

Multifunctional Single-Site Catalysts for Alkoxycarbonylation of Terminal Alkynes

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A multifunctional copolymer $(PyPPh_2-SO_3H@porous organic polymers, POPs)$ was prepared by combining acidic groups and heterogeneous P,N ligands through the copolymerization of vinyl-functionalized 2-pyridyldiphenylphosphine (2-PyPPh_2) and *p*-styrene sulfonic acid under solvothermal conditions. The morphology and chemical structure of the copolymer were evaluated using a series of characterization techniques. Compared with traditional homogeneous Pd(OAc)_2/2-PyPPh_2/*p*-toluenesulfonic acid catalyst, the copolymer supported palladium catalyst (Pd–PyPPh_2-SO_3H@POPs) exhibited higher activity for alkoxycarbonylation of terminal alkynes under the same

conditions. This phenomenon could be attributed to the synergistic effect between the single-site Pd centers, 2-PyPPh₂ ligands, and SO₃H groups, the outstanding swelling properties as well as the high enrichment of the reactant concentration by the porous catalyst. In addition, the catalyst could be reused at least 4 times without any apparent loss of activity. The excellent catalytic reactivity and good recycling properties make it an attractive catalyst for industrial applications. This work paves the way for advanced multifunctional porous organic polymers as a new type of platform for heterogeneous catalysis in the future.

Introduction

Since the first report of alkoxycarbonylation of terminal alkynes by Reppe and co-workers in 1939, this reaction has attracted considerable attention^[1] owing to its high atom economy process (Scheme 1 A) and the usefulness of α , β -unsaturated carboxylic acids and their derivatives in large-scale fine chemical synthesis.^[2] So far, palladium based homogeneous catalyst systems consisting of Pd(OAc)₂, 2-PyPPh₂ (Py=pyridine), and acidic promoters exhibit high activity and selectivity for this reaction at mild conditions.^[3] Notably, 2-PyPPh₂ plays a critical dual role in achieving high catalytic efficiency through its ability to function as a bidentate P,N-coordinated ligand, whereas

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a second P-coordinated N-protonated 2-PyPPh₂ favors proton transfer in the rate determining protonolysis step (Scheme 1 B).^[3a, c] Moreover, the N atom of the pyridyl ring also works as an acceptor of the alcoholic proton, thus favoring the cleavage of the product. Replacement of 2-PyPPh₂ by PPh₃ or other heteroaromatic rings without N atoms results in a dramatic decrease in catalytic activity.^[3b, 4] Furthermore, Brönsted acids, which are normally employed as promoters, also play a key role in the reaction; no product was obtained without the use of Brönsted acids in the reaction mixture. Therefore, soluble acids with appropriate acidic strength and coordinative properties, such as methane sulfonate, trifluoromethane sulfonic acid, and *p*-toluene sulfonic acid (TsOH), have often been employed.^[3b,f]

Such homogeneous catalytic systems play an extremely important role in the field of modern catalysis owing to their high activity and selectivity. However, the recovery and reuse of the homogeneous catalyst is still a major challenge that needs to be addressed from the viewpoint of green and sustainable chemistry. The use of precious organometallic catalysts is not widespread owing to problems associated with their recycling and metal contamination of the products.^[5]Immobilization of the homogeneous catalyst on an insoluble support (e.g., silica, alumina) definitely facilitates the recovery procedure using simple filtration, but their chemical nature limits their potential for the chemical modification process.^[6] In the case of alkoxycarbonylation of terminal alkynes, Doherty and co-workers have immobilized 2-PyPPh₂ on an insoluble polymeric support. In such a catalytic system, additional soluble acids need to be added to achieve high activity.^[4] Minimizing the liquid acidic corrosion of the reactor and pollution of the

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Scheme 1. (A) Palladium catalyzed hydrocarbonylation of terminal alkynes. (B) Mechanism of the alkoxycarbonylation of alkynes in the presence of the $Pd(OAc)_2/2$ -PyPPh₂/acidic promoters catalytic system. (C) Syntheses of Pd-PyPPh₂-SO₃H@POPs catalyst. Reagents and conditions: i) H₂O, THF, AIBN, 120°C; ii) 1 M H₂SO₄; iii) Pd(OAc)₂, THF.

environment has become an important factor to be addressed for commercial exploitation.^[7]

Recently, porous organic polymers (POPs) have emerged as a versatile platform for the deployment of catalysts owing to their porous nature, high stability, and flexibility in building block design.^[8] Generally, catalytic POPs can be divided into two major classes: POPs that are self-polymerized with only one monomer and POPs that are co-polymerized by two (or more) different monomers. Compared with self-polymerized POPs, copolymerized POPs have a clear advantage of integrating two (or more) active sites into one multifunctional material and playing a synergistic role during catalysis. In addition, compared with the homogeneous system, ligands, and other active groups are greatly concentrated by confining them in the heterogeneous space of POPs, which will further enhance their synergistic effects.^[9] Moreover, it has been recognized that polymers that are polymerized through vinyl-functionalized monomers exhibit excellent mobility of the active sites, which plays an important role in the improvement of the catalytic performance.^[10]

As far as we know, multifunctional POPs catalysts are rare owing to the difficulty of functionalizing the building blocks. Therefore, in this work, we report the preparation of a novel co-polymerized multifunctional POPs material (PyPPh₂-SO₃H@POPs) through an elegant design of vinyl-functionalized ligand (which contain both P and N) and vinyl-functionalized benzene sulfonic acid (Scheme 1). Palladium is immobilized onto PyPPh₂-SO₃H@POPs as the active metal center through impregnation. According to the mechanism in the alkoxycarbonylation of terminal alkynes, the synergistic effect of the Pd active sites, 2-PyPPh₂ ligands, and -SO₃H groups plays a key role in accelerating the reaction rates. Bearing this requirement in mind, and given the extraordinary advantage of co-polymerized POPs, which could concentrate several active sites in a confined pore field to strengthen the synergistic effect, we firstly prepared the multifunctional PyPPh2-SO3H@POPs supported palladium catalyst Pd–PyPPh₂–SO₃H@POPs and used it for alkoxycarbonylation of terminal alkynes. Compared with the soluble acids, the immobilization of the $-SO_3H$ group on the heterogeneous Pd–PyPPh₂–SO₃H@POPs catalyst prevented the corrosion of the equipment and environmental pollution. From the viewpoint of atom economy and green chemistry, the heterogeneous POPs catalyst, which combines excellent reactivity and reductive corrosion as well as facile product separation, has potential applications in chemical industry. Furthermore, the excellent activity and stability of the Pd–PyPPh₂– SO₃H@POPs heterogeneous catalyst pave the way towards the design of sustainable, efficient, and reliable catalysts.

Results and Discussion

The Pd–PyPPh₂–SO₃H@POPs catalyst was prepared according to Scheme 1 C. The monomer of 2-vinyl-functionalized diphenyl-2-pyridylphosphine (2V-P,N) was synthesized according to the method described in Scheme 2.^[11] The copolymer of 2vinyl-functionalized 2-PyPPh₂ with *p*-styrene sulfonic acid (PyPPh₂–SO₃H@POPs) was prepared by solvothermal copolymerization of 2V-P,N with sodium *p*-styrene sulfonate below 120 °C, followed by treating with H₂SO₄. After drying at 80 °C under reduced pressure, PyPPh₂–SO₃H@POPs was obtained as a white powder. The Pd–PyPPh₂–SO₃H@POPs using a solution of



Scheme 2. Synthesis of 2V-P,N. Reagents and conditions: (i) BuLi, ZnCl₂, Py, THF, -40 °C; (ii) PCl₃, THF, Py, -10 °C; (iii) Styryl magnesium bromide, THF, 0 °C.



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Pd(OAc)₂ in tetrahydrofuran (THF). For comparison, three other POPs, porous 2-vinyl-funtionalized 2-PyPPh₂ polymer (PyPPh₂@POPs), 3-vinyl-funtionalized PPh₃ polymer (PPh₃@POPs), and PPh₃ with *p*-styrene sulfonic acid (PPh₃– SO₃H@POPs), which have only one or two functionalized sites, were also synthesized and used as supports to prepare the corresponding catalysts, denoted as Pd–PyPPh₂@POPs, Pd– PPh₃@POPs, and Pd–PPh₃–SO₃H@POPs, respectively, using the same procedure as for Pd–PyPPh₂–SO₃H@POPs.

The permanent porosity of PyPPh2-SO3H@POPs was confirmed by N₂ sorption isotherms (Figure 1A). The curve collected at 77 K revealed that the copolymer possessed a surface area of 44.3 m^2g^{-1} and a total pore volume of 0.133 m^3g^{-1} . The scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) images of PyPPh₂-SO₃H@POPs are shown in Figure 1B and C, which indicate that the copolymer has rough surfaces and a considerable number of pores. Furthermore, thermogravimetric analysis shows that PyPPh₂-SO₃H@POPs has superior thermal stability, with an initial decomposition temperature of 310 °C(Figure 1D), which is comparable to that of Nafion NR50 (330 °C), one of the most stable resins.^{[6d] 13}C magic angle spinning (MAS) NMR spectra were used to characterize the PyPPh2-SO3H@POPs polymer (Figure 1 E). The new peak at 31.5 ppm was assigned to the polymerized vinyl groups. The interaction between Pd and exposed phosphine atom in the copolymer carrier was investigated by ³¹P solid state NMR (Figure 1F). A single peak at -4.53 ppm was detected, which was attributed to the P atoms of the PyPPh₂–SO₃Na@POPs support.⁽⁴⁾ For Pd–PyPPh₂–SO₃H@POPs, in addition to the peak of -4.53 ppm assigned to the uncoordinated P in PyPPh₂–SO₃H@POPs, a peak at 21.5 ppm was also identified, which was attributed to the P atoms coordinated with Pd^{II} species. The results indicated that there was a strong coordinative bond between the Pd atoms and the exposed phosphorous atoms on the surface of the porous PyPPh₂–SO₃H@POPs support. Extended X-ray absorption fine structure (EXAFS) analysis results also supported the presence of coordination bonds.^[11]

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Pd–PyPPh₂–SO₃H@POPs clearly show the isolated individual Pd species (indicated by the arrows) uniformly dispersed within the porous structures of the PyPPh₂–SO₃H@POPs support (Figure 2 A and B). In addition, scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDS) mapping images (Figure 2 C, D, E, and F) reveal the highly dispersed character of all the functional elements (P, S, N, and Pd), which are well integrated in our material.

The XPS spectra of $Pd-PyPPh_2-SO_3H@POPs$ catalysts (fresh and used) are shown in Figure 3. Clearly, Figure 3 A shows the



Figure 1. (A) N_2 sorption isotherms and pore size distributions, (B) SEM image and (C) TEM image, (D) TG curve and (E) ¹³C NMR of PyPPh₂-SO₃H@POPs, (F) ³¹P NMR of PyPPh₂-SO₃Na@POPs (top) and ³¹P NMR of Pd-PyPPh₂-SO₃H@POPs (bottom). Spinning side bands are denoted by asterisks (*).

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Figure 2. HAADF STEM image of (A) the fresh and (B) the used Pd–PyPPh₂–SO₃H@POPs catalyst; SEM-EDS mapping of Pd–PyPPh₂–SO₃H@POPs. (C) P with green color, (D) S with yellow color, (E) N with cyan color, (F) Pd with dark-red color.

signals of P, N, S, C, and O, indicating the presence of sulfonic group and a pyridyl ring in PyPPh2-SO3H@POPs. Figure 3B shows the C1s peaks at 284.6, 285.3, 286.2, and 287.7 eV, which were attributed to C--C, C--P, C--S, and C--N bonds, respectively.^[12] The O1s peak at 532.5 eV and S2p peak at 168.2 eV were associated with the -SO₃H (Figure 3C and 3D). Two peaks at approximately 399.0 and 400.1 eV were ascribed to N atoms in C–N and C–N–Pd, respectively, indicating that N coordinated with the Pd species (Figure 3 E).^[13] The P2p gives two peaks at approximately 131.4 and 133.8 eV, which correspond to P atoms in C-P and C-P-Pd, respectively (Figure 3 F).^[14] The above XPS results reveal that both 2-PyPPh₂ ligand and SO₃H group were successfully immobilized on the same copolymer. In addition, the XPS spectra (Figure 3G and H) of Pd show that the binding energy of Pd^{II} (337.8 eV) and Pd⁰ (336.0 eV) in the catalyst are higher than their typical value (Pd^{II} (337.0 eV) and Pd⁰ (335.0 eV)^[15] as well as our results of Pd binding energy in the Pd-PyPPh₂-SO₃Na@POPs sample (see Figure S3), probably originating from the Pd-H species, which are considered as the active species of the reaction. The presence of -SO₃H in the copolymer was also verified by FTIR spectroscopy. Figure 31 shows the FTIR spectra of the porous PyPPh₂@POPs and PyPPh₂-SO₃H@POPs. Compared with PyPPh₂@POPs, the bands at 1037, 1009, and 673 cm⁻¹ were attributed to the -SO₃H group in the PyPPh₂-SO₃H@POPs.^[16]

Table 1 presents the reaction performance for the methoxycarbonylation of phenylacetylene and acetylene over various catalysts. It is interesting to find that both 2-PyPPh₂ and Brönsted acid promoters play a significant role in the reaction. Pd catalysts with a pyridyl ligand exhibited much higher activities (Table 1, entries 1, and 9) than the corresponding triphenylphosphine (PPh₃) counterparts without a pyridyl ring (Table 1, Entries 3, 7, and 10). This is attributed to the critical role of 2-PyPPh₂, which serves not only as a bidentate P,N-coordinated ligand but also as a mono-coordinated ligand in the protonolysis step of the catalytic cycle.^[3c,4] No desired products were found in the reaction mixture without acid (Table 1, Entries 2, 4, 5, and 8), which is in accordance with literature reports. This could be explained by the fact that the Brönsted acid initiates the formation of the active Pd-H complex and accelerates the coordination process of alkyne to the Pd center.^[3b, f, g, 17] Both the P,N-coordinated bidentate ligand and the Brönsted acid activate the catalytic cycle. Generally speaking, heterogeneous catalysts exhibit lower activities than homogeneous catalysts owing to the low degree of exposure of the catalytic active sites. However, the heterogeneous Pd-PyPPh₂-SO₃H@POPs catalyst (Table 1, Entry 9) showed higher activity than the homogeneous counterpart (Entry 1). This phenomenon could be attributed to the following reasons: 1) The formation of a catalytically active Pd-H species is the rate controlling step during the catalytic reaction process in alkoxycarbonylation of terminal alkynes.^[3a] In our catalyst system, the different functional centers of the Pd center, 2-PyPPh₂ ligand, and SO₃H group were adjacent on the same copolymer, which favored the formation of a catalytically active Pd-H species, resulting in a catalytic synergistic effect to improve the reaction rate. 2) The PyPPh₂-SO₃H@POPs solid has outstanding solvation and swelling properties in the presence of organic solvents.^[9] For example, when the polymer was added into the THF solvent, the volume was remarkably enlarged because of the absorption of THF and then swelling of the PyPPh₂-SO₃H@POPs polymer (see Figure S4). The outstanding swelling properties of the catalyst make the active sites on the framework flexible and movable, which play an important role in the improvement of the catalytic performance. 3) The interface between the heterogeneous catalyst and the reaction system favors the enrichment of the reactants on the catalyst surface, which accelerates the reaction rate.^[18] To understand this phenomenon, we measured the adsorption of methanol and phenylacetylene on the Pd-PyPPh₂-SO₃H@POPs catalyst. The methanol and phenylacetylene could be remarkably adsorbed on the catalyst with 3.95 $q q^{-1}$ and 4.38 $q q^{-1}$ catalyst, respectively.

It showed that the activity of Pd–PyPPh₂@POPs with a homogeneous acid for carbonylation of acetylene and phenylacetylene are 3591 and 1907 h⁻¹ (Table 1, Entries 6 and 16), respectively, which were higher than those of the homogeneous Pd(OAc)₂/2-PyPPh₂/TsOH as well as the heterogeneous Pd– PyPPh₂–SO₃H@POPs catalysts. To understand this phenomenon, we firstly measured the adsorption of TsOH on PyPPh₂@POPs and found that TsOH can be remarkably adsorbed on the polymer with 1.7 g g⁻¹ polymer. It is reasonable to propose that the increase in the TsOH concentration in the PyPPh₂@POPs leads to an enhancement of the activity. Then, the S content on the surface of the Pd–PyPPh₂–SO₃H@POPs

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Figure 3. (A) XPS spectra of PyPPh₂–SO₃H@POPs, XPS spectra of (B) C1s, (C) O1s, (D) S2p, (E) N1s, (F) P2p and (G) Pd in the fresh Pd–PyPPh₂–SO₃H@POPs catalyst, (H) XPS spectra of Pd in the used Pd–PyPPh₂–SO₃H@POPs catalyst. (I) FTIR spectra of (a) PyPPh₂@POPs and (b) PyPPh₂–SO₃H@POPs.

catalyst was measured by XPS. Only 0.37 mmolg⁻¹ S content on the surface of the catalyst was detected, which was lower than 0.93 mmolg⁻¹ of the total S content of the Pd–PyPPh₂– SO₃H@POPs catalyst. This suggested that the low exposure of SO₃H group on the heterogeneous catalyst affected the catalytic performance. Although the Pd–PyPPh₂@POPs catalyst enriched by homogeneous TsOH acid exhibited higher catalytic activity, a part of TsOH is still present in the methanol solution, which could lead to corrosions of the reactor and pollution of the environment.

In an attempt to glean further information about the methoxycarbonylation, acetylene was also examined as a substrate (Table 1, Entries 11–20). Similar results were observed as for the methoxycarbonylation of phenylacetylene. These results clearly indicate that both the bidentate P,N-coordinated ligand and the Brönsted acid play a key role in the alkoxycarbonylation of terminal alkynes. The effects of reaction temperature, carbon monoxide (CO) pressure, Pd loading, and the amount of SO₃H on the turnover numbers (TON) of the methoxycarbonylation of phenylacetylene were investigated. A plot of TON value versus reaction temperature showed that 85 °C was the optimal reaction temperature (Figure 4). The pressure of CO strongly impacted on the TON value of the methoxycarbonylation of phenylacetylene, and the optimal pressure was approxi-

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mately 4.8 MPa (Figure 5). The Pd loading and amount of SO_3H in the polymer also had a significant influence on the activity of Pd–PyPPh₂–SO₃H@POPs. No ester product was found in the absence of palladium (Table 2, Entry 1) whereas the appropriate Pd loading benefited the reaction, and an excess loading of Pd(OAc)₂ causes the aggregation of palladium nanoparticles, which eventually deactivated the reaction system. Figure S5 shows that the palladium particles emerged on the surface of the catalyst (with Pd loading of 0.35%) after the reaction process. The presence of a sufficient amount of SO₃H is essential in the polymer to form the Pd–H active species (Table 2, Entry 5).^[3f]

The catalytic efficiency of Pd–PyPPh₂–SO₃H@POPs was also investigated by employing various aliphatic alcohols. To our delight, the linear alcohols (Table 3, Entries 1, 2, 5, and 6) reacted with alkynes to give the desired products with good catalytic activities. Slightly lower activity was obtained in the case of branched alcohols. This may be attributed to the steric hindrance of branched alcohols, which restricts the nucleophilic attack in the reaction process.^[3g] The stability of the supported complex during the carbonylation reaction is of great concern for most anchored catalysts. Thus, the recovery and reuse of the heterogeneous Pd–PyPPh₂–SO₃H@POPs catalyst was investigated for the methoxycarbonylation of phenylacetylene



Table 1. Methoxycarbonylation of phenylacetylene and acetylene. ^[a]								
Entry	Catalyst system	Substrate ^[b]	Acid ^[c]	TON ^[d]				
1	Pd(OAc) ₂ /2-PyPPh ₂	$Ph-C \equiv CH$	TsOH	955				
2	Pd(OAc) ₂ /2-PyPPh ₂	$Ph-C \equiv CH$	no	no				
3	Pd(OAc) ₂ /PPh ₃	$Ph-C \equiv CH$	TsOH	30				
4	Pd(OAc) ₂ /PPh ₃	$Ph-C \equiv CH$	no	no				
5	Pd–PyPPh ₂ @POPs	$Ph-C \equiv CH$	no	no				
6	Pd–PyPPh ₂ @POPs	$Ph-C \equiv CH$	TsOH	1907				
7	Pd–PPh₃@POPs	$Ph-C \equiv CH$	TsOH	45				
8	Pd–PPh₃@POPs	$Ph-C \equiv CH$	no	no				
9	Pd–PyPPh ₂ –SO ₃ H@POPs	$Ph-C \equiv CH$	no	1242				
10	Pd–PPh ₃ –SO ₃ H@POPs	$Ph-C \equiv CH$	no	21				
11 ^[e]	Pd(OAc) ₂ /2-PyPPh ₂	$HC \equiv CH$	TsOH	862				
12 ^[e]	Pd(OAc) ₂ /2-PyPPh ₂	$HC \equiv CH$	no	no				
13 ^[e]	Pd(OAc) ₂ /PPh ₃	$HC \equiv CH$	TsOH	no				
14 ^[e]	Pd(OAc) ₂ /PPh ₃	$HC \equiv CH$	no	no				
15 ^[e]	Pd–PyPPh ₂ @POPs	$HC \equiv CH$	no	no				
16 ^[e]	Pd–PyPPh ₂ @POPs	$HC \equiv CH$	TsOH	3591				
17 ^[e]	Pd–PPh₃@POPs	$HC \equiv CH$	TsOH	14				
18 ^[e]	Pd–PPh₃@POPs	$HC \equiv CH$	no	no				
19 ^[e]	Pd–PyPPh ₂ –SO ₃ H@POPs	$HC \equiv CH$	no	1136				
20 ^[e]	$Pd-PPh_{3}-SO_{3}H@POPs$	$HC \equiv CH$	no	5				

[a] Reaction conditions: 15 mL methanol, 4.8 MPa CO, 0.28 mmol ligand, theoretical catalyst loading equal to 0.0019 mmol Pd(OAc)₂, 0.0078 mmol TsOH, 50 °C, 1 h; [b] 5 mmol phenylacetylene or 0.12 MPa acetylene; [c] TsOH: *p*-toluenesulfonic acid, SO₃H content was analyzed by element analysis. "No" means the reaction was carried out without TsOH being added. [d] Calculated by GC analysis, l/r = 2-20%. [e] 20 mL acetone, 5 mL methanol, 0.55 mmol ligand, 0.0036 mmol Pd(OAc)₂, 0.016 mmol TsOH.



Figure 4. The effect of the reaction temperature on the catalytic activity of the Pd–PyPPh₂–SO₃H@POPs catalyst for methoxycarbonylation of phenylace-tylene. Reaction conditions: Pd–PyPPh₂–SO₃H@POPs (0.36 µmol Pd), phenylacetylene (0.1 g), CH₃OH (15 mL), P(CO) = 4.8 MPa.

(Figure 6). The catalyst was readily separated by simple centrifugation and then reused for the next reaction. The catalyst showed good stability and could be reused at least 4 times without a significant loss of activity. This might be associated with the stability of the polymer network and a strong coordination between Pd and P ligand in the polymer. To investigate the metal leaching problem, inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to detect the content of metal in the reaction solution. It was found that the amount of Pd that leached in the first reaction solution



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Figure 5. The effect of the pressure of CO on the catalytic activity of the Pd– PyPPh₂–SO₃H@POPs catalyst for methoxycarbonylation of phenylacetylene. Reaction conditions: Pd–PyPPh₂–SO₃H@POPs (0.36 µmol Pd), phenylacetylene (0.1 g), CH₃OH (15 mL), T = 80 °C.

cetylene under different Pd loading and content of –SO ₃ H. ^[a]									
Entry	Pd Loading ^(b) [wt%]	TON	b/l ^[c]	Selectivity ^[d] [%]					
1	0	0	-	_					
2	0.1	851.7	22.7	>99					
3	0.19	995.2	23.8	>99					
4	0.35	347.6	24.8	>99					
5 ^[e]	0.23	145.6	17.0	>99					
[a] Reactio	on conditions: 15 ml	_ methanol, 4	4.8 MPa CO,	0.02 g catalyst,					

1 mmol phenylacetylene, 80 °C,1 h. [b] Pd loading was calculated by the amount used in preparing the catalyst. [c] Molar ratio of branched to linear ester. [d] The amount of unsaturated ester in the product. [e] The theoretical content of S in Pd–PyPPh₂–SO₃H@POPs is 0.50 mmol g⁻¹.

Table 3. Alkoxycarbonylation of various substrates catalyzed by Pd–PyPPh_2–SO_3H@POPs.^{[a]} \ensuremath{P}							
Entry	Alkyne ^[b]	Alcohol	<i>t</i> [h]	TON ^[c]			
1	$Ph-C\equiv CH$	ethanol	2	475			
2	$Ph-C \equiv CH$	propanol	4	842			
3	$Ph-C \equiv CH$	isopropanol	4	145			
4	$Ph-C \equiv CH$	isobutanol	4	442			
5	$HC \equiv CH$	ethanol	1	949			
6	$HC \equiv CH$	butanol	1	588			
7	$HC \equiv CH$	isobutanol	3	402			
[a] Reaction conditions: 25 mL alcohol, 4.8 MPa CO, theoretical catalyst loading equal to 3.5×10^{-4} mmol Pd(OAc) ₂ , 50 °C; [b] 5 mmol phenylacety-lene or 0.12 MPa acetylene; [c] Calculated by GC analysis.							

was 0.081 ppm, and 0.114 ppm in the second cycle, which showed a negligible amount of leaching. This might be responsible for the slight loss of activity of the catalyst after 5 cycles. To test the stability of the catalyst Pd–PyPPh₂–SO₃H@POPs and ensure the heterogeneous nature of the catalytic process, a hot filtration test was conducted. When the insoluble catalyst was removed from the hot reaction mixture by filtration, the reaction stopped and no additional products

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Figure 6. Recyclability of Pd-PyPPh2-SO3H@POPs catalyst in the methoxycarbonylation of phenylacetylene. Reaction conditions: phenylacetylene (0.1 g, 0.98 mmol), methanol (15 mL), substrate/Pd = 550, 50 °C, P(CO) = 4.8 MPa, b: branched prducts, l: linear products.



Figure 7. Hot filtration test for the Pd-PyPPh₂-SO₃H@POPs catalyst in the methoxycarbonylation of phenylacetylene. Reaction conditions: 15 mL methanol, 4.8 MPa CO, 0.02 g catalyst, 1 mmol phenylacetylene, temperature: 80 °C.

were generated (Figure 7). This indicated that the reaction occurred in a true heterogeneous manner.

Conclusions

We have successfully synthesized for the first time, a copolymer (PyPPh₂-SO₃H@POPs) that combines an active solid acid site (-SO₃H) and a bidentate P,N-coordinated ligand (2-PyPPh₂) as an environmentally benign support. The copolymer-supported Pd-PyPPh₂-SO₃H@POPs catalyst exhibited higher activities than the corresponding homogeneous Pd(OAc)₂/2-PyPPh₂/ TsOH catalytic system for alkoxycarbonylation of terminal alkynes under the same conditions, which could be explained by the synergistic effect among different functional centers on the restricted micropore environment of the co-polymerized POPs. Furthermore, the outstanding swelling properties and high enrichment of the reactants of the catalyst also play a significant role in accelerating the reaction rates. Moreover, the heterogeneous Pd-PyPPh2-SO3H@POPs catalyst could be reused at least four times without any apparent loss of catalyt-

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ic efficiency. All these results demonstrated that this novel multifunctional single-site POPs catalyst could be a powerful potential catalyst for a sustainable industrial process for the alkoxycarbonylation of terminal alkynes.

Experimental Section

General

All reagents were of analytical grade and used as purchased without further purification unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium and methanol was distilled from magnesium and iodine under argon. Acetone was refluxed with 4 A zeolite under argon.

Synthesis of PyPPh₂-SO₃H@POPs copolymer

All operations were performed under argon. According to Scheme 2, 1.17 g 3 was added into a solution containing 0.11 g azobisisobutyronitrile (AIBN) and 15 mL THF, followed by the addition of 1.2 mL H₂O, and 0.3 g p-styrene sulfonate. After stirring at room temperature for 3 h, the solution was heated to $120\,^\circ\text{C}$ with stirring. The resulting white solid was dried under reduced pressure at room temperature to give $\mbox{PyPPh}_2\mbox{-}SO_3Na@POPs.$ A 0.5 g sample of PyPPh₂-SO₃Na@POPs was treated with 50 mL 1 M H₂SO₄ and stirred for 24 h at room temperature. PyPPh2-SO3H@POPs was obtained after drying under reduced pressure at 80°C.

Synthesis of PyPPh₂@POPs polymer

PyPPh₂@POPs was synthesized according to our previous report.^[11]

Synthesis of PPh₃-SO₃H@POPs copolymer

All operations were performed under argon. 3-vinyl-functionalized PPh3 was synthesized according to the method reported previously. $^{[6d]}$ 2.28 g of 3-vinyl-functionalized PPh_3 was added into a solution containing 0.19 g AIBN and 26 mL THF, followed by the addition of 2.2 mL H₂O and 0.3 g p-styrene sulfonate. After stirring at room temperature for 3 h, the solution was heated to 120 $^\circ\text{C}$ with stirring. The resulting white solid was dried under reduced pressure at room temperature to give PPh₃-SO₃Na@POPs. A 0.5 g sample of PPh₃-SO₃Na@POPs was treated with 50 mL 1 м H₂SO₄ and stirred for 24 h at room temperature. PPh₃-SO₃H@POPs was obtained after drying under reduced pressure at 80 °C.

Synthesis of PPh₃@POPs polymer

PPh₃@POPs was prepared according to the method reported previously.[6d]

Preparation of Pd-PyPPh₂-SO₃H@POPs catalyst

All operations were performed under argon. The Pd-PyPPh₂-SO₃H@POPs catalyst was prepared by immobilizing Pd(OAc)₂ onto the $PyPPh_2-SO_3H@POPs$ support. The procedure was as follows. 1.2 g PyPPh₂-SO₃H@POPs was added into a solution of 0.0046 g Pd(OAc)₂ in 12 mL THF. After stirring for 24 h at room temperature, the mixture was dried under reduced pressure at 65 °C, and then the $Pd-PyPPh_2-SO_3H@POPs$ catalyst was obtained. In addition, the Pd-PyPPh2-SO3H@POPs catalyst could be prepared by using POL-



2V-P,N-SO₃Na as a support to immobilize Pd(OAc)₂. After drying at 65 °C, the sample was treated with H₂SO₄ (1 m) with stirring for 24 h at room temperature and then dried at 80 °C.

 $PyPPh_2@POPs$, $PPh_3-SO_3H@POPs$, $PPh_3@POPs$ were loaded with $Pd(OAc)_2$ according to the procedure describe above to prepare $Pd-PyPPh_2@POPs$, $Pd-PPh_3-SO_3H@POPs$, and $Pd-PPh_3@POPs$ catalysts, respectively.

Sample characterization

Nitrogen sorption isotherms were measured using an AutoSorb-1 instrument. The samples were outgassed for 24 h at 120 °C before measurements. The thermal stability of PyPPh₂–SO₃H@POPs was detected in a N₂ flow (20 mL min⁻¹) using a Diamond TG/DTA instrument, with a heating rate of 10 °Cmin⁻¹ up to 1000 °C. SEM and SEM-EDS mapping studies were performed on a JSM-7800F scanning electron microscope. The TEM study was performed on a JEM-2100 transmission electron microscope. HAADF STEM was performed on a JEM-ARM200F. Solid-state ³¹P NMR experiments were performed on an Infinity plus 400 spectrometer operating at 161 MHz. The FTIR spectra were measured on a NICOLET iS50 Fourier transform infrared spectrometer in the range 4000–400 cm⁻¹. All spectra were performed on a ESCALAB 250Xi Al_a radiation.

Heterogeneous methoxycarbonylation of phenylacetylene

In a typical run, a 140 mL autoclave made of Hastelloy NS334 material was charged with 0.1 g Pd–PyPPh₂–SO₃H@POPs catalyst, 0.1 g phenylacetylene, 15 mL CH₃OH, and then the reactor was sealed. After purging three times with argon, the reactor was pressurized to 4.8 MPa with CO at room temperature. The contents were heated to 50 °C within 5 min and stirred at 800 rpm for 1 h. Afterward, the reactor was cooled to room temperature with icewater, the liquid samples were centrifuged to isolate the catalyst, and then the solution was analyzed offline by Agilent 7890A gas chromatography with a HP-5 capillary column and FID detector using cumene as an internal standard.

Other polymer supported $Pd-PyPPh_2@POPs$, $Pd-PPh_3@POPs$, $Pd-PPh_3@POPs$ catalysts were used in the reaction according to the same procedure described above for the $Pd-PyPPh_2-SO_3H@POPs$ catalyst.

Homogeneous methoxycarbonylation of phenylacetylene

The procedure of homogeneous methoxycarbonylation of phenylacetylene was the same as that of the heterogeneous methoxycarbonylation of phenylacetylene except that $Pd(OAc)_2$ (0.0019 mmol), ligand (0.28 mmol,) and *p*-toluenesulfonic acid (0.0078 mmol) were used as the homogeneous catalyst.

Heterogeneous methoxycarbonylation of acetylene

In a typical run, a 140 mL autoclave made of Hastelloy NS334 material was charged with 0.1 g Pd-PyPPh₂-SO₃H@POPs catalyst, 20 mL acetone, 5 mL CH₃OH, and then the reactor was sealed. It was purged three times with argon and then pressurized to 0.12 MPa with C₂H₂ and to 4.92 MPa with CO at room temperature. The contents were heated to 50 °C within 5 min and stirred at 800 rpm for 1 h. Afterward, the autoclave was cooled to room temperature with ice—water, the liquid products were centrifuged to

isolate the catalyst, and analyzed offline by Agilent 7890 A gas chromatography with a HP-5 capillary column and FID detector using benzene as an internal standard.

Homogeneous methoxycarbonylation of acetylene

The procedure of homogeneous methoxycarbonylation of acetylene was the same as that of the heterogeneous methoxycarbonylation of acetylene except that $Pd(OAc)_2$ (0.0036 mmol), ligand (0.55 mmol), and *p*-toluenesulfonic acid (0.016 mmol) were used as a homogeneous catalyst.

Hot filtration test

Two parallel reactions were performed under the same conditions. One reaction was performed in the presence of the catalyst for 1 h, and then the solid catalyst was filtered off at the reaction temperature. The resulting filtrate was placed under the same reaction conditions as the original reaction and analyzed by GC. The other reaction was performed in the presence of the catalyst during the entire reaction process.

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Keywords: alkoxycarbonylation • multifunctional catalyst • palladium • porous organic polymers • solid acid

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FULL PAPERS

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Multifunctional Single-Site Catalysts for Alkoxycarbonylation of Terminal Alkynes High activity and easy recyclability

Multifunctional catalyst! A novel multifunctional copolymer [(PyPPh₂– SO₃H@porous organic polymers (POPs), Py = pyridine] is used as a support to prepare a heterogeneous palladium catalyst (Pd–PyPPh₂–SO₃H@POPs). The multifunctional catalyst exhibits higher activity than the corresponding homogeneous catalyst for alkoxycarbonylation of terminal alkynes. The high efficiency is attributed to the synergistic effect of the Pd center, 2-PyPPh₂, ligand and SO₃H group, which was strengthened by the high concentration of the ligand and SO₃H groups on the copolymer.