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Selective hydrogenation of cyclopentadiene in a catalytic cellulose acetate hollow-fiber reactor

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A catalytic membrane reactor was established with catalytic hollow fibers prepared by supporting polymer anchored palladium catalysts on the inside wall of cellulose acetate hollow fibers. The selective hydrogenation of cyclopentadiene was carried out in the catalytic membrane reactor at 40°C in two ways: (1) by hydrogen permeating into the hollow fibers, and (2) by hydrogen premixed in the gas phase.

Keywords: catalytic hollow fiber reactor; selective hydrogenation; cyclopentadiene; palladium catalyst

1. Introduction

Membrane catalysis has attracted considerable attention in recent years. Much effort has been devoted to the studies of using inorganic membrane reactors in various reactions such as dehydrogenation, hydrogenation, oxidation etc. [1–5]. Polymer membranes have more versatile applicability in separation processes because the polymer membranes show satisfactory diffusivity and solubility, and most of the polymers can be easily fabricated in a number of forms (hollow fiber, spiral wound, etc.). However, only a few polymer membrane reactors have been reported. To our knowledge, although some non-catalytic polymer membrane reactors have been described in the literature [6,7], there has been no report on using catalytic polymer membrane reactors in chemical reactions up to now.

The selective hydrogenation of conjugated diene is an important reaction in the fine chemical industry and organic synthesis. A number of polymer-supported palladium catalysts have been used to catalyze this reaction under mild conditions [8]. Although the selectivity of some polymer-supported palladium catalysts is very high in the liquid-phase reaction, it is generally much lower in gas-phase hydrogenation, which is more convenient in chemical industry since there is no need for the

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process of separating products from the reaction solvent and catalyst. We have previously reported [9] that the selectivity of the polymer-anchored palladium catalysts in the hydrogenation of diene to its monoene is strongly influenced by the hydrogen partial pressure in the gas-phase reaction. It is also known that, for hydrogenation, the metallic palladium membrane reactors are often more selective than the non-membrane catalysts because side reactions are repressed owing to the effectively lower hydrogen pressure [10,11]. Therefore, it is anticipated that the catalytic membrane reactor made from polymer-supported palladium complexes should efficiently catalyze the selective hydrogenation of diene just as the metallic palladium membrane reactors.

In this study, we prepared the catalytic membrane by supporting polymer anchored palladium catalyst on the inside wall of the cellulose acetate fibers, and established a catalytic membrane reactor. As a model reaction, the selective hydrogenation of cyclopentadiene to cyclopentene has been carried out in this catalytic hollow-fiber reactor.

2. Experimental

The hollow fibers used for supporting the palladium catalyst were commercially available cellulose acetate (CA) hollow fibers (Hangzhou Water Treatment Center). The CA hollow fibers have a thin outer dense layer (with an average pore diameter of about 15 Å) supported by a microporous sponge layer. The inside and outside diameters of the fibers are 0.15 and 0.45 mm respectively. Fifty fibers were held together at both ends by epoxide resin. Effective total inner and outer surface areas of the hollow fibers (50 cm each in length) in the module are 118 and 353 cm^2 respectively. The water solution of a poly(N-vinyl-2-pyrrolidone) (PVP) anchored palladium complex (which was prepared by the reaction of PVP (1.4 g) and $PdCl_2$ (0.09 g) in 40 ml water at room temperature for 24 h) was pumped through the inside pore of the hollow fibers with a circulating pump for 6 h. Then, an aqueous solution of hydrazine (5%) was pumped through the inside pore of the fibers for 1 h. After drying in vacuum at room temperature, the catalytic hollow fibers were obtained with 1.3% of the PVP anchored palladium complex retained by the inside sponge layer of the fibers (Pd content in the final catalytic membrane reactor is 1.13 mg). The catalytic CA hollow fibers prepared this way are deeply colored (greyish black) by the presence of palladium and this color cannot be washed away by water, while the original fibers are white in color. However, $PdCl_2$ itself cannot be supported on the inside wall of the fibers by this method.

Fig. 1 shows the microphotographs of the cross-sections of the original and catalytic CA fibers. It can be seen that the internal microporous layer of the fiber is black colored. This indicates that the PVP–Pd complex is retained in the microporous layer. The permeabilities of H_2 and N_2 in the original and catalytic CA fibers are given in table 1.

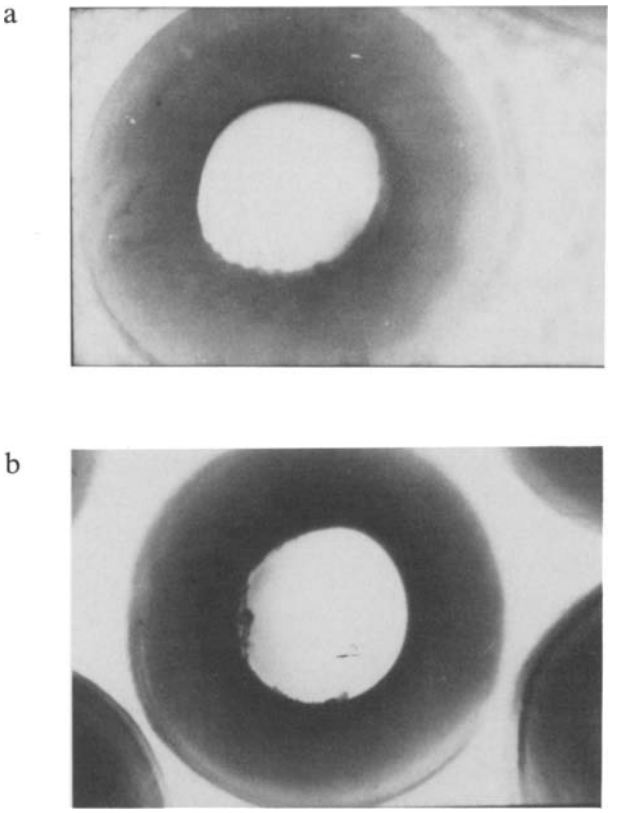

Fig. 1. Photographs of the cross-sections of the original and catalytic CA fibers. (a) Original CA fiber (120× magnification), (b) catalytic CA fiber (120×magnification).

Figs. 2 and 3 illustrate the structure of the catalytic hollow-fiber reactor and the schematic diagram of the experimental unit, respectively. The catalytic reactor consists of the catalytic hollow fibers and a jacketed glass tube. Heaters 4 and 5 were used to preheat the reactants (hydrogen and cyclopentadiene). The temperature of the circulating water passing through the jacket and heaters 4 and 5 was the same and was controlled by a thermostat. Cyclopentadiene was sufficiently preheated for a suitable vapor pressure by heater 6 and then passed by a feed of nitro-

Table 1
Permeability of H_2 and N_2 in the original and catalytic CA fibers [a]

Hollow fiber	Permeability (cm^3/cm^2 s cm Hg)		Permselectivity (α_{H_2/N_2})
	H_2	N_2	
CA	1.15×10^{-4}	2.90×10^{-5}	4.0
catalytic CA	1.10×10^{-5}	4.60×10^{-7}	23.9

[a] Driving pressure 5 atm, room temperature.

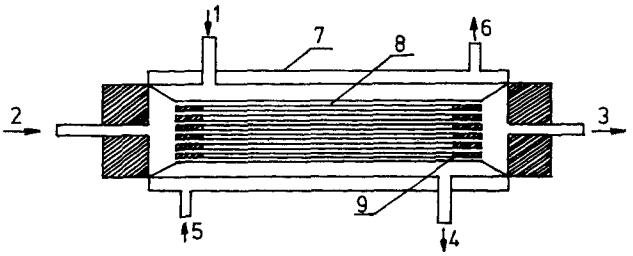

Fig. 2. Structure of the catalytic CA hollow fiber reactor. (1) $H_2 + N_2$ feed inlet; (2) cyclopentadiene feed inlet; (3) product outlet; (4) tail gas outlet; (5, 6) circulating water, inlet and outlet; (7) glass jacket; (8) catalytic CA hollow fibers; (9) epoxide resin seal.

gen through condenser 3 to the inside of the hollow fibers. The amount of the cyclopentadiene feed was controlled by adjusting the temperature of condenser 3 with a thermostat and the flow rate of nitrogen feed gas. The temperature of heater 6 was generally 10°C higher than that of condenser 3. A mixture of hydrogen and nitrogen was passed through the outside wall of the fibers. The products were analyzed with a gas chromatograph.

3. Results and discussion

The hydrogenation of cyclopentadiene was carried out in the catalytic hollow-fiber reactor at 40°C in two ways: (1) by hydrogen permeating the hollow fibers, in which a mixture of hydrogen and nitrogen flowed through the outside of the fibers and cyclopentadiene was fed with nitrogen into the inside pore of the fibers; and (2) by hydrogen premixed in the gas phase, in which cyclopentadiene was fed with a mixture of hydrogen and nitrogen into the inside pore of the fibers.

In the selective hydrogenation of cyclopentadiene to cyclopentene by permeated hydrogen, the concentration of cyclopentadiene at every section along the fibers

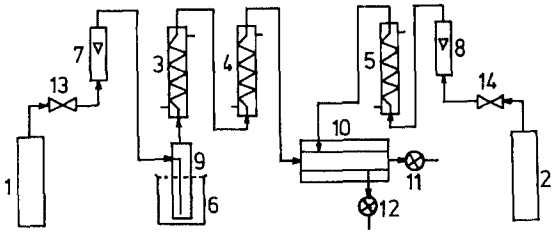

Fig. 3. Schematic flow diagram of the hydrogenation of cyclopentadiene in a catalytic CA hollow fiber reactor. (1) Carrier gas (N_2); (2) $H_2 + N_2$; (3) condenser at constant temperature with a thermostat; (4, 5, 6) preheater; (7, 8) rotameter; (9) flask containing cyclopentadiene; (10) membrane reactor; (11, 12) sampling port; (13, 14) needle valve.

can be kept much higher than that of hydrogen, so that further hydrogenation of the cyclopentene formed can be effectively inhibited by the presence of an excess of cyclopentadiene. However, the feed ratio of cyclopentadiene and hydrogen as a whole can still be maintained at 1 : 1. Nevertheless, if pure hydrogen is used on the outside of the hollow fibers, the hydrogenation selectivity is still not high enough due to a gradual decrease of the cyclopentadiene concentration along the inside pore of the fibers, while the amount of the permeated hydrogen keeps constant at every section of the fibers. For instance, a selectivity to cyclopentene of 87.5% was obtained at a cyclopentadiene conversion of 79% when pure hydrogen was used on the outside of the hollow fibers. Therefore, in the following experiments, we use a gas mixture (H_2 and N_2) instead of pure hydrogen on the outside of the hollow fibers. Thus, a concentration gradient of hydrogen can be formed between the inlet and outlet of the reactor to match with that of the cyclopentadiene, and this concentration gradient of hydrogen can be adjusted by the flow rate of the gas mixture ($H_2 + N_2$) outside the fibers. Table 2 shows the hydrogenation of cyclopentadiene by the permeated hydrogen. The gas flowing through the outside of the fibers was a mixture of hydrogen and nitrogen at a ratio of 1 : 1. It can be seen that the conversion of cyclopentadiene increases with the increase of the flow rate of the H_2 and N_2 mixture, but the selectivity for the formation of cyclopentene decreases. This is due to the fact that with the increase of the flow rate of the H_2 and N_2 mixture, the amount of the hydrogen permeating into the inside pore of the fibers is increased since the concentration gradient of the hydrogen along the outside of the fibers is decreased. This results in an increase of the hydrogenation rate of cyclopentadiene. On the other hand, with the increase of permeated hydrogen, the efficiency of cyclopentadiene inhibiting the further hydrogenation of cyclopentene to cyclopentane is decreased. When the flow rate of the H_2 and N_2 mixture is 3.7 ml/min (in this case the ratio of the H_2 flow rate and the cyclopentadiene flow rate is 1.32), both the conversion of cyclopentadiene and the selectivity of the cyclopentene are up to 91%. This indicates that under the reaction conditions, the concentrations of cyclopentadiene and the permeated hydrogen at every section along the inside pore of

Table 2
Hydrogenation of cyclopentadiene by the permeated hydrogen [a]

Flow rate of $H_2 + N_2$ (1 : 1) (ml/min)	TOF [b] ($molH_2$/molPd min)	Conversion (%)	Selectivity [c] (%)
3.4	4.7	74	93
3.7	5.9	91	91
4.0	6.2	93	88
4.7	7.4	99	74
5.6	7.9	99	66

[a] Reaction conditions: Pd content in the reactor 1.13 mg, cyclopentadiene 1.4 ml/min and nitrogen 12 ml/min inside the fibers, 40°C, 0.1 MPa.
[b] Turnover frequency related to palladium.
[c] Selectivity of cyclopentene (cyclopentene/(cyclopentane + cyclopentene)).

the fibers are well matched with each other. In this case, there is only very little unreacted H_2 left in the tail gas (less than 2%). It should be mentioned that although the permeability of cyclopentadiene and its hydrogenation products is relatively low in the CA fibers used, there is still a part of them diffused through the membrane into the outside of the fibers (corresponding to 9% of the total cyclopentadiene added).

The results of the hydrogenation of cyclopentadiene by the premixed hydrogen are listed in table 3. With the premixed hydrogen, the conversion of cyclopentadiene increases with the increase of the hydrogen partial pressure in the gas mixture, while the selectivity for the formation of cyclopentene decreases. However, the conversion of cyclopentadiene and the selectivity of cyclopentene cannot simultaneously be up to more than 90% by adjusting the hydrogen partial pressure of the gas mixture. From the data shown in table 3, it can also be seen that, when there is 27% residual cyclopentadiene and 20% H_2 remains unreacted, the selectivity for cyclopentene is up to 90%; when the residual cyclopentadiene is reduced below 2%, the selectivity for cyclopentene is only 76% or even lower. This suggests that a higher concentration of cyclopentadiene can strongly inhibit the further hydrogenation of cyclopentene.

It is worth to mention that the activity of the catalytic CA hollow fibers is very stable during the selective hydrogenation of cyclopentadiene by the permeated hydrogen or by the premixed hydrogen. This indicates that the PVP–Pd complex is firmly retained in the microporous structures of the fibers.

4. Conclusions

It is concluded that in the palladium-containing CA hollow-fiber reactor, the selective hydrogenation of cyclopentadiene can be conducted smoothly under the mild conditions of 40°C and 0.1 MPa. The selective hydrogenation of cyclopentadiene to cyclopentene can be performed more effectively by the permeated hydrogen than by the hydrogen premixed in the gas phase.

Table 3
Hydrogenation of cyclopentadiene by the premixed hydrogen [a]

H_2/C_5H_6 (v : v)	TOF (molH_2/molPd min)	Conversion (%)	Selectivity [b] (%)
1.44	8.7	99.5	52
1.22	7.2	98.1	76
1.0	4.9	73.0	90

[a] Reaction conditions: flow rate of $H_2 + N_2$ 12 ml/min, cyclopentadiene 1.4 ml/min, 40°C, 0.1 MPa.
[b] Selectivity of cyclopentene (cyclopentene/(cyclopentene + cyclopentane)).

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References

[1] V.M. Gryaznov, Vestn. Akad. Nauk SSSR (1986) 21.
[2] N.M. Mikahlenko, E.V. Khrapova and V.M. Gryaznov, Kinet. Katal. 27 (1986) 138.
[3] N. Itoh, AIChE J. 33 (1987) 1576.
[4] N.L. Basov and V.M. Gryaznov, Membr. Katal. (1985) 117.
[5] V.M. Gryaznov, V.I. Vedernikov and S.G. Gul'yanova, Kinet. Katal. 27 (1986) 142.
[6] I.K. Song, W.Y. Lee and J.J. Kim, Catal. Lett. 9 (1991) 339.
[7] I.K. Song, W.Y. Lee and J.J. Kim, Appl. Catal. A 96 (1993) 53.
[8] F.R. Hartley, *Supported Metal Complexes* (Reidel, Dordrecht, 1985).
[9] H. Gao, Y. Xu, S. Liao, R. Lui and D. Yu, J. Appl. Polym. Sci. 50 (1993) 1035.
[10] G.W. Parshall and W.A. Nugent, CHEMTECH (1988) 376.
[11] M.M. Ermilova, N.V. Orekhova, L.S. Morazora and E.V. Skakunova, Membr. Katal. (1985) 70.