



ORIGINAL ARTICLE

Preparation, characterization and catalytic activity of $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ solid heterogeneous catalyst for the synthesis of β -enaminones



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KEYWORDS

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 β -Enaminone

Abstract A series of $\text{CeO}_2\text{-ZrO}_2$ with different molybdenum (8–20 wt% MoO_3) loaded materials were prepared by homogeneous co-precipitation followed by impregnation method. The prepared materials were tested for their catalytic activity performance in the synthesis of β -enaminones by condensation of various anilines with dimedone under solvent-free conditions in microwave providing excellent yields within short reaction time. An obtained result reveals that, catalytic activity increases with increase in Mo wt% loading. The particle size of prepared materials was estimated using *Debye-Scherrer* equation. Particle size increases with increase in Mo wt% loading providing nanosized particle ranging from 7.11 to 42.09 nm. The synthesized materials were characterized by means of X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques.

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1. 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, H_2SO_4 , HCl, HNO_3 and in another hand the use of lewis acid like HF and BF_3 (Thomas, 1992; Misono and Okuhara, 1993). Despite its high selectivity, these homogeneous classical acid catalysts offer several disadvantages, such as high toxicity, corrosive nature, generate maximum waste, and are difficult to recover and reuse. In view of enviro-economical aspects, it is necessary to replace these toxic acid catalysts by newer solid heterogeneous catalyst as an excellent alternative source over these conventional acid catalysts, as they can be inexpensive, non-toxic, noncorrosive and simple to recover and reuse. Accordingly, various solid acid catalysts, such as heteropolyacids, ion exchange resins, zeolites and clays were investigated (Olah et al., 1978; Guttman and Grasselli, 1983; Dupont et al., 1995) However, the main disadvantage associated with the heteropolyacids and ion exchange resins

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is that they exhibit poor thermal stability and lose their activities at high temperature.

Metal oxide-based catalysts are active over a wide range of temperatures and show good heat resistant properties.

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 (Arata, 1990; Corma, 1995; Reddy et al., 2006; Yadav and Nair, 1999; Reddy and Sreekanth, 2003). 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 oxide exhibits 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 $\text{SiO}_2\text{-ZrO}_2$ (Rosenberg et al., 2002) and $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (Reddy et al., 2005a) combination leads to very strong acidic properties.

Literature survey shows that, MoO_3 supported on ZrO_2 also exhibits strong solid acidity and excellent catalytic properties for various organic transformations in the liquid phase (Manohar et al., 1998; Reddy and Reddy, 1999, 2000). Among the zirconia based mixed oxides, the $\text{CeO}_2\text{-ZrO}_2$ combination has emerged as a fascinating catalytic material and attracted much attention due to their superior oxygen storage/release and redox properties (Reddy et al., 2005b). The incorporation of zirconium cation into the ceria unit cell or vice versa modifies the surface acid–base sites, Ce^{4+} and Zr^{4+} ion act as Lewis acid sites and O^{2-} 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 $\text{CeO}_2\text{-ZrO}_2$ and investigated their catalytic application for the synthesis of β -enaminones.

Enaminones are novel group of compounds having significant biological as well as pharmaceutical applications (Foster et al., 1999; Michael et al., 2001; Dannhardt et al., 1998; Appelbaum et al., 2000; Edafiogho et al., 2006; Eddington et al., 2000). The classical methods for the synthesis of β -enaminones are the azeotropic removal of water by refluxing an amine with 1,3-diketone in an aromatic hydrocarbon solvent (Baraldi et al., 1983). For the synthesis of β -enaminones other improved procedure have been reported in the literature using various homogeneous and heterogeneous catalysts, such as CAN (Paira et al., 2008), heteropolyacids (Rafiee et al., 2008), $\text{BF}_3\text{-Et}_2\text{O}$ (Azzaro et al., 1981), ytterbium triflate (Dal et al., 2006), zirconium chloride (Lin and Zhang, 2007), alumina, montmorillonite (Texier and Kelin, 1986), $\text{P}_2\text{O}_5/\text{SiO}_2$ (Mohammadzadeh et al., 2009) and direct condensation of amines with diketones in water (Stefani et al., 2000). However, some of these methods are plugged by one of the drawbacks, such as drastic reaction conditions, unsatisfactory yields, long reaction times, use of expensive reagents and in some methods catalyst are destroyed in the workup procedure and could not be recovered and reused. In order to overcome these problems, the development of simple and clean catalytic route for the synthesis of β -enaminones using an eco-friendly and reusable catalyst under solvent-free conditions is of prime importance. In the last few years, microwave-induced organic reaction enhancement (MORE) has gained popularity as a nonconventional technique for rapid organic synthesis and many researchers have described accelerated organic reactions, with a large number of papers that have appeared proving the syn-

thetic utility of MORE chemistry in routine organic synthesis (Varma, 1999; Borah et al., 2002; Kidwai and Dave, 2002) 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 the present work, we have explored the use of $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ catalysts as an efficient and preferable alternative for the synthesis of β -enaminones. To the best of our knowledge, the application of $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ catalyst for the synthesis of β -enaminones has not yet been investigated. These catalytic materials were synthesized by simple co-precipitation followed by impregnation method. The preparation methods are quite simple, inexpensive and less time consuming.

2. Experimental

2.1. 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 was 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

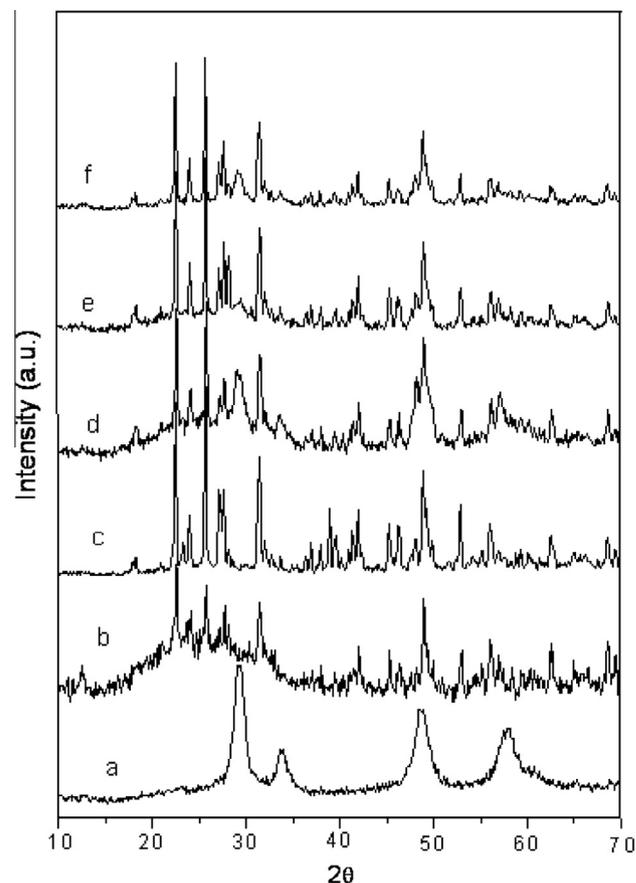


Figure 1 XRD patterns of series of (a) unsupported $\text{CeO}_2\text{-ZrO}_2$, (b) 8%, (c) 10%, (d) 12%, (e) 15%, (f) 20 wt% $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ calcined at 500 °C.

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 MoO₃/CeO₂-ZrO₂ materials, containing 8–20 wt% MoO₃ were prepared by impregnation method. To incorporate the molybdenum oxide, the requisite quantities of ammonium heptamolybdate were dissolved in excess 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.

2.2. Catalyst characterization

The X-ray powder diffraction patterns of catalyst were recorded on Bruker 8D advance X-ray diffractometer using Cu K α radiation of wavelength = 1.54060 Å, with the scanning rate of 2°/min was used for all samples. The FT-IR spectrums were recorded on JASCO-FTIR/ 4100 Japan, using dry KBr as standard reference in the range of 4000–500 cm⁻¹. In order to understand the surface morphology and to assess the surface dispersion of MoO₃ supported on CeO₂-ZrO₂, the SEM analysis was carried out with JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA. The presence of metal and their elemental composition were recorded by using energy dispersive spectroscopy.

2.3. General procedure for the synthesis of β -enaminones

Substituted aniline (1 mmol) and dimedone (1 mmol) were taken in 50 ml beaker and 0.2 g catalyst was added and well mixed with the help of glass rod. The resulting mixture was subjected to microwave irradiation at 450 W for an appropriate time (Table 3). After completion of the reaction (as monitored by TLC), 10 ml ethyl acetate was added to the reaction mixture to separate the catalyst by filtration. The solvent was evaporated and crude product was obtained. The products were characterized by ¹H NMR, IR and Mass spectroscopic techniques.

Spectral data for some of the representative compounds:

(3a): ¹H NMR (400 MHz, CDCl₃): δ 7.7 (s, 1H), 7.3 (d, 2H), 7.1 (d, J = 7.1 Hz, 3H), 5.5 (s, 1H), 2.5 (s, 2H), 2.3 (s, 2H), 1.0 ppm (s, 6H); FTIR (KBr): 3429, 3070, 1490, 1379, 1280, 1606 cm⁻¹; m/z : 215.

(3b): ¹H NMR (400 MHz, CDCl₃): δ 7.5 (s, 1H), 7.2 (d, J = 7.3 Hz, 2H), 7.1 (d, J = 7.1 Hz, 2H), 5.5 (s, 1H), 2.3 (s, J = 2.3 Hz, 2H), 2.2 (s, 2H), 1.1 ppm (s, 6H). FTIR (KBr): 3429, 3074, 1493, 1379, 1280, 1606, 605 cm⁻¹; m/z : 250.

3. Results and discussion

3.1. XRD analysis

The powder X-ray diffraction pattern of (a) pure CeO₂-ZrO₂ and (b–f) 8–20 wt% MoO₃ supported CeO₂-ZrO₂ catalysts calcined at 500 °C in the presence of air for 5 h are shown in Fig. 1.

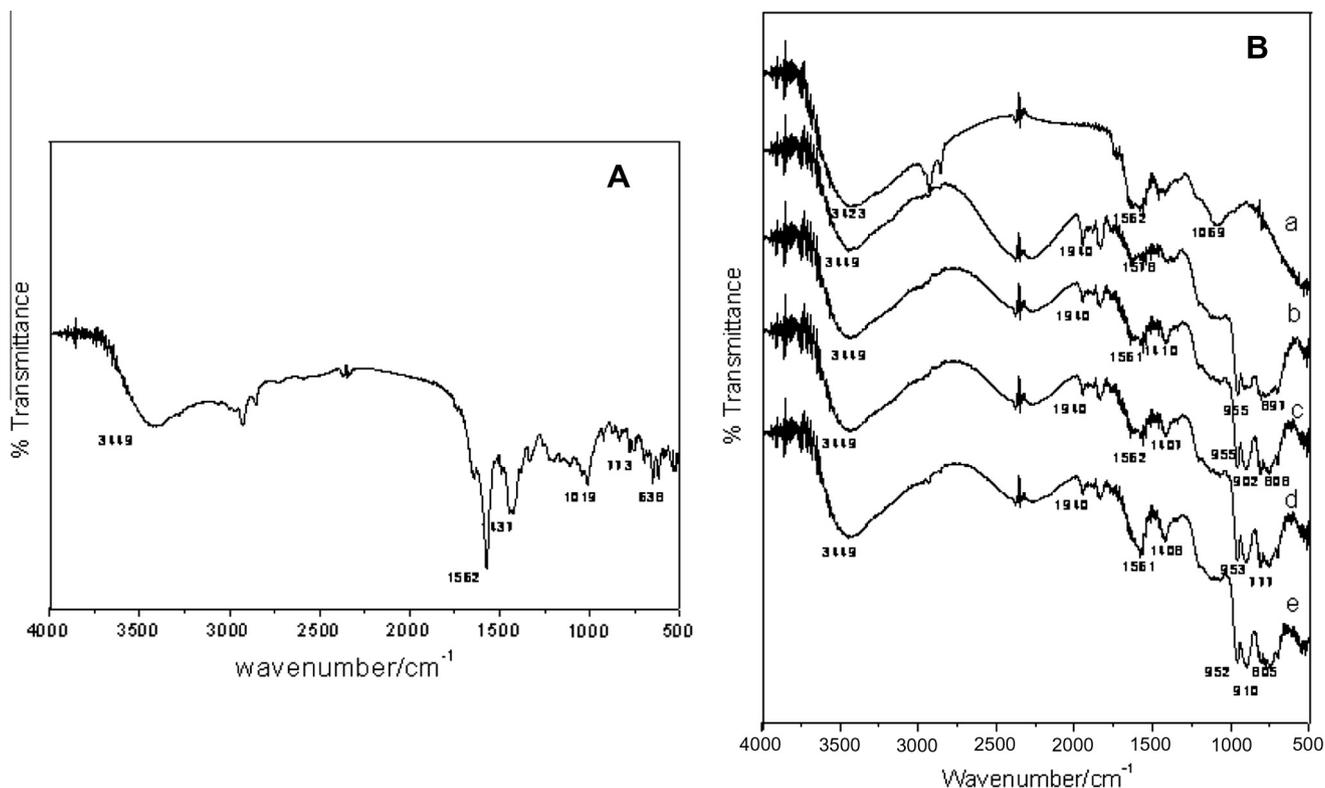


Figure 2 FT-IR spectrum of (A) unsupported CeO₂-ZrO₂, (B) (a) 8%, (b) 10%, (c) 12%, (d) 15%, (e) 20 wt% MoO₃/CeO₂-ZrO₂ calcined at 500 °C.

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), that the diffraction patterns of unsupported $\text{CeO}_2\text{-ZrO}_2$ and MoO_3 supported $\text{CeO}_2\text{-ZrO}_2$ samples differ very much indicating a strong influence of the impregnated molybdenum oxide on the surface of $\text{CeO}_2\text{-ZrO}_2$. From the 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 (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (3 3 1), respectively, indicate 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 (5 0 1), (4 1 1), (8 0 0), (7 2 0), (4 2 2), (1 1 0 2), (1 2 3), (0 1 4), (8 0 4), (0 4 0), respectively. It has been seen that, X-ray powder diffraction patterns of MoO_3 promoted $\text{CeO}_2\text{-ZrO}_2$ samples are crystalline in nature, indicating a strong interaction between the MoO_3 and $\text{CeO}_2\text{-ZrO}_2$ support.

3.2. FT-IR analysis

The FT-IR spectrums of series of $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$, using dry KBr as standard reference in the range of $4000\text{--}500\text{ cm}^{-1}$ are shown in Fig. 2. From the IR spectrum it was observed that in each sample (a–f) the peak in the range $3200\text{--}3500\text{ cm}^{-1}$ 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 peak is in the range of $1500\text{--}1600$ and $1410\text{--}1446\text{ cm}^{-1}$ due to the deformation of surface hydroxyl group (Lagashetty et al., 2007). As can be noted from the spectrum of each sample, the peak at in the range of $1010\text{--}1079\text{ cm}^{-1}$ is as-

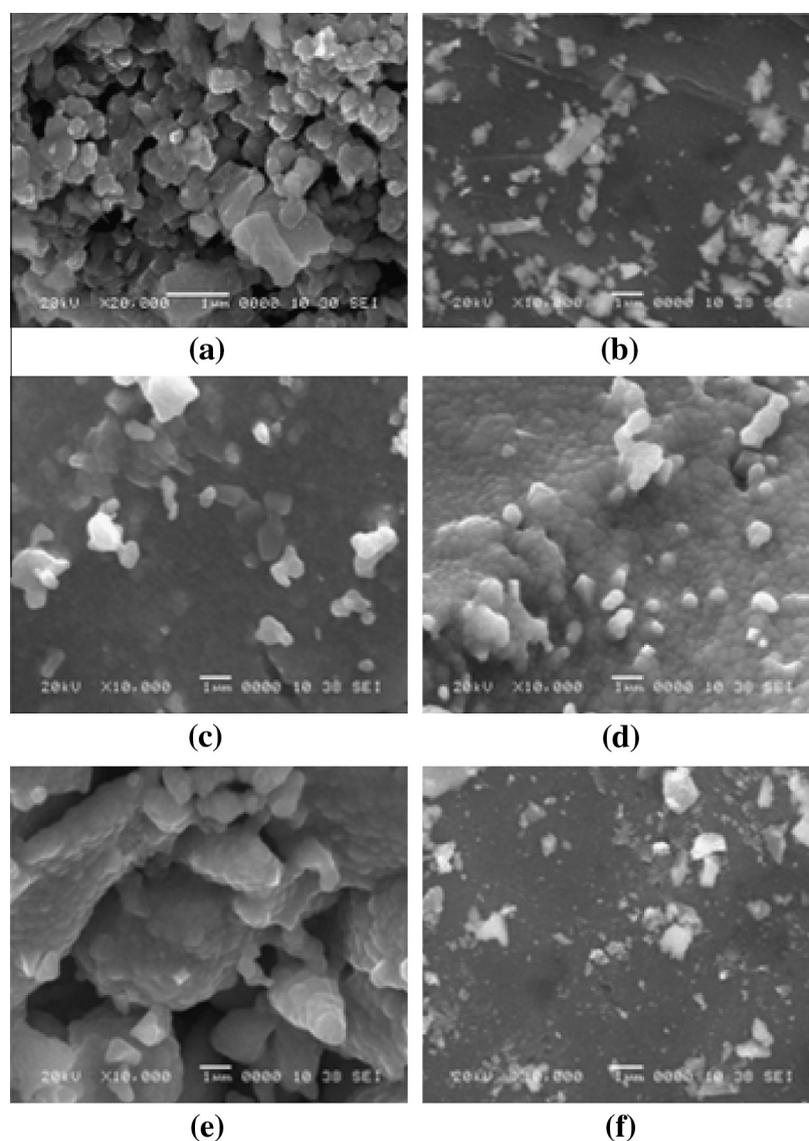


Figure 3 SEM micrograph of (a) unsupported $\text{CeO}_2\text{-ZrO}_2$, (b) 8%, (c) 10%, (d) 12%, (e) 15%, (f) 20 wt% $\text{MoO}_3/\text{CeO}_2\text{-ZrO}_2$ calcined at 500°C .

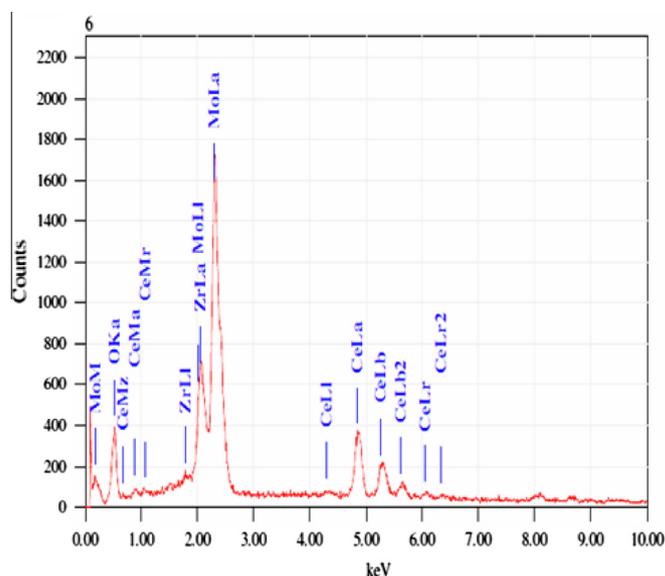


Figure 4 EDS Spectrum of 20 wt% MoO₃/CeO₂-ZrO₂ calcined at 500 °C.

signed for the M–O–M bonding (M = Mo, Ce, Zr). The bands in the range 500–991 cm⁻¹ were assigned to the Mo=O, Mo–O–Mo stretching modes of vibration for crystalline MoO₃ (Sohn and Chun, 2003). The appearance of these bands indicates that, the MoO₃ is strongly dispersed on the surface of CeO₂-ZrO₂ catalyst.

3.3. SEM analysis

Typical SEM images of series of MoO₃/CeO₂-ZrO₂ catalytic materials are presented in Fig. 3. As can be seen from Fig. 3(a) which shows the SEM image of pure CeO₂-ZrO₂ sample, it is clear that particles are homogeneously aggregated and which are 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% loaded MoO₃, it was observed that, MoO₃ is strongly interacted and highly dispersed on the surface of the CeO₂-ZrO₂ catalyst.

3.4. EDS analysis

The presence of metals and elemental compositions of the 20 wt% MoO₃/CeO₂-ZrO₂ catalyst are shown in Fig. 4, represents the elemental distribution of at Mo, Ce, Zr, and O as (0.53 at.%), (29.18 at.%), (12.67 at.%), and (57.62 at.%), respectively.

Table 1 Particle size estimation of MoO₃ supported CeO₂-ZrO₂.

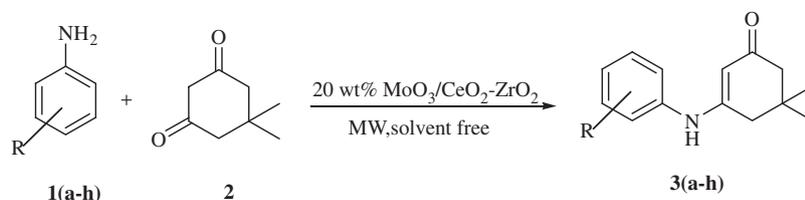
Entry	Mo wt% loading	Particle size (<i>T</i>) (nm)
1	0% CeO ₂ -ZrO ₂	7.11
2	8% MoO ₃ /CeO ₂ -ZrO ₂	23.98
3	10% MoO ₃ /CeO ₂ -ZrO ₂	33.56
4	12% MoO ₃ /CeO ₂ -ZrO ₂	38.58
5	15% MoO ₃ /CeO ₂ -ZrO ₂	42.09
6	20% MoO ₃ /CeO ₂ -ZrO ₂	33.17

Table 2 Effect of different wt% MoO₃/CeO₂-ZrO₂ in the synthesis of 3a^a (Table 3).

Entry	Mo wt% loading	At 450 W in microwave	
		Time (min)	Yield (%) ^b
1	Pure CeO ₂ -ZrO ₂	10	40
2	8% MoO ₃ /CeO ₂ -ZrO ₂	15	62
3	10% MoO ₃ /CeO ₂ -ZrO ₂	15	62
4	12% MoO ₃ /CeO ₂ -ZrO ₂	10	70
5	15% MoO ₃ /CeO ₂ -ZrO ₂	10	70
6	20% MoO ₃ /CeO ₂ -ZrO ₂	3	95

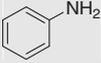
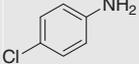
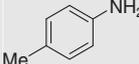
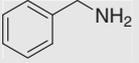
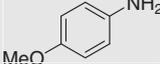
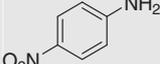
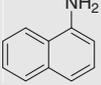
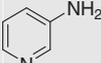
^a Reaction condition: aniline (1 mmol), dimedone (1 mmol), catalysts (200 mg), solvent free. Reaction attempted in domestic microwave (SAMSUNG).

^b Isolated yields.



Scheme 1 The synthesis of β -enaminones catalyzed by 20 wt % MoO₃/CeO₂-ZrO₂.

Table 3 Synthesis of β -enaminones derivatives catalyzed by 12 wt% MoO₃/CeO₂-ZrO₂ catalyst in microwave.

Compound	Ar-NH ₂	Time (min)	Yield (%) ^a	MP (°C)
3a		3	95(95, 95, 94) ^b	183–184
3b		3	92	190–192
3c		3	95	195–196
3d		2	85	124–126
3e		3	92	194–196
3f		2	93	193–195
3g		8	86	(Viscous oil)
3h		8	82	(Viscous oil)

^a Isolated yields.^b After consecutive run.

3.5. Crystallite size calculation

The particle sizes of different wt% MoO₃ supported CeO₂-ZrO₂ samples estimated using Debye-Scherrer equation:

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

where T = particle size, λ = wavelength, θ = diffraction angles, β = FWHM (full width half maximum).

From Table 1, it was observed that the particle size and crystallinity (from XRD) increases with increase in Mo wt% loading on CeO₂-ZrO₂.

3.6. Catalytic activity results

In order to evaluate the catalytic activities of 0, 8, 10, 12, 15 and 20 wt% MoO₃ supported on CeO₂-ZrO₂ catalysts are investigated using Scheme 1. The results in terms of reaction time and product yields obtained are summarized in Table 2. Catalytic activity results reveal that, the pure CeO₂-ZrO₂ material exhibited negligible activity in comparison with the other 8–20 wt% MoO₃ loaded CeO₂-ZrO₂ catalysts, which may be due to the poor crystallinity of the CeO₂-ZrO₂ material (Fig. 1(a)). From the X-ray diffraction patterns (Fig. 1(b–f)) it was observed that, the crystallinity increases with increase in Mo wt% loading, which indicates that, molybdenum oxide is highly crystalline in nature. Also, Table 2 shows, the 20 wt% MoO₃/CeO₂-ZrO₂ catalyst exhibits good catalytic activity for the synthesis of β -enaminones probably that might be due to the small particle size and possess better acidic sites as the acidic nature of molybdenum oxide (Williams et al., 1991; Carbucicchio and Trifiro, 1980; Bruckman et al., 1993; Ono et al., 1987; Ma et al., 2004). Therefore, it

was further used as a catalyst to prepare the various derivatives of β -enaminones (Table 3). A variety of different substituted anilines possessing an electron donating (CH₃, OCH₃, OH) and electron withdrawing groups (NO₂) offered good yield (82–95%) and reactions were completed in a very short time. We have also examined some heteroaromatic anilines, which gave reasonably good yields but demanded little more reaction time after the crystallization oily drops are formed. From the results obtained it is concluded that, the catalytic activity increases with increase in Mo wt% loading (8–20%).

Furthermore, we have investigated the reusability and recycling of 20 wt% MoO₃/CeO₂-ZrO₂ catalyst. At the end of reaction, the catalyst was recovered by simple filtration from the reaction mixture and washed with n-hexane and subjected to a second run of the reaction process. To assure that the catalyst was not dissolved in n-hexane, the catalyst was dried at 60 °C and activated at 100 °C for 1 h in (HTMF), after filtration and before using and reusing for the next reaction. The result shows that these catalysts are not soluble in n-hexane. The comparison of efficiency of 20 wt% MoO₃/CeO₂-ZrO₂ in the synthesis of 3a after three times is reported (Table 3, entry 3a). There were no significant decreases in efficiency of the recovered catalyst compared to the fresh material. The catalyst was reusable at least up to three times.

4. Conclusion

In conclusion, (1) the present paper describes a new, efficient and eco-friendly route for the synthesis of β -enaminones. (2) Among the various Mo wt% loaded CeO₂-ZrO₂ catalyst, the 20 wt% MoO₃/CeO₂-ZrO₂ catalyst exhibits excellent catalytic activity for the condensation of various aromatic and heteroar-

omatic anilines with dimedone. Most importantly this catalyst facilitates the reaction under solvent-free conditions by providing solid support in the reaction, enhances the reaction rate and thereby the excellent yields of the products. Finally, it is concluded that, the catalytic activity increases with increase in Mo wt% loading (8–20 wt%). (3) The catalyst can be prepared by simple co-precipitation followed by impregnation methods, which are easy, simple, inexpensive and less time consuming. (4) A simple procedure combined with low toxicity and reusability of the catalysts, makes this method an economic and waste-free chemical method for the synthesis of β -enaminones.

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References

- Appelbaum, F.C., Hunter, P.A., 2000. The fluoroquinolone antibacterials: past, present and future perspectives. *Int. J. Antimicrob. Agents* 16, 5.
- Arata, K., 1990. Solid super acid. *Adv. Catal.* 37, 165.
- Azzaro, M., Geribaldi, S., Videau, B., 1981. Use of Boron Trifluoride Etherate in the preparation of 2-amino-1-alkenyl ketones from β -diketones and low-boiling amines. *Synthesis* 11, 880.
- Baraldi, P.G., Simoni, D., Manfredini, S., 1983. An improved preparation of enaminones from 1,3-diketones and ammonium acetate or amine acetates. *Synthesis* 11, 902.
- Borah, R., Kalita, D.J., Sharma, J.C., 2002. Microwave promoted selective preparation of acetals and esters from aldehydes. *Indian J. Chem.* 41B, 1032.
- Bruckman, K., Grzybowska, B., Tatibouet, J.M., 1993. Methanol oxidation on MoO₃/TiO₂ catalysts. *Appl. Catal. A* 96, 279.
- Carbucicchio, M., Trifiro, F., 1980. Redox processes at the surfaces of Fe₂O₃-MoO₃/SiO₂ catalysts. *J. Catal.* 62, 13.
- Corma, A., 1995. Inorganic solid acid and their use in acid catalyzed hydrocarbon reactions. *Chem. Rev.* 95, 599.
- Dal, P.R., De, N.A., Nardi, R.M., Procopio, B.A., 2006. Erbium (III) Triflate: A valuable catalyst for the synthesis of aldimines, ketimines, and enaminones. *Synthesis* 7, 1127.
- Dannhardt, G., Bauer, U., Nowe, J.J., 1998. Non-steroidal anti-inflammatory agents. Part 23. Synthesis and pharmacological activity of enaminones which inhibit both bovine cyclooxygenase and 5-lipoxygenase. *Prakt. Chem.* 340, 256.
- Dupont, P., Vedrine, J.C., Paumard, E., Hecquet, G., Lefebvre, F., 1995. Heteropolyacids supported on activated carbon as catalysts for the esterification of acrylic acid by butanol. *Appl. Catal. A: Gen.* 129, 217.
- Edafiohgo, I.O., Ananthakshmi, K.V.V., Kombain, S.B., 2006. Anticonvulsant evaluation and mechanism of action of benzyl-amino enaminones. *Bioorg. Med. Chem.* 14, 5266.
- Eddington, N.D., Cox, D.S., Roberts, R.R., 2000. Enaminones-versatile therapeutic pharmacophores. *Curr. Med. Chem.* 7, 417.
- Foster, J.E., Nicholson, J.M., Butcher, R., Stables, J.P., 1999. Synthesis, characterization and anticonvulsant activity of enaminones. Part 6: Synthesis of substituted vinylic benzamides as potential anticonvulsants. *Bioorg. Med. Chem.* 7, 2415.
- Guttman, A.T., Grasselli, R.K., 1983. Esterification of methacrylic acid with methyl tertiary butyl ether - a process for the manufacture of methyl methacrylate. *Appl. Catal.* 9, 57.
- Kidwai, M., Dave, B., 2002. Solid support synthesis of fungicidal pyrazoles using microwaves. *Indian J. Chem.* 41B, 2430.
- Lagashetty, A., Havanoor, V., Basavaraja, S., 2007. Microwave-assisted route for synthesis of nanosized metal oxides. *Sci. Technol. Adv. Mater.* 8, 484.
- Lin, J., Zhang, L.F., 2007. ZrCl₄-catalyzed efficient synthesis of enaminones and enamino esters under solvent-free conditions. *Monatsh. Chem.* 138, 77.
- Ma, X., Gong, J., Wang, S., Gao, N., Wang, D., Yang, X., He, F., 2004. Reactivity and surface properties of silica supported molybdenum oxide catalysts for the transesterification of dimethyl oxalate with phenol. *Catal. Commun.* 5, 101.
- Manohar, B., Reddy, V.R., Reddy, B.M., 1998. Esterification by ZrO₂ and Mo-ZrO₂ ecofriendly solid acid catalysts. *Synth. Commun.* 28, 3183.
- Michael, J.P., Koning, C.B., Hosken, G.D., Stanbury, T.V., 2001. Reformatsky reactions with *N*-arylpiperidine-2-thiones: synthesis of tricyclic analogues of quinolone antibacterial agents. *Tetrahedron* 57, 9635.
- Misono, M., Okuhara, T., 1993. Preparation of solid catalyst. *Chemtech.* 11, 23.
- Mohammadzadeh, M.R., Hasaninejad, A., Bahramzadeh, M., 2009. P₂O₅/SiO₂ as a new, efficient, and reusable catalyst for the preparation of β -enaminones under solvent-free conditions. *Synth. Commun.* 39, 1152.
- Olah, G.A., Takashi, K., David, M., 1978. A convenient and improved method for esterification over Nafion-H², a superacidic perfluorinated resin-sulfonic acid catalyst. *Synthesis* 4, 929.
- Ono, T., Miyata, H., Kubokawa, Y., 1987. Catalytic activity and structure of Mo oxide highly dispersed on ZrO₂ for oxidation reactions. *J. Chem. Soc., Faraday Trans.* 183, 1761.
- Paira, M., Misra, R., Roy, S.C., 2008. Cerium (IV) Ammonium Nitrate catalyzed synthesis of β -enaminones. *Indian J. Chem.* 47, 966.
- Rafiee, E., Joshaghani, M., Eavani, S., Rashidzadeh, S., 2008. A revision for the synthesis of β -enaminones in solvent free conditions: Efficacy of different supported heteropoly acids as active and reusable catalysts. *Green Chem.* 10, 982.
- Reddy, B.M., Reddy, V.R., 1999. Mo-ZrO₂ solid acid catalyst for synthesis of substituted diphenylureas. *Synth. Commun.* 29, 2789.
- Reddy, B.M., Reddy, V.R., 2000. Influence of SO₄²⁻, Cr₂O₃, MoO₃ and WO₃ on the stability of ZrO₂ tetragonal phase. *J. Mater. Sci. Lett.* 19, 763.
- Reddy, B.M., Sreekanth, P.M., 2003. An efficient synthesis of 1-5 benzodiazepine derivative catalyzed by a solid super acid sulfated zirconia. *Tetrahedron Lett.* 44, 4447.
- Reddy, B.M., Sreekanth, P.M., Yamada, Y., Kobayashi, T., 2005a. Surface characterization and catalytic activity of sulfate-, molybdate- and tungstate-promoted Al₂O₃-ZrO₂ solid acid catalysts. *J. Mol. Catal. A: Chem.* 227, 81.
- Reddy, B.M., Lakshmanan, P., Khan, A., Lorient, S., 2005b. A surface stabilized nanosized Ce₁Zr_{1-x}O₂ solid solutions over SiO₂. *J. Phys. Chem.* 109, 13545.
- Reddy, B.M., Patil, M.K., Rao, K.N., 2006. An easy to use heterogeneous promoted zirconia catalyst for Knoevenagel condensation in liquid phase under solvent free conditions. *J. Mol. Catal. A: Chem.* 258, 302.
- Rosenberg, D.J., Coloma, F., Anderson, J.A., 2002. Modification of the Acid Properties of Silica-Zirconia Aerogels by *in Situ* and *ex Situ* Sulfation. *J. Catal.* 210, 218.
- Sohn, J.R., Chun, E.W., 2003. Spectroscopic studies on ZrO₂ modified with MoO₃ and activity for acid catalysis. *Bull. Korean. Chem. Soc.* 24, 1785.
- Stefani, H.A., Costa, I.M., Silva, D.G., 2000. An Easy Synthesis of Enaminones in Water as Solvent. *Synthesis* 11, 1526.
- Texier, B.F., Kelin, B., Hamelin, J., 1986. Pyrrole and Pyrazole Ring Closure in Heterogeneous Media. *Synthesis* 5, 409.
- Thomas, J.M., 1992. Solid acid catalysts. *Sci. Am.* 266, 112.

- Varma, S., 1999. Solvent-free organic syntheses using supported reagents and microwave irradiation. *Green Chem.* 1, 43.
- Williams, C.C., Ekerdt, J.G., Jehng, J.M., Turek, A.M., 1991. Infrared spectroscopic characterization of molybdenum carbonyl species formed by ultraviolet photoreduction of silica-supported molybdenum(VI) in carbon monoxide. *J. Phys. Chem.* 95, 8781.
- Yadav, G.D., Nair, J.J., 1999. Sulfated zirconia and its modified versions as promising catalysts for industrial processes. *Micropor. Mesopor. Mater.* 33, 1.