Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 283 (2008) 15–22
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Asymmetric hydroformylation of olefins catalyzed by rhodium nanoparticles chirally stabilized with (*R*)-BINAP ligand

Difei Han [a], Xiaohong Li [b], Huidong Zhang [a], Zhimin Liu [a], Gengshen Hu [a], Can Li [a,*]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China*

Received 28 September 2007; received in revised form 28 November 2007; accepted 1 December 2007
Available online 15 December 2007

Abstract

Rhodium nanoparticles have been conveniently synthesized by one-pot chemical reduction of aqueous rhodium chloride ($RhCl_3 \cdot 3H_2O$) dispersed in toluene solution in the presence of amphiphilic tetraoctylammonium bromide (TOAB) and chiral (*R*)-BINAP at ambient conditions. The resulting highly dispersed rhodium nanoparticles show small and narrowly distributed core sizes (1.5–2.0 nm). The chirally stabilized rhodium nanoparticles were also immobilized on silica by impregnation to give the corresponding supported catalysts. ^{31}P MAS NMR results and IR spectra of adsorbed CO confirm that chiral (*R*)-BINAP ligands stabilize the nanoparticles by coordinative interaction between phosphine and rhodium, and produce chirally catalytic active sites on the rhodium nanocatalysts. Chirally stabilized catalysts exhibit high regioselectivity and chiral induction ability for the asymmetric hydroformylation of olefins. The supported rhodium nanocatalysts show the increased activities compared to the unsupported catalysts (e.g. from 12 to 22 h^{-1} for the hydroformylation of styrene). One hundred percentage regioselectivity of branched aldehyde and up to 59% ee were obtained for the hydroformylation of vinyl acetate.

Keywords: Rhodium nanoparticles; Enantioselective hydroformylation; Chiral stabilization; Coordination; Phosphorus ligands

1. Introduction

The synthesis and characterization of metal nanoparticles have been intensively studied because of their potential applications in materials sciences, biological sciences, and chemical platforms [1,2]. Most of the metal subgroup elements can be used to prepare metal nanoparticles [3]. The stabilization of metal nanoparticles with surfactants or ligands can greatly influence their particle sizes, electron, and other properties as catalysts, photoelectric materials, molecular machines, and bio/chemical sensors [4]. Particularly, the stabilized metal nanoparticles have been extensively utilized as catalysts for hydrogenations, hydrosilylations, hydrogenolysis, oxidation, McMurry, Suzuki and Heck-Type couplings and other organic synthesis reactions [5–7]. Various ligands, such as surfactants, phosphorus or nitrogen-containing ligands, and thiols/thioethers, can be used as stabilizer to prepare the metal nanoparticles and show remarkable influence on their catalytic performance. However, chiral ligand-stabilized nanoparticles have been seldom synthesized or applied to enantioselective catalysis. Fujihara and coworkers [8,9] reported the synthesis of chirally stabilized gold and palladium nanoparticles and their application in the heterogeneous asymmetric hydrosilylation and carbon–carbon coupling reactions. Jansat et al. [10,11] synthesized ruthenium nanoparticles stabilized by diphosphite and N-donor ligands and applied these chirally stabilized catalysts to enantioselective allylic alkylation, hydrogenation and transfer hydrogenation reactions. Hyeon and coworkers [12] investigated the coordination chemistry of chiral phosphine ligands on palladium nanoparticles in detail. Researches indicate that coordinated chiral ligand may lead to chiral induction on the metal surface and stabilize the nanoparticles due to their strong chelating effect [13–16]. However, the rhodium nanoparticle catalysts stabilized with chiral phosphorus ligands appear to be an attractive and unexplored area for the development of effective heterogeneous chiral catalysts.

Chiral hydroformylation is one of the most challengable organometallic catalytic reaction and also a very useful method for the asymmetric synthesis of optically active aldehy-

* Corresponding author. Tel.: +86 411 84379070; fax: +86 411 84694447.
E-mail address: canli@dicp.ac.cn (C. Li).
URL: http://www.canli.dicp.ac.cn (C. Li).

1381-1169/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2007.12.008

des [17,18]. Chiral rhodium organometallic complexes were extensively developed for homogeneous asymmetric hydroformylation reactions. Recently, we developed chirally modified rhodium catalysts for the heterogeneous asymmetric hydroformylation of olefins [19]. Chiral phosphorus ligands were *in situ* introduced to modify the Rh/SiO_2 catalysts. Our Surface Enhanced Raman Spectroscopy (SERS) investigation on ligand modification indicates that the ligands are adsorbed onto the metal surface by coordination interaction [20]. The coordination of chiral ligands to surface rhodium sites may form chiral environment and further produce chiral induction on the metal surface. These promote us to develop chirally stabilized rhodium nanoparticles and research their application in asymmetric hydroformylation.

In this paper, we present the synthesis of novel rhodium nanoparticles stabilized with chiral phosphorus ligands and the corresponding supported catalysts. The coordination of phosphines to the nanoparticles was characterized by ^{31}P solid state NMR and IR spectra using CO as a probe. The chirally stabilized catalysts were then applied in the asymmetric hydroformylation of styrene and vinyl acetate under mild conditions, giving high regioselectivity and chiral induction ability for the branched aldehydes.

2. Experimental

2.1. General

Unless otherwise mentioned, all the manipulations were carried out with the use of standard Schlenk techniques. All the solvents used for reactions were analytical grade and treated by standard methods. Styrene and vinyl acetate were distilled before use. Chiral ligands were used as obtained without further purification. (*R*)-(+)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BIANP, >98%), and other ligands and reagents were purchased from Acros or Alfa Aesor. Rhodium trichloride hydrate (Rh > 40 wt.%) and Bis(1,5-cyclooctadiene)rhodium (I) chloride ($[Rh(COD)Cl]_2$) were used as received. Activated SiO_2 was calcined at 540 °C for 3 h before use.

2.2. Catalysts preparation

2.2.1. Preparation of rhodium nanoparticles stabilized with chiral ligands, Rh-BINAP

Rhodium nanoparticles catalysts stabilized with chiral phosphorus ligand were prepared using a modification method derived from the literature procedures [8,11]. Optically active (*R*)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP) was chosen as the chiral ligand for the stabilization of rhodium nanoparticles owing to its excellent coordination and chiral induction abilities. Rhodium trichloride hydrate ($RhCl_3$, 0.0270 g, 0.1 mmol) and tetraoctylammonium bromide (TOAB, 0.0465 g, 0.085 mmol) were dissolved in 2 ml deionized water and 2 ml toluene, respectively. The $RhCl_3$ solution was dropwise added to the surfactant solution and the mixture was stirred vigorously for 1 h under purged argon. When the rhodium color was transferred into organic phase, (*R*)-BINAP (0.1360 g, 0.2188 mmol, dissolved in 25 ml toluene) was added and the solution was stirred vigorously for another 0.5 h at room temperature. Aqueous sodium borohydride ($NaBH_4$ 0.05 g, 1.3 mmol, dissolved in 1.2 ml H_2O) was freshly prepared and added into reaction system immediately. The organic phase turned black and was further stirred for 3 h under argon atmosphere. The mixture was washed with water (2 × 50 ml) and the organic layer was separated to obtain rhodium nanoparticle solution. The resulting solid was washed with H_2O, brine and methanol/water mixture and gave rhodium nanoparticles (Rh-BINAP).

2.2.2. Preparation of chirally stabilized rhodium nanoparticles supported on silica, Rh-BINAP/SiO_2

The rhodium nanoparticles precursor containing organic layer was added to vacuum activated SiO_2 (the average pore size is 9.7 nm, S_{BET} = 375 m^2/g) and impregnated overnight. The solvent was removed in vacuum to yield a black-gray solid. The resulting solid was washed according aforementioned method to give the supported rhodium nanoparticles (Rh-BINAP/SiO_2).

The rhodium nanoparticles stabilized with achiral PPh_3 (Rh-PPh_3 and Rh-PPh_3/SiO_2) were synthesized according to the similar methods for comparison.

2.2.3. Silica immobilized homogeneous complex, $[Rh(COD)BINAP]^+OTf^-/SiO_2$

$[Rh(COD)BINAP]^+OTf^-$ was synthesized according to literature method. In a Schlenk tube under Ar, 0.1 mmol $[Rh(COD)Cl]_2$ was dissolved in 10 ml CH_2Cl_2 and 0.23 mmol $AgCF_3SO_3$ was added. The resulting mixture was stirred at room temperature for 1 h then the precipitate was filtered. To the filtrate, 0.23 mmol (*R*)-BINAP in 5 ml CH_2Cl_2 was added dropwise. The resulting mixture was stirred at RT for 3 h and then 30 ml Et_2O was slowly added. The precipitate was filtrated and dried under reduced pressure. The obtained powder was washed with Et_2O and vacuum-dried overnight to obtain the Rh-diphosphine complexes. One grams of activated SiO_2 was suspended in 5 ml CH_2Cl_2. The Rh diphosphine complex (0.1 mmol) was dissolved in 1 ml CH_2Cl_2 and added to the SiO_2/CH_2Cl_2 suspension. The reaction mixture was stirred at RT overnight and the recovered solid was washed with MeOH. The supported homogeneous catalyst was vacuum-dried at RT overnight and characterized by ^{31}P MAS NMR and IR spectroscopy.

2.3. Characterization of chirally stabilized rhodium nanoparticles

Transmission Electron Microscope (TEM) images of the catalyst samples were taken on a JEM-2000EX electron microscope. Solid-state ^{31}P MAS NMR spectra were accumulated on a Bruker DRX-400 spectrometer. IR spectra of absorbed CO on the chirally modified catalysts were collected on a Fourier transform infrared spectrometer (Thermo Nicolet NEXUS 470) with a resolution of 4 cm^{-1} and 64 scans in the region of 4000–1000 cm^{-1}. The chirally stabilized catalyst or premodified catalyst was transferred into an *in situ* IR cell, and the sample was purged with argon to remove the solvent at 120 °C.

Infrared spectra in the transmission mode were collected at reaction temperature (60 °C) after the exposure of the pre-modified catalyst to carbon monoxide.

2.4. Hydroformylation test

2.4.1. Asymmetric hydroformylation on chirally stabilized rhodium nanoparticles catalysts

The as-synthesized catalysts should be pretreated under a flow of H_2 at 453 K for 3 h before the heterogeneous asymmetric hydroformylation. The chirally stabilized catalyst (0.002 mmol Rh) together with the olefin substrate (1.2 mmol styrene or vinyl acetate in 3 ml anhydrous toluene) were transferred into an autoclave under argon atmosphere. The hydroformylation reaction were carried out under 50 atm syngas at 60 °C for 4 h. Conversion and regioselectivity (branched to linear ratio) were determined by gas chromatography (6890N, Agilent) equipped with a chiral capillary column (Chiral-Dex β-225) and the enantiomeric excess of the branched aldehyde was determined by Jones oxidation of product to the corresponding carboxylic acid followed by chiral GC analysis. The products configurations were determined by comparison of the retention time with the authentic samples.

2.4.2. Homogeneous asymmetric hydroformylation

In a typical homogeneous asymmetric hydroformylation experiment, an autoclave was filled with 0.004 mmol phosphorus ligand (0.001 mM stock solution in toluene). 0.001 mmol $[Rh(COD)Cl]_2$ (0.001 mM solution in toluene) were added under argon (L/Rh ratio of 2.0) and the solution was stirred for 2 h to *in situ* form the chiral catalyst. The substrate (2.0 mmol) was added and the subsequent operations were carried out according to the heterogeneous reaction procedure except for a reaction time of 10 h. Before GC analysis, the reaction product was concentrated and purified by flash column chromatography.

2.4.3. Recycle

The recycle experiments of catalyst and hot filtrate experiment were also performed. When the first cycle reaction was over, the reaction system was centrifuged and the solution was carefully removed under argon atmosphere. Fresh vinyl acetate substrate and solvent were added to the autoclave together with the recovered solid catalyst and then the next cycle was carried out under the same hydroformylation reaction conditions. On the other hand, filtrate recycle experiment was also performed. The reaction solution of the first cycle reaction with an incomplete conversion was filtered carefully and directly used in the next catalytic cycle.

3. Results and discussion

3.1. Synthesis of chirally stabilized rhodium nanoparticles

In our previous work, we reported the synthesis and catalytic properties of silica-supported rhodium nanoparticles modified with chiral phosphorus ligands [19]. The supported nanocatalysts were prepared by impregnation and consequently treated by calcination and hydrogen reduction at elevatory temperature. The chiral phosphorus ligands were *in situ* introduced to reaction or pre-adsorbed to modify the supported rhodium catalysts. These catalysts can give chiral inductivity for the hydroformylation of olefins. The silicas support is crucial to obtain high dispersed rhodium nanoparticles. It is attractive for us to develop the rhodium nanoparticles without the support and research the corresponding catalytic performance for the asymmetric hydroformylation.

Herein, we firstly prepared rhodium nanoparticles catalysts (Scheme 1). They can be conveniently synthesized by one-pot chemical reduction method in the absence of silica support [21]. Aqueous rhodium chloride was increasingly dissolved and highly dispersed in toluene solution in the presence of amphiphilic TOAB and the chiral stabilizer (*R*)-BINAP. Then the catalytic precursor was reduced by $NaBH_4$ at ambient conditions. The solution turned from red to black immediately, which indicated the formation of Rh(0) species. The rhodium nanoparticles were stabilized with the TOAB and chiral ligands and remained stable without aggregation.

Then the as-synthesized chirally stabilized rhodium nanoparticles were also immobilized on silica support activated in vacuum by adsorption. This supported catalyst was used for comparison with the free nanocatalysts and the supported catalysts prepared by traditional impregnation method. For the chirally stabilized methods, the chiral ligand was introduced in the synthesis procedure of rhodium nanoparticles. It is much different from that of chirally modified catalyst, in which the chiral ligand was introduced to modify the supported rhodium catalyst pre-reduced by hydrogen.

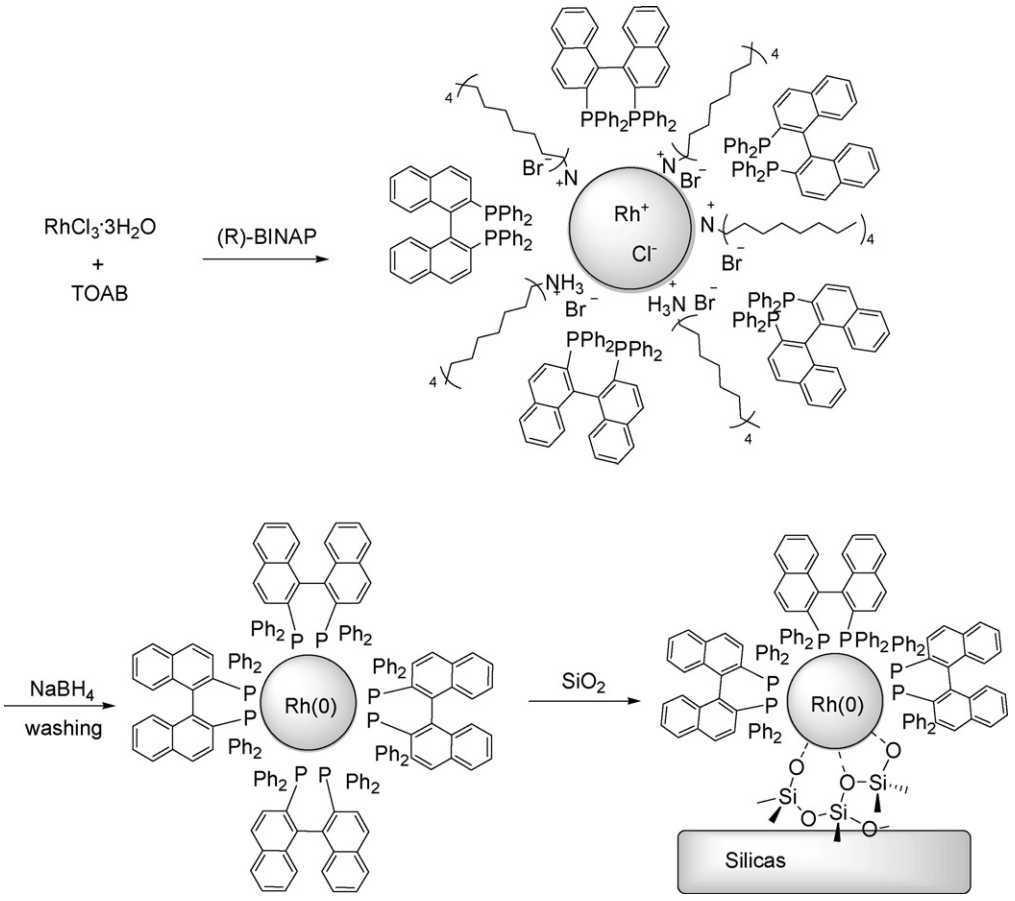
3.2. Characterization of chirally stabilized rhodium nanoparticles

3.2.1. TEM characterization

The TEM images of chirally stabilized Rh nanoparticles (Fig. 1a) and the corresponding silica-supported catalyst (Fig. 1b) show the highly dispersed rhodium nanoparticles with narrowly distributed core sizes. The average sizes of chirally stabilized rhodium nanoparticles were determined as about 1.5–2.0 nm. The particle size is similar to that of rhodium catalyst supported on silica (Fig. 1c, Rh/SiO_2, 69% dispersion and 1.7 nm diameter) prepared by incipient wet impregnation method, which was used for chirally modification. The presence of chiral phosphorus ligands benefits the formation and stabilization of rhodium nanoparticles, and provide more uniformly dispersed particle size. These results indicate that chiral stabilization is an efficient method to prepare highly dispersed rhodium nanoparticles in the absence of large surface support.

3.2.2. ^{31}P MAS NMR characterization

^{31}P MAS NMR and CO-IR spectroscopies are effective methods to investigate the metal–ligand mutual interaction of solid catalysts. The interaction between the rhodium nanoparticles and the chiral (*R*)-BINAP ligands was investigated by ^{31}P MAS NMR spectroscopy (Fig. 2). The broad signal at about 34.0 ppm



Scheme 1. The schematic synthesis of chirally stabilized rhodium nanoparticles.

for the chirally stabilized nanoparticles (Rh-BINAP/SiO_2, Fig. 2a) is assigned to the (*R*)-BINAP coordinated to rhodium atoms, which is similar to that of chirally modified catalysts (BINAP-Rh/SiO_2, Fig. 2b) and the supported organometallic complex ([Rh(COD)BINAP]$^+OTf^-$/SiO_2, Fig. 2c). This result indicates that the stabilization of rhodium nanoparticles with chiral phosphorus ligand can form quite strong P–Rh coordination interaction analogous to that of the rhodium organometallic complex. Simultaneously, the surface acid sites of support can compete with rhodium nanoparticles to adsorb the basic phosphine ligands. The signal of free (*R*)-BINAP (Fig. 2e) shifts to lower field when the chiral ligands are physically adsorbed on the silica support (Fig. 2d).

3.2.3. ATR-IR characterization

Interaction between the chiral diphosphine stabilizers with the rhodium nanoparticles was also characterized by IR spectroscopy using CO as the probe molecule (Fig. 3). CO-IR spectra of supported organometallic complexes (Fig. 3a) and Rh/SiO_2 (Fig. 3b) show ν_{CO} stretching vibration at about 2100 cm^{-1} corresponding to the rhodium gem-di-carbonyl species as the main band. These bands greatly decrease and red-shift to lower wavenumbers for BINAP-modified Rh/SiO_2 (Fig. 3c) and BINAP-stabilized rhodium catalyst (Fig. 3d). The comparatively weak band (1986 cm^{-1}) attributed to the stretching linearly adsorbed CO on the surface Rh(0) sites, appears as the main component for the chirally stabilized catalyst. These results indicate that adsorbed phosphines occupy surface Rh sites and therefore inhibit the adsorption of CO on the rhodium surface, especially for the chirally stabilized catalysts. The IR frequency of the adsorbed CO red-shifts a lot to lower frequencies in the presence of (*R*)-BINAP, which is due to the electron donor effect of phosphorus atom.

It is well-known that the phosphorus atom of ligand can donate its lone pair electrons to metal and accept the d orbital feedback from a transition metal atom. Our SERS research on the phosphorus ligand modification also confirms that the ligands adsorb on the metal surface through coordination interaction [20]. The σ-donor ability of phosphorus atom is stronger than the π-acceptor ability, and the coordination may change the surface charge property of metal nanoparticles. This result agrees to the results of CO-IR results (Fig. 3). For the chirally stabilized rhodium nanoparticles in this work, the coordination of phosphine ligands can increase the electron density of metal centre, further increase the π-back-donation from metal to other coordinative molecule. Therefore, the electron-rich surface may provide better ability for the coordination and activation of olefin and CO substrates.

The characterization results of NMR and IR spectra indicate that the chiral stabilization via the coordination of phosphines

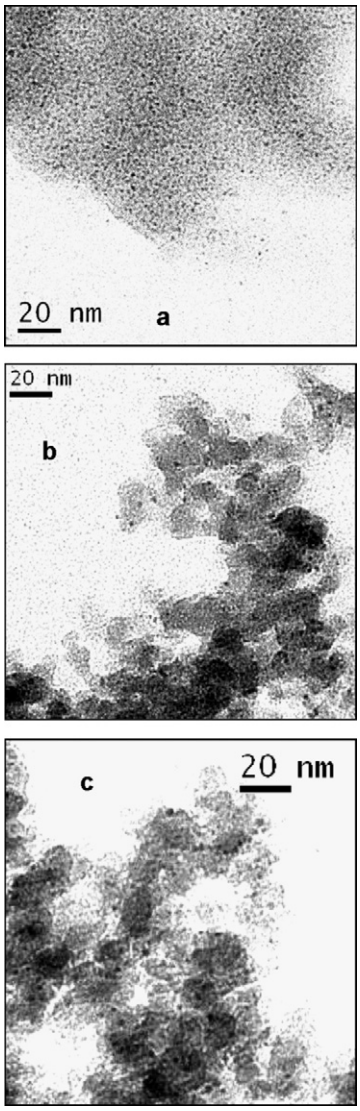


Fig. 1. TEM images of (a) Rh-BINAP (b) Rh-BINAP/SiO_2 (c) BINAP-Rh/SiO_2.

to rhodium may modify the surface electronic state and produce chirally catalytic active sites on the rhodium nanoparticles. Then, the possibility of the asymmetric induction on the chirally stabilized catalysts were studied.

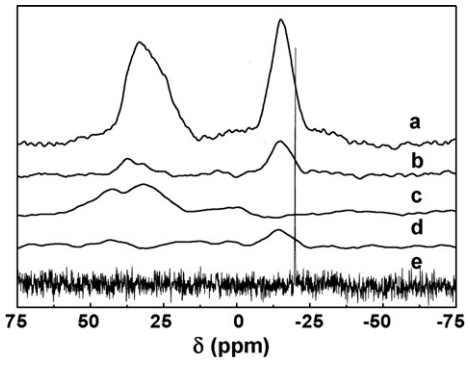


Fig. 2. ^{31}P MAS NMR spectra of (a) Rh-BINAP/SiO_2, (b) BINAP-Rh/SiO_2, (c) [Rh(COD)BINAP]$^+$OTf$^-$/SiO_2, (d) BINAP-SiO_2 and (e) ^{31}P NMR BINAP.

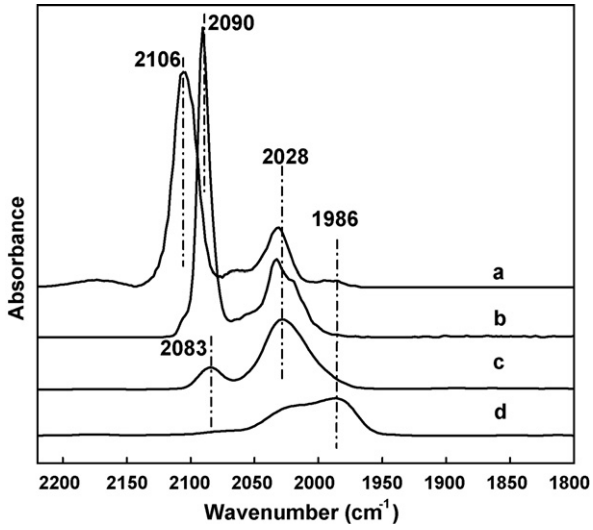
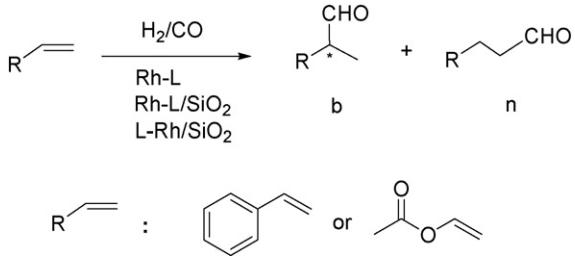


Fig. 3. IR spectra of adsorbed CO on (a) [Rh(COD)BINAP]$^+$OTf$^-$/SiO_2, (b) reduced Rh/SiO_2, (c) BINAP pre-modified Rh/SiO_2 and (d) Rh-BINAP/SiO_2 at 60 °C.



Scheme 2. Asymmetric hydroformylation of olefins on chirally stabilized rhodium nanoparticle catalysts.

3.3. Hydroformylation test

The effects of different preparation methods were tested for the asymmetric hydroformylation of styrene and vinyl acetate using the chirally stabilized catalyst, its supported analogue and the chirally modified catalyst (Scheme 2). Homogeneous catalyst and PPh_3-stabilized catalyst were also investigated for comparison.

3.3.1. Hydroformylation of styrene

The catalytic performance of chirally stabilized rhodium catalysts was investigated for the hydroformylation of styrene as the model reaction (Table 1). The introduction of chiral ligand to rhodium catalysts causes higher regioselectivity and obvious chiral induction ability than the unmodified supported catalysts. Chirally stabilized rhodium nanocatalyst (Rh-BINAP) gave 12 h^{-1} TOF, 92% branched selectivity and 25% ee (*S*-enantiomer). When supported on silica, the chirally stabilized catalyst (Rh-BINAP/SiO_2) exhibits an increased activity (22 h^{-1}), which is higher than the chirally modified Rh/SiO_2 catalyst (13 h^{-1}) and the corresponding homogenous catalyst (11 h^{-1}). The heterogeneous chiral catalysts exhibit much better branched regioselectivity (89:11–92:8) than the homogeneous catalyst (85:15). The supported catalyst stabilized with achiral

Table 1
Asymmetric hydroformylation of styrene on chirally stabilized rhodium nanoparticles[a]

Entry	Catalyst	Conv. (%)	TOF[b] (h^{-1})	*b*/*n*	Ee[c,d] (%)
1	Rh/SiO_2	99	212	67:33	0
2	Rh-BINAP	5	12	92:8	25 (*S*)
3	$Rh\text{-}BINAP/SiO_2$	9	22	89:11	26 (*S*)
4	$BINAP\text{-}Rh/SiO_2$	6	13	92:8	30 (*S*)
5	Homo.	5	11	85:15	31 (*S*)
6	$Rh\text{-}PPh_3/SiO_2$	99	239	85:15	0

[a] Reactions were carried out with 2 μmol rhodium catalyst and 1.2 mmol olefin in toluene (3 ml) at 60 °C under 50 bar syngas ($CO:H_2 = 1:1$) for 4 h.
[b] Calculated by the rhodium dispersion.
[c] Determined by means of GC with a chiral β-cyclodextrin column.
[d] The products configurations are determined by comparison of the elution order with the authentic samples.

PPh_3 ligand ($Rh\text{-}PPh_3/SiO_2$) was also tested for comparison. No chiral inductivity and lower regioselectivity against higher activity ($239\ h^{-1}$) were obtained. The presence of chiral ligand can remarkably influence the hydroformylation performance of rhodium nanoparticles.

3.3.2. Hydroformylation of vinyl acetate

The hydroformylation of vinyl acetate was also performed on chirally stabilized rhodium catalysts (Table 2). The chirally stabilized catalyst (Rh-BINAP) exhibits superior branched regioselectivity (99:1) and up to 59% enantioselectivity, which are much higher than those of the hydroformylation of styrene. Its supported catalyst ($Rh\text{-}BINAP/SiO_2$) gave complete branched aldehyde and an increased activity ($5\ h^{-1}$). While, a slight reduction of enantioselectivity (56% ee) was observed on the supported catalyst. The chirally stabilized catalysts exhibit higher regioselectivity and enantioselectivity than the corresponding homogeneous catalyst. Achiral PPh_3-stabilized rhodium nanoparticles ($Rh\text{-}PPh_3/SiO_2$) shows high racemic hydroformylation activity ($126\ h^{-1}$), which is even higher than the ligand-free catalyst ($90\ h^{-1}$) with almost complete regioselectivity of branched product.

It is difficult for monodentate PPh_3 to form stable and rigid chiral environment on metal surface due to the lack of chirality and chelation ability. And the competitive adsorption of carbon monoxide possibly reduces the coordination of PPh_3 to the rhodium catalyst under reaction conditions [22]. The PPh_3-stabilized nanocatalyst exhibit higher activity than that of the unmodified catalyst. This result is even more attractive considering that some of the active sites was occupied by phosphines for the ligand-stabilized catalysts, while all the surface sites can be accessed for the unmodified rhodium catalysts. The electron-donating coordination of PPh_3 may increase the surface electron density and thus activate the surface rhodium sites, which can benefit the coordination and activation of substrates. These may be the reasons for the high activity and regioselectivity of racemic reaction on the PPh_3-stabilized nanocatalyst.

The chirally stabilized rhodium catalysts exhibited lower activity than the ligand-free and PPh_3-stabilized rhodium catalysts. This indicates that the coordination of chiral phosphorus ligands to the rhodium nanoparticles may form steady chiral environment on the surface, and simultaneously inhibit the access and complexation of substrates to the surface metal sites. It is recognized that the steady coordination of chelating biphosphine ligands to the surface sites should account for the decreased activity, although it may produces chiral induction environment on the rhodium surface and also activate the catalytic sites by electron donation. Accordingly, the chirally stabilized nanoparticles can induce chirality for the asymmetric hydroformylation of olefins.

3.3.3. Recycle

Catalyst recycling experiments were performed to test the stability of the heterogeneous catalysts. The durability of the catalytic system was investigated by employing it in several consequent hydroformylation reactions for vinyl acetate (Table 3). The reused catalyst exhibited similar catalytic performance to the first catalytic cycle. After a few cycles, reaction performance can be maintained by newly adding (*R*)-BINAP ligand.

To further confirm that the catalyst is stable and the catalytic reaction indeed occurs on the chirally stabilized catalyst, the reaction of the hot filtration was performed. The catalyst was separated from the reaction mixture after the previous reaction. Then colorless filtrate was maintained under the same hydroformylation conditions. Although the

Table 2
Asymmetric hydroformylation of vinyl acetate on chirally stabilized rhodium nanoparticles[a]

Entry	Catalyst	Conv. (%)	TOF[b] (h^{-1})	*b*/*n*	Ee[c,d] (%)
1	Rh/SiO_2	42	90	98:2	0
2	Rh-BINAP	1	3	99:1	59 (*S*)
3	$Rh\text{-}BINAP/SiO_2$	2	5	100:0	56 (*S*)
4	$BINAP\text{-}Rh/SiO_2$	7	15	100:0	59 (*S*)
5	Homo.	1	3	98:2	54 (*S*)
6	$Rh\text{-}PPh_3/SiO_2$	56	135	99:1	0

[a] Reactions were carried out with 2 μmol rhodium catalyst and 1.2 mmol olefin in toluene (3 ml) at 60 °C under 50 bar syngas ($CO:H_2 = 1:1$) for 4 h.
[b] Calculated by the rhodium dispersion.
[c] Determined by means of GC with a chiral β-cyclodextrin column.
[d] The products configurations are determined by comparison of the elution order with the authentic samples.

Table 3
Recycle of chirally stabilized catalyst for the hydroformylation of vinyl acetate[a,b]

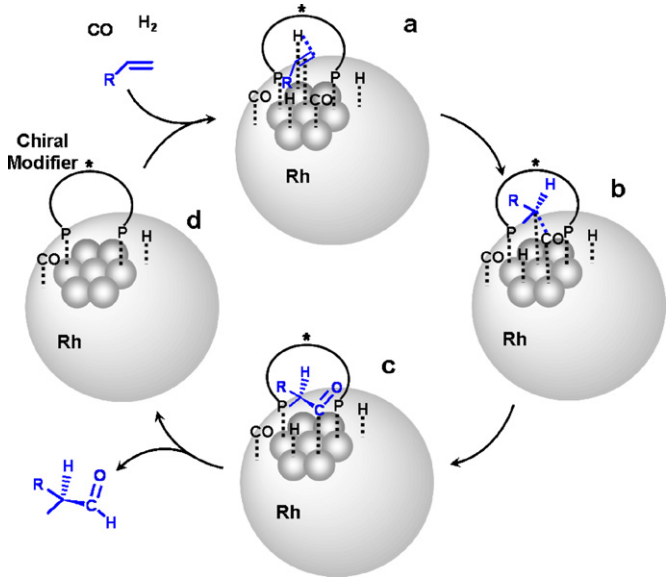
Cycle	Conv. (%)	TOF[c] (h^{-1})	*b*/*n*	Ee[d] (%)
1st	2.0	4	99/1	55
2nd	2.8	6	99/1	51
3rd[e]	2.5	5	99/1	55
4th	2.5	5	99/1	50

[a] Rh:L:Sub. = 1:1:600.
[b] Reactions were performed in toluene (3 ml) at 60 °C under 50 bar syngas ($CO:H_2 = 1:1$) for 4 h.
[c] Calculated by the rhodium dispersion.
[d] Determined by means of GC with a chiral β-cyclodextrin column.
[e] (*R*)-BINAP was added.

mechanic stirring probably damages the catalysts to some extent, no further changes in conversion and enantioselectivity were observed after the filtrate reaction for 4 h. These results indicate that the catalytic activity is definitely attributed to the reaction on the chirally stabilized rhodium catalyst and no obvious change was observed for the catalysts on use.

3.4. Mechanism Discussion

The phosphorus ligand can be adsorbed onto the metal surface via the coordination interaction between the phosphorus atoms and the metal atoms [20,23]. In this work, the ^{31}P MAS NMR and CO-IR results indicate that the (*R*)-BINAP ligands steadily adsorb onto the metal surface through coordination and produce chirally stabilized active sites on the rhodium nanocatalyst. As a result, the chirally stabilized rhodium catalysts exhibit chiral induction ability for the hydroformylation of olefins. The bidentate phosphines of chiral ligand may chelate to nearby rhodium sites to give stable coordination structure. Correspondingly, the chirality of coordinated ligand transfers to the nanocatalyst and form chiral environment on the rhodium surface. The coordinated phosphines and abundant spillover hydrogen can increase the electron density of rhodium surface and benefit the adsorption and activation of olefins and CO. The rigid chiral environment formed by chelated (*R*)-BINAP ligand together with the nanocatalyst surface exhibits good regioselectivity and enantioselectivity for hydroformylation. The activation and reaction of substrates may not necessarily occur on the same rhodium atom coordinated by the ligand, but on the neighboring active sites of the catalyst. The coordinated C=C bond can easily interact with abundant hydrogen atoms and activated CO on the catalyst surface. The surrounding chiral environment may stereoselectively direct the addition of hydrogen to alkene and the migratory insertion of the as-formed alkyl group into the nearby coordinated CO, which influence the branched to linear ratio and enantio-differentiation, respectively. It is presumed that the hydroformylation reaction proceeds the catalytic recycle through surface multi-site synergetic mechanism on the chirally stabilized rhodium nanocatalyst (Scheme 3).



Scheme 3. The proposed mechanism of asymmetric hydroformylation on chirally stabilized rhodium nanocatalysts.

4. Conclusion

This work reports the preparation of rhodium nanoparticles stabilized with chiral diphosphorus ligand and their silica-supported analogues. The presence of chiral phosphorus ligands can result in the formation of chirally stabilized rhodium nanoparticles with uniformly high dispersity (1.5–2.0 nm). ^{31}P MAS NMR and CO-IR results of (*R*)-BINAP-stabilized nanocatalysts indicate that the diphosphine ligands strongly adsorb onto rhodium surface sites through the coordination interaction, leading to the formation of chiral environment on the rhodium nanoparticles. Therefore, the chirally stabilized rhodium nanoparticles can catalyze the asymmetric hydroformylation of olefins under mild conditions and exhibit high regioselectivity and chiral inductivities (92:8 *b*/*n*, 26% ee for styrene and 99:1 *b*/*n*, 59% ee for vinyl acetate, respectively). When supported on silica, the chirally stabilized rhodium nanocatalyst showed the increased activities ($12\,h^{-1}$ vs. $22\,h^{-1}$) for the hydroformylation of styrene. Achiral PPh_3-stabilized rhodium nanoparticles exhibited high racemic activity and increased regioselectivity. A surface multi-site synergetic mechanism was presumed for the asymmetric hydroformylation on the chirally stabilized rhodium nanocatalyst. Chiral stabilization method through the coordination of chiral ligand could be used as a potential convenient strategy for the preparation of heterogeneous chiral catalysts.

Acknowledgements

Financial support for this work was provided by the National Natural Science Foundation of China (NSFC, Grants 20621063 and 20423004).

References

[1] A.C. Templeton, W.P. Wuelfing, R.W. Murray, Acc. Chem. Res. 33 (2000) 27.
[2] W. Herrmann, Chem. Eng. Technol. 21 (1998) 549.
[3] H. Bönnemann, G. Braun, W. Brijoux, R. Brinkmann, A. Schulze Tilling, K. Seevogel, K. Siepen, J. Organomet. Chem. 520 (1996) 143.
[4] M.-C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
[5] A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757.
[6] H. Bönnemann, R.M. Richards, Eur. J. Inorg. Chem. 10 (2001) 2455.
[7] N. Toshima, T. Yonezawa, New J. Chem. 22 (1998) 1179.
[8] M. Tamura, H. Fujihara, J. Am. Chem. Soc. 125 (2003) 15742.
[9] R. Tatumi, T. Akita, H. Fujihara, Chem. Commun. (2006) 3349.
[10] S. Jansat, M. Gómez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillón, B. Chaudret, J. Am. Chem. Soc. 126 (2004) 1592.
[11] S. Jansat, D. Picurelli, K. Pelzer, K. Philippot, M. Gómez, G. Muller, P. Lecante, B. Chaudret, New J. Chem. 30 (2006) 115.
[12] S.U. Son, Y. Jang, K.Y. Yoon, E. Kang, T. Hyeon, Nano Lett. 4 (2004) 1147.

[13] H.A. Wierenga, L. Soethout, J.W. Gerritsen, B.E.C. van de Leemput, H. van Kempen, G. Schmid, Adv. Mater. 2 (1990) 482.
[14] H. Bönnemann, G.A. Braun, Angew. Chem. Int. Ed. 35 (1996) 1992.
[15] W.W. Weare, S.M. Reed, M.G. Warner, J.E. Hutchison, J. Am. Chem. Soc. 122 (2000) 12890.
[16] K.S. Weddle, J.D. Aiken III, R.G. Finke, J. Am. Chem. Soc. 120 (1998) 5653.
[17] F. Agbossou, J.F. Carpentier, A. Mortreaux, Chem. Rev. 95 (1995) 2485.
[18] B. Breit, W. Seiche, Synthesis 1 (2001) 1.
[19] D. Han, X. Li, H. Zhang, Z. Liu, J. Li, C. Li, J. Catal. 243 (2006) 318.
[20] G. Hu, Z. Feng, D. Han, J. Li, G. Jia, J. Shi, C. Li, J. Phys. Chem. C 111 (2007) 8632.
[21] V. Mévellec, A. Nowicki, A. Roucoux, C. Dujardin, P. Granger, E. Payen, K. Philippot, New J. Chem. 30 (2006) 1214.
[22] S. Gladiali, J.C. Bayon, C. Claver, Tetrahedron: Asymmetry 6 (1995) 1453.
[23] G. Westermark, I. Persson, Colloids Surf. A 144 (1998) 149.