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Heterogeneous asymmetric hydroformylation of olefins on chirally modified Rh/SiO_2 catalysts

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Abstract

Heterogeneous chiral catalysts were prepared by modifying silica-supported rhodium (Rh/SiO_2) with chiral phosphorus ligands. The chirally modified Rh/SiO_2 catalysts exhibited high activity, regioselectivity, and enantioselectivity for the asymmetric hydroformylation of styrene and vinyl acetate. Up to 72% ee and 100% selectivity of branched aldehyde for the hydroformylation of vinyl acetate were obtained for (*R*)-BINAP–Rh/SiO_2 catalysts. It is noteworthy that the modification of Rh/SiO_2 with (*S*,*S*)-DIOP resulted in increased activity for the hydroformylation of vinyl acetate and gave a TOF of 128 h^{-1}, even higher than that of the unmodified Rh/SiO_2 catalyst (90 h^{-1}). It is found that chiral modifiers with bidentate phosphines and an optimized modifier/rhodium molar ratio close to 1.0 were prerequisites for chiral induction on the chirally modified catalysts. ^{31}P MAS NMR results and IR spectra of adsorbed CO indicated that the chiral modification via the coordination of phosphines to rhodium produces chirally active sites on the Rh/SiO_2 catalysts.

Keywords: Heterogeneous catalysis; Enantioselective hydroformylation; Chiral modification; Coordination; Phosphorus ligands

1. Introduction

Enantioselective hydroformylation of olefins, one of the most challenging organometallic catalytic reaction involving chemoselectivity, regioselectivity and enantioselectivity, is of great importance in the synthesis of fine chemicals and pharmaceuticals [1,2]. Three readily available components—olefins, carbon monoxide and hydrogen—can be converted into optically active aldehydes in a single catalytic reaction step, making this transformation a highly efficient and atom-economical carbonylation reaction. Although asymmetric hydroformylation has been widely investigated as an important strategy in chiral synthesis, few catalytic processes are currently applied on a commercial scale [3]. This may be due primarily to the difficulties in controlling the selectivities of hydroformylation and the separation and recycling of the catalysts from the reaction system.

Compared with homogeneous catalysts, heterogeneous catalysts offer the potential advantages of easy separation and recycling of catalysts, easy purification of products, and the possible continuous or multiple processing of chiral compounds. In addition, the confinement effect originating from surfaces and pores of supports may afford the opportunity to enhance the enantioselectivity of asymmetric reactions. Many approaches have been used to realize heterogeneous catalysis, including heterogenization of homogeneous catalysts by covalent immobilization, encapsulation or adsorption of homogeneous catalysts, and modification of supported metal catalysts, as well as conducting the reactions in ionic liquid or liquid biphasic systems [4–10]. Modification of either metal or supported metal catalyst by adsorption of chiral organic compounds termed modifiers is a promising strategy for developing heterogeneous chiral catalysts [11–18]. A typical example is the cinchonidine modified Pt/Al_2O_3 catalyst, which shows excellent performance for chiral hydrogenation of α-ketoesters. Structurally well-defined metal nanoparticles modified with chiral ligand has also been prepared and applied in heterogeneous asymmetric hydrosilylation [19]. As far as we know, heterogeneous

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asymmetric hydroformylation generally has been conducted on catalysts prepared via covalent immobilization of homogeneous complexes on organic supports [20,21]. Catalysts based on chirally modified noble metal and inorganic supports have been rarely reported, and the enantioselectivity was rather low (maximum ee of 9.0%) [22,23]. Consequently, it is desirable to develop efficient heterogeneous hydroformylation catalysts with high regioselectivity and enantioselectivity. The chiral modification of supported metal turns out to be one of the attractive approaches for achieving this goal.

In this work, we studied heterogeneous asymmetric hydroformylation on chirally modified Rh/SiO_2 catalysts. Several representative chiral phosphorus ligands, such as (*R*)-BINAP, (*S*)-MeO-BIPHEP, and (*S*,*S*)-DIOP, were used as the chiral modifiers. Up to 72% ee and 100% selectivity of branched aldehyde for the hydroformylation of vinyl acetate were obtained on the Rh/SiO_2 catalysts modified with (*R*)-BINAP. Very interestingly, the modification of Rh/SiO_2 with (*S*,*S*)-DIOP results in significantly enhanced activity for the hydroformylation of vinyl acetate, as well as a higher TOF (128 h^{-1}) than that of the unmodified catalyst (90 h^{-1}).

2. Experimental

2.1. Chemicals

Unless noted otherwise, all of the manipulations were carried out using standard Schlenk techniques. All of 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*)-BINAP, >98%), (*S*,*S*)-(+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane ((*S*,*S*)-DIOP, >98%) and (*S*)-6,6′-dimethoxy-2,2′-bis(diphenylphosphino)-1,1′-biphenyl ((*S*)-MeO-BIPHEP) was purchased from Fluka or Aldrich. Phosphite-pyridine ligand was obtained as synthesized in home laboratory. 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. Catalyst preparation

2.2.1. Preparation of supported rhodium catalysts modified with chiral ligands, L–Rh/SiO2

Activated SiO_2 support (1.0 g) was impregnated with $RhCl_3$ (0.025 g, 0.1 mmol) aqueous solution under ultrasound for 4 h, followed by a drying at 60 °C in vacuum overnight. The catalyst precursor was calcined in air flow at 300 °C for 3 h and then reduced using hydrogen at 400 °C for 3 h. Typically, 2 ml of toluene solution of modifier (0.001 M) was added to 0.02 g of reduced catalyst at room temperature, and the catalyst sample with the modifier solution was directly transferred into a reactor to avoid exposing the sample to air. The Rh/SiO_2 catalyst in the modifier solution can also be purged with hydrogen until the solvent was evaporated at an elevated temperature (60 °C) to obtain the chirally modified catalyst. Then the chirally modified catalyst was transferred into the reactor using a Schlenk technique.

2.2.2. Homogeneous complex catalyst immobilized on SiO2, [Rh(COD)BINAP]+OTf−/SiO2

$[Rh(COD)BINAP]^+OTf^-$ was synthesized according to procedures outlined in the literature [24]. In a Schlenk tube under Ar, 0.1 mmol $[Rh(COD)Cl]_2$ was dissolved in 10 ml of CH_2Cl_2 and 0.23 mmol $AgCF_3SO_3$ was added. The resulting mixture was stirred at room temperature for 1 h, after which the precipitate was filtered. To the filtrate, 0.23 mmol (*R*)-BINAP in 5 ml of CH_2Cl_2 was added dropwise. The resulting mixture was stirred at room temperature for 3 h, after which 30 ml of 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. Then 1 g of activated SiO_2 was suspended in 5 ml CH_2Cl_2. The Rh diphosphine complex (0.1 mmol) was dissolved in 1 ml of CH_2Cl_2 and added to the SiO_2/CH_2Cl_2 suspension. The reaction mixture was stirred at room temperature overnight, and the recovered solid was washed with MeOH. The supported homogeneous catalyst was vacuum-dried at room temperature overnight and characterized by ^{31}P MAS NMR and IR spectroscopy.

2.3. Characterization

Transmission electron microscopy (TEM) images of the catalyst samples were taken on a JEM-2000EX electron microscope. X-ray diffraction (XRD) patterns were recorded on a Rigaku Rotaflex (Ru-200B) diffractometer (CuK_α, Rigaku Co.). The mean size of rhodium particles and the degree of dispersion on support was determined by pulse titration of CO on a CHEMBET-3000 chemisorption analyzer (Quanta Chrome). The CO chemisorption of the samples was measured at 40 °C after the samples were pretreated in a hydrogen flow at 400 °C for 3 h. The degree of dispersion and the mean particle size (cubic model) were estimated from the CO uptake. 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 modifier was introduced onto the reduced Rh/SiO_2 through adsorption of the catalyst in a modifier-containing toluene solution overnight. The premodified catalyst was then transferred to an in situ IR cell, and the sample was purged with argon to remove the solvent at 120 °C. Infrared spectra in the diffuse reflectance mode were collected at reaction temperature (60 °C) after the premodified catalyst was exposed to carbon monoxide.

2.4. Asymmetric hydroformylation

2.4.1. Asymmetric hydroformylation on L–Rh/SiO_2 catalysts

A typical heterogeneous asymmetric hydroformylation was carried out in an autoclave, and the reaction system was magnetically stirred. The chirally modified catalyst (0.02 g, 1.0 wt% Rh, 0.002 mmol) and substrate (1.2 mmol) together in anhydrous toluene (3 ml) were transferred into the reactor, and the autoclave was sealed and replaced with 50 atm hydrogen for three times. Subsequently, the pressure of syngas in the autoclave was increased to 50 atm. The reaction system was heated to 60 °C and stirred for 4 h. After the desired reaction time, the reaction was terminated, and the mixture of products was filtered to separate the heterogeneous catalyst. Conversion and branched-to-linear ratios were determined by gas chromatography (6890N, Agilent) equipped with a chiral capillary column (Chiral-Dex β-225, HP19091G-B213, 30 m × 0.32 mm × 0.25 μm, Agilent, N_2 69 kPa) and a flame ionization detector using an internal standard method. The enantiomeric excess of the branched aldehyde was determined by Jones oxidation of product to the corresponding carboxylic acid, followed by chiral gas chromatography (GC) analysis. The product configurations were determined by comparing the elution order 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). Then 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 form the chiral catalyst in situ. The substrate (2.0 mmol) was then added, and the subsequent operations were carried out according to the heterogeneous reaction procedure for a reaction time of 10 h. Before the GC analysis, the reaction product was concentrated and purified by flash column chromatography.

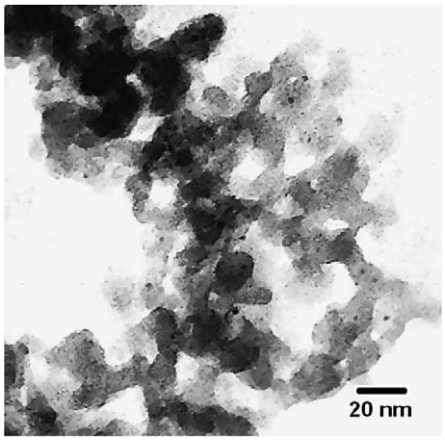
2.4.3. Recycling

The recycling of recovery catalysts and filtrate were also investigated. After the first reaction cycle was completed, the reaction system was centrifuged, and the solution was carefully removed under argon atmosphere. Fresh 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. A filtrate recycling experiment was also performed. The reaction solution of the first reaction cycle with an incomplete conversion was filtered carefully and directly used in the next catalytic cycle.

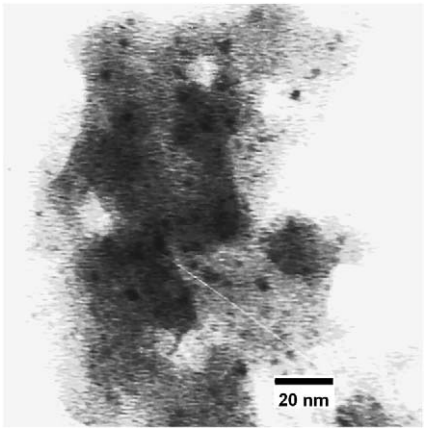
3. Results

3.1. Catalyst characterization

The metal dispersion and particle sizes of supported rhodium catalyst were measured by CO chemisorption. The dispersion of 1.0 wt% Rh/SiO_2 was estimated as 69%. The TEM images



(a)



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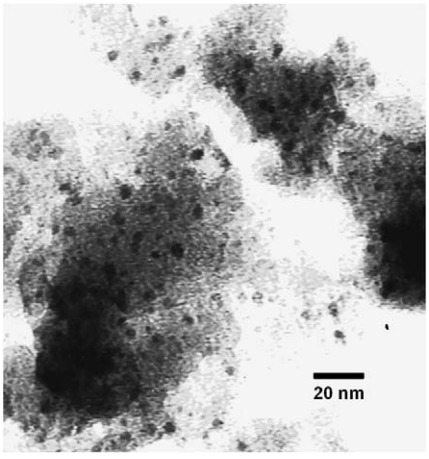
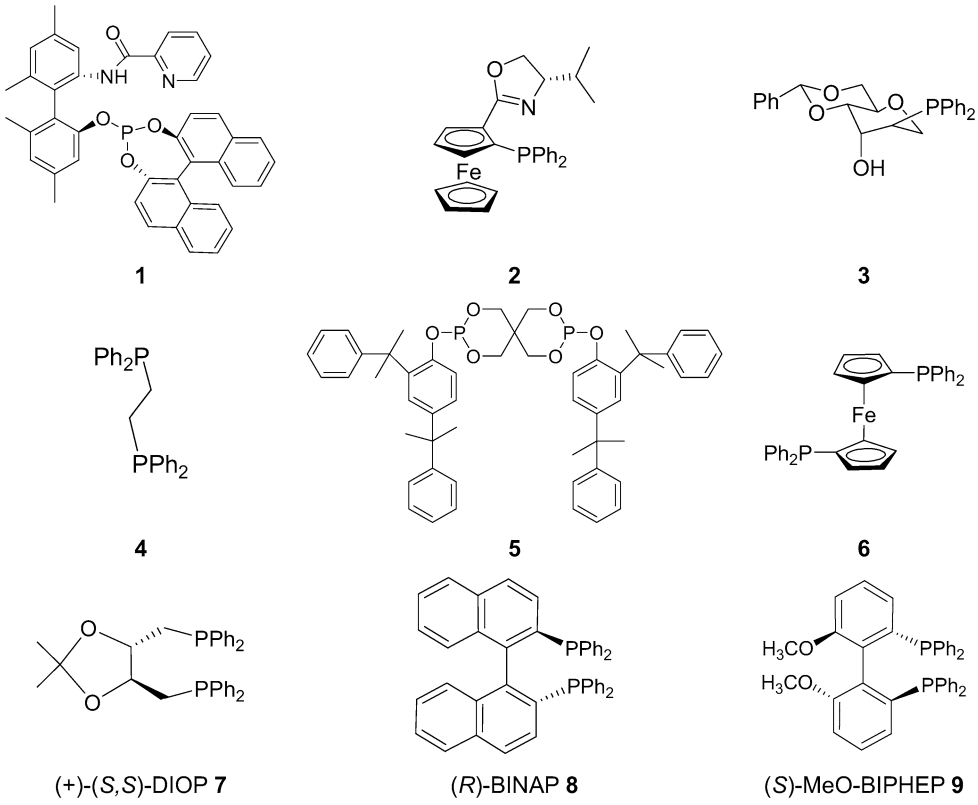


(c)

Fig. 1. TEM images of (a) 1.0 wt% Rh/SiO_2, (b) 3.0 wt% Rh/SiO_2, and (c) 5.0 wt% Rh/SiO_2.

(Fig. 1) show that highly dispersed rhodium nanoparticles were prepared and the average sizes of rhodium nanoparticles for the catalysts with 1.0, 3.0, and 5.0 wt% rhodium loading were 1.5–2.0, 3.0–4.0, and 5.0–6.0 nm, respectively, and also in good agreement with the results of chemisorption. The XRD patterns of 1.0 wt% Rh/SiO_2 (Fig. 2a) and 3.0 wt% Rh/SiO_2 (Fig. 2b) show no obvious diffraction peak of the rhodium crystalline phase. For the 5.0 wt% Rh/SiO_2 (Fig. 2c), diffraction peaks at $2\theta = 40.8°$, 47.4°, and 69.3° due to the crystalline phase



Scheme 1. The phosphorus modifiers used in this study.

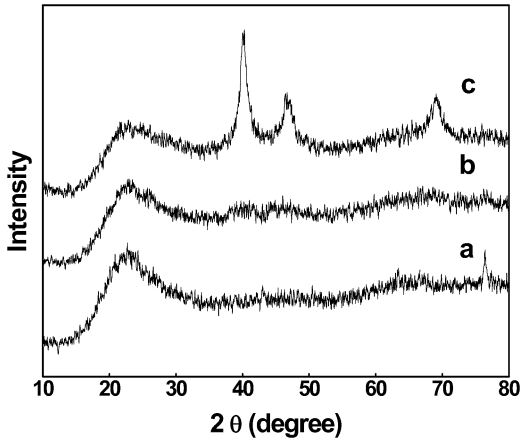


Fig. 2. The XRD patterns of (a) 1.0 wt% Rh/SiO_2, (b) 3.0 wt% Rh/SiO_2, and (c) 5.0 wt% Rh/SiO_2.

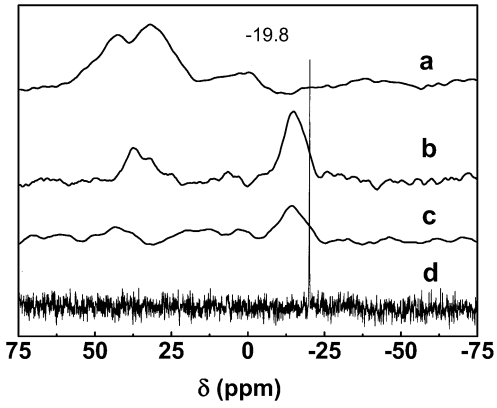


Fig. 3. ^{31}P MAS NMR spectra of (a) $[Rh(COD)BINAP]^+OTf^-/SiO_2$, (b) (*R*)-BINAP–$Rh/SiO_2$, (c) (*R*)-BINAP–$SiO_2$, and (d) ^{31}P NMR of (*R*)-BINAP.

are seen, which represent the indices of (111), (200), and (220) planes of rhodium phase, respectively [25].

The phosphorus ligands used to modify the supported rhodium catalysts are listed in Scheme 1. Modifiers **1**, **2**, and **3** are chiral mono-phosphorus ligands. Some achiral bidentate phosphorus ligands **4**, **5**, and **6** were also used in this work. Modifiers (*S*,*S*)-DIOP (**7**), (*R*)-BINAP (**8**), and (*S*)-MeO-BIPHEP (**9**) are chiral diphosphines with chelating ability. Fig. 3 shows the ^{31}P MAS NMR spectra of $[Rh(COD)BINAP]^+OTf^-/SiO_2$ and (*R*)-BINAP–Rh/SiO_2. The spectra of (*R*)-BINAP adsorbed on SiO_2 (Fig. 3c) and free BINAP (Fig. 3d) are also given for comparison. The broad signal at about 37.0 ppm of the chirally modified Rh/SiO_2 (Fig. 3b) is assigned to the (*R*)-BINAP adsorbed on rhodium atoms, which is similar to that of the supported $[Rh(COD)BINAP]^+OTf^-/SiO_2$. The chemical shift of P atom is shifted from −19.8 ppm for the free BINAP (Fig. 3d) to about −15.0 ppm for the adsorbed (*R*)-BINAP on the SiO_2 support (Fig. 3c). A similar signal is also observed for (*R*)-BINAP–Rh/SiO_2 (Fig. 3b), indicating that some of the chiral modifiers adsorb on the support simultaneously. The ^{31}P NMR results indicate that the modification of the supported rhodium nanoparticles with chiral phosphorus ligand can form a quite strong interaction via the coordination bond between the P atoms and the surface rhodium sites. The modification interaction formed by

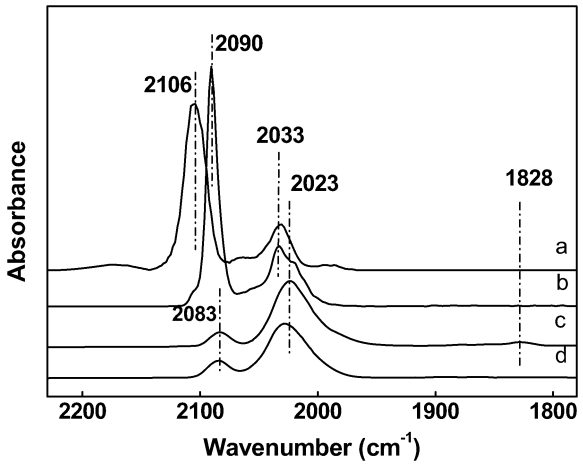


Fig. 4. IR spectra of adsorbed CO on (a) $[Rh(COD)BINAP]^+OTf^-/SiO_2$, (b) Rh/SiO_2, (c) (*S*,*S*)-DIOP–Rh/SiO_2, and (d) (*R*)-BINAP–Rh/SiO_2 at 60 °C.

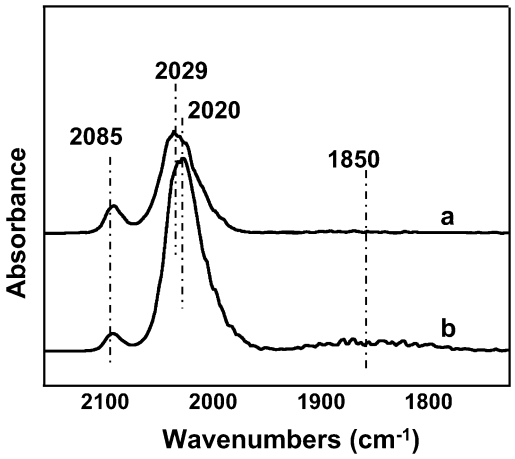


Fig. 5. IR spectra recorded from the (a) CO adsorption and (b) CO and H_2 coadsorption on (*R*)-BINAP–Rh/SiO_2 at 60 °C.

the adsorption of phosphorus ligands on Rh/SiO_2 is analogous to the coordination of the chiral ligand to the metal center in the homogeneous organometallic complexes.

Interaction of the chiral diphosphine modifiers with the supported rhodium catalysts was also probed by IR spectroscopy using CO adsorption on the chirally modified catalysts (Fig. 4). CO chemisorption on rhodium is an effective method for identifying the surface rhodium species [26,27]. The bands at 2106 and 2031 cm^{-1} for the immobilized homogeneous complexes $[Rh(COD)BINAP]^+OTf^-/SiO_2$ (Fig. 4a) are due to $\nu_{sym}CO$ and $\nu_{asy}CO$ of rhodium *gem*-di-carbonyl, which represent $Rh(I)(CO)_2BINAP$ complexes. IR spectra of adsorbed CO on unmodified Rh/SiO_2 (Fig. 4b) show bands at 2090, 2033, and 2021 cm^{-1}. The band at 2090 cm^{-1} corresponds to $\nu_{sym}CO$ of rhodium *gem*-di-carbonyl, and the band at 2033 cm^{-1} is due to linearly adsorbed CO. The shoulder band at 2021 cm^{-1} is due to the asymmetric stretching mode of *gem*-di-carbonyl. Fig. 4c displays the IR spectra of adsorbed CO on Rh/SiO_2 modified with (*S*,*S*)-DIOP. The intensity of *gem*-di-carbonyl band at 2090 cm^{-1} is obviously decreased compared with the spectra of unmodified sample, and a slight red shift to 2083 cm^{-1} is observed. This indicates that adsorbed phosphines occupy surface Rh sites and thus inhibit the adsorption of CO on the rhodium surface. The band due to $\nu_{asy}CO$ of the di-carbonyl is no longer detected. The band at 2023 cm^{-1}, due to the linearly adsorbed CO on the surface Rh sites of the chirally modified Rh/SiO_2, appears as a red shift of 10 cm^{-1} compared with that of unmodified Rh/SiO_2. The weak band at 1828 cm^{-1} can be assigned to the adsorbed CO on bridge sites. Similar bands are also observed in the spectra of CO adsorbed on Rh/SiO_2 modified with (*R*)-BINAP, except for the presence of the band of bridged CO.

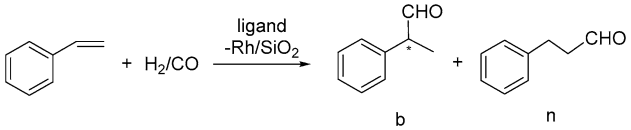
Fig. 5 shows IR spectra of CO and H_2 coadsorbed on (*R*)-BINAP–Rh/SiO_2 catalyst. After the introduction of hydrogen, the band strength of linearly adsorbed CO is greatly increased, accompanied by a red shift from 2029 to 2020 cm^{-1}, whereas the $\nu_{sym}CO$ of rhodium *gem*-di-carbonyl becomes weaker. In addition, a broad band of bridged CO appears in the range of 1900–1800 cm^{-1}. This result indicates that the coadsorbed H_2 benefits the adsorption and activation of CO on Rh sites of the chirally modified heterogeneous catalyst. The IR spectrum of CO adsorbed on chirally modified samples is much different from the IR spectra of the homogeneous complex and the unmodified catalyst. The spectra of adsorbed CO on (*S*,*S*)-DIOP and (*R*)-BINAP modified catalysts (Fig. 4, spectra c and d) show the band at 2023 cm^{-1} as the main component, due to linearly adsorbed monocarbonyls on Rh(0) sites of chirally modified Rh/SiO_2. The symmetric stretching vibration at 2083 cm^{-1} belong to $Rh(I)(CO)_2$ species is dramatically decreased and appears just as a very weak band, whereas this band is dominant in the spectrum for unmodified Rh/SiO_2. The $\nu_{asy}CO$ can hardly be recognized.

3.2. Heterogeneous asymmetric hydroformylation of styrene on chirally modified Rh/SiO_2

Vinyl compounds, such as styrene and vinyl acetate, were chosen as model substrates for the asymmetric hydroformylation. These substrates represent different types of terminal olefins with unique reactivity and selectivity in the hydroformylation reactions. The hydroformylation of vinyl aromatics has been applied to the synthesis of optically active nonsteroidal anti-inflammatory agents that are functional 2-arylpropanoic acids, such as (*S*)-Naproxen.

Table 1 gives the results of asymmetric hydroformylation of styrene on Rh/SiO_2 with different Rh loadings. Almost 100% chemoselectivity of aldehyde is obtained. The regioselectivity is expressed as the ratio of branched to linear aldehyde (b/n). Unmodified Rh/SiO_2 catalysts give low regioselectivities (b/n < 85/15) and racemic products. Chirally modified catalysts show higher regioselectivities (b/n > 90/10) but lower activities than unmodified catalyst. Catalysts with higher Rh loadings have larger Rh particle sizes and lower activities, possibly due to their lower dispersion of rhodium and less accessible catalytic sites on the surface than the catalysts with lower Rh loadings. Rh/SiO_2 catalyst with 1.0 wt% rhodium loading gives the highest activity with or without the presence of (*R*)-BINAP (entries 3 and 4). Because relatively low Rh loading provides

Table 1
Asymmetric hydroformylation of styrene on (*R*)-BINAP–Rh/SiO_2 with different rhodium loadings[a]



Entry	Rhodium loading (wt%)	Rh size (nm)	Modifier	Conversion[b] (%)	b/n	Ee (%)
1	0.5	<1.5	–	75	78/22	0
2	0.5	<1.5	(*R*)-BINAP	<1	90/10	26
3	1.0	1.5–2.0	–	99	67/33	0
4	1.0	1.5–2.0	(*R*)-BINAP	6	92/8	30
5	2.0	2.0–3.0	–	38	84/16	0
6	2.0	2.0-3.0	(*R*)-BINAP	2	91/9	29
7	3.0	3.0–4.0	–	32	80/20	0
8	3.0	3.0–4.0	(*R*)-BINAP	<1	91/9	28
9	5.0	5.0–6.0	–	28	77/23	0
10	5.0	5.0–6.0	(*R*)-BINAP	<1	90/10	28

[a] 0.02 g Rh/SiO_2 catalysts (pore size, 9.7 nm) modified with 2 μmol (*R*)-BINAP, 1.2 mmol styrene.

[b] Reactions were performed in 3 ml toluene at 60 °C under 50 bar syngas ($CO:H_2 = 1:1$) for 4 h. More than 99% selectivity of aldehydes was obtained.

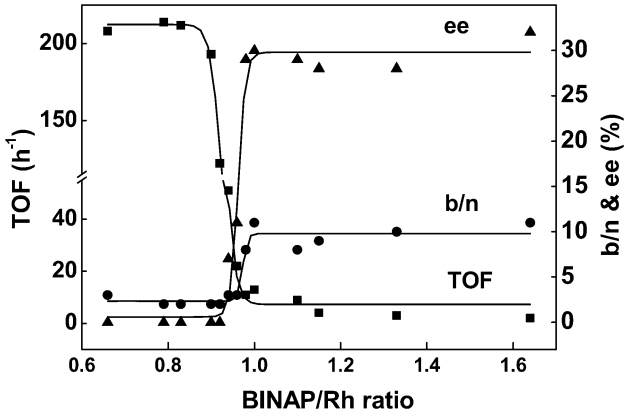


Fig. 6. The effects of BINAP/Rh ratio on the catalytic performance for the hydroformylation of styrene on (*R*)-BINAP–Rh/SiO_2 catalysts.

good catalyst efficiency, Rh/SiO_2 catalyst with rhodium loading of 1.0 wt% (particle size of 1.5–2.0 nm) was adopted for this work.

To optimize the quantity of chiral modifier adsorbed on the catalyst, the effects of modifier/rhodium ratio on reaction performance were investigated for 1.0 wt% Rh/SiO_2 catalyst modified with (*R*)-BINAP (Fig. 6). The variation of BINAP/rhodium ratio (from 0.66 to 1.64) results in a significant change in reaction performance of the hydroformylation of styrene. At a BINAP/Rh ratio of <0.9, the modified catalysts exhibit high activity, but racemic products. This situation does not change until sufficient BINAP is added. When the BINAP/Rh ratio is increased from 0.9 to 1.0, both regioselectivity and enantioselectivity increase significantly, accompanied by a decrease in activity. The regioselectivity is increased from 67/33 to 92/8, and up to 30% ee is achieved. On further increases in the BINAP/Rh ratio, the activity and selectivity remain nearly unchanged.

Table 2
Asymmetric hydroformylation of styrene on Rh/SiO_2 catalysts modified with different ligands[a]

Entry	Catalyst	Rh:L:Sub.	Conversion (%)	TOF[b] (h^{-1})	b/n	Ee (%)
1	Rh/SiO_2	1:–:600	99	212	67:33	0
2	**1**-Rh/SiO_2	1:2:600	14	30	84:16	6(*S*)
3	**2**-Rh/SiO_2	1:2:600	39	83	68:32	0
4	**3**-Rh/SiO_2	1:2:600	99	210	85:15	0
5	**4**-Rh/SiO_2	1:1:600	16	34	86:14	0
6	**5**-Rh/SiO_2	1:1:600	33	71	65:35	0
7	**6**-Rh/SiO_2	1:1:600	59	121	75:25	0
8	**7**-Rh/SiO_2	1:1:600	63	135	60:40	12(*S*)
9	**8**-Rh/SiO_2	1:1:600	6	13	92:8	30(*S*)
10	**9**-Rh/SiO_2	1:1:600	5	10	92:8	25(*R*)

[a] Rh/SiO_2 (pore size, 9.7 nm, 0.02 g, 1.0 wt%) modified with different ligands as catalysts; Rh:P:Sub. = 1:2:600.

[b] Reactions were performed in toluene (3 ml) at 60 °C under 50 bar syngas ($CO:H_2 = 1:1$) for 4 h. Calculated by the rhodium dispersion.

The BINAP/Rh molar ratio of 1.0 (P/Rh, 2.0) was used as an optimized value in the subsequent experiments.

The hydroformylation of styrene was investigated on Rh/SiO_2 modified with the chiral ligands listed in Scheme 1 (Table 2). The unmodified supported rhodium catalyst (entry 1) gives only very low regioselectivity (b/n = 67/33) and racemic products, although it shows high activity (TOF = 212 h^{-1}). The monophosphorus chiral pyridine-phosphite ligand **1** (entry 2), which has been successfully used in organometallic-catalyzed enantioselective carbon–carbon formation reactions [28], gives an enantioselectivity of 6% ee and a medium regioselectivity (b/n = 84/16). Ferrocene- and carbohydrate-derived monophosphine ligands **2** and **3** exhibit no enantioselectivity but relatively high activity (entry 3 and 4). The catalysts with chiral monophosphorus modifiers give low chiral induction and regioselectivity. The catalysts modified with achiral bidentate phosphorus ligands **4**, **5**, and **6** show no chiral induction, but some can promote the formation of branched aldehyde (entries 5, 6, and 7).

The chiral diphosphines ligands with chelating ability, such as (*S*,*S*)-DIOP (**7**), (*R*)-BINAP (**8**), and (*S*)-BIPHEP (**9**), were used to modify the Rh/SiO_2 catalysts for the hydroformylation of styrene. The catalyst modified with (*S*,*S*)-DIOP (entry 8) shows much higher activity (TOF of 135 h^{-1}) but lower enantioselectivity (12% ee of *S*-configurational enantiomer) than those obtained for the catalysts modified with the chiral biphosphorus ligands **8** and **9**. This is a ligand that depresses the branched aldehyde selectivity. The highest regioselectivity (b/n = 92/8) and enantioselectivity (30% ee, *S*) are obtained for the Rh/SiO_2 catalyst modified with (*R*)-BINAP (entry 9). (*S*)-MeO-BIPHEP, a *C*-2 symmetric ligand structurally similar to (*S*)-BINAP, introduces a skeleton modification to the binaphthyl skeleton of BINAP with 6,6′-dimethoxyl substituted biphenyl. This provides an alteration in electronic property but no obvious change in the bite angle of the bidentate modifier. The Rh/SiO_2 catalyst modified with (*S*)-MeO-BIPHEP shows an optical excess of (*R*)-product with 25% ee and similar regioselectivity to that for the catalyst modified with (*R*)-BINAP

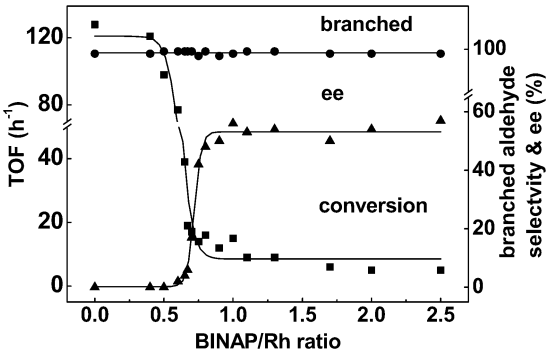


Fig. 7. The effects of BINAP/Rh ratio on the catalytic performance for the hydroformylation of vinyl acetate on (*R*)-BINAP–Rh/SiO_2 catalysts.

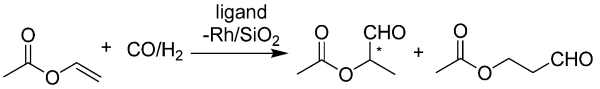
(entry 10). From these results, it can be concluded that the Rh/SiO_2 catalysts modified with chiral bidentate phosphorus modifiers with chelating ability show the better chiral induction and high regioselectivity in olefin hydroformylation.

3.3. Heterogeneous asymmetric hydroformylation of vinyl acetate

Asymmetric hydroformylation of vinyl acetate, a functional olefin with an ester group, was also investigated for its potential application in the synthesis of fine chemicals, such as optically active α-amino acids. Asymmetric hydroformylation of vinyl acetate produces mainly the chiral 2-acetoxy propionaldehyde. Fig. 7 shows the results obtained for (*R*)-BINAP–Rh/SiO_2 catalysts with different L/Rh ratios for the asymmetric hydroformylation of vinyl acetate. A variation in the BINAP/rhodium ratio from 0 to 2.5 results in a tendency of reaction performance similar to that of the hydroformylation of styrene on chirally modified Rh/SiO_2 (Fig. 6). The heterogeneous catalyst exhibits high intrinsic regioselectivity, and >99% of the branched product can be obtained for the modified catalysts. When the BINAP/Rh ratio is <0.6, the modified catalysts exhibit high activity (TOF > 90 h^{-1}) but produce the racemic products. The increase in the BINAP/Rh ratio from 0.6 to 1.0 leads to an increase in enantioselectivity from 2% to about 60%, accompanied by a decrease in conversion. Further increasing the BINAP/Rh ratio causes only a decrease in activity, with no further increase in enantioselectivity. Therefore, the BINAP/Rh ratio of 1.0 is as an optimized value used in the subsequent experiments for the heterogeneous hydroformylation of vinyl acetate.

Table 3 gives the hydroformylation results of vinyl acetate for Rh/SiO_2 catalysts modified with chiral diphosphine ligands. It is noteworthy that the (*S*,*S*)-DIOP (**7**) ligand adsorbed on Rh/SiO_2 can significantly accelerate the asymmetric hydroformylation of vinyl acetate (entry 2). Therefore, (*S*,*S*)-DIOP–Rh/SiO_2 catalyst exhibits the highest activity (TOF of 128 h^{-1}) among all of the chirally modified catalysts in this work, even higher than that of the unmodified Rh/SiO_2 (entry 1, TOF of 90 h^{-1}). The enantioselectivity (32% ee, *R*) is relatively low. (*R*)-BINAP ligand shows high chiral induction [59% ee of the (*S*)-enantiomer], and a TOF of 15 h^{-1} is obtained with (*R*)-BINAP modified catalyst (entry 3). The highest enantioselectivity (up to 72% ee) is achieved for the (*R*)-BINAP-premodified Rh/SiO_2 catalyst (entry 4). The regioselectivity is significantly high, and an almost completely branched product is obtained for the chirally modified catalysts. As far as we know, the highest regioselectivity and enantioselectivity are obtained for the hydroformylation of vinyl acetate when using (*R*)-BINAP as a chiral ligand. The (*S*)-MeO-BIPHEP-modified catalyst exhibits a slightly lower enantioselectivity and higher activity than the (*R*)-BINAP modified catalyst (entry 5). The product aldehyde has an opposite optical configuration (*R*-enantiomer). The lower steric hindrance and higher charge density of (*S*)-MeO-BIPHEP may favor the activity rather than the enantioselectivity for vinyl acetate hydroformylation.

Table 3
Asymmetric hydroformylation of vinyl acetate on Rh/SiO_2 catalysts modified with chiral ligands[a]



Entry	Catalyst[b]	Rh:L:Sub.	*T* (h)	Conversion (%)	TOF (h^{-1})	b/n	Ee (%)
1	Rh/SiO_2	1:–:600	4	42	90	98:2	0
2	**7**-Rh/SiO_2	1:1:600	4	60	128	99:1	32(*R*)
3	**8**-Rh/SiO_2	1:1:600	4	7	15	100:0	59(*S*)
4[c]	**8**-Rh/SiO_2	1:1:600	4	5	11	100:0	72(*S*)
5	**9**-Rh/SiO_2	1:1:600	4	13	27	100:0	46(*R*)

[a] Rh/SiO_2 (pore size, 9.7 nm, 0.02 g, 1.0 wt%) modified with different ligands as catalysts. Reactions were performed in toluene (3 ml) at 60 °C under 50 bar syngas ($CO:H_2$ = 1:1) for 4 h.
[b] **7** (*S*,*S*)-DIOP, **8** (*R*)-BINAP, **9** (*S*)-MeO-BINAP.
[c] (*R*)-BINAP premodified catalyst.

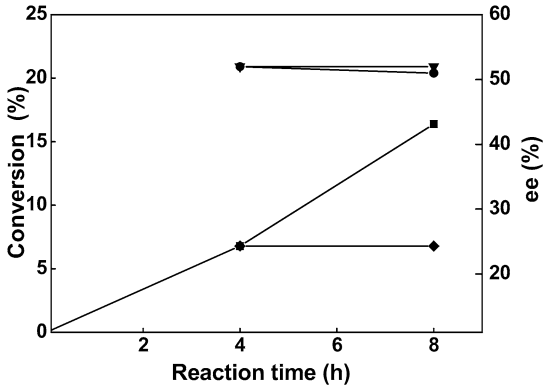


Fig. 8. Asymmetric hydroformylation of vinyl acetate: (■) conversion ((*R*)-BINAP–Rh/SiO_2), (◆) conversion (filtrate), (●) enantioselectivity ((*R*)-BINAP–Rh/SiO_2), (▼) enantioselectivity (filtrate) as functions of reaction time.

Catalyst recycling experiments were performed to test the stability of the heterogeneous catalysts. Activity and enantioselectivity similar to those of the first reaction run were obtained in the subsequent reaction cycles. After a few cycles, reaction performance can be maintained by adding (*R*)-BINAP modifier. To confirm that the catalytic reaction indeed occurs on the chirally modified catalyst, the reaction of the hot filtration was also performed (Fig. 8). The catalyst was removed from the reaction mixture before the reaction was completed, and colorless filtrate in the reaction system was maintained under the

Table 4
Homogeneous asymmetric hydroformylation[a]

Entry	Catalyst[b]	Rh:L:Sub.	Substrate	Conversion (%)	TOF (h^{-1})	b/n	Ee (%)
1	$[Rh(COD)Cl]_2$	1:–:1000	Styrene	35	35	84:16	0
2	$[Rh(COD)Cl]_2$	1:–:1000	Vinyl acetate	79	79	82:18	0
3	Rh(COD)(**7**)Cl	1:2:1000	Styrene	70	70	60:40	14(*S*)
4	Rh(COD)(**7**)Cl	1:2:1000	Vinyl acetate	65	65	99:1	28(*R*)
5	Rh(COD)(**8**)Cl	1:2:1000	Styrene	11	11	85:15	31(*S*)
6	Rh(COD)(**8**)Cl	1:2:1000	Vinyl acetate	3	3	98:2	54(*S*)
7	Rh(COD)(**9**)Cl	1:2:1000	Styrene	8	8	88:12	27(*R*)
8	Rh(COD)(**9**)Cl	1:2:1000	Vinyl acetate	5	5	98:2	44(*R*)

[a] Reactions were performed in toluene (3 ml) at 60 °C under 50 bar syngas ($CO:H_2 = 1:1$) for 10 h.
[b] **7** (*S*,*S*)-DIOP, **8** (*R*)-BINAP, **9** (*S*)-MeO-BINAP.

same hydroformylation conditions. No further changes in conversion and enantioselectivity were observed after a reaction for another 4 h, whereas the conversion increased further with the recovered catalyst. This result obviously indicates that the catalytic conversion can be attributed to the reaction on chirally modified Rh/SiO_2 catalyst.

3.4. Homogeneous asymmetric hydroformylation

The hydroformylation using homogeneous Rh(COD)(L)Cl catalyst was also performed under the general reference conditions (Table 4). $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) was used as the catalyst precursor, and a L/Rh molar ratio of 2 was adopted. Except for the hydroformylation of styrene with the (*S*,*S*)-DIOP ligand, all of the other ligands favor the branched regioselectivities. It is interesting that the higher TOF of hydroformylation of styrene than that of the corresponding homogeneous catalysts is obtained for chirally modified Rh/SiO_2 catalysts. In particular, the heterogeneous catalyst with (*S*,*S*)-DIOP as the chiral modifier gives the highest activity of 135 h^{-1}, much higher than that for the homogeneous catalyst [29]. (*R*)-BINAP ligand shows high chiral induction (59% ee of the (*S*)-enantiomer) for the hydroformylation of vinyl acetate, and a TOF of 15 h^{-1} is obtained with (*R*)-BINAP modified catalyst (Table 3, entry 3), whereas the TOF of the homogeneous counterparts are 3 h^{-1} (Table 4, entry 6) in this work and 1 h^{-1} in previous work [30,31]. Chiral modification of the Rh/SiO_2 catalyst also exerts a stronger influence on regioselectivity than that of the homogeneous catalysts. For example, the regioselectivity (b/n) of the Rh/SiO_2 catalyst for styrene is increased from 67/33 to 92/8 (Table 2, entry 1 and 9) after the modification with (*R*)-BINAP, whereas the b/n ratio for the homogeneous catalyst shows only a slight increase from 84/16 to 85/15 after the coordination of chiral ligand (Table 4, entries 1 and 5).

4. Discussion

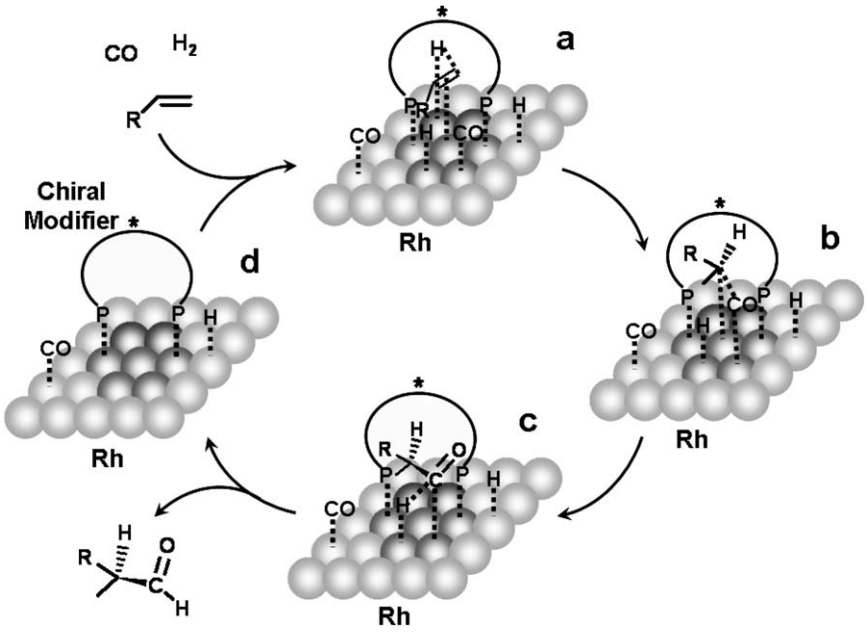
4.1. Chiral modification

It is known that phosphorus ligand can coordinate with rhodium atom through σ–π interaction to form an organometallic complex. The ligands also can be adsorbed to the metal surface via the coordination interaction between the phosphorus atoms and the metal atoms [32]. The adsorption of the chiral ligand produces a chiral environment on the metal surface, which may be somewhat analogous to that of the metal complex coordinated with chiral ligands. As a result, the chirally modified catalysts could have the asymmetric induction ability [33]. In this work, the ^{31}P MAS NMR and CO-IR results indicate that the diphosphine modifiers steadily adsorb on the metal surface through coordination. The chiral environment formed by ligand modification together with the heterogeneous surface increases the regioselectivity and enantioselectivity for hydroformylation, whereas occupation of the rhodium sites usually decreases the accessible active sites for substrates. However, it is noteworthy that the chirally modified Rh/SiO_2 catalysts exhibit higher activity and regioselectivity than their homogeneous counterparts for the asymmetric hydroformylation of olefins. Although the coordinated phosphine atoms exhibit similar status to that of homogeneous complex, the electronic density of supported Rh catalyst might be very different from that of rhodium complex. This can be proven by the large difference between their IR spectra. The chirally modified Rh/SiO_2 catalyst shows a much stronger band of linearly adsorbed CO with the presence of hydrogen. The higher electronic density of supported Rh catalyst benefits the adsorption and activation of olefins and CO. In contrast, rhodium catalyst can provide excellent hydrogen activation and transfer, which may enhance the hydroformylation activity. Thus, the coordination manner and catalytic process of the chirally modified catalyst may be somewhat different than those of homogeneous catalyst.

4.2. Effects of chiral modifier structures

Different chiral modifiers have very different effects on catalytic performance. The catalysts modified with chiral monophosphorus modifiers do not produce stereoselectivity comparable to that of catalysts modified with chiral diphosphines. It is difficult for monodentate phosphorus ligands to form a stable and rigid chiral environment on metal surface due to their poor chelation ability. It is also possible that the competitive adsorption of carbon monoxide reduces the coordination of phosphorus ligand to the rhodium catalyst under reaction conditions [34,35]. These may be the reasons for the low enantioselectivity.

The adsorbed chiral bidentate phosphorus modifier with chelating configuration can promote the chiral induction of



Scheme 2. The proposed mechanism of asymmetric hydroformylation on chirally modified Rh/SiO_2 catalyst.

these catalysts. Among the catalysts screened in this work, Rh/SiO_2 modified with (*R*)-BINAP gives the highest enantioselectivity, due to its strong chelating ability and rigid chiral structure with bulky steric hindrance. (*S*,*S*)-DIOP–Rh/SiO_2 catalyst not only induces enantioselectivity, but also exhibits the highest activity. Coordinating (*R*)-BINAP with a smaller bite angle to the active sites can form a more stable multimember chelating ring than that formed by (*S*,*S*)-DIOP [36]. Thus, one of the possible reasons for the high activity of Rh/SiO_2 catalysts modified with (*S*,*S*)-DIOP could be that more vacant sites with less steric hindrance on catalyst surface are available for the reactants. (*S*,*S*)-DIOP significantly modifies the electronic state of the Rh sites and makes them more active for the coordination and reaction. This is demonstrated by the fact that an even higher activity than that of the unmodified Rh/SiO_2 catalyst was obtained for the hydroformylation of vinyl acetate. The chiral modifiers (*R*)-BINAP and (*S*)-MeO-BIPHEP exhibit similar activity and regioselectivity, but the former produces higher chiral induction, possibly due to its greater steric hindrance.

4.3. Effects of the surface coverage of modifiers

Chiral modification can also be proven by the influence of BINAP/Rh ratio on catalytic performance for the hydroformylation of styrene and vinyl acetate (Figs. 6 and 7). When the BINAP/Rh ratio is relatively low, the active sites on catalyst are not well modified with sufficient amounts of (*R*)-BINAP. The catalyst exhibits high activity but racemic products, because most of the surface active sites are not covered by the chiral modifiers. With an increasing BINAP/Rh ratio, both regioselectivity and enantioselectivity are obviously increased, accompanied by decreased conversion near BINAP/Rh ratios of 0.9–1.0 and 0.6–0.9 for the hydroformylation of styrene and vinyl acetate, respectively. In these regions, most of the surface active sites are coordinated by chiral modifiers and show asymmetric induction. The racemic reaction on the unmodified active sites no longer dominates the reaction. When the active sites on Rh surface are fully modified with chiral ligands, the intrinsic regioselectivity and enantioselectivity are achieved. As a result of chelating effect of chiral ligands, access and coordination of substrates to the metal sites become more difficult. Accordingly, the activity of hydroformylation is decreased. From these results, it can be deduced that a well-arranged chiral array on catalyst surface is necessary for a higher enantioselectivity. This can be achieved by self-assembly of chiral ligands on the catalyst surface through coordination/disassociation equilibrium under suitable modification conditions. In this work, the premodified Rh/SiO_2 catalyst with (*R*)-BINAP shows higher ee than the catalyst modified in situ for the hydroformylation of vinyl acetate.

4.4. Catalytic behavior of the substrates with different structures

Chirally modified catalysts show higher regioselectivity and enantioselectivity for vinyl acetate than for styrene. The BINAP/Rh ratio of the initial formation of enantiomer excess for vinyl acetate is lower than that for styrene (0.6 vs 0.9). Compared with that of styrene, hydroformylation of vinyl acetate on chirally modified catalyst, such as (*R*)-BINAP–Rh/SiO_2, gives much higher activity (15 h^{-1}) than the homogeneous counterpart (3 h^{-1}). Besides the intrinsic reaction performance, the functional structure of vinyl acetate is responsible for these differences. When the C=C bond of vinyl acetate coordinates to the active site of a chirally modified catalyst, its carbonyl group may interact with the neighboring Rh site or may participate in the hydrogen activation to form a more advantageous intermediate, thereby accelerating and enhancing the chiral induction of hydroformylation. For these reasons, the hydroformylation of vinyl acetate on catalyst modified with (*S*,*S*)-DIOP exhibits

even greater activity (128 h^{-1}) than that on unmodified catalyst (90 h^{-1}) even though the modifying ligands occupy part of the Rh sites.

4.5. Proposed mechanism of asymmetric hydroformylation on chirally modified Rh/SiO_2

A modification model for the coordination or reaction of chiral ligands and reactants on chirally modified Rh/SiO_2 is proposed in Scheme 2. ^{31}P MAS NMR and CO-IR results confirm the formation of chirally modified active sites on the Rh/SiO_2 catalyst. The diphosphine modifiers strongly adsorb on Rh surface through the coordination, which may be somewhat analogous to that in the chiral ligand metal complex. The chirally modified Rh sites on the metal surface have very different catalytic performance than the homogeneous complex due to their high electronic density and intrinsic characteristics as heterogeneous catalysts. The bidentate phosphines of chiral modifiers may chelate to nearby Rh active sites to give stable cyclic coordination structures. The chirality of modifier transfers to the catalyst surface via the cyclic structure and forms a chiral environment together with the two-dimensional rigid surface. The activation and reaction of substrate may not necessarily occur on the same rhodium atom coordinated by the ligand, but may occur instead on the neighboring active sites of the catalyst. The activated C=C bond can easily interact with abundant spillover hydrogen atoms near its coordinating sites on the catalyst surface. The surrounding chiral environment may regioselectively control the addition of hydrogen to alkene (Scheme 2a), thereby affecting the branched-to-linear ratio. Migratory insertion of the as-formed alkyl group into the nearby coordinated CO is also directed by the surface chiral environment and occurs in an enantiodifferential manner (Scheme 2b). The enantioselectivity could be realized in this key step. Subsequent addition of hydrogen to the carbonyl complex forms the final aldehyde products (Scheme 2c), which dissociate from the catalyst surface in the subsequent step (Scheme 2d). The hydroformylation reaction may accomplish catalytic recycling through a multisite synergetic mechanism on the chirally modified Rh/SiO_2 surface.

5. Conclusions

Heterogeneous chiral catalysts for hydroformylation reactions were prepared by modifying Rh/SiO_2 catalysts with chiral phosphorus ligands through the coordination bonding. ^{31}P MAS NMR and IR results of CO adsorption for (*R*)-BINAP-modified catalysts indicate that the diphosphine modifiers strongly adsorb on the Rh surface through a coordination effect. The chelating ability of chiral bidentate phosphorus modifiers is crucial for achieving a better asymmetric reaction. An optimized modifier/rhodium ratio is about 1.0 for the chirally modified catalysts. Modification of Rh/SiO_2 catalyst with (*R*)-BINAP increases the regioselectivity from 67/33 to 92/8 for the asymmetric hydroformylation of styrene and provides up to 72% ee and 100% regioselectivity of branched aldehyde for the hydroformylation of vinyl acetate. (*S*,*S*)-DIOP–Rh/SiO_2 catalysts show activity as high as a TOF of 128 h^{-1} for the asymmetric hydroformylation of vinyl acetate, which is even higher than that of the unmodified catalyst (90 h^{-1}). A catalytic mechanism involving multiple surface sites on the chirally modified Rh/SiO_2 catalyst is proposed. The chirally modified Rh/SiO_2 catalysts provide the potential for asymmetric hydroformylation of olefins on heterogeneous catalysts. The further enhancement of enantioselectivity and activity of these catalysts through chiral modification is a topic for future research.

Acknowledgments

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