

Synthesis, Characterization and Catalytic Application of MoO₃/CeO₂-ZrO₂ Solid Heterogeneous Catalyst for the Synthesis of Benzimidazole Derivatives

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A series of MoO₃/CeO₂-ZrO₂ catalysts with different Mo content (8 - 20 wt %) were prepared by simple co-precipitation followed by impregnation method and were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), energy dispersive spectroscopic (EDS) techniques. The prepared materials were tested for catalytic activity by the synthesis of benzimidazole derivatives using condensation of aromatic aldehydes and o-phenylenediamine by conventional and microwave method. Obtained results reveal that the catalytic activity increases with increase in Mo wt % loading. The best catalytic activity was obtained with 20 wt % MoO₃/CeO₂-ZrO₂. The particle size or crystallite size was estimated using Debye-Scherrer equation. After completion of reaction, the catalyst can be recovered efficiently and reused with consistent activity.

Key Words: MoO₃/CeO₂-ZrO₂, XRD, FT-IR, SEM-EDS techniques, Benzimidazoles

Introduction

Nowadays, the development of environmentally benign protocol has been gaining the importance of chemical processes. Generally, organic reactions are carried out using inorganic acids such as H₂SO₄, HCl, and HNO₃ and in another hand the use of Lewis acid like HF and BF₃.^{1,2} Despite its high selectivity, these homogeneous classical acid catalysts offer several disadvantages for example high toxicity, corrosive nature, generating maximum waste, difficulty in recovery and reusability. In view of enviro-economical aspects, it is necessary to replace these toxic acid catalysts by newer solid heterogeneous catalysts as an excellent alternative source over these conventional acid catalysts, as they can be inexpensive, non-toxic, non-corrosive, easy to recover and reuse. Accordingly, various solid acid catalysts, such as heteropolyacids, ion exchange resins, zeolites and clays were investigated.³⁻⁵ However, the main disadvantage associated with the heteropolyacids and ion exchange resins like poor thermal stability and losses their activities at high temperature.

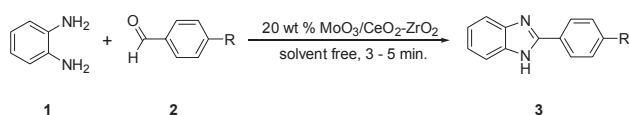
Metal oxide-based catalysts are active over a wide range of temperatures and more resistant to thermal excursions. Recently, zirconia and sulphated zirconia catalysts have gained much attention on the various organic transformations due to their super acidity, non-toxicity and high activity at low temperatures.⁶⁻¹¹ Many efforts have been made in order to improve the catalytic performance of sulfated zirconia catalysts including mixed oxides of zirconia with other transition and non-transition metals and sulfating them. Some mixed oxides exhibit strong surface acidity (Bronsted or Lewis) due to the generation of excess negative or positive charge in the model structure of the binary oxides. For example, the SiO₂-ZrO₂ and Al₂O₃-ZrO₂ combination leads to very strong acidic properties.^{12,13}

Literature survey reveals that, MoO₃ supported on ZrO₂ also

exhibits strong solid acidity and excellent catalytic properties for various organic transformations in the liquid phase.¹⁴⁻¹⁷ Among the zirconia based mixed oxides, the CeO₂-ZrO₂ combination has emerged as a fascinating catalytic material and attracted much attention due to their superior oxygen storage/release and redox properties.¹⁸ The incorporation of zirconium cation into the ceria unit cell or vice-versa modifies the surface acid-base sites, Ce⁴⁺ and Zr⁴⁺ ion acts as Lewis acid sites and O²⁻ ions as Bronsted or Lewis base sites. In this direction we have planned to study the effect of different molybdenum 8 - 20 wt % loading on CeO₂-ZrO₂ and their catalytic application for the synthesis of benzimidazole derivatives.

Benzimidazoles are very useful intermediates for the synthesis of compounds of pharmaceutical or biological interest. Benzimidazole derivatives exhibit significant activity against several viruses such as HIV,¹⁹ herpes (HSV-1),²⁰ RNA,²¹ influenza²² and human cytomegalovirus (HCMV).¹⁹ Realizing the importance of these compounds, numerous methods have been reported in the literature for the synthesis of benzimidazoles including various oxidants and catalysts such as, sulphamic acid,²³ molecular iodine,²⁴ DDQ,²⁵ atmospheric air,²⁶ Oxone,²⁷ FeCl₃·6H₂O,²⁸ In(OTf)₃,²⁹ Yb(OTf)₃,³⁰ Sc(OTf)₃,³¹ KHSO₄,³² Zirconyl chloride,³³ P-TsOH,³⁴ sodium hydrogen sulphate,³⁵ Cobalt(II) chloride,³⁶ etc. All the reported methods have their own merits for the synthesis of benzimidazoles. Despite their high efficiency for the synthesis of benzimidazoles, some of the methods are plagued by one of the drawbacks such as, high reaction temperature, prolonged reaction times, toxic solvent and inexpensive catalyst etc. Therefore, development of mild and efficient synthetic route for the synthesis of benzimidazoles continues to attract researchers attentions.

In continuation of our efforts, in the synthesis, characterization and catalytic application of mixed metal oxide as a solid heterogeneous catalyst for fine chemical synthesis.^{37,38} In this



Scheme 1

paper, we wish to report, the synthesis, characterization and catalytic application of $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ solid heterogeneous catalyst for the synthesis of benzimidazole derivatives using conventional and microwave methods (Scheme 1). The noticeable advantage of the present work is to introduce simple and eco-friendly procedure for the preparation of benzimidazoles.

Experimental Section

Catalyst preparation. The $\text{CeO}_2\text{-ZrO}_2$ (1:1) binary oxides were prepared by a homogeneous co-precipitation method. An aqueous solution containing the requisite quantities of zirconium oxychloride and ammonium ceric nitrate were prepared separately by using deionized water and mixed together with constant stirring followed by the addition of 20 mL 5% polyethylene glycol (PEG-400) as structure directing agent. This solution was hydrolyzed with 1:1 aqueous ammonia with constant stirring until the pH of solution reached to 9. A yellowish precipitate was formed and the precipitate was allowed to settle down in an electric oven at 60°C for 24 h. The resulting precipitate was filtered and washed with deionized water to remove the chloride and dried at 120°C for 12 h.

The $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ materials, containing 8 - 20 wt % MoO_3 were prepared by impregnation method. To incorporate the molybdenum oxide, the requisite quantities of ammonium heptamolybdate were dissolved in excess deionized water and the finely powdered oven-dried hydrous ceria-zirconia support was added to this solution, each mixture was stirred at 80°C for 6 h. The excess water was air-dried completely and the resulting sample was dried at 120°C for 12 h. Finally the dried powders were calcined at 500°C for 5 h in air atmosphere.

Catalyst characterization. The synthesized catalysts were characterized by using XRD, FT-IR, SEM and EDS techniques. The X-ray powder diffraction patterns of catalyst were recorded on Bruker 8D advance X-ray diffractometer using $\text{Cu K}\alpha$ radiation of wavelength at 0.154 nm. The FT-IR spectrums were recorded on JASCO-FTIR/4100 Japan, using dry KBr as standard reference in the range of $4000 - 400\text{ cm}^{-1}$. The SEM analyses were carried out with JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA. The presence and elemental composition of metal were characterized using energy dispersive spectroscopy (EDS).

General procedure for the synthesis of benzimidazoles (Microwave irradiation). In a typical general experimental procedure, a mixture of *o*-phenylenediamine (2 mmol), aromatic aldehyde (2 mmol) and catalyst (0.2 g, 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$) were taken in 100 mL beaker and well mixed with the help of glass rod and irradiated under microwave in domestic microwave oven (450 wt) for 3 - 5 minutes. The reaction mixture after being cooled was extracted with ether. The ether extract

was evaporated to leave the crude solid. The pure product and the catalyst were obtained by recrystallization of the crude solid from ethanol.

General procedure for the synthesis of benzimidazoles (Conventional method). In a typical general experimental procedure, *o*-phenylenediamine (2 mmol), aromatic aldehyde (2 mmol) and catalyst (0.2 g, 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$) were taken in 100 mL round bottom flask in ethanol medium and refluxed in ethanol for 1 - 2.5 h. The progress of reaction was monitored by TLC using ethyl acetate and *n*-hexane (7:3) as eluent. After completion of the reaction, reaction mixture was cooled at room temperature and then was poured into an ice-cold water, resulting in precipitates. The obtained solid was filtered, dried and recrystallized from ethanol to offer a pure product.

Spectral data of representative compounds: 3f: IR (KBr): 1622 (C=N) , $3446\text{ (NH)}\text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 2.38 (s, 3H), 7.18 (d, $J = 7.2\text{ Hz}$, 2H), 7.34-7.37 (m, 2H), 7.47-7.51 (m, 1H), 7.60-7.63 (m, 1H), 8.06 (d, $J = 8.0\text{ Hz}$, 2H), 12.80 (bs, 1H). **3j:** IR (KBr): 1612 (C=N) , 3360 (NH) , $3570\text{ (OH)}\text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 6.90 (d, $J = 8.4\text{ Hz}$, 2H), 7.12-7.16 (m, 2H), 7.46 (d, $J = 6.8\text{ Hz}$, 1H), 7.53 (d, $J = 7.6\text{ Hz}$, 1H), 7.99 (d, $J = 8.8\text{ Hz}$, 2H), 9.94 (bs, 1H), 12.63 (bs, 1H).

Results and Discussion

XRD analysis. The powder X-ray diffraction pattern of (a) pure $\text{CeO}_2\text{-ZrO}_2$ and (b-f) 8 - 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ catalysts calcined at 500°C in the presence of air for 5 h are shown in Fig. 1. The unsupported $\text{CeO}_2\text{-ZrO}_2$ sample exhibits broad diffraction patterns due to the poor crystallinity. As can be noted from Fig. 1 (a), the diffraction patterns of unsupported $\text{CeO}_2\text{-ZrO}_2$ and $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ samples differ very much indicating a strong influence of the impregnated molybdenum oxide on

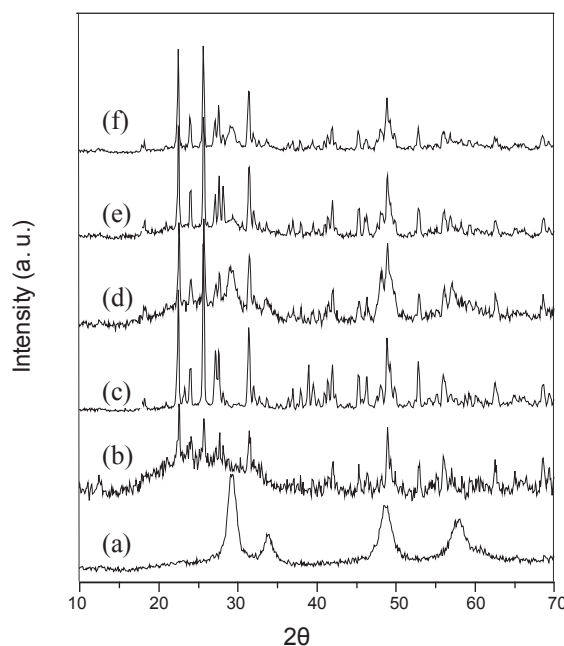


Figure 1. XRD patterns of series of (a) pure $\text{CeO}_2\text{-ZrO}_2$, (b) 8%, (c) 10%, (d) 12%, (e) 15%, (f) 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ calcined at 500°C .

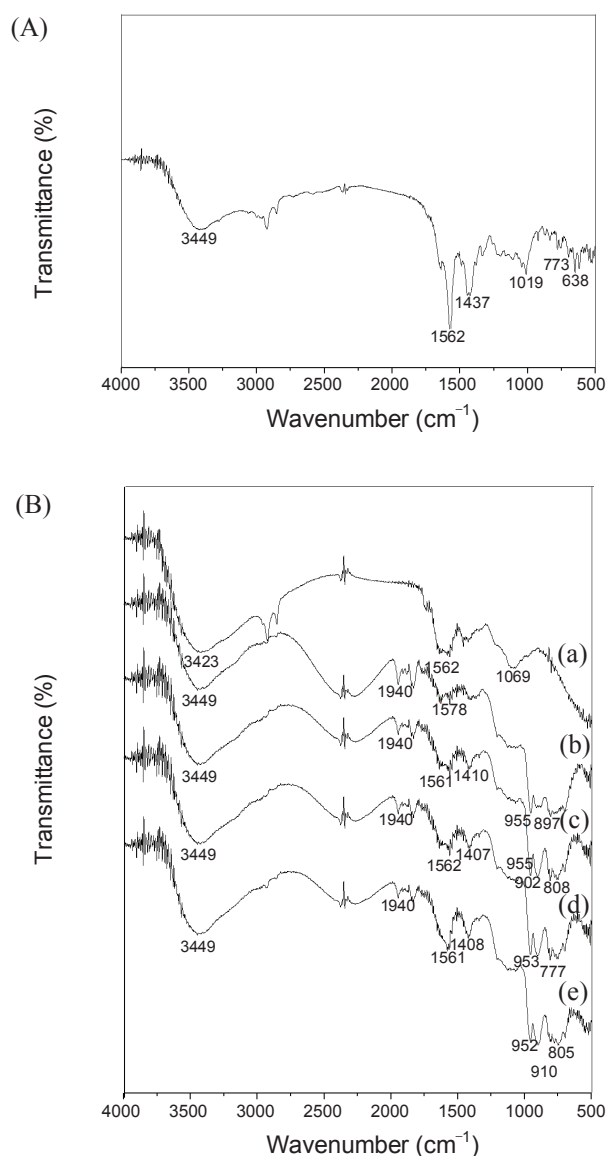


Figure 2. FT-IR spectrum of (A) pure $\text{CeO}_2\text{-ZrO}_2$, (B) (a) 8%, (b) 10%, (c) 12%, (d) 15%, (e) 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ calcined at 500 °C.

the surface of $\text{CeO}_2\text{-ZrO}_2$. Close inspection of XRD patterns pertaining to the unsupported $\text{CeO}_2\text{-ZrO}_2$ samples, an interesting observation to be noted is that the pure $\text{CeO}_2\text{-ZrO}_2$ sample exhibits diffraction patterns due to the formation of cubic solid solution, the highly intense and sharp peaks were obtained at $2\theta = 28.90^\circ, 33.56^\circ, 48.23^\circ, 57.23^\circ$ and 78.00° corresponding to the planes (111), (200), (220), (311), and (331) indicates the cubic structure of $\text{CeO}_2\text{-ZrO}_2$ [JCPDS card no. 280271]. While the orthorhombic phase could be identified in the case of 8 - 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$, the XRD patterns are displayed in Fig.1 (b-f). In each case highly intense and sharp peaks were obtained at $2\theta = 22.51^\circ, 25.70^\circ, 29.17^\circ, 41.86^\circ, 45.32^\circ, 48.93^\circ, 52.87^\circ, 57.12^\circ, 62.65^\circ, 68.63^\circ$ corresponding to the planes (501), (411), (800), (720), (422), (1102), (123), (014), (804), (040) respectively. It has been seen that X-ray powder diffraction patterns of MoO_3 promoted $\text{CeO}_2\text{-ZrO}_2$ samples are crystalline

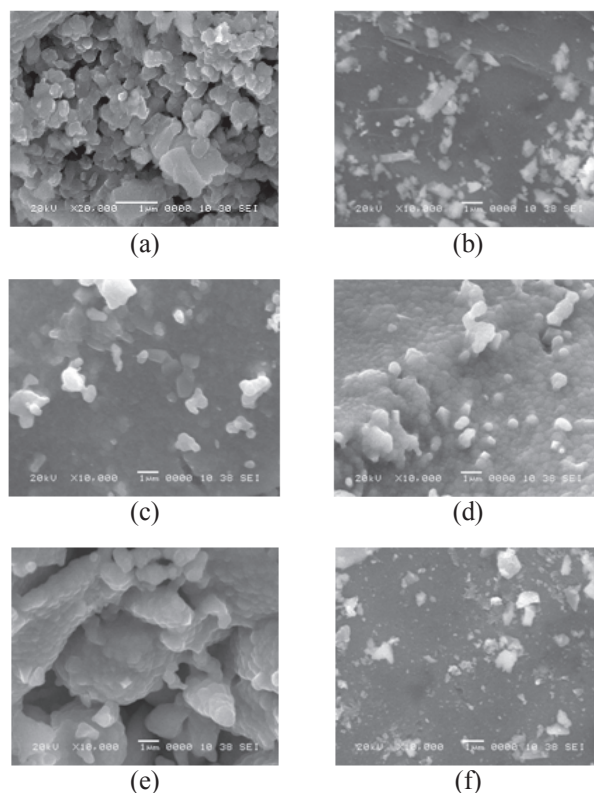


Figure 3. SEM micrograph of (a) pure $\text{CeO}_2\text{-ZrO}_2$, (b) 8%, (c) 10%, (d) 12%, (e) 15%, (f) 20 wt % $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ calcined at 500 °C.

in nature, indicating a strong interaction between the MoO_3 and $\text{CeO}_2\text{-ZrO}_2$ support.

FT-IR analysis. The IR spectra of pure $\text{CeO}_2\text{-ZrO}_2$ (A) and (8 - 20 wt %) $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ (B) are shown in Fig. 2. In the IR spectra, it was observed that in each sample (a-e) the peak in the range of 3200 - 3500 cm^{-1} appeared due to the hydroxyl group adsorbed on the surface of each catalyst and which helps to generate the Bronsted acidic sites. Similarly in all the cases the peaks in the range of 1500 - 1600 and 1410 - 1446 cm^{-1} due to the deformation of surface hydroxyl group.³⁹ As can be noted from the spectrum of each sample, the peak in the range of 1010 - 1079 cm^{-1} is assigned for the M-O-M bonding (M = Mo, Ce, Zr). The bands in the range of 500 - 991 cm^{-1} were assigned to the Mo = O, Mo-O-Mo stretching modes of vibration for crystalline MoO_3 .⁴⁰ The appearance of these bands indicates that the MoO_3 is strongly dispersed on the surface of $\text{CeO}_2\text{-ZrO}_2$ catalyst.

SEM analysis. In order to understand the surface morphology and to assess the surface dispersion of MoO_3 supported on $\text{CeO}_2\text{-ZrO}_2$, the systematic study on SEM analysis were undertaken. Typical SEM images are presented in Fig. 3. Fig. 3(a) shows the SEM image of pure $\text{CeO}_2\text{-ZrO}_2$ sample. It is clear that, particles are homogeneously aggregated and which was in irregular in shape. Also some porosity is generated, and that may be due to the addition of 5% PEG as a structure directing agent. Fig. 3 (b-f) shows SEM image of 8 - 20 wt % impregnated MoO_3 , it was observed that MoO_3 is strongly interacted and highly dispersed on the surface of the $\text{CeO}_2\text{-ZrO}_2$ catalyst.

EDS analysis. The presence and elemental compositions of the 20 wt % MoO₃ impregnated CeO₂-ZrO₂ catalyst was analyzed by the EDS techniques. The typical EDS spectrum are shown in Fig. 4 represents the elemental distribution of Mo, Ce, Zr, O as (0.53 at %), (29.18 at %), (12.67 at %), and (57.62 at %) respectively.

Crystallite size calculation. Generally, the particle size of solid materials can be estimated from X-ray line broadening and full width half maximum (FWHM) values using Debye-Scherrer equation,

$$T = 0.94 \lambda / \beta \cos \theta.$$

Where, T = Particle size, λ = wavelength, θ = diffraction an-

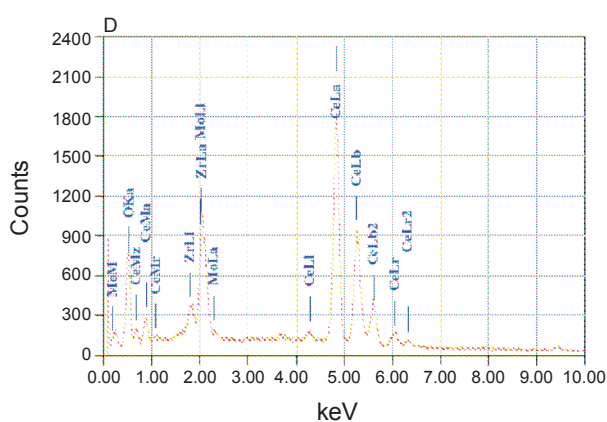


Figure 4. EDS Spectrum of 20 wt % MoO₃/CeO₂-ZrO₂ calcined at 500 °C.

Table 1. Particle size estimation of series of (8 - 20 wt %) MoO₃ impregnated CeO₂-ZrO₂

Entry	Mo wt % loading	Particle size (T) (nm)
1	0% CeO ₂ -ZrO ₂	7.11
2	8% MoO ₃ /CeO ₂ -ZrO ₂	23.98
3	10% MoO ₃ /CeO ₂ -ZrO ₂	33.56
4	12% MoO ₃ /CeO ₂ -ZrO ₂	38.58
5	15% MoO ₃ /CeO ₂ -ZrO ₂	42.09
6	20% MoO ₃ /CeO ₂ -ZrO ₂	33.17

Table 2. Synthesis of benzimidazole using 4-Chlorobenzaldehyde and *o*-phenylenediamine catalyzed by 8 - 20 wt % MoO₃/CeO₂-ZrO₂ by conventional and microwave method

Entry	Mo wt % loading	Microwave method at 450 Wt.		Conventional (reflux, at 78 °C)	
		Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)
1	0% CeO ₂ -ZrO ₂	30	40	240	55
2	8% MoO ₃ /CeO ₂ -ZrO ₂	30	50	120	60
3	10% MoO ₃ /CeO ₂ -ZrO ₂	20	60	120	55
4	12% MoO ₃ /CeO ₂ -ZrO ₂	13	63	110	65
5	15% MoO ₃ /CeO ₂ -ZrO ₂	15	65	100	65
6	20% MoO ₃ /CeO ₂ -ZrO ₂	5	94	90	86

Reaction conditions: 4-chlorobenzaldehyde (2 mmol), *o*-phenylenediamine (2 mmol) and 0.2 g catalyst in microwave at 450 wt and 10 mL ethanol (conventional, reflux). ^aIsolated Yield.

gles, λ = FWHM (full width half maximum). The particle sizes of prepared catalysts with different wt % MoO₃/CeO₂-ZrO₂ are shown in Table 1, which indicates that the particle size and crystallinity (from XRD) increases with increase in Mo wt % loading on CeO₂-ZrO₂.

Catalytic activity results. After understanding the suitability and formation of synthesized MoO₃/CeO₂-ZrO₂ catalytic material, their catalytic activity studies were undertaken. To get the best reaction condition and to find the suitable catalyst among 8 - 20 wt % MoO₃/CeO₂-ZrO₂ for the synthesis of benzimidazole, we have selected 4-chlorobenzaldehyde and *o*-phenylenediamine as a model reaction under solvent-free and reflux in ethanol by microwave and conventional methods respectively, with respect to the time and yield of products. The results obtained were summarized in Table 2. The catalytic activity result reveals that, the pure CeO₂-ZrO₂ (1:1) catalytic material exhibited negligible activity for the synthesis of benzimidazole in terms of reaction time and product yields (Table 2) by both conventional and microwave methods. But, interestingly it was observed that the catalytic activity increases with increase in Mo wt % loading resulting reduction in time and excellent yields. Among all the different Mo wt % loading, the 20 wt % MoO₃/CeO₂-ZrO₂ catalyst exhibits very good catalytic activity in the synthesis of benzimidazole derivatives (Table 2), that might be due to acidic nature of MoO₃.⁴¹ Comparatively we observed that, the conventional method consumes more energy and time providing poor yields, while microwave method consumes less energy and time providing high to excellent yields for the synthesis of benzimidazoles.

In the last few years, microwave induced organic reactions has gained popularity as a non conventional techniques for the rapid organic synthesis.⁴² It can be termed as 'e-chemistry' because it is easy, effective, economical and eco-friendly. And it is believed to be a step towards achieving green chemistry objectives in microwave. The reactions proceeds very cleanly and no undesirable side reactions were observed. To explore the generality and scope of the present method, we prepared the different derivatives of benzimidazole by reacting different substituted aromatic aldehydes and *o*-phenylenediamine which have electron donating or electron withdrawing groups under solvent free conditions in microwave. As expected in all cases benzimidazoles were obtained in good yields (Table 3).

Furthermore, in order to test the catalytic activity of the ca-

Table 3. Synthesis of benzimidazole derivatives catalyzed by 20 wt % MoO₃/CeO₂-ZrO₂ solid catalyst at 450 WT in microwave

Entry	Aldehydes	Yield ^a (%)	Time (min)	mp (°C)	
				Observed	Literature
3a	C ₆ H ₅	94	3	292	291 ³³
3b	4-Cl C ₆ H ₄	94(94,94,93) ^b	5	294	294 ³³
3c	2-Cl C ₆ H ₄	92	5	231	230 ³⁴
3d	4-NO ₂ C ₆ H ₄	94	3	310	308 ³⁴
3e	3-NO ₂ C ₆ H ₄	92	5	200	200 ³⁴
3f	4-CH ₃ C ₆ H ₄	94	3	263	261 ³⁴
3g	4-CH ₃ O C ₆ H ₄	94	3	230	228 ³⁴
3h	2-furyl	92	5	285	284 ³⁴
3i	2-OHC ₆ H ₄	92	3	236	236 ³⁵
3j	4-OHC ₆ H ₄	94	3	256	256 ³⁶

Reaction conditions: 4-chlorobenzaldehyde (2 mmol), *o*-phenylenediamine (2 mmol) and 0.2 g catalyst in microwave at 450 wt. ^aIsolated Yield. ^bAfter consecutive run.

talyst we carried out the synthesis of **3b**, (Table 3) in the absence of catalyst under solvent-free condition in microwave, no desired product was obtained within a 3 - 5 min. it means that, catalyst plays the crucial role in this transformations. Finally, we have examined the reusability of the catalyst as it is important from industrial point of view. The reusability of the catalyst was examined using the reaction of 4-chlorobenzaldehyde and *o*-phenylenediamine (Table 3, entry **3b**). Catalyst was recovered by filtration and washed it with n-hexane, dried and activated at 120 °C for 1h before catalytic run. The catalyst was successfully recycled at least three times without significant loss of activity in terms of time and yield of product.

Conclusions

In summary: (1) The present paper describes a new, efficient and eco-friendly route for the synthesis of benzimidazoles. (2) The 20 wt % MoO₃/CeO₂-ZrO₂ catalyst exhibits excellent catalytic activity for the condensation of various aromatic aldehydes and *o*-phenylenediamine. Most importantly this catalyst facilitates the reaction under solvent-free conditions providing solid supports in the reaction, enhances the reaction rate and thereby the excellent yields of the products. (3) We have also compared the time required and product yields for synthesis of benzimidazole by conventional and microwave method. Obtained results reveals that the microwave method require little time providing excellent yield of products. Therefore, we concluded that the microwave method is the best method for the synthesis of benzimidazole derivatives. (4) The catalyst can be prepared with easily available and from inexpensive reagents. They are reusable and non-hazardous. A simple procedure combined with low toxicity and reusability of the catalysts, provides an economic and waste-free chemical method for the synthesis of benzimidazoles.

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