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Preparation, Characterization and Catalytic Properties of Polyaniline-Supported Metal Complexes

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Abstract: Polyaniline-supported Sc, In, Pd, Os and Re catalysts were prepared by using a simple protocol and the thus prepared catalysts were well characterized using FTIR, XPS, UV-Vis/DRS, TGA-DTA. All the catalysts were successfully employed in a wide range of organic transformations such as cyanation and allylation of carbonyl compound, Suzuki coupling of aryl halides and boronic acids, and, most importantly, in asymmetric dihydroxylation of olefins to afford optically active vicinal diols. All the catalysts were separated from the reaction mixture by simple filtration and reused with consistent activity for five cycles without noticeable leaching of metal from the support.

Keywords: allylation; asymmetric dihydroxylation; cyanation; polyaniline; Suzuki coupling

Introduction

Although a number of homogeneous catalysts have gained wide acceptance in terms of efficiency and selectivity, the contribution of these catalysts in the overall production of chemicals is much lower than originally expected. The major drawback of homogeneous catalysis is the need to separate the relatively expensive catalyst from the reaction mixture at the end of the process. One of the most promising solutions to this problem seems to be the immobilization of the soluble catalysts onto an insoluble matrix usually polymers using a simplified protocol.[1] Microencapsulation[1c–f] and incarceration[1k–l] are newly developed, advanced techniques using polymers to contain the metal complexes inside the polymer wrap *via* pi (π) interaction and physical forces. But the preparation of polystyrene and polystyrene-derived materials for microencapsulation requires a complex procedure and the incarceration technique is tedious.

Polyaniline (PANI) is one of the most widely studied conducting polymers for electronic and optical applications[2] due to its environmental stability and interesting redox properties but only a few reports are available using not well characterized PANI-supported metal catalysts.[3] We conceived the use of interactive PANI prompted by its highly conducting and redox properties as a support that holds metal complexes securely during catalytic reactions. Furthermore, its easy preparative protocol from non-expensive starting material (aniline), controllable doping levels through an acid doping/base dedoping process, inert nature, and non-solubility in most of the organic solvents and water are essential qualities for using it as support in heterogeneous catalysis. We chose proven metal catalysts such as scandium, indium, palladium salts, osmium and rhenium oxides, which have impacted immensely on modern organic synthesis.[4] We herein disclose the preparation, characterization and evaluation of polyaniline-supported metal catalysts in a wide diversity of organic reactions.

Results and Discussion

Preparation of Polyaniline-Supported Catalysts

Scandium-doped PANI (**PANI-Sc**) was prepared by adopting a very simple protocol of stirring the solutions of $Sc(OTf)_3$ in acetonitrile with PANI at room temperature for a specified time and then the catalyst was filtered, washed, and dried. Similarly **PANI-In** from $In(OTf)_3$, **PANI-Pd** from $Pd(OAc)_2$, **PANI-Os** from OsO_4, **PANI-Re** from $MeReO_3$ (MTO) and **PANI-Os-Re** from OsO_4 and MTO were prepared.

Characterization of Polyaniline-Supported Catalysts

All the supported catalysts are well characterized using FTIR, UV-Vis-DRS, XPS and TGA-DTA. The characteristic vibrational absorbance bands of PANI and PANI-supported metal complexes are shown in Table 1. Diffuse reflectance UV-Vis spectroscopic data are shown in Table 2 and XPS data are summarized in Table 3 and Table 4. For all spectra, please see the Supporting Information.

PANI-Sc and PANI-In

PANI has quinoid (Q) and benzenoid (B) units along with amine and imine functional moieties, which can hold the metal complexes securely. In FT-IR **PANI-Sc** exhibits new absorbance bands near 634, 759 and 1024 cm^{-1} which can be assigned as ν(S–O), ν(C–S) and as $\nu(SO_2)$ as they appear in the FT-IR spectra of $Sc(OTf)_3$ at 647, 769 and 1032 cm^{-1}, respectively.[1c] **PANI-In** gives similar peaks at 636, 730 and 1026 cm^{-1}. In addition a new peak at 1130 cm^{-1} in **PANI-Sc** and at 1139 cm^{-1} in **PANI-In** indicates the presence of a charged polyaniline chain (CH in-plane bending).[5,6] Moreover, the characteristic peak for N=Q=N at 1587 cm^{-1} is shifted to 1580–1582 cm^{-1} indicating the weakening of the N=Q=N bond. UV-Vis spectra of **PANI-Sc** and **PANI-In** show some minor differences with respect to their precursors, which can be attributed to the interaction between PANI and the corresponding metal triflates. In the XPS analysis

Table 2. Diffuse reflectance UV-Vis spectral data of PANI catalysts.

Catalyst	Absorbance maxima [nm]
PANI-Sc	215–220
$Sc(OTf)_3$	220
PANI-In	215–225, 280-285
$In(OTf)_3$	220, 280
PANI-Pd	250–350
$Pd(OAc)_2$	250–350
PANI-Re	355, 375
$MeReO_3$	360
PANI-Os	290, 380
PANI-Os-Re	270–370

Table 3. XPS data of PANI-supported catalysts for the metals.

Catalyst	Binding energy [eV]
PANI-Sc	Sc signal overlapped by N signal
PANI-In	In: 446 ($3d_{5/2}$), 453.5 ($3d_{3/2}$)
PANI-Pd	Pd: 338 ($3d_{5/2}$), 343 ($3d_{3/2}$)
PANI-Os	Os: 52.3 ($4f_{7/2}$), 50.30 ($4f_{7/2}$), 55 ($4f_{5/2}$), 53.6 ($4f_{5/2}$)
PANI-Re	Re: 44.8 ($4f_{7/2}$), 46.5 ($4f_{7/2}$), 47.4 ($4f_{5/2}$), 48 ($4f_{5/2}$)
PANI-Os-Re	Os: 51 ($4f_{7/2}$), 49.6 ($4f_{7/2}$), 55 ($4f_{5/2}$), 53 ($4f_{5/2}$) Re: 44.8 ($4f_{7/2}$), 45.5 ($4f_{7/2}$), 47.2 ($4f_{5/2}$), 47.7 ($4f_{5/2}$)

Table 1. FT-IR spectral data of PANI-supported catalysts.

Catalyst	N=Q=N [cm^{-1}]	N–B–N [cm^{-1}]	$CH_{in-plane}$ bending of PANI [cm^{-1}]	Other important bands [cm^{-1}]
PANI	1587	1493	1164	–
PANI-Sc	1580	1495	1130	634, 759, 1024
PANI-In	1583	1497	1140	636, 730, 1026
PANI-Pd	1586	1495	1164	–
PANI-Os	1587	1493	1146	866 (br)
PANI-Re	1587	1496	1143	907
PANI-Os-Re	1581	1498	1142	904

Table 4. XPS data of N (1s) of PANI-supported catalysts.

Sample	–N=		–NH–		$-N^+$	
	B.E. [eV]	Share [%]	B.E. [eV]	Share [%]	B.E. [eV]	Share [%]
PANI	398	45	399.4	45	402	10
PANI-In	–	–	399.26	25.7	403.6	74.3
PANI-Pd	398.5	31.9	399.4	47.2	400.3	20.9
PANI-Os	398.1	29.4	399.19	49.7	400.374 and 402.21	15.6 and 5.3
PANI-Re	398.25	25.2	399.1	48.7	400.004	26.1

of **PANI-Sc**, Sc 3d signals are overlapped by the N 1s signals, so we studied only **PANI-In** by XPS and assumed that a similar kind of interaction is true for scandium also. After deconvoluting the N 1s signal from **PANI-In**, two peaks at 399.26 (share 25.7%) and at 403.6 eV (share 74.3%) are noticed which are assigned to amine nitrogen (–NH–) and N^+, respectively.[7] The In $3d_{5/2}$ signal appears at 446 eV. Signals for F, S, O, and C are also present. Therefore, we postulate that metal triflates form bonds with imine as well as amine nitrogens of polyaniline. The same kind of bonding is also reported for PANI doped with other strong Lewis acids such as $SnCl_4$, and $FeCl_3$.[5a,b] TGA-DTA analysis of **PANI-Sc** and **PANI-In** shows that both the catalysts give almost similar endotherms of their precursors. The probable structure is shown in Figure 1.

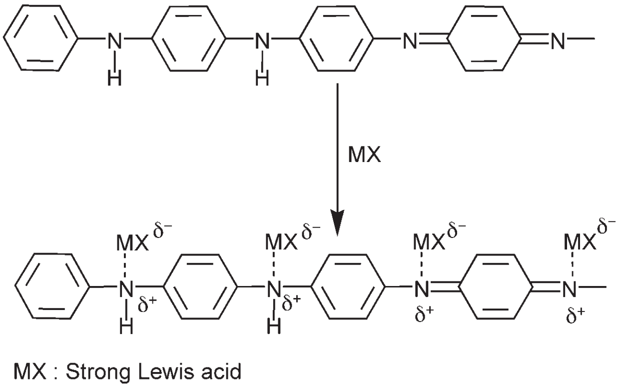


Figure 1. Structure of PANI-doped with a Lewis acid.

PANI-Pd

The preparation of the composite of polyaniline and palladium salts has been tried earlier.[8a] From the FT-IR of **PANI-Pd** prepared by us from $Pd(OAc)_2$ the presence of the acetate moiety in the resultant catalyst could not be ascertained due to the strong absorbance of PANI in the same region. Similarly, the $CH_{in\text{-}plane}$ bending is not shifted due to weak interactions, which is in accord with the earlier studies.[8] But here thermal studies appear to be fruitful in ascertaining the presence of acetate group as we observed almost near identical endotherms in the TGA-DTA of the **PANI-Pd** and $Pd(OAc)_2$ at 260–270 °C (see Supporting Information). Diffuse reflectance UV-Vis spectra of both **PANI-Pd** and $Pd(OAc)_2$ show the absorbance maxima in the same region indicating a weak interaction of $Pd(OAc)_2$ with the PANI. XPS analysis of **PANI-Pd** for N 1s shows a peak at 400.3 eV (share 20%) characteristic of charged nitrogen. A narrow scan for the Pd 3d level showing two peaks at 338 eV ($3d_{5/2}$) and at 342 eV ($3d_{3/2}$) indicates the presence of only Pd(II). These studies confirm the complexation of $Pd(OAc)_2$ with PANI.

PANI-Os

The FT-IR spectrum of **PANI-Os** shows the characteristic absorbance of charged PANI at 1146 cm^{-1}. Moreover, the difference spectrum (the FT-IR spectrum of PANI is subtracted from that of **PANI-Os**) of **PANI-Os** and PANI shows a broad band centered at 866 cm^{-1} assigned to the Os–O stretching vibration.[9] The diffuse reflectance UV-Vis spectrum of **PANI-Os** shows absorbance maxima at 290 nm, which is in accordance with other supported osmium catalysts.[9] XPS analysis of **PANI-Os** for N 1 s shows 21% of N^+ and the narrow scan for the Os $4f_{7/2}$ level shows two signals at 52.3 eV and 50.3 eV. Both the Os $4f_{7/2}$ signals correspond to Os(IV) and Os(II) oxidation states indicating reduction of the Os(VIII) oxidation state originally charged. A possible explanation for this observation is the redox reaction between PANI and osmium tetroxide as a similar kind of observation is reported for reactions of Pt^{4+} and Pd^{2+} with PANI.[8a]

PANI-Re

This presents an interesting situation because methyltrioxorhenium ($MeReO_3$: MTO) is a strong oxidizing agent as well as a Lewis acid. Here, both the Lewis acid doping and redox reactions are operating. An FT-IR spectrum of **PANI-Re** clearly shows the 1140 cm^{-1} band without any shoulder in the 1160 cm^{-1} region. Moreover a new band appeared at 907 cm^{-1} characteristic of asymmetric Re–O stretching.[1i] The diffuse reflectance UV-Vis spectrum of **PANI-Re** gives a broad absorbance in the region 360–370 nm. XPS analysis of **PANI-Re** for N 1s gives a 26% share of N^+. Moreover, a narrow scan for Re $4f_{7/2}$ level yields two peaks at 46.5 eV and 44.8 eV, which can be assigned to the Re(VII) and the lower oxidation state Re(VI), respectively.[10] A plausible explanation for these observations is that some fraction of the MTO is directly bonded to the nitrogen and the rest is involved in the redox reaction with PANI, wherein PANI gets oxidized with concomitant reduction of Re.

PANI-Os-Re

The FT-IR spectrum of **PANI-Os-Re** shows two new peaks at 1140 cm^{-1} (attributed to the charged PANI chain) and at 907 cm^{-1} (attributed to the stretching of Re–O). Moreover, the XPS analysis shows the presence of both osmium(+IV and +II) and rhenium(+VI and +VII) in the **PANI-Os-Re** catalyst.[10a]

Synthetic Applications of PANI-Supported Catalysts

PANI-Sc and PANI-In

To evaluate the synthetic utility, stability and scope of these PANI-based catalysts in diverse organic transformations. **PANI-Sc** was first used in two fundamental Lewis acid-catalyzed carbon-carbon bond forming reactions, namely cyanation and allylation of carbonyl compounds. **PANI-Sc** (3 mol%) was employed in the cyanation and allylation of anisaldehyde using trimethylsilyl cyanide (TMSCN) as cyanating reagent and tetraallyltin as allylating reagent, respectively, in dry dichloromethane to afford both the corresponding products in 95% yields in a relatively short duration (Scheme 1). Results of cyanation and allylation reactions are shown in Table 5 and Table 6. The activity of **PANI-In** in both reactions is comparable to that of **PANI-Sc** (Table 5, entry 1; Table 6, entry 1).

PANI-Pd

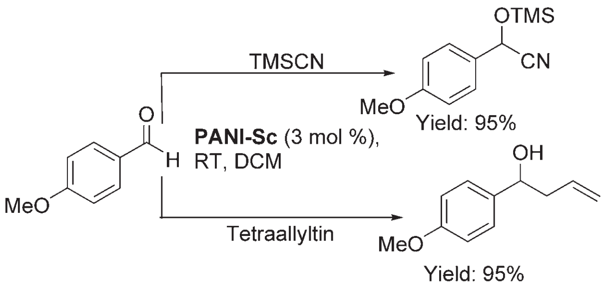
Suzuki cross-coupling of aryl halides and arylboronic acids was chosen as the model reaction to examine the catalytic efficacy of our **PANI-Pd** catalyst (Table 7). **PANI-Pd** was applied to the Suzuki cross-coupling of 4-bromotoluene with phenylboronic acid using 2 mol% of the catalyst in dioxane in the presence of Cs_2CO_3 (Scheme 2) at 100 °C without adding any external ligand to give the corresponding product

Table 5. Cyanation of carbonyl compounds using **PANI-Sc** and **PANI-In**.[a]

Entry	Substrate	Reaction time [h]	Isolated yield [%]
1	4-MeO-C_6H_4-CHO	1	95, 95[b]
2	C_6H_5-CHO	1	99
3	4-Br-C_6H_4-CHO	0.8	96
4	4-Cl-C_6H_4-CHO	0.8	94
5	4-Me-C_6H_4-CHO	1	97
6	4-NO_2-C_6H_4-CHO	0.8	98
7	2,6-$(Cl)_2$-C_6H_3-CHO	4	95
8	PhCH=CH-CHO	1	96
9	Cyclopentanone	1	94
10	Cyclohexanone	1	92
11	C_6H_5-$(CH_2)_2$-CHO	1	90

[a] *Reaction conditions:* carbonyl compound (1 mmol), TMSCN (1.2 mmol), **PANI-Sc** (3 mol%), dry dichloromethane (2 mL), room temperature.

[b] **PANI-In** (3 mol%) used as catalyst.



Scheme 1. **PANI-Sc**-catalyzed cyanation and allylation reaction.

Table 6. Allylation of carbonyl compounds using **PANI-Sc** and **PANI-In**.[a]

Entry	Substrate	Time [min]	Isolated yield [%]
1	C_6H_5-CHO	45	92, 92[b]
2	4-Me-C_6H_4-CHO	45	95
3	4-Cl-C_6H_4-CHO	40	98
4	4-MeO-C_6H_4-CHO	60	95, 94[b]
5	4-NO_2-C_6H_4-CHO	40	98
6	4-Br-C_6H_4-CHO	45	98
7	*trans*-Cinnamaldehyde	60	90, 88[b]
8	c-C_6H_{11}-CHO	50	95
9	C_6H_5-$(CH_2)_2$-CHO	50	96
10	C_6H_5-CO-CH_3	180	94
11	4-Me-C_6H_4-CO-CH_3	220	95
12	4-Cl-C_6H_4-CO-CH_3	180	95
13	4-Br-C_6H_4-CO-CH_3	160	94
14	4-MeO-C_6H_4-CO-CH_3	260	98

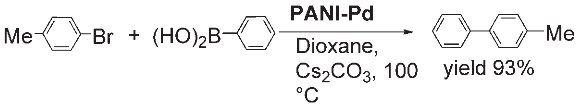
[a] *Reaction conditions:* carbonyl compound (1 mmol), tetraallyltin (0.5 mmol), **PANI-Sc** (3 mol%), dry dichloromethane (2 mL).

[b] **PANI-In** (3 mol%) used as catalyst.

Table 7. Suzuki coupling of aryl halides with arylboronic acids using **PANI-Pd.**[a]

Entry	Haloarene	Arylboronic acid	Isolated yield [%]
1	C_6H_5-I	C_6H_5-B(OH)$_2$	92
2	*p*-NO_2-C_6H_4-I	C_6H_5-B(OH)$_2$	96
3	*p*-MeO-C_6H_4-I	C_6H_5-B(OH)$_2$	90
4	*p*-Me-C_6H_4-I	C_6H_5-B(OH)$_2$	92
5	C_6H_5-I	*p*-MeO-C_6H_4-B(OH)$_2$	98
6	C_6H_5-Br	C_6H_5-B(OH)$_2$	95
7	*p*-Me-C_6H_4-Br	C_6H_5-B(OH)$_2$	93
8	*p*-NO_2-C_6H_4-Br	C_6H_5-B(OH)$_2$	98

[a] *Reaction conditions:* aryl halide (1 mmol), arylboronic acid (1.5 mmol), **PANI-Pd** (2 mol %), Cs_2CO_3 (2 mmol), 100 °C, 2–6 h.



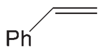
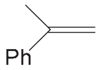
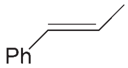
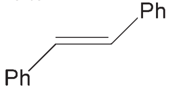
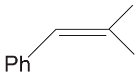
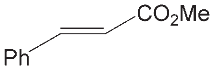
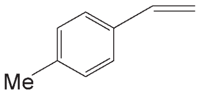
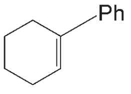
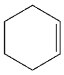
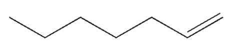
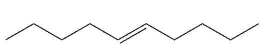
Scheme 2.

in 93 % yield within 4 h. Similarly, several other bromo- and iodoarenes are coupled with phenylboronic acids to afford excellent yields of biphenyls. It is significant to note that Pd(OAc)$_2$ as such under identical conditions gave only a 20 % yield with the formation of Pd black.

PANI-Os and PANI-Os-Re

The osmium-catalyzed asymmetric dihydroxylation (AD)[4j] of olefins provides one of the most elegant methods for the preparation of chiral vicinal diols. Although the reactions could be applied to the synthesis of pharmaceuticals, fine chemicals, and so forth, the high cost, toxicity, and possible contamination of osmium catalysts in the products restricts its use in industry. Heterogenization of the ligands on a polymer or silica gel support and eventual complexation with osmium, a possible solution to address this issue attempted by several groups, failed to recover and reuse the osmium since the coordination of anchored ligands and osmium tetroxide is in equilibrium.[1a,b,11,12] The microencapsulation technique first adopted by Kobayashi et al. to envelop osmium tetroxide in the polymer capsule[1d,e] and ion-exchange technique used by us to anchor osmate onto the surface of layered double hydroxide[9a,b] afforded recoverable and reusable osmium catalysts for asymmetric dihydroxylation. But still there is room for further development in heterogeneous dihydroxylation catalysis in terms of low loading of osmium, faster reaction rate and better yields and enantiomeric excesses of the final diols. So we were interested to test the performance of the polyaniline-supported osmium tetroxide (**PANI-Os**) catalyst in the AD reaction. To evaluate the activity, stability and scope of the **PANI-Os** catalyst in the dihydroxylation of olefins we first tried achiral dihydroxylation of *trans*-stilbene using *N*-methylmorpholine *N*-oxide (NMO) as the cooxidant.

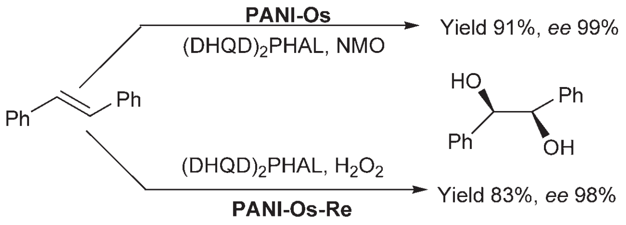
Table 8. Achiral dihydroxylation of olefins using **PANI-Os**.[a]

Entry	Substrate	Isolated yield [%]
1		93
2		93
3		94, 94[b]
4		91
5		90
6		93
7		90
8		92
9		87
10		94
11		91

[a] *Reaction conditions:* olefin (1 mmol), **PANI-Os** (0.2 mol %), NMO (1.3 mmol) in acetone:acetonitrile:water = 1:1:1 (3 mL) stirred at room temperature for 2–5 h.

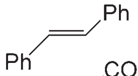
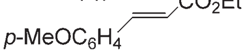
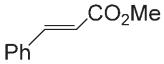
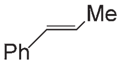
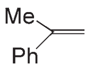
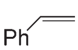
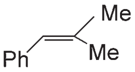
[b] Yield after the 5th cycle.

After trying several reactions we observed that in acetone-acetonitrile-water (1:1:1) as solvent only 0.2 mol % of **PANI-Os** was sufficient to give the stilbene diol in 91% isolated yield along with benzaldehyde and benzoin as side-products within 3 h at room temperature. Then several other olefins were subjected to similar reaction conditions and the results are summarized in Table 8. Encouraged by the results in achiral dihydroxylation, **PANI-Os** was employed in Sharpless asymmetric dihydroxylation[4j] of *trans*-stilbene using NMO as the oxidant and 1,4-bis(9-*O*-dihydroquinidinyl)phthalazine [$(DHQD)_2$PHAL, 1 mol%] as the chiral modifier to give 92% of the corresponding stilbene diol with 99% *ee* in 12 h (Scheme 3). Then several other olefins were also dihydroxylated with good yield and *ee*s (Table 9). Finally, in an effort to use a more benign co-oxidant like H_2O_2 and widen the scope of the PANI-supported catalyst, we employed the **PANI-Os-Re** bifunctional catalyst in the presence of H_2O_2 in the AD of olefins using Bäckvall's[13] protocol wherein the chiral modifier is also playing the role of an oxygen transfer agent (Scheme 3). The results are comparable to the results reported by Bäckvall (Table 10). To know whether any synergistic effect is operating between Os and Re, we performed one reaction with *trans*-stilbene using **PANI-Os** (2 mol%) and one with **PANI-Re** (2 mol%) separately, and the yields (80%) and *ee*s (98%) were found to be comparable to the yield using **PANI-Os-Re** (Table 10, entry 2).



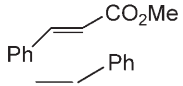
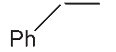
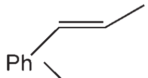
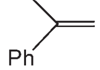
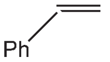
Scheme 3.

Table 9. Asymmetric dihydroxylation of olefins using **PANI-Os**.[a]

Entry	Olefin	Isolated yield [%]	*ee* [%]
1		91	99
2		93	97
3		91	86
4		94	86
5		93	73
6		93	71
7		90	62

[a] *Reaction conditions:* olefin (1 mmol), NMO (1.3 mmol), **PANI-Os** (0.5 mol%), $(DHQD)_2$PHAL (1 mol%) in acetone:acetonitrile:water = 1:1:1 (3 mL) stirred at room temperature. Olefin was added slowly over a period of 12 h.

Table 10. Asymmetric dihydroxylation of olefins using **PANI-Os-Re**.[a]

Entry	Olefin	Isolated yield [%]	*ee* [%]
1		94	98
2[b]		83	98
3		84	85
4		83	73
5		88	73

[a] *Reaction conditions:* olefin (0.5 mmol) and H_2O_2 (0.75 mmol) were added slowly and separately over 12 h to a suspension of **PANI-Os-Re** (59 mg, Os: 2 mol%, Re: 2 mol%), tetraethylammonium acetate (260 mg, 1 mmol) and $(DHQD)_2$PHAL (23 mg, 0.03 mmol) in *t*-BuOH:water = 3:1 (1.5 mL).

[b] Solvent is acetone:water = 4.4:1 (1.5 mL).

Reusability and Metal Leaching Study of the Polyaniline-Supported Catalysts

For a true heterogeneous catalyst, it is necessary to know whether the metal is leaching to the reaction mixture or not. Moreover the recyclability of the catalyst is also important.

For this, we have studied the recyclability of each catalyst in all reactions and the results are summarized in Figure 2 and Table 11. The results suggest that all the catalysts developed are maintaining their catalytic activity in repeated uses. Next we checked the leaching of metal complexes into the reaction mixture from the PANI support using ICP-AES and results are summarized in Table 12.

Conclusions

In summary, highly interactive conjugated polymer polyaniline-supported recoverable and recyclable scandium, indium, palladium, osmium and rhenium catalysts have been synthesized, characterized and

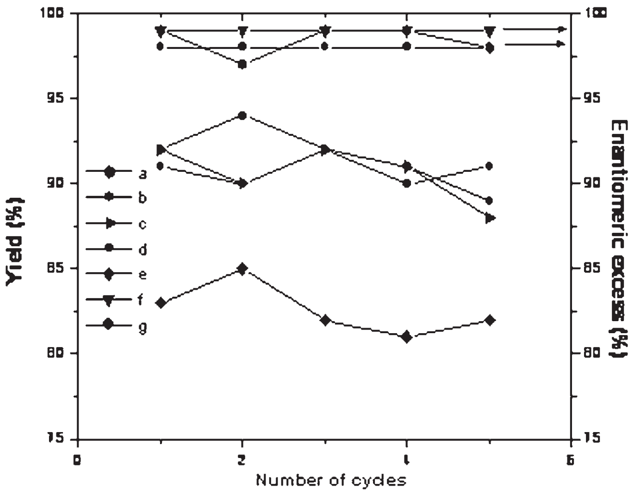


Figure 2. Yields obtained in multiple uses of (a) **PANI-Sc** in cyanation and (b) allylation of benzaldehyde, (c) **PANI-Pd** in Suzuki reaction of 4-Me-C_6H_4-Br, (d) **PANI-Os** in dihydroxylation of stilbene and (e) **PANI-Os-Re** in dihydroxylation of stilbene. The *ee* values obtained in the dihydroxylation of stilbene in multiple uses of (f) **PANI-Os** and (g) **PANI-Os-Re**.

Table 12. Metal leaching study of PANI catalysts.

Reaction	Catalyst	Amount of metal in the reaction mixture [%][a]
Cyanation	**PANI-Sc**	0.02
Cyanation	**PANI-In**	Not detected
Allylation	**PANI-Sc**	Not detected
Suzuki	**PANI-Pd**	0.05
Dihydroxylation	**PANI-Os**[b]	Not detected
Dihydroxylation	**PANI-Os-Re**[b]	Os: Not detected, Re: not detected

[a] (Amount of metal in the reaction mixture/amount of metal used) × 100.

[b] Metal detected by EDX.

successfully applied in a wide range of organic transformations. Almost consistent activity and enantioselectivity, wherever applicable, were observed in a number of cycles without noticeable leaching of the metals.

Experimental Section

General Remarks

IR spectra were recorded on a Biorad 175C FT-IR spectrometer for samples as KBr pellets. Diffuse reflectance UV spectra were recorded on a GBC Cintra 10e UV-VIS spectrometer for samples as KBr pellets. ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. Chemical shifts (δ) are reported in ppm, using TMS as internal standard for ^{1}H NMR. SEM-EDX (scanning electron microscopy-energy dispersive X-ray analysis) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. X-ray photoemission spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within ±0.1 eV. High performance liquid chromatography (HPLC) was performed using the following apparatus: Shimadzu LC-10 AT (liquid chromatograph), Shimadzu SPD-10 A (UV detector), and Shimadzu C-R6 A Chromatopac. ACME silica gel (100–200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates. ICP-AES analyses are performed using an IRIS Intrepid II XDL ICP-AES (Thermo Eelectron Corporation). All the metal complexes [OsO4, $Sc(OTf)_3$, $In(OTf)_3$, $Pd(OAc)_2$, $MeReO_3$], $(DHQD)_2$PHAL, NMO, tetraallyltin, olefins, and arylboronic acids were purchased from Aldrich and used as received. Aniline and other solvents were distilled before use. All other chemicals were procured from commercial sources and used as such without further purification.

Preparation of Polyaniline Base (PANI)

Freshly distilled aniline (4.9 g, 53 mmol) was added to water (350 mL) containing concentrated H_2SO_4 (15 mL) and the solution was kept under continuous stirring at 0 °C. To this solution ammonium persulfate (12 g, 53 mmol) in water

Table 11. Reusability of PANI supported catalysts.

Reaction	Catalyst	Yield [%] in repeated use					*ee* [%] in repeated use				
		1st	2nd	3rd	4th	5th	1st	2nd	3rd	4th	5th
Cyanation of benzaldehyde	**PANI-Sc**	99	97	99	99	98	–				
Allylation of benzaldehyde	**PANI-Sc**	92	94	92	90	91	–				
Suzuki coupling of 4-Me-C_6H_4-I and $C_6H_5B(OH)_2$	**PANI-Pd**	92	90	92	91	88	–				
Asymmetric dihydroxylation of stilbene	**PANI-Os**	91	90	92	91	89	99	99	99	99	99
Asymmetric dihydroxylation of stilbene	**PANI-Os-Re**	83	85	82	81	82	98	98	98	98	98

(125 mL) was added drop wise over 4 h. The precipitated polyaniline-sulfate salt was recovered by filtration, and the precipitate was washed with a copious amount of water followed by acetone. The thus obtained polyaniline-sulfate salt was stirred for 12 h at ambient temperature with sodium hydroxide solution (1 N, 500 mL). Then the deprotonated polyaniline base (PANI) was filtered off, and washed with water, followed by acetone.

Preparation of PANI-Sc

PANI (300 mg) was charged into a round-bottomed flask containing an acetonitrile solution (25 mL) of scandium triflate (300 mg, 0.6 mmol) and stirred under a nitrogen atmosphere for 48 h. The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air for 24 h to afford the black catalyst (440 mg). The amount of scandium was measured by ICP-AES (Sc 0.641 $\mathrm{mmol\,g^{-1}}$).

Preparation of PANI-In, PANI-Pd, PANI-Os, and PANI-Re

PANI-In, **PANI-Pd**, **PANI-Os**, and **PANI-Re** were prepared from indium triflate, $Pd(OAc)_2$, OsO_4, and $MeReO_3$, respectively, using the same procedure as stated above for **PANI-Sc**. The In, Pd, Os, and Re loadings were found to be 0.562, 0.35, 0.362, and 0.40 $\mathrm{mmol\,g^{-1}}$, respectively.

Preparation of PANI-Os-Re

PANI-Os-Re was also prepared similarly from a mixture of acetonitrile solutions of OsO_4 and $MeReO_3$. The Os and Re loading were found to be 0.17 $\mathrm{mmol\,g^{-1}}$ and 0.18 $\mathrm{mmol\,g^{-1}}$, respectively.

Cyanation of Carbonyl Compounds

The respective carbonyl compound (1.0 mmol) was taken up in dry dichloromethane (2 mL) in the presence of **PANI-Sc** (3 mol%). Then, under a nitrogen atmosphere, TMSCN (1.2 mmol) was added to the solution and kept under continuous stirring at room temperature. After the completion of the reaction (monitored by TLC), the catalyst was filtered off and washed with dichloromethane. The filtrate and washings were combined and then concentrated under reduced pressure to get the crude product. The crude product was subjected to column chromatography using ethyl acetate and hexane as eluent to obtain the pure product.

Allylation of Carbonyl Compounds

The respective carbonyl compound (1.0 mmol) was taken up in dry dichloromethane (2 mL) in the presence of **PANI-Sc** (3 mol%). Then, under a nitrogen atmosphere, tetraallyltin (0.50 mmol) was added to the solution and kept under continuous stirring at room temperature. After completion of the reaction, as judged by TLC, the catalyst was filtered off and washed with dichloromethane. The filtrate and washings were combined and stirred with 10 mL of saturated solution of ammonium chloride for 1 h and the organic layer was separated. The aqueous layer was further washed with ethyl acetate (2×10 mL) and all the organic layers were combined and concentrated under reduced pressure to get the crude product. The crude product was subjected to column chromatography and pure product was separated using a mixture of ethyl acetate and hexane.

Suzuki Coupling of Aryl Halides by PANI-Pd

In an oven-dried, 10-mL round-bottom flask, aryl halide (1 mmol), arylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), **PANI-Pd** (2 mol%), and dioxane (5 mL) were charged and stirred at 100 °C under a nitrogen atmosphere. After completion of the reaction as monitored by TLC, the catalyst was filtered. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated to get the crude product. The crude product was column chromatographed using hexane and ethyl acetate mixture as an eluent.

Achiral Dihydroxylation of Olefins Catalyzed by PANI-Os

PANI-Os (0.2 mol%) and NMO (1.3 mmol) were charged in a round-bottomed flask containing acetone-acetonitrile-water (1:1:1, 3 mL) and stirred at room temperature. To this mixture was added an olefin (1 mmol). After completion of the reaction as monitored by TLC, the **PANI-Os** catalyst was filtered and washed with acetone. Ethyl acetate was added to the combined filtrates and the organic layer was separated. After removing the solvent, the crude material was chromatographed on silica gel with EtOAc/hexane to afford the corresponding *cis*-diol.

Asymmetric Dihydroxylation of Olefins Catalyzed by PANI-Os

PANI-Os (0.5 mol%), $(DHQD)_2PHAL$ (7.8 mg, 0.01 mmol, 1 mol%), and NMO (1.3 mmol) were charged in a round-bottomed flask containing acetone-acetonitrile-water (1:1:1, 3 mL) and stirred at room temperature. To this mixture was added an olefin (1 mmol) slowly over 12 h. After completion of the reaction as monitored by TLC, the **PANI-Os** catalyst was filtered and washed with acetone. Ethyl acetate and 1 N aqueous HCl were added to the combined filtrates and the organic layer was separated. The chiral ligand was recovered from the aqueous layer. After removing the solvent, the crude material was chromatographed on silica gel with EtOAc/hexane to afford the corresponding *cis*-diol. The enantiomeric excess (*ee*) was determined by HPLC.[9a]

Asymmetric Dihydroxylation of Olefins Catalyzed by PANI-Os-Re

PANI-Os-Re (59 mg, Os: 2 mol%, Re: 2 mol%), $(DHQD)_2PHAL$ (23 mg , 0.03 mmol), and tetraethylammonium acetate (260 mg, 1 mmol) were taken in a round-bottomed flask containing *t*BuOH-water (3:1, 3 mL) and stirred at 0 °C. To this mixture an olefin (0.5 mmol) and 30% aqueous H_2O_2 (0.75 mmol) were added over a period of 10 h. After completion of the reaction as monitored by TLC, the **PANI-Os-Re** catalyst was filtered and washed with acetone. Ethyl acetate was added to the combined filtrates and the organic layer was separated. After removing the solvent, the crude material was chromatographed on silica gel with EtOAc/hexane to afford the corresponding *cis*-diol. Enantiomeric excess was determined by HPLC.[9a]

Supporting Information

FTIR, UV-Vis/DR, XPS and TGA-DTA spectra of all the polyaniline-supported catalysts.

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