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Polymer-supported diimine molybdenum carbonyl complexes as highly reusable and efficient pre-catalysts in epoxidation of alkenes

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Abstract By reaction of aldehydic polystyrene and ethylene diamine, polystyrene-imine-amine reagent was produced. Reaction of this reagent with benzaldehyde and 4-nitrobenzaldehyde resulted in polystyrene-diimines (3a and 3b). These reagents were used for the immobilization of molybdenum hexacarbonyl. The functionalized polystyrene and supported-diimine molybdenum carbonyl catalysts were characterized by FT-IR spectrum and CHN analysis. The molybdenum content of catalysts was determined by neutron activation analysis. Supported-diimine molybdenum carbonyl pre-catalysts (3aM and 3bM) were used in epoxidation of cyclooctene, and the reaction parameters such as solvent and oxidant were optimized and the epoxidation of different alkenes was investigated in optimizing these conditions. The obtained results in the presence of polymer-supported diimine molybdenum carbonyl pre-catalysts (3aM and 3bM) showed that they were very active and selective in the epoxidation of a wide range of alkenes. The reusability of the supported pre-catalysts was also studied. The results showed that they were highly reusable in epoxidation of alkenes.

Keywords Polymer-support · Molybdenum carbonyl · Diimine complex · Epoxidation

Introduction

There has been considerable recent interest in development of supported metal complex in organic transformation, and many studies in this field have been devoted to

G. Grivani (⊠) · A. Halili School of Chemistry, Damghan University, 36715-364 Damghan, Iran e-mail: grivani@du.ac.ir immobilization of transition metal complexes via covalent bonding to inorganic and organic supports [1-10]. Most of these studies have been carried out to prepare new catalysts which combine all the advantages of heterogeneous and homogeneous catalysts [11, 12]. The most important advantages came from the use of supported catalysts with ease of separation of product from reaction mixture, recovery and recycling of catalyst and simplification of the workup. Organic polymers stand among the most used solid catalytic materials for supporting the homogeneous phase because of the wide variety of coupling reactions capable of performing a covalent anchorage of the active molecules in to polymeric framework. Among these polymers, polystyrene (2 % DVB known as merifield resin) is one of the most popular polymeric materials used in synthesis because of its inexpensiveness, ready availability, mechanical robustness, facial functionalization and easily swelling by a number of solvents [5].

The design and development of heterogeneous catalysts in olefin epoxidation is considered as one of the most attractive topics in synthetic organic chemistry [13–18]. Epoxidation reaction is an important reaction in organic synthesis because the epoxides are intermediates that can be converted to a variety of products. In our previous works, we described the immobilization of molybdenum hexacarbonyl via phosphine [19], amine [20] and imine– amine linkages [21]. Here we describe the preparation of two new heterogeneous epoxidation pre-catalysts through immobilization of molybdenum hexacarbonyl with new diimine linkages and epoxidation of wide range of alkenes.

Experimental

All materials were commercial reagent grade and obtained from Merck except 18-crown ether-6 that was prepared from Aldrich. Chloromethylated polystyrene (2 % crosslinked with divinylbenzene) was purchased from Merck. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4,000 cm⁻¹ with a Perkin Elmer instrument. All GC yields based on starting materials were obtained by using Teif Gostar Fraz Co with silicon-DC 200 column.

Functionalization of polystyrene (2)

The aldehydic polystyrene and imine–amine polystyrene were prepared as we previously described [21].

Preparation of diimine polystyrene resin (3a)

In a 100 mL round-bottom flask containing 60 mL of dioxane, 3 g of resin 2 was reacted with benzaldehyde in the presence of 18-crown ether-6 (0.01 g) and refluxed. After 20 h the content was filtered off and washed thoroughly with THF and dried in an oven at 90 $^{\circ}$ C.

Preparation of diimine polystyrene resins(3b)

As described for the preparation of **3a**, except that 4-nitro benzaldehyde was used as aldehyde.

Preparation of polystyrene-supported diimine molybdenum carbonyl resins **3aM** and **3bM**

3.5 g of $Mo(CO)_6$ was added to 60 mL of dioxane in 100 mL round-bottom flask and refluxed for 1 h. Then 2 g of polystyrene–diimine resin was added to this solution and it was refluxed for 45 min else. The content was cooled to room temperature, filtered off and thoroughly washed with THF and dried in an oven at 90 °C.

General procedures of epoxidation of alkenes

To a 25 mL round-bottom flask equipped with a magnetic stirring bar 4 mL CCl₄, 0.5 mmol alkene, 1.5 mmol *tert*-butyl hydroperoxide (TBHP) and 0.012 mmol/Mo precatalyst were added and refluxed. The reaction progress was monitored by GLC.

General procedures for reusability of catalysts

The reusability of the polymer-supported diimine molybdenum carbonyl pre-catalysts was studied in repeated epoxidation reaction of *cis*-cyclooctene. The reactions were carried out as described above. At the end of each reaction, the mixture was filtered, washed with 4 mL CHCl₃/THF (in 1:3 ratio) for five times then, dried in an oven at 80 °C and reused.

Results and discussion

Aldehydic polystyrene was used as starting reagent to prepare the catalysts. This reagent was prepared readily by oxidation of chloromethylated polystyrene. Direct reaction of aldehydic polystyrene and ethylenediamine in methanol at reflux conditions resulted in polystyrene-imine-amine reagent. This functionalized polystyrene was characterized by FT-IR spectrum and CHN analysis. The carbonyl peak of aldehydic polystyrene ($v_{CO} = 1,699 \text{ cm}^{-1}$)disappeared, and new peaks appeared at 1,645 cm^{-1} and 3,422 cm^{-1} attributed to $v_{C=N}$ of imine and N–H stretching vibrations of amine of polystyrene-imine-amine bounded resin 2, respectively. By the reaction of benzaldehyde and 4-nitrobenzaldehyde with resin 2 in dioxane in the presence of 18-crown-6, polystyrene-diimine resins 3a and 3b were prepared. CHN analysis of these resins showed 85.21 % C, 7.11 % H, 1.82 % N and 84.12 % C, 7.22 % H, 2.18 % N for resins 3a and 3b, respectively. In FT-IR spectrums of resins 3a and 3b, the peaks of NH disappeared that evidently showed the formation of terminal imine bond. Further evidence for this terminal imine bond formation was obtained using 4-nitrobenzaldehyde as aldehyde reagent. For resin 3b, two new strong peaks were produced at 1,345 and 1,523 cm^{-1} that corresponded to symmetric and asymmetric stretching vibration modes of N-O bonds from -NO₂ groups. These diimine linkages were used for the immobilization of molybdenum hexacarbonyl. To a solution of molybdenum hexacarbonyl in dioxane refluxed for 1 h, each of resins 3a and 3b was added in separate reactions and refluxed for 45 min that resulted in covalent attachment of molybdenum carbonyl onto diimine polystyrenes to give polymer-supported diimine molybdenum carbonyl resins 3aM and 3bM (Scheme 1). The success of immobilization was proved by FT-IR spectrum; v_{CO} (cm⁻¹): 2,070(w), 2,010(m), 1,985 (w), 1,942 (m), 1,895 (s), 1,878 (s), 1,840 (s) for resin **3aM** and 2,070 (w), 2,008 (m), 1,980 (w), 1,938 (m), 1,891 (s), 1,882 (s), 1,840 (s) for resin 3bM. The amount of molybdenum incorporation into the polymer was also detected by neutron activation analysis (NAA) which showed values about 3.49 and 4.26 % for resins 3aM and 3bM, respectively. Based on the local symmetry of cis-[M(CO)₄(L–L)] with C_{2v} point group, four active bands can be assumed [22]. But here seven bands are seen for the two supported molybdenum carbonyl resins **3aM** and **3bM**. For each penta-carbonyl coordination (C_{4v}) and mer-tri-carbonyl coordination (C_{2v}) , three active bands can be seen in the IR spectrum, respectively [22]. Thus in addition to the tetra-carbonyl coordination of the supported ligands (3a and 3b) with the molybdenum carbonyl, the penta-carbonyl and tri-carbonyl coordination of them can be also assumed. This suggestion can be confirmed by comparison of the ratio of N/Mo in the resins 3a and 3b



and **3aM** and **3bM**. If only tera-carbonyl coordination was considered for the resins **3aM** and **3bM**, then the N/Mo ratio must be 2:1 whereas based on the CHN and NA analysis these ratios are 3.57:1 and 3.05 for **3a** and **3b** in relation to **3aM** and **3bM**, respectively. Thus the other penta and tri-carbonyl coordination modes are also present in the immobilization of the molybdenum carbonyl on the polystyrene support (Scheme 1) resulting in observation of more than four bands (seven bands) in the FT-IR spectrum of the resins **3aM** and **3bM**.

The catalytic activity of the resulting pre-catalysts was initially investigated in the epoxidation of *cis*-cyclooctene in the presence of *tert*-butylhydroperoxide (TBHP). Among the solvents of THF, chloroform, carbontetrachloride and acetonitrile, CCl_4 was chosen as the reaction solvent because higher epoxide yield was obtained in that

solvent (Table 1). In the recent years many researchers have investigated the mechanistic aspects of molybdenum(VI)-catalyzed epoxidation reaction in the presence of TBHP [23–26]. Generally they believed that TBHP is coordinated with the molybdenum(VI)-center and activated by it and then oxygen transition can be occurred to the substrate. In addition, the high epoxide yields obtained in the chlorinated solvents such as CCl₄, CHCl₃, 1,1,2,2-tetrachloroethane, and 1,2,dichloroethane [24-27] in similar to homogeneous alkene epoxidation by Mo(CO)₆ catalyst [28]. Almost all of chlorinated solvents have no coordination ability to the metal (molybdenum(VI)) center. As the coordination ability of the solvent increases the solvent competes with TBHP for coordination of the molybdenum(VI) and inhibits the TBHP coordination and retards the reaction progress, resulting in decrease of the epoxide

 Table 1 Epoxidation of cis-cyclooctene with TBHP catalyzed by
 polymer-supported molybdenum diimine (Schiff base) carbonyl precatalysts (3aM and 3bM) under reflux conditions

Solvent	Catalyst 3aM Epoxide (%) ^a	Catalyst 3bM Epoxide
THF	3	3
CH ₃ CN	1.5	1
HCCl ₃	85	87
CCl ₄	94	90

Reaction conditions: cis-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst 0.012 mmol/Mo, solvent (4 mL), reaction time: 1 h

^a GLC yield based on the starting cyclooctene

 Table 2
 Epoxidation of *cis*-cyclooctene with different oxidant catalyzed by polymer-supported diimine (Schiff base) molybdenum carbonyl pre-catalysts
 3aM and **3bM** under reflux conditions

Solvent ^b	Oxidant	Catalyst 3aM Epoxide (%) ^a	Catalyst 3bM Epoxide (%) ^a
CCl ₄ /H ₂ O	NaIO ^c ₄	d	d
	H_2O_2	3	7
	TBHP	8	9
HCCl ₃ /H ₂ O	NaIO ^c ₄	d	d
	H_2O_2	4	3
	TBHP	5	8
CH ₃ CN/H ₂ O	NaIO ^c ₄	d	d
	H_2O_2	4	5
	TBHP	6	2

Reaction conditions: cis-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst 0.012 mmol/Mo, reaction time: 1 h

^a GLC yield based on the starting cyclooctene

^b A 3:1 mixture of organic solvent: water was used

^c Tetrabutylphosphonium bromide (0.01 g) was used

^d No appreciable yield was observed

yield. Thus the observed trend for solvent effect agrees with the literatures. The effect of other different solvents and oxidants such as NaIO₄ and H₂O₂ on the epoxidation of cyclooctene under various conditions was also investigated (Tables 1, 2, respectively). It was clear that in CCl₄ in the presence of TBHP high epoxide yield was observed. This may be related to the ability of TBHP and the inability of the H₂O₂ and NaIO₄ reagents to mix with the organic substrate phase. Therefore, the epoxidation of alkenes was carried out with TBHP in CCl₄ (Table 3). The obtained results in the presence of polymer-supported diimine molybdenum carbonyl pre-catalysts (**3aM** and **3bM**) showed that these catalysts were very active and selective in the epoxidation of a wide range of alkenes (Scheme 2).

We investigated the reusability of the polymer-supported diimine molybdenum carbonyl pre-catalysts **3aM** and **3bM** in the epoxidation of *cis*-cyclooctene. These reactions were monitored by multiple sequential epoxidation of cyclooctene with TBHP (Table 4). After first run the activity of catalysts increases and the supported diimine molybdenum carbonyl pre-catalysts 3aM and 3bM consecutively were reused six times without any loss of their initial activities. The color of the resins 3aM and 3bM changes from the dark-red to the vellowish white (cream color). The FT-IR spectrum of the two pre-catalysts showed that all of the absorptions in the region of 1,800–2,100 cm⁻¹ due to the $v_{\rm CO}$ of carbonyl groups of the original pre-catalysts 3aM and 3bM disappeared after first run and two new peaks appeared in the wave numbers of 905 and 943 cm⁻¹ for **3aM** as well as 908 and 950 cm^{-1} for the **3bM**. These new bands can be attributed to the $v_{\text{sym}(Mo=O)}$ and $v_{\text{asym}(Mo=O)}$, respectively, in comparison to the spectrum of the $MoO_2(acac)_2$. Thus the active centers in these pre-catalysts are the MoO_2^{2+} moiety. Because the epoxidation reaction is carried out in the aprotic solvent (CCl_4) and the active center surrounded by the hydrophobic support (polystyrene), the two imine-bounded pre-catalysts 3aM and 3bM are relatively stable in this conditions and can be reused six times without any loss of their initial activities. In comparison to our previous researches [19–21], considering the cis-cyclooctene as a substrate and estimation of TOFs of catalysts, the activity of the two supported diimine molybdenum carbonyl pre-catalysts 3aM and 3bM is similar to the imine-amine bounded molybdenum pre-catalyst [21] but higher than those imidazole and phosphines bounded molybdenum carbonyl pre-catalysts [19, 20]. In comparison to the recent molybdenum supported catalysts [19–21, 29–33], the activity and selectivity of the pre-catalysts 3aM and 3bM were appreciable. However the reusability of the 3aM and **3bM** catalysts is lower than those catalysts immobilized by imine-amine, phosphines and imidazole bounded Mo(CO)₆ and other recent works [19-21]. It is known that the active center in the molybdenum carbonyl pre-catalysts in the presence of oxidants such as TBHP, is the MoO_2^{2+} moiety that produced in the reaction of oxidant with molybdenum carbonyl [34-36]. It seems that in supported imine-amine [21] and diimine molybdenum carbonyl pre-catalysts 3aM and 3bM the formation of the active MoO_2^{2+} moiety was easier than in supported phosphines and imidazole molybdenum carbonyl catalysts. On the other hand, the stability of the supported phosphines and imidazole molybdenum carbonyl catalysts is more than supported imine-amine and diimine molybdenum carbonyl pre-catalysts due to the higher stability of phosphines and imidazole bindings respect to hydrolyzing than imine binding.

Conclusion

In conclusion we readily functionalized the aldehydic polystyrene by ethylene diamine and then by simple

			Catalyst 3aM			Catalyst 3bM	
Entry	Alkene	Conversion (%) ^b	Epoxide selectivity (%) ^b	Time (h)	Conversion (%) ^b	Epoxide selectivity (%) ^b	Time (h)
1		94	100	1	90	100	1
2	\bigcirc	92	79 (21% benzaldehyd) ^c	2	92	82(18% benzaldehyd) ^c	1.75
3		91	69(31% acetophenon) ^c	4	93	80(20% acetophenon) ^c	3
4		61	100	2	60	100	3
5	~~~~	87	100	2.5	92	100	3
6	~~~~~	≫98	100	4	92	100	4.5
7		32	100 ^d (<i>trans</i>)	5	96	100(<i>trans</i>)	5
8		88	100(77 ^d cis, 23 trans)	5	100	100(67 ^d cis, 33 trans)	5
9		88	90(8% verbenon, 2% verbenol) ^c	3	48	93(6% verbenon, 3% verbenol) ^c	4

Table 3 Epoxidation of alkenes with TBHP catalyzed by polymer-supported diimine (Schiff base) molybdenum carbonyl pre-catalysts 3aMand 3bM under reflux conditions

Reaction conditions: alkene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.012 mmol/Mo), CCl₄ (4 mL)

^a GLC yield based on starting alkene

^b By product yield

^c Based on ¹H NMR data



Scheme 2 Epoxidation of alkenes by the polymer-supported diimine molybdenum carbonyl pre-catalysts **3aM** and **3bM**

 Table 4
 Reusability of pre-catalysts 3aM and 3bM in epoxidation of cis- cyclooctene with TBHP under reflux conditions

Run	Catalyst 3a M Cyclooctene epoxide (%) ^a	Catalyst 3bM Cyclooctene epoxide (%) ^a
1	94	90
2	96	93
3	96	95
4	94	94
5	93	93
6	93	93

Reaction conditions: *cis*-cyclooctene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.012 mmol/Mo), CCl_4 (4 mL), reaction time (1 h)

^a GLC yield based on starting alkene

reaction of this functionalized polystyrene with benzaldehyde and 4-nitrobenzaldehyde, diimine polystyrenes **3a** and **3b** were produced. These reagents were readily used for the immobilization of molybdenum hexacarbonyl and polymer-supported diimine molybdenum carbonyl pre-catalysts **3aM** and **3bM** were readily prepared. These pre-catalysts showed high activity and reusability in epoxidation of alkenes.

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