

Comparative Catalytic Behavior of Prepared Cobalt or Iron Salt of Manganese Substituted Polyoxometalate Supported on Silica in Oxidation of Benzyl Alcohol

Ghaffarzadeh Anari, Farnoosh; Aghabozorg^{,+}, Hamid Reza; Motiee, Fereshte*

Department of Chemistry, Faculty of Science, North Tehran Branch, Islamic Azad University, Tehran, I.R. IRAN

Fouladi, Shahrbanoo

Department of Chemistry, Faculty of Science, Karaj Branch, Islamic Azad University, Karaj, I.R. IRAN

ABSTRACT: Cobalt and iron salt of mono manganese substituted Keggin polyoxometalate have been prepared and supported on silica as heterogeneous catalysts. The prepared compounds were completely characterized by conventional techniques such as FT-IR, ICP-OES, XRD, FESEM, and BET. The results indicated that the primary Keggin structure remain intact in the obtained samples and the prepared particles were in the nanoscale. The surface area of silica support decreased after loading of the cobalt or the iron salt of mono manganese substituted Keggin polyoxometalate on it. Application of the prepared compounds for demonstration of the effect of transition metals such as cobalt (or iron) combined with mono manganese substituted polyoxometalate was investigated in solvent-free oxidation of benzyl alcohol, as a test reaction, using H₂O₂. The results proved that the selectivity of the silica-supported cobalt salt of mono manganese substituted Keggin polyoxometalate catalyst to benzaldehyde was more than that of the other samples. The catalyst can be reused for several runs without losing significant activity.

KEYWORDS: Polyoxometalate, Manganese, Silica, Catalyst.

INTRODUCTION

Polyoxometalates (POMs) are a large species of inorganic molecular compounds with unique metal oxygen frameworks and structures [1]. They are known as an ideal group of early transition metal oxygen anion clusters that have had wide attention for researchers since the 18th century up to now [2]. They have many applications in catalysis, biology, electronics, medicine, etc. [3-6]. Their chemical properties can be controlled by the substitution of transition metals in their structure [7]. Therefore, most

attention should be focused on the metal type of POMs because they are active sites in most chemical reactions, such as oxidative catalyzed reactions [8].

Most of the studies on the catalytic behavior of POMs have been concentrated on homogeneous solutions [9,10] because the major disadvantages of POMs are low surface area and high solubility in polar and oxidative media. Therefore, in order to achieve heterogeneous catalysts and improve the accessibility to active sites, they have been

* To whom correspondence should be addressed.

+E-mail address: hr.aghabozorg@iau-tnb.ac.ir

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supported by different solid matrices, such as silica, zirconia, activated carbon, carbon nanotube [11-14]. Silica is one of the most attractive supports, because it is chemically inert, thermally stable, harmless and inexpensive [15, 16]. For the first time, inclusion of POMs in silica support was reported by *Izumi et al* [17]. Catalysis by POM compounds in oxidation reactions is important due to their special redox properties, strong persistence against oxidants, environmental compatibility, high catalytic activity and chemical selectivity under mild condition [18, 19].

Oxidation of alcohols to aldehydes is one of the main chemical processes that needs a green oxidant, like H_2O_2 and O_2 [20, 21]. Based on POM catalysts, a variety of different catalytic systems with hydrogen peroxide have been designed [22], including substitution of transition metal ions into primary structure and exchanging the completely or partially protons with some of these metals [23, 24]. Among the various transition metal, vanadium substituted polyoxometalates have been widely investigated in alcohols oxidation [25]. Several transition metal such as cobalt, manganese, and iron in other compounds have been also developed for alcohols oxidation due to variable oxidation states and redox properties [26-28]. In this regard, study about the combination of transition metals like cobalt and iron with manganese substituted polyoxometalate supported on silica and their characteristics and catalytic oxidation activities, are very limited.

In this paper, in order to study the influence of combination of cobalt or iron with manganese substituted in POM on catalytic activity of corresponding catalysts, it was focus to design new series of compounds with applying cobalt or iron by substitution in the proton position, and manganese by substitution in POM anions. Therefore, new cobalt or iron salt of mono manganese substituted Keggin polyoxometalate supported on silica compounds were prepared and characterized. Selective oxidation of benzyl alcohol to benzaldehyde, as a test reaction was applied for study the effect of cobalt or iron with mono manganese substituted polyoxometalate anions on catalytic activity of the prepared samples.

EXPERIMENTAL SECTION

Materials

All chemicals were of analytical grade and were used without extra purification. Chemicals such as tungstophosphoric acid hydrate cryst., iron (III) nitrate

nonahydrate, cobalt (II) chloride hexahydrate, sodium hydrogen carbonate, and hydrogen peroxide 30% were purchased from Merck company and manganese (II) acetate tetrahydrate, benzyl alcohol were obtained from Exir GmbH company.

Methods

The prepared samples were characterized by conventional techniques. Fourier transform infrared spectroscopy (FT-IR) were carried out on a Bruker Tensor 27 spectrophotometer in the range of $400-4000\text{ cm}^{-1}$ using KBr pellets. BET surface area, pore volume, pore diameter and nitrogen adsorption desorption isotherms were determined by using BELSORP Mini-II employing N_2 as the adsorbate. Powder X-ray diffraction (XRD) patterns were recorded by using a PANalytical diffractometer with $Cu\ K\alpha$ radiation. Elemental analysis of the prepared samples was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-OES) on a Spectro Arcos ICP-OEC analyzer. Morphology and particle size determination of the samples were studied with field emission scanning electron microscopy (FESEM) analysis by using a MIRA3 TESCAN microscope. The products of the catalytic reactions were analyzed by a GC Varian CP-3800 gas chromatograph equipped with a capillary column ($60\text{ m} \times 0.39\ \mu\text{m} \times 0.25\ \mu\text{m}$) and a FID detector.

Synthesis of mono manganese substituted POMs ($H_3PW_{11}MnO_{40}$)

In a typical procedure, manganese acetate (0.245 g, 1 mmol) which was solved in water was added to a hot solution of $H_3PW_{12}O_{40}$ (2.880 g, 1 mmol) in water its pH was adjusted to 4.5 by using sodium hydrogen carbonate solution. The solution was stirred and heated at $90\text{ }^\circ\text{C}$ for 2 h and the resulting mixture was filtered hot and then allowed to stand overnight at room temperature. The obtained orange crystal was dried at $50\text{ }^\circ\text{C}$.

Synthesis of cobalt or iron salt of mono manganese substituted POMs [$H_{3-x}M_xPW_{11}MnO_{40}$] ($M = Co\text{ or }Fe$)

Cobalt or iron salt of mono manganese substituted polyoxometalate were synthesized by adding dropwise of a stoichiometric amount of aqueous cobalt (II) chloride or iron (III) nitrate, respectively, to a hot filtrate solution of $H_3PW_{11}MnO_{40}$. The obtained mixtures were allowed to stand overnight at room temperature and dried at $50\text{ }^\circ\text{C}$.

Preparation of 30%-cobalt or iron salt of mono manganese substituted POMs silica support [30%-($H_3xM_xPW_{11}MnO_{40}$)/SiO₂ (M = Co or Fe)]

These compounds were prepared via a two sequential-step-impregnation method on mesoporous silica. First, mesoporous silica support and a solution of the stoichiometric amount of the required salt (CoCl₂·6H₂O or Fe(NO₃)₃·9H₂O for cobalt and iron salt of mono manganese substituted polyoxometalate, respectively) were mixed in distilled water. The resulting mixture was stirred for 2 hours. After the removal of its water by a rotary evaporator, the solid powder was dried overnight at 110 °C and calcined for 4 hours at 300 °C. In the second step, the obtained product was impregnated by a solution of the appropriate amount of mono manganese substituted POMs (H₃PW₁₁MnO₄₀) using a rotary evaporator within 2 hours. After the removal of water from the mixture, the obtained sample was dried at 110 °C overnight and calcined at 300 °C for 4 hours.

Catalysts test

A mixture of benzyl alcohol and 30% aqueous hydrogen peroxide was added to a 50 ml flask equipped with a reflux condenser and a magnetic stirrer. The desired catalysts were slowly added to the mixture in a mild reaction condition (catalyst 0.05 g, benzyl alcohol/ H₂O₂: 1:3, 90 °C for 5 h). At the end of the reaction, the mixture was cooled to room temperature and catalysts were separated by a centrifuge. The calculation formulas for the conversion % and selectivity % are as follows:

$$\text{Conversion \%} = \frac{(np_1 + np_2)}{n_{\text{benzyl alcohol}}(\text{FED})} \times 100 \quad (1)$$

$$\text{Selectivity \%} = \frac{np_1}{(np_1 + np_2)} \times 100 \quad (2)$$

Where np_1 is equal to the number of moles of benzaldehyde which is produced per minute, np_2 is equal to the number of moles of benzoic acid which is produced per minute, and n benzyl alcohol is fed per minute

RESULTS AND DISCUSSION

Characterization of catalyst

FT-IR spectra of H₃PW₁₂O₄₀, and mono manganese substituted POMs (H₃PW₁₁MnO₄₀) in the range of 400–1200 cm⁻¹ are shown in Fig. 1. In the FT-IR spectrum of H₃PW₁₂O₄₀ (Fig. 1a), bands at 1080, 980, 890, and 810 cm⁻¹ are assigned to the P–O, W=O, W–O_e–W (O_e: edge-bridging oxygen atoms), and W–O_c–W (O_c: corner-bridging oxygen atoms) vibrational modes, respectively [29].

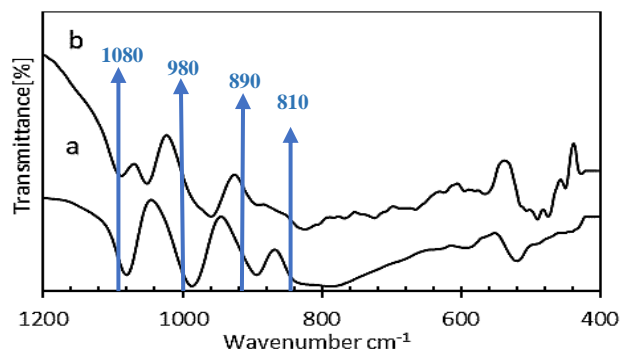


Fig. 1: FT-IR spectra of a) keggin polyoxometalate (H₃[PW₁₂O₄₀]), and b) prepared mono manganese substituted polyoxometalate (H₃PW₁₁MnO₄₀).

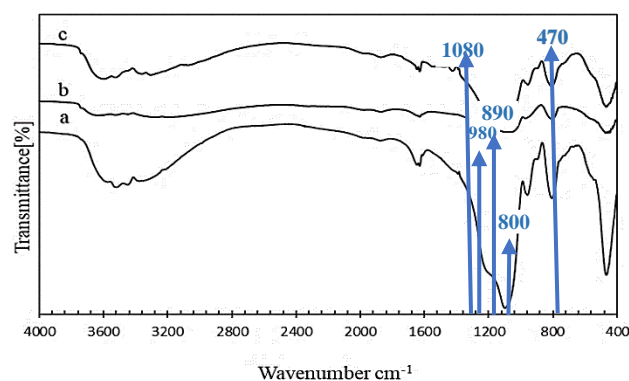


Fig. 2: FTIR spectra of a) the applied silica, b) H_{0.5}Co_{1.25}[PW₁₁MnO₄₀]/SiO₂, c) H_{1.5}Fe_{0.5}[PW₁₁MnO₄₀]/SiO₂

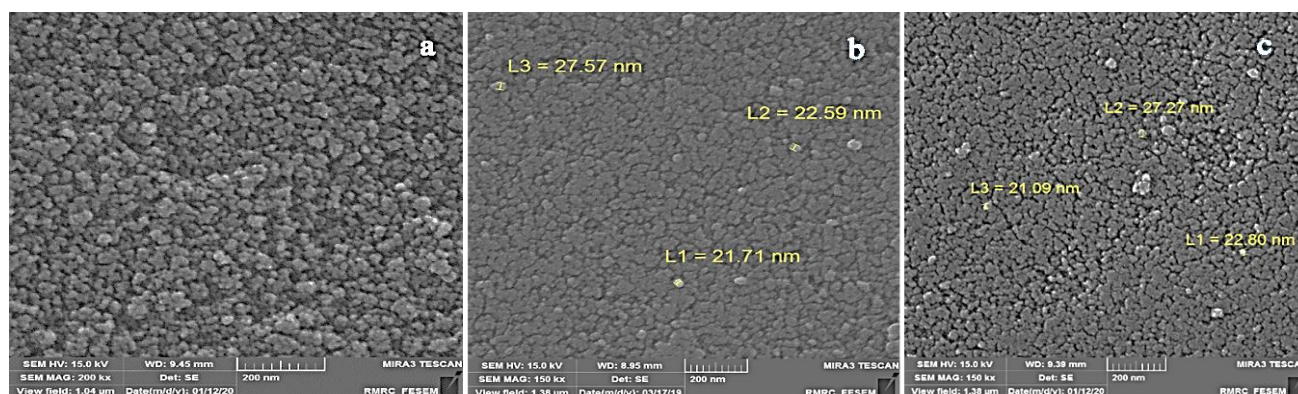
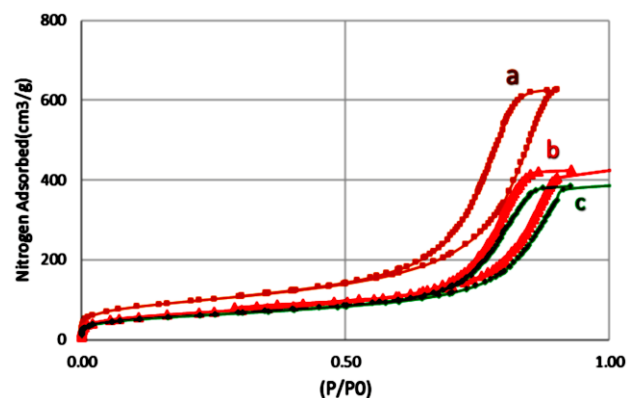
The characteristic bands of mono manganese substituted samples (Fig. 1b) showed a splitting for the P–O bond (1083 and 1041 cm⁻¹) and shifting for the others compared to the H₃PW₁₂O₄₀. The observed splitting and shifting clearly indicate that manganese (II) was introduced into the octahedral lacunary structure of POMs [30]. Thus, the FT-IR spectra clearly show the incorporation of manganese into the Keggin structure. The FT-IR spectra of the prepared cobalt or iron salt of mono manganese substituted polyoxometalate silica supported samples are compared with FT-IR spectrum of silica in Fig. 2 in the 400–4000 cm⁻¹ range. The infrared spectrum of silica (Fig. 2a) shows three characteristic bands at 1080, 800, and 470 cm⁻¹ that can be assigned to asymmetric and symmetric stretching, and bending vibration of Si–O–Si, respectively; and a band at 960 cm⁻¹ that is related to asymmetric stretching of Si–OH [31]. The spectra of the catalysts (Fig. 2b and 2c) are nearly similar to silica. The Keggin structure bands appeared at 980 cm⁻¹ and 890 cm⁻¹. The band related to P–O detected at 1080 cm⁻¹

Table 1: Elemental analysis results of the prepared compounds

Catalyst	Element (Wt%) ^a				
	Mn	Co	Fe	P	Si
$H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]/SiO_2$	0.35	0.5	-	0.2	46.5
$H_{1.5}Fe_{0.5}[PW_{11}MnO_{40}]/SiO_2$	0.34	-	0.18	0.26	46.0

^aObtained by ICP-OES method**Table 2: BET surface area, pore volume and average pore diameters of the samples**

sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Silica	337	1.00	11.52
$H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]/SiO_2$	230	0.65	11.36
$H_{1.5}Fe_{0.5}[PW_{11}MnO_{40}]/SiO_2$	210	0.60	11.32

**Fig. 3: The FESEM images of a) the applied silica, b) $H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]/SiO_2$, c) $H_{1.5}Fe_{0.5}[PW_{11}MnO_{40}]/SiO_2$** **Fig. 4: N₂ adsorption-desorption isotherms of a) the applied silica, b) $H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]/SiO_2$, c) $H_{1.5}Fe_{0.5}[PW_{11}MnO_{40}]/SiO_2$**

and overlapped by the bands related to Si—O—Si. These results suggest that the polyoxometalate is effectively dispersed on silica nanoparticles [32].

Fig. 3 shows FESEM images of the silica (Fig. 3a), cobalt, and iron salt of mono manganese-substituted

polyoxometalate samples supported on silica (Fig. 3b and 3c). These compounds have a spherical shape, similar to the original silica, with diameters between 21 and 28 nm.

The results of the elemental analysis of the catalysts obtained by inductively coupled plasma-optical emission spectrometry (ICP-OES) are shown in Table 1. These results confirmed the elemental composition of the prepared samples.

Fig. 4 shows nitrogen adsorption-desorption isotherms of the silica (Fig. 4a) and the prepared compounds (Fig. 4b and 4c). The resulting plots are type IV isotherms with characteristic hysteresis loops that are relatively similar to that of the silica [33]. BET surface area, average pore diameter, and pore volume of the samples are listed in Table 2. BET surface area, pore volume, and average pore diameter of the silica are 337 m²/g, 1.0 cm³/g, and 11.52 nm, respectively. BET surface area, pore volume, and average pore diameter of the compounds are less than those of the silica which is due to dispersion of the particles in the pores of the silica support [34].

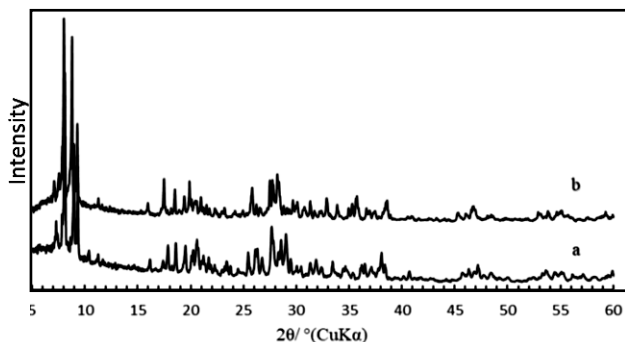


Fig. 5: XRD patterns of a) keggin polyoxometalate ($H_3[PW_{12}O_{40}]$), b) prepared mono manganese substituted polyoxometalate ($H_3PW_{11}MnO_{40}$)

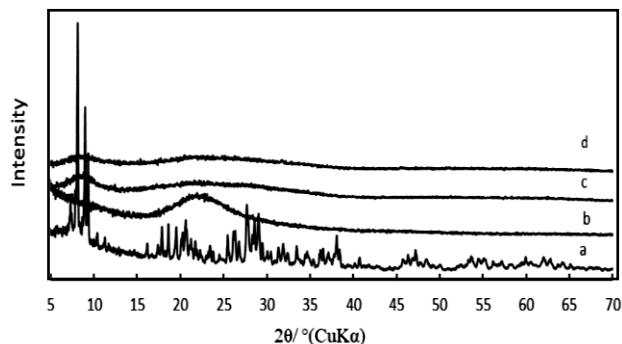


Fig. 6: XRD patterns of a) keggin polyoxometalate ($H_3[PW_{12}O_{40}]$), b) the applied silica, c) $H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]/SiO_2$, d) $H_{1.5}Fe_{0.5}[PW_{11}MnO_{40}]/SiO_2$

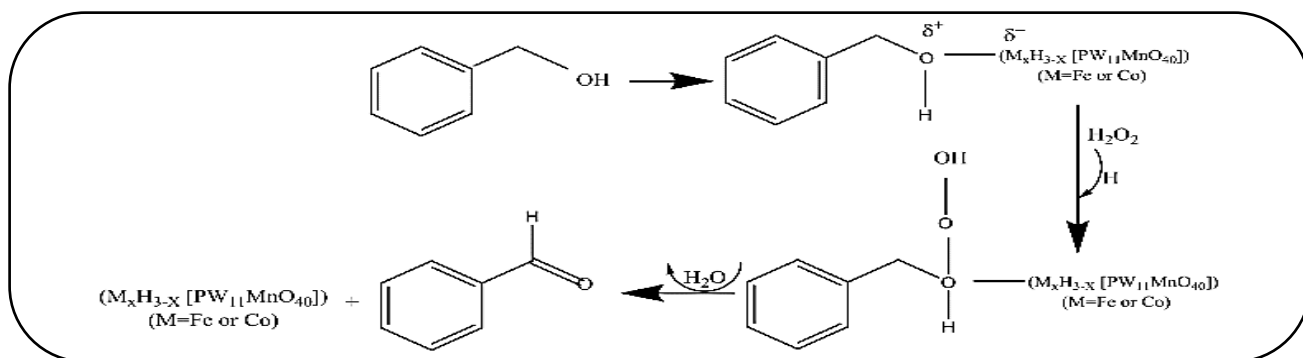


Fig. 7: Mechanism pathway of the catalysts

XRD patterns of Keggin-POM ($H_3[PW_{12}O_{40}]$), and pretreated mono manganese substituted Keggin-POM ($H_3PW_{11}MnO_{40}$) are displayed in Fig.5. These patterns are similar to each other and no further phase is observed in the XRD pattern of $H_3PW_{11}MnO_{40}$. It means that manganese has been doped into the Keggin-POM structure.

XRD patterns of Keggin polyoxometalate ($H_3[PW_{12}O_{40}]$), the silica, and both catalysts are displayed in Fig. 6. This result indicates that the diffraction peaks of Keggin polyoxometalate structure (Fig. 6a) in the compound patterns is covered with the amorphous hump of silica support (Fig. 5b). Therefore, this comparison indicates that the compounds are finely dispersed inside the channels of the silica [35].

The catalytic activity of the catalysts

Oxidation of alcohols to carbonyl compounds is very important in organic synthesis and several methods have been investigated to perform such a reaction [36, 37]. These methods involve the use of long reaction times and toxic oxidants [38]. Therefore, in order to find the best catalytic system, the solvent-free oxidation of benzyl

alcohol to benzaldehyde with H₂O₂ (30%) under mild conditions, as a test reaction was studied in the presence of the prepared catalysts. The results are listed in Table 3. In the presence of $H_3PW_{12}O_{40}$ conversion of benzyl alcohol is low (30%), but by doping of mono manganese into the structure of the polyoxometalate, the conversion increases to 45%. These results show that the incorporation of mono manganese in the structure of the polyoxometalate has essential roles in the oxidation reaction because of its variable oxidation states and redox properties. In order to improve the catalytic system, the addition of transition metals, such as cobalt and iron as counteranions in the structure of mono-manganese substituted polyoxometalate was examined. The results (Table 3) indicate that the nature of transition metal ions has a crucial role in the catalytic activity of these catalysts for the oxidation of benzyl alcohol. It seems that a synergistic effect between these transition metals and polyoxometalate increases the catalytic activity. These results are in agreement with other reports about the use of transition metals in the oxidation of benzyl alcohol [39, 40]. Based on the path mechanism (Fig. 7), POM as Lewis acid is attached to benzyl alcohol oxygen.

Table 3: Catalytic performances of the prepared catalysts for the oxidation of benzyl alcohol (Reaction condition: catalyst 0.05 g, benzyl alcohol/ H₂O₂ = 1:3, 90°C for 5 h).

Entry	Catalyst	Conversion (%)	Selectivity to benzaldehyde (%)
1	-	4	100
2	H ₃ PW ₁₂ O ₄₀	30	58
3	H ₃ PW ₁₁ MnO ₄₀	45	61
4	H _{0.5} Co _{1.25} [PW ₁₁ MnO ₄₀]	53	81
5	H _{1.5} Fe _{0.5} [PW ₁₁ MnO ₄₀]	63	76
6	H _{0.5} Co _{1.25} [PW ₁₁ MnO ₄₀]/SiO ₂	50	98
7	H _{1.5} Fe _{0.5} [PW ₁₁ MnO ₄₀]/SiO ₂	58	91

Table 4: Catalytic performances of fresh and recycled 30%-H_{0.5}Co_{1.25}[PW₁₁MnO₄₀]/SiO₂ catalyst for the oxidation of benzyl alcohol (Reaction condition: catalyst 0.05 g, benzyl alcohol/ H₂O₂ = 1:3, 90°C for 5 h).

Cycle	Conversion (%)	Selectivity to benzaldehyde (%)
Fresh	50.0	98.0
1	50.0	96.0
2	52.5	96.7
3	52.5	96.7
4	50	96.5

Due to its metals (Mn, Co, or Fe) a transition state complex is produced, containing a partial positive charge on the benzyl alcohol oxygen and a partial negative charge on metals of POM. In the next step, hydrogen peroxide as an oxidant, is added to this transition state complex. At the end, a water molecule is removed and a benzaldehyde is formed.

Therefore, H_{0.5}Co_{1.25}[PW₁₁MnO₄₀] and H_{1.5}Fe_{0.5}[PW₁₁MnO₄₀] catalysts were chosen to be loaded on a silica support. A suitable support such as silica allows the compound to disperse over a large surface and therefore, reagents will be in contact with catalyst particles much more efficiently and uniformly which will cause better selectivity. Table 3 indicates that silica has no significant effect on the reaction, but H_{0.5}Co_{1.25}[PW₁₁MnO₄₀] and H_{1.5}Fe_{0.5}[PW₁₁MnO₄₀] compounds have the main role in the reaction. The obtained results confirm that the silica-supported catalysts exhibit higher selectivity to benzaldehyde than that of the unsupported ones under the same conditions. In addition, Fe (III) catalyst as a Lewis acid is stronger than Co (II) catalyst which can lead to oxidation to deep oxidation. So the conversion increase and

selectivity decreases. Hence, H_{0.5}Co_{1.25}[PW₁₁MnO₄₀]/SiO₂ was chosen as the best one due to its higher selectivity to benzaldehyde (98%).

Recycling of the catalyst

The reusability and recyclability of a catalyst system are very important for any catalytic reaction. After completion of the reaction, the catalyst was filtered by centrifuge, washed with toluene, dried at 100 °C, and reused in a fresh reaction. In order to control the reusability of recycled, 30%- cobalt salt of mono manganese substituted polyoxometalate silica-supported, for four runs was used in selective oxidation of benzyl alcohol to benzaldehyde. The results of catalytic activity in the oxidation of benzyl alcohol for different cycles are shown in Table 4. No significant loss of catalytic activity was observed after 4 catalytic cycles. In other words, it could be used without any remarkable change in the conversion and selectivity percentage.

CONCLUSIONS

New Keggin-type cobalt and iron salt of mono manganese substituted polyoxometalate compounds were synthesized. 30%-cobalt or iron salt of mono manganese substituted polyoxometalate was loaded on silica support by impregnation method and evaluated as a catalyst in selective oxidation of benzyl alcohol to benzaldehyde, as a test reaction, using 30% aqueous H₂O₂ as a green oxidant without applying any organic solvent under mild reaction condition.

The obtained results indicated that using transition metals, such as cobalt or iron with manganese-substituted polyoxometalate had an important role in the catalytic behavior of the prepared compounds in the selective

oxidation of benzyl alcohol to benzaldehyde. Moreover, the interaction between cobalt and mono manganese substituted polyoxometalate ($H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]$) increased the selectivity of this compound to benzaldehyde than that of containing the iron. In addition, the distribution of the catalyst on the support has an important effect on the improvement of selectivity to benzaldehyde. The performance of recycled $H_{0.5}Co_{1.25}[PW_{11}MnO_{40}]/SiO_2$ after four runs didn't show any remarkable loss in the conversion and selectivity.

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