

Dodecatungstocobaltate and Sn (IV)-Substituted Polyoxometalate: Preparation, Characterization and Catalytic Performances in Solventless Synthesis of Bis(indolyl)methanes

Ezzat Rafiee*, Zohreh Zolfagharifar, Mohammad Joshaghani and Sara Eavani

Faculty of Chemistry, Razi University, Kermanshah, 67149, Iran.

Received 22 December 2011, revised 14 June 2012, accepted 19 June 2012.

ABSTRACT

Electrophilic substitution reaction of indole with various aldehydes and cyclohexanone were carried out in the presence of electron-transfer ($K_5CoW_{12}O_{40} \cdot 3H_2O$) and green Lewis acid ($[(n-C_4H_9)_4N]_3PMo_2W_9(Sn^{4+} \cdot H_2O)O_{39}$) catalysts. These catalysts were characterized by N_2 -adsorption measurements, FT-IR, UV-Vis, ^{31}P NMR, TGA, cyclic voltammetry and elemental analysis. Mechanisms for their catalytic activity are proposed. Both of these catalysts can be recovered and reused.

KEYWORDS

Dodecatungstocobaltate, Sn (IV)-substituted polyoxometalate, bis(indolyl)methanes, electrophilic substitution, solvent-free conditions.

1. Introduction

Although polyoxometalates (POMs) have been known for well over a century, only in the last few years has scientific interest in these materials begun to increase dramatically. The development, characterization and exploitation of new catalysts based on heteropoly compounds (HPCs) are exceptionally active and fast-developing fields.¹⁻³ This fact lies in the extreme variability of compositions, specific molecular architectures, environmentally friendly behaviour, acidity and redox potentials. The most common form is the Keggin structure, $[XM_{12}O_{40}]^{n-}$, characteristic of $PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$ and other derivatives.⁴ Many chemical variations possible for this common structure include substituting the central heteroatom, changing one or more of the framework metals, or substituting different cations for the protons to make their acidic or neutral salts. This broad compositional variability allows the modification of their catalytic performance from acid type to various oxidation processes. $K_5CoW_{12}O_{40}$ is the most important example of heteropoly species based on a *d*-transition-metal heteroatom that is used as an electron-transfer catalyst in some organic transformations.⁵⁻⁷ This is apparently a perfect outer-sphere one-electron oxidant due to the presence of a sheath of chemically inert oxygen atoms, which protect the central ion from undesired inner-sphere substitution reactions.⁸ Metal-substituted POMs, $[XM'_mM_{12-m}O_{40-m}]^n$, synthesized by removing of $M=O$ moieties from the saturated POM and replaced by other metals (M'), with a varied of ligands, e.g. solvent molecule, are another interesting example of HPCs. Recently, interest in the catalysis of these compounds has grown because of their unique reactivity, which depends on the composition and structure of the active sites.⁹ Substituted derivatives with multivalent cations can act as Lewis acid catalyst in organic reactions.^{10,11} These compounds are promising green catalysts since most of them are environmentally friendly and non-corrosive materials in comparison with traditional Lewis acids.

The importance of indoles and their derivatives is well recognized by synthetic as well as biological chemists. Bis(indolyl)methanes (BIMs), which contain two indole units in a molecule, are the most active cruciferous substance for promoting beneficial estrogen metabolism in women and men.¹² BIM induces apoptosis in human cancer cells and may also normalize abnormal cell growth associated with cervical dysplasia.¹³ Therefore, significant efforts have been directed towards the synthesis of these molecules. In general, BIMs are obtained from the condensation of indoles with aldehydes or ketones in the presence of protic or Lewis acids.¹⁴⁻²⁴ However, many Lewis acids are deactivated or sometimes decomposed by nitrogen-containing reactants. Even when the desired reactions proceed, more than stoichiometric amounts of Lewis acids are required and some of them generate harmful wastes that pose environmental problem. In addition, to the best of our knowledge, there is no report on the use of electron-transfer reagents as a catalyst for this conversion. Along this line and in order to extend the catalytic activities of HPCs, we now introduce $K_5CoW_{12}O_{40} \cdot 3H_2O$ and $[(n-C_4H_9)_4N]_3PMo_2W_9(Sn^{4+} \cdot H_2O)O_{39}$ (Sn^{4+} -POM) as electron-transfer and Lewis acid catalysts for the synthesis of BIMs.

2. Experimental

2.1. Materials

$[(n-C_4H_9)_4N]Br$, $SnCl_4$, KCl , HCl , $HOAc$, H_3PO_4 , sodium molybdate and sodium tungstate were obtained from Merck and $Co(OAc)_2 \cdot 4H_2O$ and potassium persulfate from Aldrich. The organic materials were commercially available and purchased from the Fluka, Merck, and Aldrich chemical companies.

2.2. Characterization Techniques

Catalyst surface areas were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Elemental analyses were performed using inductively coupled plasma (ICP atomic

* To whom correspondence should be addressed. E-mail: ezzat_rafiee@yahoo.com / e.rafiei@razi.ac.ir

emission spectroscopy) on a Spectro Ciros CCD spectrometer. UV-Vis spectra were obtained with a Shimadzu 160 spectrometer. FT-IR spectra were recorded as KBr pellets using a NICOLET FTIR NEXUS spectrometer. ^{31}P NMR spectrum was recorded on a Bruker Avance 200 MHz NMR spectrometer with CH_3CN as the solvent. Chemical shifts were referenced to 85 % H_3PO_4 . Cyclic voltammetry was performed on an Auto Lab 30 analyzer. The working electrode was glassy carbon and Pt wire and Ag/AgCl (KCl saturated) were used as the counter electrode and the reference electrode, respectively. Thermogravimetric analysis (TGA) measurements were performed on a thermal analyzer apparatus of Mettler Company (TGA-Perkin Elmer-7) from room temperature to 600 °C in a nitrogen atmosphere. Each experiment used 25–30 mg of the sample, with a heating rate of 20 °C min^{-1} .

2.3. Catalysts Preparation

2.3.1. Preparation of Sn^{4+} -POM

The synthesis of Sn^{4+} -POM started with the synthesis of $\beta\text{-Na}_8\text{HPW}_9\text{O}_{34}$. To a solution of sodium tungstate (6.0 g in 75 mL of water), 1.5 mL of H_3PO_4 (14.7 M) and 11 mL of acetic acid (17.4 M) were added. A white powder of $\beta\text{-Na}_8\text{HPW}_9\text{O}_{34}$ precipitated. For the preparation of $\alpha\text{-K}_7\text{PMo}_2\text{W}_9\text{O}_{39}$, $\beta\text{-Na}_8\text{HPW}_9\text{O}_{34}$ (11.0 g) was added to an aqueous solution of Na_2MoO_4 (20 mL, 1.0 M) and HCl (15 mL, 1.0 M). Finally, $\alpha\text{-K}_7\text{PMo}_2\text{W}_9\text{O}_{39}$ was precipitated by addition of KCl to the solution. To a solution of $\alpha\text{-K}_7\text{PMo}_2\text{W}_9\text{O}_{39}$ (3.5 g, 1.2 mmol in 25 mL of water), SnCl_4 was added in excess. After 2 h of stirring, tetrabutylammonium bromide was added until a yellowish powder of Sn^{4+} -POM precipitated. The powder was filtered and dried in a vacuum desiccator. After the synthesis, the catalyst was fully characterized.

Anal. Calcd. For $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{PMo}_2\text{W}_9(\text{Sn}^{4+}\cdot\text{H}_2\text{O})\text{O}_{39}$: C, 16.59 %; N, 1.21 %; P, 0.89 %; Mo, 5.52 %; W, 47.65 %; Sn, 3.42 %. Found: C, 18.10 %; N, 0.98 %; P, 0.92 %; Mo, 5.80 %; W, 49.51 %; Sn, 3.01 %.

2.3.2. Preparation of $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$

The synthesis of $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$ started with the preparation of sodium tungstodibocobalt(II)ate from cobaltous acetate (2.5 g, 0.01 mol) and sodium tungstate (19.8 g, 0.06 mol) in acetic acid and water. The sodium salt was then converted to the potassium salt by treatment with potassium chloride. Finally, the cobalt (II) complex was oxidized to the cobalt (III) complex by potassium persulfate (10 g). The crystals of $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}$ were dried. After the synthesis, catalyst was fully characterized and the results compared with authentic spectroscopic data.^{25–27}

Anal. Calcd. For $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$: W, 69.94 %; Co, 1.86 %; K, 6.19 %; O, 21.80 %. Found: W, 67.20 %; Co, 1.41 %; K, 6.01 %; O, 22.25 %.

2.4. Typical Procedure for the Synthesis of BIMs

Aldehyde (1 mmol) and indole (2 mmol) were mixed in the presence of appropriate amount of the catalyst at room temperature. The reaction was performed in CH_3CN (3 mL) as solvent and solventless systems. After completion of the reaction, as indicated by TLC, the catalyst was filtered (in the solventless system the mixture was diluted with ether (5 mL), and then filtered). Evaporation of the solvent under vacuum afforded a crude product which was purified by column chromatography on silica-gel using EtOAc/petroleum ether as eluent. All products were identified by comparing of their spectral data with those of authentic samples.^{28–30}

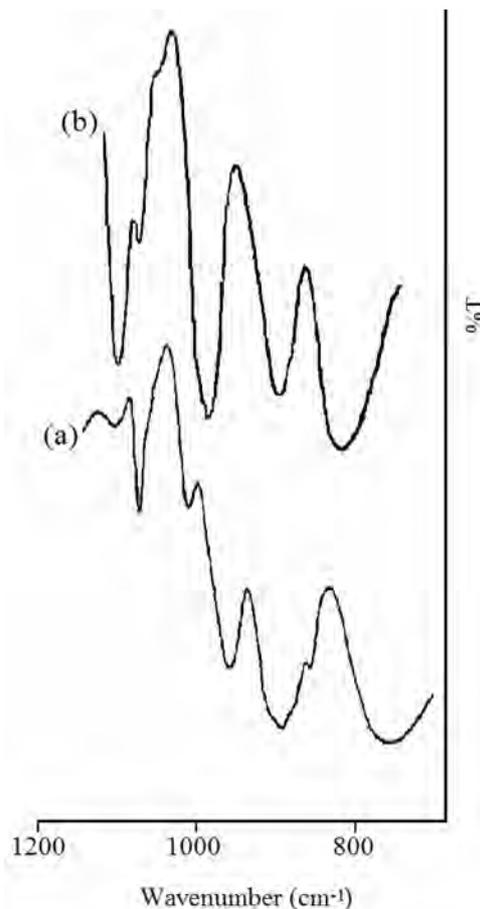


Figure 1 FT-IR spectra of (a) $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$ and (b) Sn^{4+} -POM.

3. Results and Discussion

3.1. Catalysts Characterization

The surface area of the catalysts can be estimated by the nitrogen adsorption BET technique. Both catalysts showed low BET surface areas ($<5\text{ m}^2\text{ g}^{-1}$).

As shown in Fig. 1, there were four characteristic peaks, in the region 700–1200 cm^{-1} in the FT-IR spectra of the catalysts, which can be assigned to the stretching vibrations of M-O_a , $\text{M}'=\text{O}_d$, $\text{M}'-\text{O}_b-\text{M}'$ and $\text{M}'-\text{O}_c-\text{M}'$ ($\text{M} = \text{P}$ or Co and $\text{M}' = \text{Mo}$ or W), in a Keggin structure.

The UV-Vis absorption spectrum (Fig. 2a) of $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$ in water showed an absorption maximum at 261 nm which is characteristic of the oxygen-tungsten charge-transfer band. The other absorption peak located at 210 nm should be attributed to a $\text{O}_d \rightarrow \text{W}$ band which possesses double bond character. As shown in Fig. 2b, for the Keggin Sn^{4+} -POM, two types of charge transfer bands, $\text{O}_d \rightarrow \text{M}$ and $\text{O}_{b,c} \rightarrow \text{M}$ ($\text{M} = \text{Mo}$ or W) can be observed. The $\text{O}_d \rightarrow \text{M}$ band possesses double bond character and thus appears at higher energy. Obviously, the $\text{O} \rightarrow \text{M}$ charge transfer band is independent of the substituted Sn^{4+} and no $d-d$ transition takes place.

The ^{31}P NMR spectrum of Sn^{4+} -POM in dry CH_3CN contains a single signal with $\delta_p = -11.727$ ppm indicating the presence of only one species (Fig. 3).

Analysis of the TGA curve allowed one to distinguish two types of water molecule in $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$ (Fig. 4a). The first weight loss, around 3 %, occurred from room temperature to 125 °C and is due to the loss of physisorbed water. The second one, from 125–275 °C, indicates a weight loss of 2.2 %, in agreement with approximately three waters of crystallization. The

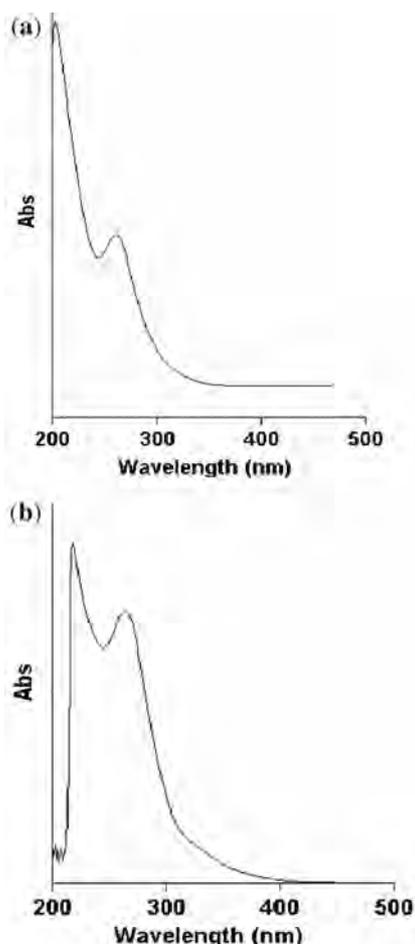


Figure 2 UV-Vis spectra of (a) $K_5CoW_{12}O_{40} \cdot 3H_2O$ in water and (b) Sn^{4+} -POM in acetonitrile.

TGA curve for Sn^{4+} -POM shows a weight loss of 3.8 %, which corresponds to six H_2O molecules per Keggin unit (Fig. 4b).

Cyclic voltammetry was employed to investigate the redox behaviour of the catalysts. The cyclic voltammetry scan of $K_5CoW_{12}O_{40} \cdot 3H_2O$ showed one reversible reduction/oxidation pair corresponding to the $Co^{III/II}$ couple (Fig. 5a). However, it was found that the $Sn^{IV/III}$ couple within Sn^{4+} -POM is an irreversible process (Fig. 5b).

3.2. Catalytic Experiments

3.2.1. Optimization of Reaction Conditions

The catalytic activities of the catalysts were assessed using the

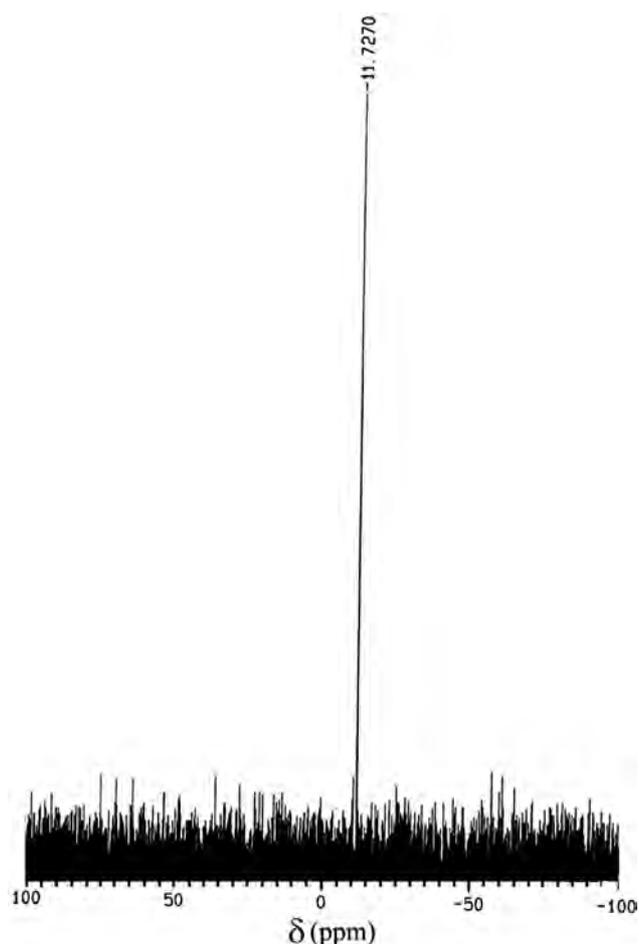


Figure 3 ^{31}P NMR spectrum of Sn^{4+} -POM.

reaction of indole with benzaldehyde as a model reaction. Initially, the catalytic tests were performed under different reaction conditions. As shown in Fig. 6, maximum yield of the product was obtained in the solventless system. With CH_3CN as solvent, the reaction proceeded smoothly and the reaction time significantly decreased under reflux condition. Since it is desirable to perform the reaction in a solventless system as a green and sustainable procedure, further investigations were done by using different amounts of catalysts in the solventless system (Fig. 7). In the case of $K_5CoW_{12}O_{40} \cdot 3H_2O$, best activity was observed at 7 mol% of catalyst to benzaldehyde and no improvement in yield or reaction time was observed when catalyst loading was increased to 10 mol% (Fig. 7a). Based on the results shown in Fig. 7b, 3 mol% of Sn^{4+} -POM to benzaldehyde

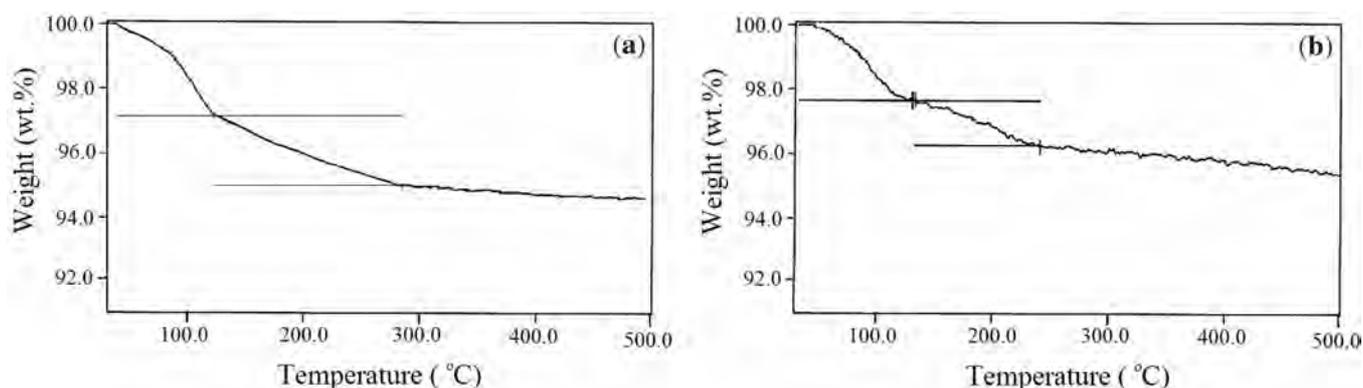


Figure 4 TGA curves of (a) $K_5CoW_{12}O_{40} \cdot 3H_2O$ and (b) Sn^{4+} -POM.

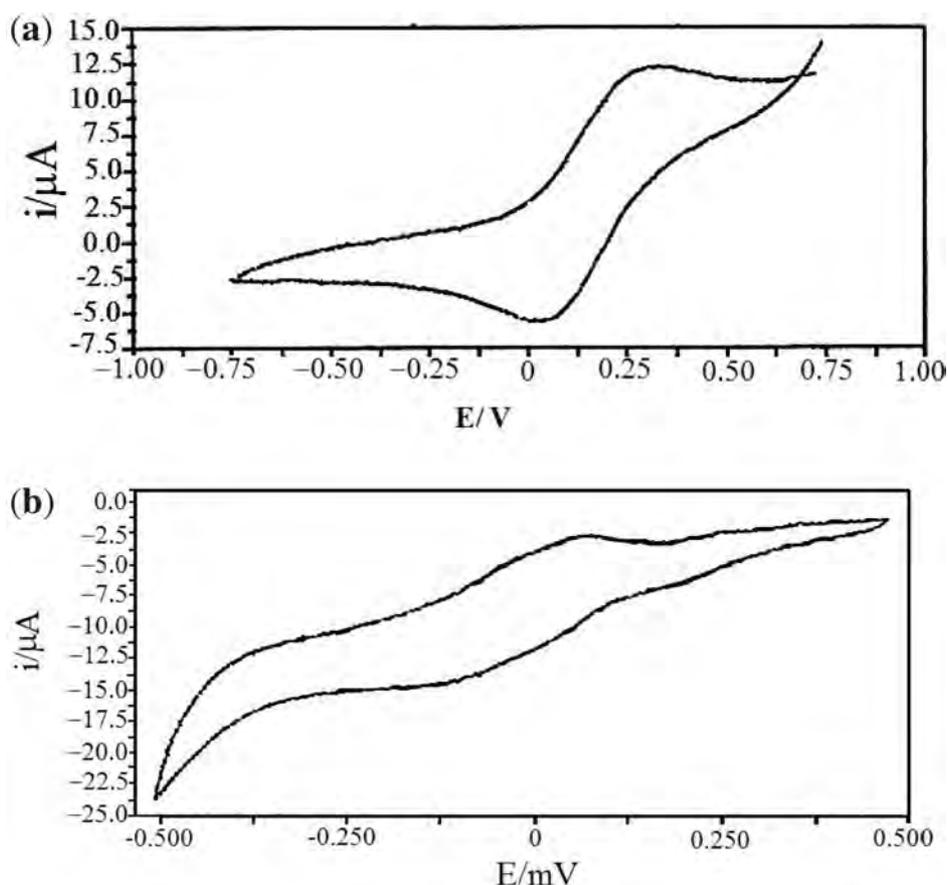


Figure 5 Cyclic voltammetry of (a) $K_5CoW_{12}O_{40} \cdot 3H_2O$ and (b) Sn^{4+} -POM.

was chosen as an ideal amount, while with a lesser amount, the reaction remains incomplete. With 7 mol% of catalyst, the reaction time decreased by only 2 minutes compared with 3 mol%.

3.2.2. Reusability of the Catalysts

To confirm the feasibility of catalyst recycling, indole (10 mmol) was mixed with benzaldehyde (5 mmol) in the presence of $K_5CoW_{12}O_{40} \cdot 3H_2O$ (1.2 g) or Sn^{4+} -POM (0.7 g) under solvent-free conditions. After completion of the reaction, the

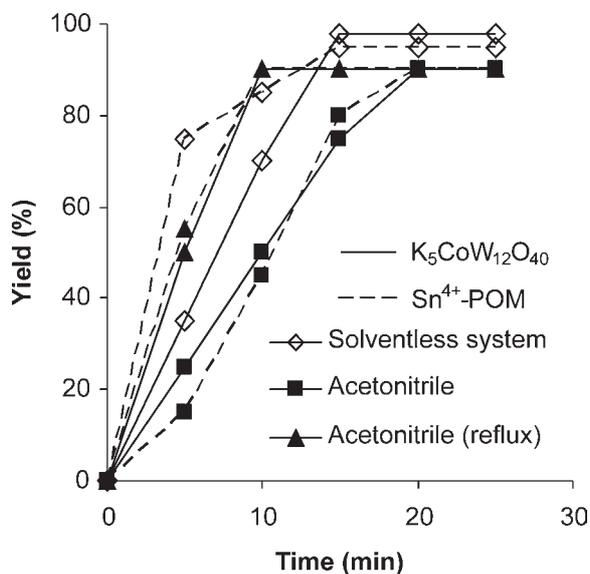


Figure 6 Effect of the reaction conditions on the condensation of indole with benzaldehyde.

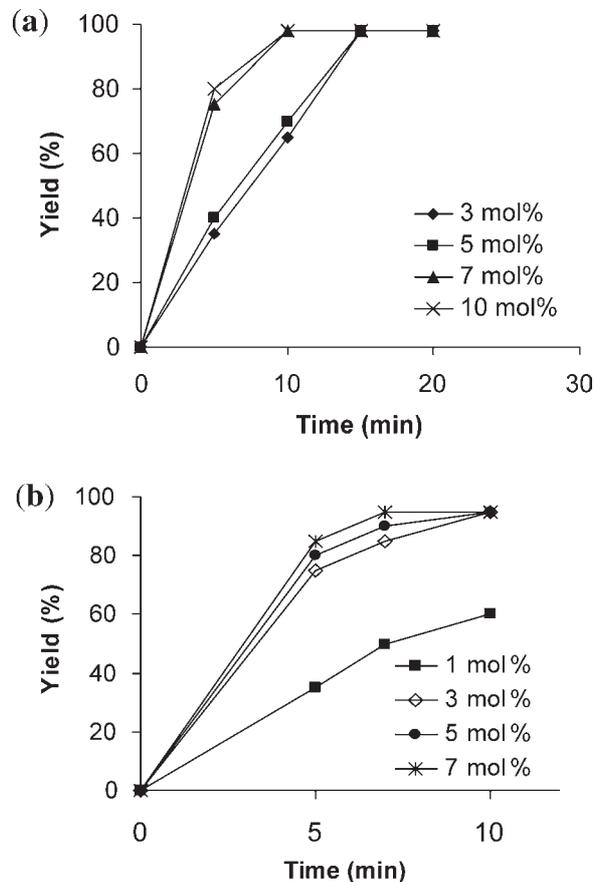


Figure 7 Effect of the amount of (a) $K_5CoW_{12}O_{40} \cdot 3H_2O$ and (b) Sn^{4+} -POM in the reaction of indole with benzaldehyde.

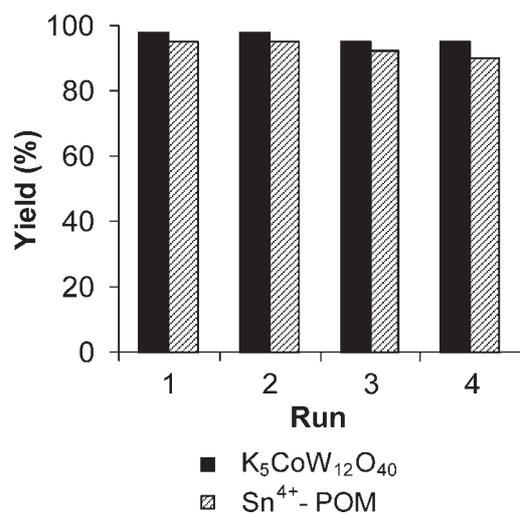
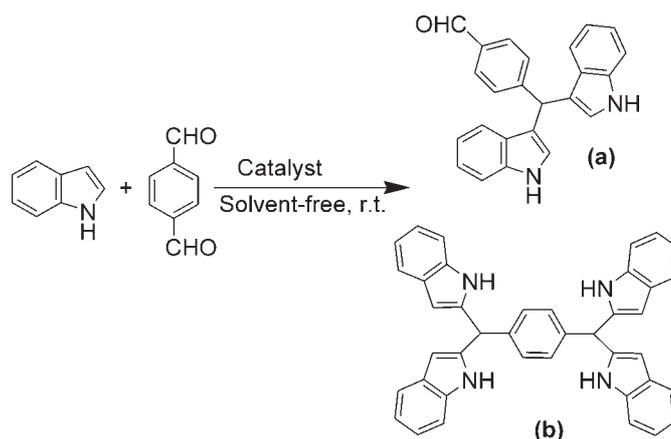


Figure 8 Reusability of the catalysts.

reaction mixture was diluted with ether and centrifuged, the supernatant removed, and the solid catalyst rinsed thoroughly several times with ether and dried. The catalyst was then reused in a second cycle with fresh reaction mixture. This procedure was repeated for four cycles. The results demonstrate that the catalysts can be reused several times without apparent loss of their catalytic activity (Fig. 8). The yield of corresponding BIM promoted by recovered catalysts was nearly the same in all four cycles.

3.2.3. Synthesis of Various BIMs

To evaluate the scope of this protocol, the optimized conditions applied to a range of substrates. As shown in Table 1, K₅CoW₁₂O₄₀·3H₂O has been applied successfully for the condensation of a variety of aldehydes and cyclohexanone with indole in a solventless system. 4-Hydroxy benzaldehyde afforded a low yield of the product in comparison with the other aldehydes (entry 4). As shown in Scheme 1, reaction of terephthalaldehyde



Scheme 1.

Reaction of indole with terephthalaldehyde.

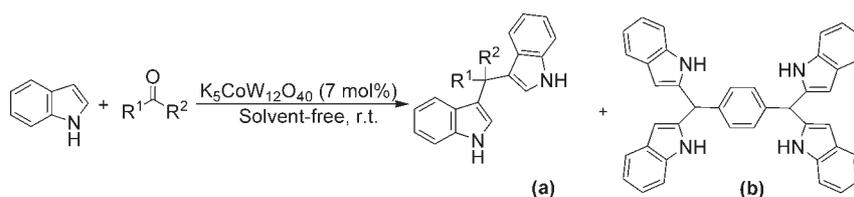
(entries 8, 9) with indole, gave the corresponding products (a) and (b). It seems that selectivity of this reaction can be controlling by the molar ratio of indole. Selective condensation of terephthalaldehyde to the corresponding BIM was achieved by using 2 mmol of indole (entry 8), while by using 4 mmol of indole the corresponding products (a) and (b) were obtained with comparable yields (entry 9).

In the presence of Sn⁴⁺-POM as catalysts, the reactions proceeded normally with excellent yields (Table 2). It was found that the reaction of 2 mmol of indole with terephthalaldehyde gave the corresponding BIM with 72 % selectivity (entry 8), while by using 4 mmol of indole the corresponding products (a) and (b) were obtained with comparable yields (entry 9).

3.3. Suggested Mechanisms

K₅CoW₁₂O₄₀·3H₂O contains a redox-active heteroatom (Fig. 5a). It has been reported that the tetrahedral Co(III) in this compound is a stronger oxidant than Co(III) in conventional

Table 1 Synthesis of various BIMs in the presence of K₅CoW₁₂O₄₀·3H₂O.

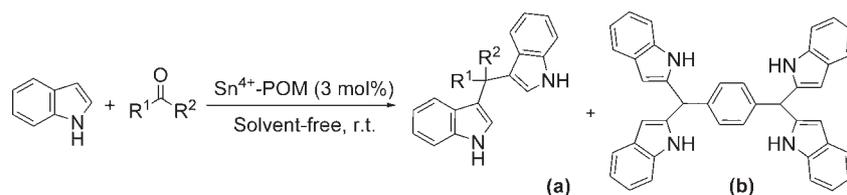


Entry	R ¹	R ²	Time /min	Yield /% ^a
1	H	C ₆ H ₅	15	98
2	H	4-Cl-C ₆ H ₄	5	95
3	H	4-NO ₂ -C ₆ H ₄	10	95
4	H	4-OH-C ₆ H ₄	15	75
5	H	4-CH ₃ -C ₆ H ₅	20	98
6	H	4-OCH ₃ -C ₆ H ₅	8	90
7	H	3,4-(OCH ₃) ₂ -C ₆ H ₃	10	95
8	H	4-CHO-C ₆ H ₄	8	80(15) ^b
9	H	4-CHO-C ₆ H ₄	10	55(45) ^{b,c}
10			10	90

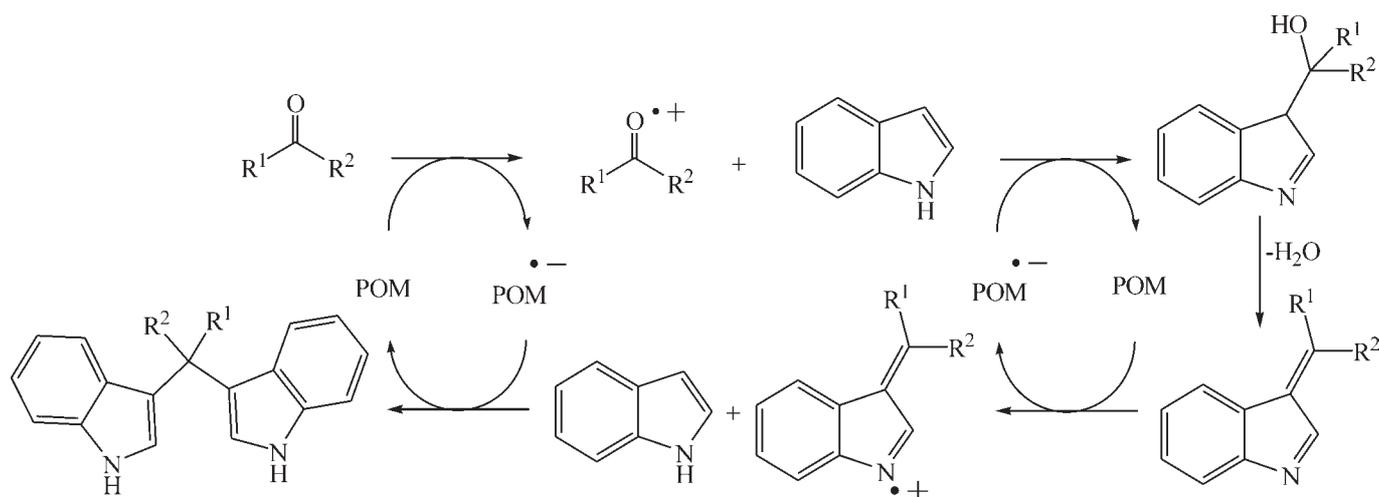
^a Isolated yield.

^b Results in brackets show the yield of product b.

^c 4 mmol of indole was used in this reaction.

Table 2 Synthesis of various BIMs in the presence of Sn⁴⁺-POM.

Entry	R ¹	R ²	Time /min	Yield /% ^a
1	H	C ₆ H ₅	10	95
2	H	4-Cl-C ₆ H ₄	5	80
3	H	4-NO ₂ -C ₆ H ₄	15	98
4	H	4-OH-C ₆ H ₄	20	90
5	H	4-CH ₃ -C ₆ H ₅	15	95
6	H	4-OCH ₃ -C ₆ H ₅	10	90
7	H	3,4-(OCH ₃) ₂ -C ₆ H ₃	15	90
8	H	4-CHO-C ₆ H ₄	15	65(25) ^b
9	H	4-CHO-C ₆ H ₄	15	50(45) ^{b,c}
10			5	98

^a Isolated yield.^b Results in brackets show the yield of the product b.^c 4 mmol of indole was used in this reaction.**Scheme 2.**Suggested mechanism in the presence of K₅CoW₁₂O₄₀·3H₂O as catalyst.

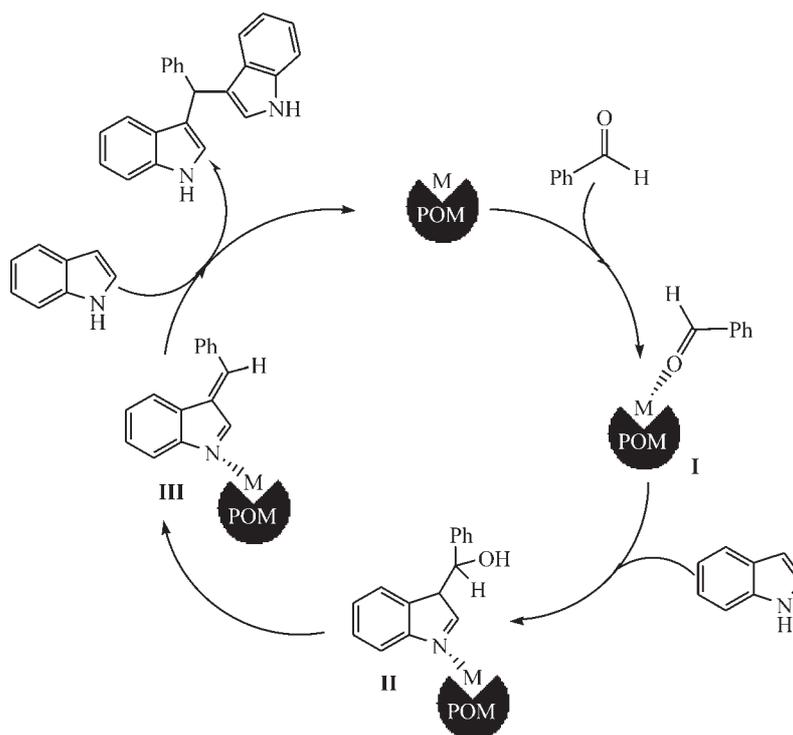
six-coordinate, hydrated complexes.³¹ It seems that the reaction of indole with carbonyl compounds probably proceeds via a one-electron transfer with the initial formation of the radical cation which is the activated species for the reaction with indole. After loss of water, an intermediate is generated (Scheme 2). The intermediate is further activated by the catalyst and serves as an electrophile to attack a second indole molecule. The possibility of a concerted electron-transfer mechanism was strongly supported by a large decrease in the reaction rate upon addition of a small amount of acrylonitrile or 2,6-di-tertbutylphenol as a radical scavenger.

Scheme 3 shows a postulated reaction mechanism in the presence of Sn⁴⁺-POM as a Lewis acid catalyst. First, this catalyst activates the carbonyl group of the aromatic aldehyde to give intermediate I, and is followed by indole attack to give II.

Then loss of H₂O from II affords III which is activated by the catalyst. Another indole is then added to III to give the final product.

4. Conclusions

This study deals with preparation, characterization and catalytic behaviour of K₅CoW₁₂O₄₀·3H₂O and Sn⁴⁺-POM in the synthesis of BIMs. These catalysts exhibited excellent catalytic activities with different reaction mechanisms. K₅CoW₁₂O₄₀·3H₂O acts as an electron-transfer catalyst due to the presence of a redox-active heteroatom, while Sn⁴⁺-POM acts as a Lewis acid catalyst due to existence of Sn (IV). These catalysts are reusable for subsequent runs. The use of environmentally benign catalysts that avoid the use of hazardous organic solvents are an important feature of these methodologies.



Scheme 3.

Suggested mechanism in the presence of Sn^{4+} -POM as catalyst.**Acknowledgements**

The authors thank the Razi University Research Council and Kermanshah Oil Refining Company for support of this work.

References

- 1 A. Bordoloi, S. Sahoo, F. Lefebvre and S.B. Halligudi, *J. Catal.*, 2008, **259**, 232–239.
- 2 S. K. Jana, Y. Kubota and T. Tatsumi, *J. Catal.*, 2008, **255**, 40–47.
- 3 J. Peng, W. Li, E. Wang and Q. Bai, *J. Chem. Soc. Dalton Trans.*, 2001, 3668–3671.
- 4 J.F. Keggin, *Nature*, 1933, **131**, 908–909.
- 5 E. Rafiee and A. Azad, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 2756–2759.
- 6 E. Rafiee and A. Azad, *Synth. Commun.*, 2007, **37**, 1127–1132.
- 7 E. Rafiee, Sh. Tangestaninejad, M.H. Habibi and V. Mirkhani, *Synth. Commun.*, 2004, **20**, 3673–3681.
- 8 I. A. Weinstock *Chem. Rev.*, 1998, **98**, 113–170.
- 9 L. Cheng, H. Sun, B. Liu, J. Liu and S. Dong, *J. Chem. Soc. Dalton Trans.*, 1999, 2619–2625.
- 10 O.A. Kholdeeva, T.A. Trubitsina, G.M. Maksimov and A.V. Golovin, R.I. Maksimovskaya, *Inorg. Chem.*, 2005, **44**, 1635–1642.
- 11 E. Rafiee, I. M. Baltork, Sh. Tangestaninejad, A. Azad, S. Moineea and Z. *Naturforsch.*, 2006, **61b**, 601–606.
- 12 M.A. Zelig, *J. Med. Food*, 1998, **101**, 67–75.
- 13 N. Amino, T. Ohse, T. Koyano and K. Umezawa, *Anticancer Res.*, 1996, **16**, 55–59.
- 14 G. Babu, N. Sridhar and P.T. Perumal, *Synth. Commun.*, 2000, **30**, 1609–1614.
- 15 D. Chen, L. Yu and P.G. Wang, *Tetrahedron Lett.*, 1996, **37**, 4467–4470.
- 16 R. Nagrajan and P.T. Perumal, *Chem. Lett.*, 2004, **33**, 288–296.
- 17 M. Chakrabarty, N. Ghosh, R. Basak and Y. Harigaya, *Tetrahedron Lett.*, 2002, **43**, 4075–4078.
- 18 A.V. Reddy, K. Ravinder, V.L. N. Reddy, T.V. Goud, V. Ravikant and Y. Venkateswarlu, *Synth. Commun.*, 2003, **33**, 3687–3694.
- 19 L. Wang, J. Han, H. Tian, J. Sheng, Z. Fan and X. Tang, *Synlett.*, 2005, 337–339.
- 20 C. Ramesh, J. Banerjee, R. Pal and B. Das, *Adv. Synth. Catal.*, 2003, **345**, 557–559.
- 21 P.R. Singh, D.U. Singh and S.D. Samant, *Synth. Commun.*, 2005, **35**, 2133–2138.
- 22 W.J. Li, X.F. Lin, J. Wang, G.L. Li and Y.G. Wang, *Synth. Commun.*, 2005, **35**, 2765–2769.
- 23 J.T. Li, H.G. Dai, W.Z. Xu and T.S. Li, *Ultrason. Sonochem.*, 2006, **13**, 24–27.
- 24 Z.H. Zhang, L. Yin and Y.M. Wang, *Synthesis*, 2005, 1949–954.
- 25 L.C.W. Baker and T.P. McCutcheon, *J. Am. Chem. Soc.* 1956, **78**, 4503–4510.
- 26 L.C.W. Baker and V.E. Simmons, *J. Am. Chem. Soc.*, 1959, **81**, 4744–4745.
- 27 F. Walmsley, *J. Chem. Ed.* 1992, **69**, 936–938.
- 28 S.J. Ji, S.Y. Wang, Y. Zhang and T.P. Loh, *Tetrahedron*, 2004, **60**, 2051–2055.
- 29 M.A. Zolfigol, P. Salehi, M. Shiri and Z. Tanbakouchian, *Catal. Commun.*, 2007, **8**, 173–178.
- 30 D.M. Pore, U.V. Desai, T.S. Thopate and P.P. Wadgaonkar, *Arkivoc*, 2008, 75–80.
- 31 P. Johnson and C.L. Hill, *J. Appl. Toxicol.*, 1999, **19**, S71–S75.