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FULL PAPER

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Aerobic $\{Mo_{72}V_{30}\}$ nanocluster-catalysed heterogeneous one-pot tandem synthesis of benzimidazoles

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A novel heterogeneous one-pot protocol is developed for tandem aerobic synthesis of benzimidazoles through dehydrogenative coupling of primary benzylic alcohols and aromatic diamines co-catalysed by Keplerate-type $\{Mo_{72}V_{30}\}$ polyoxometalate and *N*-hydroxyphthalimide (NHPI). The catalytic system also works well for the synthesis of benzimidazoles using benzaldehydes, as commonly used starting materials, in the absence of NHPI. The high activity of the solid nanocluster provides standard conditions avoiding current limitations of oxidation methods including high catalyst loadings. The spectral results and leaching experiments revealed that the nanocapsule preserved its structural integrity after being reused in consecutive runs.

KEYWORDS

$\{Mo_{72}V_{30}\}$, benzimidazoles, heterogeneous catalyst, Keplerate, tandem synthesis

1 | INTRODUCTION

Polyoxometalates (POMs), a class of versatile and discrete anionic metal oxides with unique properties, have attracted researchers' attention for several decades. They have been applied to many fields, such as catalysis,[1,2] materials[3–6] and medicine.[7] The application of POMs to catalysis is stimulated by their fascinating properties, including strong acidity, strong oxidizing ability, an unmatched range of molecular structures, efficient adsorption, inherent resistance to oxidative decomposition, high thermal stability and impressive sensitivity to light and electricity.[1]

In some cases, the shape of the POM framework is such that it forms inner cavities, which are usually filled with other molecular species. These two characteristics are found in the family of Keplerates, spherical capsules that can assemble either 102 or 132 metal atoms. For the largest members, with general formula $[M_{72}M'_{60}O_{312}(\mu\text{-}X)_{60}]^{12-}$ (M = Mo(VI), W(VI); M′ = Mo(V); X = O, S), pentagonal building blocks are linked by 30 $Mo_2O_2(\mu\text{-}X)_2$ dimers. They are recognized as nanomaterials that allow a variety of research options in several disciplines such as electronic and magnetic applications and various aspects of materials science, including catalysis.[8,9]

In the line of our research interest in catalytic applications of Keplerates,[10–14] quite recently the heterogeneous catalytic efficiency of $\{Mo_{72}V_{30}\}$ nanocluster was exploited[15] in selective aerobic oxidation of benzylic alcohols and hydrocarbons co-catalysed by *N*-hydroxyphthalimide (NHPI) in EtOAc.[16] Herein, we report that the method is also capable of dehydrogenation of alcohols followed by coupling with aromatic diamines producing benzimidazoles which are known as important building blocks for the construction of pharmaceuticals, natural products, functional materials and agrochemical compounds.[17–20] Among the methods used for the synthesis of benzimidazoles, the use of alcohols as starting materials is a suitable alternative considering economic viability and environmental integrity because of the wide availability of alcohols.[21–30]

In the study reported here, initially we explored the possibility of aerobic benzimidazole synthesis via the reaction of 1,2-diaminobenzenes and benzylic alcohols using $\{Mo_{72}V_{30}\}$ nanocluster co-catalysed by NHPI in EtOAc (Scheme 1). Subsequently, the possibility of using benzaldehydes as commonly used starting materials for condensation with diaminobenzenes for the synthesis of benzimidazoles is also described. The heterogeneous catalyst showing sustainable stability under oxidative conditions could be recovered and reused at least five times.

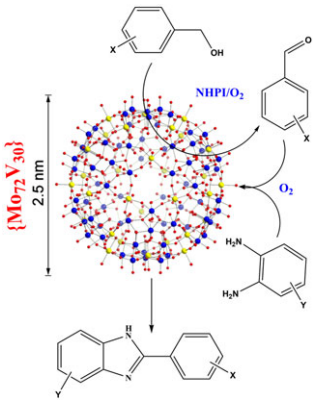
2 | EXPERIMENTAL

2.1 | General remarks

All chemicals were purchased from commercial sources. Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffractometer with Cu Ka (λ = 1.5406 Å) radiation. Fourier transform infrared (FT-IR) spectra were recorded with a Shimadzu 800 FT-IR system using a KBr pellet. UV–visible spectra were recorded with a SPECORD® 210 PLUS. Thermogravimetric analysis (TGA) was conducted with a TGA-50 (Shimadzu) at a heating rate of 10°C min^{-1} under 20 ml min^{-1} flowing air. Progress of the reactions was monitored by TLC using silica-gel SIL G/UV 254 plates and by GC with a Shimadzu GC-16A instrument using a 25 m CBP1-M25 (0.32 mm inner diameter, 0.5 mm coating) capillary column.

2.2 | Synthesis of $\{Mo_{72}V_{30}\}$

The $\{Mo_{72}V_{30}\}$ nanocluster was synthesized according to the literature.[15] A solution of $NaVO_3$ (2.6 g, 21.3 mmol) dissolved in 55 ml of water at 70°C and then cooled to room temperature was added to a solution of $Na_2MoO_{42}H_2O$ (6 g, 24.8 mmol) dissolved in 75 ml of water at room temperature. The mixture was acidified to pH 2.0 with H_2SO_4 (2 M, 14 ml) and then treated with $N_2H_6SO_4$ (0.9 g, 6.9 mmol). The solution turned dark violet and the pH increased to 2.8. After stirring for 3 h a solution of KCl (3 g, 40.2 mmol) in 20 ml of water was added to the mixture. Finally, the solution was filtered and the filtrate (solution) was left standing at room temperature. Black-purple hexagonal plates were formed overnight. The FT-IR, Raman and UV–visible spectra as well as XRD and TGA results of as-prepared $\{Mo_{72}V_{30}\}$ are given in the supporting information (Figures S1–S5).



SCHEME 1 One-pot synthesis of benzimidazoles from primary alcohols catalysed by $\{Mo_{72}V_{30}\}$ nanocapsule

2.3 | Typical procedure for synthesis of benzimidazoles from benzylic alcohols and 1,2-phenylenediamines (method A)

To a mixture of 0.1 g of benzylic alcohol (1.0 mmol) and 10 mg of $\{Mo_{72}V_{30}\}$ nanocluster (0.5 μmol, 0.05 mol%) in 2.0 ml of EtOAc was added 15 mg of NHPI (0.1 mmol, 10 mol%) and the reaction mixture was stirred under 1 atm O_2 (balloon) at 70°C for the required time. Then 1,2-phenylenediamine (0.13 g, 1.2 mmol) was added. The progress of the reaction was monitored by TLC and conversion determined by GC based on the starting alcohol. After completion of the reaction, excess amount of EtOAc was added to the mixture and the catalyst was separated by centrifugation followed by decantation (3 × 5 ml of EtOAc). Desired products were purified by plate silica chromatography eluted with *n*-hexane–ethyl acetate (10/2). Assignments of products were made from chemophysical properties as well as NMR spectral data (see supporting information).

2.4 | Typical procedure for synthesis of benzimidazoles from benzaldehydes and 1,2-phenylenediamines (method B)

To a mixture of 0.1 g of benzaldehyde (1 mmol) and 1,2-phenylenediamine (0.13 g, 1.2 mmol) in 2 ml of EtOH was added 20 mg of $\{Mo_{72}V_{30}\}$ nanocluster (1.0 μmol, 0.1 mol%) and the reaction mixture was stirred under 1 atm O_2 at 60°C for the required time. The progress of the reaction was monitored by TLC and conversion determined by GC based on the starting benzaldehyde. After completion of the reaction, excess amount of EtOH was added to the mixture and the catalyst was separated by centrifugation followed by decantation (3 × 5 ml of ethanol). Desired products were purified by plate silica chromatography eluted with *n*-hexane–ethyl acetate (10/2). Assignments of products were made from chemophysical properties as well as NMR spectral data (see supporting information).

2.5 | Recycling procedure for synthesis of benzimidazoles

After performing the reactions using the procedures of methods A and B, the residual catalyst was washed with EtOAc three times (3 × 5 ml) and dried under vacuum. It was weighed and then reused for subsequent runs.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of benzimidazoles using method A

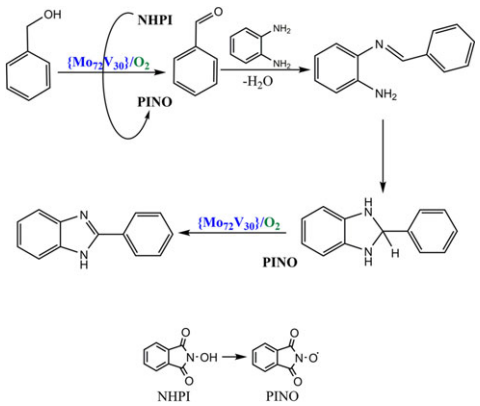
Initially, we tried to synthesize benzimidazole derivatives using dehydrogenation of benzylic alcohols followed by coupling with aromatic diamines. The data for the optimization of a model reaction using benzyl alcohol (1.0 mmol) and phenylenediamine (1.2 mmol) in the presence of molecular oxygen (1 atm, balloon) are given in Table 1. Inspection of the results in Table 1 (entries 5–9) revealed a solvent- and temperature-dependent product yield for the formation of benzimidazole. The best performance (>99%) was achieved at 70°C in EtOAc (Table 1, entry 5) and yield was significantly reduced on decreasing the temperature, reaching 5% at room temperature (Table 1, entries 6–9). Screening of the amount of catalyst and NHPI in the model system was performed with a further set of experiments. The blank reaction (catalyst-free) did not proceed in the absence or presence of NHPI. Therefore, the use of catalyst as well as NHPI for the promotion of the reaction is essential. Entries 5 and 10–14 in Table 1 show the effect of the amount of catalyst on the reaction performance. While the reaction

TABLE 1 Screening of factors in the synthesis of benzimidazole by reaction of benzyl alcohol and 1,2-phenylenediamine catalysed by $\{Mo_{72}V_{30}\}$[a]

Entry	Solvent	Temp. (°C)	Catalyst (mol%)	NHPI (mol%)	Yield (%)[b]
1	Solvent free	70	0.05	10	24
2	Water	70	0.05	10	31
3	EtOH	70	0.05	10	38
4	MeCN	70	0.05	10	86
5	**EtOAc**	**70**	**0.05**	**10**	**>99**
6	EtOAc	60	0.05	10	78
7	EtOAc	50	0.05	10	50
8	EtOAc	40	0.05	10	27
9	EtOAc	25	0.05	10	5
10	EtOAc	70	—	10	15
11	EtOAc	70	0.01	10	67
12	EtOAc	70	0.02	10	82
13	EtOAc	70	0.5	10	57
14	EtOAc	70	1	10	36
15	EtOAc	70	0.05	—	—
16	EtOAc	70	0.05	5	42
17	EtOAc	70	0.05	7.5	65
18	EtOAc	70	0.05	12.5	74
19	EtOAc	70	0.05	15	67

[a]Reactions were run for 4 h under O_2 (balloon) in 2.0 ml of solvent containing 1.0 mmol of benzyl alcohol and 1.2 mmol of 1,2-phenylenediamine.

[b]GC yield based on starting alcohol.



SCHEME 2 Proposed mechanism for aerobic synthesis of 2-phenylbenzimidazole from benzyl alcohol catalysed by $\{Mo_{72}V_{30}\}$

TABLE 2 Screening of catalyst type in synthesis of benzimidazole by reaction of benzyl alcohol and 1,2-phenylenediamine[a]

Entry	Catalyst	Catalyst amount (mol%)	Yield (%)[b]
1	$3NaVO_3$	1.5[c]	48
2	$NaMoO_4{\cdot}2H_2O$	3.6[c]	0
3	$NaVO_3$ + $NaMo_4{\cdot}2H_2O$	1.5% V + 3.6% Mo[c]	37
4	$VOSO_4$	1.5[c]	50
5	$\{Mo_{132}\}$	0.05	36
6	$\{Mo_{72}Fe_{30}\}$	0.05	0
7	**$\{Mo_{72}V_{30}\}$**	**0.05**	**>99**
8	$\{Mo_{72}Cr_{30}\}$	0.05	89
9	$\{W_{72}V_{30}\}$	0.05	68
10	$\{mimC_{18}\text{-}Mo_{72}V_{30}\}$	0.05	84
11	$\{DODA\text{-}Mo_{72}V_{30}\}$	0.05	68

[a]Reactions were run at 70°C for 4 h under O_2 (balloon) in 2.0 ml of EtOAc containing 1.0 mmol of benzyl alcohol, 1.2 mmol of 1,2-phenylenediamine and 0.1 mmol of NHPI.

[b]GC yield based on starting alcohol.

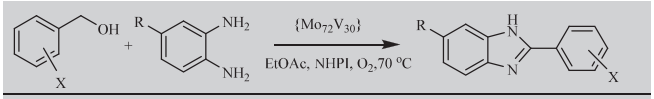
[c]The mol% of simple salts are the same as metal concentration in Keplerate POMs, i.e. 72 times Mo and 30 times V.

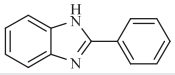
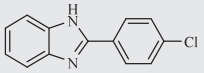
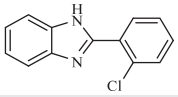
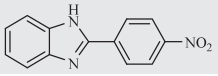
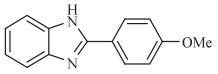
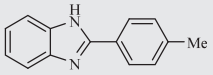
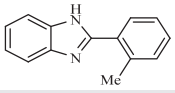
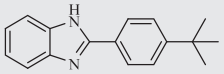
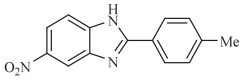
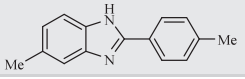
proceeded well with 0.05 mol% catalyst, increasing the catalyst loading up to 0.5 and 1 mol% decreased the corresponding yield to 57 and 36%, respectively. The formation of blackberry structures in concentrated solution of $\{Mo_{72}V_{30}\}$ macroanion reduces markedly the active sites.[31] The high dispersity of the solid nanocluster provides standard conditions avoiding current limitations of oxidation methods including high catalyst loadings.

Next, the amount of NHPI was screened. Entries 5 and 16–19 in Table 1 reveal that increasing the amount of NHPI improved the product yield, reaching a quantitative yield (95%) using 10 mol% of NHPI. These results demonstrated a co-catalyst role for NHPI in combination with $\{Mo_{72}V_{30}\}$. We also conducted the reaction under air as oxidant and found it slightly less effective than molecular oxygen (88%). Thus, the reaction exhibited the best efficiency using molecular oxygen (balloon) and a molar ratio of 2:2.4:1 for benzyl alcohol/diamine/NHPI with 0.05 mol% of catalyst in EtOAc (0.4 ml) at 70°C.

According to our previous report on alcohol oxidation,[16] a radical mechanism is reasonable for the investigated oxidative coupling reaction using NHPI and Keplerate catalyst including active Lewis acid and redox sites (Scheme 2). NHPI catalyses the oxidation reaction through initial generation of the phthalimide-*N*-oxyl (PINO) radical by abstraction of the O—H hydrogen in NHPI. The PINO radical then abstracts a hydrogen atom from a target substrate.[32,33] More evidence for hydrogen abstraction mechanism was obtained by using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the most widely used nitroxide radical.[34] The reaction proceeded with a modest yield of pertinent benzimidazole (46%) at the same time reflecting the steric hindrance about the catalytic centre involving TEMPO and transition metals of Keplerate catalyst.[16] To clarify whether NHPI is necessary for the final step of the reaction, 4-chlorobenzaldehyde (1 mmol) and 1,2-phenylenediamine (1.2 mmol) were mixed in the absence of NHPI in EtOAc under the same conditions. Benzimidazole was produced selectively in desired yield within 1 h. Thus, the method is amenable for the coupling of benzaldehydes, as commonly used starting materials, with aromatic diamines

TABLE 3 Aerobic synthesis of benzimidazoles using benzyl alcohols catalysed by $\{Mo_{72}V_{30}\}$[a]



Entry	X	R	Product	Time (h)	Yield (%)[b]
1	H	H		4	95
2	4-Cl	H		4	86
3	2-Cl	H		5	90
4	4-NO_2	H		8	68[c]
5	4-OMe	H		6	92
6	4-Me	H		6	89
7	2-Me	H		6.5	88
8	4-*t*-Bu	H		5	90
9	4-Me	NO_2		7	42[c]
10	4-Me	Me		6.5	87

[a]Reactions were run using 1.0 mmol of primary alcohols and 1.2 mmol of phenylenediamine in 2 ml of EtOAc under O_2 (1 atm, balloon) at 70°C in the presence of 0.05 mol% of catalyst, 10 mol% of NHPI.

[b]Yield of isolated products.

[c]Remainder is unreacted materials.

TABLE 4 Screening of various factors in synthesis of benzimidazole using 4-chlorobenzaldehyde and 1,2-phenylenediamine catalysed by $\{Mo_{72}V_{30}\}$[a]

Entry	Solvent	Temp. (°C)	Catalyst (mol%)	Time (min)	Yield (%)[b]
1	Solvent free	360	0.1	135	97
2	**EtOH**	**60**	**0.1**	**45**	**98**
3	Water	60	0.1	150	96
4	EtOAc	60	0.1	45	90
5	MeCN	60	0.1	95	97
6	DCE	60	0.1	145	90
7	EtOH	25	0.1	100	60
8	EtOH	40	0.1	70	98
9	EtOH	70	0.1	55	96
10	EtOH	80	0.1	120	90
11	EtOH	60	0.015	80	90
12	EtOH	60	0.03	70	90
13	EtOH	60	0.05	60	98

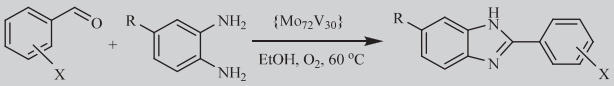
[a]Rreactions were run under O_2 (7 ml min^{-1}, bubbling) in 2.0 ml of solvent containing 1 mmol of 4-chlorobenzaldehyde and 1.2 mmol of 1,2-phenylenediamine.

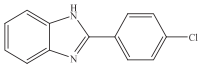
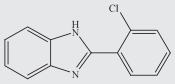
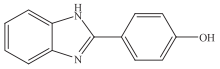
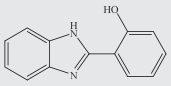
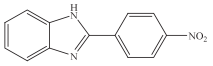
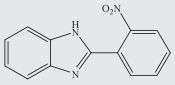
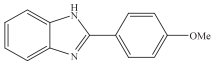
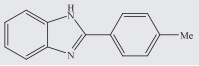
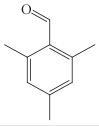
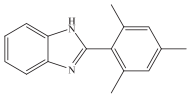
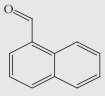
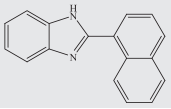
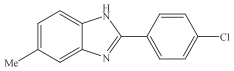
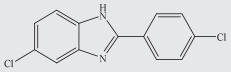
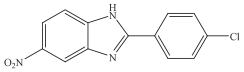
[b]GC yield based on starting 4-chlorobenzaldehyde.

for quantitative production of benimidazoles, which is the subject of next section of this work. It should be noted that, to elucidate our radical mechanism, 2,6-di-*tert*-butyl-4-methylphenol as a common radical scavenger was added to the reaction mixture, and significant retardation of benzimidazole production was observed.[16]

The catalytic potential of simple Mo and V salts as well as other Keplerate-type POMs was also evaluated in the oxidative dehydrogenation of benzyl alcohol and 1,2-phenylenediamine (Table 2). According to the results presented in entries 1–4, simple Mo and V salts were inferior catalysts for this transformation. Among various Keplerates used in this study (entries 5–9),[35–38] $\{Mo_{72}Fe_{30}\}$ was actually an inactive catalyst (entry 6), whereas $\{Mo_{72}Cr_{30}\}$ exhibited desired activity under the same conditions (entry 8). As observed for alcohol oxidation in our previous report,[16] by modification of $\{Mo_{72}V_{30}\}$ with organic cations such as 1-methyl-3-octadecaneimidazolium (C_{18}mim) and dioctadecyldimethylammonium (DODA) producing organic–inorganic nanohybrids, the yield of the corresponding products decreased to 84 and 68% (entries 10

TABLE 5 Aerobic synthesis of benzimidazoles using benzaldehydes catalysed by $\{Mo_{72}V_{30}\}$[a]



Entry	X	R	Product	Time (min)	Yield%[b]
1	4-Cl	H		45	95
2	2-Cl	H		90	94
3	4-OH	H		110	94
4	2-OH	H		190	80
5	4-NO_2	H		180	90
6	2-NO_2	H		170	96
7	4-OMe	H		150	96
8	4-Me	H		90	95
9		H		65	95
10		H		60	94
11	4-Cl	4-Me		90	93
12	4-Cl	4-Cl		55	95
13	4-Cl	4-NO_2		150	62

[a]Reactions were run using 1.0 mmol of aldehydes and 1.2 mmol of 1,2-phenylenediamine in 2.0 ml of EtOH under O_2 (1 atm, 7 ml min^{-1}, bubbling) at 60°C in the presence of 0.1 mol% of catalyst.

[b]Yield of isolated products.

and 11), respectively. Protection of active sites by the long chains of organic counter ions of the $\{Mo_{72}V_{30}\}$ surfactant-encapsulated cluster was proposed to be a good reason for such a reduction in activity.[16,39]

In order to establish the general applicability of the method, various benzyl alcohols were subjected to this protocol under the catalytic influence of the $\{Mo_{72}V_{30}\}$ nanocluster (Table 3). According to the results, benzimidazole derivatives were successfully produced with moderate to high yields. It was observed that the reaction rate was affected by electronic demands of substrates. Benzyl alcohols bearing electron-donating groups were efficiently converted to the corresponding benzimidazoles (Table 3, entries 5 and 6). Nevertheless, strong electron-withdrawing nitro group on the phenyl ring of both alcohol and amine molecules significantly retarded the reaction (Table 3, entries 4 and 9). It should be mentioned that the production of benzimidazoles using aliphatic alcohols failed, resulting from their poor oxidation reactivity for formation of aldehyde intermediates under the optimized conditions of this work.[16]

3.2 | Synthesis of benzimidazoles using method B

Next, the possibility of benzimidazole synthesis via the reaction of 1,2-diaminobenzenes and benzaldehydes as starting materials under the catalytic influence of the $\{Mo_{72}V_{30}\}$ nanocluster was examined. To optimize the reaction conditions, various factors were screened. According to data summarized in Table 4, the reaction of 4-chlorobenzaldehyde (1.0 mmol) with 1,2-phenylenediamine (1.2 mmol) in ethanol (2.0 ml) containing 0.1 mol% $\{Mo_{72}V_{30}\}$ proceeded quantitatively within 45 min under a continuous stream of O_2 at 60°C with no need for NHPI.

With an improved procedure in hand, we then focused on the evaluation of the substrate scope for synthesis of benzimidazoles. First, a set of structurally diverse aldehydes was coupled with 1,2-phenylenediamine under O_2 stream (Table 5). A broad range of benzimidazole derivatives was successfully formed with good to excellent yield using this protocol. The results indicated that an electron-withdrawing group on the phenylenediamine induced a negative influence on the reaction efficiency in this catalytic system (entry 13). It is noteworthy that, in all experiments, excellent selectivity was observed for benzimidazole formation.

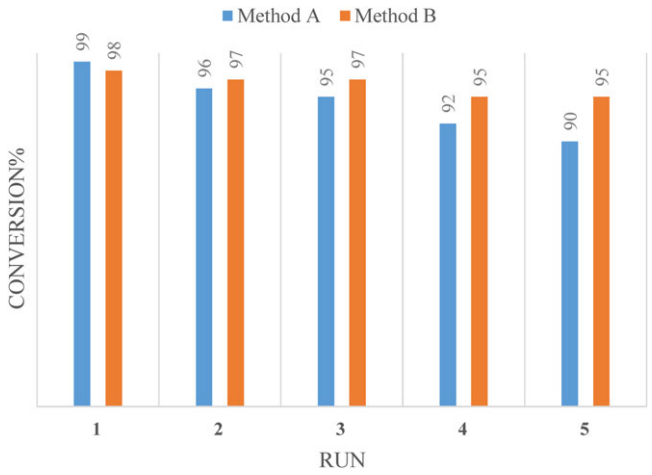


FIGURE 1 Recycling of catalytic system for synthesis of benzimidazoles (methods A and B) using $\{Mo_{72}V_{30}\}$ nanocluster according to procedures mentioned in the experimental section. Conversions were obtained using GC based on starting benzyl alcohol and 4-chlorobenzalaldehyde for methods A and B, respectively

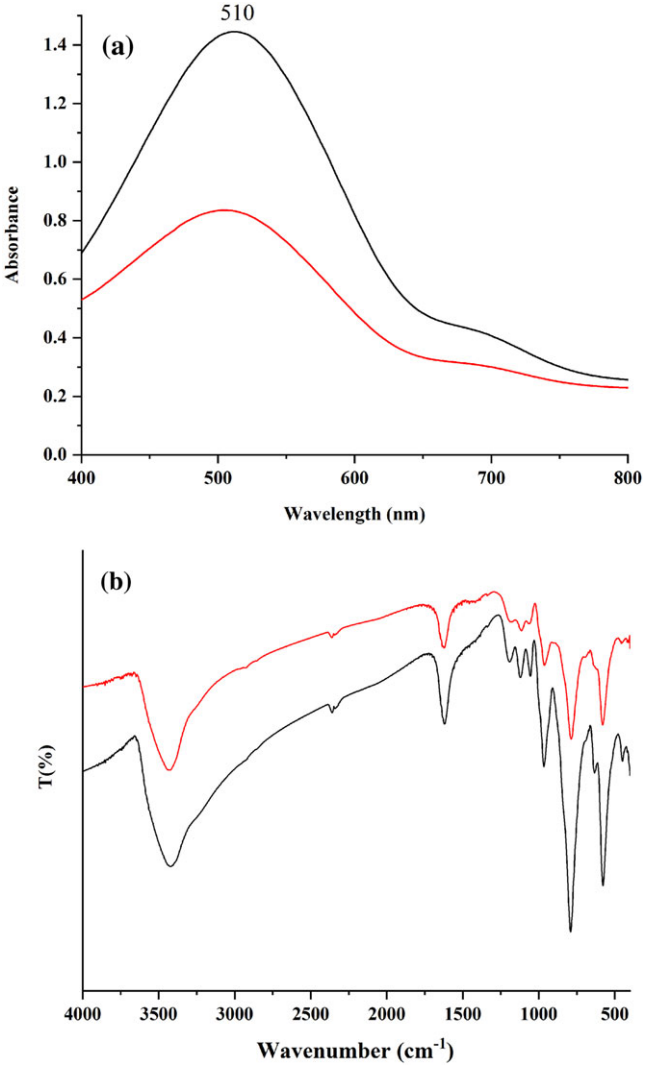


FIGURE 2 (a) UV–visible and (b) FT-IR spectra of fresh (black) and recovered (red) $\{Mo_{72}V_{30}\}$ in the synthesis of benzimidazole by method A

3.3 | Reusability and stability

The reusability and stability of a catalyst are imperative factors for practical applications of a heterogeneous system. In this line, the recyclability of the catalyst was investigated in the synthesis of benzimidazoles based on model reactions (methods A and B). After completion of the reactions, the $\{Mo_{72}V_{30}\}$ nanocluster was separated easily by centrifugation followed by decantation. The recovered catalyst was dried under air, weighed and used for subsequent runs. The catalyst gave remarkable results without noticeable loss of activity (Figure 1). Minor loss of activity in method A after the third run can be related to contamination of the catalyst surface by organic compounds. Sonication of the residual catalyst in EtOAc followed by filtration and drying under vacuum enhanced the conversion to 96% in the fifth run. Moreover, the stability of the catalyst was investigated by comparison of FT-IR and UV–visible spectra of used catalyst with those of fresh one (Figure 2). These results clearly revealed that the structure of the catalyst remained almost intact so that the reaction had no effect on the structure and properties of the catalyst. Moreover, to determine the amount of Mo and V released during the reaction, atomic absorption spectrometric measurements were performed after filtration of solid particles. The amount of elements in filtrate was not detectable using this analysis (<1 ppm) demonstrating that the $\{Mo_{72}V_{30}\}$ nanocluster rather than the products of its degradation acts as an active catalyst in these transformations.

3.4 | Comparison with previously reported methods

Finally, the merit of these operationally catalytic protocols in the synthesis of benzimidazoles was compared with previously reported methods in terms of catalyst loading, temperature, reaction time and yields of products with both benzyl alcohol (Table 6, method A) and benzaldehyde (Table 7, method B) as starting materials. Therefore, the title catalytic system is environmentally

TABLE 6 Comparison of catalytic activity of $\{Mo_{72}V_{30}\}$ nanocluster with that of other previously reported catalysts for synthesis of benzimidazole using benzyl alcohol and 1,2-phenylenediamine

Entry	Catalyst	Catalyst amount (mol %)	Conditions	Time (h)	Yield (%)	Ref.
1	**$\{Mo_{72}V_{30}\}$**	**0.05**	**EtOAc/O_2/NHPI/70°C**	**4**	**95**	**This work**
2	Co_3O_4@Al_2O_3/SiO_2	5	Solvent free/O_2/120°C	6	96	[40]
3	Ir/TiO_2–500	1	Mesitylene/Ar/120°C	18	97	[41]
4	[Ir(cod)2,6-DiAmPy(iPr)$_2$]	1.4	KO^{t}Bu/diglyme/110°C	24	85	[42]
5	TEMPO-PEG_{4000}-NHC-Cu(II)	5	Water/air/*t*-BuONa/75°C	8	96	[43]
6	dppf [1,1-bis(diphenylphosphino)ferrocene]	5	Toluene/Ar/150°C	24	74	[44]
7	2-Iodoxybenzoic acid	1	DMSO/air/25°C	5	72	[23]
8	FePC	1	Toluene/*t*-BuONa/120°C	36	89	[45]
9	$RuCl_2(PPh_3)_3$	3.3	Toluene/Ar/200°C	20	80	[26]

TABLE 7 Comparison of catalytic activity of $\{Mo_{72}V_{30}\}$ nanocluster with that of other previously reported catalysts for synthesis of benzimidazole using 4-chlorobenzaldehyde and 1,2-phenylenediamine

Entry	Catalyst	Catalyst amount (mol%)	Conditions	Time (min)	Yield (%)	Ref.
1	**$\{Mo_{72}V_{30}\}$**	**0.1**	**EtOH/O_2/60°C**	**45**	**95**	**This work**
2	$Cu(OH)_2$	10	Methanol/air/RT	240	98	[46]
3	Thiamine hydrochloride	3	DMF/air/RT	90	88	[47]
4	$LaCl_3$	10	CH_3CN/air/RT	150	91	[48]
5	*p*-Toluenesulfonic acid/graphite	19	Solvent free/air/75°C	45	79	[49]
6	Na_3AlF_6	2	EtOH/air/50°C	960	83	[50]
7	$Zn(OTf)_2$	10	EtOH/80 C/reflux	480	89	[51]
8	$NaC_{15}H_{25}S_O4$	10	Water/air/RT	35	85	[52]
9	$Fe(HSO_4)_3$	100	Water/RT	60	91	[53]

benign because of using oxygen as an ideal oxidant, EtOAc and ethanol as safe reaction media, reusing of an active catalyst, easy isolation of organic products and finally no need for toxic reagents or solvents.

4 | CONCLUSIONS

The catalytic efficiency of $\{Mo_{72}V_{30}\}$ nanocluster was exploited in dehydrogenative coupling of primary benzylic alcohols and aromatic diamines in the presence of NHPI as hydrogen acceptor for direct synthesis of benzimidazoles. The method is also capable of oxidative coupling of benzaldehydes with aromatic diamines producing benzimidazoles in high to excellent yields. The reactions exhibited high performance using low catalyst loading because of high dispersity of the solid nanocluster providing standard conditions avoiding current limitations for scale-up applications. The methods use molecular oxygen as oxidant and ethyl acetate or ethanol as safe solvents affording environmentally friendly reaction conditions for the synthesis of benzimidazoles as medicinally and pharmaceutically important compounds. Moreover, the stability of the catalyst and its potential for efficient recyclability along with easy workup procedure for isolation of products in good to excellent yields are further advantages of these procedures, highlighting their merits for applied purposes.

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REFERENCES

[1] S. S. Wang, G.-Y. Yang, *Chem. Rev.* **2015**, *115*, 4893.

[2] A. Patel, S. Pathan, *Polyoxomolybdates as Green Catalysts for Aerobic Oxidation*, Springer, New York **2015**.

[3] M. Genovese, K. Lian, *Curr. Opin. Solid State Mater. Sci.* **2015**, *19*, 126.

[4] A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239.

[5] T. Yamase, *Chem. Rev.* **1998**, *98*, 307.

[6] E. Coronado, C. J. Gomez-Garcia, *Chem. Rev.* **1998**, *98*, 273.

[7] J. T. Rhule, C. L. Hill, D. A. Judd, R. F. Schinazi, *Chem. Rev.* **1998**, *98*, 327.

[8] A. Müller, P. Gouzerh, *Chem. Soc. Rev.* **2012**, *41*, 7431.

[9] A. Müller, P. Gouzerh, *Chem. Eur. J.* **2014**, *20*, 4862.

[10] A. Rezaeifard, R. Haddad, M. Jafarpour, M. Hakimi, *J. Am. Chem. Soc.* **2013**, *135*, 10036.

[11] A. Rezaeifard, R. Haddad, M. Jafarpour, M. Hakimi, *ACS Sustain. Chem. Eng.* **2014**, *2*, 942.

[12] A. Rezaeifard, M. Jafarpour, R. Haddad, H. Tavallaei, M. Hakimi, *J. Clust. Sci.* **2015**, *26*, 1439.

[13] A. Rezaeifard, M. Jafarpour, R. Haddad, F. Feizpour, *Catal. Commun.* **2017**, *95*, 88.

[14] R. Mokhtari, A. Rezaeifard, M. Jafarpour, A. Farrokhi, *Catal. Sci. Technol.* **2018**, *8*, 4645.

[15] B. Botar, P. Kögerler, C. L. Hill, *Chem. Commun.* **2005**, *21*, 3138.

[16] A. Rezaeifard, A. Khoshyan, M. Jafarpour, M. Pourtahmasb, *RSC Adv.* **2017**, *7*, 15754.

[17] S. Yadav, B. Narasimhan, H. Kaur, *Anti-Cancer Agents Med. Chem. (Formerly Curr. Med. Chem. Agents)* **2016**, *16*, 1403.

[18] Y. Bansal, O. Silakari, *Bioorg. Med. Chem.* **2012**, *20*, 6208.

[19] S. D. Undevia, F. Innocenti, J. Ramirez, L. House, A. A. Desai, L. A. Skoog, D. A. Singh, T. Karrison, H. L. Kindler, M. J. Ratain, *Eur. J. Cancer* **2008**, *44*, 1684.

[20] H. Mehlhorn, *Encyclopedia of Parasitology*, Ed. 4, Springer-Verlag, Berlin Heidelberg **2016**.

[21] A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi, J. M. J. Williams, *Org. Lett.* **2009**, *11*, 2039.

[22] Y. Shiraishi, Y. Sugano, S. Tanaka, T. Hirai, *Angew. Chem.* **2010**, *122*, 1700.

[23] J. N. Moorthy, I. Neogi, *Tetrahedron Lett.* **2011**, *52*, 3868.

[24] F. Feizpour, M. Jafarpour, A.b. Rezaeifard, *Catal. Lett.* **2018**, *148*, 30.

[25] V. R. Ruiz, A. Corma, M. J. Sabater, *Tetrahedron* **2010**, *66*, 730.

[26] A. Eskandari, M. Jafarpour, A. Rezaeifard, M. Salimi, *New J. Chem.* **2018**, *42*, 6449.

[27] G. M. Raghavendra, A. B. Ramesha, C. N. Revanna, K. N. Nandeesh, K. Mantelingu, K. S. Rangappa, *Tetrahedron Lett.* **2011**, *52*, 5571.

[28] Y. Zhu, F. Jia, M. Liu, A. Wu, *Org. Lett.* **2012**, *14*, 4414.

[29] J. W. Kim, J. He, K. Yamaguchi, N. Mizuno, *Chem. Lett.* **2009**, *38*, 920.

[30] J. Yu, J. Xu, M. Lu, *Appl. Organometal. Chem.* **2013**, *27*, 606.

[31] P. Yin, D. Li, T. Liu, *Chem. Soc. Rev.* **2012**, *41*, 7368.

[32] F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800.

[33] Y. Ishii, S. Sakaguchi, T. Iwahama, *Adv. Synth. Catal.* **2001**, *343*, 393.

[34] S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski, *Chem. Rev.* **2013**, *113*, 6234.

[35] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem. Int. Ed.* **1998**, *37*, 3359.

[36] A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed.* **1999**, *38*, 3238.

[37] A. M. Todea, A. Merca, H. Bögge, J. Van Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry, A. Müller, *Angew. Chem. Int. Ed.* **2007**, *46*, 6106.

[38] A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, *Chem. Commun.* **2009**, 3351.

[39] D. Volkmer, A. Du Chesne, D. G. Kurth, H. Schnablegger, P. Lehmann, M. J. Koop, A. Müller, *J. Am. Chem. Soc.* **2000**, *122*, 1995.

[40] P. L. Reddy, R. Arundhathi, M. Tripathi, P. Chauhan, N. Yan, D. S. Rawat, *ChemistrySelect* **2017**, *2*, 3889.

[41] K. Tateyama, K. Wada, H. Miura, S. Hosokawa, R. Abe, M. Inoue, *Catal. Sci. Technol.* **2016**, *6*, 1677.

[42] T. Hille, T. Irrgang, R. Kempe, *Chem. Eur. J.* **2014**, *20*, 5569.

[43] Z. Wang, X. Cao, Y. Yang, M. Lu, *Synth. Commun.* **2015**, *45*, 1476.

[44] G. Li, J. Wang, B. Yuan, D. Zhang, Z. Lin, P. Li, H. Huang, *Tetrahedron Lett.* **2013**, *54*, 6934.

[45] M. Bala, P. K. Verma, U. Sharma, N. Kumar, B. Singh, *Green Chem.* **2013**, *15*, 1687.

[46] M. A. Chari, D. Shobha, S. Malayalama, Z.-A-Mosaa, *Int. J. Org. Chem.* **2013**, *3*, 243.

[47] M. Lei, L. Ma, L. Hu, *Synth. Commun.* **2012**, *42*, 2981.

[48] Y. Venkateswarlu, S. R. Kumar, P. Leelavathi, *Org. Med. Chem. Lett.* **2013**, *3*, 7.

[49] H. Sharghi, O. Asemani, S. M. H. Tabaei, *J. Heterocycl. Chem.* **2008**, *45*, 1293.

[50] A. Mobinikhaledi, A. Hamta, M. Kalhor, M. Shariatzadeh, *Iran. J. Pharm. Res.* **2014**, *13*, 95.

[51] R. Srinivasulu, K. R. Kumar, P. V. V. Satyanarayana, *Green Sustain. Chem.* **2014**, *4*, 33.

[52] S. D. Pardeshi, S. N. Thore, *Int. J. Chem. Phys. Sci.* **2015**, *4*, 300.

[53] H. Eshghi, M. Rahimizadeh, A. Shiri, P. Sedaghat, *Bull. Kor. Chem. Soc.* **2012**, *33*, 515.

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