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Simple preparation of some reusable and efficient polymer-supported tungsten carbonyl catalysts and clean epoxidation of *cis*-cyclooctene in the presence of H$_2$O$_2$

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Abstract

Tungsten hexacarbonyl was immobilized onto polystyrene (2% cross-linked with divinylbenzene) via different linkages to afford polymer-supported tungsten carbonyl catalysts. These catalysts were used for the epoxidation of *cis*-cyclooctene with hydrogen peroxide. The effect of different solvents and oxygen donors were investigated in the epoxidation of *cis*-cyclooctene with catalyst **2e** and CH$_3$CN was chosen as reaction media and H$_2$O$_2$ as oxidant. We found that the polymer-supported tungsten carbonyl catalysts were efficient and reusable catalysts in this reaction. These catalysts could be reused 3–10 times in the epoxidation of *cis*-cyclooctene.
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1. Introduction

Transition metal complexes are very effective catalysts for a wide variety of organic reactions [1], but one of the major problems associated with these homogeneous catalysts is the recovery of catalyst from the reaction medium. In recent years, there have been intense efforts to develop methods recovering and reusing the homogeneous catalysts [2]. The use of polymer-supported catalysts in organic transformations has been receiving extraordinary attention [3–6], and the design of functionalized polymers carrying catalytically active metal species has attracted considerable interest [7–18]. These immobilized metal-based reagents can offer numerous advantages over their solution-phase counterparts such as: (i) easy separation of the catalysts from reagents and reaction products; (ii) nonvolatile and nontoxic characteristics imparted to the metal complexes upon anchoring to high molecular weight polymer backbone; (iii) simplification of methods of recycling the expensive cata-

lysts; (iv) minimization of certain catalyst deactivation pathways through site isolation. These advantages can make them useful for industrial applications.

Catalytic epoxidation of alkenes is both an important industrial reaction and useful synthetic method for the production of a wide variety of fine chemicals [19,20], because they are derived directly from alkenes, a primary petrochemical source. Many single oxygen donor reagents such as NaIO$_4$, NaOCl, PhIO, ROOH, O$_2$ and H$_2$O$_2$ have been used in catalytic epoxidation of alkenes. Hydrogen peroxide is an efficient and attractive epoxidation reagent, particularly due to its low cost and the absence of pollution by effluents [21]. Over the last two decades, many highly active W(VI) alkene epoxidation catalysts have been developed in the presence of hydrogen peroxide. Recently, Gelbard et al. supported some tungstic species on organic and inorganic supports and used them in the epoxidation of alkenes in the presence of hydrogen peroxide [22–24]. In our previous work, we reported the epoxidation of alkenes by immobilized molybdenum carbonyl catalysts via imidazole and piperazine linkages [25,26]. Here, we describe the immobilization of tungsten hexacarbonyl onto polystyrene (2% cross-linked with divinylbenzene), via functionalization of polymer by different phosphine

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and amine linkages, and investigation of their catalytic activity and reusability in the epoxidation of *cis*-cyclooctene.

2. Experimental

All materials were commercial reagent grade and obtained from Merck. Chloromethylated polystyrene (2% cross-linked with divinylbenzene) was purchased from Merck. A 400 W Hg lamp was used for activation of metal carbonyl. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with a Nicolet Impact 400D instrument. ^{1}H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz spectrometer.

2.1. Functionalization of polystyrene (*1a–1h*)

2.1.1. Preparation of phosphinated polystyrenes (*1a and 1b*)

To a 80 mL DMF in a 250 mL round bottom flask were added 2 g (2.5 mmol Cl) chloromethylated polystyrene and 7.5 mmol phosphine and the mixture was stirred for 20 h at 100 °C. The reaction mixture was filtered and washed thoroughly with benzene (caution: under a hood) and was dried in vacuo for 20 h.

2.1.2. Preparation of aminated polystyrenes (*1c–1h*)

The aminated polystyrenes **1e** and **1f** were prepared by literature methods [27,28]. Other aminated polystyrenes were prepared by the following method: to a 250 mL round bottom flask equipped with a magnetic stirrer bar were added polystyrene (2 g, 2.5 mmol Cl), amine (25 mmol) and NaI (0.13 mmol) and the mixture was refluxed (Scheme 1). Then, in the case of **1c** and **1d** the reaction mixtures were washed with 6 × 40 mL of 3:1

mixture of CH$_3$CN/H$_2$O and with 3 × 40 mL CH$_3$CN, and were dried in an oven (80 °C). In the case of **1g** and **1h**, the reaction mixtures were washed with 5 × 40 mL of CH$_3$CN, 5 × 40 mL of 1:1 CH$_3$OH/1 M, Na$_2$CO$_3$, 5 × 40 mL of 1:1 CH$_3$OH/H$_2$O and with 3 × 40 mL of diethyl ether and then were dried in an oven (80 °C).

2.2. Preparation of polymer-supported tungsten carbonyl catalysts *2a–2h*

A 250 mL round bottom flask containing 2.7 g (7.7 mmol) of W(CO)$_6$ in 90 mL THF was placed under UV irradiation (400 W Hg lamp) for 45 min and then 1.5 g of phosphinated or aminated polystyrene was added to this solution and the mixture was refluxed for appropriate time (Table 2). Then the reaction mixture was filtered, thoroughly washed with THF and was dried in vaccuo for 20 h.

2.3. Characterization of catalysts

The functionalized polystyrenes and polymer-supported catalysts were characterized by elemental analysis and FT-IR spectra. The amount of P (%) and N (%) for functionalized polystyrenes **1a–1h** are given in Table 1 and W (%) and $v_{(CO)}$ for catalysts **2a–2h** are given in Table 2. The amount of phosphorus was determined by the ICP method and the chloride ion content in the resins **1a**, **1b**, **1c** and **1d** was determined by using these polymers as ion exchange resins in a column through which aqueous NaNO$_3$ solution (1 M) was passed. After elution with H$_2$O, the eluate was analyzed for its chloride ion content by the potentiometric titration method, which showed 2.53%, 2.62%, 2.41% and 2.73% (Cl$^-$) for resins **1a**, **1b**, **1c** and **1d**, respec-
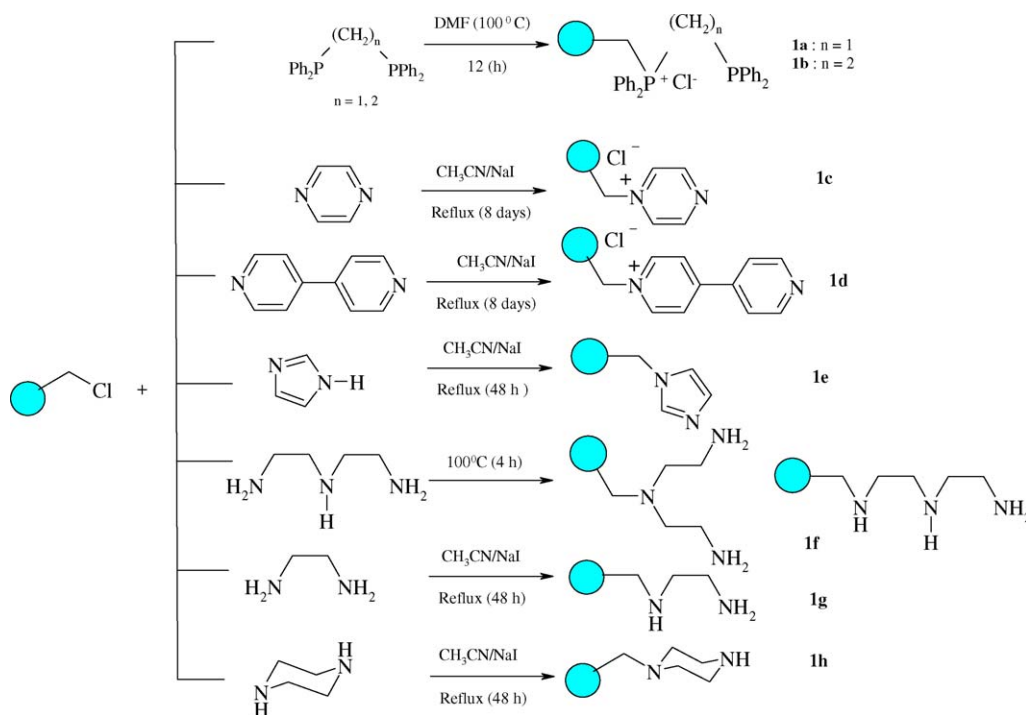
Scheme 1. Preparation of functionalized polystyrenes **1a–1h**.

Table 1
Elemental analysis of functionalized polystyrenes

Functionalized polystyrene	P (%)[a]	N (%)[b]
1a	4.28	–
1b	4.37	–
1c	–	2.17
1d	–	2.21
1e	–	3.00
1f	–	3.41
1g	–	2.29
1h	–	2.06

[a] Determined by ICP method.
[b] Determined by elemental analysis.

Table 2
Refluxing times, W (%) and $v_{(CO)}$ for polymer-supported tungsten carbonyls **2a–2h**

Catalyst	Refluxing time (h)	W (%)	$v_{(CO)}$ (cm^{-1})[a]
2a	3	13.9	2018 (w), 1911 (s), 1864 (m)
2b	3	11.4	1976 (m), 1917 (s), 1864 (m)
2c	1	10.5	2066 (w), 1913 (s), 1865 (m)
2d	1	13.0	2067 (w), 1972 (w), 1918 (s)
2e	3	13.2	2087 (w), 1967 (m), 1921 (s)
2f	20	14.0	2064 (w), 2005 (w), 1919 (s), 1868 (s), 1824 (s)
2g	22	12.9	2064 (w), 2003 (w), 1917 (s), 1864 (s)
2h	4	11.4	1968 (w), 1920 (s), 1869 (m)

[a] w: weak; s: strong; m: medium.

tively. The W (%) of resins **2a–2h** was determined by neutron activation analysis (NAA).

### 2.4. General procedure for epoxidation of cis-cyclooctene

To a 25 mL round bottom flask equipped with a magnetic stirrer bar were added 4 mL CH$_3$CN, 1 mmol alkene, 5 mmol H$_2$O$_2$ (30%) and 0.05 g catalyst and the mixture was refluxed. The reaction progress was monitored by GLC. The reaction mixture was diluted with CH$_2$Cl$_2$ (20 mL) and was filtered. The resin was washed with 4:1 mixture of THF/CHCl$_3$ and the filtrates was purified on a silica gel plates or a silica gel column. IR and ^{1}H NMR spectral data confirmed the identities of the products.

2.5. Reusability of catalysts

After each epoxidation reaction the mixture was filtered and the catalyst was washed five times with CHCl$_3$ and CH$_3$CN, successively, and was dried in an oven (80 °C) for 20 min and then was reused for the next cycle.

3. Results and discussion

The functionalized polystyrenes were readily prepared by direct reaction of phosphines and amines as shown in Scheme 1. Phosphorous and nitrogen loadings of the polystyrenes were determined by ICP and elemental analysis, respectively. Reac-
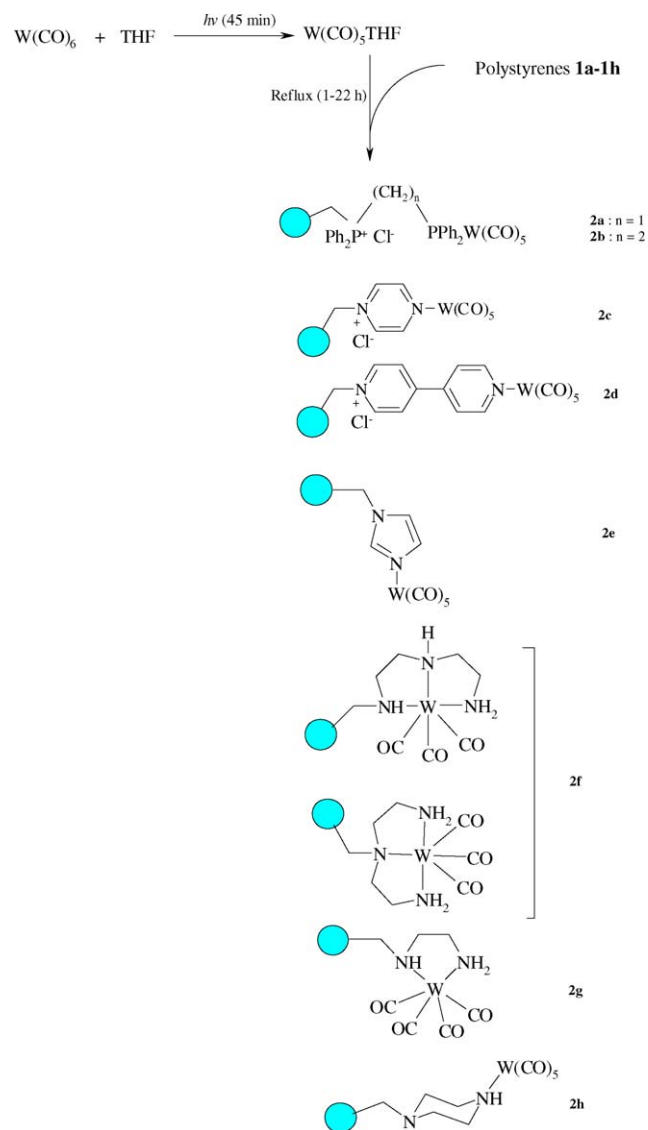
Scheme 2. Preparation of polymer-supported tungsten carbonyl catalysts **2a–2h**.

tion of these functionalized resins with a solution of W(CO)$_6$ in THF (which was activated by UV irradiation), led to attachment of tungsten hexacarbonyl onto the functionalized polystyrene via covalent bond (Scheme 2). The success of immobilization was confirmed by FT-IR spectroscopy and the amount of tungsten loading on functionalized polymer was determined by neutron activation analysis (NAA).

Then we investigated the catalytic activity of these polymer-supported tungsten carbonyl catalysts in the epoxidation of *cis*-cyclooctene. Initially, we studied the epoxidation of *cis*-cyclooctene by catalyst (**2e**) in the presence of H$_2$O$_2$. Among the acetone, THF, chloroform and acetonitrile solvents, CH$_3$CN was chosen as the reaction medium because it gave higher epoxide yields (Table 3). We also investigated the ability of different oxygen donors such as hydrogen peroxide, urea–H$_2$O$_2$ (UHP), *t*-BuOOH, NaIO$_4$/tetrabutylphosphonium bromide in the oxidation of *cis*-cyclooctene and H$_2$O$_2$ was chosen as the oxygen donor (Table 4). Then, we carried out the epoxidation of *cis*-cyclooctene with H$_2$O$_2$ by catalysts **2a–2h** in acetonitrile.

Table 3
Effect of solvent on the epoxidation of *cis*-cyclooctene with H_2O_2 catalyzed by polymer-supported tungsten carbonyl catalyst (**2e**) under reflux conditions[a]

Solvent	Epoxide yield (%)[b]	Time (h)
$(CH_3)_2CO$	5	2
THF	8	2
CH_3CN	94	1.5
$HCCl_3$	17	2

[a] Reaction conditions: *cis*-cyclooctene (1 mmol); H_2O_2 (5 mmol); catalyst (0.05 g); solvent (4 mL).
[b] GLC yield based on the starting cyclooctene.

Table 4
Epoxidation of *cis*-cyclooctene with different oxidants catalyzed by polymer-supported tungsten carbonyl catalyst (**2e**) under reflux conditions[a]

Oxygen donor	Epoxide yield (%)[b]	Time (h)
$NaIO_4$[c]	No reaction	2.5
t-BOOH	No reaction	2.5
Urea/H_2O_2	43	2.5
H_2O_2	94	1.5

[a] Reaction conditions: *cis*-cyclooctene (1 mmol); oxidant (5 mmol); catalyst (0.05 g); acetonitrile (4 mL).
[b] GLC yield based on the starting cyclooctene.
[c] Tetrabutylphosphonium bromide (0.01 g).

Catalysts **2d**–**2g** were more active in the epoxidation of *cis*-cyclooctene. The results summarized in Table 5 showed that the catalysts prepared by immobilization of tungsten hexacarbonyl via nitrogen containing linkages were more active than those prepared by phosphine containing linkages.

During the course of epoxidation of cyclooctene with H_2O_2, the cyclooctene epoxide and the solvent remained intact and no reaction occurred between epoxide and carbonyls or solvent and oxidant.

Blank experiments in the absence of catalysts showed that only 4–7% of cyclooctane oxide was produced.

The reusability of supported catalysts is one of the most important properties and as transition metal complexes are often expensive to purchase or prepare this along with other supporting advantages makes them useful for commercial applications.

Table 5
Epoxidation of *cis*-cyclooctene with H_2O_2 catalyzed by polymer-supported tungsten carbonyl catalysts **2a**–**2h** under reflux conditions[a]

Catalyst	Time (h)	Cyclooctene epoxide (%)[b]
2a	6	39
2b	6	57
2c	6	75
2d	6	90
2e	1.5	94
2f	1.5	93
2g	1.5	96
2h	4	51

[a] Reaction conditions: *cis*-cyclooctene (1 mmol); H_2O_2 (5 mmol); catalyst (0.05 g); acetonitrile (4 mL).
[b] GLC yield based on the starting cyclooctene.

Therefore, we investigated the reusability of polymer-supported tungsten carbonyl catalysts **2a**–**2h** in the epoxidation of *cis*-cyclooctene. The results are given in Table 6. Almost for all catalysts, after the first run, the activity of catalysts increased. Catalysts **2a** and **2b** preserve their activity four times and then their activities decreased. Catalysts **2c** and **2d**, in which tungsten carbonyl was linked to polymer by similar linkages, showed different behavior in repeated epoxidation of *cis*-cyclooctene. In the case of catalyst **2c**, the activity decreased after the fourth run, but catalyst **2d** was highly active upon 10 times without significant decrease in its activity. This trend was similarly observed between catalysts **2g** and **2h**; catalyst **2h** showed higher reusability than catalyst **2g**. Despite the fact that catalysts **2f** and **2g** showed higher activity in the initial step, the activities of those decreased suddenly in the third run.

Another advantage of these catalysts is clean epoxidation of *cis*-cyclooctene. In fact, in the epoxidation of cyclooctene catalyzed by supported catalysts **2a**–**2h**, no by-product was observed in the reaction mixture.

The nature of the recovered catalysts was studied by FT-IR spectra, in which the FT-IR spectra of recovered catalysts showed that the CO bands disappeared and this led to increase in the catalytic activity. The mechanism of these reactions was reported previously [29].

Table 6
Reusability of catalysts **2a**–**2h** in the epoxidation of *cis*-cyclooctene with H_2O_2 under reflux conditions[a]

Run	Cyclooctene epoxide (%)[b]							
	Catalyst **2a**	Catalyst **2b**	Catalyst **2c**	Catalyst **2d**	Catalyst **2e**	Catalyst **2f**	Catalyst **2g**	Catalyst **2h**
1	39 (6)[c]	57 (6)	75 (6)	90 (6)	94 (1.5)	93 (1.5)	96 (1.25)	51 (4)
2	50 (4)	70 (4)	83 (6)	96 (4)	93 (0.75)	86 (1.5)	87 (1.25)	83 (4)
3	53 (4)	69 (4)	80 (6)	98 (4)	93 (0.75)	52 (1.5)	65 (1.25)	91 (4)
4	36 (4)	58 (4)	69 (6)	98 (4)	93 (0.75)	35 (1.5)	25 (1.25)	95 (4)
5	19 (4)	54 (4)	54 (6)	98 (4)	93 (0.75)	–	–	94 (4)
6	–	45 (4)	43 (6)	97 (4)	93 (1)	–	–	96 (4)
7	–	–	–	96 (4)	83 (1)	–	–	94 (4)
8	–	–	–	96 (4)	78 (1)	–	–	61 (4)
9	–	–	–	95 (4)	64 (1)	–	–	–
10	–	–	–	95 (4)	52 (1)	–	–	–

[a] Reaction conditions: *cis*-cyclooctene (1 mmol); H_2O_2 (5 mmol); catalyst (0.05 g); acetonitrile (4 mL).
[b] GLC yield based on the starting cyclooctene.
[c] Refluxing times (h).

4. Conclusion

In conclusion, we prepared polymer-supported tungsten carbonyl catalysts by immobilization of tungsten hexacarbonyl onto polystyrene via different phosphine and amine linkages and we found that some of these catalysts are highly reusable and efficient in the epoxidation of *cis*-cyclooctene. Polymer-supported tungsten carbonyl catalysts immobilized by nitrogen linkages show higher activity than those immobilized by phosphine linkages.

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