



Dynamic functionalised metallogel: An approach to immobilised catalysis with improved activity

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ARTICLE INFO

Article history:

Received 25 June 2009

Received in revised form 30 October 2009

Accepted 1 November 2009

Available online 11 November 2009

Keywords:

Gel

Hybrid material

Palladium

Coordination polymer

Supported catalysis

ABSTRACT

A metal–organic gel (MOG) route to immobilised catalysts has been developed based on the reversibility of coordination bond formation in a Fe^{3+} –carboxylate MOG. The ferric gel was rationally designed based on a bifunctional ligand, 5-1*H*-benzo[*d*]imidazole-1,3-dicarboxylic acid (L1), in which the imidazole N atom may further bind to a soft ion like Pd^{2+} more strongly due to the HSAB matching. Palladium(II) was successfully loaded in the gel to yield a supported coordination catalyst. Compared with its homogeneous counterparts, the immobilised gel catalyst exhibited significantly improved catalytic activity under mild conditions as shown in Suzuki–Miyaura C–C coupling, and could be reused for several times.

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1. Introduction

Sol–gel processes have been used to produce a large number of useful solid materials for optical, magnetic, electrical, and catalytic applications [1]. The sol–gel process provides a route to efficient heterogeneous catalysts [2]. Sol–gel catalysts have many advantages for materials preparation and catalysis, such as preparation under mild conditions, homogeneous distribution of catalytic active centres, and easy removal from the reaction medium. Metal–organic gels (MOGs) are a class of supramolecular metallogels that rely on metal–ligand coordination extending into 3D structures via coordination and/or other supramolecular interactions, such as hydrogen-bonding, π – π stacking, van der Waals and hydrophobic interactions [3]. MOGs have received growing attention due to the incorporation of coordination interactions [3]. MOG-based materials may have some advantages over the materials prepared by the sol–gel processes which are normally amorphous and lack of short-range order in molecular level in spite of some regularity in mesoscale in some cases (e.g. MCM- and SBA-type silicas) [4].

Compared with traditional sol–gel materials, MOG-based materials may be of potential interest for catalytic applications due

to the following reasons. (a) A large number of organic ligands and metal ions provide a rich pool for active catalyst. (b) Short-range ordered structures of MOGs provide highly regulated metal centres or microenvironment for catalyst immobilisation [5]. (c) Stable organic ligands and metal salts are usually used as MOG precursors, which avoid the tedious manipulation in traditional sol–gel processes. (d) The wet gel itself with catalytically active centre can be also a highly porous catalyst without further processing due to its relatively inert nature compared to silica gels and others [6]. (e) To be the most important, the reversibility of coordination bond formation may make MOGs have some promising properties that traditional supports with rigid bonds (e.g. organic polymers and inorganic oxides) do not have.

In spite of the potential application of MOGs in catalysis, only a few transition metal catalysts have been immobilised by MOGs via direct incorporation [5,6] or post-modification [7] with catalytically active metal ions reported by us and others. In comparison, the latter strategy may offer a versatile entry into transition metal gel catalysts, however, it is still a challenge to synthesise a metallogel with free donor groups since the donor has a tendency to coordinate. Herein, we wish to report the synthesis and characterisation of a functionalised Fe^{3+} –carboxylate MOG based on 5-1*H*-benzo[*d*]imidazole-1,3-dicarboxylic acid (L1). The reversibility of coordination bond formation in the resulting gel was subsequently employed to immobilise Pd(II) coordination catalyst.

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2. Experimental

2.1. Methods

Scanning electron micrographs were recorded by using a Quanta 400 Thermal FE Environment Scanning Electron Microscope or a JSM-6330F Field Emission Scanning Electron Microscope. Transmission electron micrographs were recorded on a JEOL JEM-2010HR microscope. Nitrogen adsorption and desorption isotherms were measured at 77 K on a BELSORP-max system. Pd elemental analyses were performed by inductively coupled plasma atomic emission spectroscopy using a TJA IRIS HR ICP instrument. To prepare the samples for ICP-AES, a wet ash method with HClO₄-H₃PO₄ was used to digest the xerogel. The xerogel was dried in vacuum prior to analysis and a sample of 4.0 mg was added in HClO₄-H₃PO₄ (v:v=5:2, 2 mL) and heated until no yellow fume produced. The mixture was filtered to remove some flottage and diluted with HClO₄-H₃PO₄ to a volume of 25 mL. For a list of the materials used and their symbols, see Table 1.

2.2. Preparation of

2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole [8]

A new method was developed: 3,5-dimethylbenzoic acid (0.76 g, 5 mmol), 1,3-phenylenediamine (0.625 g, 5.8 mmol), polyphosphoric acid (5 mL) and phosphoric acid (3 mL) were heated at 190 °C for 15 h. The dark green reaction mixture was cooled down to about 100 °C, and poured into icy water (100 mL) while stirring to get a black solid. The solid was dissolved in 100 mL of water and the pH was adjusted to 12 with a NaOH solution (2 mol/L). Filtered and washed with ethyl acetate to get a white solid (0.705 g, yield 63%).

2.3. Preparation of 5-1H-benzo[d]imidazole-1,3-dicarboxylic acid (L1)

2-(3,5-Dimethylphenyl)-1H-benzo[d]imidazole (0.305 g, 1.37 mmol) was dissolved in a mixture of *tert*-butanol (8 mL) and water (8 mL). A hot solution of KMnO₄ (2.0 g) in H₂O (20 mL) was added at 80 °C in four portions during the course of 4 h. The reaction was carried out for 28 h. Subsequently a Na₂SO₃ solution was added to quench excess KMnO₄. After stirring for 30 min more, the reaction mixture was filtered to remove MnO₂ and the filtrate was adjusted to acidic using concentrated H₂SO₄ to obtain a white solid. The solid was recrystallised from boiling water to get the final product (0.201 g, yield 52%). L1 is soluble in DMF, DMSO, boiling H₂O, or alkaline solutions, but insoluble in alcohols, acetone, THF, chloroform, diethyl ether, and ethyl acetate. ¹H NMR (300 MHz, DMSO-*d*₆, δ): 8.62 (s, 2H; H_a), 8.55 (s, 1H; H_b), 8.34 (s, 2H; H_c), 7.58 (s, 2H; H_d); IR (KBr): ν = 3410 (vs, O-H), 2930 (m),

1710 (vs, C=O), 1674 (vs), 1449 (w), 1383 (m), 1242 (s, CN), 1175 (w), 749 (w), 677 (w); EI MS (*m/z* (%)): 282 (3) [M⁺].

2.4. Preparation of G1

L1 (11.3 mg, 0.04 mmol) in DMF (2 mL) and Fe(NO₃)₃·9H₂O (24.2 mg, 0.06 mmol) in DMF-H₂O (2 mL, v:v=1:1) were mixed together, and then left to stand. A brown gel was obtained after about 2 days. IR (KBr): ν = 3422 (s, O-H), 2980 (m), 2780 (m), 1620 (m), 1572 (w), 1383 (vs), 1239 (w), 1217 (w), 1158 (w), 757 (w), 713 (w).

2.5. Preparation of G1-Pd

Method a: A solution of Pd(COD)Cl₂ (5.7 mg, 0.02 mmol) in DMF (2 mL) was allowed to stand above a sample of G1. After diffusion for ca. 3 days, the supernatant turned from yellow to colourless and was decanted, and the resultant brown gel was washed with MeCN, yielding a gel, G1-Pd. IR (KBr): ν = 3430 (s, O-H), 1620 (m), 1572 (m), 1440 (m), 1383 (ws), 1111 (w), 713 (w), 631 (w), 472 (w); elemental analysis found (%) for the xerogel of G1-Pd: C 21.16, H 5.23, N 11.60.

Method b: A solution of L1 (11.3 mg, 0.04 mmol) and Pd(COD)Cl₂ (5.7 mg, 0.02 mmol) in DMF (2 mL) were mixed with a solution of Fe(NO₃)₃·9H₂O (24.2 mg, 0.06 mmol) in DMF-H₂O (2 mL, v:v=1:1), and then left to stand. A brown gel was obtained after about 4–5 days.

2.6. Preparation of G2-Pd

A Pd(II)-functionalised gel (G2-Pd) was prepared by placing an acetonitrile solution (2 mL) containing excess Pd(COD)Cl₂ (14.3 mg, 0.05 mol) on top of Fe-BTC gel G2 (prepared by 60.5 mg of Fe(NO₃)₃·9H₂O, and 21.2 mg of H₃BTC in 1 mL of ethanol, each [3g]). After diffusion for 10 days, the supernatant was decanted and the gel washed several times with CH₃CN until the washings were colourless. IR (KBr): ν = 3425 (s), 1630 (s), 1450 (s), 1380 (vs), 758 (w), 712 (m), 623 (w), 461 (w); elemental analysis found (%) for the xerogel of G2-Pd: C 24.60, H 4.46, N 1.72 and for the aerogel of G2-Pd: C 27.06, H 3.99, N 1.46.

2.7. Preparation of aerogels, ag1-Pd and ag2-Pd

The solvent in the wet gel was extracted with liquid CO₂ in a high pressure Soxhlet extractor. The extraction time was 8 h for G1-Pd or 4 h for G2-Pd.

Table 1
List of the materials used and their symbols.

Symbol	Material	Symbol	Material
L1		H ₃ BTC	
G1	Gel synthesised from L1 and Fe(NO ₃) ₃ ·9H ₂ O in DMF-H ₂ O	G2	Gel synthesised from H ₃ BTC and Fe(NO ₃) ₃ ·9H ₂ O in EtOH
g1	Xerogel of G1	g2	Xerogel of G2
G1-Pd	G1 modified with Pd ²⁺	G2-Pd	G2 modified with Pd ²⁺
g1-Pd	Xerogel of G1-Pd	g2-Pd	Xerogel of G2-Pd
ag1-Pd	Aerogel of G1-Pd	ag2-Pd	Aerogel of G2-Pd

2.8. General procedure for the coupling reactions of aryl/pyridyl halides with boronic acids

A typical procedure is given below on the reaction expressed in entry 1 of Table 1. Iodobenzene (102.0 mg, 0.50 mmol), phenylboronic acid (91.4 mg, 0.75 mmol), Na_2CO_3 (159.0 mg, 1.5 mmol), MeOH (5 mL) and G1-Pd (0.5 mol% of Pd(II)), were introduced to a flask under ambient atmosphere. The mixture was stirred with a magnetic stirrer bar at 60 °C. H_2O (10 mL) was added into the resultant mixture and extracted three times with Et_2O (10 mL). The ethereal extract was evaporated to dryness and analysed by GC/MS and NMR spectroscopy. For recovering, the gel was centrifuged after reaction.

Data for 4-(3,5-dimethylphenyl)pyridine: Pale yellow oil. ^1H NMR (300 MHz, DMSO-d_6): δ = 8.57 (d, 2H, $^3J_{\text{H-H}}$ = 5.5 Hz), 7.63 (d, 2H, $^3J_{\text{H-H}}$ = 6.0 Hz), 7.36 (s, 2H), 7.07 (s, 1H), 2.33 (s, 6H).

Data for 3-(3,5-dimethylphenyl)pyridine: Pale yellow oil. ^1H NMR (300 MHz, DMSO-d_6): δ = 8.82 (s, 1H), 8.52 (d, 1H, $^3J_{\text{H-H}}$ = 4.7 Hz), 8.00 (d, 1H, $^3J_{\text{H-H}}$ = 8.0 Hz), 7.43 (m, 1H), 7.30 (s, 2H), 7.04 (s, 1H), 2.34 (s, 6H).

3. Results and discussion

3.1. Gelation study and Pd(II) loading

The ligand 5-1H-benzo[d]imidazole-1,3-dicarboxylic acid (L1, Table 1) was designed with three functional groups in which two carboxylic groups are necessary to coordinate to Fe^{3+} to form a gel network [7], and the imidazole group coordinates to Fe^{3+} less strongly according to the HSAB matching. L1 was synthesised through oxidation of 2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole by KMnO_4 . DMF, DMSO, and other mixed solvents were tested as solvent for gelation and gels were successfully obtained in DMF- H_2O (referred to as G1), DMF or DMF-MeOH, judged by turning the sample upside down (Fig. 1). The time of metallogel formation increased either in DMF or in DMF-MeOH (about 9 days) compared with in DMF- H_2O (2 days). The gel obtained in DMF/ H_2O had visually better mechanical strength. Metal-ligand ratios also played an important role in the gel formation. Gels could be obtained in different L1/ Fe ratios from 1:1, 2:3 to 1:2, while only a weak flowing gel was obtained when the ratio was increased to 2:1. The colour of the metallogels turned gradually from orange to brown with increased L1/ Fe ratios. The gel with L1/ Fe ratio of 1:2 was transparent, and the other gels were turbid. When the gel G1 was heated, no gel-sol transition was observed indicating a robust gel network was formed.

In G1, the hard metal ion Fe^{3+} strongly coordinates to carboxylate groups to form the gel network as shown previously [4], however, Fe^{3+} may also coordinate to the imidazole group less strongly [9]. In contrast, binding of a soft metal ion like Pd^{2+} via



Fig. 1. A photographic image of metallogel G1.

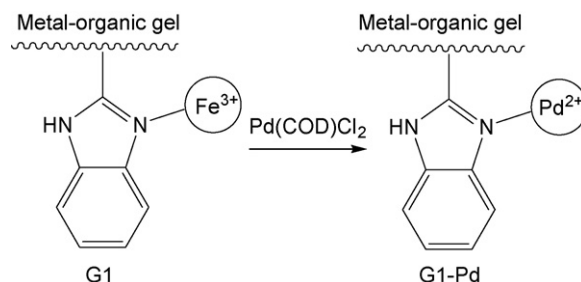


Fig. 2. Schematic representation of use of dynamic metallogel, G1, as a support for catalyst.

the imidazole N atom is favourable [10]. If Pd^{2+} is added to G1, Fe-N(imidazole) bond may cleave and new Pd-N bond may be formed instead due to the reversibility of coordination bond formation [11] (Fig. 2). In addition Pd^{2+} may be more strongly anchored in imidazole-functionalised carboxylate gel network (e.g. G1) than in a “pure” carboxylate gel (e.g. Fe^{3+} -benzenetricarboxylate gel, G2, see below). Such a new strategy may broaden the scope of available gels for catalyst immobilisation, together with other strategies of incorporation of catalytically active units directly in the framework of metallogels (Fig. 3a) [5,6], and of post-modification of metallogels with free groups available for coordination (Fig. 3b) [7].

To prove our hypothesis, two Pd(II)-functionalised gels were prepared via a post-modification method. G1 was modified by placing a DMF or MeCN solution containing $\text{Pd}(\text{COD})\text{Cl}_2$ in with the molar ratio of Pd:L1 = 1:2 on top of the gel G1. After diffusion, a brown Pd(II) gel, G1-Pd, was obtained. For comparison, a Pd(II)-functionalised gel (G2-Pd) was prepared by topping a Fe-tricarboxylate gel (G2, prepared by $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1,3,5-benzenetricarboxylic acid in ethanol) with a MeCN solution containing excess $\text{Pd}(\text{COD})\text{Cl}_2$. It is worth mentioning that G1-Pd could also be prepared via direct gelation by mixing a DMF solution of L1 and $\text{Pd}(\text{COD})\text{Cl}_2$ and a DMF/ H_2O solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with prolonged gelation time (4–5 days). Although the latter method gave a more homogeneous gel catalyst, all the samples mentioned below were prepared by the former method in order to give a blueprint of the MOG route to supported catalyst.

The resulting gels were subjected to elemental analyses. The weight percentage of Pd atoms in the xerogel of G1-Pd (g1-Pd) was determined to be 3.75% by inductively coupled plasma spectroscopic analysis, higher than that in g2-Pd (2.28%) even if only a limited amount of $\text{Pd}(\text{COD})\text{Cl}_2$ was used for G1 and excess for G2. The theoretical Pd value would be 5.3% if 100% of the used Pd(II) was immobilised. The results show that the entrapment of Pd was more efficient in G1 than in G2 as expected, resulting in a concentration decrease of the supernatant from $10^{-2} \text{ mol L}^{-1}$ to $2.4 \times 10^{-3} \text{ mol L}^{-1}$ after standing for 3 days. The surface analysis by XPS revealed the presence of Fe and Pd in both the power xerogel samples of G1-Pd and G2-Pd. Both the XPS spectra showed a

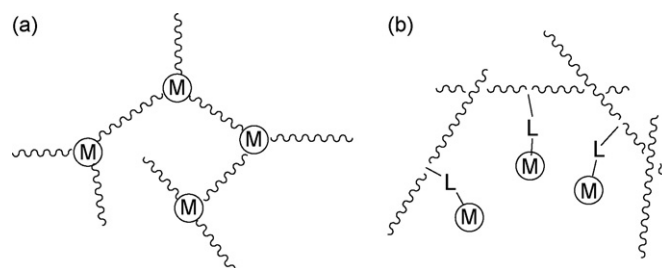


Fig. 3. Immobilisation of transition metal catalysts by metal-organic gels via direct incorporation (a) or post-modification (b).

Table 2
Comparison of $\Delta\nu$ for the gels/xerogels/aerogels.

	$\nu_{\text{asym}}(\text{CO}_2)/\text{cm}^{-1}$	$\nu_{\text{sym}}(\text{CO}_2)/\text{cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$
L1	1710	1449	261
g1	1620	1440	180
g1-Pd	1620	1440	180
H ₃ BTC	1703	1450	253
g2	1630	1450	180
g2-Pd	1630	1450	180
ag2-Pd	1630	1450	180

signal at 712 eV in the Fe 2p_{3/2} region, and analysis in the Pd 3d_{3/2} and 3d_{5/2} regions showed two signals at 338 eV and 343 eV, respectively, confirming attachment of the Pd(II) ions to the gel network. The Pd/Fe ratio was calculated to be about 1:2 for g1-Pd.

FT-IR spectra confirmed the presence of carboxylate in the metal coordination sphere for the gels and the Pd(II) gels (Table 2). In the gels, the bands due to the coordinated carboxylates are shifted to lower frequencies with respect to the free ligands. For the xerogels, strong bands at around 1380 cm⁻¹ are due to NO₃⁻. The difference between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ of around 180 cm⁻¹ suggests that the carboxylate ligands are bridging–chelating. The FT-IR spectra of the Pd-loaded gel, G1-Pd and G2-Pd, generally displayed similar bands to that of G1 and G2, respectively.

The aerogels were prepared by supercritical CO₂ drying to remove the solvent in the gel matrix. The aerogels were subjected to scanning electron micrograph (SEM) and SEM images of the aerogels of G1-Pd (Fig. 4a) and G2-Pd (Fig. 4b) revealed each an interconnected macroporous network of globular nanometer-sized particles of diameter ca. 100 nm. Transmission electron microscopy (TEM) images of the xerogel of G1-Pd confirmed a continuous

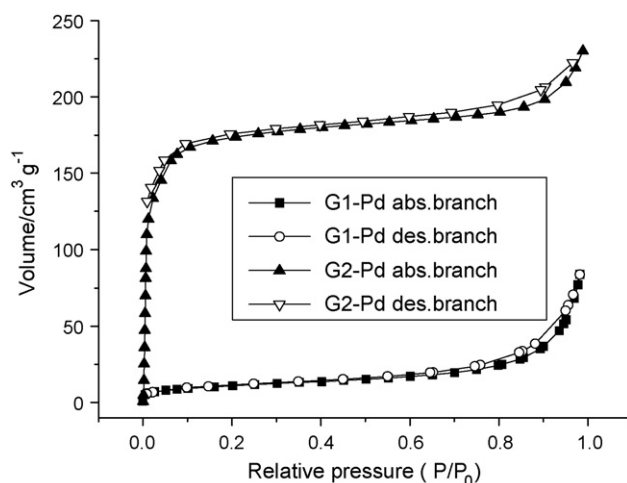


Fig. 5. Nitrogen adsorption–desorption isotherm of the aerogels of G1-Pd and G2-Pd.

amorphous network with connected particles (Fig. 4c and d). Adsorption isotherm of both the aerogels performed using N₂ gas as the adsorbate at liquid nitrogen temperature exhibited a type IV adsorption branch with a combination of H1- and H3-type hysteresis loops (Fig. 5) [12]. Detailed BET analyses showed that the aerogel of G1-Pd has a BET surface area of 38.8 m² g⁻¹ and total pore volume of 0.13 cm³ g⁻¹. In contrast, the aerogel of G2-Pd is highly porous with the BET surface area of 482 m² g⁻¹ and total pore volume of 0.36 cm³ g⁻¹. In both samples, the rise in the N₂ uptake at $P/P_0 > 0.8$ in the adsorption isotherms may arise in part

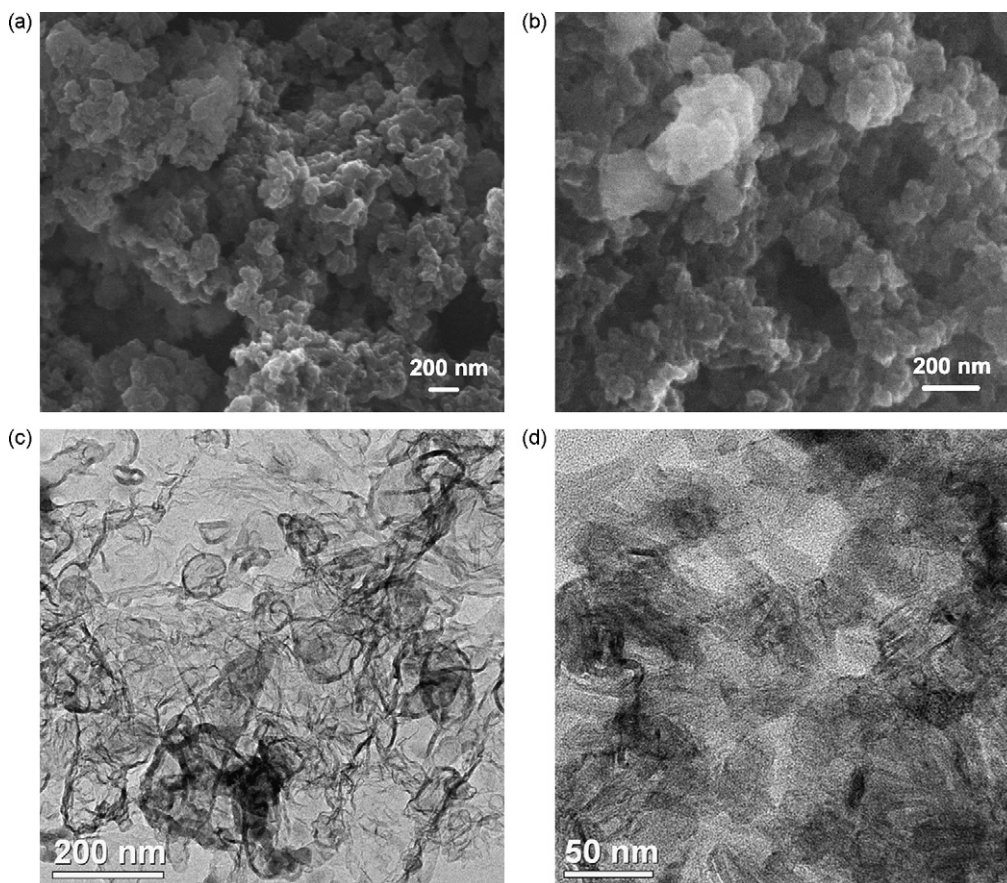


Fig. 4. (a and b) SEM images of the aerogels of G1-Pd (a) and G2-Pd (b), and (c and d) TEM images of the xerogel of G1-Pd.

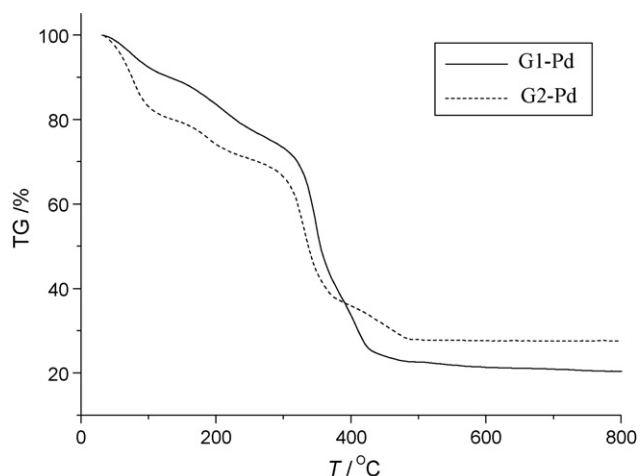


Fig. 6. TG curve of the aerogels of G1-Pd and G2-Pd under nitrogen flow.

from textural interparticular porosity associated with the meso- and macro-structures of the samples. The reduced microporosity for the aerogel of G1-Pd may result from the lower concentration of the gelator, which led to closure of micropores in the drying process. The aerogel of G2-Pd contained both micropores and mesopores, which microporous nature of the network was confirmed by the steep uptake of nitrogen at very low relative pressures [13].

The thermal stability of the aerogels was investigated with thermogravimetric analysis (TGA) under nitrogen (Fig. 6). From room temperature to 267 °C, an observed 23.7% weight loss for the aerogel of G1-Pd may be due to physisorbed or chemisorbed water or ethanol and a weight loss of 56.4% above 267 °C is accounted for the framework decomposition. The aerogel of G2-Pd showed similar thermal behaviour, and the TG analysis showed a weight loss of 29.1% from room temperature to 246 °C and the framework collapsed from 246 °C to 500 °C.

3.2. Catalytic activity

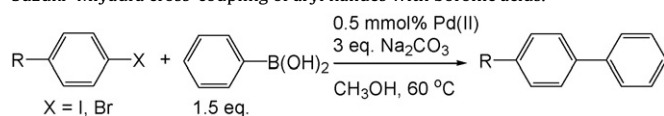
The catalytic activity of G1-Pd arising from its palladium(II) centre was evidenced in the Suzuki–Miyaura cross-coupling reac-

tion (Table 3). The coupling reactions were examined in different solvents, such as MeOH, DMF, and H₂O at 60 °C under aerobic conditions with 0.5 mol% catalyst loading. An excellent yield of 91% after 15 min was achieved in MeOH in the reaction of bromobenzene and phenylboronic acid, whereas poor yields were achieved in DMF (9% after 15 min, 18% after 5 h) or H₂O (10% after 15 min). Thus MeOH was chosen as solvent in the following reactions. G1-Pd efficiently catalysed the coupling reactions of aryl halides with phenylboronic acids. The coupling reactions of iodobenzene with phenylboronic acid gave nearly quantitative yield catalysed by the wet gel of G1-Pd within 0.5 h. The wet gel of G1-Pd also showed excellent activity towards aryl bromides. 4-Bromoacetophenone could couple with boronic acid quantitatively after 0.5 h. The reactions of bromobenzene and 4-bromoanisole with phenylboronic acid afforded yields of 91% after 15 min and 72% after 0.5 h, respectively. As expected, aryl chlorides are stubborn and G1-Pd showed relatively modest activity towards them. Chlorobenzene, 4-chloroacetophenone or 4-chloroanisole did not give attractive results catalysed by the wet gel or xerogel, and a best yield of 27% was achieved for chlorobenzene after 3.0 h in DMF at 110 °C.

G1-Pd was also shown to be an effective catalyst in the coupling reactions of bromopyridines and 3,5-dimethylphenylboronic acid/3,5-difluorophenylboronic acid (Table 4). However, G1-Pd had no activity in the coupling of aryl halides (iodobenzene or 4-bromoacetophenone) with 4-pyridylboronic acid in the tested reactions. The catalytic activity of the xerogel of G1-Pd was also examined. As expected, the xerogel generally showed lower activity compared to the wet gel probably due to the lower surface area and decreased substrate accessibility of catalytic sites.

To study its origin of the excellent catalytic activity of G1-Pd, coupling of phenylboronic acid and 4-bromoanisole were performed as a control reaction (Fig. 7) due to its importance in comparing highly active palladium catalysts [14]. In contrast to the good yield of 72% after 0.5 h catalysed by the gel of G1-Pd, no catalytic activity was observed in the absence of palladium (no Pd, G1 itself as catalyst), and only poor activity was achieved in the presence of only Pd(COD)Cl₂ (1% of Pd) and 2 equiv. of benzimidazole (17% yield after 2 h), or in the presence of Pd(COD)Cl₂ and L1 only with no gelation (12% yield after 5 h). These results confirm that the observed good catalytic behaviour is unique to the immo-

Table 3
Suzuki–Miyaura cross-coupling of aryl halides with boronic acids.^a



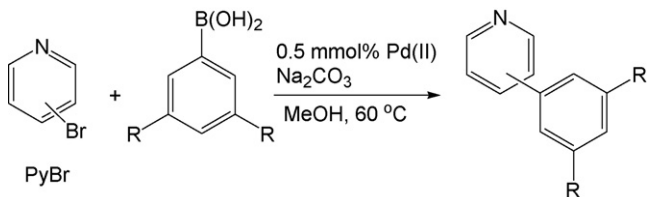
Entry	Catalyst	X, R	GC yield/% (time/h)
1	G1-Pd (wet gel)	X=I, R=H	93 (0.25), >99 (0.5)
2	G1-Pd (xerogel)	X=I, R=H	92 (0.25), >99 (0.5)
3	G1-Pd (wet gel)	X=Br, R=H	91 (0.25) ^b
4	G1-Pd (wet gel)	X=Br, R=COCH ₃	95 (0.25), >99 (0.5)
5	G1-Pd (wet gel)	X=Br, R=OCH ₃	54 (0.25), 72 (0.5), 74 (2.0)
6	G1-Pd (xerogel)	X=Br, R=OCH ₃	29 (0.25), 57 (0.5), 69 (1.0), 71 (2.0)
7	G1-Pd (wet gel)	X=Cl, R=H	20 (0.25), 26 (0.5), 29 (1.0), 46 (11) ^c
8	G1-Pd (xerogel)	X=Cl, R=H	8 (0.5), 10 (2.0)
9	G1-Pd (wet gel)	X=Cl, R=COCH ₃	14 (1.0), 18 (3.0) ^c
10	G1-Pd (xerogel)	X=Cl, R=COCH ₃	6 (1.0), 12 (3.0) ^c
11	G1 (no Pd)	X=I, R=H	Trace (2.0)
12	G2-Pd (wet gel)	X=Br, R=OCH ₃	10 (0.25), 12 (0.5), 19 (1.0), 30 (2.0), 44 (3.0)
13	Pd(COD)Cl ₂ (1 mol%)	X=Br, R=OCH ₃	16 (1.0), 24 (2.0), 26 (3.0)
14	Pd(COD)Cl ₂ (1 mol%) + 2 equiv. benzimidazole	X=Br, R=OCH ₃	7 (0.25), 15 (1.0), 17 (2.0)
15	Pd(COD)Cl ₂ + L1	X=Br, R=OCH ₃	12 (0.5) ^b

^a Reaction conditions: 0.5 mmol of aryl halide, 0.75 mmol of PhB(OH)₂, 0.5 mol% of Pd(II) of the catalyst, 1.5 mmol of Na₂CO₃, 6 mL of CH₃OH at 60 °C under ambient atmosphere.

^b Yield remained unchanged till 5 h.

^c Performed in DMF at 110 °C.

Table 4
Suzuki–Miyaura cross-coupling catalysed by 0.5 mol% of Pd(II) of G1–Pd.



Entry	Catalyst	PyBr	R	GC yield/% (time/h)
1	Wet gel	4-Bromopyridine	R = Me	70 (0.25), 97 (0.5), >99 (1.0)
2	Xerogel	4-Bromopyridine	R = Me	56 (0.25), 82 (0.5), 91 (0.75), >99 (1.25)
3	Wet gel	3-Bromopyridine	R = Me	95 (0.25), >99 (0.5)
4	Xerogel	3-Bromopyridine	R = Me	63 (0.25), 71 (1.0), 77 (2.0)
5	Wet gel	2-Bromopyridine	R = Me	39 (0.25), 42 (0.5), 67 (1.0), 68 (2.0), 76 (3.0), 86 (6.0)
6	Xerogel	2-Bromopyridine	R = Me	10 (0.25), 30 (1.0), 32 (2.5)
7	Wet gel	4-Bromopyridine	R = F	58 (3.0)
8	Wet gel	3-Bromopyridine	R = F	13 (1.0), 39 (3.0), 77 (7.0), 93 (27)
9	Xerogel	3-Bromopyridine	R = F	2 (0.5), 4 (4.0), 8 (5.0)
10	Xerogel	2-Bromopyridine	R = F	3 (0.5), 10 (1.0), 16 (2.0)

bilisation of Pd(II) in the gel matrix of G1–Pd. In fact, solid-phase catalysts are commonly difficult to retain or raise their activities compared to their homogeneous counterparts, even if a better performance of immobilised catalysts than homogeneous catalysts has been reported in a limited number of cases, for example, some solid-supported Pd catalysts show higher activities than homogeneous catalysts [15]. The higher activity of G1–Pd is probably due to the higher stability and confined environment or cooperativity resulting from the entrapment of catalytic centres in the supporting gel network.

As an important feature of G1–Pd, its dynamic support property arising from the introduction of benzimidazole group was evidenced in the comparison of the catalytic activity of G1–Pd and G2–Pd (no benzimidazole group, “purely” carboxylate) (Fig. 7). In the coupling reaction of 4-bromoanisole with phenylboronic acid, a lower modest yield of 44% was achieved after 4 h catalysed by the gel of G2–Pd. Thus the introduction of benzimidazolyl group is believed to play an important role in the improvement of catalytic activity of G1–Pd. The results therefore agree well with our hypothesis that G1 is dynamic.

Interestingly, G1–Pd could be reused for several times in contrast to its homogeneous counterparts (Table 5). The gel catalyst

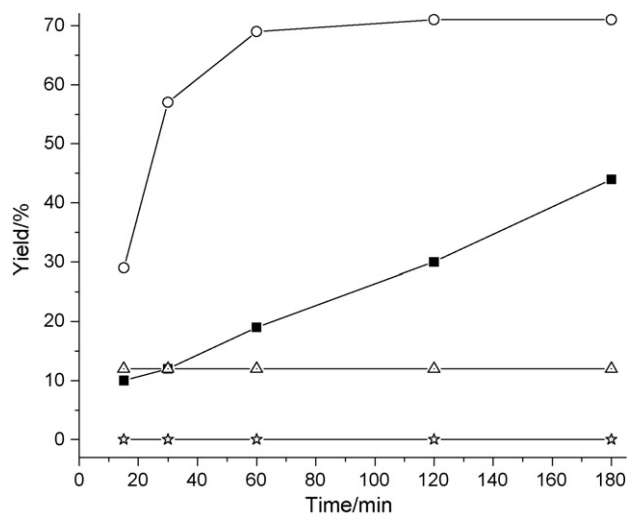


Fig. 7. Suzuki–Miyaura coupling of 4-bromoanisole and phenylboronic acid (catalyst: circle, G1–Pd (with 0.5 mol% of Pd); square, G2–Pd (with 1 mol% Pd); triangle, L1/Pd(COD)Cl₂ = 2:1 (with 0.5 mol% of Pd); star, G1 or G2).

Table 5
Suzuki–Miyaura coupling of 4-bromopyridine with 3,5-difluorophenylboronic acid using G1–Pd as recovered catalyst.

Entry	Run	Time/h	GC yield/%
1	1st	3	58
2	2nd	3	53
3	3rd	3	45
4	4th	16	26

was readily recovered by simple filtration due to their heterogeneous nature. As an example, the gel could be reused for three runs with yields of 58%, 53%, and 45%, respectively, in the reaction of 4-bromopyridine and 3,5-difluorophenylboronic acid. The catalytic activity was gradually diminished in the first three runs, and thereafter the activity dropped considerably (26% yield, after 16 h) in the fourth run. This trend was also observed for the xerogel of G1–Pd, G2–Pd and other reactions (e.g. the coupling of 4-bromopyridine and 3,5-dimethylphenylboronic acid), which was also reported for some other supported Pd catalysts [16]. It was to note that no palladium black was formed and collapsing of gels did not appear in the reactions. The reactivity loss is attributed to slow continuous leaching of the Pd active component resulting from destruction of the gel catalyst by the reaction medium. Therefore stable MOG systems need to be investigated for future gel catalysts.

4. Conclusions

In summary, we have described the anchoring of palladium(II) to a dynamic Fe–carboxylate network by a metal–organic gel methodology and their use as efficient and recoverable catalysts for Suzuki–Miyaura coupling of aryl/pyridyl bromides with boronic acids under mild conditions. The approach may theoretically work for other soft metal catalysts such as Pt, Rh, and Ir as well. Interestingly, the supported Pd²⁺ gel catalyst showed enhanced catalytic activity in the Suzuki coupling under mild conditions, compared with its homogeneous analogue. This behaviour is observed for metallogel for the first time, to the best of our knowledge. It may offer a new approach to active supported catalysts. The recyclability of the catalyst was performed in the reactions of 4-bromopyridine and 3,5-difluorophenylboronic acid or 3,5-dimethylphenylboronic acid. The catalyst could be reused for several times.

As a novel strategy, the present method paves a way to employ the unique dynamic property of MOGs to immobilise transition metal catalysts. The Fe–N(imidazole) bond in the Fe–carboxylate gel, G1, may break to form new Pd–N bond in the presence of

Pd²⁺. This bond cleavage and generation arises from their different binding ability with imidazole. Different from direct functionalisation with organic ligand or catalytically active metal complex via sol–gel method or other methods [17], the reversibility of coordination bond formation in MOGs may offer a new chance for immobilisation of transition metal complexes. Future work is to develop chemically, mechanically and thermally stable MOG in various reaction media for heterogeneous catalysts. This approach may also be interesting in preparation of various metal-containing materials by incorporation of metal complexes into a networked matrix.

Acknowledgements

We gratefully acknowledge the SEM (SRF for ROCS), the NSF of China (Grants 20525310, 20773167, J0730420) and the 973 Program of China (Grant 2007CB815302) for support.

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