

# Selective hydrogenation of cyclopentadiene in mono- and bimetallic catalytic hollow-fiber reactors

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## Abstract

The mono- and bimetallic catalytic polymeric hollow-fiber reactors were established with catalytic polymeric cellulose acetate (CA) hollow fibers prepared by supporting the polymer-anchored mono- or bimetallic catalyst in/on the inner wall of the hollow fibers. The selective hydrogenation of cyclopentadiene to cyclopentene was efficiently carried out in the above catalytic polymeric hollow-fiber reactors, especially in the  $\text{NaBH}_4$  reduced bimetallic PVP–Pd–0.5Co/CA hollow-fiber reactor under mild conditions of 40°C and 0.1 MPa. It was found that there was a remarkable synergic effect of palladium and cobalt reduced by  $\text{NaBH}_4$  in the bimetallic PVP–Pd–0.5Co/CA hollow-fiber reactor, which results in a 97.5% conversion of cyclopentadiene and a 98.4% selectivity for cyclopentene. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic hollow-fiber reactor; Polymer-anchored mono- and bimetallic catalysts; Synergic effect; Selective hydrogenation; Cyclopentadiene

## 1. Introduction

The selective hydrogenation of cyclopentadiene to cyclopentene is a very useful reaction in the fine chemical industry and organic synthesis. Cyclopentene is of commercial interest as a raw material for the manufacture of polycyclopentene. Generally, this reaction can be realized by using heterogeneous catalysts under relatively higher pressure and temperature. If the complex catalysts such as polymer-supported palladium catalysts are used, the reaction can be conducted under mild conditions [1,2]. The se-

lectivity for the desired product is higher in the liquid-phase reaction than that in the gas-phase reaction, while the latter is more convenient in chemical industry since there is no need for the process of separating products from the reaction solvent and catalyst. Recently, many of the inorganic or organic catalytic membranes instead of non-membrane catalysts have been used for partial oxidation reaction, dehydrogenation reaction, selective hydrogenation reaction, etc., and the selectivity is relatively high because side reactions are repressed [3–7]. However, most of the investigations on the catalytic membranes have been focused on the application of metal or inorganic membranes [8–17], the reports concerning the organic membrane reactors in which the membrane plays both the role of

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catalyst and separating material or the latter are still few [5–7,18–20].

In our recent study, we have found that the selective hydrogenation of cyclopentadiene in the gas-phase reaction can efficiently be carried out in a monometallic catalytic cellulose acetate hollow-fiber reactor [5,6,21], but the conversion of cyclopentadiene and the selectivity for cyclopentene cannot be more than 95% simultaneously. It is well known that many bimetallic catalysts have been reported in the homogeneous and polymer-anchored catalysis for the enhancement of reaction rates, selectivities or activities of the catalysts [22–29]. Furthermore, it has been found that when using a bimetallic catalytic hollow-fiber reactor for the selective hydrogenation of butadiene in crude 1-butene, there is a remarkable synergic effect of the bimetallic catalyst in the reactor for inhibiting the isomerization of 1-butene and improving the selectivity for 1-butene [30]. So it is reasonable to expect that the bimetallic polymeric hollow-fiber catalysts may be effective for improving the selectivity for cyclopentene and/or the conversion of cyclopentadiene still further.

In this paper, we study the catalytic performance of mono- and bimetallic catalytic hollow fibers, which were prepared by supporting the soluble polymer-anchored mono- or bimetallic complex on/in the inner micropores of the hollow fibers, using the selective hydrogenation of cyclopentadiene as a model reaction. The polymer-anchored mono- or bimetallic catalyst supported in the hollow fibers was reduced by  $\text{NH}_2\text{NH}_2$  or  $\text{NaBH}_4$ . The improvement of the selectivity for cyclopentene was significant and the synergic effect of the bimetallic catalyst was remarkable.

## 2. Experimental

### 2.1. Materials

Cellulose acetate (CA) hollow fibers were provided by the Hangzhou Water Treatment

Center. The CA fibers had a thin dense outer layer supported by a microporous sponge inner layer. The inside and outside diameters of CA hollow fibers were 0.15 and 0.45 mm, respectively. The pore diameter of the porous layer of CA was around 2–20 Å. Poly(*N*-vinyl-2-pyrrolidone) (PVP,  $K = 27\text{--}33$ ), ethyl cellulose (EC,  $M_w = 62,000$ ) and melamine-formaldehyde resin (AR) were the products of BASF, Dow and Dalian, respectively. Cyclopentadiene is separated from the  $\text{C}_5$  fraction of the petroleum factors.

### 2.2. Preparation of the polymer-anchored mono- and bimetallic catalysts

The aqueous solution of PVP-anchored palladium complex (PVP–Pd) was prepared by the reaction of PVP (1.14 g) and  $\text{PdCl}_2$  (0.09 g) in 120 ml water at room temperature for 48 h. The aqueous solution of EC- or AR-anchored palladium complexes (EC–Pd or AR–Pd) was prepared by the reaction of EC (0.6 g) or AR (4.0 g) with  $\text{PdCl}_2$  (0.023 g or 0.06 g) in 150 ml or 100 ml water at room temperature for 48 h, then the polymer-anchored monometallic catalyst, PVP–Pd, EC–Pd or AR–Pd was obtained. To the monometallic catalyst, a second transition metal component,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (Co:Pd = 0.5 (mole ratio)) was added and stirred at room temperature for 24 h, and the polymer-anchored bimetallic catalyst (PVP–Pd–0.5Co(OAc)<sub>2</sub>, EC–Pd–0.5Co(OAc)<sub>2</sub> or AR–Pd–0.5Co(OAc)<sub>2</sub>) was prepared. PVP–Co(OAc)<sub>2</sub> was prepared by using a similar procedure.

### 2.3. Preparation of the catalytic hollow fibers

Seventy CA fibers (50 cm in length) were held together at both ends by epoxy resin. An aqueous solution of PVP–Pd, EC–Pd, AR–Pd, PVP–Co(OAc)<sub>2</sub>, PVP–Pd–0.5Co(OAc)<sub>2</sub>, EC–Pd–0.5Co(OAc)<sub>2</sub> or AR–Pd–0.5Co(OAc)<sub>2</sub>, was pumped through the inside of the CA hollow fibers with a circulating pump for 6 h. Then, an

aqueous solution of  $\text{NH}_2\text{NH}_2$  or  $\text{NaBH}_4$  (5%) was pumped through the inside of the fibers for 2 h. After drying at room temperature, the catalytic hollow fibers were obtained. The monometallic PVP–Pd, EC–Pd, AR–Pd or PVP– $\text{Co}(\text{OAc})_2$  catalyst or bimetallic PVP–Pd– $0.5\text{Co}(\text{OAc})_2$ , EC–Pd– $0.5\text{Co}(\text{OAc})_2$  or AR–Pd– $0.5\text{Co}(\text{OAc})_2$  catalyst was retained in the microporous sponge layer of the CA hollow fibers [6]. Fourteen kinds of catalytic polymeric reactors (R-1–R-14) were established with the above mentioned catalytic hollow fibers. Table 1 gives the details of the membrane reactors.

#### 2.4. Selective hydrogenation of cyclopentadiene in the catalytic hollow-fiber reactors

The hydrogenation procedure is similar to that reported in a previous paper [6]. The gas phase cyclopentadiene passed through the inner side of the hollow fibers and a mixture of hydrogen and nitrogen passed through the outer side of the fibers.

Cyclopentadiene, cyclopentene and cyclopentane were analyzed by GLC with a 2 m DEGS column at  $50^\circ\text{C}$ .  $\text{H}_2$  was analyzed with a 1 M carbon molecular sieve column at  $20^\circ\text{C}$ . The

conversion of cyclopentadiene and the selectivity for cyclopentene were calculated as follows:

$$\begin{aligned} \text{Conversion (\%)} &= [1 - D/(D + E + A)] \times 100 \\ \text{Selectivity (\%)} &= [E/(E + A)] \times 100 \end{aligned}$$

$D$ ,  $E$  and  $A$  are the relative concentrations (wt.%) of cyclopentadiene, cyclopentene and cyclopentane in the effluent flow of the inner side of the fiber reactor, respectively.

### 3. Results and discussion

Table 2 shows the results of the selective hydrogenation of cyclopentadiene with six different monometallic palladium catalytic hollow-fiber reactors. It can be seen that the catalytic hollow fibers reduced by different reducing agents, PVP–Pd/CA/ $\text{NH}_2\text{NH}_2$ , PVP–Pd/CA/ $\text{NaBH}_4$ , EC–Pd/CA/ $\text{NH}_2\text{NH}_2$ , EC–Pd/CA/ $\text{NaBH}_4$ , AR–Pd/CA/ $\text{NH}_2\text{NH}_2$  and AR–Pd/CA/ $\text{NaBH}_4$  are all active for the selective hydrogenation of cyclopentadiene under mild conditions of  $40^\circ\text{C}$  and 0.1 MPa.

Table 1  
Details of 14 kinds of catalytic hollow-fiber reactors

Reactor <sup>a</sup>	Supported Pd complex	Catalytic fibers	Reducing agent	Pd content <sup>b</sup> (mg)
R-1	PVP–Pd	PVP–Pd/CA	$\text{NH}_2\text{NH}_2$	1.13
R-2	PVP–Pd	PVP–Pd/CA	$\text{NaBH}_4$	1.15
R-3	EC–Pd	EC–Pd/CA	$\text{NH}_2\text{NH}_2$	1.39
R-4	EC–Pd	EC–Pd/CA	$\text{NaBH}_4$	1.36
R-5	AR–Pd	AR–Pd/CA	$\text{NH}_2\text{NH}_2$	1.21
R-6	AR–Pd	AR–Pd/CA	$\text{NaBH}_4$	1.24
R-7	PVP–Pd– $0.5\text{Co}(\text{OAc})_2$	PVP–Pd– $0.5\text{Co}(\text{OAc})_2$ /CA	$\text{NH}_2\text{NH}_2$	1.19
R-8	PVP–Pd– $0.5\text{Co}(\text{OAc})_2$	PVP–Pd– $0.5\text{Co}(\text{OAc})_2$ /CA	$\text{NaBH}_4$	1.10
R-9	EC–Pd– $0.5\text{Co}(\text{OAc})_2$	EC–Pd– $0.5\text{Co}(\text{OAc})_2$ /CA	$\text{NH}_2\text{NH}_2$	1.29
R-10	EC–Pd– $0.5\text{Co}(\text{OAc})_2$	EC–Pd– $0.5\text{Co}(\text{OAc})_2$ /CA	$\text{NaBH}_4$	1.32
R-11	AR–Pd– $0.5\text{Co}(\text{OAc})_2$	AR–Pd– $0.5\text{Co}(\text{OAc})_2$ /CA	$\text{NH}_2\text{NH}_2$	1.17
R-12	AR–Pd– $0.5\text{Co}(\text{OAc})_2$	AR–Pd– $0.5\text{Co}(\text{OAc})_2$ /CA	$\text{NaBH}_4$	1.12
R-13	PVP– $\text{Co}(\text{OAc})_2$	PVP– $\text{Co}(\text{OAc})_2$ /CA	$\text{NH}_2\text{NH}_2$	0
R-14	PVP– $\text{Co}(\text{OAc})_2$	PVP– $\text{Co}(\text{OAc})_2$ /CA	$\text{NaBH}_4$	0

<sup>a</sup>The diameter and the length of the reactor are 20 mm and 500 mm, respectively.

<sup>b</sup>Palladium content in the whole reactor.

Table 2

Selective hydrogenation of cyclopentadiene with six different kinds of monometallic catalytic hollow-fiber reactors

Reaction conditions: CPD 3 ml/min, H<sub>2</sub>/N<sub>2</sub> 2:1, H<sub>2</sub>+N<sub>2</sub> 6 ml/min, H<sub>2</sub>/CPD 1.33/1, 40°C, 0.1 MPa.

Reactor	Catalytic fibers	Reducing agent	Conversion (%)	Selectivity <sup>a</sup> (%)
R-1	PVP-Pd/CA	NH <sub>2</sub> NH <sub>2</sub>	91.0	91.0
R-2	PVP-Pd/CA	NaBH <sub>4</sub>	92.7	93.4
R-3	EC-Pd/CA	NH <sub>2</sub> NH <sub>2</sub>	61.2	78.8
R-4	EC-Pd/CA	NaBH <sub>4</sub>	63.4	80.3
R-5	AR-Pd/CA	NH <sub>2</sub> NH <sub>2</sub>	29.1	79.6
R-6	AR-Pd/CA	NaBH <sub>4</sub>	33.6	82.5

<sup>a</sup>Selectivity for cyclopentene.

It is also shown in Table 2 that the hydrogenation activity and selectivity of the catalytic hollow fibers depend on both the polymer-anchored palladium complex and the reducing agent. Different coordination groups on the soluble polymers may cause the variation of the coordination state of palladium active species and then affect the behavior of the membrane catalyst. When NaBH<sub>4</sub> is used instead of NH<sub>2</sub>NH<sub>2</sub> as reducing agent for the same monometallic catalytic hollow fibers, both the conversion of cyclopentadiene and selectivity for cyclopentene increase. A main reason is that the valence state and the structure of the active species of the monometallic palladium catalyst can affect the catalytic property of the catalytic polymeric hollow fibers because the reduction abilities of NH<sub>2</sub>NH<sub>2</sub> and NaBH<sub>4</sub> are different. As Schlesinger et al. [31–35] have reported that the reduction of Pd<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, etc. by NaBH<sub>4</sub> gives palladium-boride, cobalt-boride and other corresponding borides. Accordingly, when polymer-anchored monometallic palladium catalyst on the hollow fibers is reduced by NaBH<sub>4</sub>, polymer-protected palladium boride catalytic active species can be formed which exhibits relatively higher hydrogenation activity and selectivity than those reduced by NH<sub>2</sub>NH<sub>2</sub>. From the results of the hydrogenation reaction, we find that the PVP-Pd/CA/NaBH<sub>4</sub> is more appropriate for high cyclopentadiene conversion and cyclopentene

selectivity than the other five catalytic hollow fibers.

It is known that, for the selective hydrogenation reaction with the coordination catalyst, the selectivity for the reaction depends both on the relative coordinate ability and on the concentration (or the partial pressure) of the substrate and hydrogen surrounding the active center of the catalyst. When the catalytic polymeric hollow-fiber reactors are used for the selective hydrogenation of cyclopentadiene, the cyclopentadiene and hydrogen are introduced to the inner and outer sides of the hollow fibers, respectively. The hydrogen can permeate from the outer side to the inner side of the fibers and react with cyclopentadiene, so by adjusting the reaction parameters, especially the flow rate or the H<sub>2</sub>/N<sub>2</sub> mole ratio of the H<sub>2</sub> and N<sub>2</sub> mixture outside the fibers, the concentration gradients of hydrogen and cyclopentadiene can be formed between the inlet and outlet of the reactor, and can be well matched with each other at every section along the inner side wall of the fibers, which will result in a relatively high selectivity for cyclopentene. Tables 3 and 4 show the selective hydrogenation of cyclopentadiene in the catalytic membrane reactor R-2 under different flow rates and H<sub>2</sub>/N<sub>2</sub> mole ratios of the H<sub>2</sub> and N<sub>2</sub> mixture, respectively. It can be seen that the conversion of cyclopentadiene increases with the increase of the flow rate or the H<sub>2</sub>/N<sub>2</sub> mole ratio of the H<sub>2</sub> and N<sub>2</sub> mixture, but the selectivity for the formation of cyclopentene decreases. This is due to the fact that with the increase of the flow rate or the H<sub>2</sub>/N<sub>2</sub> mole ratio of the H<sub>2</sub>

Table 3

Selective hydrogenation of cyclopentadiene in reactor R-2 under different flow rate of the H<sub>2</sub> and N<sub>2</sub> mixture

Reaction conditions: CPD 3 ml/min, 40°C, 0.1 MPa.

Flow rate of H <sub>2</sub> +N <sub>2</sub> (2:1) (ml/min)	H <sub>2</sub> /CPD	Conversion (%)	Selectivity (%)
5.6	1.24:1	85.2	95.6
6	1.33:1	92.7	93.4
6.4	1.42:1	94.5	86.2
6.8	1.51:1	98.6	74.3

Table 4

The effect of  $H_2/N_2$  mole ratios of the  $H_2$  and  $N_2$  mixture on the selective hydrogenation of cyclopentadiene in reactor R-2  
Reaction conditions: CPD 3 ml/min,  $H_2 + N_2$  6 ml/min, 40°C, 0.1 MPa.

$H_2/N_2$ (mole ratio)	$H_2/CPD$	Conversion (%)	Selectivity (%)
1	1:1	84.1	97.6
2	1.33:1	92.7	93.4
5	1.66:1	98.8	42.1
$H_2$	2:1	100	0.3

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 and over-hydrogenation of cyclopentene. If pure hydrogen is used at the outer side of the hollow fibers, the selectivity of cyclopentene is very low. In this case, the partial pressure of cyclopentadiene decreases gradually along the inner side wall of the fibers, while the amount of permeated  $H_2$  remains constant at every section of the fibers. Thus, at the end of the reactor, the partial pressure of  $H_2$  is much higher than that of cyclopentadiene, so it results in a low selectivity of cyclopentene. By the application of the  $H_2$  and  $N_2$  gas mixture, this shortcoming can be avoided.

It has been tested that in this kind of catalytic membrane reactor, small amount of cyclopentadiene, cyclopentene and cyclopentane (about 2%

of the total cyclopentadiene added to the reactor) permeated from the inner to the outer side of the CA fibers.

In order to further improve the conversion of cyclopentadiene and the selectivity for cyclopentene, six bimetallic polymeric hollow-fiber reactors are established with the bimetallic hollow fibers prepared by supporting  $NH_2NH_2$  or  $NaBH_4$  reduced polymer-anchored bimetallic palladium–cobalt catalyst on the inner wall of CA hollow fibers.

Table 5 gives the results of the selective hydrogenation of cyclopentadiene with eight different mono- and bimetallic membrane reactors. A remarkable synergic effect of palladium and cobalt reduced by  $NaBH_4$  is observed whether in PVP–Pd–0.5Co(OAc)<sub>2</sub>/CA, EC–Pd–0.5Co(OAc)<sub>2</sub>/CA or AR–Pd–0.5Co(OAc)<sub>2</sub>/CA bimetallic hollow fibers in reactor R-8, R-10 and R-12, respectively. For example, when the reaction is carried out in R-8, the conversion of cyclopentadiene and the selectivity for cyclopentene can be up to 97.5% and 98.4% after 3 h compared with those of 92.7% and 93.4%, respectively, in the monometallic palladium hollow-fiber reactor R-2. While the monometallic cobalt hollow fibers in reactor R-14 are inactive for the selective hydrogenation of cyclopentadiene under the same reaction conditions. The data in Table 5 also show that when the bimetallic PVP–Pd–0.5Co(OAc)<sub>2</sub>/CA, EC–Pd–0.5Co(OAc)<sub>2</sub>/CA or AR–Pd–0.5Co(OAc)<sub>2</sub>/CA hollow fibers in R-7, R-9

Table 5

Selective hydrogenation of cyclopentadiene with different bimetallic catalytic hollow-fiber reactors  
Reaction conditions: CPD 3 ml/min,  $H_2/N_2$  2:1,  $H_2 + N_2$  6 ml/min,  $H_2/CPD$  1.33/1, 40°C, 0.1 MPa.

Reactor	Catalytic fibers	Reducing agent	Conversion (%)	Selectivity (%)
R-7	PVP–Pd–0.5Co(OAc) <sub>2</sub> /CA	$NH_2NH_2$	91.4	91.2
R-8	PVP–Pd–0.5Co(OAc) <sub>2</sub> /CA	$NaBH_4$	97.5	98.4
R-9	EC–Pd–0.5Co(OAc) <sub>2</sub> /CA	$NH_2NH_2$	60.9	79.0
R-10	EC–Pd–0.5Co(OAc) <sub>2</sub> /CA	$NaBH_4$	66.5	84.2
R-11	AR–Pd–0.5Co(OAc) <sub>2</sub> /CA	$NH_2NH_2$	29.4	79.5
R-12	AR–Pd–0.5Co(OAc) <sub>2</sub> /CA	$NaBH_4$	33.8	82.9
R-13	PVP–Co(OAc) <sub>2</sub> /CA	$NH_2NH_2$	0	0
R-14	PVP–Co(OAc) <sub>2</sub> /CA	$NaBH_4$	0	0

and R-11, respectively, are reduced by  $\text{NH}_2\text{-NH}_2$ , there is no obvious bimetallic synergic effect since the conversion of cyclopentadiene and the selectivity for cyclopentene are nearly the same as those using  $\text{NH}_2\text{NH}_2$  reduced monometallic palladium hollow fibers in R-1, R-3 and R-5, respectively.

A possible explanation for the synergic effect of the bimetallic catalytic hollow fibers is that when PVP-Pd-0.5Co(OAc)<sub>2</sub>/CA, EC-Pd-0.5Co(OAc)<sub>2</sub>/CA or AR-Pd-0.5Co(OAc)<sub>2</sub>/CA bimetallic hollow fibers is reduced by  $\text{NH}_2\text{NH}_2$  and  $\text{NaBH}_4$ , different polymer-protected bimetallic catalytic active species are formed.  $\text{Pd}^{2+}$  can be reduced to  $\text{Pd}^+$  or  $\text{Pd}^0$  by  $\text{NH}_2\text{NH}_2$ , but  $\text{Co}^{2+}$  cannot be reduced by  $\text{NH}_2\text{NH}_2$ . While, when  $\text{NaBH}_4$  is used as the reducing agent for the bimetallic polymer-anchored Pd-0.5Co(OAc)<sub>2</sub>/CA catalyst, different polymer-protected palladium boride-cobalt boride could be formed which displays much higher catalytic activity and selectivity than those reduced by  $\text{NH}_2\text{NH}_2$  for the selective hydrogenation of cyclopentadiene.

The data in Table 5 also show that the PVP-Pd-0.5Co(OAc)<sub>2</sub>/CA bimetallic hollow fibers reduced by  $\text{NaBH}_4$  is more appropriate for high cyclopentadiene conversion and cyclopentene selectivity than the other two kinds of bimetallic hollow fibers EC-Pd-0.5Co(OAc)<sub>2</sub>/CA and AR-Pd-0.5Co(OAc)<sub>2</sub>/CA.

It is worth mentioning that the activity of the catalytic CA hollow fibers is stable during the selective hydrogenation. The membrane catalyst keeps the hydrogenation activity and selectivity after 300 h reaction by permeated hydrogen. This indicates that the polymer-anchored mono- or bimetallic catalyst is firmly retained in the microporous structures of the fibers.

#### 4. Conclusion

The  $\text{NaBH}_4$  reduced Pd-Co bimetallic catalytic hollow fibers, PVP-Pd-0.5Co(OAc)<sub>2</sub>/CA/ $\text{NaBH}_4$ , in the hollow-fiber reactor, exhibit

very high hydrogenation activity and selectivity for the selective hydrogenation of cyclopentadiene.

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