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Preparation and application of coconut shell activated carbon immobilized palladium complexes†

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Coconut shell activated carbon (CSAC) granules were used as carriers to immobilize palladium complexes. Boehm titration showed that the hydroxyl content of the carbon surface reached 0.376 mmol g^{-1} after 20% HNO₃ treatment. Ethylenediamine, benzyl malononitrile and propyl malononitrile were successfully grafted onto the oxidized CSAC. The bidentate nitrogen ligands complexed Pd²⁺ samples were characterized by FT-IR, XPS, ICP and N₂ adsorption–desorption. In oxidative carbonylation of phenol, three bidentate ligand grafted catalysts were evaluated in a high pressure reaction vessel. The results showed that the ethylenediamine grafted catalyst had a phenol conversion of 12.06% and a diphenyl carbonate (DPC) selectivity of 91.03%. In comparison, the benzyl malononitrile grafted catalyst displayed a phenol conversion of 6.22% and a DPC selectivity of 81.02%. Additionally, the ethylenediamine and the benzyl malononitrile grafted catalysts were also investigated in a continuous packed-bed reactor. The results showed that the phenol conversion and the DPC selectivity were comparative to those obtained in a high pressure reaction vessel.

1. Introduction

It is very attractive to heterogenize homogeneous catalysts in order to facilitate catalyst recycling and to avoid corrosive reaction mixtures.^{1–7} Homogeneous palladium catalysts have been applied for oxidative carbonylation of phenol with CO and O_2 .^{8–11} The oxidative carbonylation of phenol has been considered as a promising candidate for non-phosgene diphenyl carbonate (DPC) synthesis, in that palladium complex catalysts have displayed high catalytic efficiency attributed to high reactivity of CO and phenol at the palladium center, and due to the *cis*-configuration between CO and phenoxide on the palladium center and adequate steric repulsion caused from their ligands.^{12,13}

To facilitate recovery of the noble palladium catalyst in homogeneous reactions, polymers,^{14,15} SiO₂,^{16–18} zeolites,¹⁹ mixed oxides,^{20–23} double-layered hydroxides and mesoporous silica have been investigated to support palladium complexes.^{24–28} However, polymers cannot bear high temperatures. Some supports are nonporous and have a low specific surface area. Moreover, the active components located on the outside surface of the supports easily leach out, leading to deactivation of heterogeneous catalysts.²⁹ Compared to nonporous materials, porous materials have been proved to have favorable features for immobilization owing to their large surface area, high pore volume and opened structures. An SBA-15 tethered titanium complex was reported by Burkett et al.24 Cu2+ complex grafted MCM-41 was prepared by Sharma et al.25 Jones et al.²⁶ prepared zirconium complexes on SBA-15. Asefa et al.27 synthesized Zn complex-functionalized SBA-15 catalysts. These mesoporous silica supported catalysts are powdery substances. Therefore, their catalytic performances are limited to a slurry reactor. The catalyst must be separated after each batch, leading to partial loss of catalysts and increasing the production cost. Meanwhile, it is inconvenient to recycle an ultrafine catalyst. A packed-bed reactor has many attractive features, such as no need to separate the catalyst from the product, the ease of scale-up from a single tube to a pilot plant, and continuous operation for large scale synthesis of chemicals under constant operating conditions. To process mesoporous silica immobilized metal complexes into macrosized granules for application in a packed-bed reactor, the catalyst powder is normally mixed with an adhesive binder and subjected to annealing at high temperature. However, organic ligands would burn during the annealing procedure.



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Therefore, binderless granular carriers are more suitable for immobilizing organic ligand containing catalysts in industrial applications.

Although carbon supported metals or metal oxides have been prepared using deposition–precipitation or impregnation techniques,^{30–33} carbon has not yet been exploited to covalently immobilize metal complexes. Coconut shell activated carbon (CSAC) is a cheap, readily available and non-toxic material. It has high mechanical strength, good abrasion resistance and an inherent granular structure, which is important for a continuous packed-bed process.³⁴ In this paper, the CSAC granules were controllably oxidized to generate phenolic groups, followed by grafting bidentate nitrogen ligands to immobilize palladium ions as shown in Scheme 1. To explore the application of the CSAC granule immobilized Pd²⁺ catalysts in oxidative carbonylation of phenol, their catalytic performances were evaluated in a packed-bed reactor as well as in a high pressure reaction vessel.

2. Experimental

2.1 Materials

CSAC granules (20–40 mesh) were obtained from Jinweida Activated Carbon Co. (Beijing, China). *N*-[3-trimethoxysilylpropyl]ethylenediamine (AEAPTMS), 4-(chloromethyl)phenyltrichlorosiliane (CMPTCS) and (3-chloropropyl)trimethoxysilane (CPTMS) were purchased from Sigma-Aldrich Chemical Co. HNO₃, HCl, NaOH, CH₃CH₂ONa, CH₂(CN)₂, PdCl₂, CuCl₂, NaI and benzonitrile were purchased from Jinchun Chemical Reagent Co. (Shanghai, China). Anhydrous ethanol, toluene, dichloromethane and dimethylfuran (DMF) were obtained from Guanghua Chemical Reagent Co. (Guangzhou, China).

2.2 Oxidation of CSAC

Raw CSAC granules were subjected to oxidation prior to grafting bidentate nitrogen ligands. The CSAC granules were placed into a Soxhlet extractor and washed with deionized water at 100 °C for 12 h, and then dried at 105 °C for 24 hours. 13.0 g of the washed raw CSAC was oxidized with 300 mL of 20 wt% HNO₃ in a backflow device at 85 °C for 4 h. The oxidized CSAC were thoroughly washed with distilled water and then dried at 105 °C for 24 h.

2.3 Grafting of ethylenediamine ligand

Three types of bidentate nitrogen ligand grafted CSACs were prepared as presented in Scheme 1. 10.0 g of the oxidized CSAC granules and 0.67 g of $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$ (AEAPTMS) were mixed with 300 mL toluene and refluxed for 2 h under nitrogen atmosphere first, then 0.1 mL of DI water was added and refluxed for 4 h. The solid was separated by suction filtration, and then washed successively with ethanol and dichloromethane. The physically adsorped AEAPTMS was extracted with ethanol in a Soxhlet extractor for 24 h. The resulting samples were dried at 70 °C.

2.4 Grafting of benzyl malononitrile ligand

0.78 g of 4-(chloromethyl)phenyltrichlorosiliane (CMPTCS) and 0.41 g of anhydrous ethanol were dissolved in 300 mL toluene. The mixture was stirred for 10 h at 80 °C under nitrogen atmosphere, and then 10.0 g of the oxidized CSAC, 0.1 mL of DI water and 0.5 mL of anhydrous pyridine were added. The product was suction-filtered after stirring for 9 h at 100 °C. The physically adsorped CMPTCS was extracted successively with toluene and dichloromethane for 24 h. After



Scheme 1 Preparation processes of three bidentate nitrogen ligand complexed Pd²⁺ catalysts.

vacuum drying at 70 °C for 8 h, 8.0 g of the CMPTCS silanized CSAC was stirred with 300 mL of DMF containing 0.18 g NaCH(CN)₂ and 0.10 g NaI under nitrogen atmosphere, and refluxed for 48 h at 90 °C. The resulting material was treated by Soxhlet extraction with ethanol for 24 h, and followed by vacuum drying at 70 °C for 8 h.

2.5 Grafting of propyl malononitrile ligand

10.0 g of the oxidized CSAC, 0.60 g of $(MeO)_3Si(CH_2)_3Cl$ (CPTMS) and 300 mL toluene were mixed and stirred for 2 h under nitrogen atmosphere, then 0.1 mL of DI water was added and refluxed for 4 h at 80 °C. The solid was separated by suction filtration, and washed successively with ethanol and dichloromethane. The physically adsorped CPTMS was extracted with ethanol in a Soxhlet extractor for 24 h. Afterwards, malononitrile ligands were grafted in the same way as described above.

2.6 Complexation of metal ions

Pd(PhCN)₂Cl₂ was prepared according to a literature procedure.³⁵ 2.0 g of PdCl₂ was dissolved in 20 mL benzonitrile and refluxed for 4 h at 100 °C. Yellow needle-like Pd(PhCN)₂Cl₂ crystals precipitated after cooling down to room temperature. The solid was separated by suction filtration, and vacuum drying at 60 °C for 24 h. 5.0 g of bidentate nitrogen ligand grafted ACs were added in 50 mL CH₂Cl₂ containing 0.77 g of Pd(PhCN)₂Cl₂ and 0.27 g of CuCl₂. The mixture was stirred at room temperature for 48 h, followed by filtration and washing with CH₂Cl₂. The product was Soxhlet-extracted with CH₂Cl₂ for 24 h to remove physically adsorbed Pd(PhCN)₂Cl₂ and CuCl₂, and vacuum dried at room temperature to achieve the catalysts.

2.7 Characterization

The surface oxygen-containing functional groups on the raw and the oxidized CSAC were quantitatively and qualitatively determined by Boehm titration.³⁶ It depends on the amount and the strength of the alkali reacted with the oxygencontaining groups. In the experiment, 0.2 g of the CSAC was separately added into four 100 ml conical flasks, containing 20 ml of 0.02 M HCl, NaOH, NaHCO₃, and Na₂CO₃ solutions, respectively. The flasks were gently shaken for 48 h on a Wrist Shaker, and then filtered. The filtrate was titrated with 0.02 M HCl aqueous solution.

BET surface areas and pore sizes of the CSAC based samples were measured from N_2 absorption-desorption using a TriStar 3000. FT-IR spectra were recorded from KBr pellets using a Bruker Tensor 27 spectrometer. XPS analyses were conducted on an AXIS ULTRA^{DLD} spectrometer (Kratos) with achromatic Al(MONO) K α X-radiation (1486.6 eV) as the X-ray source. The C 1s binding energy of the graphitic peak was fixed at 284.6 eV for calibration. The complexed palladium and copper in the CSAC was quantified by X Series(X7) ICP with Elga-PURELAB ultra analytic water purification system. The ²⁹Si MAS NMR spectra were recorded on a Varian VNMR400 instrument equipped with a 4 mm probe. The ²⁹Si MAS NMR experiments employed a spinning speed of $v_{\rm R}$ = 3 kHz, a relaxation delay of 15 s, and typically 5000 scans. The ²⁹Si chemical shifts was referenced to tetramethylsilane (TMS). The spectra were modified by the MestReNova software.

2.8 Oxidative carbonylation of phenol

Catalytic activities of three Pd^{2+} complexed catalysts were investigated in a high pressure reaction vessel. A schematic diagram of the batch catalytic reaction is shown in Fig. S1.† The oxidative carbonylation of phenol is shown in Scheme 2. It was performed by mixing the catalyst (1.0 g), 3 Å molecular sieves (2.5 g), phenol (0.32 mol) and solvent (30 mL). The molar ratio of $Pd^{2+}/TBAB$ (tetrabutylammonium bromide)/BQ (benzoquinone) is 1/10/20, and the pressure ratio of CO to O₂ is 10. The stirring speed is 600 rpm, and the reaction time is 5 h. Phenol and diphenyl carbonate were identified and quantified by a capillary gas chromatograph with an FID detector (GC4000A Gas Chromatograph, SE-54 Column, 30 m, 0.25 mm).

The ethylenediamine and the benzyl malononitrile complexed Pd^{2+} catalysts were also evaluated in a fixed-bed reactor. A schematic diagram of the reaction is shown in Fig. S2.† The packed column has an inner diameter of 5 cm and a length of 60 cm. 30 g of catalyst and 5 g of 4 Å molecular sieves were mixed and placed at the middle of the column with both ends filled with quartz granules. The reaction solution has a weight composition of 15% phenol, 1% TBAB, 1% BQ and 83% CH₂Cl₂. For all experiments, the reaction temperature was maintained at 100 °C and the reaction pressure was maintained at 2.5 MPa (CO/O₂ = 19/1). The liquid flow rate was 5 mL min⁻¹ and the gas flow rate was 200 mL min⁻¹.

3. Results and discussion

3.1 Oxidation of the CSAC

The Boehm's titration results suggested that the total concentration of surface oxygen-containing groups in the raw CSAC was 0.234 mmol g^{-1} . Among them, the concentration of carboxylic and lactonic groups was 0.111 mmol g^{-1} , and the concentration of phenolic hydroxyl was 0.118 mmol g^{-1} . However, the concentration of carboxylic and lactonic groups was increased to 0.400 mmol g^{-1} after oxidization by 20% HNO₃. Meanwhile, the concentration of phenolic hydroxyl groups was increased to 0.376 mmol g^{-1} . Fig. 1 displays the C 1s binding energies of the raw CSAC and the oxidized CSAC. Both spectra showed a main peak at 284.9 eV, ascribed to graphitic carbon.³⁷ In addition, a small peak at 285.7 eV is assigned to aliphatic carbons (C–COH or C–COO).³⁷



Scheme 2 The oxidative carbonylation of phenol.



-COO, respectively.³⁷ In contrast to the raw CSAC, the 20% HNO_3 treated CSAC displayed a more intense peak at 286.8 eV, indicating that some carbon atoms were oxidized to phenolic hydroxyl groups. The area ratio of the peak at 286.8 eV to the peak at 284.9 eV was 0.176 for the oxidized CSAC and 0.081 for the raw CSAC.

3.2 Grafting of ethylenediamine ligand

Grafting of ethylenediamine ligand onto the CSAC was accomplished by aminosilylating the oxidized AC with AEAPTMS. The FT-IR spectra of the oxidized CSAC and the AEAPTMS silanized CSAC are shown in Fig. 2. In the FT-IR spectra of oxidized CSAC (Fig. 2a), the bands at 1400, 1068 and 1629 cm⁻¹ are assigned to bending vibration of C–OH, C–O stretching vibration of alcohols or esters, and C==O stretching vibration of carboxyl in aromatic ring,³⁸ respectively. In Fig. 2b, the band at 729 cm⁻¹ is assigned to out-of-plane bending vibration of Ar–O–Si,³⁹ which resulted from combination of –Si–(OMe)₃ with phenolic hydroxyl. In comparison to Fig. 2a, the intensity of 1400 cm⁻¹ is much weaker in the IR spectrum of the AEAPTMS silanized CSAC owing to condensation



Fig. 2 FT-IR spectra of (a) oxidized CSAC and (b) AEAPTMS silanized CSAC.

of phenolic hydroxyl with the silane. Two IR bands at 777 and 1101 cm⁻¹ are assigned to out-of-plane bending vibration of -NH- and stretching vibration of R-NH₂,⁴⁰ respectively. It further suggests that AEAPTMS was successfully grafted onto the oxidized CSAC. The existence of Si and N was further indicated in the XPS spectrum as shown in Fig. S3b.[†] The peaks at 102 and 399.8 eV are ascribed to electron binding energies of Si 2p and N 1s,⁴¹ respectively. Comparatively, such signals were not observed in the oxidized CSAC (Fig. S3a⁺). In the solid state ²⁹Si NMR spectrum (Fig. 3a), the strong resonance centered at -60 ppm is ascribed to [C-Si(OSi)₂(OC)],⁴² suggesting that one silane was condensed with one phenolic hydroxyl group and crosslinked with two neighboring silanes. A weak resonance at -110 ppm was observed in the spectra. The resonance was associated with the silicon in (SiO)₄*Si (Q4).⁴³ This may be due to minor impurity, which comes from CSAC or the environment.

3.3 Grafting of benzyl malononitrile ligand

The oxidized CSAC was silanized with CMPTCS, as suggested by the FT-IR spectrum as well as the ²⁹Si NMR spectrum in Fig. 3b. In Fig. 4b, condensation of phenolic hydroxyl with the silane was demonstrated by the out-of-plane bending vibration of Ar-O-Si at 727 cm⁻¹.³⁹ Therefore, it can be found that the intensity of 1400 cm⁻¹, assigned to bending vibration of C-OH, was obviously decreased in comparison to the oxidized CSAC (Fig. 4a). In addition, the band at 773 cm⁻¹ is assigned to C-Cl stretching vibration,40 and the bands at 1452 and 1591 cm⁻¹ are assigned to the stretching vibration of C=C in benzene ring.40 The XPS spectrum in Fig. S4b† also showed the presence of Si and Cl in the CMPTCS silanized CSAC. After nucleophilic substitution of C-Cl and NaCH(CN)₂, the band at 773 cm⁻¹ disappeared, as seen in Fig. 4c, suggesting that malononitrile ligand was grafted onto the silanized CSAC. Meanwhile, the band of the C=N stretching



Fig. 3 ²⁹Si MAS NMR spectra of (a) ethylenediamine complexed catalyst, (b) benzyl malononitrile complexed catalyst, (c) propyl malononitrile complexed catalyst.



Fig. 4 FT-IR spectra of (a) oxidized CSAC, (b) CMPTCS silanized CSAC and (c) benzyl malononitrile grafted CSAC.

vibration was observed at 2248 cm^{-1,40} In Fig. S4c,† N element can also be detected by the XPS spectrum.

3.4 Grafting of propyl malononitrile ligand

To prepare propyl malononitrile ligand grafted CSAC, the oxidized CSAC was first reacted with the -(CH2)3Cl ligand containing silane. The CSAC was also successfully silanized with CPTMS, as evidenced by presence of the band at 727 cm^{-1} and reduction in the intensity of 1400 cm⁻¹ as seen in Fig. 5b. Meanwhile, the C-Cl stretching vibration at 786 cm⁻¹ can be observed as well.⁴⁰ In the same way, the silane may attach with one phenolic hydroxyl group and crosslink with two neighboring silanes. Grafting of the malononitrile ligand was accomplished by a nucleophilic reaction of (CH₂)₃Cl and NaCH(CN)₂, which was corroborated by the disappearance of C-Cl stretching vibration at 786 cm⁻¹ and the presence of C=N stretching vibration at 2248 cm^{-1} as shown in Fig. 5c. Their XPS spectra in Fig. S5[†] further confirmed the existence of the respective characteristic elements in the CPTMS silanized CSAC and the propyl malononitrile ligand grafted CSAC.

3.5 Complexation of metal ions

The electron binding energies of N 1s and Pd²⁺ 3d_{5/2} are sensitive to the chemical environment of the atoms. Table 1 presents the XPS data before and after complexation with palladium ions. The binding energies of $Pd^{2+} 3d_{5/2}$ in the three bidentate nitrogen ligand complexed Pd²⁺ were lower than that of PdCl₂ due to electron donation from nitrogen. Meanwhile, the binding energies of N 1s increased after complexing with metal ions. Among the three bidentate nitrogen ligand complexed Pd²⁺, it can be seen that the ethylenediamine ligand complexed Pd^{2+} has the lowest $Pd^{2+} 3d_{5/2}$ binding energy and that a highest N 1s binding energy, which means that ethylenediamine is more electron donating compared to malononitrile. Successful complexation of metal ions was confirmed by FT-IR spectroscopy, as seen in Fig. 6. The bands at 462-467 and 849-857 cm⁻¹ were ascribed to stretching vibrations of Pd-N and Cu-N, respectively.44,45



Fig. 5 FT-IR spectra of (a) oxidized CSAC, (b) CPTMS silanized CSAC and (c) propyl malononitrile grafted CSAC.

Table 1 XPS data of the samples before and after complexation with metal ions

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		Ethylenedia	mine ligand	Benzyl malone	Benzyl malononitrile ligand		Propyl malononitrile ligand	
Samples	$PdCl_2$	Before ^a	After ^b	Before ^a	After ^b	Before ^a	After ^b	
Pd 3d5/2/(eV)	337.8	_	337.0	_	337.2	_	337.2	
N 1s/(eV)	_	399.8	400.3	399.9	400.1	399.9	400.1	



Fig. 6 FT-IR spectra of (a) ethylenediamine complexed catalyst, (b) benzyl malononitrile complexed catalyst and (c) propyl malononitrile complexed catalyst.

The content of palladium and copper in the three samples were determined by ICP-AES (as seen in Table 2). High Pd²⁺ loading may increase the number of catalytic active sites, which has a significant effect on catalytic performance. Cu²⁺ ions behave as a cocatalyst. Hatanaka et al.⁴⁶ have proposed that a possible mechanism of oxidative carbonylation of phenol to DPC is a "multi-step electron transfer" catalytic cycle, in which the chemical state of palladium changed between Pd^{2+} and Pd(0). Pd(0) is inactive in the reaction,⁴⁷ so Pd(0) must be transformed to Pd²⁺ by the cocatalyst during the reaction to keep the catalytic activity. The experimental results in Table S1[†] show that the ethylenediamine ligand complexed metal catalyst has the highest palladium and copper loading contents of 1.79% and 1.10%, respectively. Despite there being many factors influencing metal ions loading in the CSAC, the stronger electron-donating ability of the ethylenediamine ligand may be an important reason for the higher metal ion loading.

Table 3 displays the BET surface areas and average pore sizes of the samples. The raw CSAC has a BET surface area of 788.9 m² g⁻¹, and an average pore size of 3.39 nm. After treatment by HNO₃, the BET surface area of the CSAC slightly decreased to 767.6 m² g⁻¹, and the average pore size increased to 3.43 nm. A possible explanation for this is that some micropores in CSAC collapsed during the oxidation process and some impurities were dissolved by HNO₃. However, the BET surface areas and the average pore sizes of the three bidentate nitrogen ligand complexed Pd²⁺ catalysts apparently declined due to grafting of guest species on the CSAC. Their pore size distributions are shown in Fig. S6.†

3.6 Catalytic activity

DPC synthesis by oxidative carbonylation of phenol was carried out in a high pressure reaction vessel. The effect of temperature on the phenol conversion was investigated at a pressure of 7 MPa with CH₂Cl₂ as solvent. The conversion of PhOH over the three bidentate nitrogen ligand complexed Pd²⁺ catalysts increased with temperature as shown in Fig. 7. It was also noticed that the ethylenediamine and benzyl malononitrile complexed Pd²⁺ not only showed a higher phenol conversion compared to the propyl malononitrile complexed Pd2+, but also displayed a more obvious phenol conversion versus temperature change. The three catalysts have relatively stable DPC selectivities at temperatures lower than 100 °C as seen in Fig. 7. They are 91.0%, 90.5% and 80.8% for the ethylenediamine, benzyl malononitrile and propyl malononitrile complexed Pd²⁺ catalysts, respectively. Although high temperature benefited the phenol conversion, DPC selectivities apparently decreased as the temperature increased from 100 to 130 °C, since more side reactions would occur, generating o-phenylene carbonate, phenol dimers etc.48

Although the reaction occurs mainly in the liquid phase, phenol conversion is also affected by CO and O_2 pressure due to the change of the reactant concentrations in the solvent. For the reaction of oxidative carbonylation of phenol

Table 2	Contents	of active	species	in	three	catalysts	
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	Fresh catalysts (wt%)		After 75 h of catalytic performance in packed bed (wt%)		
Catalysts	Pd^{2+}	Cu ²⁺	Pd^{2+}	Cu ²⁺	
Ethylenediamine grafted CSAS	1.79	1.10	1.65	1.01	
Benzyl malononitrile grafted CSAS	1.22	0.71	1.16	0.66	
Propyl malononitrile grafted CSAS	0.82	0.52	_	_	

Table 3 BET surface areas and average pore sizes of the samples

Samples	Raw CSAC	Oxidized CSAC	Ethylenediamine complexed Pd ²⁺	Benzyl malononitrile complexed Pd ²⁺	Propyl malononitrile complexed Pd ²⁺
BET surface area (m ² g ⁻¹)	788.9	767.6	490.1	505.2	437.9
Average pore diameter (nm)	3.39	3.43	2.17	2.07	2.02



Fig. 7 Effect of temperature on the phenol conversion and DPC selectivity at pressure of 7 MPa with CH_2Cl_2 as solvent.

to DPC, the number of gaseous reactant molecules decreases after reaction. Thus, enhancement of pressure is favorable for the phenol conversion according to the principles of chemical equilibrium.⁴⁹ Therefore, it was observed that the phenol conversions increased with pressure as shown in Fig. 8, but almost leveled off as the pressure reached 7 MPa for all three catalysts because of equilibrium restrictions, which is also indicated in the literature.⁵⁰

In order to assess the effect of solvent on the oxidative carbonylation of phenol, the commonly used solvents, C₆H₆, CH₂Cl₂, THF and DMF, were tested in the reaction. The conversion rate of phenol and the DPC selectivity are shown in Fig. 9. The phenol conversion was increased in the presence of solvents compared to the solvent-free reaction, probably because the activated phenoxycarbonyl intermediate interacts with the solvent and is solvated, lowering the potential energy, so the activation energy decreases and the rate of the reaction increases. In addition, the polarity of the solvent plays a minor role. The polarities of C₆H₆, CH₂Cl₂, THF and DMF are 3, 3.4, 4.2 and 6.4, respectively. It is found that the phenol conversion had a slight increase with the polarity of solvent. The charge density of the phenoxycarbonyl intermediate is greater than the charge density of the initial reactants, so the electrostatic contribution decreases the Gibb's free energy of the transition state.

In terms of the three bidentate ligand complexed Pd^{2+} catalysts, the ethylenediamine complexed Pd^{2+} catalyst has the highest phenol conversion and DPC selectivity, since it has the largest pore size, and the ethylenediamine ligand has the strongest electron-donating ability and enhances loading capacity of palladium ions. In the same way, the benzyl malononitrile complexed Pd^{2+} catalyst has a higher Pd^{2+} content and a larger pore size than the propyl malononitrile complexed Pd^{2+} catalyst, so it showed a higher catalytic efficiency. In addition, this positive effect is also probably due to the steric hindrance of benzene group. It has been reported



Fig. 8 Effect of pressure on the phenol conversion and DPC selectivity at 100 $^\circ$ C with CH₂Cl₂ as solvent.



Fig. 9 Effect of solvent on the phenol conversion and DPC selectivity at 100 $^{\circ}\text{C}$ and a pressure of 7 MPa.

that the cleavage of the Pd–C bond in the phenoxycarbonyl intermediate is the rate-determining step,¹⁴ the presence of the benzene group might accelerate the cleavage rate by steric repulsion.

CSAC tends to be harder, more resistant to abrasion, and lower in ash than similar grades of coal or wood-based carbons. Therefore, the CSAC granules can be directly used as catalyst carriers for application in a packed-bed continuous process. The ethylenediamine and benzyl malononitrile complexed Pd²⁺ catalysts were also evaluated in a packed-bed reactor. In the reaction, the liquid flow rate was 5 mL min^{-1} and the gas flow rate was 200 mL min⁻¹. After 10 h of running, the reaction liquid was analyzed. For the ethylenediamine complexed Pd²⁺, the conversion rate of phenol and the DPC selectivity were 12.03% and 93.05%, respectively. Meanwhile, the benzyl malononitrile complexed Pd²⁺ had a phenol conversion rate of 9.36% and a DPC selectivity of 90.82%. Their phenol conversion and DPC selectivity were comparative to those achieved in a high pressure reaction vessel. TOF was 10.6 mol DPC/(mol Pd h⁻¹) for the ethylenediamine complexed catalyst, and 11.9 mol DPC/(mol Pd h⁻¹) for the benzyl malononitrile complexed one. Generally speaking, a catalyst would display a higher TOF in a batch reaction. When batch reactions were carried out in CH₂Cl₂ under a pressure of 5 MPa at 100 °C, TOF values were 34.5 and 55.0 mol DPC/(mol Pd h⁻¹) for the ethylenediamine and benzyl malononitrile complexed catalysts, respectively.

The catalysts displayed relatively good catalytic stabilities in the packed-bed reactor. After 75 h of running, the conversion rates of phenol were 11.5% and 8.9% for the ethylenediamine and benzyl malononitrile complexed Pd²⁺ catalysts, respectively. The DPC selectivities nearly remained unchanged. Relatively stable catalytic performance is mainly due to the strong interaction of metal ion and organic complex. Bidentate ligand nitrogen complexes generally display stronger chelation with metal ions than monodentate ligand complexes. Furthermore, most of the active components are located inside the pores of the supports. The leaching of active species is very small after 75 h of catalytic reaction in packed bed reactor, as seen in Table 2. It cannot be ruled out that catalytic performance in a packed bed may reduce the leaching of active species compared to that in a slurry reactor. In Fig S7,† the presence of the bands ascribed to stretching vibrations of Pd-N and Cu-N indicated the stability of the catalysts in a packed bed reactor.

For comparison, catalytic tests of other supported catalysts found in references were carried out in a high pressure reaction vessel. Ishii *et al.*¹⁴ tethered palladium–pyridyl complexes on polymer support. The results showed that TOF reached 11.31 mol DPC/(mol Pd h⁻¹). Fan *et al.*⁴⁸ anchored palladium complexes on silica functionalized by 1,2-diaminocyclohexane. The yield of DPC was 12.0%, and TOF was 12 mol DPC/ (mol Pd h⁻¹). However, the Pd loss reached 3.0% after one batch operation in the vessel. Xue *et al.*⁴¹ reported a DPC yield of 20.3% over Pd–Cu–O/SiO₂ under certain conditions, and TOF was 15.1 mol DPC/(mol Pd h⁻¹). Song *et al.*¹⁵ used 5% Pd/AC as catalyst, the yield of DPC was 14.3% with a selectivity of 66.5%. Takagi *et al.*⁵¹ researched the Pd–Pb–NMe₄Br catalyst, the reported yield was 9.55%, and DPC selectivity was 78.8%.

4. Conclusions

Bidentate nitrogen ligands were successfully grafted onto the CSAC by silanization of the oxidized AC. Among three bidentate ligand complexed Pd2+ catalysts, the ethylenediamine ligand has a relatively stronger electron-donating ability and complexes more metal ions. The ethylenediamine grafted AC has a bigger BET surface area and larger average pore size. Therefore, it exhibited a higher catalytic efficiency. In addition to the reaction temperature and pressure, the polarity of solvent has an influence on the oxidative carbonylation of phenol. More polar solvent may accelerate phenol conversion. The CSAC granules immobilized metal complexes can be directly applied in a packed bed reactor and exhibited good catalytic performance, which is an obvious advantage over mesoporous molecular sieves. These results imply the CSAC granules can be extended to immobilize other organic group containing catalysts, such as enzymes, ionic liquids, etc., for application in a packed bed reactor.

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