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ARTICLE TYPE

A Green Procedure for Direct Oxidation of Organic Halides to Aldehydes and Ketones Catalyzed by Molybdate-Based Catalyst

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A molybdate-based heterogeneous magnetic catalyst was synthesized and used in direct oxidation of various primary and secondary organic halides to corresponding aldehydes and ketones using 30% H₂O₂ as oxidant in ethanol. Various organic halides were oxidized to their corresponding aldehydes and ketones in good to excellent yields. The catalyst system can be easily separated by applying an external magnet and reused in 6 run without any significant loss of catalytic activity. The catalyst was fully characterized by techniques of FT-IR, SEM, TEM, EDS, XRD, VSM, ICP-AES, and elemental analysis (CHN).

Introduction

Aldehydes and ketones are important classes of chemicals which serve as important precursors and intermediates for many drugs, vitamins and fragrances [1-2]. One of the methods for the synthesis of aldehydes and ketones is direct oxidation of organic halides [3-4]. The oxidation of benzyl halides into aldehydes is a well-known transformation in organic synthesis, although the oxidation of aliphatic halides to aldehydes is not common and performed far more difficult than oxidation of benzyl halides [5-7].

Up to now, several methods have been developed for direct oxidation of halides to their corresponding carbonyl compounds. The Hass-Bender [5] and Sommelet [6] reactions are two well-known methods for such a conversion. These methods have some drawbacks. The former method is only suitable for para-substituted benzylic halides and the latter is well for active halides such as benzyl, allyl halides, and α -halo-ketones.

Various reagents have recently been developed as the oxygen donor for this transformation in decades. Some of these reagents are Mg-Al hydrotalcite [8], pyridine N-oxide [9], V₂O₅ [10], NaIO₄-DMF [11], quinolinium chlorochromate [12], H₅IO₆ in [C₁₂mim][FeCl₄] [13], amine oxide [14-16]. However, some of these methods suffer from drawbacks such as long reaction time, high temperature, low yields, being harmful to environment and difficult separation of the product from the reaction mixture. From environmental and green chemistry viewpoint, there is a great need to develop new and green procedures with a broad substrate scope that address the mentioned drawbacks for the direct oxidation of organic halides to their corresponding carbonyl compounds.

For this target, the use of molecular oxygen or hydrogen peroxide as a primary oxidant in the presence of a catalyst is particularly attractive. Hydrogen peroxide is a non-toxic, cheap and effective oxidizer reagent. In addition, the oxidation reaction by hydrogen

peroxide can be controlled easier than molecular oxygen and air. In recent years, various types of molybdenum based catalyst systems have been used in oxidation reactions. For example, Na₂MoO₄·2H₂O is widely used as a catalyst for hydrodesulfurization from petroleum [17-20]. Although using Na₂MoO₄·2H₂O as a catalyst needs homogeneous reaction condition and therefore the catalyst is difficult to recover and reuse. Use of recycled catalysts is required for reducing the catalytic cost and green processes. One way to attain this goal is to immobilize the catalytic system onto a large surface area of solid carrier.

Fe₃O₄ magnetic nanoparticles (MNPs) have been frequently used as a support for recyclable catalysts because of their unique magnetic property and also their large surface area [21-23]. Fe₃O₄ nanoparticles can be easily oxidized in air and dissolved in acidic solutions. To solve this drawback, Fe₃O₄ could be coated by other materials which can protect them from being dissolved in acidic solutions and oxidation in air. Silica is one of the best materials that can be used for coating of Fe₃O₄. Silica is chemically inert and does not affect the redox reaction at the core surface. Also, nonmagnetic shell can suppress the particle-particle magnetic bipolar interaction and prevent them from aggregating and agglomeration [22-24].

We surmised that molybdate-based magnetic catalyst could affect the direct oxidation of organic halides to carbonyl compounds. Therefore, we planned to explore the use of the supported molybdate anion on Fe₃O₄@SiO₂ magnetic nanoparticles for the oxidation of organic halides to the carbonyl compounds, wherein H₂O₂ was used as an oxidant in ethanol as green solvent.

There is no report in which molybdate-based magnetic catalyst has been directly employed for oxidation of organic halides to their corresponding carbonyl compounds.

The reaction proceeded well for various organic halides to afford high yields of aldehydes/or ketones. This heterogeneous catalytic

system can be recycled and reused without any significant loss of catalytic activity

Experimental

Materials and methods

FT infrared (FT-IR) spectra were recorded on ABB Bomem MB100 spectrometer with potassium bromide (KBr) pellets. Scanning electron microscopy (SEM) was performed on KYKY-EM3200. An energy dispersive detector (EDS) coupled to the microscope was used to identify chemical elements of the prepared catalyst. X-ray diffraction (XRD) pattern was recorded on APD 2000, using Cu K α radiation (50 kV, 150 mA) in the range $2\theta=10-120^\circ$. Transmission electron microscopy (TEM) was performed on Philips CM30.

The room-temperature magnetization in the applied magnetic field was performed by a homemade vibrating sample magnetometer (Meghnatis Daghigh Kavir Company, Iran) from -10000 to +10000 Oersted. Inductively coupled plasma-atom emission spectrometer (ICP-AES) was performed on Perkin-Elmer Optima 3300 DV. Elemental analysis (CHN analysis) was performed in duplicate by a model Perkin Elmer, USA (2400, Series II).

Preparations

Fe₃O₄

Fe₃O₄ nanoparticles were synthesized according to previous published method [25]. Briefly, FeCl₂ (5.4 g) and FeCl₃ (2 g) were dissolved in 25 ml of 2 M hydrochloric acid at room temperature under mechanical stirrer until salts dissolved completely. 40 ml of 25% aqueous ammonia was added dropwise into the mixture at room temperature under argon atmosphere. Then, the black precipitate of magnetic nanoparticles (MNPs) was formed immediately and followed by stirring about 1 h with mechanical stirrer. The Fe₃O₄ nanoparticles were separated by an external magnet and washed with the double distilled water (five times), then vacuum-dried at 50 °C overnight.

Fe₃O₄@SiO₂

The synthesized Fe₃O₄ magnetic nanoparticles were homogeneously dispersed in ethanol (35 ml) and deionized water (6 ml). 1.5 ml of tetraethyl orthosilicate (TEOS) was added slowly to the mixture and sonicated for 15 min. 1 ml of 25% aqueous ammonia was added slowly over 10 min under mechanical stirrer and then the mixture was heated at 50 °C for 6 h. The magnetic nanoparticles with a thin layer of silica (Fe₃O₄@SiO₂) were separated by an external magnet and washed three times with ethanol and dried under vacuum.

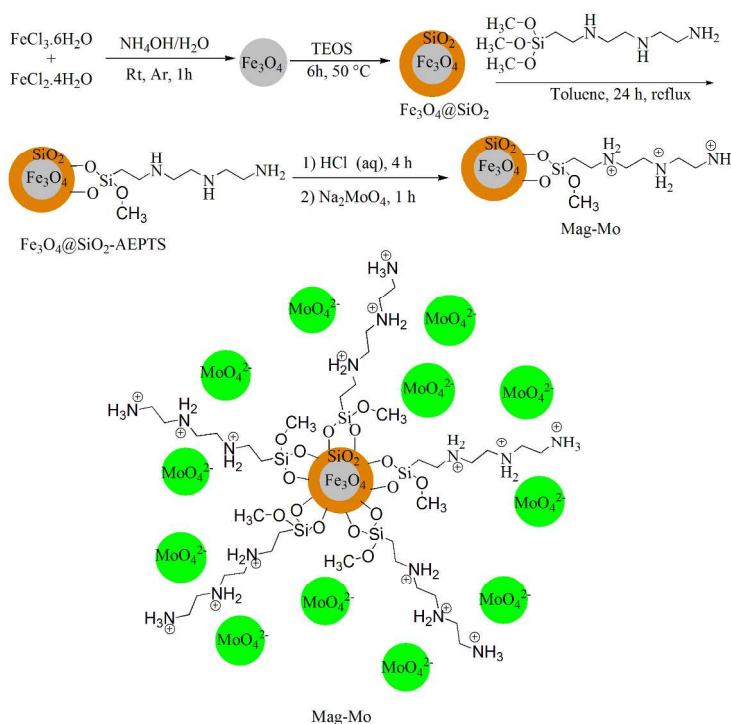
Fe₃O₄@SiO₂-AEPTS

1 g of dry Fe₃O₄@SiO₂ was added to 25 ml of dry toluene and sonicated for 10 min to produce a homogeneously mixed solution. Then, 1 ml of 3-[2-(2-Aminoethylamino)ethylamino]propyl-

trimethoxysilane (AEPTS) was added and heated to reflux for 24 h. The solid material was separated, washed with methanol and ethanol, and then dried overnight in an oven at 60 °C. This product will be referred to as Fe₃O₄@SiO₂-AEPTS.

Mag-Mo catalyst

The synthesized Fe₃O₄@SiO₂-AEPTS (1 g) was reacted with excess of HCl (1 M, 5 ml) solution for 4 h and then separated by magnet, washed with water and ethanol, and then dried in vacuum desiccator at 60 °C overnight to afford surface bound ammonium chloride. Finally, the prepared material (1 g) was added to an aqueous solution of the Na₂MoO₄ (0.15 g) at room temperature. The mixture was stirred for 1 h, magnetically separated, washed several times with water and ethanol, and then dried to afford the Fe₃O₄@SiO₂-AEPTS supported molybdate anion (**Mag-Mo**) (Scheme 1).



Scheme 1. Preparation of magnetically recoverable heterogeneous nanocatalyst Mag-Mo

General procedure for oxidation of organic halides

A mixture of organic halide (1 mmol), 30% H₂O₂ (4 equiv), **Mag-Mo** catalyst (73 mg) were stirred in ethanol (5 ml) under reflux condition. Completion of the reaction was indicated by thin layer chromatography (TLC) (n-hexane/ethylacetate 10:1) and gas chromatography (GC). After completion of the reaction, the reaction mixture was cooled, and the catalyst was separated by an external magnet. Then, 10 ml of water was added and the product was extracted by ether (3 × 5 ml). After drying with anhydrous sodium sulfate, the organic residue was analyzed by GC and then purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) to afford the desired product. The separated catalyst was washed with EtOH and used directly for a subsequent

round of reaction without further purification. All reaction products were identified by GC chromatogram, IR spectra and melting point as compared with authentic samples.

Results and discussion

Preparation and characterization of Mag-Mo catalyst

The first step, the bare Fe_3O_4 was prepared by using a $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixture via the conventional coprecipitation method (Scheme 1). Then, the SiO_2 was used to protect the magnetic core material against agglomeration and oxidation. 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (AEPTS) was employed to modify the surface of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ to yield the amino-modified MNPs ($\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-AEPTS}$). Finally, these synthesized magnetic materials were treated with HCl and then

Na_2MoO_4 to generate Mag-Mo catalyst.

Fig. 1 shows the XRD result of **Mag-Mo** catalyst. The six main peaks in XRD at $2\theta = 30.4, 35.9, 43.4, 53.8, 57.4,$ and 62.9 correspond to (220), (311), (400), (422), (551), and (440) diffraction planes of Fe_3O_4 MNPs which are in good agreement with the standard XRD data for the cubic Fe_3O_4 phase of inverse spinel crystal structure (JCPDS Card number 89-43191) [26]. The XRD result of **Mag-Mo** catalyst shows that the main peaks associated to Fe_3O_4 MNPs do not change after the attachment of AEPTS organic functional group and immobilization of molybdate anion on the Fe_3O_4 surface, indicating no change in the crystal structure of the Fe_3O_4 core during the functionalization process. The average size of the particles was estimated to be 29 nm for **Mag-Mo** using the Debye-Scherrer equation according to the (311) reflection.

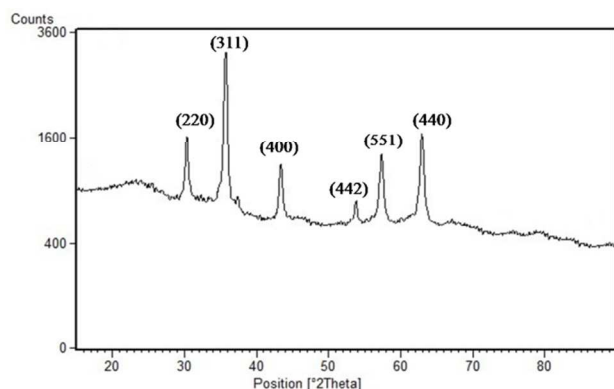


Fig. 1 XRD pattern of **Mag-Mo** catalyst

The magnetic property of uncoated Fe_3O_4 nanoparticles, $\text{Fe}_3\text{O}_4@/\text{SiO}_2$, and **Mag-Mo** catalyst were characterized by using the vibrating sample magnetometer (VSM). Fig. 2 shows the magnetic hysteresis loops of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ (b), and **Mag-Mo** catalyst (c) in an applied field of -10 000 to 10 000 Oe at 298 K. The hysteresis loops of all of the magnetic particles exhibited superparamagnetic behavior and had little hysteresis, remanence and coercivity. The saturation magnetization of the **Mag-Mo** catalyst is about 42 emu g^{-1} (Fig. 2) which is relatively

lower than the unsupported Fe_3O_4 due to the non-magnetic properties of silica and the presence of AEPTS and molybdate anion moieties in the prepared catalyst. This saturation magnetization of **Mag-Mo** catalyst shows that the catalyst could be easily separated by applying an external magnet that minimizes the loss of the catalyst during the separation stage.

The IR spectrum of **Mag-Mo** shows peaks corresponding to molybdate anion, which clearly differ from that of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-AEPTS}$. The spectrum of **Mag-Mo** catalyst (Fig. 3b) shows the peaks at 886 cm^{-1} , which could be assigned to the Mo=O stretch mode of the characteristic vibrations of molybdate anion [27- 28]. Moreover, absorption band at 2926 cm^{-1} is attributed to C-H stretching vibration of CH_2 groups in AEPTS. As shown in Fig. 3b, peaks at 580 cm^{-1} and 1104 cm^{-1} are related to stretching vibration of Fe-O and Si-O bonds, respectively. The bands at 464 cm^{-1} and 798 cm^{-1} are due to the deformation of Si-O bond [29].

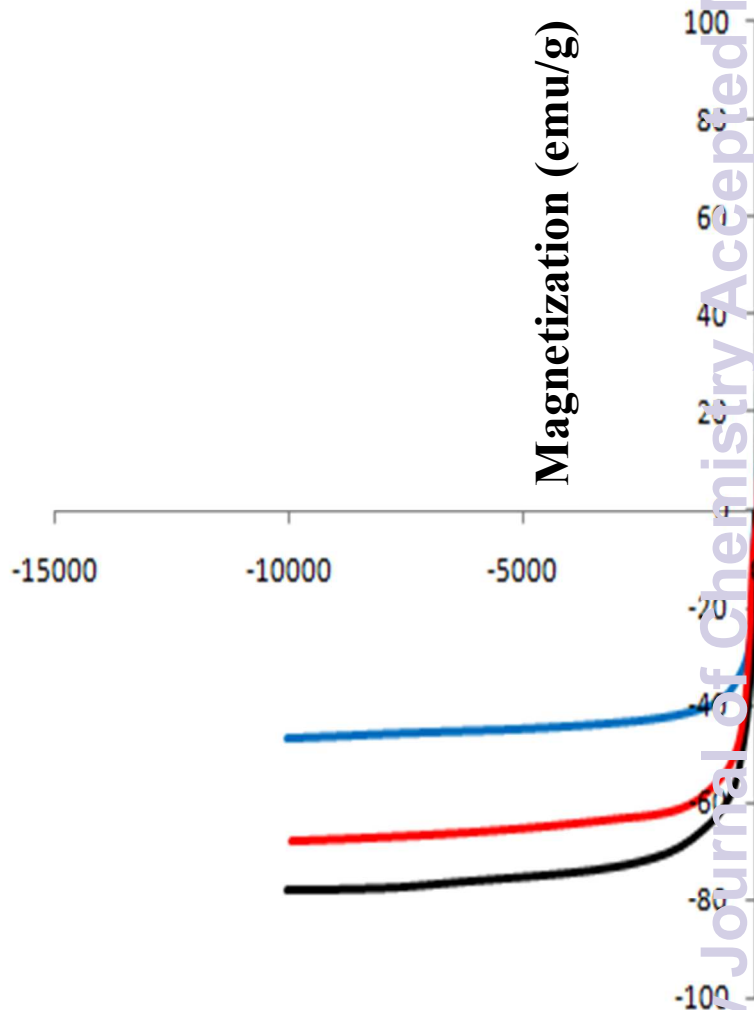


Fig. 2 Magnetization curves of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ (b), and **Mag-Mo** catalyst (c). The inset is a photograph of **Mag-Mo** catalyst under an external magnetic field.

Finally, the broad peak at 3477 cm^{-1} and the band around 1629 cm^{-1} are due to the O-H vibration and the bending vibration of water molecules adsorbed on the surface, respectively [27- 28]. The stretching vibration of -N-H bonds in **Mag-Mo** catalyst may have an overlap with the O-H vibration of water molecules adsorbed on the surface at 3477 cm^{-1} .

In order to investigate the morphology and particle size of **Mag-Mo** catalyst, scanning electron microscopy (SEM) and transition electron microscopy (TEM) images of **Mag-Mo** are shown in Fig. 4. These images indicate that the size of nanoparticles is between 30-40 nm, and the particles are also semi-spherical and uniform. As seen from EDS analysis in Fig. 4c, the molybdenum peak clearly confirms the presence of a molybdate anion in **Mag-Mo** catalyst. The loading of AEPTS group on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surface

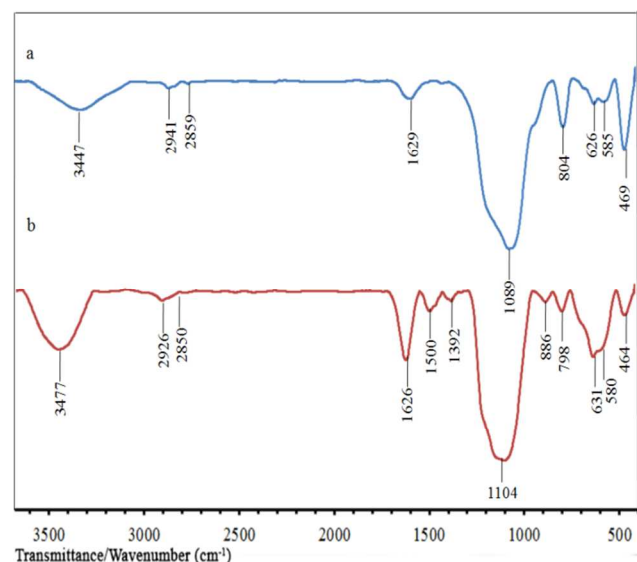


Fig. 3 IR spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-AEPTS}$ (a) and **Mag-Mo** catalyst (b)

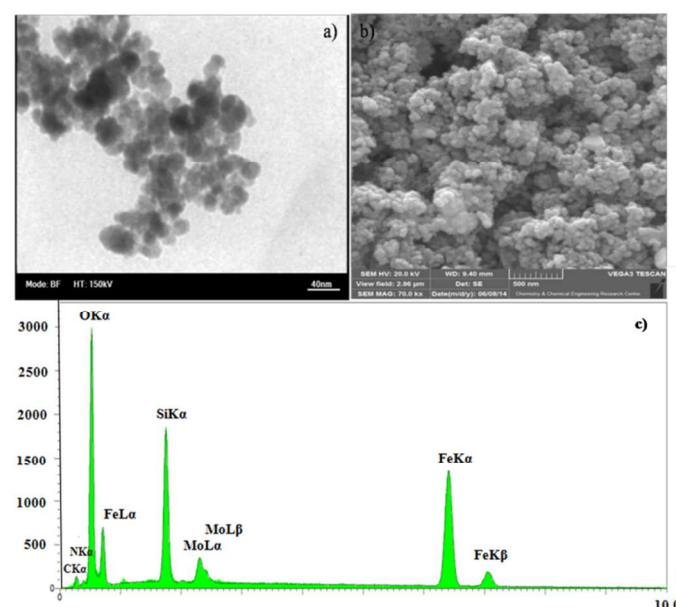


Fig. 4 TEM (a), SEM (b) and EDS (c) images of **Mag-Mo** catalyst.

was calculated using quantitative elemental analysis (CHN), which approximately confirmed a loading of 0.37 mmol.g^{-1} . Inductively coupled plasma atomic emission analysis (ICP-AES) was used to obtain an insight into the accurate amount of Mo in the **Mag-Mo** catalyst. ICP-AES indicated that the Mo content is about 0.41 mmol.g^{-1} .

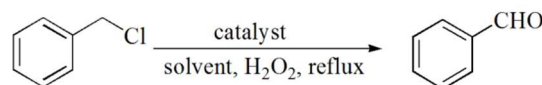
Catalytic activity of **Mag-Mo** catalyst for direct oxidation of organic halides to aldehydes and ketones

To investigate the catalyst activity of **Mag-Mo** catalyst, we have chosen the oxidation of organic halides to aldehydes and ketones with H_2O_2 catalyzed by **Mag-Mo** catalyst. In order to get an insight into the optimum catalytic conditions for the oxidation process, the oxidation reaction of benzyl chloride was used as a model substrate. The effect of solvent, temperature and the amount of **Mag-Mo** catalyst on the oxidation reaction was investigated in order to improve the efficiency of the reaction.

To obtain suitable solvent for the oxidation reaction, the reaction was carried out in various solvents (Table 1). The results for various solvents indicated that not only conversion of benzyl chloride to benzaldehyde in ethanol is high, but also selectivity towards benzaldehyde is also good.

After choosing ethanol as the best solvent, the effect of temperature and the amount of **Mag-Mo** catalyst on the oxidation reaction was investigated. As seen from Table 1, in the absence of **Mag-Mo** catalyst (entry 8), benzaldehyde was obtained only 39% in 24 h. When the catalyst (1 mol% (24 mg)) was added to the reaction mixture (entry 3), the yield of reaction increased from 39% to 82% and the time and selectivity of reaction decreased to 8 h and 98%, respectively. It was found that the amount of catalyst could remarkably promote conversion of benzyl chloride to benzaldehyde and decrease the time and selectivity of reaction. As seen from Table 1, with the increase of **Mag-Mo** catalyst amount from 1% to 4%, the selectivity of the reaction decreased generally depending on the catalyst value used in the oxidation reaction. For example, with the increase of catalyst value from 3% to 4%, the selectivity decreased from 97% to 94%. Thus, we performed the reaction in the presence of 3% catalyst to get the highest yield and selectivity values.

Table 1. Optimization of the reaction conditions for benzyl chloride oxidation to benzaldehyde^a



Entry	Solvent	Catalyst mol% (g)	Time (h)	Yield (%) ^b	Selectivity (%)
1	THF	1 mol% (0.024)	8	53	95
2	H ₂ O	1 mol% (0.024)	8	60	88
3	EtOH	1 mol% (0.024)	8	82	98

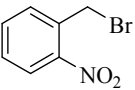
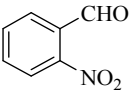
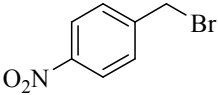
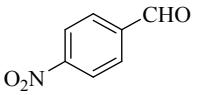
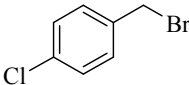
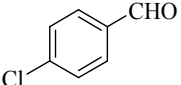
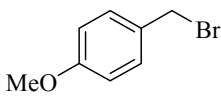
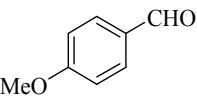
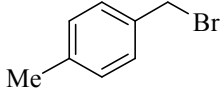
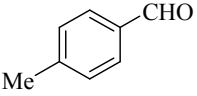
4	MeOH	1 mol%(0.024)	8	76	97
5	CH ₃ CN	1 mol%(0.024)	8	79	98
6	n-Hexane	1 mol%(0.024)	8	37	99
7	Toluene	1 mol%(0.024)	8	40	98
8	EtOH	-	24	39	100
9	EtOH	1 mol%(0.002)	8	79 ^c	96
10	EtOH	2 mol% (0.048)	4	89	99
11	EtOH	3 mol% (0.073)	4	94	97
12	EtOH	4 mol% (0.097)	4	94	94
13	EtOH	3 mol% (0.073)	4	38 ^d	99

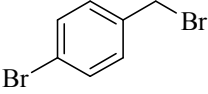
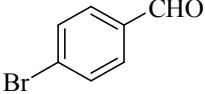
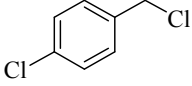
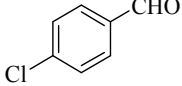
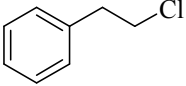
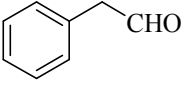
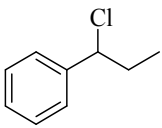
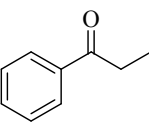
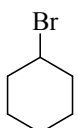
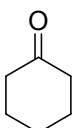
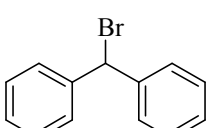
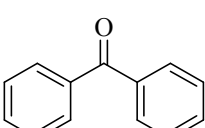
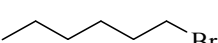
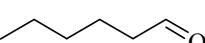
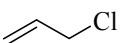
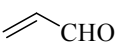
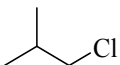
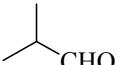
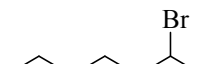
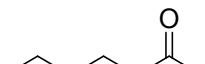
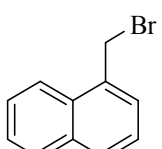
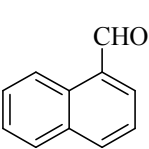
^aReaction conditions: benzyl chloride (1 mmol), 30% H₂O₂ (4 equiv), solvent (5 ml), under reflux condition. ^bIsolated yield. ^cNa₂MoO₄ was added. ^dRoom temperature.

As seen in Table 1, temperature has remarkably effect on the yield of benzaldehyde. With increasing temperature from room temperature to reflux condition, the yield of benzaldehyde increased from 38% (entry 13) to 94% (entry 11). Moreover, over-oxidation of benzaldehyde to benzoic acid occurred with the increase of time to 10 h, and the selectivity of the desired product was reduced. The applicability of this protocol was studied by oxidation of primary and secondary organic halides to their corresponding

aldehydes and ketones under the optimized conditions. As seen from Table 2, a wide variety of functionalized benzyl halides with electron-donating and withdrawing substituents was used in the oxidation reaction. Generally, benzyl halides with electron-donating substituents produced good to excellent yields, while benzyl halides containing withdrawing groups exhibited slightly lower conversions. Over oxidation was also seen in the oxidation of organic halides to their corresponding carbonyl compounds. For example, the primary benzyl halides were oxidized to their corresponding carboxylic acids. The selectivity values for all substrates are summarized in Table 2. As seen from Table 2, the selectivity values for primary benzyl halides are lower than other substrates. Our results indicate that benzyl halides could be easily converted to their corresponding aldehydes in good to excellent yield, although conversion of aliphatic halides to aldehydes is far more difficult than oxidation of benzylic halides. For example, 1-bromo hexane was converted to corresponding aldehyde with only 62% yield in 7 h (entry 12). The primary allyl chloride was also converted into the oxidation product in a relatively good yield (entry 13). When these conditions were applied to cyclohexyl bromide, the corresponding ketone was obtained as the product without formation of cyclohexene.

Table 2. Oxidation of organic halides to aldehydes and ketones.^a

Entry	Substrate	Product	Time (h)	Yield (%) ^b	Selectivity
1			8	87	96
2			9	83	97
3			4	93	94
4			4	96	92
5			4	95	95

6			4	92	96
7			4	91	97
8			7	72	99
9			6	89	97
10			8	70	99
11			6	92	99>
12			7	62	99
13			5	90	93
14			6	60	99
15			8	65	99>
16			4	96	97

^aReaction conditions: organic halide (1 mmol), catalyst (3 mol%, 73 mg), H₂O₂(4 equiv), EtOH (5 mL) under reflux condition. ^bIsolated yield.

Table 3. Comparison of the activity of various catalysts in the oxidation reaction of benzyl chloride.

Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield %	[ref]
1	H ₅ IO ₆	[C ₁₂ mim][FeCl ₄]	30	2	94	[13]
2	Na ₂ MoO ₄	H ₂ O	90	18	72	[30]

3	V ₂ O ₅	H ₂ O	100	6	70	[10]
4	Mg–Al hydrotalcites	DMSO	140	10	80	[8]
5	H ₅ IO ₆ /V ₂ O ₅	[bmpy][PF ₆]	50	3	92	[7]
This work	Mag-Mo	EtOH	78	4	94	-

The efficiency of **Mag-Mo** catalyst was compared with other catalyst systems in literature for the oxidation reaction of benzyl chloride (Table 3). Some of these procedures (entries 2–4) are associated with disadvantages such as long reaction time, high temperature, and low yields. In comparing our work and the reactions done in ionic liquid solvents (entries 1 and 5), the magnetic property of **Mag-Mo** heterogeneous catalyst provides the easy separation of catalyst from reaction mixture only by applying an external magnetic field, although the catalyst separation, recycling and reuse is difficult in ionic liquids.

Catalyst recycling

One of the issues in using heterogeneous catalyst is its recyclability and reusability. In with this line, recyclability of the catalyst was investigated in the oxidation of benzyl chloride. After each reaction cycle, the **Mag-Mo** catalyst was separated with an external magnet, washed with ethanol, and used in subsequent reaction. According to Fig. 5, only a slight reduction in the yield of benzaldehyde was observed after 6 consecutive runs.

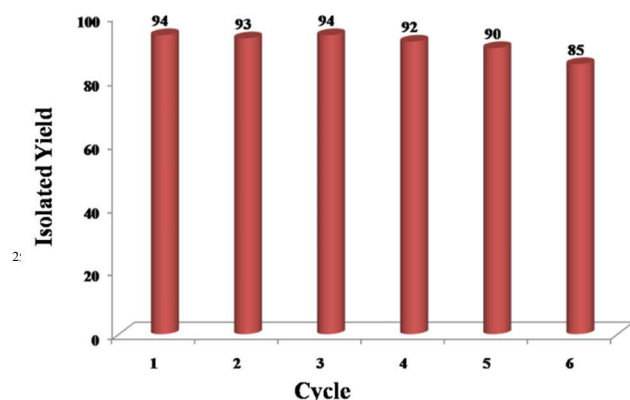


Fig. 5 The recycling experiment of **Mag-Mo** catalyst in the oxidation reaction of benzyl chloride to benzaldehyde under optimized conditions. The oxidation reaction was quenched after 4 h at each step.

Conclusion

In this study, a molybdate-base magnetic catalyst (**Mag-Mo**) was prepared for direct oxidation of organic halides to corresponding aldehydes and ketones using 30% H₂O₂ as oxidant in ethanol. In these conditions, a wide range of organic halides with electron-donating and withdrawing substituents could be oxidized to corresponding products with good conversions. This catalytic system is very easy to handle and can be recycled and reused in 6 run without any significant loss of catalytic activity. Moreover, this catalyst system can be easily prepared from commercially available starting materials.

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Notes and references

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