

Preparation and performance of anchored heterogenized rhodium complex catalyst for hydroformylation

Jiquan Zhao^{a,*}, Yuecheng Zhang^{a,b}, Jianping Han^a, Yongjie Jiao^a

^a School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, PR China

^b School of Pharmaceuticals and Biotechnology, Tianjin University, Tianjin 300072, PR China

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Abstract

In order to solve the difficult problem in separation of homogeneous catalyst from the reaction mixture, heterogenized rhodium carbonyl complex catalyst for hydroformylation of olefins was prepared by copolymerization of functionalized 3-aminopropyltriethoxysilane with tetraethoxysilane (TEOS) via the sol–gel method. The catalyst was characterized by FT-IR, X-ray photoelectron spectroscopy (XPS), ICP and N₂ absorption. The activity, selectivity and stability of this catalyst for 1-hexene hydroformylation have been examined. It was concluded the activity depended on the surface area of the catalyst matrix, which varied according to the pH in the sol–gel process. The conversion of 1-hexene reached 98.8%, with a selectivity of 99.6% of aldehydes and the *n/i* ratio of 0.86 under optimized conditions. Furthermore, it showed excellent stability and reusability, the catalyst was used for six times without obvious loss of activity.

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1. Introduction

The fatal problem for hydroformylation of olefins in the homogeneous catalysis is the difficult separation of catalyst from the reaction mixture. In the past three decades, many efforts have been made to resolve this problem [1,2]. Various methods [3–5] of heterogenization for overcoming it have appeared in recent years. From the pre-works, we can know that the sol–gel technique is a promising method for obtaining heterogenized catalysts, because of its diversity, mildness in the procedure, matrix stability and prevention of catalyst from leaching [6–8]. Generally, there are two sol–gel methods for heterogenizing homogeneous catalysts. One is physically encapsulating complex into solid matrix, the other is by the combination of anchoring and sol–gel process. For the latter method, the complexes are anchored to the matrix by chemical linkage except for direct encapsulation in the former. It is expected the catalyst heterogenized by this way is more stable and leaching-proof. So it is interesting and useful to find new anchoring method for obtaining stable heterogenized complex catalyst.

Herein, we present an easy and practical heterogenization method by forming amide bond to anchor Rh carbonyl complex with a carboxy group to the SiO₂ matrix by a sol–gel technique. The catalyst was characterized by FT-IR, XPS, ICP and N₂ absorption. The immobilized catalyst was applied to the hydroformylation of 1-hexene.

2. Experimental

2.1. Materials and methods

Triphenylphosphine, acrylic acid, tetraethoxysilane (TEOS), *N*-hydroxysuccinimide and 1,3-dicyclohexylcarbodiimide (DCC) were purchased from Aldrich. THF was distilled from sodium. Other solvents were dried and distilled prior to use as usual. Water was distilled under N₂ prior to use. The complex of [Rh(CO)₂Cl]₂ was prepared by the McCleverty's method [9].

2.2. Characterization of the catalysts

The H NMR spectrum was measured on a Bruker AC-P 300 (300 MHz for proton) spectrometer. FT-IR spectra were

* Corresponding author. Tel.: +86 22 26564279; fax: +86 22 26564733.
E-mail address: zhaojiquan@jsemail.hebut.edu.cn (J. Zhao).

recorded in KBr pellet, using a Bruker Vector 22 spectrophotometer, in the range 400–4000 cm^{-1} . To determine the metal content, the sample was dissolved in concentrate HNO_3 and HF, and then the metal content of these solutions was determined by a T.J.A ICP-9000(N+M) type ICP-AES instrument. X-ray photoelectron spectroscopy (XPS) measurements of the heterogenized catalysts were recorded in a PHI5300 ESCA instrument at 10^{-7} Pa, the pass energy of 50 eV and using nonmonochromatized Mg $K\alpha$ as the radiation source. N_2 adsorption measurements were performed at 77 K on a Micromeritics ASAP 2010 sorptometer. Prior to measurement, all samples were dried under 110°C for 3 h, and then degassed for 15 h at 110°C . Surface areas were determined from the BET equation, while pore volumes were determined from the BJH equation.

2.3. The analysis of the products

Reaction products were analyzed on a Shandong Lunan Ruihong Gas Chromatograph, SP-6800A, equipped with an SE 30 capillary column, $30.0\text{ m} \times 0.25\text{ mm}$ and an FID detector. Nitrogen was the carrier gas. The products were also characterized by a Trace-DSQ GC-MS system with a CP Sil CB-MS capillary column, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ (Thermo Electron Cooperation, USA).

2.4. Synthesis of diphenylphosphine propionic acid

The synthesis was performed under nitrogen using standard Schlenk techniques. To 4.0 g of triphenylphosphine in 25 ml of THF was added 0.4 g of metallic lithium. The mixture was stirred for 6 h, then the lithium left was removed by filtration [10]. To the filtrate, 1.4 g of *t*-butyl chloride dissolved in 15 ml of THF was slowly added at 0°C . The solution obtained was heated up to reflux for 0.5 h, and then cooled to 20°C . To the solution was slowly added 1.1 g of acrylic acid in 25 ml of THF, and the solution obtained was stirred for 2 h. The THF was distilled off and the residue was dissolved in 15 ml of water. The aqueous solution obtained was extracted with diethyl ether to remove impurities. The aqueous layer was acidified with 2N of hydrochloric acid and some precipitate took place. The precipitate collected was recrystallized from ethanol. The pure ligand diphenylphosphine propionic acid was obtained. IR (KBr): 3070, 3016, 2924, 2854, 1709, 1432, 1256, 736 and 695 cm^{-1} ; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 2.29–2.46 (m, 4H, $-\text{CH}_2-$), 7.24–7.43 (m, 10H, Ar-H); EI-MS m/z : 258 ($\text{M}^+ + 1$); mp 126.7 – 127.3°C (literature [11], 127 – 128°C).

2.5. Preparation of the heterogenized catalyst

The preparation of the heterogenized catalyst was performed under nitrogen using standard Schlenk techniques. To 1.000 g of diphenylphosphine propionic acid (A) in 25 ml of THF were added 0.452 g of *N*-hydroxysuccinimide and 0.834 g of DCC. The mixture was stirred at 25°C for 24 h and then it was filtrated. To the filtrate was added 0.858 g of

3-aminopropyltriethoxysilane. The mixture was stirred for 24 h, then the solvent was distilled off and a solid product (B) was obtained. B was dissolved in 50 ml of toluene. To the solution was slowly added 0.240 g of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in 10 ml of toluene, and the solution obtained was stirred for 4 h, then the toluene was distilled off to produced C. C was dissolved with 10 ml of ethanol. Fifteen milliliters of TEOS and 7.5 ml of distilled water were added to the above solution under stirring to get a homogeneous solution. To the solution, hydrochloric acid was added to adjust the pH to 3. The stirring was continued under 60°C until gelation was completed. The gel was dried under 50°C till a constant weight was obtained and then washed with boiling water until the pH of the washing water reached 7. Finally, the heterogenized catalyst (D) was obtained after the gel was extracted with toluene in a Soxhlet extractor for 10 h.

2.6. Hydroformylation reaction

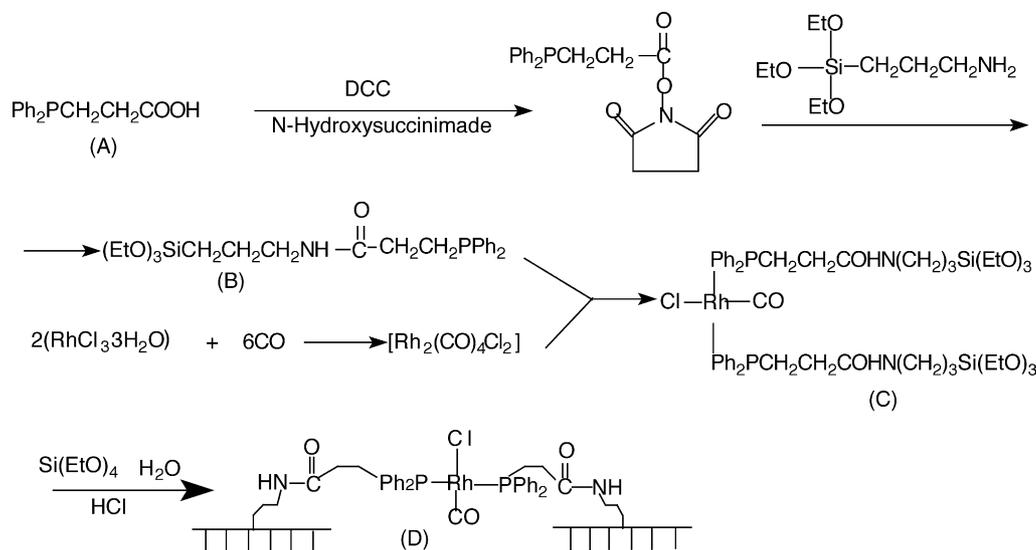
All the hydroformylation reactions were carried out in a 250 ml stainless steel autoclave with a magnetic stirrer supplied by Weihai Autoclave Cooperation, China. An amount of 0.238 g of the heterogenized catalyst was introduced into the autoclave under a nitrogen atmosphere. The resulting solution composed of 1-hexene (5 ml, 0.04 mol) and toluene (50 ml) was charged into the reactor by suction. The reaction vessel was purged with carbon monoxide and hydrogen two times alternatively and then filled with H_2 and CO to the needed pressure ($\text{H}_2:\text{CO} = 1:1$). The mixture was heated up to the needed reaction temperature and stirred magnetically at 800 rpm for 9 or 10 h. After the reaction completed, the mixture was cooled to ambient temperature and analyzed by GC.

For the recycle test experiments, the heterogenized catalyst was allowed to settle down and the supernatant liquid was extruded out. The residual catalyst was washed with toluene and dried under vacuum. The solvent and reactants were introduced into the vessel according to the same procedure as above and the reaction was run under the same reaction conditions as in the first run. For determining the rhodium leaching, the rhodium content of the catalyst was analyzed by XPS and ICP before and after the cycle.

3. Results and discussion

3.1. Preparation of the catalyst

As shown in Scheme 1, an active ester was synthesized first via the reaction of diphenylphosphine propionic acid with *N*-hydroxysuccinimide and used directly. By employing the reaction of this active ester with the amino group of 3-aminopropyltriethoxysilane, the functionalized ligand 3-aminopropyltriethoxysilane $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCOCH}_2\text{CH}_2\text{PPh}_2$ (B) was prepared. The conditions of the process were mild and easy, and the reaction was almost quantitative. This ligand reacted with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ smoothly to give the corresponding homogeneous complex (C) with group $-\text{Si}(\text{OEt})_3$ [12] which allowed the complex to be copolymerized



with TEOS to give the heterogenized catalyst (D) by the sol–gel technique.

3.2. Catalyst characterization

For elucidation of the structure, the oxidation state, the surface area of the matrix and the content of rhodium, the catalyst was characterized by FT-IR, XPS, N_2 adsorption and ICP. Fig. 1 is the FT-IR spectra of diphenylphosphine propionic acid (a), the homogeneous complex (b) and the heterogenized catalyst (c). Comparison of the three IR spectra shows that the rhodium complex is anchored and entrapped into the SiO_2 matrix. The $\nu(C=O)$ of the acyl that appeared at 1709 cm^{-1} in the spectrum of diphenylphosphine propionic acid (a) shifts to 1648 cm^{-1} in the homogeneous complex (b), which suggests the formation of amide. A sharp band centered at 1973 cm^{-1} in the homogeneous complex (b) is attributed to vibration of CO coordinated to Rh [13]. This vibration shifts to 1981 cm^{-1} after encapsulation, which indicates the strength of CO coordination with Rh is enhanced after the complex is anchored and entrapped in the matrix. The other characteristic bands at 2927, 2860, 1550, 1435,

1087, 740 and 698 cm^{-1} in (b) can be apparently identified in (c).

The XPS spectra gave the corresponding binding energies and molar fractions of phosphorus, rhodium and silicon atoms on the surface of the fresh catalyst and the catalyst after the first and the seventh runs, respectively. The results are shown in Fig. 2 and Table 1. From Fig. 2, we can know that the binding energies of the elements in the catalyst agreed well with those in literature [5], which indicated that rhodium was present in the 1+ oxidation state as in the homogeneous complex. This fully supports the idea that the complex suffered from no damages in the preparation procedures and the catalytic reaction. Thus this method for preparing the heterogenized catalyst is reliable and the catalyst obtained will have good recyclability in the catalytic reaction.

3.3. The effect of pH in the sol–gel process on the catalysis of the catalyst

Generally, the catalysis of heterogenized catalyst via the sol–gel technique depends on the conditions including encapsulating temperature, drying temperature, the molar ratio of water to TEOS and the pH employed in the sol–gel process. From experimental results, we found that pH was the most important factor in determining the catalysis of the heterogenized complex. Table 2 presents the conversion and selectivity towards aldehyde in the hydroformylation of 1-hexene in presence of the catalysts

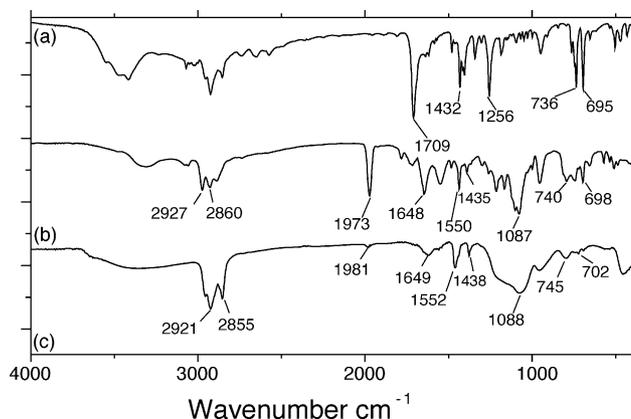


Fig. 1. FT-IR spectra of: (a) the ligand diphenylphosphine propionic acid, (b) the homogeneous catalyst and (c) the heterogenized catalyst.

Table 1
Surface atomic concentration of the heterogenized catalyst determined by XPS

Catalyst	Mole fraction of elements (%)				
	Si	P	Rh	$n(\text{Rh})/n(\text{Si})$	$n(\text{Rh})/n(\text{P})$
Fresh	39.60	1.07	0.43	0.011	0.40
Running 1 time	35.86	1.01	0.19	0.0053	0.19
Running 7 time	41.41	1.02	0.17	0.0041	0.17

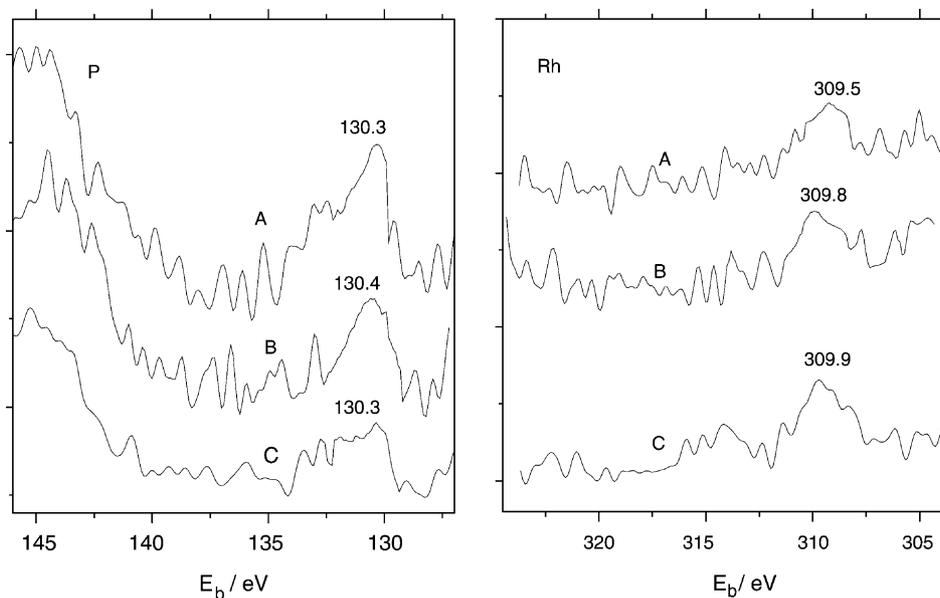


Fig. 2. XPS profile of P and Rh ions in the heterogenized catalyst: (A) fresh heterogenized catalyst; (B) heterogenized catalyst of running 1 time; (C) heterogenized catalyst of running 7 time.

encapsulated in different pHs. It can be seen that the highest conversion (91.0%, corresponding 1172 of the TON) of 1-hexene was obtained when the catalyst prepared at pH 4 (entry 3) was employed in the hydroformylation of 1-hexene at 100 °C under 5 MPa, while the conversion was only 81.2% for the catalyst prepared at pH 2. It seems that the pH had no remarkable effect on the selectivity of the catalyst for the hydroformylation of 1-hexene.

For elucidating why this happened, N₂ adsorption was employed to analyze the surface area, pore volume and average pore diameter of the catalysts. The results are given in Table 3. The catalytic activity obviously relates with the internal structure of the catalysts. It is noted that the surface area, pore volume and average pore diameter of the catalyst prepared at pH 4 are 389 m²/g, 0.20 cm³/g and 20 Å, respectively, larger than those prepared at other pHs. Large surface area allows more active center to be exposed to reactants, giving more chances of substrates contacting the catalytic active center of the catalyst and enhancing the activity of the catalyst. Therefore, the catalyst obtained at pH 4 is the best in activity among all the catalysts. The catalytic property is also related with the pore diameter and

pore volume of the catalyst. Large pores facilitate the fast diffusion of substrates to the active center, which also increases the catalytic activity of the heterogenized catalyst. Here, all average pore diameters of the catalysts are larger than the diameter of 1-hexene, which allows 1-hexene to enter into the matrixes smoothly, so the diameter is not the key factor determining the catalytic activities of the catalysts.

Although the heterogenized catalyst showed excellent conversion, high selectivity towards aldehyde and TON in the hydroformylation of 1-hexene, the *n/i* ratio of the aldehyde was relatively low. The *n/i* ratio for all the catalysts in the hydroformylation of 1-hexene was not higher than 0.90. The low value of *n/i* ratio may be derived from the fact that ligand anchored to the matrix could not move freely to the catalytic center as that in the homogenous analogues, which caused no steric effect enhancing the increase in the *n/i* ratio. Perhaps, this problem can be solved by lengthening the anchoring linker. The other reason might be that the heterogenized catalyst has a strong isomerization activity derived from the matrix.

Because the heterogenized catalyst prepared at pH 4 showed the highest activity, it was studied intensively. The reaction parameters influencing the catalytic activity were investigated and optimized.

Table 2
Hydroformylation of 1-hexene with the catalysts prepared at different pH values

Entry	pH	Conversion (%)	Selectivity		TON
			Aldehyde (%)	<i>n/i</i>	
1	2	81.2	99.4	0.81	1046
2	3	85.3	99.4	0.86	1113
3	4	91.0	99.3	0.89	1172
4	5	86.8	99.6	0.84	1121

Reaction conditions: catalyst—0.238 g, Rh-content in catalyst—1.34%, w/w; P_{CO/H₂} = 5.0 MPa (CO:H₂ = 1:1); temperature—373 K; 1-hexene—5 ml (0.04 mol); solvent—toluene, volume—50 ml; reaction time—9 h; TON—mole of aldehydes formed/mole of Rh.

Table 3
N₂ adsorption results of the catalysts

Entry	pH	Surface area ^a (m ² /g)	Pore volume ^b (cm ³ /g)	Average pore diameter ^c (Å)
1	2	290.78	0.11	15.14
2	3	312.37	0.14	17.93
3	4	388.58	0.20	20.32
4	5	314.16	0.13	16.55

^a Calculated from the BET equation.

^b Calculated from the BJH equation.

^c Average pore diameter = 4 × pore volume/surface area.

Table 4
Effect of temperature on the reaction

T (°C)	Conversion (%)	Selectivity		TON
		Aldehyde (%)	<i>n/i</i>	
90	85.2	100.0	0.94	1104
100	96.8	99.3	0.87	1246
110	91.2	98.0	0.84	1159
120	89.0	95.8	0.78	1105

Reaction conditions: catalyst—0.238 g; Rh-content in fresh catalyst—1.34%, w/w; $P_{\text{CO}/\text{H}_2} = 4.0$ MPa (CO:H₂ = 1:1); 1-hexene—5 ml (0.04 mol); solvent—toluene, volume—50 ml; reaction time—10 h; TON—mole of aldehydes formed/mole of Rh.

3.4. Effect of temperature

The hydroformylation of 1-hexene catalyzed by the heterogenized catalyst prepared at pH 4 was studied at 90–120 °C and the results obtained are shown in Table 4. An increase in the conversion of 1-hexene was observed with the increase in the temperature from 90 to 100 °C. The highest conversion of 1-hexene was obtained at 100 °C. At this temperature, the conversion was 96.8% and the TON reached 1246. Then, the conversion decreased with the increase in the temperature mainly because isomerization of 1-hexene was enhanced at high temperature. It was observed both the selectivity towards aldehyde and the *n/i* ratio for the aldehyde decreased with the increase in the temperature, which was also due to the increase in the isomerization of 1-hexene at elevated temperature.

3.5. Effect of pressure

The activity of the catalyst for the hydroformylation of 1-hexene was studied at different pressures at 100 °C and the results are given in Table 5. It was found the conversion increased with increasing pressure of synthesis gas (CO:H₂ = 1:1) when the pressure was lower than or equal to 5.0 MPa. As the pressure increased from 3 to 5 MPa, the conversion increased from 80.2 to 98.7%, but the selectivity towards aldehyde kept almost constant. The reason may be higher H₂ pressure can stabilize the rhodium hydride that is the key intermediate in the hydroformylation cycle. Once the pressure was higher than 5.0 MPa, the conversion began to decrease with the increase in the pressure, which conformed to the kinetics of hydroformylation. The *n/i*

Table 5
Effect of pressure on the reaction

Pressure (MPa)	Conversion (%)	Selectivity		TON
		Aldehyde (%)	<i>n/i</i>	
3.0	80.2	99.6	0.83	1059
4.0	96.8	99.3	0.87	1246
5.0	98.7	99.6	0.86	1274
6.0	97.8	99.7	0.89	1264

Reaction conditions: catalyst—0.238 g, Rh-content in fresh catalyst—1.34%, w/w, CO:H₂ = 1:1; temperature—373 K; 1-hexene—5 ml (0.04 mol); solvent—toluene, volume—50 ml; reaction time—10 h; TON—mole of aldehydes formed/mole of Rh.

Table 6
Effect of solvent on the reaction

Solvent	Conversion (%)	Selectivity		TON
		Aldehyde (%)	<i>n/i</i>	
Toluene	98.7	99.6	0.86	1274
Cyclohexane	98.9	99.2	0.71	1272
1,4-Dioxane	98.4	99.9	1.03	1274
<i>N,N</i> -Dimethylformamide	20.5	100.0	2.18	266

Reaction conditions: catalyst—0.238 g, Rh-content in fresh catalyst—1.34%, w/w, $P_{\text{CO}/\text{H}_2} = 5.0$ MPa (CO:H₂ = 1:1); temperature—373 K; 1-hexene—5 ml (0.04 mol); solvent—toluene, volume—50 ml; reaction time—10 h; TON—mole of aldehydes formed/mole of Rh.

ratio for the aldehyde increased from 0.83 to 0.87 as the pressure increased from 3 to 4 MPa, but it did not greatly change when the pressure increased from 4 to 5 MPa.

3.6. Effect of solvent

Solvents also have influence on the hydroformylation of olefin. In order to study the effect of solvent, several solvents were employed in the hydroformylation of 1-hexene catalyzed by the above catalyst. As shown in Table 6, the conversion was higher than 98% when toluene, cyclohexane and 1,4-dioxane were used as solvents. However, if *N,N*-dimethylformamide was employed, the conversion was only 20.5%. It was also observed that both the selectivity towards aldehyde and the *n/i* ratio increased with the increase in the solvent polarity. The selectivity towards aldehyde was 99.2% and the *n/i* ratio was 0.71 when cyclohexane was employed. However, the selectivity reached 100% and the *n/i* ratio increased to 2.18 in *N,N*-dimethylformamide. These results can be explained by the solvating effect. That is, the polar solvent molecules could surround the active center of the catalyst to generate a solvent cage which slowed down the substrate to contact the catalyst and decreased the reaction rate. Furthermore, the solvent molecules in the cage enhance the coordination of the substrate to the Rh with the terminal carbon atom or that with fewer substitutes, which also pushed the isomerization of hexenes shifted to 1-hexene.

From above results, the optimized conditions for the hydroformylation of 1-hexene were obtained. When the reaction was carried out at the optimized conditions (at 100 °C under 5 MPa in toluene for 9 h), the conversion of 1-hexene was 98.8%, with a selectivity of 99.6% towards aldehyde and the *n/i* ratio of 0.86.

3.7. Recycle test of the heterogenized catalyst

The goal of heterogenizing homogeneous catalyst is to find a catalyst with good catalytic performance and reusability. The heterogenized catalyst was used in subsequent catalytic runs to obtain information as to its reusability. The results are presented in Table 7. The conversion decreased by 2.9% in the second run but it decreased by only 0.9% in the sixth run compared to the second run. The drop of conversion during the recycle runs should come from the leaching of rhodium. The conversion cannot reflect the actual catalyst deactivation. Table 7 also gives

Table 7

Recycle test results of the heterogenized catalyst for hydroformylation of 1-hexene

Recycle runs	Conversion (%)	Selectivity		TON	TOF
		Aldehyde (%)	<i>n/i</i>		
1	98.2	99.6	0.86	1268	126.8
2	95.3	99.8	0.83	1406	140.6
3	87.8	100.0	0.80	1297	129.7
4	96.7	99.7	0.85	1425	142.5
5	93.3	99.8	0.82	1376	137.6
6	94.4	99.5	0.87	1389	138.9
7	88.1	99.7	0.86	1298	129.8

Reaction conditions: catalyst—0.238 g, Rh-content in fresh catalyst—1.34%, w/w, in the catalyst of running 1 time—1.17%, w/w; $P_{\text{CO}/\text{H}_2} = 5.0$ MPa ($\text{CO}:\text{H}_2 = 1:1$); temperature—373 K; 1-hexene—5 ml (0.04 mol); solvent—toluene, volume—50 ml; reaction time—10 h; TON—mole of aldehydes formed/mole of Rh; TOF—mole of aldehydes formed/((mole of Rh)h).

the TOF. It can be seen that the TOF had not reduced markedly during the recycle test. Compared with that in the second run, the TOF in the sixth run decreased by 1.2%. The selectivity towards aldehydes and the *n/i* ratio almost kept constant.

XPS and ICP were used to determine the leaching of rhodium in the recycle runs. As shown in Table 1, 50% of rhodium atom in the outer surface was lost after the first run. The heavy losses of rhodium can be attributed to that the rhodium on the surface of the matrix was not encapsulated by the matrix but only anchored by phosphino ligand, while CO in the system could replace the phosphino ligand from rhodium in the hydroformylation conditions.

The XPS results cannot give the real leaching situation of the catalyst because it cannot detect the atoms entrapped in the matrix. For obtaining the accurate rhodium leaching of the heterogenized catalyst, the rhodium contents of the fresh catalyst, the catalysts after the first and seventh runs were analyzed by ICP, which were 1.34, 1.17 and 1.18%, respectively. From these results, we can know 12.7% of the rhodium atom was leached after the first run, but no rhodium leaching took place in the subsequent runs. From the ICP and XPS results, we concluded that the rhodium leaching (12.7%) mainly came from the outer surface of the matrix, while the complex entrapped in the matrix did not leach enormously with the combination of protection by

anchoring and encapsulation. From these results, we also conclude besides the rhodium leaching, the impurities deposited on the surface of the matrix, which blocked the substrates entering to contact the catalyst, might be another reason to decrease the conversion.

4. Conclusions

A novel heterogenized rhodium carbonyl complex catalyst for hydroformylation was prepared by the combination of chemically anchoring and the sol-gel encapsulation methods. The catalyst has high activity, selectivity and stability but low *n/i* ratios in the hydroformylation of 1-hexene. It can be separated easily from the product and reusable in numerous catalytic cycles without much deterioration of the catalytic activity.

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