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Platinum nanoparticles confined in imidazolium-based ionic polymer for assembling a microfluidic reactor with enhanced catalytic activity

Haobin Fang, Junxing Chen, Yali Xiao, Jianyong Zhang*

MOE Laboratory of Polymeric Composite and Functional Materials, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

* Correspondence author.

E-mail addresses: zhjyong@mail.sysu.edu.cn (J. Zhang).

Graphical Abstract



Highlights

- Fused-silica capillary is modified by ionic polymer loaded with well-dispersed Pt nanoparticles.
- A catalytic microfluidic reactor is assembled for nitroreduction and hydrosilylation.
- The microfluidic reactor shows improved activity and multiple uses.

Abstract

A synthetic strategy is developed to grow Pt nanoparticles supported by imidazolium-based ionic polymers (Pt/ImIP-2BrB) on the inner surface of fused-silica capillary. The imidazolium-based ionic polymers ImIP-2BrB are prepared from condensation of tetrakis[4-(1-imidazolyl)phenyl]methane and 1,4-bis-bromomethyl-benzene and are employed to

support Pt nanoparticles. The capillary coated with Pt/ImIP-2BrB is further assembled to achieve a catalytic microfluidic reactor. The catalytic activity is probed in either the reduction of nitrobenzene derivatives or the hydrosilylation of phenylacetylene with triethylsilane by flowing through the microfluidic reactor. The catalytic microfluidic reactor demonstrates significantly enhanced activity about 2-8 times in comparison with the corresponding reactions under batch conditions. The reactor greatly reduces the amount of Pt upon achieving similar yields. It also shows good recyclability without significant decrease of the activity.

Keywords: platinum nanoparticles, ionic polymers, microfluidic reactor, nitroreduction

1. Introduction

Noble metals like Au, Pd, Pt are widely applied as catalysts in a number of organic transformations such as nitroreduction [1,2], aerobic oxidation [3], coupling reaction [4,5], hydrogenation reaction [6,7], etc. Altough the high cost limits their application, it is still irreplaceable. Metal nanoparticles (NPs) loaded on porous materials have been developed as efficient heterogeneous catalysts because reduced metal dosage and downsizing nanoparticles can achieve a large proportion of active surface atoms [8-24]. Among various porous materials, imidazolium-based ionic polymers incorporating ionic building blocks can load kinds of metal nanoparticles through electrostatic interaction or ion exchange with corresponding metal salts [25-29]. Stable and well-dispersed nanoparticles may be encapsulated in the imidazolium-based ionic polymers to result in improved catalytic efficiency and stability. However, heterogeneous catalysts generally suffer from decreased catalytic efficiency compared with homogeneous catalysts, and specific technology is needed to improve the catalytic efficiency [30].

Microfluidic reactors have been extensively explored to improve the efficiency of organic synthesis in recent years [31-35]. In comparison with the reactions performed under batch conditions, the microfluidic systems have a range of advantages such as easy automatical control of reaction temperature and reagent consumption, improved transfer efficiency of heat, mass and kinetics of diffusion-limited reactions [36-40]. Catalysts in a confined region offer a large number of active sites exposed to reagents and precise selection for products [41-45]. In addition the reaction in microfluidic reactors is safer for hazardous chemicals. So the high reaction efficiency,

environmental sustainability, and easy control make the microfluidic systems promising in various fields [46-54].

Based on the above considerations, an open-tubular microfluidic system with coating Pt NPs supported on imidazolium-based organic polymer is herein reported. Imidazolium-based ionic polymer (ImIP-2BrB) [55] is coated on the inner surface of microfluidic capillary to support Pt NPs. The positive network of ImIP-2BrB can entrap PtCl₆²⁻ ions for subsequent formation of Pt NPs. In the capillary, the polymer acts as a carrier allowing Pt NPs to be stably loaded on the capillary wall. In the catalytic process, the polymer can stabilize Pt NPs and prevent the loss or agglomeration of Pt NPs. The open-tubular capillary reactor with Pt/ImIP-2BrB coating is applied to catalyze nitroreduction [56-59] and hydrosilylation reactions [60-67]. The technology greatly reduces the amount of Pt with remarkably improved catalytic activity and recyclability.

2. Experimental section

2.1 Materials and methods

Chemicals and solvents were obtained from commercial sources and used as received without further purification unless otherwise stated. (3-Bromo-propyl)triethoxysilane [68] and tetrakis[4-(1H-imidazole-1-yl)phenyl]methane [55] were synthesized according to the previous reports. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis was carried out using an ultra-high resolution SU8010 FE-SEM. For SEM measurements, the material was dispersed in EtOH using sonication, and then deposited on aluminum foil. Transmission electron microscopy (TEM) investigations were performed on a FEI Tecnai G2 Spirit 120 kV or 300 kV TEM system. For TEM measurement, the material was dispersed in EtOH with the aid of sonication, and then dropped on a carbon coated copper grid. Powder X-ray diffraction (XRD) data was collected on a Rigaku Smart Lab diffractometer (Cu-K α_1 radiation, $\lambda =$ 1.54056 Å). NMR spectra were obtained on a Bruker Avance 400 MHz Superconducting Fourier Transform Nuclear Magnetic Resonance Spectroscopy instrument. Pt analysis was performed using a Thermo ScientifiCAP RQ ICP-MS instrument. Before the analysis, the material on the coated capillary was digested by aqua regia at 150 °C for 3 d. Infrared spectra were recorded on a Perkin Elmer Frontier FT-IR spectrometer with KBr pellets in the range 4000-400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was using X-ray Photoelectron Spectroscopy/ESCA

(ESCALAB 250). Thermo analyses were using a NETZSCH TG STA 449 F3 Jupiter system under N_2 atmosphere.

2.2 Coating of Pt/ImIP-2BrB in capillary

Pre-bromination of the inner surface of capillary. A capillary (ID = 0.53 mm, L = 30.0 m) was rinsed with acetone for 30 min, 3 mol L⁻¹ NaOH for 2 h, and 3 mol L⁻¹ HCl aqueous solution for 2 h, in turn. Then the capillary was rinsed with distilled water for 10 min and EtOH for 10 min in turn, and dried in Ar stream for 2 h. Subsequently the capillary was filled with a solution of 3-bromopropyl-triethoxysilane in dry toluene (2%, *v:v*) and kept for 1 d at 80 °C. The solution was removed and the capillary was rinsed with dry toluene for 10 min and EtOH for 10 min in turn, and dried in Ar stream for 4 h.

Coating of ImIP-2BrB in the capillary. The above pre-treated capillary (L = 1000 mm) was filled with a mixed solution of tetrakis[4-(1-imidazolyl)phenyl]methane (TIM) and 1,4-bis-bromomethyl-benzene (2BrB) in CHCl₃ (c_{TIM} = 0.046 mol L⁻¹, c_{2BrB} = 0.091 mol L⁻¹, mixed in a 1:1 volume ratio). The injection speed was controlled by a syringe at 0.2 mL min⁻¹. The capillary was sealed and kept for 2 d at 80 °C. Then the solution was removed by flushing the capillary with Ar. The capillary was rinsed with CHCl₃ for 10 min.

The above processes (pre-bromination and ImIP-2BrB coating) were repeated for three times.

Pt NPs incorporating in capillary. H_2PtCl_4 in EtOH (2.5 mmol L⁻¹) was injected into the above capillary at 0.2 mL min⁻¹. The capillary was sealed and kept for 1 d at RT. NaBH₄ solution in EtOH (0.2 mol L⁻¹) was injected into the capillary at 0.2 mL min⁻¹ continuously during 1.5 h. The solution was removed by flushing the capillary with Ar. The capillary was rinsed with water for 10 min and ethanol for 10 min in turn. The coating thickness was ca. $31.7 \pm 0.7 \mu m$ according to SEM. ICP showed that the Pt content was 0.00025 mmol for 1000 mm capillary.

2.3 Nitroarene reduction in capillary reactor and recyclability

Typical procedure: A solution of nitrobenzene (0.062 g, 0.5 mmol) in THF (4 mL) was mixed with a solution of reducing agent, NaBH₄ (0.095 g, 2.5 mmol) in water (2 mL). 1 mL of the resulting mixture was taken to be continuously introduced into the coated capillary (ID = 0.53 mm, L = 1000 mm) using a syringe, and the mixture passed through the capillary with constant flow

rate (6 μ L min⁻¹) at RT (~25 °C). The reaction time in the coated capillary was about 1.0 h. Then the effluent was collected and extracted with ethyl acetate (0.5 mL). The organic layer (1 μ L) was tested using gas chromatography. For subsequent use, the capillary reactor was rinsed with H₂O, EtOH and dried by flushing the capillary with Ar.

2.4 Nitroarenereduction under batch conditions

General procedure: Nitroarene derivatives (1.0 mmol) in THF (4 mL) and NaBH₄ (0.189 g, 5.0 mmol) in water (2 mL) were mixed, and Pt/ImIP-2BrB-2.5 catalyst (10.0 mg, 0.6 mol% Pt based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.2 mL) was taken and extracted with H₂O (1 mL) and ethyl acetate (1 mL) in turn, and the organic layer (1 μ L) was tested. After the mixture was stirred at RT for 2 h, and filtered, the filtrate was extracted with ethyl acetate (3×10 mL) and washed by 10 mL water. The combined organic phase was dried by anhydrous MgSO₄ and the crude product was further purified by flash column chromatography on silica gel. The product was dried in vacuum and confirmed by NMR. 4-Toluidine (0.091 g, 85%), 3-toluidine (0.085 g, 79%), 2-toluidine (0.080 g, 75%), 4-aminophenol (0.076 g, 70%), 1,4-phenylenediamine (0.089 g, 82%), 4-tert-butylaniline (0.118 g, 79%), 4-anisidine (0.107 g, 87%).

2.5 Hydrosilylation in capillary reactor and recyclability test

Typical procedure: Phenylacetylene (0.102 g, 1.0 mmol) and triethylsilane (0.116 g, 1.0 mmol) were mixed in 5 mL toluene. The resulting solution was taken to be continuously introduced into the coated capillary (ID = 0.53 mm, L = 2000 mm) using a syringe at 80 °C. The reaction was kept for 4 h (flow rate, 2 μ L min⁻¹) and then cooled down to RT. The 0.5 mL effluent from the end of the coated capillary was collect at intervals and evaporated to dryness in vacuum and analyzed by ¹H NMR using 1,4-dioxane (0.1 mmol) as the standard. After the reaction, the capillary was rinsed with toluene for subsequent use and the residual solution was removed by Ar.

2.6 Hydrosilylation under batch conditions

Typical procedure: Phenylacetylene (0.102 g, 1.0 mmol), triethylsilane (0.116 g, 1.0 mmol), 20, 10 or 5 mg catalyst (1.2, 0.6 or 0.3 mol%) were mixed in toluene (5 mL) under Ar at 80 °C.

The reaction mixture was stirred for 4 h and then cooled down to RT. The reaction mixture was dried in vacuum, extracted with 0.5 mL CDCl₃, filtrated and analyzed by ¹H NMR spectroscopy with 1,4-dioxane as standard. The isomeric content was determined based on the alkene coupling constants in the ¹H NMR spectra and/or analysis of chemical shifts.

3. Results and discussion

3.1 Preparation of the coating capillary

The synthetic route for the growth of Pt/ImIP-2BrB on the surface of fused-silica capillary is presented in Fig. 1. First, the inner surface of a capillary is brominated by (3-bromo-propyl)triethoxysilane treatment [56]. The resulting capillary is denoted as C-Br. Subsequently, the imidazole groups of tetrakis[4-(1H-imidazole-1-yl)phenyl]methane (TIM) are alkylated on its N atoms with 1,4-bis(bromomethyl)-benzene (2BrB) to generate extended imidazolium-based ionic polymer with cationic imidazolium crosslinks, ImIP-2BrB. In the meantime, the coupling reaction of TIM with the dangling -Br groups on the capillary surface leads to strong covalent linkage between ImIP-2BrB and capillary, which benefits a uniform and stable modified layer. Finally, due to the cationic nature, ImIP-2BrB layer grown on the capillary surface readily adsorbs PtCl6²⁻ anions. Following an in situ reduction induced by NaBH₄ solution, Pt NPs are formed and stabilized within the porous channels of the ImIP-2BrB layer.





Fig. 1. a) Synthetic route to C-Pt/ImIP-2BrB, and b) schematic representation of the microfluidic reactor assembled from Pt/ImIP-2BrB-coated capillary.



Fig. 2. a-d) SEM and e) TEM images of Pt/ImIP-2BrB layer on the capillary, and f) particle size distribution (Pt/ImIP-2BrB growth parameters, $c_{\text{TIM}} = 0.023 \text{ mol } \text{L}^{-1}\text{and } c_{2\text{BrB}} = 0.091 \text{ mol } \text{L}^{-1}$ in CHCl₃ in 1:1 volume ratio). The bars represent 40.0, 30.0, 10.0, 2.00, and 5 nm, respectively, from a to e.

3.2 Characterization of the coating capillary

The morphology of the resulting Pt NPs supported on ImIP-2BrB within the microfluidic capillary (denoted as C-Pt/ImIP-2BrB) is characterized using SEM and TEM (Fig. 2). SEM of the capillary cross section confirms the growth of a Pt/ImIP-2BrB layer with a thickness of 42.3±4.0 μ m. The morphology of the material on the capillary was macroscopically composed of interconnected spheres which is in agreement with that of the material obtained under batch conditions. TEM reveals nanoparticles of 1.8±0.2 nm for C-Pt/ImIP-2BrB which is close to the size of the Pt NPs (1.92±0.33 nm) obtained under batch conditions according to our previous study [55]. High resolution TEM shows atomic lattice fringes of Pt NPs with a spacing of 0.23 nm

which corresponds to Pt(111) planes and proves the existence of crystalline Pt NPs in ImIP-2BrB within the microfluidic capillary (Fig. S1) [69,70]. Energy dispersive X-ray spectroscopy (EDX) analysis of the coating layer shows the Pt, C, N and Br elements indicating the successful coating of the polymer on the capillary (Fig. S2). Powder X-ray diffraction (PXRD) shows that the polymer ImIP-2BrB is amorphous before loading Pt NPs (Fig. S3). After loading of Pt NPs, the signal at $2\theta \approx 40^{\circ}$ ascribed to the Pt(111) lattice plane of Pt NPs is too broad to be observed clearly, which is presumably attributed to the small size and high dispersion of crystalline Pt NPs [59, 60].

FT-IR of Pt/ImIP-2BrB scraped from the capillary shows characteristic peaks at around 1665 and 1615 cm⁻¹, which are attributed to the imidazolium C=C and C=N stretching vibrations, respectively (Fig. S4) [61]. The polymer after Pt loading shows almost identical spectrum to the corresponding polymer before Pt loading, indicating that the polymeric structure is well maintained [55,59,60]. X-ray photoelectron spectroscopy (XPS) survey spectra of Pt/ImIP-2BrB on the capillary possess characteristic signals of Pt 4f, Br 3d, Si 2p, C 1s, N 1s, and O 1s (Fig. S5). The Pt 4f region is divided into two spin-orbital pairs. The binding energy peaks at 75.0 eV (Pt $4f_{5/2}$) and 71.7 eV (Pt $4f_{7/2}$) are assigned to Pt(0) species [60,62,63]. The results indicate successful coating of the polymer on the capillary.

Thermogravimetric analysis (TGA) profile shows that Pt/ImIP-2BrB and ImIP-2BrB scraped from the capillary show similar thermal stability (Fig. S6). For ImIP-2BrB the continuous weight loss before 100 °C is related to the removal of moisture or free solvent. Both the materials decompose when the temperature is above about 200 °C.

3.3 Assembling of the microfluidic reactor

The microfluidic equipment includes a syringe pump, an injector, a capillary coated by Pt/ImIP-2BrB and a vessel for collecting the product. The injector and coated capillary were connected by a Luer taper. The starting solution mixture in the injector was injected into the coating capillary by the syringe pump that controls the flow rate. The flow rate of the solution mixture and the length/volume of the coated capillary (ID = 0.53 mm, L = 1000 mm) determine the reaction time (of passing through the capillary) (Fig. 1). For the hydrosilylation reaction, an oil bath is needed to heat the coating capillary. The Pt NPs in the reactor was determined to be $2.5 \times$

10⁻⁴ mmol m⁻¹ by ICP. The Pt NPs in the reactor has similar size but lower content in comparison with the material prepared under the batch conditions.

3.4 Reduction of nitroarene derivatives

The catalytic performance of the microfluidic reactor was evaluated in the reduction of nitroarene derivatives to corresponding anilines, which is an important transformation in organic chemistry. The reaction was first performed under batch conditions for optimized conditions (Table 1). First, the molar ratio of nitrobenzene:NaBH₄ was optimized. The selectivity was only 64% (azobenzene/azoxybenzene compounds are main by-products) when the molar rate of nitrobenzene:NaBH₄ was 1:3, while it was higher up to 99% when nitrobenzene:NaBH₄ was 1:5 (with >98% conversion after 2 h). It indicates that insufficient NaBH₄ results in poor selectivity. Next the activity of the material with different size of Pt NPs was also studied. Pt/ImIP-2BrB-2.5 with smaller size of Pt NPs (1.92 ± 0.33 nm) showed better selectivity (e.g., >99% for the reduction of nitrobenzene) and shorter reaction time (e.g., 1 h for the reduction of 1-chloro-4-nitrobenzene) than Pt/ImIP-2BrB-5.0 (2.86 ± 0.56 nm). Therefore the optimized reaction was performed with 1:5 molar ratio of nitrobenzene and NaBH₄ and 10 mg of Pt/ImIP-2BrB (Pt 0.64 mol% to the nitrobenzene) in 6 mL THF/H₂O (*v*:*v* = 2:1) at RT (~25 °C) under Ar atmosphere.

The reaction was then performed in the microfluidic reactor. The reaction mixture (e.g., nitrobenzene (0.17 mmol) and NaBH₄ (0.83 mmol) in THF-H₂O (v:v = 2:1)) was taken to be introduced into the capillary using a syringe pump. Nitrobenzene was catalytically reduced and the product was collected at the end of the capillary and tested using gas chromatography and NMR (Fig. S7-S26). The Pt amount in the reactor was determined using inductively coupled plasma, and apparent turnover frequency (TOF) for all the catalytic reactions was calculated as the amount of nitrobenzene that a mole of Pt can convert per unit time [64]. Then the TOF for the reactions performed in the microfluidic reaction system was compared with the reactions under batch conditions. Most of the nitrobenzene derivatives catalysed by C-Pt/ImIP-2BrB showed about 2-4 times higher TOF when compared with those by Pt/ImIP-2BrB under batch conditions. For example, the reduction of 2-nitrotoluene (46 vs. 284) and 1-tert-butyl-4-nitrobenzene (75 vs. 594)

by C-Pt/ImIP-2BrB showed about 8 times higher TOF compared with those by Pt/ImIP-2BrB under batch conditions. The substrates bearing electron-donating groups, such as 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene and 4-nitroanisole, provided good conversion and selectivity to corresponding products (98% and 99% for 2-nitrotoluene, 94% and 89% for 3-nitrotoluene, 92% and 93% for 3-nitrotoluene, 98% and 95% for 4-nitroanisole). The steric hindrance at ortho-, meta- and para-positions of nitrotoluene has little effect on the catalytic reactions. Additionally the reduction of 1-tert-butyl-4-nitrobenzene also gave 92% conversion and 96% selectivity indicating that the bulky steric effect was also little. Functional groups, such as -OH and -NO₂, were well tolerated in the catalytic system and gave good conversion and selectivity.

1-Chloro-4-nitrobenzene gave 90% conversion and only 76% selectivity of 4-chloroaniline, and 4-nitrobenzaldehyde gave only 82% conversion and 62% selectivity of 4-aminobenzyl alcohol due to the electron-withdrawing groups like -Cl and -CHO [64, 65]. The TOFs are also much higher than those under batch conditions. The present Pt catalyst in microfluidic reactor showed higher TOFs than the reported Pt NPs-based catalysts for nitroreduction (Table S1) [8-11]. The reported TOFs range from 2 to 262 h⁻¹ for several nitrobenzene derivatives, while the present microfluidic reactor achieves more than 600 h⁻¹ for most of the nitrobenzene derivatives. The higher TOFs may be caused by the larger proportion of Pt NPs that are exposed to the substrates. When the Pt NPs catalyst is transformed into a confined ionic polymer layer of the microfluidic channel, the contact is significantly enhanced between substrates and the Pt NPs catalytically active sites [66, 67].

$R \xrightarrow{NO_2} \frac{\text{Cat. , NaBH_4}}{\text{THF/H}_2\text{O, RT}} \xrightarrow{R} \xrightarrow{NH_2}$								
Entry	R	Catalyst ^a	Pt conter /mmol	nt Time/h	Conv./%	Sel./%	TOF _{max} /h ⁻¹	
1	4-H	Pt/ImIP-2BrB-2.5	0.0064	1	>99	>99	156	
2		Pt/ImIP-2BrB-5.0	-	1	>99	94	-	
3°		Pt/ImIP-2BrB-5.0	-	2	98	64	-	
4		C-Pt/ImIP-2BrB	0.00025	1	>99	>99	666	
5	4-Cl	Pt/ImIP-2BrB-2.5	0.0064	1	95	67	99	
6		Pt/ImIP-2BrB-5.0	-	3	97	62	-	

Table 1	Reduction	of nitro	obenzene	e derivativ	es to anilines	catalyzed	by	Pt/ImIP-	2BrB.

7		C-Pt/ImIP-2BrB	0.00025	2	90	76	233
8	4-Me	Pt/ImIP-2BrB-2.5	0.0064	2	99	96	74
9		C-Pt/ImIP-2BrB	0.00025	1	98	99	660
10	2-Me	Pt/ImIP-2BrB-2.5	0.0064	3	99	90	46
11		C-Pt/ImIP-2BrB	0.00025	2	94	89	284
12	3-Me	Pt/ImIP-2BrB-2.5	0.0064	3	98	99	50
13		C-Pt/ImIP-2BrB	0.00025	2	92	93	291
14	4-OH	Pt/ImIP-2BrB-2.5	0.0064	0.5	98	93	285
15		C-Pt/ImIP-2BrB	0.00025	1	95	99	640
16	$4-NO_2$	Pt/ImIP-2BrB-2.5	0.0064	1	99	>99	155
17		C-Pt/ImIP-2BrB	0.00025	1	98	97	646
18 ^e	4-CHO	Pt/ImIP-2BrB-2.5	0.0064	6	79	40	8
19 ^e		C-Pt/ImIP-2BrB	0.00025	5	82	62	69
20	4-CMe ₃	Pt/ImIP-2BrB-2.5	0.0064	2	>99	96	75
21		C-Pt/ImIP-2BrB	0.00025	1	92	95	594
22	4-OMe	Pt/ImIP-2BrB-2.5	0.0064	3	>99	>99	52
23		C-Pt/ImIP-2BrB	0.00025	3	98	95	211

^a Pt/ImIP-2BrB-2.5 and Pt/ImIP-2BrB-5.0 were synthesized according to ref [41]. ^b Batch reaction conditions: nitroarene (1.0 mmol), NaBH₄ (5.0 mmol), Pt/ImIP-2BrB-2.5 (0.64 mol%) in 6 mL THF-H₂O (2:1, ν/ν) at RT; Microfluidic reaction conditions: 1.0 m capillary (Pt, 0.16 mol%), C-Pt/ImIP-2BrB with a coating thickness of 31.7±0.7 µm, nitroarene (0.17 mmol) and NaBH₄ (0.83 mmol) in 1 mL or 2 mL H₂O-THF (2:1, ν/ν) at RT. ^c the molar ratio of nitroarene and NaBH₄ was 1:3. ^d Conversion [%] and selectivity [%] were determined by GC and NMR. ^e The product was determined to be 4-aminobenzyl alcohol.



Fig. 3. Histogram of the multiple uses of C-ImIP-2BrB for the nitroreduction of nitrobenzene.

Reaction conditions: nitrobenzene (0.083 mmol), NaBH₄ (0.42 mmol) in 2 mL THF-H₂O-EtOH (8:3:1, *v*:*v*:*v*) at RT for 1 h.



Fig. 4. Three-phase test plots for the nitroreduction of nitrobenzene. A solution of nitrobenzene (0.5 mmol) in THF (4 mL) was mixed with a solution of reducing agent, NaBH₄ (2.5 mmol) in 2 mL H₂O/EtOH (v:v = 2:1). The reaction mixture flowed through the Pt/ImIP-2BrB capillary (10 cm) with reaction time of 2 min (11 µL min⁻¹), and conversion was monitored. (a) When conversion reach 68%, the solution collected from the Pt/ImIP-2BrB capillary was introduced into a raw capillary with no catalyst loaded (black line); (b) Fresh solution was introduced into the first Pt/pIM-2BrB capillary, and conversion was monitored (red line).

Multiple uses were performed in the capillary reactor for the nitroreduction of nitrobenzene. The catalytic activity of C-Pt/ImIP-2BrB maintained for at least 8 recycling runs (Fig. 3). Initial time-conversion plots also showed that no significant activity loss was observed (Fig. S27). The Pt content after 8 runs was experimentally measured to be 0.00021 mmol m⁻¹ and the size of Pt NPs was 2.0 ± 0.4 nm, which are close to those prior to initiating the reduction (0.00025 mmol m⁻¹ and 1.8 ± 0.2 nm), and a spacing of atomic lattice fringes of Pt NPs was still 0.24 nm which corresponds to Pt (111) planes, showing that the Pt NPs catalyst was stable (Fig. S28-S30). SEM of the capillary cross section showed the Pt/ImIP-2BrB layer with a thickness of 39.7±6.7 µm which is close to that before the catalytic reaction (42.3 ± 4.0 µm) and the morphology of polymer on the capillary did not change after 10 runs. Further verification that the Pt NPs were not leaching was carried out with a three-phase test for the nitroreduction of nitrobenzene. With reaction time

of 2 min and 4 min (10 cm, 11 μL min⁻¹), the conversion reached 43% and 68% respectively. After 68% conversion was reached, the reaction solution from the Pt/ImIP-2BrB capillary was injected to a new raw capillary which did not contain any catalyst, and the solution did not react and remains at 68% conversion (Fig. 4). This indicates that no active Pt NPs leached from the Pt/pIM-2BrB capillary, otherwise an increase in conversion would have been observed for the solution from the raw capillary [71]. The microfluidic reactor remains its catalytic activity after the multiple uses. This proves that Pt NPs and polymer in the capillary is stable after modification of the capillary using the present method together with other evidences. Polymers do not fall off from the capillary wall and Pt NPs are captured firmly within the polymers during the reactions. Thus the microfluidic reactor continues to catalyze the reactions without clogging or degradation.

3.5 Hydrosilylation reaction

Hydrosilylation was performed in the microfluidic reactor and the reactions were detected by ¹H NMR [53, 68-70]. The hydrosilylation of phenylacetylene and triethylsilane was chosen as a model hydrosilylation system. Reaction conditions were first optimized under batch conditions, and the best performance was observed when toluene was chosen as the solvent and the Pt content of Pt/ImIP-2BrB was 0.6 mol% (Table S2, Fig. S31, S32). The yield was 66% with the α : β -(E) isomeric ratio 40:60 (no β -(Z) isomer was observed) and the TOF was calculated to be 28 h⁻¹. The hydrogen signals on the alkene of both products were detected according to ¹H NMR (α product, 6.2, 5.9 ppm; β -(E) product, 7.3, 6.8 ppm). Then the hydrosilylation of phenylacetylene and triethylsilane was performed in the microfluidic reactor with the coated capillary (ID = 0.53 mm, L = 2000 mm) at 80 °C. The flow rate was about 2 μ L min⁻¹ and the reaction time was about 4 h. The yield was 79% and the α : β -(E) isomeric ratio was 56:44 after 4 h in toluene. The TOF was 395 h⁻¹, which is over ten times higher than that under batch conditions.

The microfluidic reactor (C-Pt/ImIP-2BrB) was also assessed in other hydrosilylation reactions. When 1-phenyl-1-propyne or 4-ethynyltoluene was chosen to react with triethylsilane, characteristic signals were detected at 6.1 ppm (α product) and 6.7 ppm (β -(E) product) for 1-phenyl-1-propyne (Fig. S33) and at 5.9, 5.6 ppm (α product) and 6.9, 6.4 ppm (β -(E) product) for 4-ethynyltoluene (Fig. S34). The yield and isomeric ratio was 65%, 29:71, and 50% 50:50 with TOF was 217 and 167 h⁻¹, respectively. They are remarkably higher than those under batch

conditions (yield 45% and 39%, TOF 13 and 11 h⁻¹). NMR signals were detected at 5.9, 5.6 ppm (α product) and 6.9, 6.4 ppm (β -(E) product) for 1-ethynyl-4-fluorobenzene, at 6.1, 5.8 ppm (α product) and 7.1, 6.7 ppm (β -(E) product) for 4-ethynylanisole (Fig S35). For 1-ethynyl-4-fluorobenzene, low yield (6%) and TOF (20 h⁻¹) was observed, while no product was detected for 4-ethynylanisole (Fig S36). These results suggest that the presence of electron-withdrawing substituent groups of CH₃O and F inhibits the catalytic efficiency. Therefore the microfluidic reactor efficiently catalyzes the hydrosilylation reaction between triethylsilane and phenylacetylene and its derivatives with electron-donating groups.

R ¹	R	² + HSiEt ₃ — Cat.	R ¹	R^2 H SiEt ₃	R ¹	R ² Si β-(E)	Et ₃
Entry	Alkyne	Cat.	Pt content /mmol	Time/h	Yield	TOF /h ⁻¹	Isomeric ratio α · β - $(E)^{c}$
1 ^a	$R^1 = H$,	Pt/ImIP-2BrB	6×10 ⁻³	4	66	28	40:60
2 ^b	$R^2 = H$	C-Pt/ImIP-2BrB	5×10 ⁻⁴	4	79	395	56:44
3 ^a	$R^1 = H$,	Pt/ImIP-2BrB	6×10 ⁻³	6	45	13	27:73
4 ^b	$R^2 = CH_3$	C-Pt/ImIP-2BrB	5×10 ⁻⁴	6	65	217	29:71
5 ^a	$R^1 = CH_3$,	Pt/ImIP-2BrB	6×10 ⁻³	6	39	11	37:63
6 ^b	$R^2 = H$	C-Pt/ImIP-2BrB	5×10 ⁻⁴	6	50	167	50:50
7 ^a	$R^1 = F$,	Pt/ImIP-2BrB	6×10 ⁻³	10	10	1.7	30:70
8 ^b	$R^2 = H$	C-Pt/ImIP-2BrB	5×10 ⁻⁴	6	6	20	28:72
9 ^a	$\mathbf{R}^{1}=\mathbf{C}\mathbf{H}_{3}\mathbf{O},$	Pt/ImIP-2BrB	6×10 ⁻³	24	1	0.03	0:100
10 ^b	$R^2 = H$	C-Pt/ImIP-2BrB	5×10 ⁻⁴	24	-	-	-

Table 2. Hydrosilylation of alkynes with triethylsilane.

^a Batch reaction conditions: Triethylsilane (1.0 mmol), alkyne (1.0 mmol) and 10 mg Pt/ImIP-2BrB (0.6 mol% Pt) in toluene (5 mL) at 80 °C. ^b Microfluidic reaction conditions: Triethylsilane (1.0 mmol), alkyne (1.0 mmol) in toluene (5 mL) using the capillary reactor (ID = 0.53 mm, L = 2000 mm) coated by Pt/ImIP-2BrB (5×10^{-4} mmol Pt). ^c Yield and isomeric ratio were determined by ¹H NMR using 1,4-dioxane as the standard.

The microfluidic reaction system could be reused as shown in the hydrosilylation of

phenylacetylene and triethylsilane (Fig. 5). The catalytic activity of C-Pt/ImIP-2BrB maintained for at least 5 recycling runs with around 79-72 yields and α : β -(E) isomeric ratio 55:45 (TOF 395-360 h⁻¹), indicating good recyclability for the reactor under heating conditions. In comparison with other Pt-based catalyst systems [17-19, 25], the present system is easy to be recycled with controllable reaction conditions, and it may be potentially applied in automated control field.



Fig. 5. Histogram of the recyclability test of C-ImIP-2BrB for hydrosilylation between triethylsilane and phenylacetylene. Reaction conditions: triethylsilane (1.0 mmol) and phenylacetylene (1.0 mmol) in toluene (5 mL) at 80 °C.

4. Conclusion

In summary, a novel strategy has been developed to fabricate a catalytic microfluidic reactor via coating Pt/ImIP-2BrB along the inner surface of microfluidic capillary. The inner surface of the fused-silica capillary was coated with dangling bromo groups as anchors for the ImIP-2BrB and subsequent in situ growth of ImIP-2BrB along the surface was performed. The ImIP-2BrB layer is prepared from nucleophilic substitution reactions between TIM and 2BrB, and employed to support Pt NPs. Then the coated capillary is further assembled into an open-tubular microfluidic reactor and the thickness of the Pt/ImIP-2BrB in the capillary was 31.7 ± 0.7 µm and the Pt NPs was 1.8 ± 0.2 nm and 2.5×10^{-4} mmol m⁻¹. The Pt/ImIP-2BrB microfluidic reactor shows various catalytic applications as shown in either the nitroreduction or the hydrosilylation reaction. The microfluidic reactor shows significantly higher catalytic efficiency in terms of TOFs (about 2-10 folds) than the corresponding catalyst under batch conditions. The significantly enhanced TOFs

suggest that capillary confinement plays a crucial role in increasing the efficiency of catalytic active sites and reducing the amount of noble metal catalysts. It is also noticed that the selectivity is improved in some reactions under microfluidic conditions. Additionally the microfluidic reactor exhibits good recyclability for multiple uses without significant activity decrease for the reduction of nitroarene and the hydrosilylation reaction. These results demonstrate the significance of improving the current catalytic activity of supported noble metal catalysts by combination with microfluidic technology and porous materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/xxxxxx.

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