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Efficient and selective green oxidation of alcohols by MOFderived magnetic nanoparticles as recoverable catalyst

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A simple and highly efficient synthesis strategy for green oxidation of alcohols to corresponding carbonyl products is developed using a heterogeneous non-noble magnetic Fe₃O₄@C catalyst. The magnetic nanocomposites were prepared by one-pot thermal decomposition of a Fe-containing MOF and fully characterized by powder X-ray diffraction (PXRD), N₂ physical adsorption, atomic absorption spectroscopy (AAS), element analysis, scanning electronic microscopy (SEM), and transmission electron microscopy (TEM). The catalytic activities of Fe₃O₄@C materials were investigated in the selective oxidation of alcohols in neat water using hydrogen peroxide as green oxidant under base-free conditions. Besides the high activity and selectivity to the target products, the proposed catalytic system features a broad substrate scope for both aryl and alkyl alcohols. Moreover, the magnetically catalyst could be easily separated by using an external magnetic field and reused for at least four times without significant loss in catalytic efficiency under the investigated conditions.

Introduction

The oxidation of alcohols to the corresponding aldehydes, ketones and carboxylic acids is commonly recognized as one of the most widely used and important oxidation reactions in organic synthesis. Typically, the chemoselective oxidation of alcohols to aldehydes or ketones without traceable overoxidation products (i.e., carboxylic acids) is attractive for the preparation of fine chemicals owing to the nature of aldehydes or ketones as an intermediate for producing carbonyl products, which are of great importance and versatility for the chemical industry and pharmaceutical synthesis.¹ Numerous efforts on developing efficient catalysts towards these oxidations have been progressed and reported a lot. In most cases, noble-metalbased (e.g., Au, Pd and Ru) catalysts show excellent activities and selectivities for this chemical proceses.²⁻⁴ However, the high price and shortage of noble metals resources limit the usage of these noble-metal-based catalyst. Therefore in recent years, there has been increasing demand for catalysts with less cost though high efficiency and selectivity towards the desired products, as well as environmentally benign. Some non-noble transition-metal-based catalyst systems (e.g., Co, Fe, Cu, and Mn) have been successfully developed for the oxidation of alcohols.⁵⁻⁸ Nevertheless, in competition with noble-metal-catalysts, the activity or selectivity in the reactions of aerobic alcohol oxidation is somehow lower for the non-noble catalysts, even in term of the scope and functional group tolerance of substrates.⁹ Besides, there are still persistent problems in this field: on one hand, a large excess of base additives or stoichiometric amounts of hazardous oxidizing agents (e.g., metal oxidants and peroxy acids) are conventionally utilized aiming to promote the activity and selectivity of this transformation, 10-13 which would cause drawbacks such as high cost, waste, by-products, and serious environmental issues. More importantly, liquid phase oxidation of alcohols by dioxygen or hydrogen peroxide is highly desired since they are relatively convenient and acceptable; the oxidants having high contents of active oxygen are cheap, mild and environmental friendly owing to the producing of water as the sole by-product. On the other hand, some of these reported oxidation reactions were carried out in organic solvents, for instance, toluene,9 acetonitrile,^{11,14} dimethyl sulfoxide (DMSO),¹⁵ which would cause the environmental pollution and the waste of resources. In general, the development of highly-efficient heterogeneous catalytic systems for the selective green oxidation of alcohols attracts keen interest continuously in both organic synthesis and green chemistry.

In addition, carbon nanocomposites containing inorganic oxides have become one kind of preferred functional materials attributed to their extensive applications covering diverse fields, among which magnetic nanomaterials have been invoked as an easy-recoverable material thus received increasing attentions. The unique physical and chemical properties of magnetic nanomaterials make them of great potential in various applications such as electrochemical,^{16,17} removal of wastewater,¹⁸ oils and dyes,^{19,20} magnetic storage media, drug delivery and cell separation etc.²¹⁻²⁴ In particular, the special magnetic characteristic plays decisive role in the separation procedure after usage by addition of external magnetic field, which have been proved to be simple and convenient. Over the past decade, functionalized magnetic nanoparticles have been

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ARTICLE

utilized as efficient and recoverable catalyst for various organic transformations, which represent excellent catalytic activities.²⁵⁻ 29 Α commonly-used method to synthesize nanocomposites is to utilize metal-organic frameworks (MOFs) as one component or precursors. In the recent two decades, MOFs have emerged as a new class of porous materials that can undergo self-assembly with metal ions and organic ligands. Owing to the highly-ordered structures, relatively huge surface areas and large pore volumes, MOFs have been widely utilized in a variety of fields such as gas storage/separation,^{30,31} catalysis,³² sensing,^{33,34} biomedical field,^{35,36} etc. However, the stability of MOFs is normally lower than the traditional porous materials such as zeolites and active carbons considering the low coordination bond energy between the ligands and metal ions of MOFs, which would likely led to the collapse of the framework during reactions thus impede the practical applications to the extent. Hence researchers thought from another side that to utilize this so-called "disadvantage" of MOFs to prepare more stable nanoporous materials. As a consequence, MOFs being considered as one component or alternative precursors to construct nanocomposites including metal/carbon hybrids has become the focus in the MOF-based chemistry. This new approach that to utilize MOFs in preparation of metal oxides or metal/carbon nanomaterials via a simple thermolysis procedure has been aroused in recent years. From a theoretical perspective, metal oxides are expected as products when the pyrolysis takes place in air and metal/carbon composites could be the produced in an inert atmosphere. Great progress has been made in the synthesis of porous carbon,³⁷ metal/metal oxides³⁸ and metal/metal oxide@C composites with various structures and compositions³⁹ ever since the development of this new approach to functional materials; the corresponding applications are also widely investigated especially in electrochemistry, including supercapacitors, batteries, fuel cells, sensing and catalysis. To date, efforts for such MOF-derived materials in liquid-phase catalytic oxidation reactions have been rarely done.40-44 Our research work aimed to fill up this field starting with developing this non-noble magnetic heterogeneous catalystbased system for selective oxidation of alcohols with green oxidants.

In continuation with recent research endeavours from the group, $^{2c,40-42,44-46}$ here we report the design and synthesis of novel non-noble magnetic heterogeneous catalysts, Fe₃O₄@C (B-x, where x indicates the temperature for preparing the catalyst) for selective oxidation of alcohols in neat water using hydrogen peroxide as green oxidant under base-free conditions. The proposed catalytic system features a good substrate scope for a variety of aryl and alkyl alcohols with a high selectivity for the target oxidation products. Moreover, the catalysts could be easily recovered and reused for a number of times without significant loss in activity and selectivity.

Experimental

General information

Commercially available chemicals and regents involved in this study were used without further purification unless otherwise indicated. Powder X-ray diffraction patterns of the MIL-88B and Bx were recorded on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu Ka radiation (40 kV, 30 mA, 0.1543 nm). Elemental analysis was performed on an Elementar Vario EL III equipment by weighing samples of 0.2-0.3 mg and packing with aluminium foil for the measurement. BET surface area and pore sizes were obtained from N2 adsorption/desorption isotherms at 77K with a Micromeritics ASAP 2020M instrument. The Fe contents of the B-x samples were measured by atomic adsorption spectroscopy (AAS) with a Hitachi Z-2300 instrument. The stability of MIL-88B was evaluated by TGA at a heating rate of 10 °C·min⁻¹ under N₂ atmosphere. The surface topography of MIL-88B and B-x as well as the elemental mapping were investigated by scanning electron microscope (SEM, MERLIN of ZEISS) and transmission electron microscope (TEM, JEOL, JEM-2010HR).

Preparation of MIL-88B

The Fe-containing MOF precursor, MIL-88B, was prepared according to the literature reports.⁴⁷ In a typical synthesis procedure, a mixture of FeCl₃•6H₂O (0.748 g, 2.77 mmol), 1,4-benzenedicarboxylic acid (0.460 g, 2.77 mmol) in *N*,*N*-Dimethylformamide (DMF, 120 mL) were transferred to a Teflon-lined autoclave, in which the mixture was then heated at 150 °C for 7 days. After cooling down to room temperature, the solid was collected by centrifugation, followed by washing with DMF and ethanol, then dried under vacuum at 60 °C to afford orange colour powder.

Preparation of B-x by thermolysis of MIL-88B

The typical thermolysis procedure for the preparation of the magnetic particle-embedded porous carbon materials is described as follows: the as-synthesized MIL-88B was heated at a heating rate of 1 °C/min from room temperature to 150 °C and maintained at this temperature for 2 h under argon atmosphere. Then increasing temperature to the target (i.e., 500 °C, 600 °C, 700 °C or 800 °C) lead to the formation of the hybrid composites. After calcination, the sample was cooled down to room temperature and collected. The obtained black powder was denoted as B-x (where x represents the temperature for thermolysis procedure).

General procedures for the catalytical oxidation of alcohols

A mixture of alcohol (0.5 mmol), $H_2O_2 30 \text{ wt.}\%$ (1.5 mmol), H_2O (3 mL) and catalyst (Fe 10 mol%) was placed in a Schlenk tube. The reaction solution was stirred at 110 °C for a certain course. At the end of a reaction, the catalyst was isolated and a sample of the liquid mixture was subjected to GC-MS analysis after extraction with ethyl acetate. (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

Recycling of catalyst

The recyclabilities of the catalysts were examined in the optimized reaction system. The catalyst was firstly re-collected after the former

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catalytic reaction by placing a magnet close to the Schlenk tube. The powders were adsorbed on the wall near the magnet side of the tube in seconds. After removing the supernatant solution from the mixture, the collected powders were thoroughly washed with ethanol, dried under vacuum to remove the residual solvent, and then reutilized as catalyst for subsequent runs under the identical reaction conditions as described above, except using the recycled catalyst.

Results and discussion

Characterization of MIL-88B and B-x

The powder X-ray Diffraction (XRD) patterns of MIL-88B (Fig. 1) matched well with the simulated and also the reported XRD patterns,⁴⁸ confirming the structure of the as-synthesized MOF material in this work. Thermogravimetric Analysis (TGA) curves of MIL-88B indicated that the MOF structure began to decompose when the temperature was increased to 400 °C under nitrogen (Fig.S1, ESI[†]). Therefore, the calcination temperatures for carbonization of MIL-88B were varied from 500 °C to 800 °C. The resulting composite was denoted as B-x, where x indicates the MOF thermolysis temperature. XRD patterns of B-x materials (Fig. 2) exhibited five diffraction peaks at around 30.1°, 35.4°, 53.1°, 56.9° and 62.5° , respectively, which were characteristics of Fe₃O₄ (JCPDS No. 19-0629). In addition, we have performed XPS measurements on the B-600 catalyst. The XPS survey spectrum of B-600 (Fig. S2a, ESI[†]) mainly showed the peaks of three elements present in the composite (i.e., Fe, O, C). Two strong peaks at 724.5 and 711.0 eV, assigned to Fe 2p_{1/2} and Fe 2p_{3/2} of Fe₃O₄,⁴⁹ respectively, were observed in the XPS spectrum (Fig. S2b, ESI[†]). As shown in the N₂ adsorption/desorption isotherms, micropores were only present in MIL-88B (Fig. S3, ESI⁺, and Table 1); after thermolysis, the observation of hysteresis loops at higher P/P_0 indicated the presence of mesopores in B-x materials (Fig. 2, and Table 1). Significant reduces in the specific surface areas of the B-x composites varied from around 237 m² g⁻¹ (B-500) to 198 m² g⁻¹ (B-800) were observed as compared with 1104 m² g⁻¹ of MIL-88B, probably owing to the collapse of crystal structure. The chemical compositions of the resulting B-x materials were characterized by elemental analysis and AAS. Contents of Fe, C, and O elements were mainly detected and summarized in Table 1.



Fig. 1 Powder XRD patterns of as-synthesized MIL-88B: (a) simulated, (b) as-synthesized.

Sample	S _{BET} (m ² g ⁻¹)	Pore Pore	Content (wt%)				
		Volume (cm ³ g ⁻¹)	Size (Å)	C ^a	H ^a	Fe ^b	O ^c
MIL-88B	1104	0.41	0.5	38.6	4.0	19.2	37.8
B-500	237	0.15	2.3	62.1	0.5	20.1	16.9
B-600	214	0.65	2.4 and	66.2	0.4	23.8	03
B-000			4.1	00.2	0.4	23.0).5
B-700	204	0.42	2.6	30.7	0.7	45.0	23.4
B-800	198	0.59	2.8	22.2	0.2	42.9	34.5

Table 1 Properties of Fe-based materials

^a Measured by elemental analysis. ^b Measured by AAS. ^c Calculated.

The surface morphology of B-x was subsequently investigated by SEM (Scanning Electron Microscopy). As shown in Fig. 3, all Bx exhibited similar particle shapes to those of the parent MIL-88B. However, the composite surface was distorted to rough when the calcination started, indicating the decomposition and carbonization of the MOF frameworks. Elemental mapping (Fig. 3, C1-C3)



Fig. 2 (a) The powder XRD patterns of the B-x materials. All samples show six well-resolved peaks which are identified as Fe₃O₄ (JCPDS No. 19-0629). (b) Nitrogen adsorption/desorption isotherms at 77 K for B-x materials. Black for B-500, red for B-600, blue for B-700, purple for B-800.



Fig. 3 SEM images of (a) MIL-88B, (b) B-500, (c) B-600, (d) B-700, (e) B-800, and elemental mapping of B-600: (C1) Fe, (C2) C, (C3) O.



Fig. 4 (a)–(c) TEM images of Fe_3O_4 nanoparticles of B-600. (d) The corresponding size distribution of Fe_3O_4 particles for B-600.

revealed a uniform distribution of Fe, C, and O in the material. The high dispersion nature of Fe₃O₄ in the porous carbons was further demonstrated by high-resolution transmission electron microscopy (HRTEM) (Fig. 4). It was obvious that Fe₃O₄ was dispersed on the carbon in B-600 with a uniform particle size of 12.5±3.6 nm. A high-resolution TEM image of B-600 confirmed the existence of crystallized Fe₃O₄ nanoparticles which were tightly surrounded by graphitized carbon. Moreover, no significant aggregation of Fe₃O₄ nanoparticles was observed, which could be attributed to the isolation effect of carbons formed from carbonization of the terephthalic acid linkers in MIL-88B. As the pyrolysis temperature increased, the Fe₃O₄ nanoparticles tended to aggregate gradually, as shown in Figure S3. Transmission Electron Microscopy (TEM) micrographs (Fig. 4 and Fig. S4, ESI[†]) revealed magnetic nanoparticles homogeneously dispersed in B-x materials. Magnetic nanoparticles obtained at higher thermolysis temperatures exhibited relatively larger sizes. These results suggested that the thermolysis temperature and organic ligands played important roles in reducing the particle size of Fe₃O₄ particles.

Catalytic activity in aerobic oxidations of alcohols under basefree conditions

Table 2 Optimization	of reaction cond	itions for oxidat	tion of benzyl
alcohol to benzaldehy	de.		



Entry	Catalyst	Solvent	Con. (%) ^a	Sel. (%) ^a
1	No	Toluene	5	99
2	B-500	Toluene	14	99
3	B-600	Toluene	21	99
4	B-700	Toluene	12	99
5	B-800	Toluene	9	99
6	B-600	Acetonitrile	22	96
7	B-600	DMF	13	95
8	B-600	DMA	19	94
9	B-600	H_2O	39	95
10	B-600	Acetone	18	95
11	B-600	DMSO	7	99
12	B-600	Dimethylbenzene	8	99
13	B-600	n-Hexane	7	99
14	B-600	Ethanol	30	95
15 ^b	B-600	H_2O	70	95
16 ^c	B-600	H_2O	71	95
17^{d}	B-600	H_2O	91	92
18^{e}	B-600	H_2O	93	91
$19^{\rm f}$	B-600	H_2O	99	91

Reaction conditions: benzyl alcohol (0.5 mmol), catalyst (10 mol% Fe), solvent (3 mL), $H_2O_2(1.5 \text{ mmol})$, 80 °C, 15 h. ^a Conversion and selectivity were based on the yield determined by GC-MS with an external standard. Benzoic acid was detected as by-product. ^b 50 °C , 48 h. ^c 70 °C , 48 h. ^d 90 °C , 48 h. ^e 100 °C , 48 h. ^f 110 °C , 48 h.

The catalytic activities of these magnetic nanopraticles materials were subsequently tested in alcohol oxidation using benzyl alcohol transforming to benzaldehyde as a model reaction, hydrogen peroxide as the oxidant; reactions were performed under moderate base-free condition. As illustration in Table 2, blank test (without catalyst) showed almost no reactivity (Table 2, entry 1). To our delight, the as-synthesized magnetic nanocomposites showed promising activity in this transformation. First, the B-x materials were examined as catalysts for the aerobic oxidation of benzyl alcohol in toluene at 80 °C. Although the conversions were somewhat low under these conditions, it was noteworthy that the aldehyde selectivities achieved by the B-x composites were all

Journal Name

Table 3 Oxidation of various alcohols by B-600 in water.

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	I I	B-600	Ĭ	
		H ₂ O ₂ , H ₂ O		
E. t.	Q-h-trate	Con.	C -1 (0/)ª	
Entry	Substrate	(%) ^a	Sel. (%)"	
1	J OH	86	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	99
2	ОН	93		99
3	ОН	91		99
4	NH ₂ OH	>99	NH2 O	99
5	н,соссо	88	H3COCO O	99
6	Огран	84	O ₂ N O	99
7	F	96	F C C C C C C C C C C C C C C C C C C C	99
8	сі	94	ci Co	99
9	С	83		99
10	Вг	>99	Br	99
11	OH C	81		99
12	OH CH	82		99
13	CI OH	89	g C	99
14	Br	91	Br	99
15	OH	81		99
16	но	91	0	90
17 ^b	Слон	98		96

Table 3 (Contd.)



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Reaction conditions: substrate (0.5 mmol), B-600 (10 mol% Fe), H_2O (3 mL), H_2O_2 (1.5 mmol), 110 °C, 48 h. ^a Conversion and selectivity were determined by GC-MS with an external standard. ^b 60 h. ^c 72 h. ^d 96 h.

nearly 100% (Table 2, entries 2–5). Among all the B-x materials, B-600 (*i.e.*, the material prepared at 600 °C) was most active (Table 2, entry 3), therefore was selected as catalyst for further optimization and investigation. The B-600 catalyst for the alcohol oxidation was then tested under different solvent systems, among which water was revealed to be the best (Table 2, entry 9). It appears that solvation effect might hugely influence the conversion of benzyl alcohol to the desired products. H₂O, which possesses the strongest polarity of all the investigated solvents, was preference to this reaction system. Although, the role of water for benefiting this reaction system is unclear, it is reasonable to consider water as a safe, cheap and green solvent if this reaction system could be performed in water.

Inspired by these intriguing results, we further optimized the oxidation reaction conditions. It is well known that the reaction temperature would affect the transformation in the term of both conversion and selectivity. As revealed in Table 2 (entries 15–19), slightly increase of temperature 50 °C to 110 °C led to an obvious increase of the conversion from 70.16% to an almost quantitative transformation with the reaction time prolonged to 48 h (Table 2, entry 19); in addition, the selectivities seemed satisfactory with a faintest decrease, probably owing to the producing of a very small amount of by-products at high temperatures. Thus after screening the reaction parameters and taking the balance between conversion and selectivity into consideration, the optimized reaction conditions could be obtained as follows: 10 mol% B-600 as the catalyst, H₂O as the solvent, hydrogen peroxide as the green oxidant, and reaction temperature at 110 °C for 48 h.

The substrate scope and the functional group tolerance of the selective green alcohol oxidation over the B-600 materials was then investigated under the optimized reaction environment (Table 3). First, different primary and secondary benzylic alcohols bearing electron-donating or -withdrawing functional groups afforded the

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Fig. 5 (a) Magnetic separation of the Fe₃O₄@C catalyst after reaction; (b) recycling of the B-600 in the oxidation of benzyl alcohol to benzaldehyde. Reaction conditions: benzyl alcohol (0.5 mmol), B-600 (10 mol% Fe), H₂O (3 mL), H₂O₂ (1.5 mmol), 110 °C, 48 h.

corresponding substituted aldehyde or ketones in good to excellent yields within 48 h (entries 1-14). As shown in Table 3, studies with substituted benzyl alcohols reveal that the conversion to aldehydes or ketones are not significantly controlled by the electron-donating and electron-withdrawing abilities of the substituents, nor sensitive to the substituent position on the benzene ring, which could be explained by the proposed mechanism for this transformation: the oxidation of benzyl alcohol derivatives proceeds via a hydrogen atom abstraction procedure of C-H bond activation, which should be the rate-determining step in the alcohol oxidation as demonstrated in the kinetic studies in other systems for alcohol oxidation.^{2c,50} The difference in activities between these alcohols could be ascribed to their compositions and structures. For the secondary benzylic alcohols such as 1-phenylethanol and its derivatives as well as diphenylmethanol, the convertions to the corresponding ketones were found in good yet relatively smaller yields comparing with those of primary benzylic alcohols (entry 11–15), which were likely caused by the steric effect of the secondary alcohols at the a-CH position. This is consistent with the proposed mechanism that hydrogen atom abstraction reaction requires significant interaction between the target C-H bond and the active centre of the catalyst, which is likely hindered by the other group in the secondary benzylic alcohols, thus end up with a decreased activity. Besides, 1,4-Benzenedimethanol could also undergo oxidation to 1,4-Benzene dicarboxaldehyde in 91% yield (entry 16).

In addition, we also investigated the oxidation reactions with heterocyclic alcohols such as 1-pyridinemethanol, furfuryl alcohol. The activities were well if prolonging reaction time to 60 h (entries 17-18). Moreover, a range of aliphatic alcohols were also demonstrated suitable for the formation of the corresponding products, achieving moderate to good yields within 72 h (entries 19, 21-22). For the cases in which the conversion was not satisfying, it could be remarkably improved by simply prolonging the reaction

time without any obvious reduces in selectivities. For example, 2hexanol was efficiently oxidized in excellent yield (86 %) with a 95 % selectivity towards 2-hexanone after 96 h of reaction (entry 20). Notably, the excellent selectivity to the target oxidation products could be obtained for all the investigated substrates.

Finally, we investigated the reusability of the highly active B-600 catalyst in the green oxidation of benzyl alcohol to benzaldehyde in aqueous medium. After the former run, the catalyst was dispersed in water, it can be easily separated out in a solid form with the assistance of an external magnet (Fig. 5). AAS analysis of the separating solution confirmed that the content of Fe in the solution was under the detection limit, indicating that no significant leaching of the active Fe3O4 was detected during the reaction process. The used catalyst was washed several times with acetic ester and methanol, and then dried in vacuum. Results included in Fig. 5 revealed no appreciable loss of conversion after at least four reaction runs. Powder XRD characterization proved that the structure of the catalyst was mostly preserved (Fig. S5, ESI⁺), indicating the stability of the material under the investigated conditions. Moreover, at ca. 60% conversion, the reaction solution was quickly filtrated at the reaction temperature, the resulting solution would undergo a slow conversion and reach to a conversion of 65% when the total reaction time was extended to 60 h, probably owing to the oxidation of substrates by H₂O₂, strongly suggesting that the reaction proceeded mostly on the heterogeneous surface (Fig. S6, ESI[†]).

Conclusions

In summary, we have developed a non-noble, highly efficient, and reusable magnetic heterogeneous catalyst for selective green oxidation of alcohols. The Fe₃O₄@C composites, synthesized by one-step thermolysis of cheap metal-containing organic framework of MIL-88B under an inert atmosphere, were proved to be highly active and selective in the oxidation of a broad substrate scope for both aryl and alkyl alcohols in the absence of any base additives in neat water. Moreover, the catalysts are magnetically separable and reusable, maintaining its high performance in this transformation for at least four recycles. Although the explanation of the solvation effect and the exact mechanism for the oxidation of alcohols over this catalytic system is still unclear, the combination of cheap, green and efficient, versatility and recyclability, as well as mild reaction conditions (in the absence of bases in neat water) makes this system an attractive alternative pathway for various oxidation processes. Further investigations to better understand the precise mechanism of this catalytic system in alcohol oxidation as well as in other oxidation processes are currently in progress.

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Graphical Abstract

A magnetic $Fe_3O_4@C$ heterogeneous catalyst derived from MOFs is highly efficient and selective in oxidation of alcohols with neat water and base-free conditions.

Neat ater, base-free R OH R C R=Aryl R'=Aryl, alkyl o R R P 🔘 : C (: Fe₃O₄ Yield: >80% Selectivity: 99%