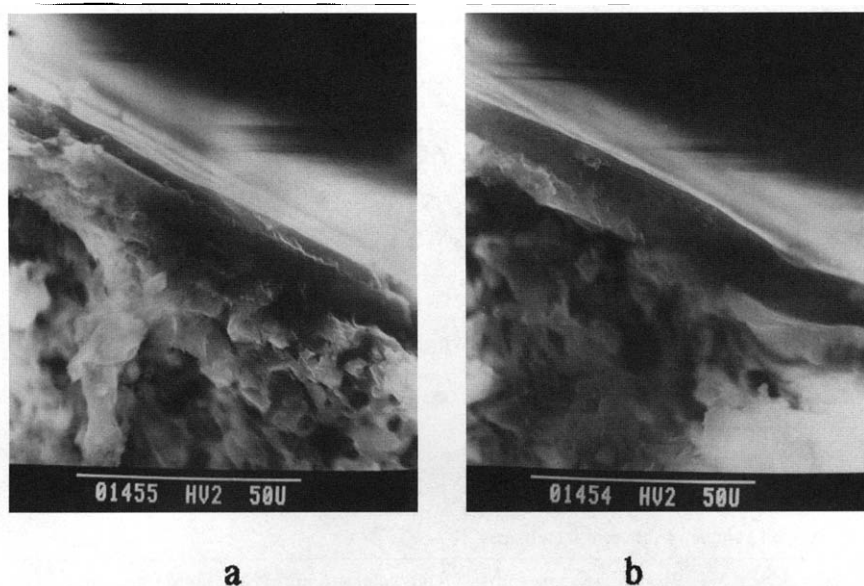


Fig. 2. Electron micrograph of the cross-section (a) Pd-Ru/ γ -Al₂O₃ (b) Pd-Ag/ γ -Al₂O₃ membrane.

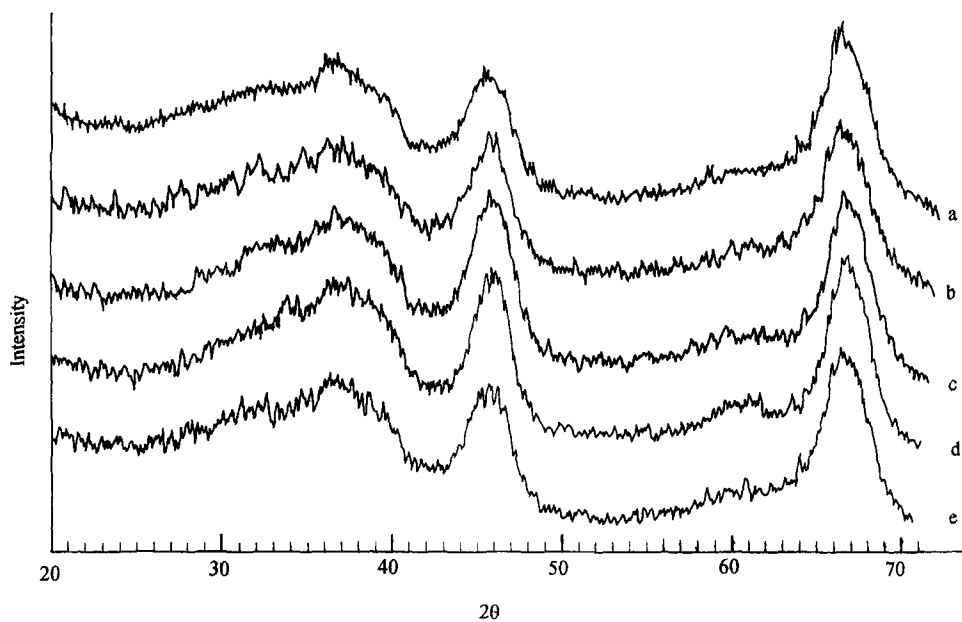


Fig. 3. XRD Pattern of different membranes. (a) Pd/ γ -Al₂O₃, (b) Pd-Ag/ γ -Al₂O₃, (c) Pd-Ni/ γ -Al₂O₃, (d) Pd-Rh/ γ -Al₂O₃, (e) Pd-Ru/ γ -Al₂O₃

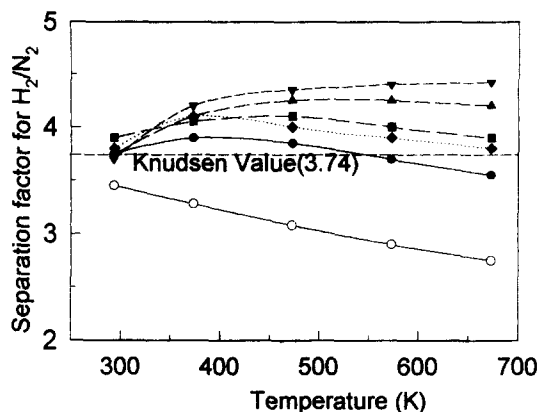


Fig. 4. Effect of temperature on the separation factor of different membranes. (▼) Pd-Ru/ $\gamma\text{-Al}_2\text{O}_3$, (▲) Pd-Ag/ $\gamma\text{-Al}_2\text{O}_3$, (■) Pd-Rh/ $\gamma\text{-Al}_2\text{O}_3$, (◆) Pd/ $\gamma\text{-Al}_2\text{O}_3$, (●) Pd-Ni/ $\gamma\text{-Al}_2\text{O}_3$, (○) pure $\gamma\text{-Al}_2\text{O}_3$. $\Delta P=1.5 \times 10^4$ KPa, $P_{\text{H}_2}/P_{\text{N}_2}=1.0$, Sweepflow rate=40 ml/min.

separation factor of the pure $\gamma\text{-Al}_2\text{O}_3$ membrane is lower than the theoretical Knudsen value(3.74), and decreases with the increase of the temperature, which is a little higher than the result of Chai et al. [12]. While for the Pd-M modified alumina membranes, the separation factor exceeds the theoretical Knudsen diffusion value, and almost rises with the increase of the temperature. The separation factor for different membranes increased as the following: $\gamma\text{-Al}_2\text{O}_3 < \text{Pd-Ni}/\gamma\text{-Al}_2\text{O}_3 < \text{Pd}/\gamma\text{-Al}_2\text{O}_3 < \text{Pd-Rh}/\gamma\text{-Al}_2\text{O}_3 < \text{Pd-Ag}/\gamma\text{-Al}_2\text{O}_3 < \text{Pd-Ru}/\gamma\text{-Al}_2\text{O}_3$. There is improvement of the selective permeation of H_2 in the Pd-M/ $\gamma\text{-Al}_2\text{O}_3$ composite membranes compared to pure alumina membranes, which can only be caused by the change of the transport mechanism. There is the selective surface diffusion [8] which enhances the separation performance. By introduction of the second metal M, such as Ru or Rh or Ag (the metal Ru or Rh itself absorb hydrogen strongly), there would be an interaction of the two metals and a Pd-M alloy effect appeared. Just as the palladium alloy membrane had exhibited [6,7], the Pd-M/ $\gamma\text{-Al}_2\text{O}_3$ membrane showed improved perm-selectivity to Pd/ $\gamma\text{-Al}_2\text{O}_3$ membrane.

3.2. Performance of the membrane reactors

The yield of acetaldehyde in various membrane reactors in relation to reaction temperature was shown in Fig. 5. The yield of acetaldehyde increased with increasing temperature in each reactor. The yield in conventional reactor was less than the equilibrium value, but for the modified membrane reactors, the yield of the acetaldehyde highly exceeded the equilibrium value. Particularly for the membrane reactors incorporating the Pd-Ru/ $\gamma\text{-Al}_2\text{O}_3$ membrane, the yield of acetaldehyde increased by 15% compared with the thermodynamic equilibrium values. And the yield of Pd-Ni/ $\gamma\text{-Al}_2\text{O}_3$ membrane reactor was slightly lower than that of Pd/ $\gamma\text{-Al}_2\text{O}_3$ membrane reactor. The variation of the yield for various

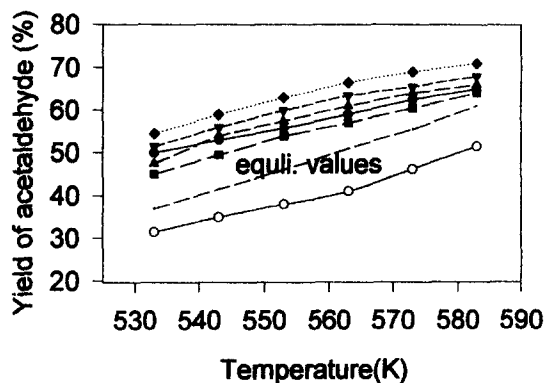


Fig. 5. Effect of reaction temperature on the yield of acetaldehyde in different reactors. (○) Conventional reactor, (◆) Pd–Ru/ γ -Al₂O₃, (▼) Pd–Ag/ γ -Al₂O₃, (▲) Pd–Rh/ γ -Al₂O₃, (●) Pd/ γ -Al₂O₃, (■) Pd–Ni/ γ -Al₂O₃.

membrane reactors was in accordance to the separation factor for different membranes. As the pressure difference (ΔP) between the retentate (feed) side and permeate side is always kept at 20 KPa, the back diffusion of the sweep argon gas is very small, and there is little decrease of the partial pressure of the reactants. The effect of the decrease of the partial pressure to the changes of the dehydrogenation yield can be ignored. It is the selective removal of the hydrogen results in the enhancement of the performance of the membrane reactors. In the Pd–Ru/ γ -Al₂O₃ membrane reactor, the modified membrane offers the best perm-selectivity of H₂, so the effect of the removal of the hydrogen is the most significant. The equilibrium is heavily displaced and shifted to the production side, which can be further confirmed by Fig. 7. The acetaldehyde yield in the membrane reactors is still much higher than that in the conventional reactor or equilibrium values when there is no sweep argon gas.

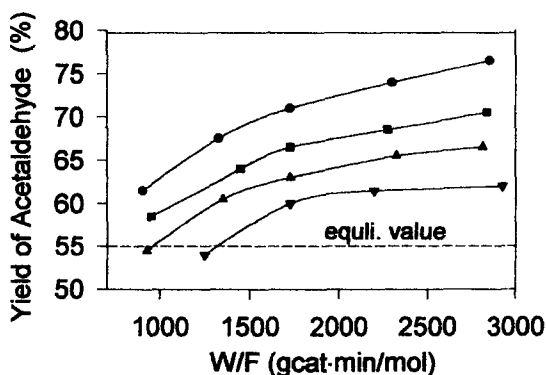


Fig. 6. Effect of W/F on the yield of acetaldehyde in different reactors. (●) Pd–Ru/ γ -Al₂O₃, (■) Pd–Ag/ γ -Al₂O₃, (▲) Pd–Rh/ γ -Al₂O₃, (▼) Pd–Ni/ γ -Al₂O₃. Reaction temperature: 553 K, Sweepflow rate: 40 ml/min.

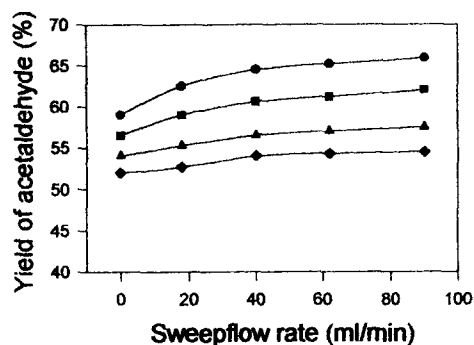


Fig. 7. Effect of sweepflow rate in different reactors. (●) Pd-Ru/γ-Al₂O₃, (■) Pd-Ag/γ-Al₂O₃, (▲) Pd-Rh/γ-Al₂O₃, (▼) Pd-Ni/γ-Al₂O₃.

The effect of feed rate of ethanol on the yield of acetaldehyde is shown in Fig. 6. The W/F varied between 700–3000 g·cat·min/mol. The figure shows that the feed rate played an important role in the efficiency of the membrane reactor. The yield of the acetaldehyde increased with increasing W/F , especially in the Pd-Ru/γ-Al₂O₃ membrane reactor. The increase of W/F leads to a longer contact time of the reactant with the catalyst bed and membrane. This was discussed in detail in our previous work [9].

Fig. 7 shows the effect of flow rate of argon on the yield of the membrane reactors. It shows that with the increase of the purge of argon passing through the inner tube to carry away the permeated hydrogen, the yield would increase continuously. The acetaldehyde yield increased most significantly in Pd-Ru/γ-Al₂O₃ membrane reactor when sweeping rate was increased.

4. Conclusion

Pd-M/γ-Al₂O₃ composite membranes were prepared by a Boehmite sol modified with binary metal salts. The characterization of membranes by SEM, XRD, nitrogen adsorption shows that membranes are uniform with average pore size 5–7 nm, and the metals introduced are highly dispersed in the membranes. Introducing a second metal into the membrane leads to the reduction of the pore size of the Pd modified membrane. It can also be suggested that there is an interaction between the two metals, just like the conventional active catalyst on porous supports. The binary metals modified alumina membranes showed a behaviour like that of palladium alloy membranes, there is the improvement of the permselectivity for hydrogen. A very high yield of direct dehydrogenation of ethanol to acetaldehyde can be achieved. All this shows prospects for industrial process of the direct catalytic dehydrogenation of ethanol to acetaldehyde.

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