Characterization and Catalytic Activity of Polymer Supported Ruthenium Schiff Base Complexes Towards Catechol Oxidation

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ABSTRACT: Ruthenium(III) complexes of the Schiff bases formed by the condensation of polymer bound aldehyde and the amines, such as 1,2-phenylenediamine (PS-opd), 2-aminophenol (PS-ap), and 2-aminobenzimidazole (PS-ab) have been prepared. The magnetic moment, EPR and electronic spectra suggest an octahedral structure for the complexes. The complexes of PS-opd, PS-ap, and PS-ab have been assigned the formula [PS-opdRuCl$_3$(H$_2$O)], [PS-apRuCl$_2$(H$_2$O)$_2$], [PS-ab-RuCl$_3$(H$_2$O)$_2$], respectively. These complexes catalyze oxidation of catechol using H$_2$O$_2$ selectively to o-benzoquinone. The catalytic activity of the complexes is in the order [PS-ab-RuCl$_3$(H$_2$O)$_2$] > [PS-opdRuCl$_3$(H$_2$O)] $\gg$ [PS-apRuCl$_2$(H$_2$O)$_2$]. Mechanism of the catalytic oxidation of catechol by ruthenium(III) complex is suggested to take place through the formation of a ruthenium(II) complex and its subsequent oxidation by H$_2$O$_2$ to the ruthenium(III) complex. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 997–1002, 2007

Key words: polystyrene supported complexes; Schiff base; ruthenium(III); catalysis; catechol oxidation

INTRODUCTION

Crosslinked polymers with specific properties are widely used as catalyst supports[1] as they are inert, nontoxic, and nonvolatile, and offer advantageous features of heterogeneous catalysis such as thermal stability, selectivity, and recyclability to homogeneous systems. They can induce specific control over catalytic and coordinating ability of the ligand. The ease of separation from the reaction products leads to operational flexibility.[2] Moreover, the amount of metal present on the surface of such catalysts is very small, which is of economic significance in the case of expensive metals like ruthenium, rhodium, and palladium. Earlier reports of catalytic activity of various metal ions such as Rh(I), Ru(III), and Pd(II) anchored to different crosslinked polymers with *N*-donor ligands prompted us to use ligands with nitrogen and oxygen as donor groups.[3–5] Although the Schiff bases are the most widely used ligands, only a few Schiff bases have been immobilized to polystyrene matrix.[1,2,6–8] Immobilization onto polymer supports through covalent attachment is one of the important means to solve the problem of decomposition of many complexes during catalytic reaction.[9] Ru(II) and Ru(III) complexes are widely known for their catalytic activity.[10–13]

Herein we report the preparation and characterization of ruthenium(III) complexes of the Schiff bases obtained by condensation of polystyrene bound aldehyde and 1,2-phenylenediamine (PS-opd), 2-aminophenol (PS-ap) or 2-aminobenzimidazole (PS-ab). Although complete characterization of the polymer supported complexes is impossible, attempts were made to understand the environment surrounding the metal ion using elemental analyses, spectroscopic (IR, UV/visible, EPR), thermogravimetric, magnetic moment, and surface area studies. These studies are necessary for the proper understanding of their involvement in catalytic reactions. The catalytic properties of these complexes have been demonstrated by studying the oxidation reaction of catechol with H$_2$O$_2$.

EXPERIMENTAL

Materials and methods

Chloromethylated polystyrene beads of 200–400 mesh size crosslinked with 2% divinylbenzene and containing 12% chlorine (Fluka), *o*-phenylenediamine (Loba Chemie), sodium bicarbonate, 2-aminobenzimidazole (Merck), 2-aminophenol (Merck), RuCl$_3$ · 3H$_2$O (Merck), catechol (Loba Chemie), and hydrogen peroxide (30% aqueous solution -Merck) were used as obtained.

TABLE I
Physical and Analytical Data of Polymer Supported Ligands and Complexes

Sample	Color	Elements (%) found			
		Metal	C	H	N
PS-opd	Pale yellow	–	63.55	7.19	1.88
[PS-opdRuCl$_3$(H$_2$O)]	Grayish black	4.00	62.04	6.79	1.65
PS-ap	Pale orange	–	66.81	7.25	2.48
[PS-apRuCl$_2$(H$_2$O)$_2$]	Dark gray	1.53	65.75	6.26	1.79
PS-ab	Pale yellow	–	61.87	6.37	2.88
[PS-abRuCl$_3$(H$_2$O)$_2$]	Gray	2.26	60.86	5.81	2.75

Solvents employed were either of 99% purity or purified by known laboratory procedures.[14]

Elemental analyses of the ligands and complexes were done by an Elemental model Vario EL III. The metal percentage present in the complexes were determined using ICP-AES spectrometer (Thermo Electron, IRIS Intrepid II XSP DUO). Surface area of the samples were measured by multipoint BET method using Micromeritics Gemini 2360 surface area analyzer. Nitrogen gas was used as the adsorbate at liquid nitrogen temperature. Magnetic susceptibility measurements were done using a vibrating sample magnetometer. UV-visible absorption spectra of polymer anchored complexes were recorded in Nujol by a layering mull of the sample on the inside of one of the cuvettes while keeping the other one layered with Nujol as reference (Varian Cary 5000). IR spectra were recorded as KBr pellets (Schimadzu 8000, Japan). The X band EPR spectra were recorded on a Varian E-112 spectrometer at liquid nitrogen temperature. Thermal analyses were done on a Perkin–Elmer, Diamond TG/DTA analyzer at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

Preparation of ligands

Chloromethylated polystyrene beads were functionalized with aldehyde group according to the reported procedure.[15] A mixture of chloromethylpolystyrene (20.0 g), dimethylsulphoxide (300 mL), and sodium bicarbonate (19.0 g) was stirred at 138–140°C for 12 h. The resultant resin was filtered, washed with hot ethanol and methylene chloride. It was then dried *in vacuo* over anhydrous calcium chloride. Polymer bound aldehyde (10.0 g) was swollen in dioxan

(50 mL) for 24 h. Afterwards dioxan was decanted off and amine (2.0 g of 1,2-phenylenediamine, 4.0 g of 2-aminophenol, or 4.0 g of 2-aminobenzimidazole) in absolute ethanol was added. This mixture was refluxed on a water bath for 10 h. The polymer bound Schiff base was filtered, washed several times with dioxan, and ethanol and dried *in vacuo* over anhydrous calcium chloride.[16]

Preparation of complexes

The polymer bound Schiff base (3.0 g) was swelled in chloroform for 1 h. It was filtered and an excess of metal chloride (1 mmol: 0.26 g RuCl$_3$.3H$_2$O) was added and the reaction vessel was sealed. The mixture was shaken for 5 h on a mechanical shaker. The resulting polymer bound metal complex was filtered, washed with methanol, chloroform and acetone and dried *in vacuo* over anhydrous calcium chloride.

Catalytic oxidation of catechol

Kinetic study

The catalytic activities of the complexes towards oxidation of catechol by H$_2$O$_2$ were determined kinetically. A standard solution of catechol in methanol (1×10^{-2} mol dm^{-3}) was prepared afresh before each set of kinetic runs. Hydrogen peroxide (30% w/v; 1 mL) was diluted to 100 mL in a standard flask and was used as such for the catalytic studies. The concentration of the stock solution was estimated permanganometrically.[17]

All the kinetic runs were carried out in 9:1 methanol-water mixtures at room temperature. For following

TABLE II
IR Spectral Data of Polymer Supported Ligands and Complexes (cm^{-1})

PS-opd	[PS-opdRuCl$_3$(H$_2$O)]	PS-ap	[PS-apRuCl$_2$(H$_2$O)$_2$]	PS-ab	[PS-abRuCl$_3$(H$_2$O)$_2$]	Assignments
1650	1638	1653	1644	1641	1637	$\nu_{C=N}$
		1502	1511			ν_{C-O}
	863		874		868	$\nu_{coord\ water}$
	594		544		545	ν_{M-N}

TABLE III
Surface Area and Pore Volume Data of Polymer Supported Complexes

S. no.	Sample	Surface area (Sq m/g)	Pore volume (mL/g)
1	Polymer bound aldehyde	142	0.1479
2	[PS-opdRuCl$_3$(H$_2$O)]	46	0.1174
3	[PS-apRuCl$_2$(H$_2$O)$_2$]	33	0.0989
4	[PS-abRuCl$_3$(H$_2$O)$_2$]	39	0.1098

the reaction kinetics, catechol solution was mixed with the catalyst and the reaction was initiated by adding H$_2$O$_2$ solution. The reaction was monitored spectrophotometrically with respect to time against suitable blank at two wavelengths, at 390 nm where the product of the reaction, o-benzoquinone, absorbs and at 780 nm where the product does not absorb. Any absorbance detected at 780 nm corresponds to the scattering due to the catalyst particles. To get the actual absorbance of the product, the absorbance due to scattering was deducted.[18] The initial rates of the reaction were obtained by fitting the concentration versus time data into the polynomial of the form $[C] = a_0 + a_1t + a_2t^2 + ——$ and obtaining the slope of the curve at $t = 0$.[19] The activity of the catalysts was compared in terms of the initial rates of the reaction.

The reaction between catechol and H$_2$O$_2$ in the absence of the catalyst and that between catechol and catalyst in the absence of H$_2$O$_2$ were also monitored separately using similar procedure and in these cases rate of the reaction was found to be negligibly small.

RESULTS AND DISCUSSION

Characterization of the complexes

The elemental analysis data of the ligands and their complexes are given in Table I. The data indicate the formation of the complexes. The infrared frequencies are given in Table II. All the ligands exhibit a band in the region 1640–1660 cm^{-1}, which can be assigned to the azomethine >C=N linkage[20] of the Schiff base. This band shows a negative shift by 12–15 cm^{-1} in the complexes suggesting coordination of azomethine nitrogen to the metal ion in the complexes. The ligand PS-ap shows a band at 1502 cm^{-1} due to ν_{C-O}

(phenolic). This band undergoes a positive shift to 1511 cm^{-1} in [PS-apRuCl$_2$(H$_2$O)$_2$] suggesting the bonding of phenolic oxygen of the ligand to ruthenium(III).[21] IR spectrum of the free ligand PS-ab shows band at 1440 cm^{-1} due to $\nu_{C=N}$ of the imidazole ring which is unaffected by complexation. Bands seen at 594, 544, and 545 cm^{-1} in the spectra of the complexes [PS-opdRuCl$_3$(H$_2$O)], [PS-apRuCl$_2$(H$_2$O)$_2$], and [PS-abRuCl$_3$(H$_2$O)$_2$] respectively, might be due to the M-N stretching vibration.[22] A sharp band seen in the region 860–880 cm^{-1} indicates the presence of coordinated water.[23] The broad band in the region 3400–3500 cm^{-1} observed in all the complexes is due to the presence of water molecule. Other bands are seen to be little affected by coordination and might be arising from the polymer part.

Surface area and pore volume measurement studies reveal that the surface area and pore volume of the polymer bound aldehyde has been considerably reduced when it is converted into the complexes (Table III). This indicates the inclusion of the complexes in the pores of the polymer.[24]

Thermo gravimetric analysis shows stability of polymer-anchored complexes up to 340°C (Table IV). Below 100°C, the weight loss observed is due to physisorbed water. As the molecular weight of the polymer supported complexes are very large, only a very small percentage of coordinated water is expected (1% in [PS-opdRuCl$_3$(H$_2$O)], 0.5% in [PS-apRuCl$_2$(H$_2$O)$_2$], and 1.5% in [PS-abRuCl$_3$(H$_2$O)$_2$]). A corresponding mass loss has been observed in the thermal decomposition range 120–200°C.[25]

The experimentally observed magnetic susceptibilities of all the present polymer supported Schiff base complexes of ruthenium were negative. This is probably due to the low concentration of the metal and the very large diamagnetic susceptibility of the atoms present in the polymer matrix. The absolute magnetic susceptibility values of the complexes were calculated using approximate molecular weight of the repeating complex unit containing one metal atom, according to a reported procedure.[26] A value of ~ 2 B.M was obtained for the complex, which is as expected for Ru(III) low spin octahedral complexes.[27]

The electronic spectral data (Table V) of the complexes also suggest the octahedral nature of the complexes. It has been reported that in a number of

TABLE IV
Thermogravimetric Data of Polymer Supported Complexes

Compound	I stage			II stage		
	Temperature range (°C)	% Weight loss	Peak T (°C)	Temperature range (°C)	% Weight loss	Peak T (°C)
[PS-opdRuCl$_3$(H$_2$O)]	50–100	17	96	389–450	32	418
[PS-apRuCl$_2$(H$_2$O)$_2$]	50–100	13	92	344–500	35	373
[PS-abRuCl$_3$(H$_2$O)$_2$]	50–100	21	99	369–440	30	410

TABLE V
Electronic Spectral Data of Polymer Supported Complexes

Sample	Absorptions (cm^{-1})	Tentative assignments
[PS-opdRuCl$_3$(H$_2$O)]	30300	Charge transfer
	26110 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$
	19920	$^2T_{2g} \rightarrow {}^4T_{2g}$
	16130	$^2T_{2g} \rightarrow {}^4T_{1g}$
[PS-apRuCl$_2$(H$_2$O)$_2$]	29070	Charge Transfer
	25510 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$
	16660	$^2T_{2g} \rightarrow {}^4T_{1g}$
[PS-abRuCl$_3$(H$_2$O)$_2$]	30860	Charge Transfer
	28490 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$
	17540	$^2T_{2g} \rightarrow {}^4T_{1g}$

Table foot note: sh = shoulder.

ruthenium complexes charge transfer absorptions occur at relatively low energies. In the present complexes, the high intensity transitions around 20,000 and 30,000 cm^{-1} are assigned as charge transfer bands.[28,29] The ground state for the low spin octahedral complexes is $^2T_{2g}$ and the excited states are $^2A_{2g}$, $^2T_{1g}$, ^2E_g. In [PS-apRuCl$_2$(H$_2$O)$_2$] the absorption peak seen as shoulder on the high intensity charge transfer band at 29,070 cm^{-1}, is assigned to the transition $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$. As the crystal field parameters are quite large, the expected electronic transitions $^2T_{2g} \rightarrow {}^2E_g$, usually occur in the region of absorptions of the charge transfer bands and are frequently obscured in all the complexes.[30] However two spin forbidden transitions, $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$, can frequently be observed in the octahedral complexes. The bands occurring in the region 12,000–18,000 cm^{-1} have been assigned to the spin forbidden transitions.[30,31]
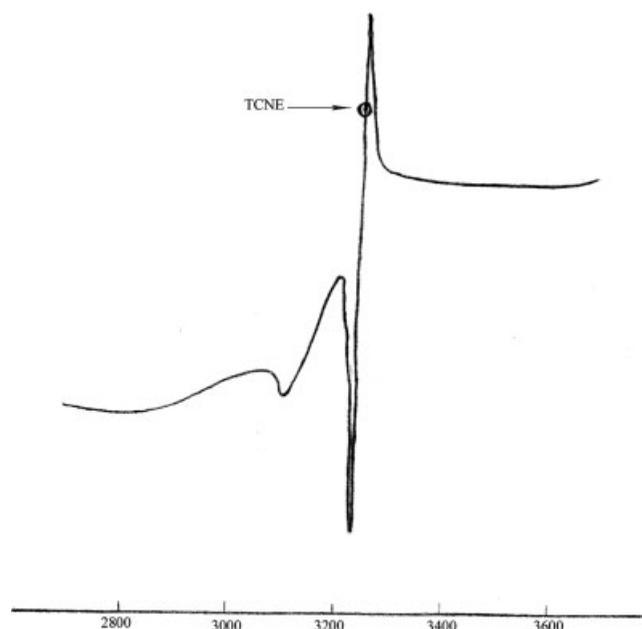
All the polymer supported complexes are seen to be EPR active giving two g values (Table VI), which has been attributed to the axial symmetry of the octahedral molecule (Fig. 1). Suggested structures of the complexes are presented in Figure 2.

Catalytic activity study

Catechol oxidation by H$_2$O$_2$ is known to give the product, o-benzoquinone.[32] In the presence of the

TABLE VI
EPR Spectral and Magnetic Moment Data of Polymer Supported Complexes

| Complex	$g_{\parallel}$ values	$g_{\perp}$ values	Magnetic moment (B. M)
[PS-opdRuCl$_3$(H$_2$O)]	2.1	1.99	1.8
[PS-apRuCl$_2$(H$_2$O)$_2$]	2.1	2.01	2.1
[PS-abRuCl$_3$(H$_2$O)$_2$]	2.1	1.99	1.9

Figure 1 EPR spectrum of [PS-apRuCl$_2$(H$_2$O)$_2$].

polymer supported complexes, the reaction was found to be selective towards the formation of o-benzoquinone. The plots of absorbance versus time were shown in Figures 3–5. The obtained initial rates of the reaction are given in Table VII. These rates show that all the three ruthenium(III) complexes catalyze the oxidation. The percentage conversion of catechol to
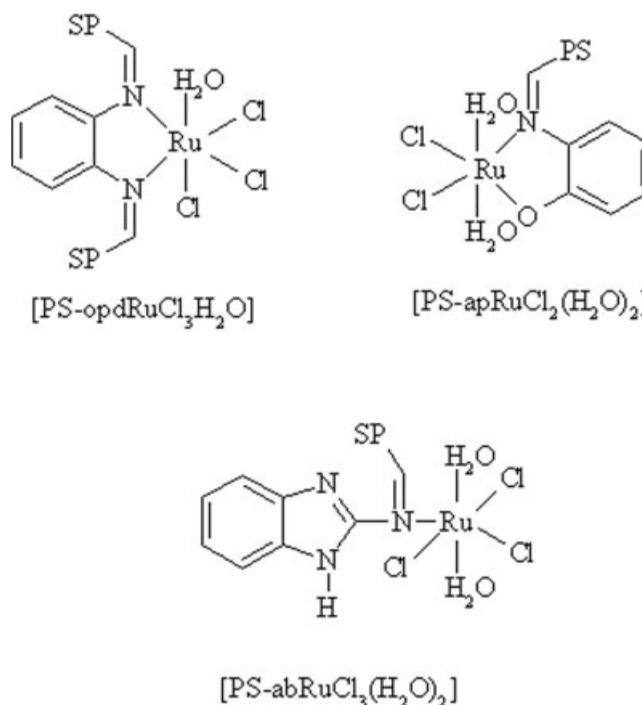
Figure 2 Proposed structures of polymer anchored complexes.
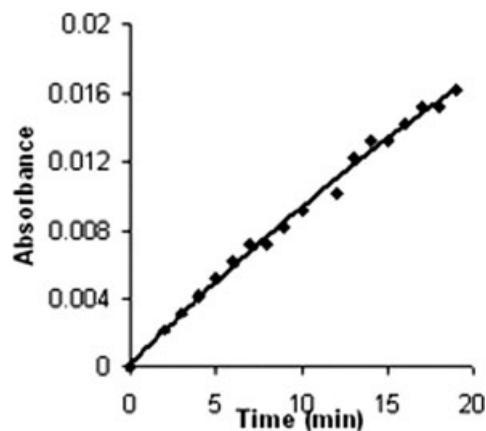
Figure 3 Kinetic plot of absorbance versus time for cate-chol-H_2O_2 reaction catalyzed by [PS-opdRuCl$_3$H$_2$O].
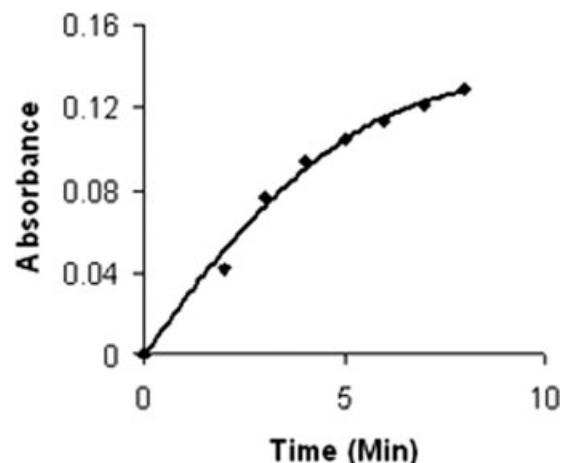
Figure 5 Kinetic plot of absorbance versus time for cate-chol-H_2O_2 reaction catalyzed by [PS-abRuCl$_3$(H$_2$O)$_2$].

o-benzoquinone in 30 min and TOF (h^{-1}) were also calculated and presented in Table VII. In the presence of [PS-abRuCl$_3$(H$_2$O)$_2$] 63% conversion was achieved in 30 min with a TOF (h^{-1}) of 5631. [PS-opdRuCl$_3$(H$_2$O)], [PS-apRuCl$_2$(H$_2$O)$_2$] complexes show activity with lesser percent conversion and TOF. The oxidation of catechol by hydrogen peroxide in the presence of the ruthenium(III) complexes can proceed either by oxidation of catechol by ruthenium(III) complex leading to the formation of ruthenium(II) state and the subsequent oxidation of ruthenium(II) by H_2O_2[33] or by another mechanism, involving oxidation of ruthenium(III) to ruthenium(V) state by H_2O_2 followed by reduction of ruthenium(V)[11] by catechol. The catalytic activity of the complexes is in the order [PS-abRuCl$_3$(H$_2$O)$_2$] > [PS-opdRuCl$_3$(H$_2$O)] ≫ [PS-apRuCl$_2$(H$_2$O)$_2$]. It is reported that the phenolate oxygen stabilizes the higher oxidation states of ruthenium while imine nitrogen stabilizes the lower oxidation state of

ruthenium.[34] As has been mentioned earlier, IR studies of these complexes showed that PS-ab binds to the metal atom through one imino nitrogen, PS-opd binds through two imino nitrogens and ps-ap binds through one phenolate oxygen and one imino nitrogen. As the rates of the reaction of [PS-abRuCl$_3$(H$_2$O)$_2$] and [PS-opdRuCl$_3$(H$_2$O)] are higher than that of the [PS-apRuCl$_2$(H$_2$O)$_2$], a lower oxidation state (Ru^{II}) is thought to be involved in this catalytic reaction. The lower value of [PS-opdRuCl$_3$(H$_2$O)] than that of [PS-abRuCl$_3$(H$_2$O)$_2$] may be due to the steric hindrance caused by the involvement of two polymer chains at the reaction center. If the reaction proceeded through ruthenium(V) formation, a reverse trend in the activity of the complexes would have been observed.

CONCLUSIONS

Ruthenium(III) complexes with polymer-anchored Schiff base ligands PS-opd, PS-ap, and PS-ab have been suggested to have an octahedral structure with axial symmetry. The complexes exhibit potential ac-
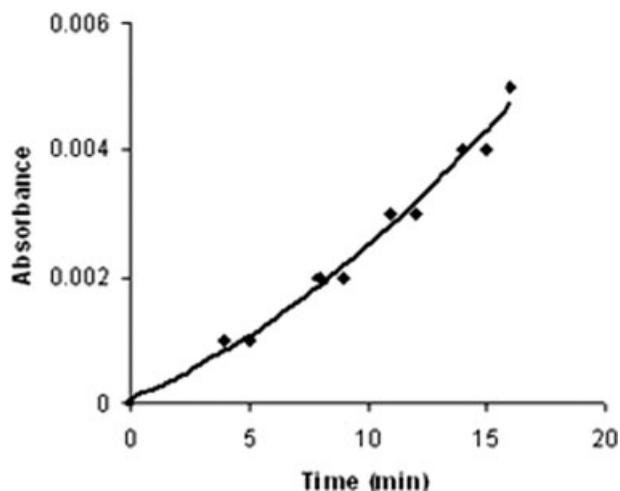
Figure 4 Kinetic plot of absorbance versus time for cate-chol-H_2O_2 reaction catalyzed by [PS-apRuCl$_2$(H$_2$O)$_2$].

TABLE VII
Initial Rates and Percent Conversion of Catechol-H_2O_2 Reaction Using Polymer Supported Complexes of Ruthenium

Catalyst	Initial rate/unit weight of ruthenium $\times 10^5$ (mol dm^{-3} s^{-1} g^{-1})	Conversion (%) in 30 min	TOF (h^{-1})*
[PS-opdRuCl$_3$(H$_2$O)]	12.2	43.1	2172
[PS-apRuCl$_2$(H$_2$O)$_2$]	2.9	7.8	1040
[PS-abRuCl$_3$(H$_2$O)$_2$]	473.1	63.0	5631

[Catechol] = 1 × 10^{-2} mol dm^{-3}. [H$_2$O$_2$] = 1 × 10^{-2} mol dm^{-3}.
* TOF (h^{-1}) = No. of moles of substrate converted per mole of ruthenium in the polymer catalyst in 1 h.

tivity for the oxidation of catechol to *o*-benzoquinone by hydrogen peroxide. The results indicate that ruthenium(II) intermediate complex is involved in the catalytic reaction.

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