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Highly Efficient Heterogeneous Hydroformylation over Rh-Metallated Porous Organic Polymers: Synergistic Effect of High Ligand Concentration and Flexible Framework

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KEYWORDS. Hydroformylation, porous organic polymer, Rh-based catalyst, quasi-homogeneous catalyst, heterogeneous catalyst.

ABSTRACT: A series of diphosphine ligand constructed porous polymers with stable and flexible frameworks have been successfully synthesized under the solvothermal conditions from polymerizing the corresponding vinyl-functionalized diphosphine monomers. These insoluble porous polymers can be swollen by a wide range of organic solvents, showing similar behavior to those of soluble analogues. Rather than just as immobilizing homogeneous catalysts, these porous polymers supported with Rh species demonstrate even better catalytic performance in the hydroformylations than the analogue homogeneous catalysts. The sample extraordinary performance could be attributed to the combination of high ligand concentration and flexible framework of the porous polymers. Meanwhile, they can be easily separated and recycled from the reaction systems without losing any activity and selectivity. This excellent catalytic performance and easy recycling heterogeneous catalyst property make them be very attractive. These diphosphine ligand constructed porous polymers may provide new platforms for the hydroformylation of olefins in the future.

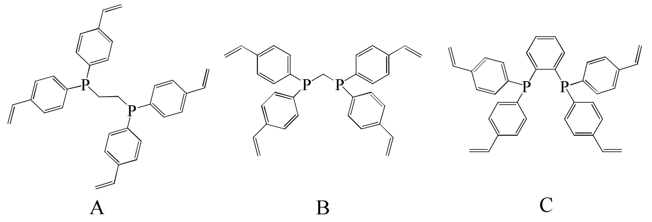
INTRODUCTION

As one of the largest industrial processes, the hydroformylation of olefins is normally performed by the rhodium-based homogeneous catalysts.[1] Because of the fully accessible and highly tunable active species, the homogeneous catalysts have important advantages in catalytic activity and selectivity over the heterogeneous catalysts. Nevertheless, the heterogeneous catalysts are more desirable for industrial applications owing to the convenience of recovering and recycling of the catalysts.[2,3] During the past three decades, intensive efforts have been devoted to immobilizing homogeneous catalysts onto solid supports for introducing the advantages of heterogeneous catalysts into homogeneous catalytic systems.[4] However, the immobilization process often causes significant decrease of catalytic activity and selectivity due to the low concentration of organic ligands in the vicinity of metal species. In order to overcome this disadvantage, interesting materials have been developed in which the organometallic complexes are physically adsorbed on water,[5] ionic liquid,[6] or polyelectrolyte-anchored[7] high surface area solids. These composites have the adjustable organic ligand concentration and demonstrate superior catalytic activity and selectivity in the hydroformylation of olefins. However, the relatively low stability of the physical adsorption causes the leaching of active species including the organic ligands and the metal species. Therefore, it is a challenge to prepare highly efficient heterogeneous hydroformylation catalysts with both adjustable concentration of organic ligands and avoidance of leaching for active species.

Until now, immobilizing organometallic complexes onto high surface solids is still an excellent strategy to combine the advantages of homogeneous and heterogeneous catalysts. Among many porous supporting materials, porous organic polymers (POPs)[8] as an emerging class of porous materials, could be a promising candidate for their high surface areas, excellent stabilities, and designable pore walls. If POPs are composed by only organic ligands themselves, the porous organic ligands (POLs) should have very high ligand concentration.[9] As we know that the diphosphine ligands are the top selective ligands for forming the desirable products in the hydroformylation processes over rhodium-based homogeneous catalysts,[10] it is proposed to synthesize insoluble porous polymerized diphosphine ligands served as both organic ligands and supports to prepare highly efficient heterogeneous catalysts for the hydroformylations.

It has been well recognized that the mobility of active sites in the solid catalysts plays an important role in the improvement of the catalytic performance.[11] Recently, a porous polymer with outstanding swelling property has been synthesized through polymerizing vinyl-functionalized monomers under solvothermal conditions.[12] The swollen polymers can be characterized as solution, although they are the elastic solids rather than the viscous liquids.[13] The swollen polymers endow the organic framework with surprisingly high flexibility. In this context, the swollen porous polymers with excellent mobility of catalytic sites adopted onto the framework are expected to enhance the catalytic performance.

To demonstrate the "proof-of-concept", in this contribution a solvothermal synthesis method was employed to polymerize the vinyl-functionalized diphosphine monomers, and a series of insoluble porous organic polymers were achieved (Figure 1). It is also very exciting to observe that they have outstanding swelling properties in a wide range of organic solvents. These porous diphosphine ligand polymers adopted the Rh species exhibit extraordinary catalytic performance in the hydroformylation of styrene, octene, and dodecene. Especially, the Rh species anchored porous polymer, which is composed by 1, 2-bis(diphenylphosphino)ethane moieties (dppe), demonstrates even better performance than their corresponding homogeneous analogues. The more important benefit is that catalysts can be easily separated and recycled from the reaction system without losing any activity and selectivity. The most important character is that the solid materials can be swollen by a range of organic solvents, like their homogeneous counterparts. Rather than just as the immobilized heterogeneous catalysts, this "quasi-homogeneous" catalytic character makes them have the potential to be developed using in industrial fields.



Monomers	Polymeric ligands	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
A	POL-dppe	959	1.15
B	POL-dppm	892	1.07
C	POL-dppb	846	0.81

Figure 1. Structures of vinyl-functionalized diphosphine ligand monomers and textural parameters of the corresponding porous polymers. (A) 1,2-bis(diphenylphosphino)ethane (dppe), (B) bis(diphenylphosphino)methane (dppm), and (C) 1,2-bis(diphenylphosphino)benzene (dppb).

RESULTS AND DISCUSSION

Synthesis and Characterization. As a representative sample among our synthesized porous diphosphine ligand polymers, the preparation of porous polymer constructed by dppe ligand is illustrated thoroughly. It was prepared through a free-radical polymerization of vinyl-functionalized dppe monomer in THF at 100 °C for 24 h. The resultant solid was washed with THF and then dried at 50 °C under vacuum. The white solid product (POL-dppe) was finally obtained in nearly quantitative yield.

The viny-functionalized diphosphine monomers such as dppe, bis(diphenylphosphino)methane (dppm), and 1,2-bis(diphenylphosphino)benzene (dppb) (Figure 1) have been obtained by the one-pot synthesis method. In this synthetic route, the commercially available dichlorophosphines were reacted with (4-vinylphenyl) magnesium bromide (Figures S1-S6) to produce those vinyl-functionalized diphosphine monomers. This easy-to-get feature of vinyl-functionalized diphosphine monomers made the numbers of porous polymers easily scale-up.

^{13}C MAS NMR spectra were used to characterize the POL-dppe polymer. The signals ranged from 125 to 145 ppm (Figure 2A and Figure S7) are assignable to the aromatic carbons of the POL-dppe polymer, and the signal at 25.3 ppm is attributed to the "-CH_2CH_2-" linker. The strong signal at 43.8 ppm is attributed to the polymerized vinyl groups.[9] Additionally, ^{31}P MAS NMR spectrum shows just one signal at -15.1 ppm (Figure 2B), which is at the same position as the ligand. These observations indicate that the dppe moieties were stable during the solvothermal polymerization process. The POL-dppe polymer are air stable chemicals because no obvious changes have been observed when the white POL-dppe solid was exposed to air for one month. TG analysis demonstrates that the weight loss of the POL-dppe

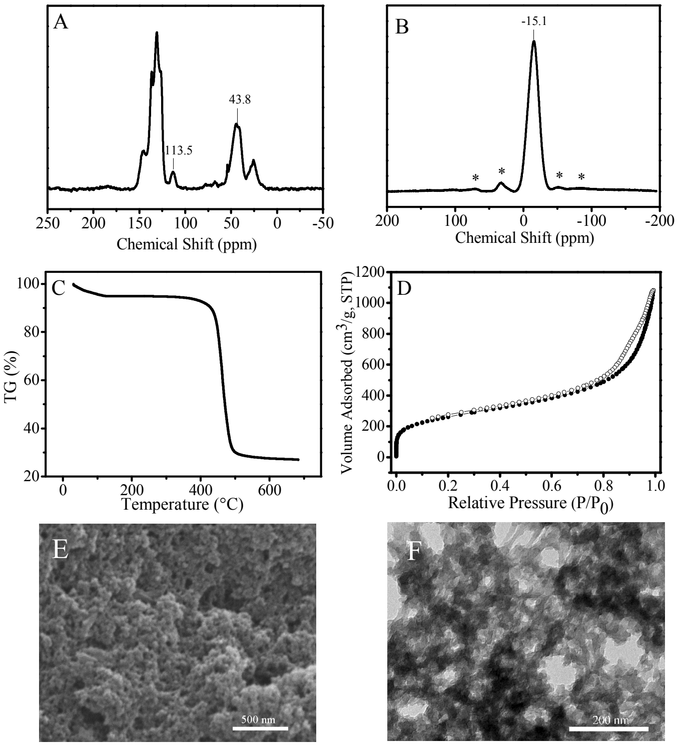


Figure 2. (A) ^{13}C MAS NMR spectrum, (B) ^{31}P MAS NMR spectrum, (C) TG curve, (D) N_2 sorption isotherms, (E) SEM image, and (F) TEM image of POL-dppe polymer.

polymer starts over 400 °C (Figure 2C), which indicates that the POL-dppe polymer is thermally stable. The powder X-ray diffraction (XRD) pattern reveals that the POL-dppe solid are amorphous (Figure S8). The permanent porosity of the POL-dppe polymer was confirmed by N_2 sorption isotherms. The curve collected at -196 °C (Figure 2D) exhibits combined features of type I and type IV with two obviously steep steps in the $P/P_0<0.01$ and $0.70<P/P_0<0.98$ regions, which suggests that there are micro- and meso- pores in the polymer. Based upon the calculations of the nonlocal density functional theory method (NLDFT), the pore sizes of two types are distributed around 0.7-1.5 and 2.8-150 nm (Figure S9), respectively. The Brunauer-Emmett-Teller (BET) surface area of POL-dppe polymer is estimated at 943 m^2/g with a total pore volume of 1.51 cm^3/g. Scanning electron micrograph (SEM, Figure 2E) and transmission electron micrograph (TEM, Figure 2F) images of POL-dppe polymer further confirm the existence of hierarchical porosities. This hierarchical porous structural property of POL-dppe polymer is very favorable for the diffusion of reactants and products in the catalytic transformation processes.

It is also very interesting to illustrate that the POL-dppe solid have outstanding solvation and swelling properties in a wide range of organic solvents. For example, when the POL-dppe polymer was added into the toluene solvent, the volume was enlarged remarkably because of the toluene absorption and then swelling of the POL-dppe polymer (Figure S10). The swollen polymers make their framework flexible and freely movable. This swelling property let the organic ligands in the POL-dppe polymer be more accessible for the organometallic complexes.

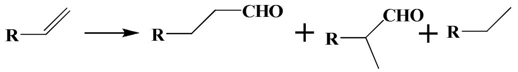
Rh species supported POL-dppe polymers (Rh/POL-dppe) have been obtained by treating POL-dppe polymer with $Rh(CO)_2(acac)$ in the toluene solvent. The Rh/POL-dppe catalysts with various Rh loading amounts still demonstrate very high surface areas, large pore volumes, and outstanding swelling properties. For example, POL-dppe with 2.0 wt.% Rh loading (hereafter denoted Rh/POL-dppe, the dppe/Rh ratio in this catalyst is about 10) gives the BET surface area and pore volume of 856 m^2/g and 1.41 cm^3/g, respectively (Figures S11 and S12). After the toluene solvent was introduced, the volume of the Rh/POL-dppe catalyst is largely expanded (Figure S13). X-ray photoelectron spectroscopy (XPS) spectra of the Rh/POL-dppe catalyst (Figure S14) demonstrate the values of $Rh3d_{5/2}$ and $Rh3d_{3/2}$ about 308.9 and 313.5 eV, which are lower than the values 309.9 and 314.6 eV of $Rh(CO)_2(acac)$. Simultaneously, the P2d binding energy of the Rh/POL-dppe catalyst exhibits a higher value (131.5 eV) than that (130.9 eV) of the POL-dppe polymer. All XPS experimental results strongly support that there is a strong interaction between dppe ligand and Rh species in the Rh/POL-dppe catalyst.[14a] The IR spectrum of Rh/POL-dppe shows a characteristic peak of P-Rh-P at 650 cm^{-1}, indicating successful coordination of dppe moieties in the POL-dppe with the Rh species (Figure S15).[14b]

Evaluation of catalytic performance. The catalytic capabilities of the Rh/POL-dppe catalysts in the hydroformylation of olefins were evaluated by using styrene as a model substrate. The hydroformylation reactions were operated at 80 °C under 1 MPa of CO/H_2 ($CO/H_2=1:1$) with 0.05 mol% of the catalyst based on Rh species. The Rh/POL-dppe catalysts (at optimized Rh loading at 2.0 wt.%, Figure S16) exhibit excellent chemo- and regioselectivities [nearly quantitative aldehydes yield and 87.8% regioselectivity for branched aldehyde (2-phenyl propionaldehyde)]. Scheme S1 suggests the possible mechanism. More importantly, there is almost no change in terms of the chemo- and regioselectivities over the whole reaction time (Figure 3A). In the multiple repeating reactions, the chemo- and regioselectivities are well retained and after recycling for 5 times the catalysts still preserve the similar activity and regioselectivity (Figure 3B). These catalytic testing results confirm that this catalyst has excellent stabilities and recyclabilities. Meanwhile, the information from inductively coupled plasma optical emission spectroscopy (ICP-OES) shows that the Rh species in the filtrate after each run are undetectable (less than 10 ppb). After separating the solid catalysts, further hydroformylation tests have been operated onto the residual liquids and the residual is completely inactive. All above experimental results indicate that leaching of Rh species from the catalyst is negligible. It is reasonable to propose that both the high concentration of free ligands in the porous polymers and strong interaction between Rh species and ligands resulted in the scarcely any leaching. However the other heterogeneous catalysts, such as Rh/SiO_2, do not stop the leaching of the metal species because of the less organic ligands and weaker interactions.[15] Obviously, the leaching of metal species (catalytic active sites) is not favorable for the catalytic process.

It has been reported that improving the regioselectivity of branched aromatic aldehydes over 90% in the hydroformylation of styrene could be very useful in the pharmaceutical industry.[16] In order to optimize the distribution of products over the Rh/POL-dppe catalyst, different experimental conditions were tested. Table S1 demonstrates the effect of temperature on the catalytic performance, and lower temperature is more favorable for improving the regioselectivity of the Rh/POL-dppe catalyst. For example, at 110 °C the regioselectivity for the branched aldehyde is about 72.5%, and this number was increased up to 94.9% when the temperature was reduced to 50 °C. Figure S17 shows the dependence of the syngas pressure on the product selectivity. Increasing the pressure from 1.0 to 4.0 MPa caused a regioselectivity enhancement of the branched aldehyde from 87.8% to 93.5%. But when the pressure is over 5.0 MPa, there is no obvious effect on the regioselectivity (93.3%).

It also needs to be mentioned that the Rh/POL-dppe catalyst can effectively suppress producing of ethylbenzene (Table S1), which is a conventional byproduct of heterogeneous catalyzed hydroformylation of styrene.[17] Above catalytic experimental results indicate that the Rh/POL-dppe catalyst has a higher selectivity than the conventional heterogeneous catalysts. This phenomenon can be reasonably attributed to that sufficient dppe ligands in the proximity of Rh species in Rh/POL-dppe catalyst prevent the formation of ligand free rhodium species, which are active sites for the formation of the ethylbenzene byproduct.[1]

Table 1. Catalytic data in hydroformylation of *n*-octene and *n*-dodecene.[a]



Entry	Catalyst	Reactant	Conv. (%)	Aldehydes(%)[b]
1	Rh/POL-dppe	*1*-octene	96.9	99.3 (n/i=2.46)
2[c]	Rh/POL-dppe	*1*-octene	96.7	99.3 (n/i=2.45)
3[d]	Rh/POL-dppe	*1*-octene	96.7	98.9 (n/i=2.43)
4[e]	$Rh(CO)_2(acac)$	*1*-octene	98.8	50.1 (n/i=1.07)
5	Rh/dppe	*1*-octene	99.5	52.3 (n/i=1.32)
6	Rh/*2*dppe	*1*-octene	99.5	65.2 (n/i=1.35)
7	Rh/*5*dppe	*1*-octene	96.7	91.3 (n/i=2.62)
8	Rh/10dppe	*1*-octene	54.7	97.9 (n/i=2.42)
9	Rh/POL-dppe	*1*-dodecene	95.5	96.2 (n/i=2.45)
10	$Rh(CO)_2(acac)$	*1*-dodecene	94.5	45.5 (n/i=0.95)
11	Rh/dppe	*1*-dodecene	90.8	61.3 (n/i=0.97)
12	Rh/*2*dppe	*1*-dodecene	88.9	65.9 (n/i=1.44)
13	Rh/*5*dppe	*1*-dodecene	95.1	91.9 (n/i=2.46)
14	Rh/*10*dppe	*1*-dodecene	10.9	69.7 (n/i=0.93)

[a] Reaction conditions: olefin (5.0 mmol), toluene (10 mL), 90 °C, CO/H_2=1:1 (2.0 MPa), S/C=2000, 2.5 h for *n*-octene and 3.0 h for *n*-dodecene; [b] Selectivity (n/i: molar ratio of linear to branched aldehyde in the products) and other products are iso-olefins; [c] Reuse; [d] Recycle for 5 times; [e] The selective of paraffin was 0.3%. Rh/*y*dppe means that the mole ratio of dppe/Rh in the homogeneous catalytic systems is *y*.

Hydroformylation of long-chain olefins to yield aldehydes and alcohols is of great interest because of their widely industrial applications, such as producing detergents, plasticizers, and surfacetants.[1] Table 1 demonstrates the hydroformylation data of *n*-octene and *n*-dodecene over the Rh/POL-dppe catalyst. More importantly, the Rh/POL-dppe catalyst exhibit higher selectivity for producing the corresponding aldehydes than the homogeneous catalysts with various Rh/dppe ratios. Furthermore, dependences of the *n*-octene conversion on the time in the hydroformylation show that, in spite of the insoluble nature, Rh/POL-dppe exhibits a slight higher activity than the optimized homogeneous control Rh/*5*dppe (Figure S18), confirming the excellent catalytic properties of the Rh/POL-dppe catalyst. Moreover, the Rh/POL-dppe catalyst can be readily recycled without observable loss of catalytic activity and selectivity for at least ten runs (Table S2). More importantly, kinetic profiles of the fresh and ten-times-recycled Rh/POL-dppe reveal that they afford the similar activities, confirming its long-term stability (Figure S19). All experimental results indicate that the Rh/POL-dppe catalyst could be applied in industrial field as the Rh-based heterogeneous catalysts.

Importance of high ligand concentration and flexible framework. It has been well documented that the ligand concentration of rhodium-phosphine catalytic system strongly influences the activity, and selectivity of homogeneous hydroformylation.[1] Normally, a large excess of ligand is usually required for realizing the good chemo- and regioselectivities.[18] In order to understand the effect of ligand concentration on the catalytic performance of heterogeneous catalysts, a series of porous polymers bearing dppe ligands were prepared through a solvothermal copolymerization synthetic route with incorporating different amounts of divinylbenzene. After metalation with $Rh(CO)_2(acac)$ (2.0 wt.% Rh), these catalysts with different dppe concentration were finally obtained, and they are represented by Rh/PDVB-*x*-dppe, where *x* stands for the mass ratio of vinyl-functionalized dppe monomer in the polymers (Table S3). According to the experimental results, the catalytic activity and selectivity have been improved by increasing dppe ligand ratio in the frameworks (Figure 3C). For example, the Rh/PDVB-*0.1*-dppe just gives a 60.6% conversion and 50.2% regioselectivity for branched aldehyde along with the formation of ethylbenzene byproduct (selectivity at 2.0%). While the Rh/PDVB-*0.8*-dppe exhibits a >99.8% conversion and 74.9% branched aldehyde selectivity with a complete disappearance of ethylbenzene. Those results also prove that the high ligand concentration play very important roles in improving the catalytic activity and selectivity in the hydroformylation processes. Meanwhile the incorporation of DVB in the POL-dppe framework affected the product selectivity. According to the catalytic data, during the hydroformylation of styrene the Rh/POL-dppe is more selective than the Rh/PDVB-*0.8*-dppe catalyst (87.8% over 75.4%, Figure S20). In order to identify the effects of insertion of DVB on the Rh/POL-dppe catalyst, the same dppe/Rh ratio was maintained by keeping the Rh loading weight of Rh/POL-dppe and Rh/PDVB-*0.8*-dppe at 2.0 wt.% and 1.6 wt.%, respectively. The only difference in two catalysts is the spatial continuity of the dppe ligand; therefore it is reasonable to propose that the wonderful spatial continuity of the Rh/POL-dppe catalyst is another important factor to contribute the excellent catalytic performance. The distinguished structural continuity of the Rh/POL-dppe catalyst is always reserving a high local ligand concentration around the Rh species.

The POL-dppe polymer can swell in various organic solvents, and the framework of swollen polymers could be characterized as solution. This “quasi-homogeneous” character of Rh/POL-dppe catalysts even makes them have a better catalytic performance than the “real homogeneous” Rh/dppe catalysts. The free movement of ligands in the POL-dppe framework has been investigated by ^{31}P static solid-state NMR technique due to the uniform chemical environment and the high natural abundance of ^{31}P nuclei. The static spectrum of the POL-dppe polymer exhibits a broad signal for the combination of the wide distribution of chemical shifts and the broad chemical shift anisotropic line shapes under the solid state (Figure 4a). However, after introducing of toluene solvent to the solids, the swollen polymers demonstrated a sharp signal, which is almost at the same chemical shift position as its analogue in solution (Figure 4b).[10a] This observation proves that large part of the dppe ligands in the framework do have a high mobility in the swollen state. In order to confirm the importance of

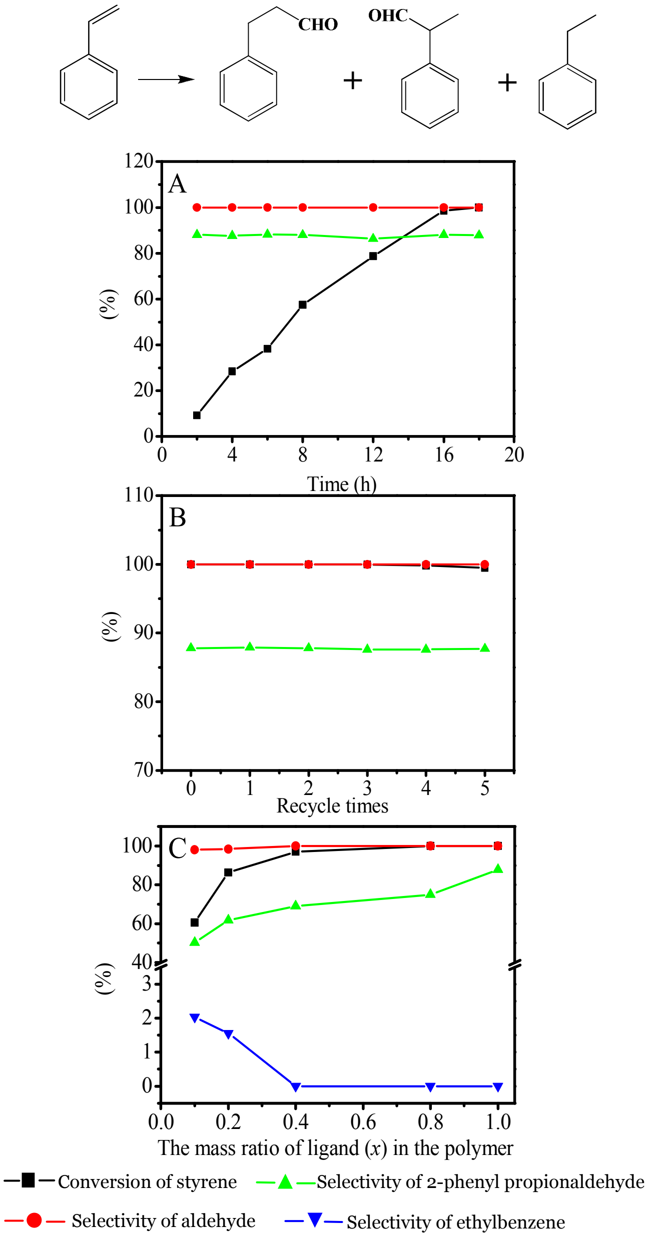


Figure 3. Catalytic performance in styrene hydroformylation of (A) dependence of the catalytic activities and selectivities on the time over the Rh/POL-dppe catalyst, (B) recycling tests of the Rh/POL-dppe catalyst, and (C) dependence of catalytic activities and selectivities on the dppe ligand concentration in the Rh/PDVB-*x*-dppe catalysts. Reaction conditions: styrene (5.0 mmol), toluene (10 mL), 80 °C, CO/H_2=1:1 (1.0 MPa), S/C=2000, 18 h, and Rh loading at 2.0 wt.%. *x* stands for the mass ratio of vinyl-functionalized dppe monomer in the polymers.

the swelling property, a nonporous polymerized dppe with poor swelling property (NPOL-dppe) has been synthesized through polymerizing the vinyl-functionalized dppe monomer under the presence of acetic ether solvent. Even after introducing an excess of toluene solvent, the ^{31}P static solid-state NMR spectrum of NPOL-dppe polymer just exhibits a broad signal (Figure 4c). The hydroformylation of styrene shows that the catalytic properties of Rh/NPOL-dppe (2.0 wt.% Rh) are poor (65.2% styrene conversion with 67.7% branched aldehyde selectivity). Furthermore, porous dppe polymer with poor swelling property (POL-dppe-PS, BET surface area at 947 m^2/g) has also been synthesized through a polymerization process of the vinyl-functionalized dppe monomer in the presence of a small amount of THF solvent. The catalytic performance of Rh/POL-dppe-PS catalyst (92.4% styrene conversion and 80.6% branched aldehyde selectivity) is not good as that of the Rh/POL-dppe catalyst with excellent swelling property under the same reaction conditions. XPS spectra reveal that the binding energies of P2p and Rh3d in Rh/NPOL-dppe and Rh/POL-dppe-PS are similar to those of Rh/POL-dppe (Figure S21), suggesting their similar bonding nature of Rh species with the dppe moieties. Above research results clearly illustrate that the swelling property of Rh/POL-dppe catalyst plays very important roles in the catalytic performance of these heterogeneous catalysts. Through comprehensive experiments, it is confirmed that both the high ligand concentration and swelling properties of Rh/POL-dppe catalysts made them has the extraordinary catalytic performance.

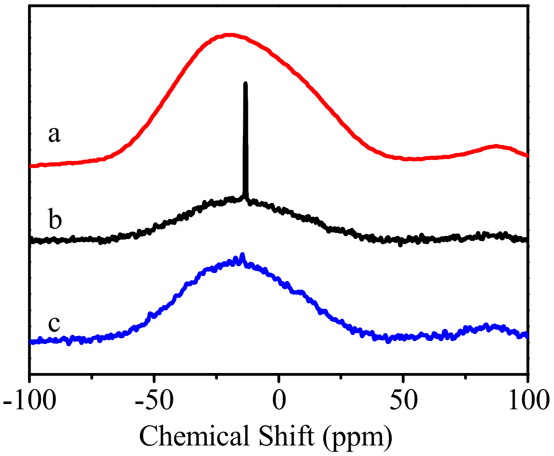


Figure 4. ^{31}P static solid-state NMR spectra of (a) dried POL-dppe polymer, (b) POL-dppe polymer in the presence of toluene, and (c) NPOL-dppe polymer in the presence of toluene.

SUMMARY AND CONCLUSION

In conclusion, a series of diphosphine ligand constructed porous polymers were synthesized through polymerizing the vinyl-functionalized diphosphine monomers. As a protocol catalyst among the Rh species loaded porous polymers, the Rh/POL-dppe catalysts have been thoroughly studied in the hydroformylation of olefins. They demonstrated excellent catalytic performance in terms of activity and selectivity. Through the multiple comparing experimental studies, it is reasonable to suggest that the wonderful catalytic performance of these porous polymers should be attributed to the extremely high ligand concentration (the ratio of dppe to Rh in the Rh/POL-dppe catalyst is about 10) and the excellent mobility of dppe ligands in the framework in the swollen state. These Rh-metallated porous organic polymers exihibit “quasi-homogeneous” catalytic behavior. As solids in nature, they are also easily separated and recycled from the reaction system without losing any activitiy and selectivity. Like enzymes, these catalysts realize the homogeneous catalysis under the heterogeneous medium state. Therefore, these porous polymers provide new perspectives for synthesizing heterogeneous catalysts with the homogeneous catalytic character.

METHOD

Synthesis of vinyl-functionalized diphosphine monomers. As a representative sample, 1,2-bis(dichlorophosphino)ethane (15 mmol in 30 mL of THF) was added slowly at 0 °C to (4-vinylphenyl)magnesium bromide solution, which was synthesized from 4-bromostyrene (60 mmol) and magnesium powder (70 mmol). After stirring at RT for 2 h, 50 mL of saturated NH_4Cl aqueous was added to quench the reaction. The organic phase was separated, and water phase was extracted with an excess of diethyl ether. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuum. The obtained crude product was purified by silica gel chromatography (5%EtOAc/Petroleum ether) to afford vinyl-functionalized dppe monomer as a white solid.

Synthesis of diphosphine ligand constructed porous polymers. One typical example, 2.0 g of vinyl-functionalized dppe monomer was dissolved in 20 mL of THF, followed by addition of 50 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of THF under vacuum, a solid monolith was obtained and denoted as POL-dppe.

ASSOCIATED CONTENT

Supporting Information

Synthesis, characterization and catalytic data details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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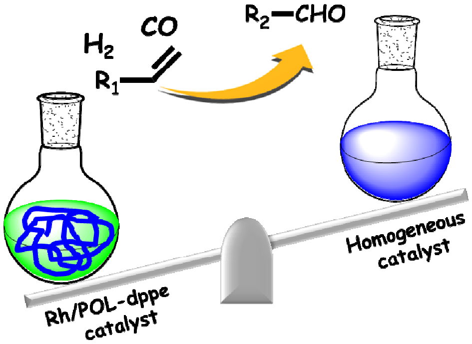
H2
CO
R1
R2—CHO
Rh/POL-dppe catalyst
Homogeneous catalyst