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The 2V-P,N polymer supported palladium catalyst for methoxycarbonylation of acetylene

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Graphical Abstract



Highlights

2-PyPPh2 ligand based porous organic polymer (POL-2V-P,N) was successfully synthesized

The Pd/POL-2V-P,N catalyst exhibits higher activity than the corresponding homogeneous complex

The reused catalyst exhibited similar activity as that of the fresh catalyst

Abstract

Heterogenization of homogeneous catalyst by immobilizing complex on the surface of polymer supports promotes the design of the catalysts which combine the advantages of heterogeneous and homogeneous catalysts. The porous 2-vinyl-functional diphenyl-2-pyridylphosphine (2V-P,N) polymer (POL-2V-P,N) was successfully synthesized under solvothermal conditions. The POL-2V-P,N polymer was characterized by nitrogen physisorption, thermogravimetry (TG), scanning electron microscope (SEM) and transmission electron microscopy (TEM). The heterogenized homogeneous Pd/POL-2V-P,N catalyst was synthesized by immobilizing $Pd(OAc)_2$ on the POL-2V-P,N, which was used as not only support but also as ligands. The catalyst was investigated by means of ³¹P NMR, X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopic (XPS) and FT-IR and tested for the methoxycarbonylation of acetylene. According to the results of ³¹P NMR, XPS and EXAFS, there existed coordination bonds between palladium and the exposed phosphorous and nitrogen atoms of the porous POL-2V-P,N support. The XPS and FT-IR results showed that Pd⁰ species were present on the Pd/POL-2V-P,N catalyst. The heterogenized Pd/POL-2V-P,N palladium complex catalyst with high surface area and large pore volume displayed excellent activity for the methoxycarbonylation of acetylene as compared with the corresponding homogeneous palladium diphenyl-2-pyridylphosphine complex (Pd-P,N) under the same conditions. The used Pd/POL-2V-P,N catalyst also exhibited excellent activity under the same conditions. In addition, the hot filtration tests indicated that the reaction occurred in a heterogeneous way.

Keywords: 2V-P,N Polymer; palladium; homogeneous reaction; heterogenized catalyst; methoxycarbonylation of acetylene

1. Introduction

Acrylic esters are important bulk chemicals which are widely used in textile, leather finishes, polymer synthesis etc[1-3]. Since Reppe and co-works reported alkoxycarbonylation of terminal alkynes firstly in 1939, carbonylation of acetylene with CO and alcohol, a non-petroleum approach, has been extensively studied as potential route for direct synthesis of acrylic esters[4]. In addition, as a highly versatile process of high atom economy (Scheme 1), acrylic acid and their derivatives could be synthesized in one step[5-7].

So far, the homogeneous palladium catalyst system consisting of 2-pyridyl-diphenylphosphine $(2-PyPPh_2)$, palladium acetate $(Pd(OAc)_2)$ and a sulfonic acid have received great attention due to their high activity in the carbonylation of alkynes and selectivity under mild conditions[8-13]. Drent et al. employed the complex catalysts for methoxycarbonylaiton of propyne giving turn over numbers as high as 40,000 molproduct molcat⁻¹ h⁻¹[14, 15]. Tang and co-workers reported that the catalyst exhibited high activity for hydrocarbonylation of acetylene[16, 17]. It is especially worth mentioning that the organic ligand 2-PyPPh₂ is of critical importance in the reaction that replacement of it by a phenyl group or a heteroaromatic ring without N atoms results in a dramatic decrease in catalytic activity [14, 15, 18]. This is attributed to that 2-PyPPh₂ functions as a bidentate ligand, and this type of P-coordinated N-promoted 2-PyPPh₂ ligand facilities rapid proton transfer in the rate determining protonlysis step. In addition, the N atom of the pyridyl ring can also work as acceptor of the alcoholic proton, thus favouring the cleavage[18].

Such kind of above homogeneous catalytic system play an extremely important role in the field of modern catalysis due to their high activity and selectivity. However, the difficulties of recovery and recycling restrict their more extensive application[19]. A series of approaches have been developed to solve this problem [20], the main one is to heterogenize the metal complex, where silica-based materials and magnetic nanoparticles are the most commonly used materials for such supports[21-25]. However, their chemical nature limits their potential for chemical modification process. Moreover, the catalytic moieties are usually in homogeneously distributed and pendent into the pore volume thus deactivating the catalytic system[26]. Recently, porous organic polymers (POPs) have emerged as a versatile platform for the development of highly efficient catalysts due to their porous nature and high surface area [27-29]. Recently, we developed a porous organic ligand (POL-PPh₃) supported Rh catalysts with high activities and stabilities for hydroformylation of olefins[30, 31]. Sun et al. reported a hierarchical porous ionic organic polymer as a new platform for heterogeneous phase transfer catalysis[32]. Therefore, the POPs

supported catalysts have great potential to be developed using in industrial fields. Doherty *et al.* immobilized 2-PyPPh₂ to an insoluble solid support, but the process they employed for copolymerization is difficult to operate[33]. Inspired by the POPs material, we have successfully synthesized a POL-2V-P,N porous organic polymer under solvothermal conditions and prepared the insoluble POPs supported palladium complex catalyst. The synthesized heterogenized homogeneous catalyst showed high activity for the methoxycarbonylation of acetylene with CO and CH₃OH to produce methyl acrylate.

2. Experimental

2.1. Materials

All materials (A.R. grade) were obtained from commercial sources and used without further purification unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium and pyridine (py) from calcium hydride under argon. Acetone was refluxed with 4A zeolite and methanol with magnesium and iodine under argon.

2.2. Preparation of POL-2V-P,N

All operations were carried out under anaerobic anhydrous conditions. The synthesis of POL-2V-P,N is shown in Scheme 2. $[2-C_5H_4NZnCl \cdot C_5H_5N]_2$ was prepared according to the method of Budzelaar et al.[34]. The prepared $[2-C_5H_4NZnCl \cdot C_5H_5N]_2$ was dissolved

in THF/pyridine mixture (3:1, 240 ml), then the solution was cooled to -10° C and then added dropwise to a THF/pyridine (1:1, 120 ml) solution of PCl₃ (0.12 mol). Finally, the reaction mixture was warmed up to room temperature, stirred for 25 h and filtered to give 2-pridyldichlorophosphine.

The *p*-styrylmagnesium bromine was synthesized as described by Leebrick et al[35]. 2-pridyldichlorophosphine was added to the solution of the *p*-styrylmagnesium bromine at 0 $^{\circ}$ C and stirred for 2 h[36]. Then the reaction mixture was quenched by adding 200 ml of H₂O, extracted by 500 ml of ethyl acetate and the products were purified by column chromatography (petroleum ether, silica gel). Then 2-vinyl-functional diphenyl-2-pyridylphosphine was obtained.

The polymerization reaction of 2-vinyl-functionalized diphenyl-2-pyridylphosphine (1.0 g, 3.18 mmol) in THF solution (10ml) was induced with AIBN (1 mol%, 0.05 g, 0.03 mmol) and the solution was heated to 100°C and held for 24 h. The resulting white solid was dried under reduced pressure at 65 °C to synthesize the polymer of 2-vinyl-functional diphenyl-2-pyridylphosphine (hereafter referred to as POL-2V-P,N).

2.3. Preparation of Pd/POL-2V-P,N catalyst

The heterogenized Pd/POL-2V-P,N catalyst was prepared by stirring

a solution of $Pd(OAc)_2$ (0.0053 g) in 15 ml of THF containing 1.0 g POL-2V-P,N polymer solid at room temperature for 24 h. The solvent was removed under vacuum, and the resulting solid washed with CH₃OH at room temperature with a Soxhlet apparatus and dried under reduced pressure to obtain the Pd/POL-2V-P,N catalyst.

2.4. Carbonylation reactions

The carbonylation reactions were carried out in a 140 ml autoclave which was made of Hastelloy NS334 material following by a procedure similar to that described by Tang[16]. In a typical run, Pd/POL-2V-P,N catalyst (0.0046 mmol), and *p*-toluenesulfonic acid monohydrate (0.0115 mmol), were dissolved in a mixture of 20 ml acetone and 5 ml CH₃OH and transferred to the autoclave. After replaced three times with argon, the reactor was pressured to 0.12 MPa with C₂H₂ and then to 4.92 MPa with CO at room temperature. The autoclave was heated to 50 °C within 5 min and stirred at 800 rpm for 1h. Afterwards the reactor was cooled to room temperature, and the gas samples and liquid samples were analyzed online by Agilent 7890A gas chromatography with a TDX-01 packed column and off-line with a HP-5 capillary column, respectively.

2.5. Hot filtration test

Two parallel reactions were carried out under the same reaction conditions (see 2.4), and one of the reaction mixtures was filtered off at the reaction temperature after 1 h (the content of methacrylate is 0.28 g). The filtrate was then transferred into the autoclave and the reaction was restarted under the same conditions as the original reaction. The result catalyzed by the filtrate was compared with that of the parallel reaction.

2.6. Characterization

The BET surface area, pore volume, and BJH pore distribution were measured by adsorption-desorption of N2 at 77 K using an AutoSorb-1 instrument. 53.8 mg sample was degassed under vacuum at 120 $^{\circ}$ C for 21 h prior to measurement. The thermal stability of POL-2V-P,N was detected in N₂ flow (20 ml min⁻¹) using a STA 449 F3 TG-DSC instrument, with a heating rate of 10°C.min⁻¹ up to 1000 °C. SEM study was carried out on a JSM-7800F scanning electron microscope. TEM measurement was performed on a JEM-2100 transmission electron microscopy. Pd leaching was determined by ICP-OES on a Perkin-Elmer optima 7300DV instrument. Solid-state ³¹P NMR experiments were carried out on an Infinity plus 400 spectrometer operating at 161 MHZ. The FT-IR spectra were measured on a NICOLET iS50 Fourier transform infrared spectrometer in the range of 4000-400 cm⁻¹. All spectra were recorded with 32 scans with a resolution of 4 cm⁻¹. XPS spectra were performed on an ESCALAB 250Xi AIa radiation. Pd K-edge X-ray absorption fine structure (EXAFS) spectra of the prepared catalysts were obtained at the BL14W1 beamline of SSRF, SINAP (Shanghai, China) with the use of a Si(311) crystal monochromator. The storage ring was operated at 3.5 GeV with injection currents of 200 mA. Pd foil was used as reference samples, and all the X-ray absorption spectra were measured in the transmission mode. All spectra of the as-synthesized catalysts were conducted in the fluorescence mode. The raw data were energy-calibrated (Pd K-edge energy of Pd foil) at 24,350 eV, first inflection point, background-corrected, and normalized using the IFEFFIT software. Fourier transformation of the EXAFS data was applied to the k3-weighted functions. For the curve-fitting analysis, Pd-C, Pd-P, Pd-N path parameters were obtained from the ab initio multiple scattering codes FFEF6.

3. Results and discussion

3.1. Characterization

3.1.1. Characterization of POL-2V-P,N

Fig.1. shows the TG curve of the POL-2V-P,N sample, N₂ sorption isotherms, SEM and TEM images. TG analysis was utilized to examine the thermal stability of the POL-2V-P,N. The TG curve showed a minute weight loss at about 200 $^{\circ}$ C owing to the removal of physically absorbed solvent in Fig. 1A). The biggest weight loss was observed in the range of 400-500 $^{\circ}$ C due to the decomposition of the polymer. It indicated that the POL-2V-P,N was a highly thermally stable material. As shown in Fig. 1B), the N₂ sorption isotherms exhibited a hysteresis loop at a relative pressure(P/P₀) of 0.45-0.95, suggesting that the polymer is filled with mesopore. Accordingly, the BET surface area, pore volume, and BJH average pore size of POL-2V-P,N were 475 m².g⁻¹, 0.64 cm³.g⁻¹, and about 2.7 nm, respectively. It implied that the polymer possessed high surface area and large pore volume. The morphologies of the polymer were further characterized by SEM and TEM (Fig. 1 C) and D)). Both of the SEM and TEM images also showed the presence of mesopore, which was consistent with the result of N₂ sorption isotherm (Fig. 1B)).

3.1.2. Characterization of Pd/POL-2V-P,N catalyst

Solid-state ³¹P NMR for the POL-2V-P,N support and the heterogenized Pd/POL-2V-P,N catalyst were carried out to detect the interaction between Pd and the polymer, and the result was shown in Fig. 2. A single peak at -4.53 ppm belonged to uncoordinated P atoms was detected for the polymer support. For the Pd/POL-2V-P,N, except for -4.53 ppm peak, a new peak at 19.77 ppm appeared, which was attributed to P atom coordinated with palladium (Fig. 2 b). It implied that there was truly an interaction between palladium and the exposed phosphorous atoms on the surface of porous POL-2V-P,N support, and the POL-2V-P,N was used as not only support but also ligands simultaneously.

To determine the chemical environment of Pd, the spent

Pd/POL-2V-P,N catalyst (0.247 wt%) was characterized by EXAFS (Fig. 3.). The curve-fitting analysis for the EXAFS Fourier-transformed spectra at Pd-K edge for the catalyst revealed the existence of a Pd-P bond at 2.35 Å, a Pd-N bond at 2.15 Å and Pd-C bonds at 2.03 Å (Table 2). All the observations above revealed clearly that coordination bonds were formed between Pd and the exposed P and N atoms of POL-2V-P,N support[37]. It also demonstrated a similar bonding characteristics to that of the corresponding homogeneous catalysts [38, 39] in the coordination sphere around Pd in the catalyst. This result was consistent with those obtained from ³¹P NMR.

X-ray photoelectron spectroscopic (XPS) analysis was performed for the fresh and spent catalysts (Fig. 4.). Two peaks at 338.0 and 343.2 eV for fresh catalyst were assigned to $3d_{5/2}$ and $3d_{3/2}$ for Pd²⁺ species, while the other two peaks at 336.2 and 341.3 eV were assigned to $3d_{5/2}$ and $3d_{3/2}$ for Pd⁰ species, respectively[40]. The corresponding binding energies of the spent catalysts were lower than that of the fresh catalyst, probably due to the electron donating effect of CO on the Pd species[41]. The relative Pd⁰ percentage was 7.6 % for the fresh catalyst, which was calculated from the area of the $3d_{5/2}$ peak. However, the Pd⁰ percentage enhanced to 22.0 % for the spent catalyst. It implied that Pd²⁺ species were reduced to Pd⁰ species during the catalytic reactions. This result was analogous with those reported in literature [18, 40]. It is well known that Pd²⁺ species acted as catalytic active sites for methoxycarbonylation of acetylene [16, 17]. Meanwhile, it has also been shown that Pd⁰ species are involved in catalytic cycle[18].

XPS spectra of P of the fresh catalyst were shown in Fig. 5. Two peaks at about 131.4 and 133.8 eV were ascribed to P atoms in C-P and C-P-Pd, respectively, indicating that P coordinated with Pd species[42]. The result was coincident with those obtained from ³¹P NMR and EXAFS.

To glean further information about the carbonylation reaction process, the Pd/POL-2V-P,N catalysts were characterized with FT-IR by CO probe molecule (Fig. 6.). According to the literature[43, 44], ligand has a big influence on the palladium carbonyls. The bands at 2002 cm⁻¹ and 1946 cm⁻¹ were assignable to Pd⁰(CO)_n/POL-2V-P,N species, which were close to that reported for the (d¹bpe)Pd⁰(CO)₂[44]. Importantly, Willner's report has revealed that substitution of Pd⁰ with Pd²⁺ caused a lower electron density, thus decreasing the back-donation to the carbonyl ligand and leading a blue shift in the carbonyl stretching frequency[45]. Therefore, the bands at 2071 and 1987cm⁻¹ could probably ascribed to Pd²⁺(CO)_n/POL-2V-P,N species. This was coincident with the results of XPS which indicated both Pd⁰ and Pd²⁺ species were present during the catalytic cycle.

3.2. Catalytic tests

3.2.1. Comparison between homogeneous and heterogenized catalyst

For a comparison, both of the homogeneous Pd-N,P catalyst and the heterogenized Pd/POL-2V-P,N catalyst were employed in the methoxycarbonylation of acetylene under the same conditions, as shown in Table 1. The Pd-N,P complex $(4.6 \times 10^{-3} \text{ mmol Pd}(\text{OAc})_2, 0.63 \text{ mmol})$ 2-pyPPh₂) gave 1238.8 h⁻¹ TOF (Entry 1). The result was lower than Tang's report [17] which pointed out that higher activity was obtained at lower pressure. The initial partial pressure was 1.0 MPa in Tang's study, while it was 4.8 MPa in this experiment. Thus, the lower TOF (1238.8 h^{-1}) was ascribed to the higher initial partial CO pressure. Higher activity (TOF 2983.3 h^{-1}) was achieved over Pd/POL-2V-P,N catalyst with 4.6× 10^{-3} mmol Pd(OAc)₂ and 0.63 mmol POL-2V-P,N (Entry 2).

It was found that the molar ratio of P ligand to Pd has a significant role on catalytic activity [16, 17]. The effect of different ratio of P/Pd of the two types of catalyst was investigated in our study. When the content of Pd(OAc)₂ increased, the molar ratio of P/Pd decreased. It led to drop of the catalytic activity of the heterogenized Pd/POL-2V-P,N catalyst as well as the homogeneous Pd/N,P catalyst. The similar observation has been reported in the Pd-catalyzed carbonylation of aryl arenesulfonates[46].

It was obvious that the heterogenized Pd/POL-2V-P,N catalysts exhibited excellent activity with the molar ratio of P/Pd ranging from 90 to 137, which were higher than that of the corresponding Pd/N,P

homogeneous catalyst under the same conditions. According to the results of ³¹P NMR, XPS, EXAFS and FT-IR, the Pd species of the Pd/POL-2V-P,N catalyst was coordinated with the exposed phosphorous and nitrogen atoms of the POL-2V-P,N, and its bonding characteristics was similar to that of the corresponding homogeneous catalysts. It means that both of the catalytic active species of the heterogenized Pd/POL-2V-P,N catalyst and Pd/N,P homogeneous catalyst are Pd/N,P complex. However, the former was located on the surface of the POL-2V-P,N support, but the latter was soluble species in the reaction solutions. Thus. excellent catalytic performance of the the Pd/POL-2V-P,N catalyst might originate from the high surface area (475 $m^2 g^{-1}$) and large pore volume (0.64 cm³ g⁻¹) of the POL-2V-P,N polymer, which allowed the substrates more accessible to the active metal sites.

3.2.2 Effect of initial partial pressure of carbon monoxide

Fig. 7. shows the effect of initial partial pressure of CO to the catalytic activity of the heterogenized Pd/POL-2V-P,N catalyst. The reaction rate increased rapidly with the increasing of CO partial pressure from 1.11 MPa to 4.96 MPa, then the increasing of TOF value slowed down when CO partial pressure was further raised to 5.83 MPa. However, the TOF value decreased when the CO partial pressure is above 5.83 MPa. This result was distinguished from the result of the homogeneous Pd-P,N catalyst with high activity at low initial partial pressure of CO (1.0 MPa)

reported by Tang[17]. It could be speculated that high pressure of CO favored for the CO coordination with Pd active species located in the pore of the POL-2V-P,N support, thus improving the reaction rate. Meanwhile, too high CO pressure suppressed coordination of other reactant such as C_2H_2 and CH₃OH with the catalytic active species, and thus inhibited the reaction process.

3.2.3 Effect of *p*-toluenesulfonic acid concentration

Fig. 8. shows the effect of *p*-toluenesulfonic acid concentration (H^+/Pd) to the behavior of methoxycarbonylation of acetylene reaction over Pd/POL-2V-P,N catalyst. The catalytic activity enhanced rapidly when the *p*-toluenesulfonic acid concentration increased to an H⁺/Pd ratio of 23. Nevertheless, keep increasing the ration of H⁺/Pd from 23 to 51, there was only a slight improving of catalytic activity. And the catalytic activity decreased when the H⁺/Pd ratio was higher than 51, which indicated that the appropriate amount of *p*-toluenesulfonic acid facilitated methoxycarbonylation of acetylene.

3.2.4. Effect of temperature to catalytic performance

The effect of temperature to the catalytic performance is shown in Fig. 9. The catalytic activity increased rapidly when the reaction temperature was raised, and then it reached a maximum TOF value at 63° C. However, the catalytic activity decreased with further increase of

temperature. It is probably due to that the interaction between Pd species and POL-2V-P,N support weakened at higher temperature, and even led to decomposition of catalyst with the further increase of temperature[17].

3.3. Catalyst reusability

The reusability of the Pd/POL-2V-P,N catalyst for the methoxycarbonylation of acetylene was investigated (Fig. 10.). After completion of the reaction (1h), the catalyst was separated by centrifugation, which kept the catalyst away from the air[47]. After recycling three times, a conversion of 77.9 % was obtained with the recycled catalyst, which is a little higher than the first cycle of 72.3 %. This might be attributed to the formation of the Pd-H active species in the reaction. Pd leaching of the heterogenized Pd/POL-2V-P,N catalyst in reaction solution was detected by ICP-OES. It was found that after the first run the amount of Pd leaching was about 0.16%, and after the second and third runs it was about 0.097% and 0.12% of the initial Pd, respectively. This indicated that the Pd/POL-2V-P,N catalyst could be reused in the methoxycarbonylation of acetylene reaction. The stability of the catalyst might be attributed to the stable structure of palladium coordination with the exposed phosphorous and nitrogen atoms of the porous POL-2V-P,N support.

3.4 Hot filtration test

The result of hot filtration test for the Pd/POL-2V-P,N catalyst in methoxycarbonylation of acetylene is shown in Fig. 11. The results revealed that no additional methacrylate was generated after the solid catalyst was filtered off, which confirmed that the catalytic active species came from the surface of heterogeneous catalysts rather than the leaching Pd species in solution, suggested that the reaction occurred in a truly heterogeneous manner[33, 37].

3.5 Proposed mechanism

³¹P NMR and EXAFS experiments results revealed that there was a strong interaction between Pd and POL-2V-P,N support. Usually, two mechanisms, namely the "metal-carbalkoxy" and "metal-hydride", were proposed [13, 15, 17, 18, 48]. The reaction mechanism of the Pd/POL-2V-P,N catalysts for methoxycarbonylation of acetylene was proposed, as shown in Scheme 3, which was similar to that of the homogeneous Pd(OAc)₂/2-PyPPh₂ complex[13, 18]. The Pd-H active species (I) were formed when Pd/POL-2V-P,N was treated with Brönsted acid. Then the alkyne inserted into a Pd-H bond to give a (σ -vinyl)-palladium complex (III). Following that, CO adsorbed on palladium and inserted into the Pd-C bond to afford an acylpalladium complex (V). Subsequently, alcoholysis of the acylpalladium complex yielded the expected ester, simultaneously regenerating the Pd-H active species. In the above catalytic process, Pd active sites were located in the

POL-2V-P,N support with high surface area and large pore volume, which might facilitate substrates like C_2H_2 , CO and CH_3OH to interact with Pd active sites, thus leading to higher catalytic activity for methoxycarbonylation of acetylene.

4. Conclusions

In summary, POL-2V-P,N was successfully synthesized by polymerizing 2-vinyl-functional diphenyl-2-pyridylphosphine. And the heterogenized homogeneous Pd/POL-2V-P,N catalyst was prepared by immobilizing Pd(OAc)₂ on the POL-2V-P,N support. The results of ${}^{31}P$ NMR, XPS, EXAFS and FT-IR of the Pd/POL-2V-P,N catalyst indicated that Pd was coordinated with the exposed P and N atoms of the 2V-P,N polymer. The heterogenized Pd/POL-2V-P,N catalyst showed higher activity for methoxycarbonylation of acetylene than that of the corresponding Pd-P,N complex under the same conditions. It might originate from the high surface area and large pore volume of the 2V-P,N-POL polymer, which allowed the substrates more accessible to the Pd active sites. The recovered Pd/2V-P,N-POL catalyst also displayed excellent activity under the same conditions. Our approach provides a the preparation of highly method for efficient heterogenized homogeneous catalytic system with characteristic of easy separation and recycling.

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Figure Captions



Fig. 1. A) TG curves, B) N₂ sorption isothermes, C) SEM image, and D) TEM image of POL-2V-P,N



Fig. 2. Solid-state ³¹P NMR spectra. (a) POL-2V-P,N (b)Pd/ POL-2V-P,N catalyst. Spinning side bands are denoted by asterisks (*).



Fig. 3. EXAFS spectra of the spent Pd/POL-2V-P,N catalyst.



Fig. 4. XPS spectra of Pd in (a) the fresh Pd/ POL-2V-P,N catalyst, (b) the spent catalyst



Fig. 5. XPS spectra of P of the fresh Pd/ POL-2V-P,N catalyst



Fig. 6. FT-IR spectra of Pd/POL-2V-P,N catalyst: (a) the fresh catalyst (b) the spent catalyst



Fig. 7. Effect of CO initial partial pressure on catalytic activity. Conditions: $Pd(OAc)_2 4.6 \times 10^{-3}$ mmol, P-TSA 0.4 mmol, acetone 20 ml, CH₃OH 5 ml, initial partial pressure: $P(C_2H_2)=0.12$ MPa, reaction time: 60 min, reaction temperature: 50°C.



Fig. 8. Effect of p-toluenesulfonic acid concentration on catalytic activity Conditions: $Pd(OAc)_2$ 4.6×10⁻³ mmol, acetone 20 ml, CH₃OH 5 ml, initial partial pressure: $P(C_2H_2)=0.14$ MPa, P(CO)=4.8 MPa, reaction time: 60 min, reaction temperature: 50 °C.



Fig. 9. Effect of reaction temperature on catalytic activity. Conditions: Pd(OAc)₂ 4.6×10^{-3} mmol, p-toluenesulfonic acid: 0.115mmol, acetone 20 ml, CH₃OH 5 ml, initial partial pressure: P(C₂H₂)=0.12 MPa, P(CO)=4.8 MPa, reaction time: 60 min.



Fig. 10. Reusability of the Pd/POL-2V-P,N catalyst in methoxycarbonylation of acetylene. Conditions: $Pd(OAc)_2 4.6 \times 10^{-3}$ mmol, acetone 20 ml, CH₃OH 5 ml, initial partial pressure: $P(C_2H_2)=0.12$ MPa, P(CO)=4.8 MPa, reaction time: 60 min, reaction temperature: 63 °C.



Fig. 11. Hot filtration test for the Pd/POL-2V-P,N catalyst in methoxycarbonylation of acetylene. Conditions: $Pd(OAc)_2 \ 8.2 \times 10^{-4}$ mmol, acetone 20 ml, CH₃OH 5 ml, initial partial pressure: $P(C_2H_2)=0.1$ MPa, P(CO)=4.8 MPa, reaction temperature: 57 °C. Hot filtration was applied at 1h.

$HC \equiv CH + CO + H_2O \xrightarrow{Cat.} H_2C = CH - COOH$ $HC \equiv CH + CO + ROH \xrightarrow{Cat.} H_2C = CH - COOR$

Scheme 1. Catalyzed carbonylation of acetylene with carbon monoxide to

acrylates of acrylic acid



Scheme 2 Synthesis of POL-2V-P,N. Reagents and conditions: (i) BuLi, ZnCl₂, Py, THF, -40 $^{\circ}$ C; (ii) PCl₃, THF, Py, -10 $^{\circ}$ C; (iii) StyryMgBr, THF, 0 $^{\circ}$ C; (iv) AIBN, THF.



Scheme 3. Reaction mechanism for methoxycarbonylation of acetylene over the Pd/POL-2V-P,N catalyst.

Tables

| Entry | Catalysts | N(Pd) (\times | P/Pd | Selectivity | TOF (h^{-1}) |
|-------|---------------|------------------------|------------|-------------|----------------|
| | | 10 ⁻³ mmol) | more ratio | to MA (%) | |
| | | | | | |
| 1 | Pd-N,P | 4.6 | 137 | 89.4 | 1238.8 |
| 2 | Pd/POL-2V-P,N | 4.6 | 137 | 92.6 | 2983.3 |
| 3 | Pd-N,P | 5.5 | 115 | 97.7 | 1122.6 |
| 4 | Pd/POL-2V-P,N | 5.5 | 115 | 90.4 | 1701.8 |
| 5 | Pd-N,P | 7.0 | 90 | 93.5 | 799.0 |
| 6 | Pd/POL-2V-P,N | 7.0 | 90 | 94.9 | 1573.3 |

 Table 1. Comparison of Homogeneous and heterogenized catalyst.

Conditions: 0.63 mmol ligand, p-toluenesulfonic acid 0.115 mmol, acetone 20 ml, CH₃OH 5 ml, initial partial pressure: $P(C_2H_2)=0.14$ MPa, P(CO)=4.94 MPa, reaction temperature: 63°C, reaction time: 60 min. MA: methyl acrylate.

Table 2. Best-fit values of EXAFS structural parameters for thePd/POL-2V-P,N catalyst

| sample | Path | N | R(Å) | $\sigma 2(\text{\AA}^2)$ | $\Delta E_0(eV)$ | R-factor |
|---------------|-------|---|--------------|--------------------------|------------------|----------|
| | Pd -P | 1 | 2.35(±0.020) | 0.001 | 15.8 (±2.8) | |
| Pd/POL-2V-P,N | Pd -N | 1 | 2.15(±0.027) | 0.006(±0.003) | 15.2(±0.1) | 0.0078 |
| | Pd-C | 2 | 2.03(±0.023) | 0.002(±0.004) | 0 | |