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Exploration of cinnamaldehyde hydrogenation in Co–Pt/γ-Al_2O_3 catalytic membrane reactors

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The feasibility of Co–Pt/γ-Al_2O_3 catalytic membrane reactors for cinnamaldehyde hydrogenation has been explored. The results of hydrogenation in four membrane reactors with different configurations indicate that the effect of the gas transport limitation is more important than the liquid diffusion limitation. The membrane with the catalytic layer situated on the gas side shows the highest activity due to the minimized gas transport limitation.

Keywords: cinnamaldehyde hydrogenation, three-phase membrane reactor, mass transfer limitation

1. Introduction

Selective hydrogenation of α,β-unsaturated aldehyde to produce unsaturated alcohol has attracted attention because of its importance in the fine chemicals industry [1,2]. However, the mass transfer resistance has been recognized as the key problem in carrying out these multiphase reactions involving hydrogen, due to its limited solubility in liquid. Therefore, cinnamaldehyde, a typical member of α,β-unsaturated aldehydes, is conventionally hydrogenated in a slurry reactor with powdered catalysts under stirring and high pressures [2,3], in order to improve the hydrogen mass transfer and the contact of gas–liquid–solid phases. For three-phase hydrogenation processes, much research work has been focused on new reactor configurations for minimizing the mass transport limitation. Vos [4] converted a heat exchanger into a cross-flow reactor for the hydrogenation of liquid p-xylene and 1,4-di-*tert*-butylbenzene. Akyurtlu [5] studied a tubular catalytic porous-wall configuration for three-phase reactions. More recently, several reports and new ideas [6–9] about catalysis in three-phase membrane reactors were presented at the Third International Conference on Catalysis in Membrane Reactors (ICCMR-3). However, the feasibility of three-phase membrane reactors for the selective hydrogenation of cinnamaldehyde has never been reported. The above together with the tedious problem of powdered catalyst separation and recovery in the slurry reactors motivated the exploration of cinnamaldehyde hydrogenation in catalytic membrane reactors. This paper focuses on the feasibility of Co–Pt/γ-Al_2O_3 catalytic membrane reactors for cinnamaldehyde hydrogenation.

2. Experimental

A tubular α-Al_2O_3 membrane with outer diameter of 15 mm, inner diameter of 11.5 mm and pore size of 0.6 μm was used as the support. A thin toplayer of mesoporous γ-Al_2O_3 membrane was deposited on the support membrane by slip casting of γ-AlOOH sol [10,11]. Cobalt and platinum were incorporated in the thin layer of γ-Al_2O_3 by a deposition–precipitation method with a $Co(NO_3)_2$ and H_2PtCl_6/urea solution [12,13]. The weight ratio of Co/Pt is chosen as 100/5 according to our previous paper [14]. The morphology of the membrane cross-section was examined by scanning electron microscopy (SEM) on a JSM-5600LV equipment. Energy dispersive X-ray analysis (EDX) was performed on an Oxford ISIS-300 equipment to detect the distribution of cobalt and platinum in the membrane.

The schematic diagram of the membrane reactor is shown in figure 1. Liquid reactant of cinnamaldehyde/ethanol solution (10/90 vol%) was introduced into the tube side, and hydrogen was fed into the shell side of the mem-

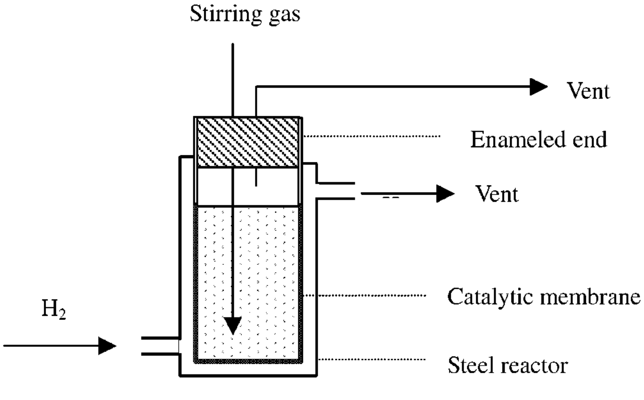

Figure 1. Schematic of three-phase membrane reactor for the hydrogenation of cinnamaldehyde.

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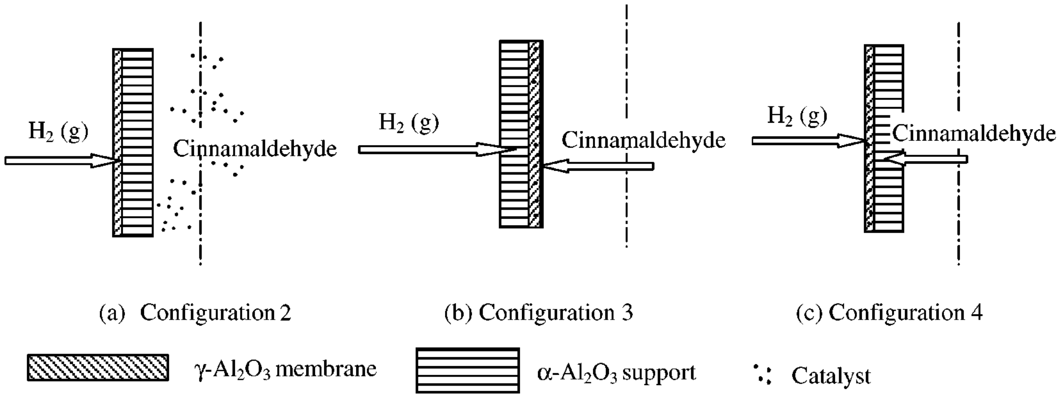

Figure 2. Schematic illustration of different membrane configurations.

brane. Nitrogen (10 ml/min) was fed into the tube side as a bubbling gas in order to mix well the mixture of cinnamaldehyde/ethanol solution. The volume of the solution is 10 ml normally. Reactions were conducted at 50 °C and 1.6 atm, followed by withdrawing 0.2 μl samples with a syringe from the reaction system at certain intervals. A GC-8820 instrument analyzed the products of hydrogenation with a FID detector and a PEG-20M column of 30 m.

Different membrane configurations were designed to evaluate the relative significance of the gas and liquid transport limitations. They are illustrated schematically in figure 2. In configuration 2, the membrane is pure γ-Al_2O_3 located on the outer surface of support α-Al_2O_3. The catalysts were put together with liquid reactant in the tube side. In configuration 3, the catalytic membrane was deposited on the inner side and deposited on the outer side in configuration 4.

3. Results and discussion

A SEM micrograph of the catalytic membrane cross-section is shown in figure 3. The thickness of the toplayer of the γ-Al_2O_3 membrane can be well recognized to be around 12 μm. γ-Al_2O_3 provides a support with a large BET surface area of 320 m^2/g [10] to disperse the active species. The thin γ-Al_2O_3 with 4.8 nm pore size [11] confines the deposited cobalt in the toplayer with a uniform distribution, as detected by EDX line scanning across the cross section of the membrane. But platinum is not detected due to its too low concentration.

According to the literature data, the major products of the hydrogenation reaction of cinnamaldehyde are dihydrocinnamaldehyde (B), cinnamyl alcohol (C) and 3-phenyl-1-propanol (D), as illustrated in figure 4. B is the thermodynamically favored product, and C is the aimed product. Reactions in different configurations were carried out under the same conditions and the results are shown in table 1. In our laboratory, 10 wt% Co–0.5 wt% Pt/Al_2O_3 has been shown to be an excellent catalyst with selectivity to product C as high as 95% in a slurry reactor [15]. However, in the membrane reactors of this paper, the selectivity is relatively lower, and the selectivity to B is sometimes observed to be as high as 20% during the experiments. This is probably related to the state of the catalysts, since the hydrogenation of the two unsaturated bonds C=O and C=C is sensitive to the state of the active catalysts. However, further work is underway to clarify the reasons.

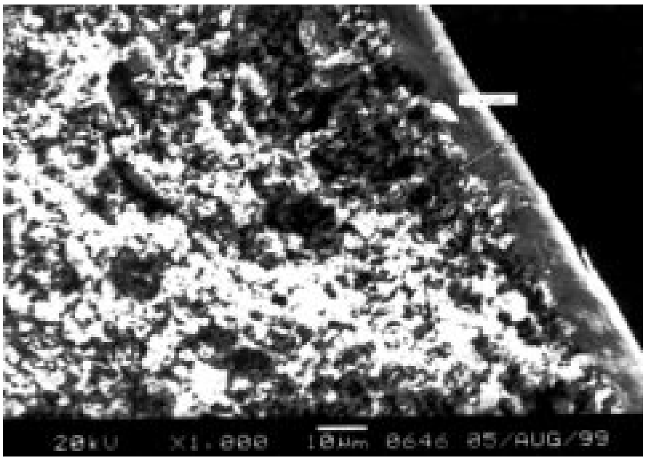

Figure 3. SEM micrograph of the cross-section of the catalytic membrane.

The performance in configuration 1 confirmed that pure γ-Al_2O_3/α-Al_2O_3 membrane almost does not contribute to the cinnamaldehyde hydrogenation. In configuration 2, powdered 10 wt% Co–0.5 wt% Pt/γ-Al_2O_3 catalysts (containing 25 mg Co, prepared by impregnation [15]) were put in the tube side of the pure γ-Al_2O_3/α-Al_2O_3 membrane. After 10 h, the conversion of cinnamaldehyde was still as low as 2.1%. In configuration 3, namely a Co–Pt/γ-Al_2O_3 membrane reactor, with Co and Pt catalysts deposited on the inner wall of the membrane, cinnamaldehyde was rapidly converted to cinnamyl alcohol with a selectivity of 69%. By contrast, the conversion of cinnamaldehyde in configuration 4 was much higher than that in the former three membrane reactors. After 1 h, the conversion was 7.8%, which was twice that in configuration 3. The difference in activities was even much more significant with the stream of time. The comparison between these two configurations is more obviously seen in figure 5. In configuration 4, Co and Pt catalysts were deposited on the outer wall of the

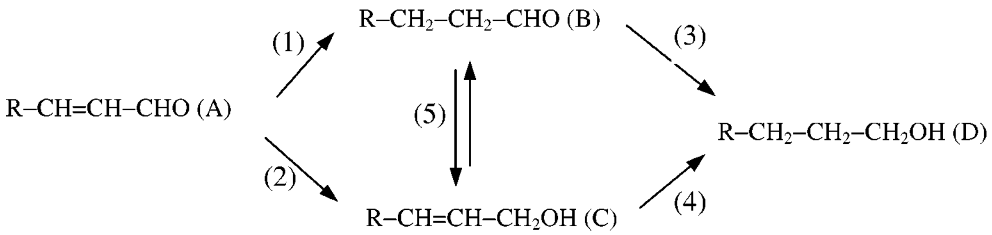

Figure 4. Possible reaction pathways in the hydrogenation of cinnamaldehyde.

Table 1
Selective hydrogenation of cinnamaldehyde in different membrane reactors.

No.	Configuration	Time (h)	Conversion (%)	Selectivity of C=O
1	γ-Al_2O_3/α-Al_2O_3	1	–[a]	–
		10	0.6	56
2	γ-Al_2O_3/α-Al_2O_3 + Co–Pt/γ-Al_2O_3 catalyst[b]	1	–	–
		10	2.1	57
3	Co–Pt/γ-Al_2O_3[c] membrane (inner)	1	3.8	69
		10	8.8	65
4	Co–Pt/γ-Al_2O_3[d] membrane (outer)	1	7.8	68
		10	43.7	75

[a] Conversion or selectivity undetectable.
[b] 25 mg Co.
[c] 25 mg Co deposited on the inner wall of the membrane.
[d] 23 mg Co deposited on the outer membrane wall.

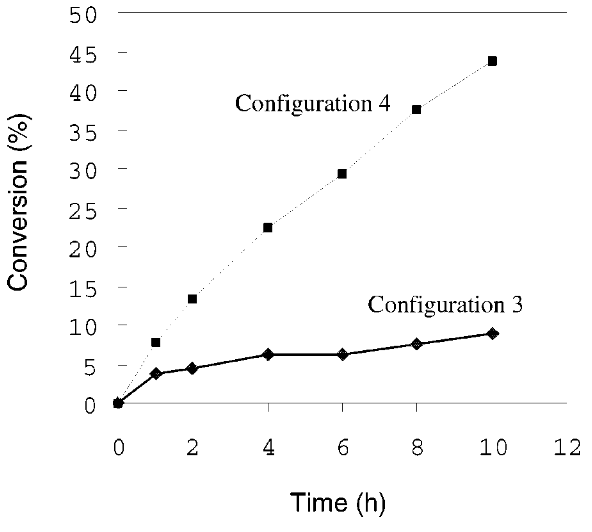

Figure 5. Comparison of cinnamaldehyde hydrogenation in different membrane reactor configurations. Configuration 3: catalytic membrane is located on the inner wall. Configuration 4: catalytic membrane located on the outer wall.

γ-Al_2O_3 membrane. Thus, it can be seen that different configurations of membrane reactors can influence greatly the activity in cinnamaldehyde hydrogenation.

Different activities in the latter three reactors are attributed to the different diffusion paths for the gas and the liquid. In all membranes, the pores are filled with liquid because of the capillary forces. In configuration 2, the catalysts are immersed in the liquid directly. The gas has to diffuse first through liquid channels of the membrane pores, and then through the liquid film covering the solid catalysts, as in the case of conventional three-phase hydrogenation. It is well known that the availability of hydrogen on the catalyst surface can strongly affect the conversion and selectivity in heterogeneous hydrogenation [16]. In configuration 3, the catalysts incorporated into the γ-Al_2O_3 membrane on the inner membrane wall are more accessible to hydrogen than those immersed in the liquid reactant. Therefore, it is reasonable that the catalytic membrane in configuration 3 shows higher activity than that in configuration 2. However, hydrogen still has difficulty in access to the catalysts in the inner wall of the membrane in this configuration, although the liquid diffusion limitation has been minimized. In the case of configuration 4, the contact between gas, liquid and solid is improved, because hydrogen does not necessarily diffuse through a liquid film covering the solid catalysts, as in a conventional reactor [17]. In contrast, hydrogen is directly adsorbed and activated on the catalytic layer of Co–Pt/γ-Al_2O_3. The liquid reactant contacts with the catalysts and the activated hydrogen by capillary forces of the membrane pores. Although there is liquid diffusion limitation for the product cinnamyl alcohol, the activity is still much higher than that in configuration 3, which is controlled by the gas transport limitation. The results in configurations 3 and 4 show that the effect of cinnamyl alcohol diffusion in the membrane pores is less significant than that of hydrogen transport limitation on the activity of cinnamaldehyde hydrogenation. If the gas transport limitation is minimized, a high activity can be expected in catalytic membrane reactors.

By incorporating the catalysts into the thin membrane, the tedious separation and recovery of catalyst from the slurry reactor can be avoided. Through feeding gas on the catalyst side and the liquid on the other side, the gas transport limitation is reduced and hydrogen is more efficiently supplied to the catalysts. However at the same time, the liquid diffusion limitation, especially the products diffusion in the pores, will become relatively more significant compared to the slurry reactor, although it has been shown that gas transport limitation is a more important issue in the membrane reactor. So further work is directed to study the extent of liquid diffusion limitation on the hydrogenation of cinnamaldehyde.

These results are preliminary but promising. However, mathematical modeling and systematical experiments are necessary in order to learn the reaction mechanism in the membrane reactors. Optimum conditions are to be found to obtain higher conversion and selectivity.

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References

[1] J. Jenck and J.E. Germain, J. Catal. 65 (1980) 141.

[2] A. Giroir-Fendler, D. Richard and P. Gallezot, Stud. Surf. Sci. Catal. 41 (1988) 171.

[3] D. Richard, P. Fouilloux and P. Gallezot, in: *Proc. 9th Int. Congress on Catalysis*, Calgary (Chemical Institute of Canada, Ottawa, 1988) p. 1074.

[4] R. de Vos, G. Smedler and N.-H. Schöön, Ind. Eng. Chem. Process Des. Dev. 25 (1986) 197.

[5] J.F. Akyurtlu, A. Akyurtlu and C.E. Hamrin, Jr., Chem. Eng. Commun. 66 (1988) 169.

[6] J.A. Dalmon, in: *III Int. Conf. Catal. Membrane Reactors*, Copenhagen, Denmark, September 1998, p. L3.

[7] O.M. Ilinitch, F.P. Cuperus, L.V. Nosova and E.N. Gribov, in: *III Int. Conf. Catal. Membrane Reactors*, Copenhagen, Denmark, September 1998, p. 011.

[8] W.F. Maier, C. Lange, I. Tilgner and B. Tesche, in: *III Int. Conf. Catal. Membrane Reactors*, Copenhagen, Denmark, September 1998, p. 022.

[9] J.W. Veldsink, O.M. Ilinitch and F.P. Cuperus, in: *III Int. Conf. Catal. Membrane Reactors*, Copenhagen, Denmark, September 1998, p. 7.

[10] A.W. Li, H.B. Zhao, J.H. Gu and G.X. Xiong, Sci. Chin. B 40 (1997) 31.

[11] A.W. Li, H.B. Zhao, J.H. Gu and G.X. Xiong, Chin. Sci. Bull. 42 (1997) 791.

[12] H.B. Zhao, D.J. Draelants and G.V. Baron, Catal. Today 56 (2000) 229.

[13] L.M. Knijff, P.H. Bolt, R. van Yperen, A.J. van Dellen and J.W. Geus, in: *Preparation of Catalysts*, Vol. V, eds. B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1991) p. 165.

[14] B.J. Liu, G.X. Xiong, W.S. Yang and S.S. Sheng, Mol. Catal. 13 (1999) 424 (in Chinese).

[15] G.X. Xiong, B.J. Liu, X.L. Pan, W.S. Yang and S.S. Sheng, Chinese Patent 99 1 12959.8.

[16] P.N. Rylander, *Catalytic Hydrogenation in Organic Synthesis* (Academic Press, New York, 1979).

[17] J. Zaman and A. Chakma, J. Membr. Sci. 92 (1994) 1.