



Mesoporous mixed metal oxide nanocrystals: Efficient and recyclable heterogeneous catalysts for the synthesis of 1,2-disubstituted benzimidazoles and 2-substituted benzothiazoles

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ABSTRACT

Present communication elicits the use of mesoporous mixed metal oxide nanocrystals of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$ as heterogeneous catalysts for the preparation of series of medicinally significant 1,2-disubstituted benzimidazoles and 2-substituted benzothiazoles. These nanocrystalline catalysts exhibited remarkable catalytic activity with a high substrate to catalyst weight ratio (20:1) to achieve the synthetic targets in the range of yield 81–96%. The solvent-free microwave assisted synthesis of these compounds was an advantageous way which resulted in excellent yields in much lesser time (0.75–1.5 min) in comparison to conventional heating. The use of catalyst in eco-friendly green protocol and its reusability up to four cycles with similar catalytic response are the unique features of the heterogeneous catalysis. This protocol provided greater selectivity, cost-efficiency, clean reaction profiles, simple work-up procedure and high yields.

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1. Introduction

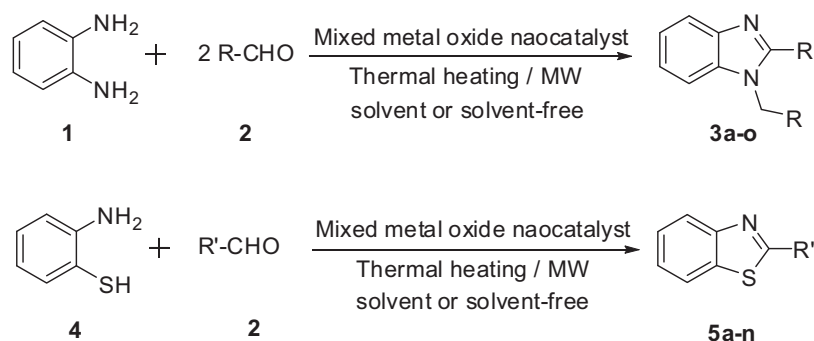
The chemistry of benzimidazole and benzothiazole structural motifs has blossomed rapidly in diverse areas of medicinal chemistry owing to their potential involvement as key component for various pharmacological activities [1–6]. The high profiles of biological applications displayed by compounds associated with benzimidazole and benzothiazole nuclei have prompted extensive studies for their synthesis [7,8]. Most of the methods reported so far for the synthesis of benzimidazoles involves the condensation of 1,2-phenylenediamines with carboxylic acid derivatives [9] or aldehydes [10] in presence of strong acids such as polyphosphoric acid or mineral acid or under oxidative condition. The use of palladium [11] and copper-catalyzed [12] intramolecular N-arylation starting from o-haloanilines has also been reported as other alternative. Recently, the use of $\text{SiO}_2/\text{ZnCl}_2$ [13], cerium (IV) ammonium nitrate (CAN) [14] as the catalyst and solvent-free protocols [15] has been described. Conventionally, 2-substituted benzothiazoles are synthesized by the condensation of 2-aminothiophenol with carboxylic acid derivatives [16]. 2-Aryl benzothiazoles can be prepared by direct coupling of benzothiazoles with aryl bromides [17] or by the cycliza-

tion of the intermediate radical formed after initial oxidative coupling between thiophenols and aromatic nitriles [18]. However, most of these methods suffer from several bottlenecks such as the requirement of drastic reaction conditions (strong acids, high temperatures), prolonged reaction time, limitation of being restricted to only aromatic aldehydes, use of toxic and expensive reagents/catalyst, use of hazardous solvents, low yields, formation of by-products and tedious work-up procedure. As a consequence, search for new methods/reagents/catalysts to overcome these limitations is still an important experimental challenge to synthetic organic chemists.

Recent advances in nanotechnology have led to an increasing demand for multifunctional materials. Highly ordered mesoporous materials function as excellent catalysts owing to their high surface area and surface functionalities. Thus, synthesis of ordered mesoporous materials has attracted great deal of research interest in the last few years [19]. Of late, we successfully explored the use of mixed metal oxide nanocrystals for the decontamination of yperite [20]. In continuation of our work on new synthetic strategies [21,22], herein, we report the efficient application of mesoporous mixed metal oxide nanocrystals of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$ as heterogeneous catalysts for the synthesis of pharmacologically significant 1,2-disubstituted benzimidazoles **3a–o** and 2-substituted benzothiazoles **5a–n** (Scheme 1) by the condensation of 1,2-phenylenediamines **1** or 2-aminothiophenol **4** with aromatic and aliphatic aldehydes **2**, respectively.

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Scheme 1. Synthesis of 1,2-disubstituted benzimidazoles (3a-o) and 2-substituted benzothiazoles (5a-n) using mixed metal oxide nanocatalysts.

2. Experimental

2.1. Materials

Aluminium-sec-butoxide, vanadyl acetylacetonate, copper acetylacetonate, iron acetylacetonate, 1,2-phenylenediamines, 2-aminothiophenol, various aromatic and aliphatic aldehydes were purchased from Sigma-Aldrich, India.

2.2. Catalyst preparation

Mesoporous mixed oxide nanocrystals of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$ were prepared by aero gel process: A 1000 mL round bottom flask was charged with aluminium-sec-butoxide (10.0 g) under constant nitrogen flow. It was dissolved in 100 mL of butan-2-ol to form a clear solution. To this solution, copper acetylacetonate/iron acetylacetonate/vanadyl acetylacetonate was added and the solution was stirred for 2 h. Now a mixture of 500 mL of toluene and 150 mL of butan-2-ol was added and the contents were allowed to stir for 30 min. To this solution, 2.0 mL of ultrapure water was added and the stirring was continued for overnight period in order to obtain the soft gel. This soft gel was then transferred to a Parr autoclave which was flushed initially with nitrogen and pressurized to 100 psi under continuous shaking. The reactor was slowly heated to 300 °C and the pressure raised to 1000 psi. As soon as the autoclave has acquired 300 °C the reactor was vented to ambient pressure. The autoclave was then allowed to cool and flushed with nitrogen. Mesoporous mixed oxide alumina thus obtained was heated at 500 °C under vacuum [23].

2.3. Catalyst characterization techniques

XRD patterns were obtained in an X Pert Pro Diffractometer, Panalytical, Netherlands, using $\text{Cu K}\alpha$ radiation. The Scherer formula was used to calculate the crystallite size of the materials:

$$\text{Crystallite size} = \frac{(0.9\lambda 180)}{B \cos \theta \pi} \text{ \AA}$$

where, $B = \sqrt{(\text{FWHM}^2 - 0.3^2)}$ and λ is X-ray wave length (1.54 Å).

FWHM is full width half maxima of the peak and θ is Bragg's angle.

FWHM was calculated from the peak having highest intensity in all the samples using X Pert high score plus LTU software.

SEM-EDAX measurements were done on a FEI instrument. N_2 BET measurements were done on ASAP 2020 of Micrometrics, USA.

2.4. Catalytic activity: synthesis of 1,2-disubstituted benzimidazoles and 2-substituted benzothiazoles

Method A: To a mixture of 1,2-phenylenediamine (0.108 g, 1 mmol) and aromatic/aliphatic aldehyde (2 mmol), catalytic amount (0.0054 g, 5 wt% of 1,2-phenylenediamine) of mesoporous mixed metal oxide nanocrystals ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ or $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ or $\text{Al}_2\text{O}_3\text{-CuO}$) was added using 2 mL of acetonitrile as solvent at room temperature under stirring. The reaction progress was monitored by TLC. After stirring for 10–45 min, under heating condition at 60 °C, the reaction mixture was cooled to room temperature and it was dissolved in ethanol (10 mL) and then poured into ice-water (30 mL). Ethyl acetate (10 mL) was added and the catalyst was separated out by filtration from the extraction mixture. The organic extract was dried over anhydrous sodium sulfate and excess of solvent was removed under reduced pressure so as to obtain the product. It was then purified by column chromatography over silica gel using hexanes/EtOAc (9:1, v/v) as the eluting solvent system, yielding the pure products.

Method B: In a typical procedure, aldehydes (2 mmol), 1,2-phenylenediamines (1 mmol), and the catalyst (5 wt% of 1,2-phenylenediamine) were placed in a 10 mL glass tube under solvent-free condition. The vessel was then sealed with a septum, placed into the microwave cavity and irradiated under a constant 150 W magnetron output power (at 109 °C) for 0.75–1.5 min. After allowing the mixture to cool to room temperature, the reaction vessel was opened. It was dissolved in ethanol (10 mL) and then poured into ice-water (30 mL). The product was then purified according to that described in Method A.

An identical procedure for the synthesis of 2-substituted benzothiazoles was employed using 2-aminothiophenol (0.11 mL, 1 mmol) and aromatic/aliphatic aldehyde (1 mmol) in the presence of catalytic amount (5 wt% of 2-aminothiophenol) of mesoporous mixed metal oxide nanocrystals of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ or $\text{Al}_2\text{O}_3\text{-CuO}$ under conventional heating condition (60 °C) as well as under the influence of microwave irradiation at 150 W (at 109 °C).

3. Results and discussions

3.1. Characterization of catalysts

Synthesized nanocrystals were characterized by X-ray diffraction studies as per the patterns depicted in Fig. 1. In all the diffraction patterns of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (a), $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ (b) and $\text{Al}_2\text{O}_3\text{-CuO}$ (c), broadened peaks centered at 19.3, 37.5, 39.2, 45.6, 60.5 and 66.6 typical of (1 1 1), (3 1 1), (2 2 2), (4 0 0), (5 1 1) and (4 4 0) were observed. They can be attributed to the presence of $\gamma\text{-Al}_2\text{O}_3$ in the above materials. XRD data also represented that, these materials are of less crystalline in nature and they had a completely

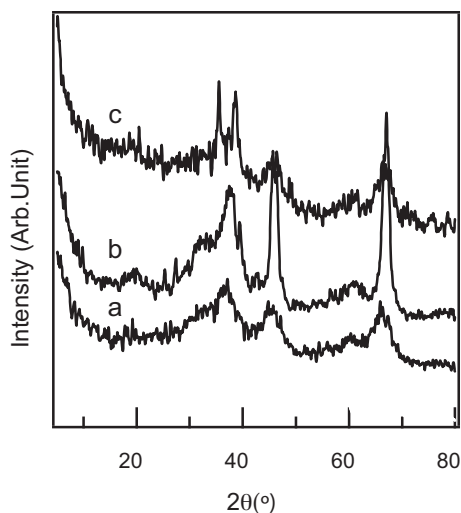


Fig. 1. XRD pattern of (a) Al₂O₃-Fe₂O₃, (b) Al₂O₃-V₂O₅ and (c) Al₂O₃-CuO.

amorphous pattern due to particle size broadening. It is clearly revealed from the literature that, with the broadening of XRD peaks along with the emergence of relatively lower crystallinities are in accordance to the lower crystallite size [24].

In order to confirm this, crystallites size of Al₂O₃-Fe₂O₃, Al₂O₃-V₂O₅ and Al₂O₃-CuO materials was determined by the Scherrer equation. The values of crystallite size diameter were found to be 4.2 nm, 6.4 nm, 3.7 nm for Al₂O₃-Fe₂O₃, Al₂O₃-V₂O₅ and Al₂O₃-CuO, respectively. Size of crystallites Fe₂O₃, V₂O₅ on alumina could not be calculated due to the amorphous nature of diffraction patterns. Materials were further characterized by scanning electron microscopy (SEM) [Fig. 2 (a–c)]. Scanning electron micrographs show the aggregates of nanocrystallites having size less than 50 nm. These aggregates appeared to be formed from particles of size smaller than 50 nm as indicated by XRD data. These nanoparticles were seemed to orient randomly in irregular fashion to minimize the steric, electric charge repulsions thereby resulting into a porous structure. It also seemed that, size of the aggregates influenced the size of the voids. Larger sized particle formed larger sized voids and smaller sized aggregates formed smaller sized voids on aggregation. SEM data indicated that the aggregates of Al₂O₃-Fe₂O₃, Al₂O₃-V₂O₅ and Al₂O₃-CuO were having the values of void diameters ranging approximately between 10 and 50 nm. These values come in the range of mesoporous materials.

In order to characterize and determine the porous structure and the value of the surface area of Al₂O₃-Fe₂O₃, Al₂O₃-V₂O₅ and Al₂O₃-CuO, N₂ BET adsorption studies were performed. A type IV isotherm with hysteresis curve was obtained by such nitrogen adsorption isotherm (Fig. 3), which represents characteristic fea-

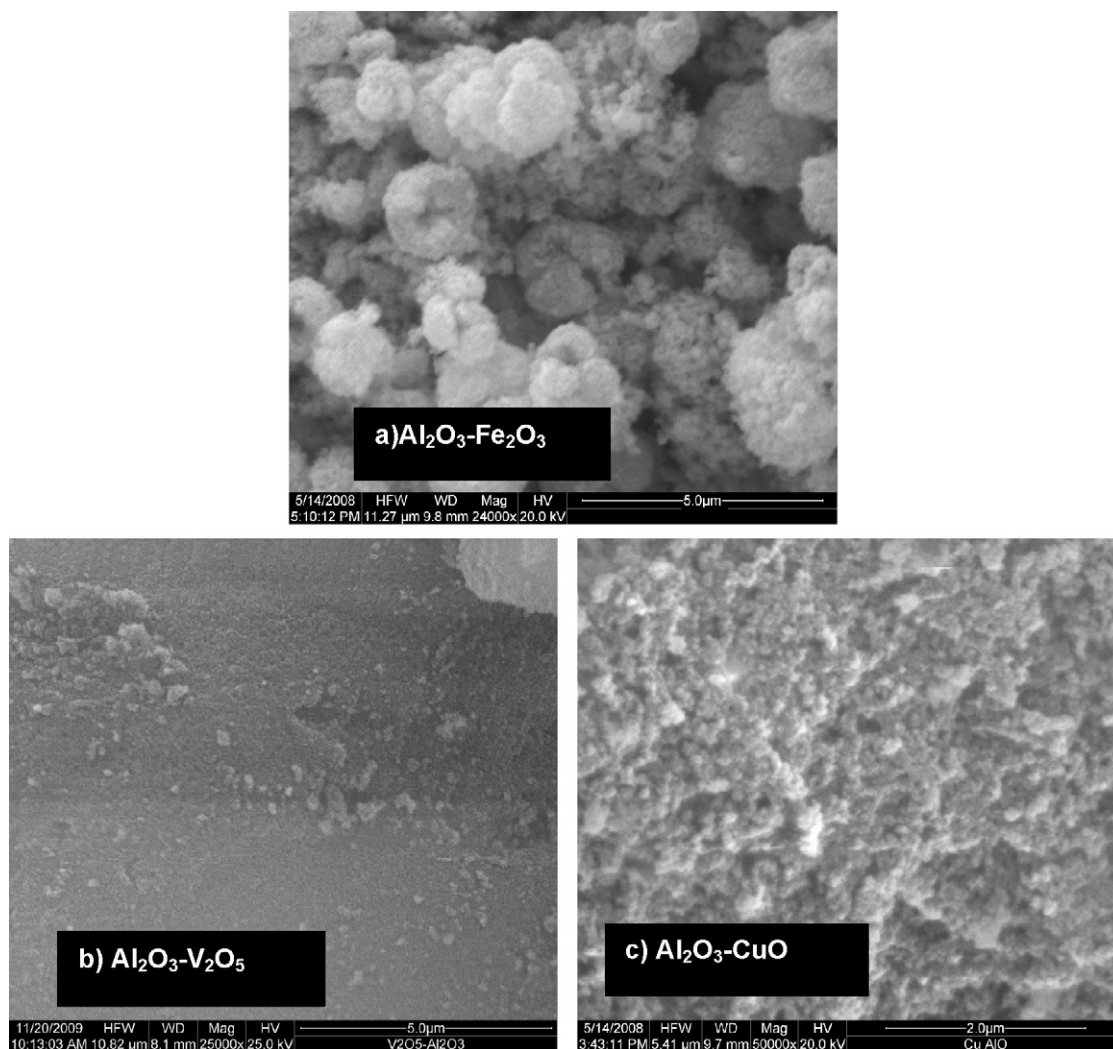


Fig. 2. SEM images of (a) Al₂O₃-Fe₂O₃, (b) Al₂O₃-V₂O₅ and (c) Al₂O₃-CuO.

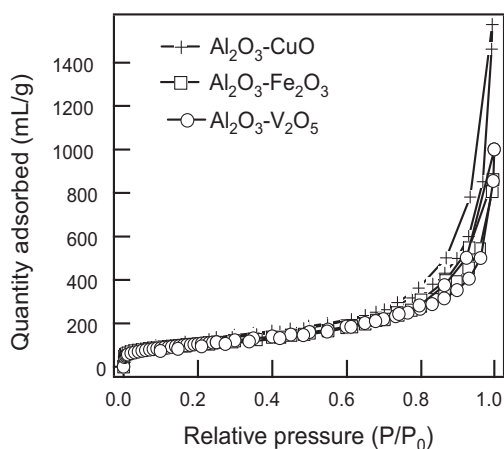


Fig. 3. Nitrogen adsorption isotherms.

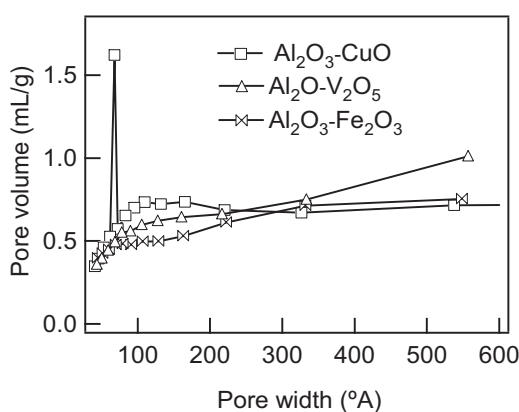


Fig. 4. Pore size distribution data of (a) $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, (b) $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and (c) $\text{Al}_2\text{O}_3\text{-CuO}$.

Table 1
BET Surface area and pore volume values for $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$.

Sl. no.	Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)
1.	$\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$	376	1.00
2.	$\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$	384	1.10
3.	$\text{Al}_2\text{O}_3\text{-CuO}$	418	1.38

ture of mesoporous materials. It is revealed from the isotherms that materials possess cylindrical pores with opening at both the ends. Furthermore, $\text{Al}_2\text{O}_3\text{-CuO}$ was found to have more number of pores than $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ or $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$.

Surface area of these materials was found to be ranging from 376 to 418 m^2/g . They exhibited meso and macroporosity with the pore volume range from 1.0 to 1.38 mL/g . The pore size distribution data is depicted in Fig. 4.

The surface area and pore volume values obtained from the above studies are presented in Table 1. Data indicate that $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ exhibited wide meso-pore size distribution with maxima centered at 7.1 nm, whereas, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$ exhibited wide pore size distribution unlike $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$. The pores as understood perhaps were formed by aggregation of nanocrystals. However, during the formation of nanocrystals of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, they nucleate, crystallize and aggregate in a manner to create pores of 7.1 nm width. In case of $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$, they possibly follow a different route of crystallization and orientation followed by aggregation due to different symmetry.

Table 2
Effect of catalyst concentration for the synthesis of 1-benzyl-2-phenyl benzimidazole (3a).

Entry	Catalyst conc. (wt%)	Reaction time ^a (min)	Yield (%) ^b
1	1	1.5	52
2	2.5	1.5	67
3	5	1.5	89
4	10	2.0	85
5	20	2.5	79

Reaction condition: The mixture of 1,2-phenylenediamine (1 mmol) and benzaldehyde (2 mmol) with different concentration of catalyst was irradiated under microwave.

^a All the reactions monitored by TLC.

^b Isolated yield.

Table 3
Recyclability of the catalyst for the synthesis of 1-benzyl-2-phenyl benzimidazoles (3a).

Entry	Cycle	Yield ^a (%)
1	Cycle 1	89
2	Cycle 2	83
3	Cycle 3	70
4	Cycle 4	62

Reaction condition: The mixture of 1,2-phenylenediamine (1mmol) and benzaldehyde (2mmol) with mixed metal oxide nanocrystals (5 wt% of 1,2-phenylenediamine) was irradiated under microwave for 1.5 min.

^a Yields after consecutive cycles.

Due to broadening of diffraction peaks it was quite uncertain to confirm the presence of Fe_2O_3 or V_2O_5 nanocrystals in the matrix of Al_2O_3 . Therefore, for this sake, samples were analyzed by energy dispersive analysis of X-rays. Data was calculated as wt% of either Al, or Fe or Cu or V or O. In $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ sample, 39.37 wt% of Al, 34.65 wt% of O, 12.32 wt% Fe were observed. In $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$, 38.21 wt% of Al, 28.12 wt% of O, 20.95 wt% V were observed. In $\text{Al}_2\text{O}_3\text{-CuO}$, 31.28 wt% of Al, 41.82 wt% of O, 5.27 wt% Cu were observed. It is inferred from these data that, either metal oxides are forming small clusters of nanocrystallites that are located on the surface of Al_2O_3 which are in close contact with each other and form an interface with more number of active sites or they form small crystallites that are mixed with Al_2O_3 in a uniform manner.

In order to investigate the optimum reaction conditions, a set of control experiments on benzaldehyde and 1,2-phenylenediamine was carried out in the presence of catalytic amount of each of $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Al}_2\text{O}_3\text{-CuO}$ systems separately under solvent-free conditions using MW irradiations. It was observed that, all the three catalytic systems efficiently accelerated the reaction towards the formation of desired product, although $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$ were found to be little superior over $\text{Al}_2\text{O}_3\text{-CuO}$ owing to their enhanced surface properties. The optimum weight percentage of the catalyst was also studied (1, 2.5, 5, 10, 20 wt% of 1,2-phenylenediamine) and it was revealed that 5 wt% of the catalyst was the optimum weight percentage. The results are presented in Table 2.

3.2. Reusability of the catalyst

At the end of the reaction, the catalyst was filtered off, washed with mixture of hot ethanol and water, dried at 100 °C for 3 h, and reused as such for subsequent experiments (up to four cycles) under similar reaction conditions. It was noticed that yields of the product remained comparable in these experiments (Table 3), and thereby pointing the recyclability and reusability of the catalyst without any significant loss in catalytic activity.

When the reaction was carried out with 1,2-phenylenediamine and aldehyde in 1:1 molar ratio under microwave, then a mixture of mono and di-substituted product were formed. But when 1:2 molar ratio was used then the desired 1,2-disubstituted benzimi-

Table 4
Synthesis of 1,2-disubstituted benzimidazoles (3a–o) using mixed metal oxide nanocatalysts.

Entry	R	Product	Time ^a (min)		Yield ^b (%)	
			Method A	Method B	Method A	Method B
1	C ₆ H ₅	3a	12	1.0	84	89
2	4-MeC ₆ H ₄	3b	27	1.5	85	88
3	4-MeOC ₆ H ₄	3c	34	1.5	87	90
4	4-(Me) ₂ NC ₆ H ₄	3d	45	1.0	83	89
5	4-(Me) ₃ CC ₆ H ₄	3e	22	1.0	81	88
6	3-EtO-4-HOC ₆ H ₃	3f	35	1.25	89	92
7	4-FC ₆ H ₄	3g	21	0.75	88	93
8	5-Br-2-HOC ₆ H ₃	3h	27	1.5	85	89
9	3-NO ₂ C ₆ H ₄	3i	10	1.5	87	91
10	4-F ₃ COC ₆ H ₄	3j	25	0.75	84	89
11	3,4-Cl ₂ C ₆ H ₃	3k	14	1.0	85	88
12	Furyl	3l	12	1.0	90	93
13	C ₆ H ₅ CH=CH	3m	37	0.75	84	94
14	CH ₃ -CH ₂ -CH ₂	3n	20	1.0	78	89
15	CH ₃ -(CH ₂) ₄ -CH ₂	3o	24	1.0	82	88

Reaction condition: 1,2-phenylenediamine (1 mmol), benzaldehyde (2 mmol), mixed metal oxide nanocrystals (5 wt% of 1,2-phenylenediamine), CH₃CN (2 mL) (for method A).

^a All the reactions monitored by TLC.

^b Isolated yield.

Table 5
Synthesis of 2-substituted benzothiazoles (5a–n) using mixed metal oxide nanocatalysts.

Entry	R'	Product	Time ^a (min)		Yield ^b (%)	
			Method A	Method B	Method A	Method B
1	C ₆ H ₅	5a	13	1.0	87	89
2	2-EtC ₆ H ₄	5b	22	1.0	85	92
3	4-HOC ₆ H ₄	5c	16	1.0	84	95
4	3,4,5-(MeO) ₃ C ₆ H ₂	5d	33	1.5	83	90
5	4-EtOC ₆ H ₄	5e	15	1.0	85	94
6	4-EtO-3-MeOC ₆ H ₃	5f	24	1.5	83	93
7	4-(Me) ₂ HCC ₆ H ₄	5g	17	1.0	87	96
8	4-BrC ₆ H ₄	5h	10	1.0	87	93
9	4-ClC ₆ H ₄	5i	11	1.0	89	92
10	5-Br-2-MeOC ₆ H ₃	5j	28	1.5	89	91
11	4-NO ₂ C ₆ H ₄	5k	23	1.5	88	94
12	2-F ₃ CC ₆ H ₄	5l	13	1.0	86	89
13	CH ₃ -CH ₂ -CH ₂	5m	10	1.0	79	89
14	CH ₃ -(CH ₂) ₄ -CH ₂	5n	15	1.0	80	89

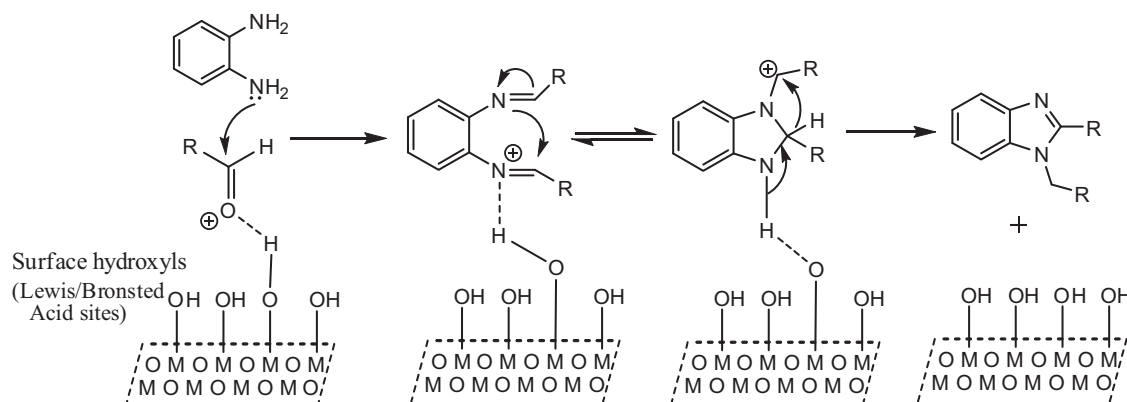
Reaction condition: 2-aminothiophenol (1 mmol), benzaldehyde (1 mmol), mixed metal oxide nanocrystals (5 wt% of 2-aminothiophenol), CH₃CN (2 mL).

^a All the reactions monitored by TLC.

^b Isolated yield.

dazole was formed with excellent selectivity and yields. However, trace amount of monosubstituted product was also formed in some cases, which was separated by column chromatography. Moreover, by applying microwave dielectric heating, the reaction time was significantly reduced with the increase in the product yield as compared to conventional heating.

It is evident from the data in Tables 4 and 5 that, the proposed synthetic procedure works well with mono, di (Table 4, entries 6, 8 and 11 and Table 5, entries 6 and 10) and even tri-substituted (Table 5, entry 4) aryl aldehydes. The effect of substitution present on aromatic aldehyde on the reaction rate and the overall yield was also studied. As shown, a variety of benzaldehydes bearing

**Fig. 5.** Proposed mechanism for the synthesis of 1,2-disubstituted benzimidazoles.

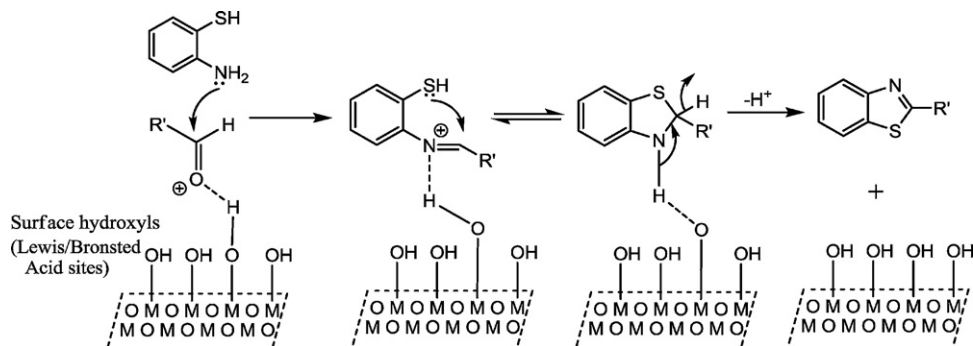


Fig. 6. Mechanistic pathway for the preparation of 2-substituted benzothiazoles.

electron-donating (Table 4, entries 2–7 and Table 5, entries 2–9) and electron-withdrawing substituents (Table 4, entries 8–11 and Table 5, entries 10–12) were successfully employed to prepare the corresponding benzimidazoles 3a–o and benzothiazoles 5a–n derivatives in excellent yields. Furfural (Table 4, entry 12) and cinnamyl aldehyde (Table 4, entry 13) also afforded the desired products in excellent yields. Moreover, this synthetic strategy was further extended to aliphatic aldehydes, viz., butyraldehyde, heptanal to obtain the desired 1,2-disubstituted benzimidazoles (Table 4, entries 14 and 15) and 2-substituted benzothiazoles (Table 5, entries 13 and 14) in reasonably good yield.

In order to demonstrate the synthetic potential of this protocol the same procedure was extended for one-pot synthesis of benzothiazole class of compounds. An overview of synthetic highlights delineating the synthesis of 2-substituted benzothiazoles is depicted in Table 5.

The proposed mechanistic path for the formation of 1,2-disubstituted benzimidazoles is presented in (Fig. 5).

The possible mechanistic path for the synthesis of 2-substituted benzothiazole is given in Fig. 6. The used metal oxides species contains Lewis acid sites and Bronsted acid sites in addition to basic surface sites. These acidic sites react with carbonyl oxygen of aldehyde by forming surface bound hydrogen bonded species. Surface of nanocrystalline Al_2O_3 was found to be basic in nature. Further addition of transition metal oxides would increase the number of Lewis acid sites, Bronsted acid sites and basic sites thereby increasing the reactivity of metal oxides as catalyst.

4. Conclusion

In conclusion, a simple, efficient and environmentally benign method has been developed for the synthesis of 1,2-disubstituted benzimidazoles and 2-substituted benzothiazoles by using mesoporous mixed metal oxide nanocrystals having high surface area and high catalytic activity. This one-pot, mixed metal oxide catalyzed synthetic method is an unprecedented, inexpensive and rapid alternative for the generation of structurally diversified benzimidazole and benzothiazole derivatives. The catalytic system along with microwave dielectric heating was instrumental in reducing the reaction times and increasing yields. The environmental compatibility and excellent reusability of the catalyst and ease of isolation of product are among the other added advantages that make this approach an attractive alternative for the synthesis of these heterocycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.03.027.

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