Magnetic Nanoparticles Linked to Pyridinium Hydrotribromide Groups as Catalyst for Selective Oxidation of Alcohols and Protection of Alcohols

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Abstract

In this research, a novel and efficient magnetic nanoparticle catalyst linked to pyridinium hydrotribromide (Fe_3O_4@ $PyHBr_3$) was synthesized in three steps using reaction of 3-(aminopropyl)triethoxysilane (APTES) with 4-(bromomethyl)pyridine hydrobromide followed by reaction with Fe_3O_4 magnetic nanoparticles and at last step grinding with KBr and HIO_4 in a mortar. Fe_3O_4@ $PyHBr_3$ was characterized by FT-IR, CHN, XRD, SEM, TGA and VSM analysis. This magnetic nanoparticles was used as catalyst in the selective oxidation of alcohols to aldehydes and ketones using 30% H_2O_2 as an oxidant in short times and high yields. No over-oxidation of the alcohols was observed. The catalyst was recycled efficiently for five consecutive cycles without any significant loss in its catalytic activity. Furthermore, trimethylsilylation and tetrahydropyranylation of alcohols were performed in the presence of this catalyst.

Keywords: Magnetic nanoparticles; pyridinium hydrotribromide; oxidation of alcohols; tetrahydropyranylation; trimethylsilylation

1. Introduction

Organic tribromides are widely used as selective brominating reagents for various organic functionalities[1-6] and also as efficient catalysts for oxidation of some organic substrates such as alcohols,[7] aldehydes,[8] and sulfides,[9,10] trimethylsilylation[11,12] or tetrahydropyranylation[13] of alcohols, α-thiocyanation[14] or thioacetalization[15] of ketones and heterocyclic ring synthesis.[16]

Typical organic tribromides are tetrabutylammonium tribromide (TBATB),[2,9] pyridinium hydrotribromide (PyHTB),[4-6,14] benzyltrimethyl ammonium tribromide (BTMATB),[7] 2-carboxyethyltriphenyl phosphonium tribromide (CTPTB)[11] and benzyltriphenyl phosphonium tribromide.[13,15] This reagents have received great attention in organic synthesis and have been established to be premiere to liquid bromine, NBS, Br_2/HBr, and many other traditional brominating reagents because of their easy-handling, mildness, efficiency, and selectivity. They are stable and crystalline solids that qualified for releasing a stoichiometric amount of bromine. Other advantages are their recoverability and reusability when they used as catalyst.

In recent years, Br_3^- immobilized on polymer[1,17] or magnetic nanoparticles (MNPs)[16,18-20] or other solid supports[21] have received enormous attention. Among them, organic tribromide immobilized on magnetic nanoparticles can be readily separated from reaction mixture by using an external magnet, without the need for filtration or other workup processes. Using magnetic nanoparticles (MNPs) as support for catalyst enabling efficient recovery of the catalyst. This can solve the problems associated with separation of nanoparticles.[22,23] Although several immobilized tribromides have been synthesized but in most cases their preparation involves using liquid Br_2 and/or HBr, [16-21] which leads to an environmental problem.

Many improved methods have been reported in the literature for the synthesis of organic tribromides which are considered to be environmental benign. In these improved methods, an oxidant system was used for the oxidation of organic bromide to organic tribromide such as $(NH_4)_2S_2O_8/H^+$,[7] $NaOCl/H^+$,[10] $KMnO_4$ /H^+,[11] H_5IO_6,[12] oxone®,[15] MCPBA,[3] H_2MoO_4 or V_2O_5/ H_2O_2,[24] and CAN.[25] In spite of introducing these oxidation methods in the literature, many of the recently reported methods for synthesis of magnetic nanoparticles (MNPs)[16,18-20] or polymer supported[1,17] bromine sources involve liquid Br_2 and/or HBr, which still cause environmental concerns. Therefore, development of newer strategies that do not require the use of molecular bromine or metals and strong mineral acids is still a challenge for synthesis of immobilized organic tribromide especially magnetic nanoparticles supported catalysts.

In this work, we report a novel method for synthesis of supported pyridinium hydrotribromide on Fe_3O_4 magnetic nanoparticles (MNPs) via oxidation of immobilized organic bromide to tribromide using periodic acid (H_5IO_6) as a cheap, nontoxic, efficient, and easy to handle oxidant. Fe_3O_4@ $PyHBr_3$ was used as catalyst in the selective oxidation of alcohols to aldehydes and ketones using 30% H_2O_2. Furthermore, trimethylsilylation and tetrahydropyranylation of alcohols were performed in the presence of this catalyst.

2. Experimental Section

2. 1. Instrumentation, analysis and raw materials

All products are known and were characterized by comparison of their physical data with those of known samples or by their spectral data. Infrared (IR) spectra were recorded on KBr matrix with Perkin Elmer RXI spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 or $CDCl_3$ using tetramethylsilane (TMS) as internal standard on a Bruker Avance DRX spectrometer. Thermogravimetric analysis (TGA) was conducted on BAHR thermo analyse STA 503 instrument. XRD patterns were recorded on a Bruker D8-advance diffractometer. Elemental analysis was performed using a Costech Elemental Combustion System CHNS-O (ECS 4010). Field emission scanning electron microscopy (FESEM) was carried out using a MIRA3 TESCAN instrument. A vibrating sample magnetometer (VSM) Lakeshore7400 was used for characterization of the magnetic properties at room temperature.

2.2. Preparation of the Fe_3O_4 Magnetic Nanoparticles (Fe_3O_4 MNPs)

Fe_3O_4 MNPs were prepared according to the method described in the literature.[26] Typically, $FeCl_3.6H_2O$ (5.406 g, 20 mmol) and $FeCl_2.4H_2O$ (1.988g, 10 mmol) were dissolved in distilled water (75 mL) in a three-necked bottom (250 mL) under N_2 atmosphere. Then, NaOH (10 M, 10 mL) was added into the solution with vigorous mechanical stirring until PH of the solution raised to 11. The temperature of mixture was raised to 80 °C. The mixture stirred for 1 h in an ultrasonic bath. The black precipitate was isolated by a magnet, washed with double-distilled water until neutrality and then washed with ethanol (2×20 mL) and dried at 60 °C in a vacuum oven.

2.3. Synthesis of Fe_3O_4@$PyHBr_3$ MNPs

To a solution of (3-aminopropyl)triethoxysilane, APTES (1.771 g, 8 mmol) in $CHCl_3$ (10 mL), was added 4-(bromomethyl) pyridine hydrobromide (2.024 g, 8 mmol). The mixture was heated at reflux condition for 24 h. Then the solvent was evaporated and the product (APTES-MPyHBr) was dried. To a solution of APTES-MPyHBr (2 g) in toluene (10 mL), was added Fe_3O_4 MNPs (1.2 g) and the mixture was heated for 12 h under N_2 atmosphere at reflux condition. The Fe_3O_4@PyHBr Magnetic nanoparticles were isolated by a magnet, washed with CH_2Cl_2 (3×20 mL) and dried at 60 °C in a vacuum oven. Analytical data for Fe_3O_4@PyHBr: C, 18.65; H, 3.02; N, 4.86%.

A mixture of Fe_3O_4@PyHBr (3 g), KBr (1.27 g, 10.67 mmol) and HIO_4 (2.70 g, 14.07 mmol) in a mortar for 30 min. was grinded at room temperature. The color of the mixture was changed from orange to dark brown. The Fe_3O_4@$PyHBr_3$ MNPs were washed with H_2O (3×15 mL) and then with ethanol (3×15 mL) and dried at 60 °C in a vacuum oven. Analytical data for Fe_3O_4@$PyHBr_3$: C, 12.96; H, 1.67; N, 3.65%.

2.4. Typical Procedures

2.4.1. Oxidation of 4-nitrobenzyl alcohol

Fe_3O_4@$PyHBr_3$ MNPs (0.070 g, 0.091 mmol) was added to a mixture of 4-nitrobenzyl alcohol (0.153 g, 1 mmol) and H_2O (1 mL) followed by the addition hydrogen peroxide (30%, 0.45 mL, 4 mmol) and the resulting mixture was heated at 50 °C. The progress of the reaction was followed by TLC using *n*-hexane-ethyl acetate (7:3) as eluent. After the completion of the reaction (75 min.), the catalyst was separated by a magnet. Then, the reaction mixture was extracted with diethyl ether (3×5 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give 4-nitrobenzaldehyde (0.128 g, 0.85 mmol); mp: 104-106°C.

FT-IR (KBr), ν (cm^{-1}): 3107 (w), 3066 (w), 2956(s), 2926 (s), 2854 (s), 1706 (s), 1608 (s), 1544 (s), 1454 (s), 1378 (s), 1360 (s), 1346 (s), 1197 (s), 852 (s), 818 (s), 740 (s).

^{1}HNMR (DMSO-d_6), δ (ppm): 8.12-8.17 (m, 2H), 8.39-8.42 (m, 2H), 10.15 (s, 1H).

2.4.2. Trimethylsilylation of benzyl alcohol

Fe_3O_4@$PyHBr_3$ MNPs (0.070 g, 0.091 mmol) was added to a mixture of benzyl alcohol (0.108 g, 1mmol) and HMDS (0.113 g, 0.7 mmol) in CH_2Cl_2 (5 mL) and the resulting mixture was mechanically stirred at room temperature. The progress of the reaction was followed by TLC using *n*-hexane-ethyl acetate (7:3) as eluent. After the completion of the reaction (10 min.), the catalyst was separated by a magnet. Then, the reaction mixture was extracted with diethyl ether (3×5 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give benzyl trimethylsilylether (0.166 g, 0.92 mmol).Colourless liquid; b.p. 93^{o}C; lit. b.p. 92^{o}C.

FT-IR (KBr, cm^{-1}): 2957, 1250, 1094, 727.

^{1}HNMR ($CDCl_3$) δ (ppm): 0.18 (s, 9H), 4.29 (s, 2H), 7.26-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ: 0.09, 70.7, 127.1, 127.3, 129.0, 145.7.

2.4.3. Tetrahydropyranylation of 4-chlorobenzyl alcohol

Fe_3O_4@$PyHBr_3$ MNPs (0.070 g, 0.091 mmol) was added to a mixture of 4-chlorobenzyl alcohol (0.143 g, 1mmol) and DHP (0.126 g, 1.5 mmol) in CH_3CN (5 mL) and the resulting mixture was mechanically stirred at room temperature. The progress of the reaction was followed by TLC using *n*-hexane-ethyl acetate (7:3) as eluent. After the completion of the reaction (3 h), the catalyst was separated by a magnet. Then, the reaction mixture was extracted with diethyl ether (3×5 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give 4-chlorobenzyl tetrahydropyranylether (0.213 g, 0.94 mmol).

FT-IR (KBr), ν (cm^{-1}): 3070 (w), 2944(s), 2871 (s), 1442 (m), 1343 (m), 1128 (s), 1029 (s), 754 (s).

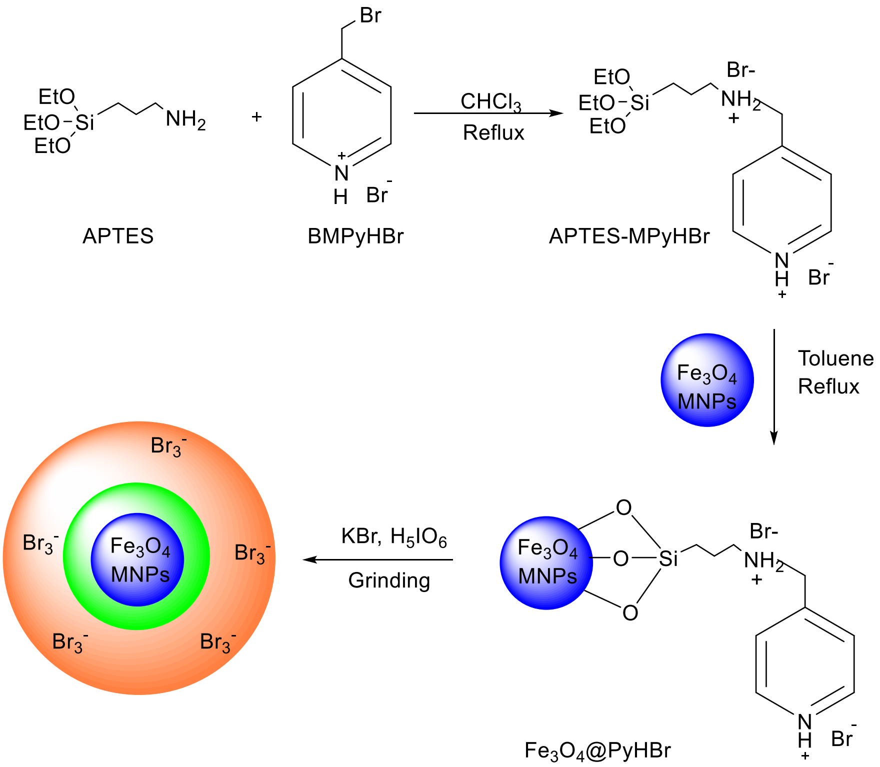
^{1}HNMR ($CDCl_3$), δ (ppm): 1.57-1.60 (m, 2H), 1.64-1.65 (m, 2H), 1.66-1.78 (m, 2H), 3.56-3.60 (m, 1H), 3.91-3.96 (m, 1H), 4.50-4.52 (d, 1H), 4.72-4.74 (t, 1H), 4.77-4.80 (d, 1H), 7.30-7.36 (m, 4H).

3. Results and Discussion

The synthesis of Fe_3O_4 MNPs linked to pyridinium hydrotribromide (Fe_3O_4@ $PyHBr_3$) was accomplished in three steps. First, APTES-MPYHBr was synthesized through the reaction of 3-(aminopropyl)triethoxysilane (APTES) with 4-(bromomethyl)pyridine hydrobromide (BMPYHBr) in $CHCl_3$ at reflux conditions followed by reaction with Fe_3O_4 magnetic nanoparticles and at last step grinding with KBr and HIO_4 in a mortar (Scheme 1). Fe_3O_4 MNPs were prepared according to the method described in the literature.[26] Typically, $FeCl_3.6H_2O$ (20 mmol) and $FeCl_2.4H_2O$ (10 mmol) were dissolved in distilled water (75 mL) under N_2 atmosphere. Then, NaOH (10 M) was added into the solution with vigorous mechanical stirring until PH of the solution raised to 11. The temperature of mixture was raised to 80 °C. The mixture stirred for 1 h in an ultrasonic bath. The black precipitate was isolated by a magnet, washed with plenty water and then with ethanol and dried at 60 °C in a vacuum oven.

Fe_3O_4@ $PyHBr_3$ was characterized by FT-IR, CHN, XRD, SEM, TGA and VSM analysis. The FT-IR spectrum as well confirms the preparation of the catalyst in each step (Figure 1). Fe_3O_4@ $PyHBr_3$ nanoparticles possess a sharp absorption bands in 2927 cm^{-1} and a band in 1222 cm^{-1} due to stretching and bending (wagging) vibration of CH_2 groups, respectively (Figure 2). Also, broad absorption bands in 1045 and 1115 cm^{-1} due to stretching vibration of Si-O bonds, 3421

cm^{-1} band that confirms N-H group which is overlapped by the hydroxyl group (Fe_3O_4 is an OH-rich surface), 1630 cm^{-1} band of O-H deformed vibration and characteristic absorption band of Fe-O bond of bulk Fe_3O_4 in 585 cm^{-1}.



Scheme 1. Synthesis of Fe_3O_4@ $PyHBr_3$ magnetic nanoparticles

Elemental (CHN) analysis results showed that the carbon, hydrogen, and nitrogen content of Fe_3O_4@ $PyHBr_3$ was 12.96, 1.67 and 3.65 (wt.%), respectively, equivalent to a loading of 1.3 mmol of nitrogen groups (Br_3^- content) per gram of catalyst. Also, (CHN) analysis results showed that the carbon, hydrogen, and nitrogen content of Fe_3O_4@ PyHBr (monobromide) was 18.65, 3.02 and 4.86 (wt.%), respectively. By comparing the total weight percentages of carbon, hydrogen and nitrogen in the two samples Fe_3O_4@PyHBr and Fe_3O_4@$PyHBr_3$ (26.53 and 18.28, respectively), a ratio of 1.45 is obtained, which is very close to 1.36, calculated from the chemical formula of organic segment of these compounds.

X-ray powder diffraction (XRD) analysis was used to characterize the crystalline structure of the Fe_3O_4@ $PyHBr_3$. XRD diffraction pattern is shown in figure 3 which matches with literature.[26]

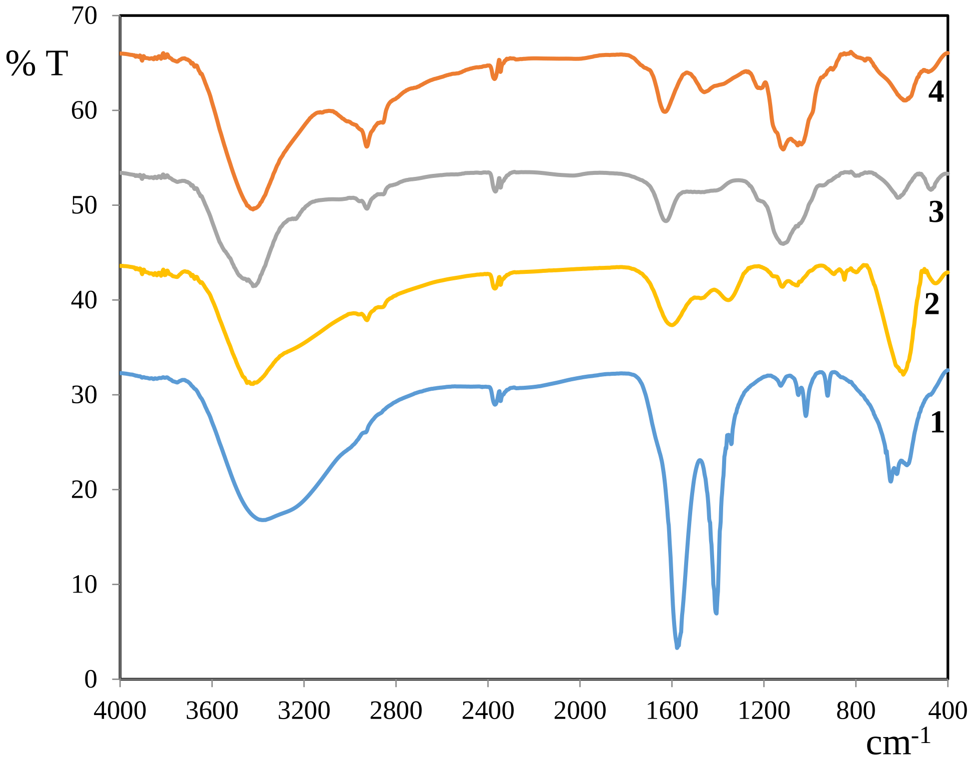


Figure 1. FT-IR spectrum of Fe_3O_4 MNPs (1); Fe_3O_4@ PyHBr MNPs (2); Fe_3O_4@ PyHBr$_3$ MNPs (3); APTES-MPYHBr (4)

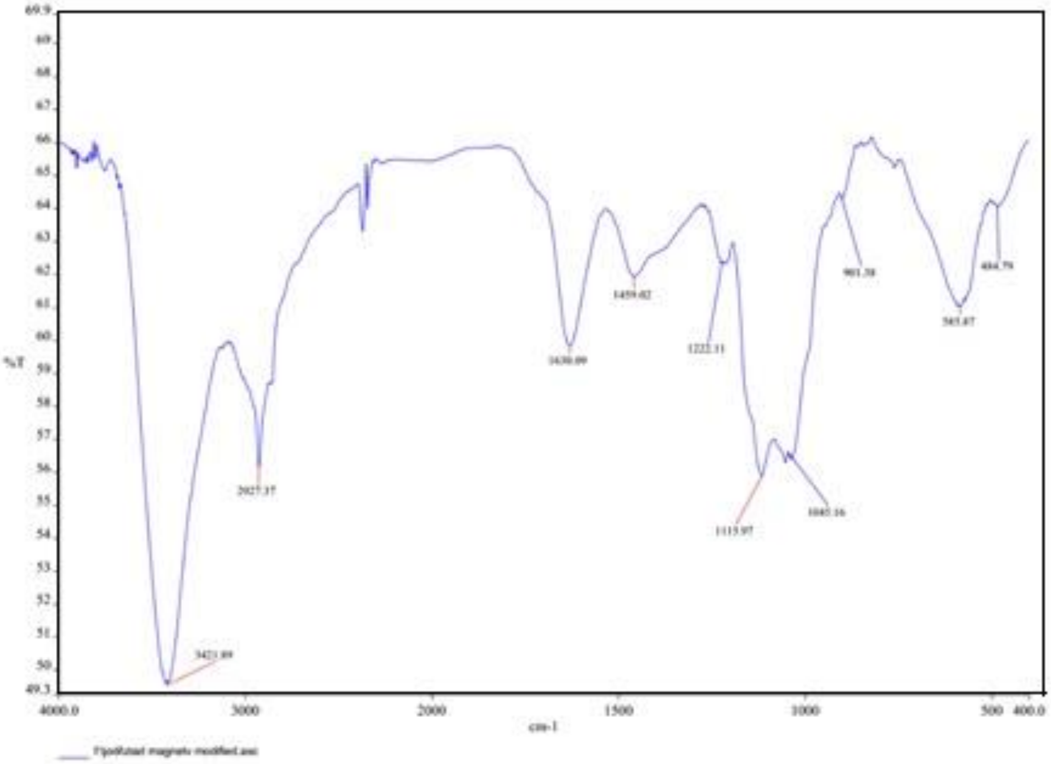


Figure 2. FT-IR spectrum of Fe_3O_4@ PyHBr$_3$ MNPs (KBr)

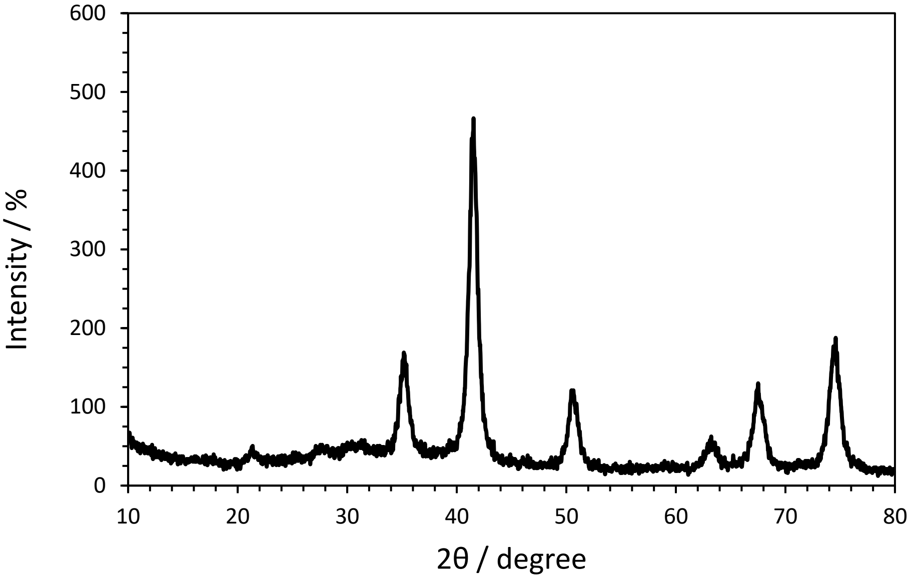


Figure 3. XRD pattern of Fe_3O_4@ $PyHBr_3$ MNPs

Field emission scanning electron microscopy image of Fe_3O_4 @ $PyHBr_3$ magnetic nanoparticles shows that the particles dimension are in the range of 35-40 nm (Figure 4).

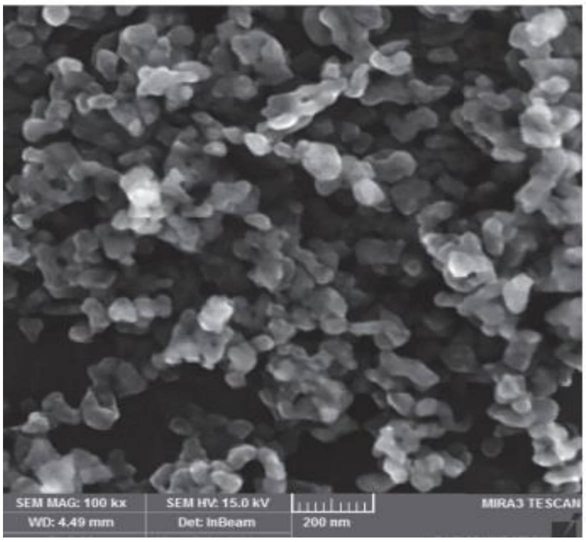


Figure 4. Field emission scanning electron micrograph of Fe_3O_4@ $PyHBr_3$ MNPs

The magnetic properties were characterized by a vibrating sample magnetometer (VSM) at room temperature. The amount of saturation magnetization of Fe_3O_4 @ $PyHBr_3$ MNPs is about 50 emu g^{-1}, which is less than the pure Fe3O4 MNPs (74 emu g^{-1}). The reduction of measured saturation magnetization is due to the presence of organic matter around Fe_3O_4.

TGA analysis of Fe_3O_4 MNPs and Fe_3O_4@$PyHBr_3$ MNPs were also investigated. Comparison of the respective thermograms shows that while no significant weight loss is observed for Fe_3O_4 entire thermogram (Figure 5, black thermogram), decomposition of the Fe_3O_4 @ $PyHBr_3$ started at about 200 ° C and it lost about 15% of its weight in two stages, which is most likely related to the decomposition and removal of the organic part.

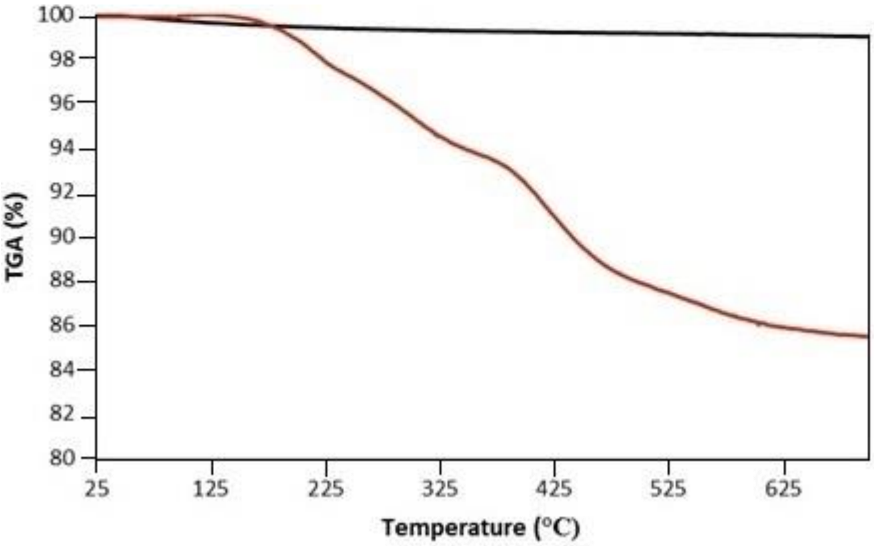
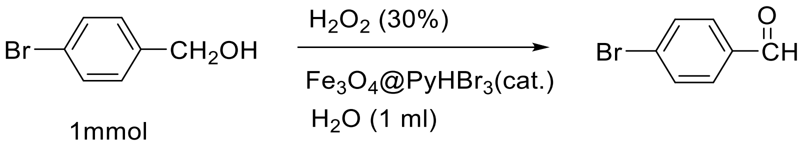


Figure 5. Thermograms of pure Fe_3O_4 MNPs (black) and Fe_3O_4 @ $PyHBr_3$ MNPs (red)

Oxidation of alcohols is one of the important reactions in the synthesis of organic compounds.[27-35] Some of these reactions occur under harsh conditions, such as high temperatures, the use of unfavorable environmental solvents, and the use of toxic oxidants including transition metal compounds that produce harmful by-products. Usually, compounds such as chromic acid, dichromate/H^+, PCC, PDC have been used to oxidize alcohols.[31] Due to the limitations of existing methods, efforts are being made to carry out environmentally safe reactions. The goal of these efforts is the catalytic oxidation of alcohols using inexpensive green oxidants such as air, oxygen and hydrogen peroxide and with the help of heterogeneous (solid) catalysts and harmless and environmentally friendly solvents. Hydrogen peroxide, H_2O_2 is an attractive oxidant for liquid phase reactions.[31-35] This water-soluble oxidizer is safe, inexpensive and has a high oxygen content that does not require buffer, and in addition, because its by-product is water, it is considered a green and environmentally friendly oxidizer.

After synthesis of supported pyridinium hydrotribromide on Fe_3O_4 MNPs, we investigated the effectiveness of Fe_3O_4@$PyHBr_3$ MNPs as catalyst in oxidation of benzyl alcohols by 30% hydrogen peroxide. In order to optimize the reaction conditions, oxidation of 4-bromobenzyl alcohol were investigated by different amounts of 30% hydrogen peroxide, different amounts of Fe_3O_4@$PyHBr_3$ catalyst and different reaction temperatures (Scheme 2).



Scheme 2. Oxidation of 4-bromobenzyl alcohol by hydrogen peroxide in the presence of Fe_3O_4@ $PyHBr_3$

In order to explore the optimum amount of hydrogen peroxide, the reaction of 4-bromobenzyl alcohol (1 mmol) were investigated by different molar ratios of H_2O_2 to alcohol in the presence of 0.020 g of catalyst at 50 ˚C in H_2O (1 mL) (Table 1, entries 1-4). According to the results reported in table 1, it was observed that using 4 mmol H_2O_2, the reaction had a higher conversion (60%) and a shorter time (60 minutes), but this time in order to increase conversion, additional amounts of catalyst were used (Table 1, entries 5 to 6 and 9). As the results show, increasing the amount of catalyst increased the conversion. The effect of reaction temperature was also examined (Table 1, entries 6 to 8). At 25°C and 70°C, the conversion was 65% and 90%, respectively.

Table1. Optimization of oxidation of 4-bromobenzyl alcohol by 30% H_2O_2[a]

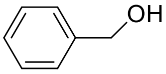
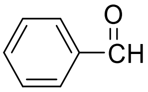
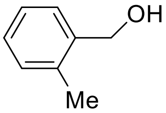
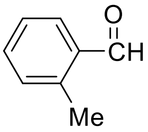
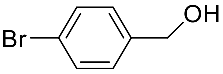
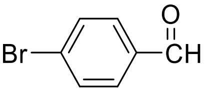
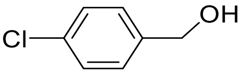
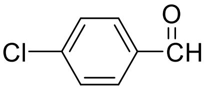
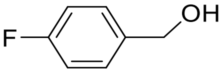
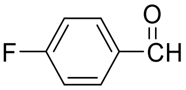
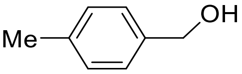
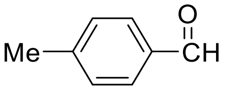
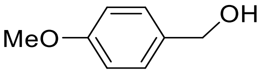
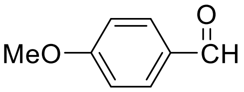
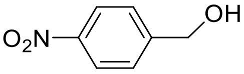
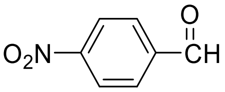
Entry	$\frac{H_2O_2}{alcohol}$ Molar ratio	Catalyst (g)	T (˚C)	Reaction time (min.)	Conversion (%)
1	1	0.02	50	120	30
2	2	0.02	50	120	45
3	3	0.02	50	90	50
4	4	0.02	50	60	60
5	4	0.04	50	45	80
6	4	0.07	50	20	100
7	4	0.07	25	60	65
8	4	0.07	70	20	90
9	4	0.08	50	18	100
10	3	0.07	50	40	80
11	4	0.23[b]	50	40	96
12	4	-	50	240	5

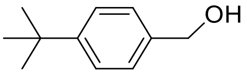
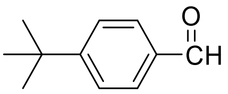
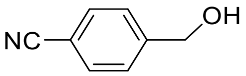
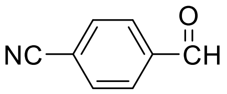
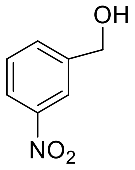
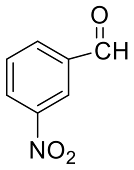
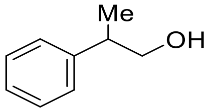
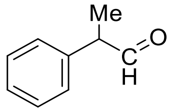
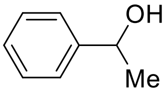
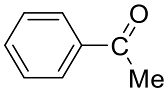
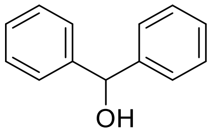
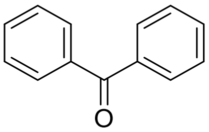
[a] The reaction was performed using 4-bromobenzyl alcohol (1 mmol) in H_2O (1 mL).
[b] Fe_3O_4 MNPs was used as catalyst.

The reaction was also performed using Fe_3O_4 (0.23 g) and it was found that the reaction time was longer than that of the Fe_3O_4@$PyHBr_3$ catalyst (Table 1, entry 11). When the reaction was performed without the use of a catalyst, after 4 hours the desired product was produced with a very small conversion (Table 1, entry 12).

According to the results reported in Table 1, the optimal conditions of this reaction are 4 mmol of 30% hydrogen peroxide as oxidant, 0.070 g (9.1 mol%) of Fe_3O_4 @ $PyHBr_3$ as catalyst at 50°C (Table 1, entry 6). Using these optimal conditions, 4-bromobenzaldehyde was obtained in 20 minutes with an excellent conversion rate of 100%. The reaction of benzyl alcohol and other benzyl alcohols with electron donor and electron acceptor substituents was performed under these optimal conditions, the results of which are shown in Table 2. Benzyl alcohols with electron donor group (Table 2, entries 2, 6, 7, 9) were oxidized in shorter periods of time than alcohols with strong electron acceptor group (Table 2, entries 8, 10, 11). The secondary benzyl alcohols (entries 13 and 14) were also oxidized to the corresponding ketones. The study showed that the oxidation time of a non-benzyl alcohol, 2-phenyl-1-propanol, was longer than that of benzyl alcohols (Table 2, entry 12). In addition, in the case of the primary alcohols, no additional oxidation was observed for the formation of carboxylic acid, which is a reason for the mildness and selectivity of the present method.

Table 2. Fe_3O_4@ $PyHBr_3$ MNPs catalyzed oxidation of alcohols to carbonyl compounds [a]

Entry	Substrate	Product	Reaction Time (min.)	yield[b] (%)
1			20	88
2			10	95
3			20	95
4			30	93
5			35	90
6			25	98
7			15	90
8			75	85

9			18	86
10			60	97
11			60	88
12			80	91
13			35	94
14			10	95

[a] Reaction conditions: substrate (1 mmol), Fe_3O_4@ $PyHBr_3$ MNPs (0.07 g, 9.1 molar%), aqueous hydrogen peroxide (4 mmol, 30%), H_2O (1 mL), at 50 °C.

[b] Isolated yields.

After the completion of the reaction, the catalyst was separated by a magnet. In order to evaluate the performance of Fe_3O_4 @ $PyHBr_3$ catalyst after recovery, the catalyst used in each reaction was separated by a magnet and reused in the next reaction after rinsing with CH_2Cl_2 (3×5 mL). The results of catalyst recovery for 4-bromobenzyl alcohol oxidation showed that it can be used up to 5-cycles without any considerable reduction in reaction yield (Table 3).

Table 3. Recyclability of Fe_3O_4 @ $PyHBr_3$ catalyst

Run	1	2	3	4	5
Yield (%)	95	90	88	85	80
Time (min.)	20	20	20	20	20

The efficiency of this catalyst can also be elucidated by comparing the results obtained in this study for the oxidation of benzyl alcohol with the results reported in the literature. For this purpose, in Table 4, a number of recent methods are given along with the temperature, reaction time and yield.

Table 4. Comparison of the presence method with other methodologies reported for oxidation of benzyl alcohol

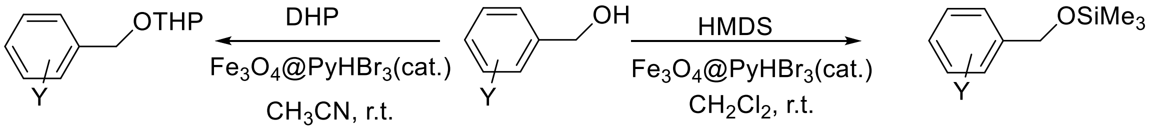
Reagents	Reaction time (min.)	Temperature (°C)	Yield (%)	Ref.
PVP-Br_3	70	r.t.	94	[17]
Silica-supported *DABCO-Br_3	60	80	95	[21]
H_2O_2 (1.1 eq), {[K.18-Crown-6]Br_3}$_n$	30	80	81	[33]
H_2O_2 (3 eq), **DBDMH (0/5 eq)	120	60	85	[34]
H_2O_2 (1.3eq), $MgFe_2O_4$ MNPs	55	60	88	[35]
H_2O_2, $K_8[BW_{11}O_{39}H]_{13}H_2O$	360	90	98	[31]
H_2O_2,VHPW/MCM-41/NH_2	480	80	97	[32]
H_2O_2, Fe_3O_4@PyHBr_3	20	50	88	-

*DABCO =1,4-diazabicyclo[2.2.2]octane

**DBDMH= 1,3-Dibromo-5,5-dimethylhydatoin

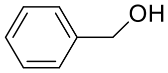
Trimethylsilylation and tetrahydropyranylation of benzyl alcohols were investigated in the presence of Fe_3O_4@ PyHBr_3 (Scheme 3). According to the optimal conditions obtained for 4-bromobenzyl alcohol, trimethylsilylation of various alcohol were performed using Fe_3O_4@ PyHBr_3 (0.07 g, 9.1 molar%), HMDS (0.7 mmol) in CH_2Cl_2 (5 mL) at room temperature (Scheme 3, Table 5). Also, tetrahydropyranylation of alcohols were accomplished using Fe_3O_4@ PyHBr_3 (0.07 g, 9.1 molar%), DHP (1.5 mmol) in CH_3CN (5 mL) at room temperature (Scheme 3, Table 5).

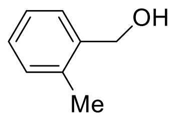
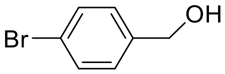
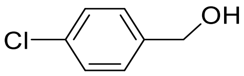
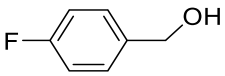
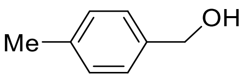
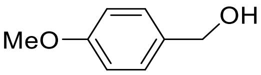
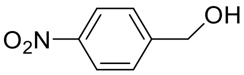
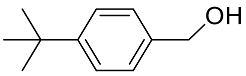
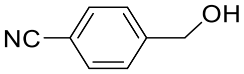
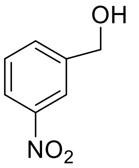
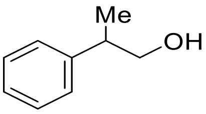
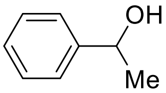
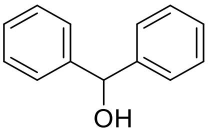
These results show that for all types of benzyl alcohols with electron donor and electron acceptor substituents, the corresponding trimethylsilyl ethers has been obtained in a short time and with excellent yields. Reaction times are shorter for benzyl alcohols including electron donor substituents with respect to benzyl alcohols having strong electron acceptor substituents.



Scheme 3. Trimethylsilylation and tetrahydropyranylation of benzyl alcohols in the presence of Fe_3O_4@ PyHBr_3

Table 5. Fe_3O_4@ PyHBr_3 MNPs catalyzed trimethylsilylation and tetrahydropyranylation of alcohols

Entry	Substrate	Trimethylsilylation^a		Tetrahydropyranylation^b	
		Time (min.)	Yield^c (%)	Time (min.)	Yield^c (%)
1		10	92	120	86

2		12	85	150	80
3		10	95	120	96
4		20	88	180	94
5		25	96	200	87
6		10	94	120	92
7		8	96	90	98
8		45	80	245	80
9		10	88	100	95
10		30	80	175	90
11		35	86	210	75
12		20	80	240	70
13		50	82	240	70
14		30	89	150	85

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[a] Reaction conditions: substrate (1 mmol), Fe_3O_4@ $PyHBr_3$ (0.07 g, 9.1 molar%), HMDS (0.7 mmol), CH_2Cl_2 (5 mL), at room temperature.

[b] Reaction conditions: substrate (1 mmol), Fe_3O_4@ $PyHBr_3$ (0.07 g, 9.1 molar%), DHP (1.5 mmol), CH_3CN (5 mL), at room temperature.

[c] Isolated yield.

These results show that the corresponding tetrahydropyranyl ethers are obtained with high yields for primary benzyl alcohols with either electron-acceptor or electron-donor substitutions. However, benzyl alcohols has shorter reaction times if they have electron-donor substitutions.

4. Conclusion

In conclusion, magnetic nanoparticles attached to pyridinium hydrotribromide (Fe_3O_4@PyHBr$_3$) were synthesized and the structure of magnetic nanoparticles was investigated using infrared spectroscopy, CHN, TGA, XRD, FE-SEM and VSM analyzes. Also, the efficiency of this magnetic nanoparticle in the oxidation reactions of alcohols to aldehydes and ketones was investigated. The results showed that Fe_3O_4@PyHBr$_3$ was very effective as a catalyst in the oxidation of alcohols by H_2O_2 as a green oxidant. This method has very mild reaction conditions as well as the advantages of easy separation and reusability of the catalyst, very short reaction times, high yields and using H_2O as green solvent. In the case of the primary alcohols, no additional oxidation was observed for the formation of carboxylic acid, which is a reason for the mildness and selectivity of the present method. The use of this magnetic catalyst in the reactions of trimethylsilylation and tetrahydropyranylation of alcohols were also investigated and it was found that it has many advantages such as easy separation of catalyst, good yields and mild reaction conditions.

Acknowlegements

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