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Research Note

Ossification: A new approach to immobilize metal complex catalysts—applications to carbonylation and Suzuki coupling reactions

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Abstract

A simple approach for immobilization of transition metal complexes is reported here based on the transformation of the complex into its intrinsically insoluble counterpart, thus generating solid molecular catalysts. This approach that we call "ossification" is based on a principle, in which the water-soluble analogues of the metal complexes are precipitated out from aqueous solutions as insoluble ionic ensembles having catalytically active metal-centered coordination environments and robust framework. The approach has been illustrated for Pd complex catalyzed carbonylation and Suzuki coupling reactions. "Ossification" was found to be an economically and environmentally attractive alternative to other exotic immobilization methodologies.

Keywords: Immobilization; Heterogeneous catalysts; Palladium complex; Ossification; Carbonylation; Suzuki coupling

1. Introduction

The homogeneous metal complex catalysts are well known for their high activity and selectivity for a wide variety of reactions [1,2]. Despite several discoveries of novel metal complex catalysts and their applications for efficient synthesis of a variety of products, their utility has been limited due to the difficulties in catalyst–product separation and economic utilization [3]. An obvious solution is to develop an appropriate methodology for immobilization of the soluble catalysts to give active, selective, stable, and non-leaching catalysts. Over the years, several attempts have been made to immobilize homogeneous catalysts based on the principles of phase differentiation, which led to the development of biphasic catalysis [4], immobilization using anchoring, tethering, encapsulation techniques, and precipitation of products/catalysts by solvent selection/manipulation of physical parameters [3]. In only a few cases have truly heterogenized catalysts with commercially acceptable performance been developed, and the search for new but simple methodologies is open to investigation. Recently, Lin et al. [5,6] reported hybrid solids composed of modified zirconium phosphonates with pendant chiral ligands holding Ru catalysts for the asymmetric hydrogenation reactions. These catalysts are efficient, but the handling of highly sensitive chiral phosphonates, the longer reaction times (∼20 h), and the tedious and intricate synthetic methodology of the catalysts are some of the most important drawbacks of the system. In this report, we present a very simple and efficient immobilization approach in which the metal complex is first converted to its water-soluble analogue by known methods and then transformed to almost completely insoluble forms.

Our new approach of immobilization called *ossification* involves the preparation of inherently insoluble catalytically active molecules by a process, resembling the self-assembly of robust insoluble biomaterials (e.g., shells, bones, coral reefs) from simpler soluble precursor molecules and ions. In our two-step protocol of synthesis, the metal complexes are first made aqueous-soluble by introducing non-coordinating anionic functionalities such as sulphonate ($–SO_3^-$), carboxylate ($–CO_2^-$), and others, to any of the ligands by well-established methods [7,8]. This derivatization of the ligand and thus of the complex is followed by their transformation to solid materials/precipitates by treatment with the heavier group IIA cations, such as Sr^{2+},

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Ba^{2+}, and others. These group IIA metal sulphonates are inherently insoluble in water and most of the organic solvents, and are high-melting and non-subliming solids. Thus, we can obtain molecular solids with intact catalytically active transition-metal-centered environments (see the schematic in Fig. 1) with a solid appendage, and thereby a whole new range of molecularly heterogenized metal complex catalyst entities, by an extremely simple synthesis approach. To prove the general applicability of the protocol, we have chosen different palladium complex catalysts for application to different classes of reactions with diverse reaction conditions. We have selected two important classes of C–C bond formation reactions: hydrocarboxylation and Suzuki cross-coupling reactions.

We selected a class of palladium complex catalysts having one hemilabile chelating ligand as a benchmark. The $N^{\cap}O$ and $N^{\cap}N$ chelating ligands selected were *pyca* [2-picolinate], *acpy* [2-acetylpyridine], *pycald* [pyridine-2-carboxaldehyde], and *bipy* [2,2′-bipyridyl]. The Pd(pyca)(PPh_3)(OTs) and other similar complexes were synthesized as described previously [9,10]. The complexes were derivatized by simply replacing the PPh_3 ligand with its –SO_3H derivative, triphenylphosphine trisulphonate (TPPTS), thus forming aqueous-soluble counterparts [11,12] [e.g., Pd(pyca)(TPPTS) complex] by a partitioning technique. The regulated addition of these aqueous solutions to a solution of Ba^{2+} or Sr^{2+} produced a pale-yellowish precipitate. The ossified complexes were designated as *ossified*-Pd(pyca)(TPPTS) (catalyst 1A), *ossified*-Pd(acpy)(TPPTS) (catalyst 1B), *ossified*-Pd(pycald)(TPPTS) (catalyst 1C), and *ossified*-Pd(bipy)(TPPTS) (catalyst 1D). The catalytic materials may be empirically represented as $Ba_{3x}[Pd(L)(TPPTS)]_{2y}\cdot zH_2O$, where $x, y, z \geqslant 1$ (integer) and L is the bidentate chelating ligand as mentioned earlier. The characterization of these catalysts and their performances for carbonylation and Suzuki coupling reactions are discussed below.

2. Experimental

2.1. Ossification of Pd complexes

A typical two-step ossification process for synthesis of immobilized Pd complexes is described here, using Pd(pyca)-(PPh_3)(OTs) complex as a representative example. In the first step, Pd(pyca)(PPh_3)(OTs) complex (0.357 g, 0.5 mmol) was dissolved in $CHCl_3$ (7 mL), then partitioned with an aqueous solution of TPPTS-Na salt (0.286 g, 0.5 mmol in 10 mL H_2O) to get a yellow solution. Only stoichiometric amount of TPPTS was used for synthesis of a pure aqueous-soluble complex to avoid any excess of free TPPTS in aqueous solution of the complex. Washing the aqueous phase with organic solvent is necessary to remove any adhering organic-soluble precursor complex; thus, this aqueous phase was washed thoroughly with $CHCl_3$ to remove all organic-soluble precursors. In the second step, regulated addition of this aqueous solution to a saturated aqueous solution of $Ba(NO_3)_2$ (10 mL) with vigorous stirring under argon blanket immediately yielded pale yellow precipitate. The slurry was stirred for 2 h at room temperature, for another 4 h at 333 K, and then filtered. Residue was subjected to Soxhlet extraction treatment with water and acetone for 12 h each and dried in air. All of the other catalysts (catalysts 1B, 1C, and 1D) were synthesized in the same fashion. The synthesized catalysts were characterized using various techniques, including powder XRD and ^{31}P CP MAS NMR using a Bruker MSL 300-MHz instrument. The ^{31}P NMR spectra were recorded at 202.456 MHz using 85% H_3PO_4 as an external standard. X-ray photoelectron spectra (XPS) of the catalysts were recorded on a VG-Microtech ESCA 3000 spectrometer using the MgK_α emission ($E = 1253$ eV) under a vacuum of $\sim 10^{-9}$ Torr. Scanning electron microscopy (SEM) was performed using a Philips XL 30 instrument, with the catalysts suspended in isopropanol and cast on gold-plated discs, followed by drying under vacuum and coating with a conducting material.

2.2. Carbonylation reactions

Hydrocarboxylation[1] reactions were carried out in a 50-mL Parr autoclave reactor composed of Hastelloy C-276 material following a procedure similar to that described previously [9]. For a typical reaction, the solid catalyst and the liquid-phase reactant/solvent were charged in the reactor, sealed, and flushed. The contents were heated to the desired temperature, and then the reactor was filled with CO to the desired pressure The progress of the reaction was followed by observing the pressure drop in the CO reservoir as a function of time, and the reaction was stopped on completion of CO absorption. Afterward, the reactor was brought to ambient temperature, its content gas was released and flushed three times with N_2, and liquid-phase samples were analyzed for reactant/product composition using a HP GC 6890 gas chromatograph fitted with a HP-FFAP capillary column (25 m × 0.33 mm × 0.2 µm). Gas chromatography–mass spectroscopy (GC-MS) analyses of the samples were performed using an Agilent 5973 N Mass Selective Detector attachment.

2.3. Suzuki cross-coupling reactions

For a typical Suzuki reaction experiment, the necessary liquid reactants and solid catalyst were charged in a round-bottomed flask fitted with a condenser and refluxed for a specified time. The intermediate samples were collected, and reaction progress was monitored by GC. The final reaction mixture after cooling was analyzed for the quantitative composition of reactants and products by GC using a HP GC 6890 device fitted with a HP-5 MS capillary column (30 m × 0.25 mm × 0.25 µm). Products were identified by GC-MS using a Agilent 5973 N Mass Selective Detector, using a similar capillary column.

3. Results and discussion

Catalysts 1A, 1B, 1C, and 1D were characterized to gain insight into the nature of ossified catalysts before evaluation of

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[1] Hazardous CO involved, authors suggest safe and expert handling during experiments.

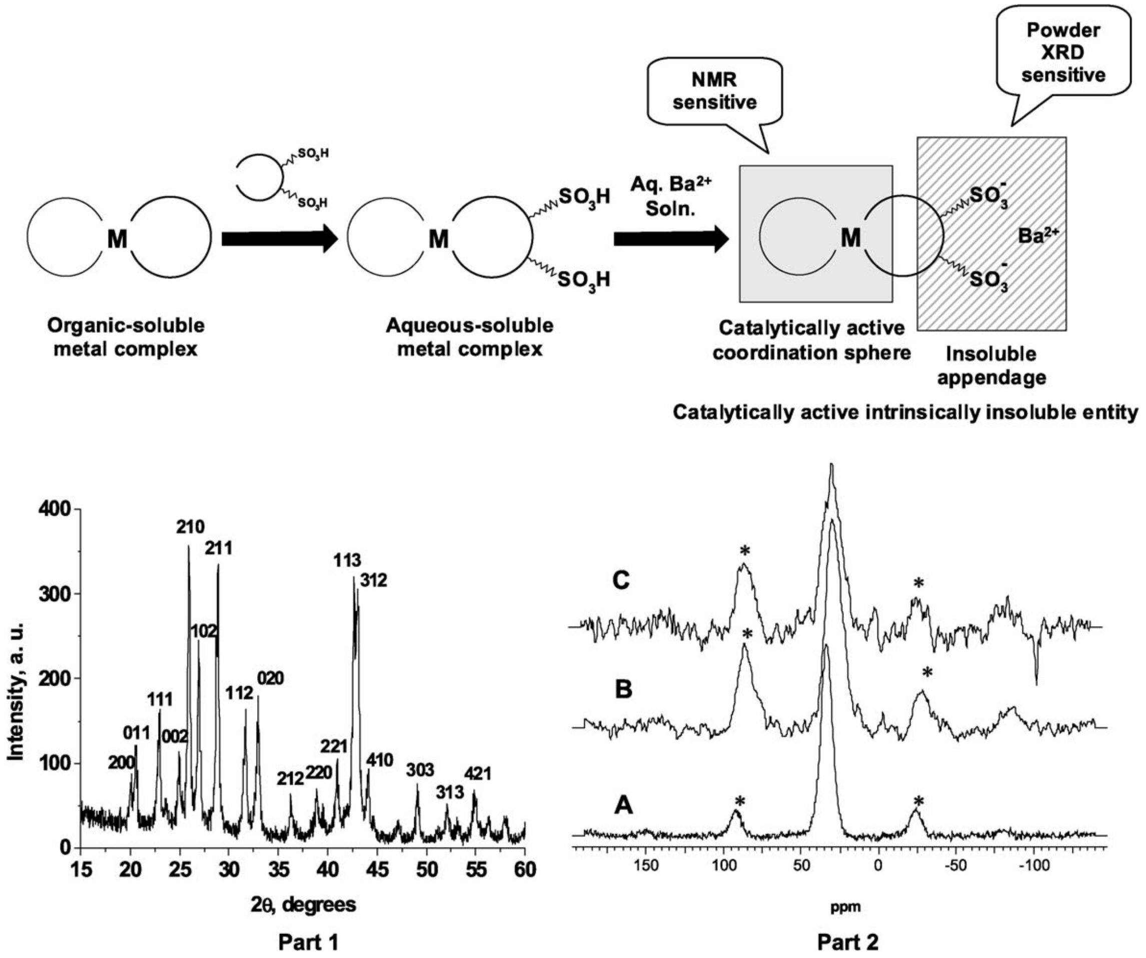
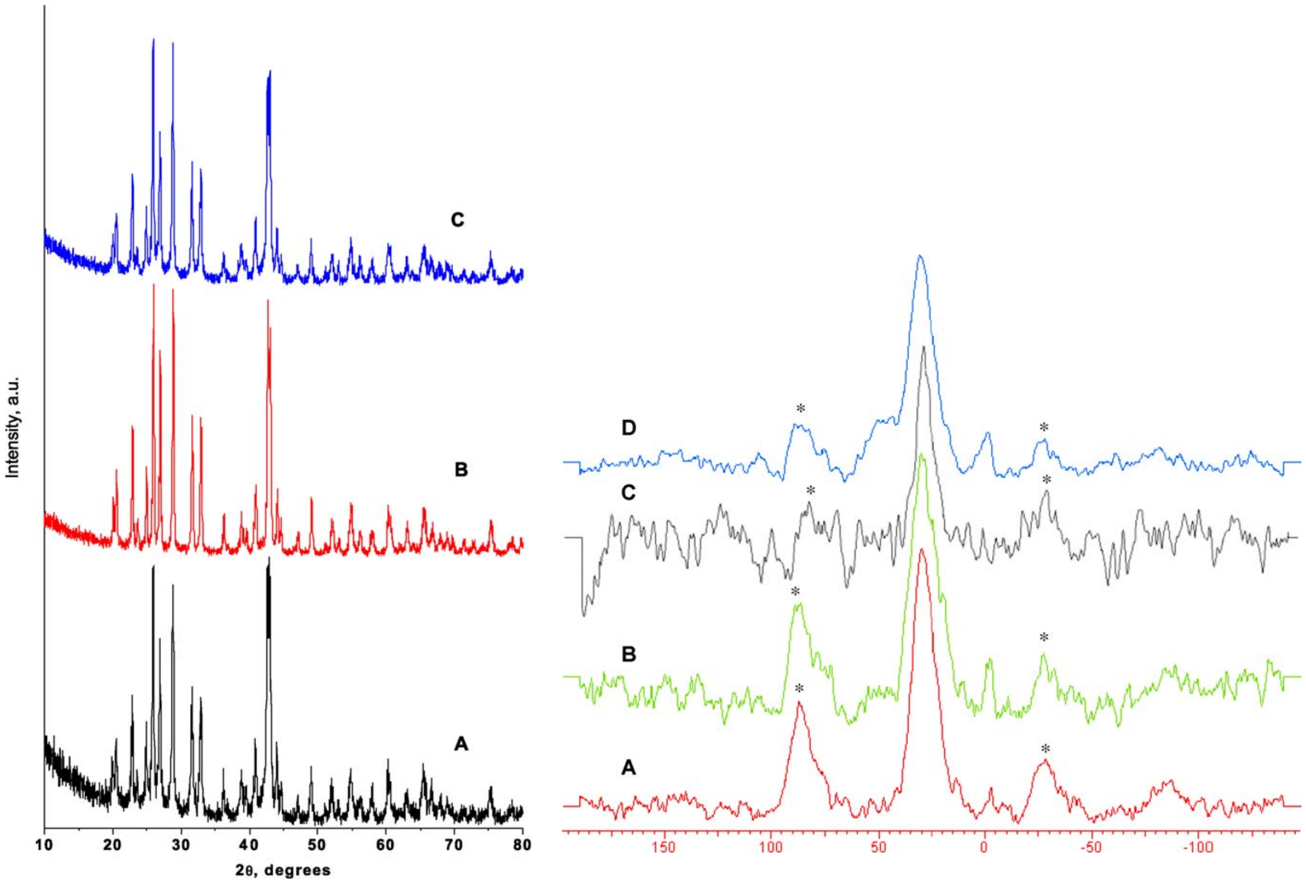


Fig. 1. Schematic representation of ossification methodology showing the characterization strategies. Part 1: Powder XRD pattern of Ba-salt of Pd(pyca)(TPPTS) complex [catalyst 1A]. The numbers inside the graph are the Miller indices of the respective Bragg's planes. Part 2: ^{31}P CP MAS NMR spectra of catalysts. (A) Pd(pyca)(PPh$_3$)(OTs), (B) ossified Pd(pyca)(TPPTS) complex using barium [catalyst 1A], (C) catalyst 1A after 4 recycles. * in NMR spectra represent sidebands at 7 kHz.

their catalytic performance. The powder XRD pattern of the *ossified*-Pd(pyca)(TPPTS) (catalyst 1A) complex is shown in Fig. 1, Part 1. The formation of the Ba-sulphonate catalyst composite (Ba salt of the sulphonated triphenylphosphine coordinated to the Pd center) can be confirmed from the characteristic d-values, which are similar to those in the literature for inorganic BaSO$_4$, with very slight variation in the intensities of the principle peaks. The powder XRD patterns of the Ba-ossified forms of other complexes (catalysts 1B, 1C, and 1D) showed similar results (Fig. 2, Part I), proving the formation of the Ba–sulphonate ion pair and generality of the synthesis protocol. Solid-state ^{31}P CP-MAS NMR experiments were used to investigate the Pd–P linkage after ossification. The spectrum of the pure Pd(pyca)(PPh$_3$)(OTs) complex (Fig. 1, Part 2, curve A) showed an intense peak at δ_{iso} 33.44 ppm, corresponding to the single P atom in the complex. The spectrum for the ossified counterpart (catalyst 1A) showed a chemical shift of δ_{iso} 29.83 ppm (singlet) (Fig. 1, Part 2, curve B). However, the ^{31}P NMR of the water-soluble complex Pd(pyca)(TPPTS)(OTs) in D$_2$O showed two signals at δ 36.13 ppm (N *cis* to TPPTS, weak) and δ 35.31 ppm (N *trans* to TPPTS, strong) [12]. This can be attributed to the introduction of the –SO$_3$H group into the phenyl rings of PPh$_3$, which makes the P atom more electron-deficient, causing a downfield shift compared with the organic-soluble counterpart. For the ossified complex, formation of the solid Ba–sulphonate ion pair and the lattice effects quench the electron-withdrawing effect of the –SO$_3^-$ group; in addition, the reduced mobility in the solid state creates an upfield shift of the ^{31}P signal. The spectrum of Ba salt of free TPPTS shows a singlet at δ_{iso} of −4.3 ppm. The absence of any such signal for the ossified complex shows that the Pd complex maintained its integrity after ossification. The ^{31}P CP-MAS NMR spectra of the other ossified complexes (catalysts 1B, 1C, and 1D) also showed formation of the Ba–sulphonate ion pair and retention of integrity of the complexes (Fig. 2, Part II). The appearance of the peak positions at slightly different positions for the different complexes were in compliance with the stereo-electronic outplay of the respective chelating ligands. A variation of nucleophilicity of ligands in the order as pyca > acpy > pycald > bipy was also evident from the ^{31}P signals of their respective ossified complexes. The FTIR data for ossified Pd-pyca complex (catalyst 1A) showed Pd–N, O=C–O, and C=O stretching vibrations at 568, 1327, and 1667 cm^{-1}, respectively, which agree nicely with those of the



Part I

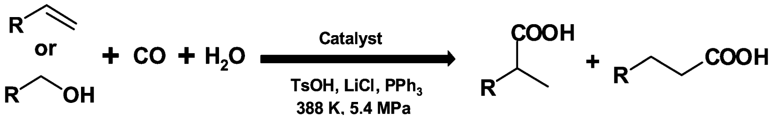
Part II

Fig. 2. Characterization of the ossified Pd-complexes using Ba^{2+} ions. Part I: Powder XRD patterns of (A) Pd(acpy)(TPPTS) complex [catalyst 1B], (B) Pd(pycald)(TPPTS) complex [catalyst 1C], (C) Pd(bipy)(TPPTS) complex [catalyst 1D]. Part II: ^{31}P CP-MAS NMR spectra of the ossified catalysts using Ba^{2+} ions; (A) ossified Pd(pyca)(TPPTS) complex [catalyst 1A], (B) ossified Pd(acpy)(TPPTS) complex [catalyst 1B], (C) ossified Pd(pycald)(TPPTS) complex [catalyst 1C], (D) ossified Pd(bipy)(TPPTS) complex [catalyst 1D]. * in the spectra indicate the side bands at 7 kHz.

pure complex (568, 1330, and 1667 cm^{-1}, respectively). The scanning electron microscopy (SEM) images of the ossified complex 1A showed irregular polyhedral macrocrystallites with an average size of 450 nm (see supplementary information, Fig. S1). The XPS results of representative ossified catalyst 1A are as follows (see supplementary information, Fig. S2). The peaks at 342.9 and 337.6 eV indicate the $3d_{3/2}$ and $3d_{5/2}$ states of Pd(II), with the characteristic band gap of 5.3 eV. Similarly, peaks at 804.7 and 789.2 eV are indicative of the $3d_{3/2}$ and $3d_{5/2}$ states of Ba(II), respectively, with the characteristic 15.5 eV band gap. The other elements also matched in the binding energy values of their respective oxidation states. The other ossified Pd-complexes (catalysts 1B, 1C, and 1D) showed similar results in XPS. The synthesis methodology also involved Soxhlet extraction of the catalyst materials using water and acetone for 12 h each, which showed no leaching of the Pd or Ba in to the waste solvents. These confirmed our immobilization strategy on stability aspect and the immobilized Pd-complex catalysts (otherwise, the derivatized Ba sulphonates) were no less stable than our model $BaSO_4$ molecule.

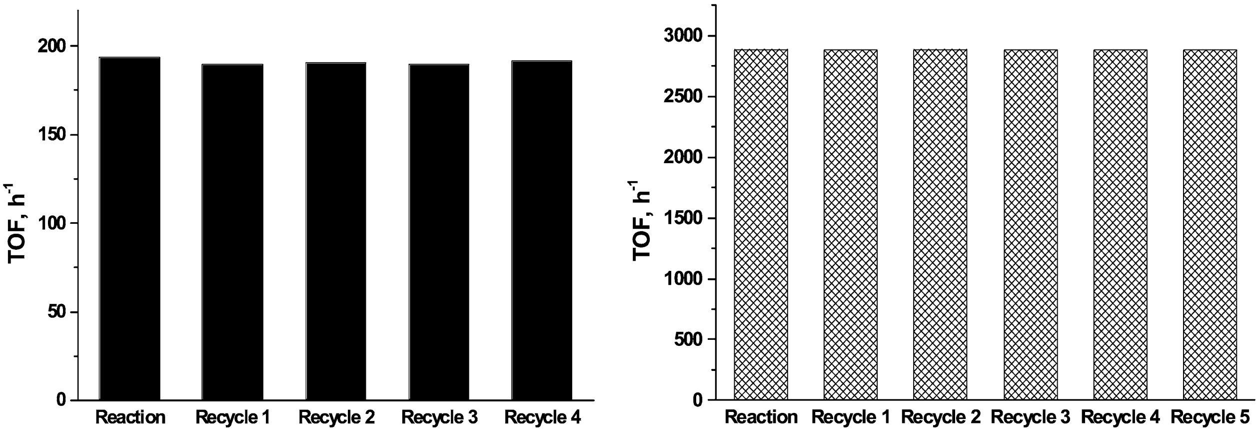
Hydrocarboxylation of aryl olefins and alcohols were performed using an ossified Pd-complex catalyst (catalyst 1A). The catalyst showed excellent performance with respect to high activity and regioselectivity to the branched isomer products for different substrates, as shown in Table 1. It was observed that the TONs for all of the substrates were >1000 with regioselectivity of $>99\%$ to the branched isomer and conversions $>92\%$. Compared with the previous cases, the ossified catalyst (catalyst 1A) had a higher TON than the biphasic catalyst [11,12] but was inferior to the Pd/C [13] and anchored Pd-complex catalysts [14]. However, the regioselectivity was better than all of them. The stability of the catalyst was tested through leaching experiments. A typical reaction was stopped intermittently, and the hot-filtered reaction mixture was analyzed for Pd-content by atomic absorption spectroscopy (AAS). The analysis showed almost no loss of Pd from the catalyst ($8.8 \times 10^{-5}\%$ loss of total Pd content). It is noteworthy that the ossified catalyst showed greater stability than any of the heterogeneous Pd catalysts (Table 1). Further, the ossified catalyst 1A was recycled four times (Fig. 3, Part I) successfully (cumulative TON ∼5780 after 4 recycles for styrene), with only marginal variation in activity ($<1\%$) and practically the same regioselectivity. The recycled catalyst 1A was characterized using ^{31}P CP-MAS NMR (δ_{iso} 29.54 ppm), which showed no variation compared to the original catalyst (Fig. 1, Part II, curve C). The XPS data of the used catalyst 1A show retention of oxidation states of Pd, Ba,

Table 1
Comparison of performance of ossified Pd-complex catalysts with previous reports for hydrocarboxylation of olefins and alcohols



Entry	Substrate	Catalyst system	Conversion (%)	Selectivity (%)		TON	Time (h)	TOF (h^{-1})	Pd-loss in reaction	Remarks
				iso	*n*					
1	S[a]	Homogeneous Pd(pyca)(PPh_3)(OTs)[b]	97	99.01	0.98	468	0.18	2600	–	Tedious catalyst-product separation and reuse
2	S	Pd/C[c]	92	98	1.9	13340	4.6	2900	37.5%	Heavy leaching obtained, activity might be due to leached Pd
3	S	Aq. biphasic Pd(pyca)(TPPTS)[d]	94.5	92	7.2	428	1.42	302	0.225%	Catalyst deactivates in air, recycles active only under CO atmosphere
4	S	Pd(pyca)(PPh_3)(OTs) anchored inside MCM-41[e]	98.12	99.3	0.68	5556	12	463	3.5×10^{-4}%	Cumbersome multi-step catalyst synthesis involving sensitive/exotic reagents
5	S	Catalyst 1A[f]	96	99.9	–	1160	6	194	8.8×10^{-5}%	Extremely easy catalyst synthesis method, highly stable recyclable and truly heterogeneous catalyst with negligible leaching
6	4-Me-S	Catalyst 1A[f]	94	99.8	0.1	1102	6	184		
7	4-tBu-S	Catalyst 1A[f]	92	99.2	0.7	1100	6	183		
8	IBPE[g]	Catalyst 1A[f]	93	99.8	0.1	1050	11	96		
9	S	Catalyst 1B[f]	94	98.2	1.78	1050	7	150		Comparable performance with respect to catalyst 1A
10	S	Catalyst 1C[f]	93	97.8	2.09	1106	7	158		
11	S	Catalyst 1D[f]	95	99.0	0.88	1099	7	157		

[a] S = styrene.
[b] Reaction conditions as in Ref. [9].
[c] Reaction conditions as in Ref. [13].
[d] Reaction conditions as in Ref. [11].
[e] Reaction conditions as in Ref. [14].
[f] Reaction conditions: substrate 9.6 mmol; catalyst 100 mg; LiCl 1.7 mmol; TsOH 0.85 mmol; PPh_3 0.038 mmol; H_2O 27 mmol; solvent methyl ethyl ketone (MEK); T 388 K; P_{CO} 5.4 MPa. Pd-contents: catalyst 1A = 0.44%, catalyst 1B = 0.48%, catalyst 1C = 0.45%, catalyst 1D = 0.46%.
[g] IBPE = 1-(4-isobutylphenyl)ethanol.



Part I Part II

Fig. 3. Recycle study results using ossified Pd(pyca)(TPPTS) complex [catalyst 1A]. Part I: Hydrocarboxylation of styrene, reaction conditions: styrene 9.6 mmol; catalyst 100 mg; LiCl 1.7 mmol; TsOH 0.85 mmol; PPh_3 0.038 mmol; H_2O 27 mmol; solvent MEK; T 388 K; P_{CO} 5.4 MPa. Part II: Suzuki cross-coupling reaction of Ph–I and $PhB(OH)_2$. Reaction conditions: iodobenzene 1.5 mmol; phenylboronic acid 1.8 mmol; catalyst 25 mg; K_2CO_3 4.5 mmol; solvent EtOH, 20 ml; reflux.

and the other elements similar to that of the pristine catalyst 1A. The comparative performance of catalysts 1A, 1B, 1C, and 1D for styrene carbonylation shows excellent performance with respect to activity and selectivity for carbonylation reaction (Table 1, entries 9–11). Thus, by ossification we can get truly heterogeneous analogs of the homogeneous complex catalysts with promising application in reactions such as carbonylation.

In another example of application of the ossified Pd-complex catalysts, we performed Suzuki cross-coupling reactions (sche-

Table 2
Comparison of performance of ossified Pd-complex catalysts with a selected few heterogeneous Pd-catalysts for Suzuki coupling reaction

Entry	Substrate[a]	Catalyst system[b]	S/Pd[c]	Conversion (%)	Selectivity (%)	TON	Time (h)	TOF (h^{-1})	Pd-leaching	Ref.
1	Ph–I	Pd-hollows	32	99	100	31	3.0	10	Nil	[16]
2	Ph–Cl	NanoPd-layered double hydroxide	100	93	–	93	10.0	9.3	Not determined	[17]
3	4-NO_2–Ph–I	Cyclodextrins capped Nano-Pd	100	98	–	96	2.0	48	Not determined ~50% after 4th recycle	[18]
4	4-MeO–Ph–Br	Nano-Pd loaded on organosilicas	105	98	–	102	5.0	20		[19]
5	Ph–Br	Pd-hydroxyapatite	50000	80	–	40000	4.0	10000	Nil	[20]
6	Ph–I	Pd-AS	2000	98	–	1960	24.0	82	Nil	[21]
7	Ph–I	Pd-AS	1250000	100	100	1250000	36.0	34722		
8	4-Cl–AcPh[d]	Palladacycle anchored to siliceous supports	25	>99	95	24	2.0	12	Present but inactive for reaction of Ar–Cl	[23]
9	4-Br–Ph–OH	Pd-sepiolite	1000	99	100	990	20.0	49.5	Not determined	[24]
10	4-Br–Ph–OH	Pd-sepiolite	1000000	94	100	940000	24.0	39167		
11	4-MeO–Ph–Br	Pd-perovskite	526316	75	–	399000	336.0	1187	High	[25]
12[e]	Ph–I	Catalyst 1A	1445	100	99.9	1445	0.5	2890	<0.3 ppm	–
13[f]	Ph–I	Catalyst 1A	216818	96	100	208146	3.0	69382	Nil	–
14[g]	Ph–I	Catalyst 1A	1084092	95	100	1029887	3.0	343296	Nil	–
15[e]	Ph–I	Catalyst 1B	1324	98	99.6	1298	0.5	2596	–	–
16[e]	Ph–I	Catalyst 1C	1413	97	99.5	1370	0.5	2741	–	–
17[e]	Ph–I	Catalyst 1D	1381	99	99.8	1368	0.5	2736	–	–

[a] Aryl halide is mentioned, other reactant is $PhB(OH)_2$.

[b] Reaction conditions as mentioned in the respective references and the term Pd represents either Pd-complexes or nanoclusters.

[c] S/Pd = substrate/palladium ratio.

[d] 4-Cl–AcPh = 4-chloroacetophenone.

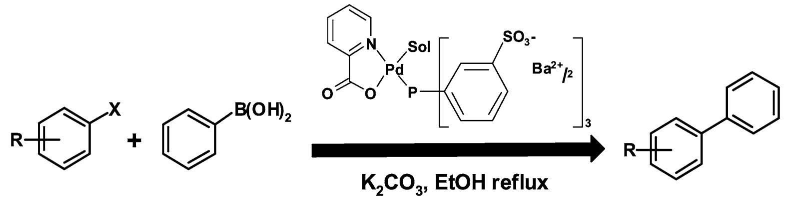
[e] Reaction conditions: substrate 1.5 mmol; $PhB(OH)_2$ 1.8 mmol; catalyst 25 mg; K_2CO_3 4.5 mmol; solvent EtOH, 20 ml; reflux. Pd-content in catalysts: catalyst 1A = 0.44%, catalyst 1B = 0.48%, catalyst 1C = 0.45%, catalyst 1D = 0.46%, respectively.

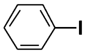
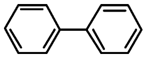
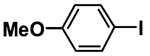
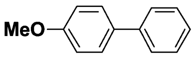
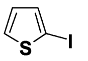
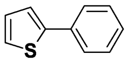
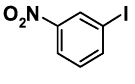
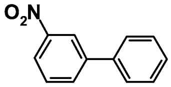
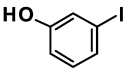
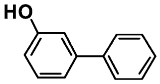
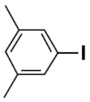
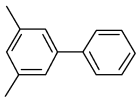
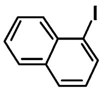
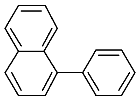
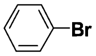
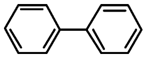
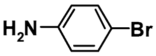
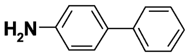
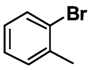
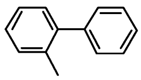
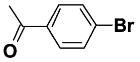
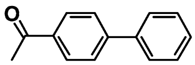
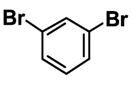
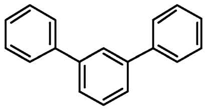
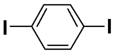
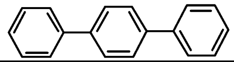
[f] Ph–I 45 mmol; $PhB(OH)_2$ 54 mmol; catalyst 5 mg; K_2CO_3 135 mmol; solvent EtOH, 150 ml.

[g] Same as in entry 13 but catalyst 1 mg.

me in Table 3). The reaction was optimized using iodobenzene and phenylboronic acid, and the standardized conditions were applied for all reactions except the reaction time. It was observed from the optimization studies that 1.2 equivalents of phenylboronic acid with respect to the aryl halide (mono) were necessary for efficient coupling. Several bases (e.g., Na_2CO_3, NaOAc, KO*t*-Bu, Na_3PO_4) were tested, and K_2CO_3 was deemed the best from an activity and biaryl selectivity performance standpoint, with a relative amount of 3 equivalents with respect to the aryl halide. Reactions in ethanol showed the best performance among the other solvents (e.g., methanol, acetone, chloroform, hexane, toluene) tested. The Suzuki coupling reactions of iodobenzene and phenylboronic acid were performed with all of the four ossified Pd-complex catalysts (catalyst 1A, 1B, 1C, and 1D), showing that the ossified Pd-pyca complex (catalyst 1A) had the best performance with 100% conversion and 99.9% chemoselectivity to biphenyl with an excellent TOF (2890 h^{-1}) within a very short reaction time of 0.5 h (Table 2, entries 12, 15, 16, and 17). However, the other ossified catalysts (1B, 1C, and 1D) also showed comparably good performance. An intermediate hot-filtered sample of the reaction mixture was analyzed by AAS for Pd content for catalyst 1A to evaluate Pd leaching in solution during the reaction. The results showed that <0.3 ppm of Pd was present in solution. Comparing these findings with previous reports using heterogeneous Pd-metal catalysts [15–19] and heterogenized Pd-complex catalysts [20–25] reveals that many of the examples described previously used very high substrate-to-catalyst ratios, resulting in very high TONs. Working in a similar range of substrate-to-catalyst ratios (~2,00,000 to 10,00,000), we obtained very high TONs, comparable to the previously reported highest values [21] but at a comparatively shorter reaction time (3 h). Thus, we have achieved turnover frequencies (TOFs) in the range of 68,000 to >3,00,000 h^{-1}, which is to the best of our knowledge the highest for any heterogeneous Pd-catalyzed Suzuki coupling reaction. Catalyst 1A was recycled five times to evaluate its stability and reusability at high catalyst concentrations (S/Pd ratio ~1400). The catalyst was seen to recycle very efficiently with retention of the activity and selectivity aspects after five recycles (Fig. 3, Part II), and a cumulative TON of ~8667 was achieved. The Suzuki coupling reaction was also carried out using different functionalized aryl halides (Table 3) at similar substrate-to-catalyst ratios (~1000), enabling faster reactions and easier handling. These reactions showed excellent activity and hetero-biaryl selectivity. All of the iodoarenes showed >99% conversion in shorter reaction times than the aryl bromides, with good selectivity. In some cases, <1% biphenyl was obtained as a byproduct. A trimeric cyclic boroxine was detected in the GC-MS spectra when Na_3PO_4 was used as a base, probably due to the longer reaction time required when using Na_3PO_4. Thus, ossified Pd-complex catalysts have proven to be efficient, stable, and recyclable for Suzuki coupling reactions with extremely high activity.

Table 3
Suzuki coupling reactions[a] of different aryl halide with $PhB(OH)_2$ using ossified Pd-complex, catalyst 1A



Entry	Substrate	Conversion (%)	Product	Selectivity (%)		TON	Time (h)	TOF (h^{-1})
				Biaryl	Others			
1		100		99.9	–	1415	0.5	2890
2		98.0		99.2	0.7	1416	1.0	1416
3		99.9		99.0	0.9	1444	1.0	1444
4		100		99.9	–	1445	0.42	3440
5		99.9		99.0	0.9	1445	0.88	1642
6		99.9		99.1	0.88	1444	0.67	2155
7		99.9		99.8	0.15	1444	0.70	2065
8		89		99.8	–	1402	1.5	858
9		74		98.2	0.67	1070	4.5	238
10		83		99.1	0.8	1200	4.0	300
11		97		99.0	0.8	1401	2.5	560
12[b]		96		99	0.9	1387	2.0	694
13[b]		99.9		99.8	0.1	1443	0.8	1805

[a] Reaction conditions: substrate 1.5 mmol; phenylboronic acid 1.8 mmol; catalyst 25 mg; K_2CO_3 4.5 mmol; solvent EtOH, 20 ml; reflux. Pd-content of catalyst 1A: 0.44%.

[b] 3.6 mmol phenylboronic acid used.

4. Conclusion

The aim of this work was to demonstrate the novel and facile heterogenization concept, which we call *ossification*, and then illustrate the versatile applicability of the thus-immobilized catalysts. For this purpose, different palladium complex catalysts were chosen as potential candidates and were immobilized. A detailed characterization of the catalysts by ^{31}P CP-MAS NMR, powder XRD, and XPS proved the concept beyond ambiguity from a synthesis viewpoint. The applicability of thus immobilized palladium complexes needed to be tested under stringent reaction conditions to validate the stability issue. Thus, the *ossified Pd-complex catalysts* were been demonstrated for two different types of palladium-catalyzed reactions, such as carbonylation (under high temperature and high pressure, in the presence of protic acids and alkali-metal salt promoters) and Suzuki cross-coupling reactions (strongly basic and aerated reaction media). The immobilized catalysts' excellent performance with respect to activity, selectivity, and stability, coupled with their recyclability and convenient synthesis methodology, are noteworthy. Excellent results (highest reported TOF $\sim$3,43,296 h^{-1}, with TON $>$ 10,00,000) were obtained for the Suzuki coupling experiments. Moreover, the synthesis methodology is generic, and most aqueous-soluble metal complexes may be easily transformed to their solid molecular counterparts by ossification and hence may be applicable to numerous metal complex-catalyzed reactions. Ossification of metal complexes has potential as a universal, easy-to-use immobilization strategy with wider applicability. These may be considered considerable advancements in the search for truly heterogeneous and stable catalysts for the development of sustainable technology.

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Supplementary information

The online version of this article contains additional supplementary material.

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