

Partial Hydrogenation of Benzene Catalyzed by Pt/*N-n*-Propyl Chitosan Hybrid Membrane

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ABSTRACT: The partial hydrogenation of benzene by a Pt nano-cluster/*N-n*-propyl chitosan hybrid membrane was investigated in this article. Monodispersed Pt nano-clusters were prepared by the reduction of H_2PtCl_6 with ethylene glycol under microwave conditions. TEM, FTIR, XRD, $^1\text{H-NMR}$, and XPS were used to characterize the structure of Pt nano-particles, *N-n*-propyl chitosan and Pt/*N-n*-propyl chitosan hybrid membrane, respectively. Experimental results showed that Pt/*N-n*-propyl chitosan hybrid membrane catalyst gave a high selectivity for cyclohexene of 85.2% in the liquid phase hydrogenation of benzene, while the selectivity of cyclohexene was only 58.2%

over the Pt/chitosan hybrid membrane catalyst. It was worth noting that there was no cyclohexene in the product when the catalyst was only Pt nano-particles without chitosan hybrid membrane. So the chitosan or modified-chitosan membranes played an important role in the controlling to the hydrogenation of benzene, and the relationship of the swelling degree and the catalytic activity was discussed in detail. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2140–2146, 2012

Key words: membranes; Pt nano-cluster; chitosan; cyclohexene; catalysts

INTRODUCTION

Cyclohexene is an important chemical raw material with active double bond, which has widespread use in the pharmaceutical and petroleum industry.¹ Especially in polymer field, the production route of Nylon 6 or 66 with cyclohexene as the raw material is simple and low-cost.^{2,3} Although cyclohexene is an intermediate product of benzene hydrogenation, cyclohexane is always produced because of the kinetically favored hydrogenation of cyclohexene to cyclohexane.⁴ Thus, investigation of catalyst for the partial hydrogenation of benzene to cyclohexene is the key.

Several metals can be used as hydrogenation catalysts, such as Pt, Pd, Ru, and Ni, in which Pt has the highest catalytic activity for benzene hydrogenation.⁵ Dini et al.^{6,7} found that cyclohexene was a reaction product of benzene hydrogenation when the Pt/polyamide was used as catalysts. In their studies, the highest selectivity to cyclohexene was 48.0%, but the conversion of benzene was 0.4%, while the conversion of benzene got to 25.9%, but then the selectivity to cyclohexene was only 0.1%. In addition, Domínguez et al.⁸ reported that when catalysts of

0.5% Pt supported on gallia/alumina were used in benzene hydrogenation, the only product was cyclohexane. Nagahara reported a particularly efficient catalyst composed of Ru-black promoted with ZnO. In their studies, the yield of 56% and the selectivity of 80% were believed to be high enough to develop an industrial process.⁹ Recently, William et al have studied the activities for low-temperature hydrogenation of benzene by Pt/Ni bimetallic catalysts supported on $\gamma\text{-Al}_2\text{O}_3$. It was observed that the bimetallic catalysts were more active than either parent metal catalyst, but in this article cyclohexane was the only observed reaction product.¹⁰

In our previous studies, we have investigated the fabrication of Pt nano-cluster/polyimide hybrid membrane and its catalytic activity to the partial hydrogenation of benzene, in which the selectivity to cyclohexene reached to 72.4%.¹¹ Thus it can be supposed that benzene may contact the active center of catalyst in the hybrid membrane through swelling method, and the controlling of the hydrogenation to obtain higher selectivity of cyclohexene can be realized by controlling the swelling degree of membrane. However, the preparation process of polyimide is complex and costly, so in this research the cheap and abundant natural polymer chitosan (CS) was chosen.

Chitosan is the N-deacetylated derivative of chitin, which is suitable functional material because of its biocompatibility, biodegradability, nontoxicity, adsorption properties, etc.¹² In addition, the large number of $-\text{NH}_2$ and $-\text{OH}$ in CS has good chelating ability to metal.¹³ However, CS is a polar molecular,

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and there are a large number of hydrogen bonds in CS, making its poor solubility in most organic solvents. Our group has studied the fabrication of Pt nano-cluster/CS membrane and its catalytic activity to the partial hydrogenation of benzene, in which the selectivity to cyclohexene reached 58.2%, and the conversion of benzene was only 0.54%. To improve the catalytic activity of Pt/CS membrane, the modification to chitosan was carried out and some alkyl derivatives were synthesized. The alkyl groups may reduce the hydrogen bonds and the introduction of branched chain may also lead to some change of the crystallinity of CS. It was supposed that these factors could change the swelling property of membrane in the nonpolar solvents such as benzene, and then would finally improve the catalytic activity of Pt hybrid membrane to the partial hydrogenation of benzene.¹⁴

In this article, we focused on the synthesis of *N-n*-propyl chitosan (PCS) at various levels of the extent of N-substitution (ES) and the corresponding Pt/PCS hybrid membranes. The structures of Pt, PCS and Pt/PCS were characterized by TEM, XRD, XPS, ¹H-NMR, and FTIR. The swelling degrees of Pt/PCS hybrid membrane in benzene, cyclohexene and cyclohexane were discussed, and finally the partial hydrogenation of benzene catalyzed by Pt/PCS hybrid membrane was investigated.

EXPERIMENTAL

Preparation of *N-n*-propyl chitosan

Preparation of *N-n*-propyl chitosan was similar to the literature.¹⁵ Firstly, chitosan was dissolved in 0.2 M acetic acid solution and diluted with ethanol. Then add ethanol solution of propionaldehyde with different concentrations to the chitosan solution. The reaction mixture was stirred at 80°C for 6 h, and the pH of the solution was adjusted to 5 by adding 1 M NaOH solution. Then, different amounts of 10% aqueous solution of NaBH₄ were added to the above solution. After reaction under stirring at 80°C for 3 h, adjust pH = 10 by 10% aqueous NaOH solution. The precipitate was washed with distilled water, ethanol and ether for several times. Finally the precipitate was extracted (Soxhlet) by ethanol/ether (1 : 1) for 48 h. The final product was gained and dried overnight under vacuum at 45°C.

Preparation of hybrid membrane catalysts

To get monodispersed Pt nano-clusters for a higher catalytic activity, H₂PtCl₆·6H₂O was reduced under microwave irradiation as reported in our previous paper.¹¹ A certain amount of prepared PCS was completely dissolved in 3% acetic acid solution, after

deaeration, the platinum nano-clusters were added into the PCS solution with stirring, and then vibrated under the ultrasonic wave for 30 min. After that, the solution was poured onto the glass, and then dried overnight at 60°C. With the evaporation of solvent, the hybrid membrane was formed. The prepared membrane was soaked in 10% NaOH solution for 30 min, washed with distilled water to neutrality, and then dried under 80°C. Finally, the uniformly dispersed platinum nano-cluster/*N-n*-propyl chitosan hybrid membrane was obtained.

Catalytic evaluation

The liquid phase hydrogenation of benzene was performed in autoclave under the H₂ pressure of 5 MPa, 150°C for 2 h. The reaction products were determined by gas chromatography with FID detector (GC-17A ATF, Shimadzu, 30 m, 0.25 mm ID, stainless steel column filled with 100% dimethyl polysiloxane).

Characterization of catalysts

The morphology of Pt nano-clusters and Pt/CS membrane were determined by TEM (FEI TACNAI G2 F20 S-Twin) with 200 kV. FTIR spectra were determined on NEXUS 470 Fourier transform infrared spectroscopy. XRD patterns were acquired on a Bruker D8 advance X-ray diffractometer with Cu-Kα radiation. ¹H-NMR was measured on a Bruker AVANCE 400 MHz spectrometer with D₂O/CF₃CO₂D (1 : 1) as solution. XPS data were recorded on VG Multilab 2000 instrument with Al-Kα line as the excitation source (300 W, 100 eV), and all of the binding energy values were referenced to the C1s peak of contaminant carbon at 284.6 eV. The thickness of membranes was determined by the CHY-C2 thickness gauge.

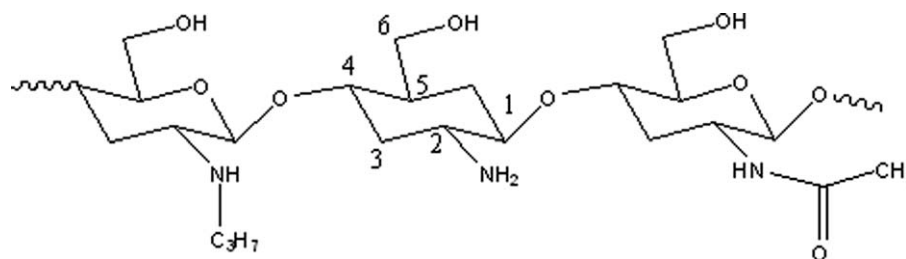
RESULTS AND DISCUSSION

Characterization of *N-n*-propyl chitosan

The extents of N-substitution in *N-n*-propyl chitosan were determined by ¹H-NMR and the corresponding calculation formula was shown in Eq. (1):

$$ES(\%) = \frac{\frac{1}{3}CH_3}{H_2 + \frac{1}{3}NHAc} \times 100\% \quad (1)$$

In this equation, ES (%) is the extent of N-substitution, CH₃ is the integral area of methyl protons, H₂ is the integral areas of the protons at the C-2 carbon of glucosamine (GlcN) and NHAc is the integral area of *N*-acetylglucosamine (GlcNAc) protons.¹⁶ The general chemical structure of *N-n*-propyl chitosan was shown in Scheme 1. The ES of PCS were calculated



Scheme 1 The general structure of *N-n*-propyl chitosan.

and listed in Figure 1. In Figure 1, all the spectra exhibited the characteristic $^1\text{H-NMR}$ pattern of chitosan, such as the multiple peaks at δ 3.2–2.6 ppm due to H3, H4, H5, H6, and two single peaks at δ 2.3 and 1.2 ppm due to the H2 proton of the GlcN and *N*-acetyl protons of GlcNAc, respectively. The $^1\text{H-NMR}$ spectrum of *N-n*-propyl chitosan was similar to the one of chitosan except the additional signals of the propyl group which appeared as the multiplet and singlet at δ 0.9 and 0.17 ppm due to methylene and methyl protons, respectively.

The FTIR spectra of CS and PCS were shown in Figure 2. The FTIR spectrum of PCS was similar to that of CS, but the intensity of the absorption band at 2975 cm^{-1} was gradually increased with the increasing degree of substitution of propyl. The intensity of the absorption band at 1594 cm^{-1} due to N–H deformation of amino groups was gradually decreased. In addition, a new absorption band at 1416 cm^{-1} was observed which were assigned to C–H deformation of the propyl group.

Characterization of Pt particles and Pt/*N-n*-propyl chitosan hybrid membrane

The TEM photographs of Pt particles and the Pt/CS hybrid membrane were shown in Figure 3. As shown in Figure 3, the average diameter of the Pt particles was about 5 nm. It showed that microwave

provided an effective method for the synthesis of stable, smaller diameter and mono-dispersed Pt nano-clusters. From the TEM photograph of the Pt/CS membrane, it could be found that Pt particles were uniformly dispersed in chitosan membrane and the size of Pt particles in Pt/CS hybrid membrane was also about 5 nm.

XRD patterns of CS, PCS, Pt/CS, and Pt/PCS membranes were shown in Figure 4. From Figure 4A, it could be seen that the introduction of branched chains in PCS led to some changes in the crystallinity of CS membrane, as shown in the peak of 20–30°. Compared with CS, the crystallinity of PCS decreased mainly due to the introduction of propyl branched chains. It destroyed the intermolecular hydrogen bonds of chitosan molecular chains, making the branching degree of chitosan increased and the corresponding molecular arrangement regularity decreased. For Pt nano-clusters, there are four distinct peaks at 39.9°, 46.3°, 67.6°, and 81.8°, corresponding to metallic Pt (111), (200), (220), and (311) planes, respectively, which showed that the platinum nano-clusters under the condition of microwave irradiation had good crystallinity. For Pt/CS and Pt/PCS hybrid membranes in Figure 4B, the above peaks corresponding to metallic Pt had almost no changes, which indicated that Pt in the hybrid membrane maintained good crystallinity.

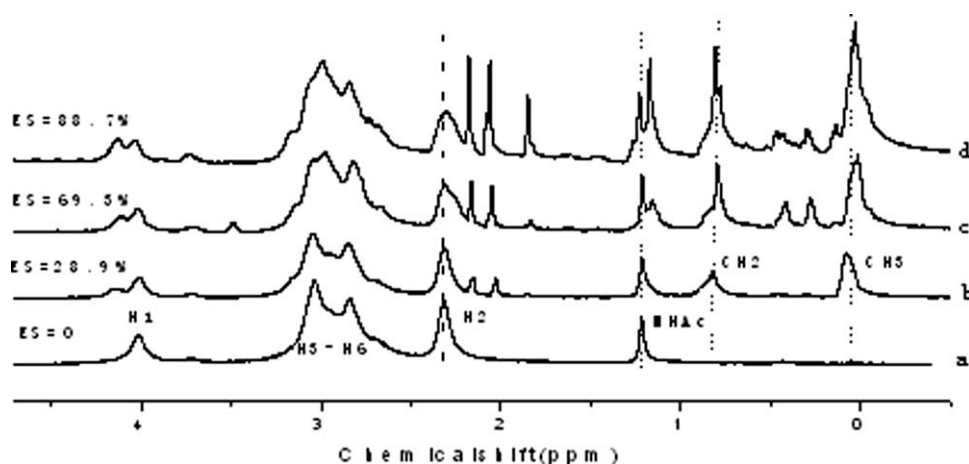


Figure 1 $^1\text{H-NMR}$ spectra of CS and PCS with different ES (a: CS; b–d: PCS).

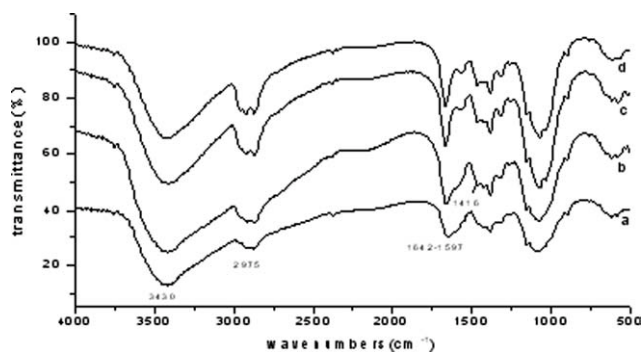


Figure 2 FTIR spectra of CS and PCS with different ES [a: CS; b: PCS (ES = 28.9%); c: PCS (ES = 69.3%); d: PCS (ES = 88.7%)].

XPS spectra for *N-n*-propyl chitosan membrane with 28.9% of ES and the corresponding Pt/*N-n*-propyl chitosan hybrid membrane were shown in Figure 5. As revealed in Figure 5A, the binding energy of O1s at 532.53 eV for PCS membrane shifted to 532.20 eV for Pt/PCS hybrid membrane, which implied that there was an electron transfer from oxygen to platinum. Similarly, in Figure 5B, the binding energy of N1s at 399.42 eV for PCS membrane shifted to 399.28 eV for Pt/PCS hybrid membrane, which could be explained that an electron transfer from nitrogen to platinum happened too.

Partial hydrogenation of benzene catalyzed by Pt/CS and Pt/PCS

The liquid hydrogenation of benzene was carried out with Pt/CS and Pt/PCS hybrid membrane with different ES as catalysts, and the results were listed in Table 1. Cyclohexene and cyclohexane can be both obtained in the hydrogenation of benzene and cyclohexene as the partial hydrogenation product

appeared when CS or PCS membrane with loaded Pt nano-clusters as catalyst. It was worth noting that cyclohexane was the only product and there was no cyclohexene produced when the catalyst was only Pt nano-particles without chitosan hybrid membrane. As depicted in Table 1, with the increasing of the extent of substitution of *N-n*-propyl, the conversion of benzene was gradually increased, while the selectivity of cyclohexene increased at first and then decreased. With 28.9% of ES, the selectivity of cyclohexene was as high as 85.2%.

To investigate the nature of the catalytic reaction, the swelling degrees of membranes in various solvents were determined. The thickness of membranes and the swelling degrees of CS and PCS with different ES loaded with or without platinum nano-clusters in benzene, cyclohexene, and cyclohexane, respectively, were shown in Table 2. As shown in Table 2, with the increasing of the extent of *N*-substitution, the thickness of membranes were increased, and accordingly the swelling degrees of membranes were increased too. The order of swelling degree was cyclohexene > benzene > cyclohexane, irrespective of loaded Pt or without Pt. The swelling degrees of Pt/CS and Pt/PCS with different ES were decreased significantly compared with that of CS and PCS without Pt. With the increasing of extent of substitution of *N-n*-propyl, the swelling degrees of PCS membranes in benzene, cyclohexene, and cyclohexane were all increased, which was mainly due to the enlargement of spacing between molecular chains with the decrease of the crystallinity of PCS and the increase of the membrane thickness. The most significant increasing appeared in benzene, which probably led to the increasing of the conversion of benzene in liquid hydrogenation catalyzed Pt/*N-n*-propyl chitosan membrane with increasing ES. In contrast, the swelling degree of

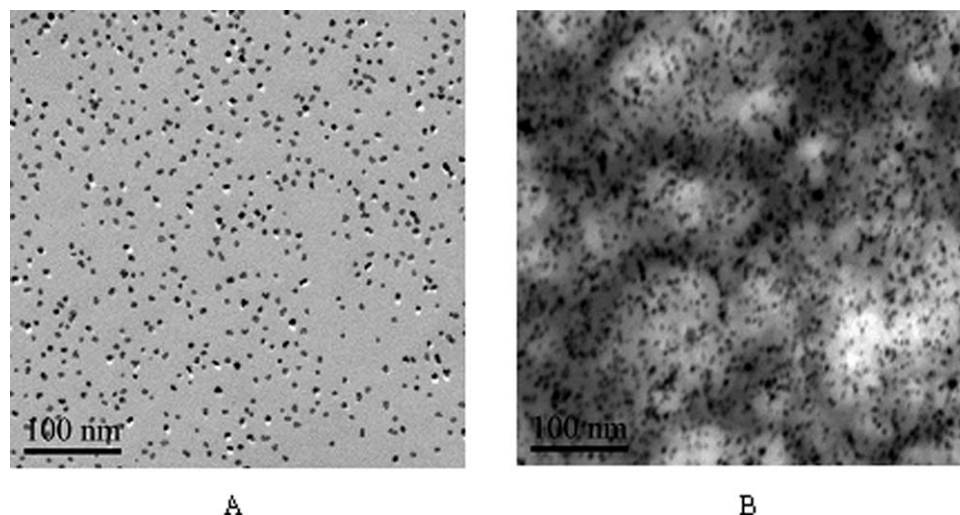


Figure 3 TEM photographs of Pt particles (A) and Pt/CS membrane (B).

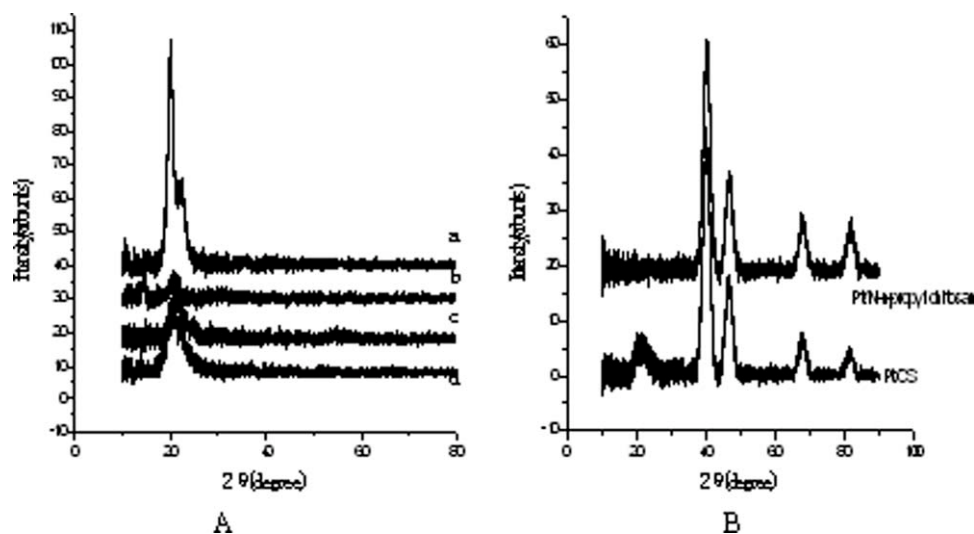


Figure 4 (A) XRD patterns of CS and PCS membranes with different ES [a: CS; b: PCS (ES = 28.9%); c: PCS (ES = 69.3%); d: PCS (ES = 88.7%)]; (B) XRD patterns of Pt/CS and Pt/PCS with 28.9% ES hybrid membranes.

membrane with different ES in cyclohexene and cyclohexane both showed slight increasing trend.

Generally, cyclohexene as the partial hydrogenation product of benzene is difficult to be obtained, because of the thermodynamics favored hydrogenation of cyclohexene to cyclohexane. The above experimental results showed that CS membrane played an important role in the partial hydrogenation of benzene to cyclohexene. As reported by our group previously,¹⁷ we conjecture that benzene may contact the active center of catalytic hydrogenation through swelling into Pt/CS hybrid membrane, so the swelling process is important to the catalytic reaction.

The schematic representation of the hydrogenation of benzene over Pt/CS hybrid membrane catalyst was shown in Figure 6. In the reaction progress,

benzene and hydrogen diffused into the chitosan hybrid membranes and adsorbed with platinum nano-clusters, and then catalytic hydrogenation reaction occurred. Firstly, because of the existence of membrane, the contact of H₂ and Pt was inadequate, which had an important influence on the hydrogenation rate of benzene, making the reaction to the direction of producing cyclohexene. Secondly, because there was concentration difference of cyclohexene among the catalyst surface, membrane, and oil phase, as shown in Figure 6, cyclohexene had a tendency to diffuse from the catalyst surface to the oil phase. Furthermore, there are many polar groups around the catalytic center, such as hydroxyl, amino etc, so once cyclohexene is produced in the reaction, it can quickly diffuse from membrane with the help

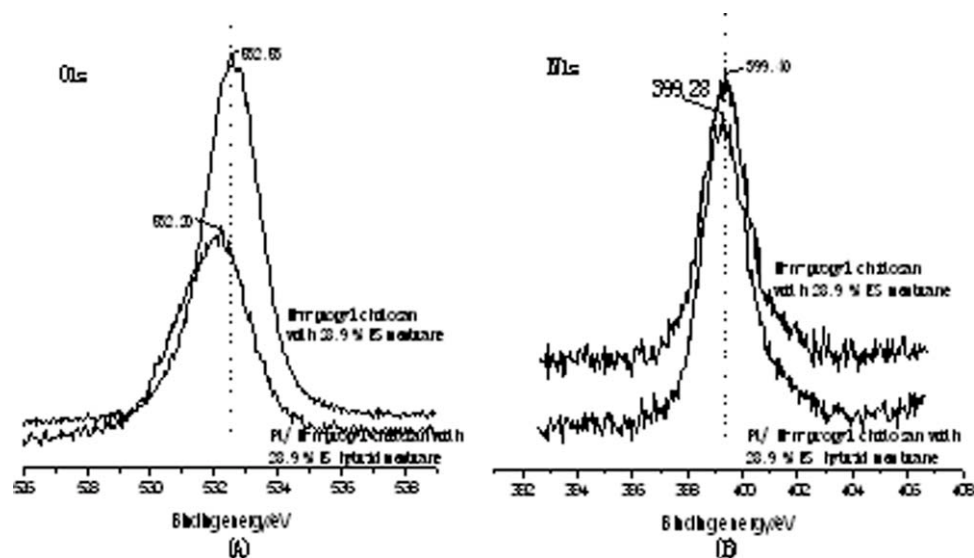


Figure 5 XPS spectra of O1s (A) and N1s (B) in *N-n*-propyl chitosan with 28.9% ES membrane and Pt/*N-n*-propyl chitosan with 28.9% ES hybrid membrane.

TABLE I
Hydrogenation of Benzene Catalyzed by
Pt/CS and Pt/PCS

Catalyst	ES of PCS (%)	Conversion of benzene (%)	Selectivity to cyclohexene (%)
Pt	–	1.08	0
Pt/CS	–	0.54	58.2
Pt/PCS	28.9	0.69	85.2
Pt/PCS	69.3	0.82	73.6
Pt/PCS	88.7	1.36	38.6

Reaction conditions: C_6H_6 : 30 mL, catalyst: 0.40 g, m (Pt)/m (CS or PCS): 20%, T: 150°C, p (H_2): 5 MPa, Time: 2 h.

of the van der Waals force between these polar groups and cyclohexene molecules, which avoids the probability of further hydrogenation to convert to cyclohexane. Finally, the characterization results showed that there was an electron transfer from oxygen and nitrogen in CS to platinum. It could probably change the electron environment of Pt in hybrid membrane compared with pure Pt nano-clusters, then influence the absorption of benzene with Pt, and finally influence the catalytic property to the hydrogenation of benzene.

The both increasing of swelling degrees of Pt/PCS membranes with different ES in benzene and cyclohexene has two-aspect effects on the reaction. On the one hand, the increasing of swelling degree of membrane in benzene led to the more contacting time of reactant to the catalytic center, which resulted in the increasing of conversion of benzene. In addition, the increasing of swelling degree of membrane in cyclohexene led to the longer staying time of cyclohexene in membrane with catalytic center, which may lead to the further hydrogenation of cyclohexene to produce cyclohexane. On the other hand, the number of amino groups in chitosan diminished with the increasing degree of substitution, making the interaction of amino groups and Pt

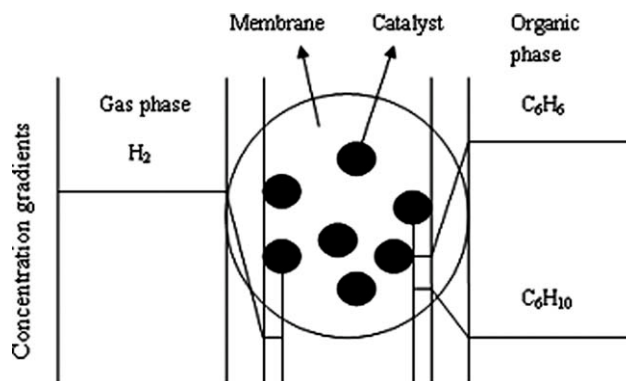


Figure 6 Schematic representation of the concentration gradients of hydrogen, benzene and cyclohexene in the selective hydrogenation of benzene over Pt/CS hybrid membrane catalyst.

decreased, which could change the catalytic activity of platinum to the partial hydrogenation of benzene. As a result, the selectivity of cyclohexene was increased at first, and then decreased with the increasing of ES.

CONCLUSIONS

In summary, the Pt nano-cluster/chitosan and Pt nano-cluster/*N-n*-propyl chitosan with different ES hybrid membranes were prepared, and their catalytic activities for partial hydrogenation of benzene were investigated. With increasing the extent of substitution of *N-n*-propyl, the conversion of benzene was gradually increased, while the selectivity of cyclohexene increased at first and then decreased with the highest selectivity of 85.2%. These catalytic results had a close relationship to the swelling degrees of different membranes in benzene, cyclohexene and cyclohexane. It was supposed that hybrid membrane played an important role in the controlling of catalytic hydrogenation of benzene,

TABLE II
Degree of Swelling of CS, PCS, Pt/CS, and Pt/PCS in Benzene, Cyclohexene, and Cyclohexane

Sample	ES of PCS (%)	Thickness of membrane/ μm	Degree of swelling (%)		
			Benzene	Cyclohexene	Cyclohexane
CS	–	110	1.34	2.96	1.26
PCS	28.9	111	1.88	2.98	1.33
PCS	69.3	112	2.27	3.04	1.38
PCS	88.7	114	2.35	3.13	1.44
Pt/CS	–	111	1.06	2.63	0.98
Pt/PCS	28.9	112	1.43	2.66	1.15
Pt/PCS	69.3	115	1.71	2.72	1.20
Pt/PCS	88.7	116	1.89	2.78	1.24

Degree of swelling of membrane can be expressed as $A = (m - m_0)/m_0$, where m is the mass of the swollen sample, and m_0 is the mass of the nonswollen sample. Swelling time: 24 h.

and the catalytic selectivity to produce cyclohexene could be improved by the modification of chitosan structure.

References

1. Ronchin, L.; Toniolo, L. *Catal Today* 1999, 48, 255.
2. Hu, S. C.; Chen, Y. W. *Ind Eng Chem Res* 2001, 40, 3127.
3. Nagahara, H.; Ono, M.; Konishi, M.; Fukuoka, Y. *Appl Surf Sci* 1997, 121, 448.
4. Liu, S. C.; Liu, Z. Y.; Liu, Y. L.; Wu, Y. M.; Wang, Z. *J Rare Earths* 2006, 24, 456.
5. Huang, Z. J.; Fang D. Y. *Chemical Technology*; High Edu Press: Beijing, 2001, 181.
6. Dini, P.; Dones, D.; Montelatici, S.; Giordano, N. *J Catal* 1973, 30, 1.
7. Harrison, D. P.; Rase, H. F. *Ind Eng Chem Fundam* 1967, 6, 161.
8. Domínguez, F.; Sánchez, J.; Arteaga, G.; Choren, E. *J Mol Catal A* 2005, 228, 319.
9. Nagahara, H.; Konishi, M. U.S. Pat. 4,734,536 (1988).
10. William, W. L.; Dionisios, G. V.; Jingguang, G. C. *J Catal* 2010, 271, 239.
11. Long, S.; Zhang, A. Q.; Liu, H. F.; Li, L.; Ding, L. Q. *Chin J Catal* 2009, 30, 276.
12. Majeti, N. V.; Ravi, K. *React Funct Polym.* 2000, 46, 1.
13. Eric, G. *Separ Purif Technol* 2004, 38, 43.
14. Douglas, B.; Odilio B. G. A. *Int J Biol Macromol* 2007, 42, 198.
15. Warayuth, S.; Supawan, T.; Varawut, T.; Mrunal, T.; William. H. D. *Int J Biol Macromol* 2008, 43, 79.
16. Warayuth, S.; Supawan, T.; Varawut, T.; William. H. D. *Carbohydr Res* 2009, 344, 2502.
17. Zhai, H.; Zhang, A. Q.; Li, L.; Long, S.; Liu, H. F. *Chin Ind Catal* 2011, 19, 32.