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Introduction

2-Benzimidazole and its derivatives are important aromatic nitrogen heterocycles due to their ubiquitous presence and wide applications in many pharmaceutical and biological areas as antiulcer agents, antihypertensives, antivirals, antifungals, anticancer agents, and antihistamines, as well as in organic synthesis.¹⁻⁶ The widespread interest in 2-benzimidazoles has prompted extensive studies on their synthesis and a series of methods has been subsequently developed in recent decades. The coupling of o-phenylenediamines with carboxylic acids⁷ or their derivatives⁸ is an established general method to prepare benzimidazoles, but the harsh reaction conditions and relatively low yields limit its applications. Alternatively, the oxidative cyclodehydrogenation of aniline Schiff bases, generated in situ from the condensation of o-phenylenediamines with aldehydes,9 over various oxidants or catalysts has become popular due to the high efficiency and green nature of this approach. The generally employed oxidants or catalysts

An ammonium molybdate deposited amorphous silica coated iron oxide magnetic core—shell nanocomposite for the efficient synthesis of 2-benzimidazoles using hydrogen peroxide†

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An ammonium molybdate deposited amorphous silica coated iron oxide (Fe₃O₄@SiO₂) magnetic coreshell nanocomposite was prepared and tested in the application to the synthesis of 2-benzimidazoles from aromatic aldehydes and o-phenylenediamines using hydrogen peroxide as an oxidant at room temperature. It was found that the yields were fundamentally influenced by the nature and position of the substituents on the phenyl ring. Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS) confirmed that the active ammonium molybdate species are highly dispersed on the surface of the Fe₃O₄@SiO₂ magnetic core–shell nanocomposite, accounting for its good activity. A method was eventually developed for the synthesis of 2-benzimidazoles highlighting the good activity and easily recyclable nature of this magnetic catalyst.

> include $In(OTf)_3$,¹⁰ FeCl₃,¹¹ DDQ,¹² I₂,¹³ NH₄OAc,¹⁴ SDS,¹⁵ IBD,¹⁶ DMP,¹⁷ NaHSO₃,¹⁸ Na₂S₂O₅,¹⁹ Scolecite,²⁰ Dowex 50W,²¹ H₂O₂-HCl,²² H₂O₂-Bu₄NI,²³ and H₂O₂-CAN.²⁴ The application of these reagents has resulted in the efficient synthesis of benzimidazoles, but some procedures still have problems such as the use of toxic or precious metal catalysts, and the difficulties in catalyst recycling. These problems have limited the practical applications of this approach and there has been a great demand for the application of a green oxidant and a recyclable catalyst for the synthesis of 2-benzimidazoles.

> On the other hand, polyoxometalates have been widely used as homogeneous or heterogeneous catalysts in organic synthesis due to their excellent catalytic activity, good solubility, and non-toxicity.²⁵⁻²⁹ For instance, Iraj et al.²⁸ have reported the synthesis of various oxazolines and imidazolines over tungstophosphoric acid, and excellent yields were achieved in a short time. Autino et al.29 have obtained good results under solvent-free conditions in the synthesis of substituted coumarins from phenols and β-ketoesters over Wells-Dawson polyoxometalates. However, the difficulty in efficient recycling of the used polyoxometalates has limited their further application, mainly ascribed to their high solubility in water. Thus, preparation and application of supported polyoxometalates have attracted much attention in recent years.30,31 For example, García-Gutierrez et al.31 have developed an efficient γ-Al₂O₃ supported ammonium molybdate catalyst for the ultradeep oxidative desulfurization of diesel fuel using hydrogen



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peroxide as an oxidant. Recently, magnetic core–shell nanocomposites have become popular as novel supported catalysts due to their chemically modifiable surface, magnetically separable nature and good stability.^{32–34} For instance, Wu *et al.*³³ have reported a magnetically separable Fe₃O₄@SiO₂@Pd-Au nanocomposite for the liquid-phase hydrodechlorination of 4-chlorophenol under mild conditions, exhibiting an excellent catalytic performance. An *et al.*³⁴ have prepared a novel Fe₃O₄@SiO₂@AgCl:Ag nanocomposite *via* the visible-light reduction method and tested it in the decomposition of organic pollutants. This catalyst can be effectively recycled many times without the loss of its activity. However, to the best of our knowledge, no work on the synthesis of 2-benzimidazoles over core–shell structured nanocomposites has been reported.

In continuation of our previous work,³⁵ we herein report our recent research into the green and efficient synthesis of 2-benzimidazoles from aromatic aldehydes and *o*-phenylenediamines *via* a hydrogen peroxide oxidation system involving a novel ammonium molybdate deposited $Fe_3O_4(@SiO_2 magnetic$ core–shell nanocomposite ($Fe_3O_4(@SiO_2(@(NH_4)_6MO_7O_24))$). This catalyst exhibits good catalytic performance in the synthesis of 2-benzimidazoles and can be easily recycled. The mechanism of this transformation will be discussed in this paper and the structure of this core–shell nanocomposite has been confirmed.

Results and discussion

Initially, the synthesis of 2-phenylbenzimidazole as a representative of 2-benzimidazole, from benzaldehyde and *o*-phenylenediamine, was carried out over hydrogen peroxide and different polyoxometalates or surfactant combinations, and the results are listed in Table 1. As can be seen, the selectivity for 2-phenylbenzimidazole was only 48.3%, together with formation of appreciable quantities of Schiff base intermediates, in the absence of a catalyst. Gratifyingly, among the catalysts studied, ammonium molybdate was found to markedly improve the selectivity of 2-phenylbenzimidazole, achieving 97.7% in 180 min, much higher than other catalysts. On the other hand, 2-phenylbenzimidazole was obtained with 48.7% selectivity in the presence of air without hydrogen peroxide, whereas it decreased to 14.4% in the absence of both hydrogen peroxide and air (Table 1, entries 8 and 9), indicating that ammonium molybdate itself has poor catalytic activity. Therefore, we speculated that peroxomolybdate intermediates or other peroxides, generated from ammonium molybdate with hydrogen peroxide and air, account for the high activity of this catalytic system. Furthermore, we also examined the effect of reaction time. It was found that, although the conversion still remained at a high level, the selectivity for 2-phenylbenzimidazole decreased dramatically from 97.7% to 17.4% when the reaction time was decreased from 180 min to 60 min, whereas it was nearly unchanged when the reaction time was prolonged from 180 min to 240 min. Thus, 180 min is regarded as the appropriate reaction time for this catalytic system.

To solve the difficulty of efficient recycling of the used ammonium molybdate and shorten the reaction time, we proposed to prepare a new supported ammonium molybdate catalyst. Considering that magnetic separation is more attractive and efficient than traditional filtration or centrifugation, we decided to immobilize ammonium molybdate on a

 Table 1
 Effect of different catalytic systems on the synthesis of 2-phenylbenzimidazole^a



Entry	Oxidant	Catalyst	Time (min)	Conversion ^{b} (%)	Selectivity ^b (%)
1	H ₂ O ₂		180	93.2	48.3
2	H_2O_2	$H_{2}PW_{12}O_{40}$	180	95.4	64.9
3	H_2O_2	Na ₂ WO ₄	180	96.0	20.3
4	H_2O_2	Na ₂ MoO ₄	180	98.0	71.6
5	H_2O_2	$(NH_4)_6MO_7O_{24}$	180	94.1	97.7
6	H_2O_2	TBAB	180	92.4	38.4
7	H_2O_2	CTAB	180	98.4	29.2
8		$(NH_4)_6MO_7O_{24}$	180	98.3	48.7
9		$(NH_4)_6 MO_7 O_{24}^{c}$	180	96.2	14.4
10	H_2O_2	$(NH_4)_6MO_7O_{24}$	120	96.7	62.1
11	H_2O_2	$(NH_4)_6MO_7O_{24}$	60	97.9	17.4
12	$\tilde{H_2O_2}$	$(NH_4)_c MO_7O_{24}$	240	93.5	94.4

^{*a*} Reaction conditions: benzaldehyde (1.0 mmol), *o*-phenylenediamine (1.1 mmol), EtOH (5.0 mL), catalyst (0.04 mmol), H_2O_2 (0.2 mL). ^{*b*} Determined by HPLC based on the starting material. ^{*c*} Operated under a nitrogen atmosphere. TBAB = tetrabutyl ammonium bromide. CTAB = cetyl trimethyl ammonium bromide.



Fig. 1 Stepwise preparation of Fe $_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$ magnetic core-shell nanocomposites.

Table 2 Effect of ammonium molybdate supported on $Fe_3O_4@SiO_2$ on the synthesis of 2-phenylbenzimidazole a

Entry	Catalyst	Solvent	Conversion ^c (%)	Selectivity (%)
1	Catalyst-free	EtOH	95.2	11.6
2	$(NH_4)_c MO_7O_{24}$	EtOH	96.2	11.9
3	$Fe_3O_4(a)SiO_2$	EtOH	87.3	18.3
4	$Fe_{3}O_{4}$ (a) SiO_{2} (a)	EtOH	92.0	94.0
	$(NH_4)_6MO_7O_{24}$			
5	$Fe_{3}O_{4}(0)(NH_{4})_{6}MO_{7}O_{24}$	EtOH	81.0	97.1
6	Fe ₃ O ₄ @SiO ₂ @	Solvent-	71.8	94.7
	$(NH_4)_6MO_7O_{24}$	free		
7	Fe ₃ O ₄ @SiO ₂ @	H_2O	47.1	86.2
	$(NH_4)_6MO_7O_{24}$			
8	Fe ₃ O ₄ @SiO ₂ @	EtOH	92.6	96.8
	$(NH_4)_6 MO_7 O_{24}^{b}$			

^{*a*} Reaction conditions: benzaldehyde (1.0 mmol), *o*-phenylenediamine (1.1 mmol), solvent (5.0 mL), catalyst (0.22 g, including 0.04 mmol $(NH_4)_6Mo_7O_{24}$), H_2O_2 (0.2 mL), 30 min at room temperature. ^{*b*} Ultrasound heating for 30 min at room temperature. ^{*c*} Determined by HPLC based on the starting material.

 $Fe_3O_4@SiO_2$ magnetic core-shell nanocomposite by combining the Stöber and the equilibrium adsorption methodology, as illustrated in Fig. 1. Thus, a novel $Fe_3O_4@SiO_2@$ $(NH_4)_6Mo_7O_{24}$ catalyst was first prepared and applied to the synthesis of 2-benzimidazoles (Table 2).

As envisaged, the Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ catalyst could be effectively separated from the reaction mixture by an external magnetic field after the completion of reaction. Of note, the selectivity for 2-phenylbenzimidazole increased markedly to 94.0% in 30 min, whereas it was only 11.9% over the unsupported ammonium molybdate, 11.6% in the absence of any catalyst and 18.3% over Fe₃O₄@SiO₂. On the other hand, the conversion of benzaldehyde was only 81.0% when catalyzed by ammonium molybdate directly immobilized onto Fe_3O_4 (Fe_3O_4 (NH_4)₆Mo₇O₂₄) by the same method, although the selectivity for 2-phenylbenzimidazole was similar. Thus, it appears that ammonium molybdate supported on Fe₃O₄@SiO₂ not only solves the problem of separation of ammonium molybdate from the reaction mixture but also improves the dispersion of the active ammonium molybdate on the surface of SiO₂, accounting for the high activity of Fe₃O₄@SiO₂@ $(NH_4)_6 Mo_7 O_{24}$.



Fig. 2 Reusability studies on Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ for the synthesis of 2-phenylbenzimidazole. Reaction conditions: benzaldehyde (1.0 mmol), o-phenylenediamine (1.1 mmol), EtOH (5 mL), catalyst (0.22 g, including 0.04 mmol (NH₄)₆Mo₇O₂₄), H₂O₂ (0.2 mL) at room temperature.

Furthermore, the effect of solvents was also investigated under the same reaction conditions (Table 2). It became apparent that the conversion of benzaldehyde decreased in other solvents compared to ethanol. Considering that application of ultrasound often can reduce the reaction time dramatically,³⁵ this reaction was also carried out under ultrasound but we only observed a slight increase in the conversion and selectivity. Thus, $Fe_3O_4(@SiO_2(@(NH_4)_6MO_7O_{24}))$ was finally chosen as the catalyst of choice for the synthesis of 2-phenylbenzimidazoles in ethanol as the solvent of choice.

In addition, the stability of Fe_3O_4 @SiO₂@(NH₄)₆Mo₇O₂₄ was investigated. The recovered Fe_3O_4 @SiO₂@(NH₄)₆Mo₇O₂₄ was easily separated with an external magnet after reaction and then recycled under the same reaction conditions. The results depicted in Fig. 2 show that Fe_3O_4 @SiO₂@ (NH₄)₆Mo₇O₂₄ can be recycled five times without an appreciable loss of its catalytic activity, demonstrating its good stability as a catalyst for the synthesis of 2-phenylbenzimidazole. Furthermore inductively coupled plasma (ICP) analysis revealed that the amount of Mo in the supernatant after the reaction is very low and nearly negligible, indicating that there is almost no loss of the ammonium molybdate active species during the recycle, in agreement with the stability results.

Catalyst characterization

The physicochemical properties of ammonium molybdate and the magnetic core-shell nanocomposites were measured and selected results are summarized in Table 3. ICP results indicated that the Mo content of $Fe_3O_4(@SiO_2(@(NH_4)_6MO_7O_{24}$

 Table 3
 Selected physicochemical properties of ammonium molybdate

 and the magnetic core-shell nanocomposites

Sample	Mo loading ^a (wt%)	Surface area $(m^2 g^{-1})$	Pore volume $(10^{-2} \text{ cm}^3 \text{ g}^{-1})$
(NH ₄) ₆ M0 ₇ O ₂₄	_	3.4	1.1
Fe ₃ O ₄ (a)SiO ₂	_	27.5	5.8
Fe ₃ O ₄ @SiO ₂ @(NH ₄) ₆ Mo ₇ O ₂₄	10.0	8.3	2.4

^a Based on ICP results.



Fig. 3 XRD patterns of $(NH_4)_6Mo_7O_{24}$ and the core-shell nanocomposites. (a) $(NH_4)_6Mo_7O_{24}$, (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO₂@ $(NH_4)_6Mo_7O_{24}$. The inset shows the SAED image of Fe₃O₄@SiO₂@ $(NH_4)_6Mo_7O_{24}$.

was 10.0%, in agreement with the actual loading amount of ammonium molybdate. The surface area and pore volume of $Fe_3O_4(a)SiO_2(a)(NH_4)_6MO_7O_{24}$ were higher than those of ammonium molybdate, but much lower than those of $Fe_3O_4(a)SiO_2$, probably owing to the active ammonium molybdate species present in the pores and assembled on its surface.

Fig. 3 shows X-ray diffraction (XRD) patterns of ammonium molybdate and the corresponding magnetic core-shell nanocomposites. The characteristic diffraction peaks of ammonium molybdate appear around 12.5°, 25.1°, 37.3° and 41.4°, confirming the presence of crystalline ammonium molybdate.³⁶ Fe₃O₄(a)SiO₂ shows characteristic diffraction peaks at about 30.4°, 35.8°, 43.5°, 53.5°, 57.6° and 63.3°, just like those of pure Fe₃O₄ (JCPDS: 00-003-0862), indicating that the embedded Fe₃O₄ retains its crystalline structure after SiO₂ coating, while the SiO₂ exists in an amorphous state. However, the diffraction peaks of Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ are similar to those of Fe₃O₄@SiO₂ with no characteristic diffraction peak corresponding to ammonium molybdate being observed, indicating that the active ammonium molybdate species either exists in an amorphous state or is highly dispersed on the surface and in the pores of Fe₃O₄@SiO₂. Selected-area electron diffraction (SAED) patterns obtained from the shell edges of Fe_3O_4 O_2 O_2 $(NH_4)_6MO_7O_{24}$ are characterized by successive diffraction rings (inset in Fig. 3), demonstrating the crystalline structure of Fe₃O₄ in Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄, in accordance with the XRD results.

The nitrogen adsorption-desorption isotherms and the pore size distribution curves of $Fe_3O_4(@SiO_2(@(NH_4)_6MO_7O_{24}))$ are shown in Fig. 4. The nitrogen sorption isotherms of both magnetic core-shell nanocomposites resembled typical type IV isotherms³⁷ together with a hysteresis loop of type H3 in the P/P_0 range of 0.4–1.0, arising



Fig. 4 Nitrogen adsorption-desorption isotherms and the pore size distributions (the inset) of the core-shell nanocomposites (a) $Fe_3O_4@SiO_2 and$ (b) $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$.

from capillary condensation. The pore size distribution curve of $Fe_3O_4(@SiO_2$ showed a sharp peak at 3.9 nm and fluctuations between 5 and 40 nm (inset), which might be due to the micropore nature and interstices between the primary particles, improving the adsorption ability of $Fe_3O_4(@SiO_2,$ whereas the pore size distribution curve of $Fe_3O_4(@SiO_2(@))$ (NH₄)₆Mo₇O₂₄ merely fluctuated over a wide range, indicating only interstices between the primary particles.³⁸ Thus, we speculate that the active ammonium molybdate species are deposited on the $Fe_3O_4(@SiO_2$ magnetic core-shell nanocomposite, obstructing the micropores and some interstices, in agreement with its smaller BET surface area and pore volume.

The surface morphology and the particle distributions of the corresponding magnetic core-shell nanocomposites were recorded by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). From Fig. 5a and b, it can be seen that each nanocomposite contains several uniform spherical shaped Fe₃O₄ nanoparticles (approximately 6 nm in diameter) in one SiO₂ shell. The existence of the ammonium molybdate species on the surface of Fe₃O₄@SiO₂ nanocomposites was difficult to confirm from the TEM and HRTEM investigations (Fig. 5c and d), indicating that the ammonium molybdate species were highly dispersed on the surface or in pores and were not in a crystalline state. Further analysis of particle distributions showed that Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ has a little larger average particle size (approximately 62 nm) than Fe₃O₄@SiO₂ (approximately 58 nm) (Fig. 5, insets in a and c), although both of them intend to form larger aggregates due to the magnetic nature of Fe₃O₄. This suggests that the active ammonium molybdate species might assemble on the surface of Fe₃O₄@SiO₂ to form a monolayer, in agreement with the scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy results (Fig. S1 and S2[†]).

Scanning transmission electron microscopy (STEM) images of Fe_3O_4 (SiO_2(NH_4)_6MO_7O_{24} are depicted in Fig. 6, together



Fig. 5 TEM and HRTEM images of (a and b) $Fe_3O_4@SiO_2$ and (c and d) $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$ nanocomposites. (Insets a and c: the particle distributions of $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$.)

with a representative high-angle annular dark-field (HAADF) image and elemental mapping of the nanocomposite. The results demonstrate the presence of the expected molybdenum in the structure of this nanocomposite, as confirmed by the mapping of the related Si, Fe and O elements (Fig. 6c–g). The distribution of the molybdenum supports our previous assumption that the ammonium molybdate species were highly dispersed on the surface and in the pores of Fe₃O₄@SiO₂ nanocomposites.

X-ray photoelectron spectra (XPS) of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ are shown in Fig. 7. It was found that no Fe element was detected on the surface of either nanocomposites, demonstrating that the Fe₃O₄ nanoparticles were well coated with the pyknotic SiO₂ shell. Furthermore, two peaks related to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ (inset) could be observed on the surface of Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄. Their binding energies are 232.7 and 235.8 eV, respectively, suggesting the presence of the $(Mo_7O_{24})^{6-}$ structure, as also reported in previous literature.³⁹ Further thermogravimetric (TG) and differential thermogravimetric (DTG) measurements (Fig. S3[†]) confirmed that Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ is relatively stable within 473 K, whereas (NH₄)₆Mo₇O₂₄·4H₂O will only lose its crystalline water during the preparation process, in agreement with the above XPS results.

The room temperature hysteresis loops of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ nanocomposites are shown in Fig. 8. As can be seen, the saturation magnetization (M_s) value of Fe₃O₄@SiO₂ is 37.6 emu g⁻¹ at an applied field of 20 000 Oe, whereas the M_s value of Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ decreases to 28.0 emu g⁻¹, ascribed to the deposition of



Fig. 6 (a) STEM image of $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$. (b) HAADF-STEM image of $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$, with elemental mapping of (c) Si, (d) Fe, (e) O, (f) Mo, and (g) their overlap shown in the bottom row.

 $(NH_4)_6Mo_7O_{24}$ on the surface of Fe₃O₄@SiO₂. Moreover, the magnetization curves showed no remanence or coercivity in both samples, suggesting their superparamagnetic character.⁴⁰ Thus, the Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ nanocomposites can be easily separated from the reaction mixture by an external magnetic field (inset in Fig. 8), but pure ammonium molybdate cannot be separated.

Speculation of the reaction mechanism

A plausible mechanism of this reaction is proposed based on the experimental results and previous literature observations,^{23,24,31} as shown in Scheme 1. Intermediate 2 is initially formed *via* cyclization of Schiff base intermediate 1, which is formed by rapid condensation from benzaldehyde and *o*-phenylenediamine in the absence of the catalyst, as Zhu²³ and Bahrami²⁴ have described. Then, the intermediate 2 reacts with the *in situ* generated peroxomolybdate intermediates 6,³¹ from the oxidation of the supported molybdate species 5 by hydrogen peroxide, to afford the key intermediate 3, together with the regeneration of 5 and irreversible loss of



Fig. 7 XPS spectra of (a) $Fe_3O_4@SiO_2$ and (b) $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$ nanocomposites. The inset in (b) shows the high resolution XPS spectra of the Mo element in $Fe_3O_4@SiO_2@(NH_4)_6Mo_7O_{24}$.





Fig. 8 Room temperature hysteresis loops of the core–shell nanocomposites. (a) Fe₃O₄@SiO₂ and (b) Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄. The inset shows photographs of Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ before (left) and after (right) magnetic separation by an external magnetic field.

water. Finally, the rapid oxidative dehydrogenation of intermediate **3** generates the desired 2-phenylbenzimidazole.⁴¹

Synthesis of derivatives

To evaluate the versatility of this method, a series of aromatic aldehydes was then examined with *o*-phenylenediamines under the optimum reaction conditions, as shown in Table 4. In all cases, the reaction was carried out over periods of 30 min to 65 min. All products were characterized by FT-IR, ¹H NMR, ¹³C NMR and HRMS spectroscopy. As expected, all aromatic aldehydes reacted smoothly with *o*-phenylenediamine to provide the corresponding 2-benzimidazoles in good to excellent isolated yields. Furthermore, reactions of the *p*-substituted aldehydes possessing electron-withdrawing groups, such as –Cl and –NO₂, underwent much faster reaction than those possessing electron-donating groups, such as –OCH₃ and –OH, suggesting that the electron-withdrawing groups are favorable for this transformation. In contrast, comparing the reaction results of substituted benzaldehydes with the –Cl group in



Scheme 1 A plausible mechanism for the synthesis of 2-phenylbenzimidazole.

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Entry	Diamine	Aldehyde	Product	Time (min)	$\operatorname{Yield}^{b}(\%)$
1	NH ₂ NH ₂	Сно		30	90.3
2	NH ₂ NH ₂	СІ—		30	94.6
3	NH ₂ NH ₂	СІ		45	93.0
4	NH ₂ NH ₂	СІ		35	90.4
5	NH ₂ NH ₂	O ₂ N-CHO		35	90.9
6	NH ₂ NH ₂	МеО-СНО	N N H	65	87.3
7	NH ₂ NH ₂	н ₃ сСно	N H H CH3	40	89.7
8	NH ₂ NH ₂	но-Сно	М С С С С С С С С С С С С С С С С С С С	65	88.9
9	NH ₂ NH ₂	СНО		60	91.7
10	H ₃ C NH ₂ NH ₂	СНО	H ₃ C N	35	95.2
11	Br NH ₂ NH ₂	Сно		35	93.7
12	O ₂ N NH ₂ NH ₂	СНО	O ₂ N, N	45	91.0

Table 4 Synthesis of 2-benzimidazoles from aldehydes and diamines^a

^{*a*} Reaction conditions: aldehyde (1.0 mmol), diamine (1.1 mmol), EtOH (5.0 mL), catalyst (0.22 g, including 0.04 mmol (NH₄)₆Mo₇O₂₄), H₂O₂ (0.2 mL). ^{*b*} Yields of isolated products.

various positions, the steric factors of the substituents are proven to have less influence on the reaction rate. Thus, we can conclude that electronic factors are the main controlling factors in this transformation rather than steric factors. Moreover, the reaction of benzaldehyde with some substituted *o*-phenylenediamines also gave the corresponding 2-benzimidazoles smoothly in excellent yields, indicating the wide versatility of this method.

Conclusions

In summary, we have developed a green and efficient one-pot synthetic route to prepare 2-benzimidazoles from aldehydes and *o*-phenylenediamines using hydrogen peroxide as an oxidant at room temperature. A novel $Fe_3O_4(@SiO_2@(NH_4)_6-MO_7O_{24})$ magnetic core-shell nanocomposite has been prepared and demonstrated to be a highly efficient catalyst for this transformation. It can be recycled and reused several times without any appreciable loss of its initial catalytic activity. The noteworthy advantages of this method are its high efficiency, rapid and easy isolation of the used catalyst, and green and mild reaction conditions, which make it an attractive and useful contribution to present methodologies.

Experimental section

Catalyst preparation

The Fe_3O_4 (SiO_2) (NH_4)₆ Mo_7O_{24} magnetic core-shell nanocomposite was prepared by a combination of the Stöber and equilibrium adsorption methodology, described as follows.

The core-shell Fe₃O₄@SiO₂ nanocomposite was first prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) on the surface of Fe₃O₄ nanoparticles in a similar manner to the protocol reported in previous literature.⁴² In a typical procedure, 1.4 g Fe₃O₄ powder was first dispersed in 70 mL deionized water. An absolute ethanol solution containing 5.0 mL 25 wt% aqueous ammonia was then added to the magnetite suspension with stirring at 303 K over 15 min. After that, 4.0 mL TEOS was added slowly and the mixture was vigorously stirred for 12 h. Finally, the Fe₃O₄@SiO₂ was washed with absolute ethanol several times, collected using a magnet, dried and then kept under vacuum for further use.

 $Fe_3O_4(3)SiO_2(0)(NH_4)_6MO_7O_{24}$ was then prepared by the following run: the prepared $Fe_3O_4(3)SiO_2$ nanocomposite (1.0 g) was first impregnated with an aqueous solution of 0.25 g ammonium molybdate at room temperature. The wet samples were dried at room temperature overnight and then dried at 403 K in air for 2 h. Finally, the $Fe_3O_4(3)SiO_2(3)(NH_4)_6MO_7O_{24}$ nanocomposite thus obtained was kept under vacuum for further use.

Instruments and methods

The amount of Mo in the supernatant after the reaction was tested by ICP on an Agilent7500a spectrometer. The Mo content of the Fe₃O₄@SiO₂@(NH₄)₆Mo₇O₂₄ magnetic coreshell nanocomposite was determined by ICP on a Varian Vista-MPX spectrometer. BET surface areas and pore volumes of the catalysts were tested by nitrogen physisorption at 77 K on Micromeritics Tristar II 3020 apparatus. Before measurements, the samples were dried at 393 K for 2 h. Powder XRD patterns were obtained with a Bruker D8 diffractometer using a Cu Ka radiation source at 40 kV and 100 mA with a step size of 0.01° 2θ over the range 10-80°. TEM images were acquired with a FEI Tecnai G2 F20 X-Twin microscope at an extraction voltage of 3950 V, gun lens 1 and spot size 1. STEM/EDX maps were obtained at a spot size of 6 and the diffraction pattern was acquired with a camera length of 300 mm. The average particle sizes were estimated on the basis of 50 particles. XPS analysis was carried out on a PHI 1600 spectrometer using monochromatic Mg K α as the excitation source. The catalyst was mounted on the sample holder, where the background pressure was lower than 2×10^{-8} Torr. All the binding energy

(BE) values were calibrated by the C 1s peak of contaminant carbon at 284.6 eV. Magnetization curves were obtained on a LDJ9600-1 Superconducting quantum interference device at room temperature.

General procedure for the synthesis of 2-benzimidazoles

A mixture of aromatic aldehydes (1.0 mmol) and *o*-phenylenediamines (1.1 mmol) was first stirred in ethanol (5.0 mL) at room temperature. The catalyst (0.22 g, including 0.04 mmol (NH₄)₆Mo₇O₂₄) and 30.0% H₂O₂ (0.2 mL) were then added to the above mixture and reacted at room temperature for the requisite period of time while monitoring the reaction progress by TLC or HPLC. The reaction mixture was analyzed by HPLC using a BaseLine C₁₈ column (150 mm × 4.6 mm) with a mobile phase of methanol–water (7:3 by volume) at a 0.6 mL min⁻¹ constant flow.

After completion of the reaction, the catalyst was first separated using an external magnet for recycling and the residual reaction mixture was diluted with ethyl acetate (30.0 mL). Then, the solution was concentrated and the products were finally isolated by column chromatography on 200– 300 mesh silica gel using petroleum ether–ethyl acetate = $6:1 \sim 4:1$ as an eluent. Analytical and spectroscopic data of the series of 2-benzimidazoles are given in the ESI.†

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