

Novel molybdenum-cerium based heterogeneous catalysts for efficient oxidative coupling of benzylamines under eco-friendly conditions

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Abstract This work demonstrates that MoO_x/CeO₂–ZrO₂ solid acid acts as a promising catalyst in the solvent-free oxidative-coupling of benzylamine into dibenzylimine with O₂ as the oxidant. The benzylamine conversions were found to be ~27, 51, 74, and 99 % for CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂, and MoO_x/CeO₂–ZrO₂ catalysts, respectively. The MoO_x/CeO₂–ZrO₂ catalyst also efficiently converts various substituted- and secondary-benzylamines under solvent-free conditions with O₂ resulting in moderate to excellent yields. Remarkably, a high selectivity of ~99.6–99.9 % towards the dibenzylimine product was found for all reaction conditions. The outstanding performance of MoO_x/CeO₂–ZrO₂ catalyst was attributed to high specific surface area, improved structural defects, and superior acid properties.

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Graphical Abstract



The MoO_x/CeO_2 -ZrO₂ catalyst show an outstanding performance in the oxidation of benzylamine and its derivatives, which is attributed to abundant acidic sites, large number of oxygen vacancies, and superior BET surface area.

Introduction

The oxidative coupling of amines to imines is an important organic transformation in chemical synthesis. Imines are crucial building blocks for the synthesis of dyes, fragrances, fungicides, agrochemicals, oxazolidines, pharmaceuticals, nitrones, amides, chiral amines, hydroxyamines, anti-inflammatory agents, lipoxygenase inhibitors, anti-cancer agents, polymer compounds, and biologically active compounds [1-14]. Additionally, imines are key intermediates in a number of reactions, such as addition, reduction, aziridination, β -lactamization, cyclization, condensations, and aza-Diels-Alder reactions [4]. The oxidative coupling of amines is traditionally performed with stoichiometric amounts of high valent inorganic oxidants, such as chromate or permanganate, as well as with organic oxidants, like 2-iodoxybenzoic acid and N-tert-butylphenylsulfinimidoylchloride [15-18]. The use of these oxidants leads to the generation of large amounts of metal/organic waste, which is undesirable from the viewpoint of the 12 Green Chemistry Principles. On the other hand, oxidative coupling of amines using O2 as the oxidant has received tremendous attention in recent years [14, 19]. O₂ is an abundant and green oxidant, and gives only water as the by-product in the oxidation reactions [4, 20].

Several catalysts based on Pd [1, 11, 21, 22], Pt [23], and Au [10, 24] have been reported for the oxidation of amines. The requirement of large catalyst quantities and the expensive nature of these metals limit their applicability in the chemical industry. It has been recently demonstrated that ceria-based materials act as efficient catalysts in the selective oxidative coupling of various benzylamines [4]. The properties, such as high surface area, enriched structural defects, and importantly, abundant acid properties are found to be the key factors for the observed catalytic

efficiency of ceria-based catalysts. It is therefore believed that, by modifying the properties of ceria-based materials, their catalytic efficiency can be improved for the oxidative coupling of amines [25, 26].

In this work, we have synthesized MoO_x/CeO_2 and MoO_x/CeO_2 –ZrO₂ catalysts along with the CeO₂ and CeO₂–ZrO₂ using facile preparation methods, and their catalytic efficiency was evaluated for the oxidation of benzylamine using O₂ under solvent-free conditions. MoO_x based materials are widely used catalysts in several reactions because of their strong acid properties [27–29]. For this reason, MoO_x was selected as a promoter in this study. Much attention has been paid to correlate the physicochemical properties of the catalysts with their catalytic efficiency for the benzylamine oxidation.

Experimental

Catalyst preparation

The CeO₂–ZrO₂ (1:1, mole ratio) binary oxide was prepared by a simple and economical coprecipitation method. The desired amounts of Ce(NO₃)₃·6H₂O (Aldrich, AR grade) and ZrO(NO₃)₂·XH₂O (Fluka, AR grade) precursors were dissolved separately in double distilled water and mixed together under mild stirring conditions. Aq. NH₃ solution (2.5 w/w%) was added slowly to the above solution until the pH of the solution reached ~ 8.5. The resulting yellowish precipitates were filtered off and washed with double distilled water several times to remove the anion impurities. Finally, the obtained cake was dried at 393 K for 12 h and calcined at 773 K for 5 h in an air atmosphere.

To synthesize 10 wt% MoO₃ supported on CeO₂–ZrO₂, the required quantity of CeO₂–ZrO₂ was dispersed in deionised water under stirring conditions at room temperature. The requisite amounts of $(NH_4)_6Mo_7O_{24}$ ·4H₂O were dissolved in deionised water and mixed with CeO₂–ZrO₂ solution under stirring conditions. The remaining procedure follows the same as the above. Pure CeO₂ and MoO_x/CeO₂ are also prepared using the same procedure.

Catalyst characterization

The physicochemical characterization of the catalysts was undertaken using X-ray diffraction (XRD), Raman spectroscopy, X-ray photo electron spectroscopy (XPS), Barrett–Joyner–Halenda (BJH) pore size distribution, Brunauer–Emmett–Teller (BET) surface area, and NH₃-temperature programmed desorption (TPD) techniques. The detailed procedure related to characterization methods used in this work is presented in the supporting information.

Catalytic activity

Catalytic performance of the samples was studied for the oxidation of benzylamine with O_2 as the oxidant under solvent-free conditions. Reactions were conducted in a 10 mL round bottom flask by taking 0.2 mmol of substrate and 100 mg of catalyst

under the O_2 flow (20 mL min⁻¹). After completion of the reaction, the catalyst and the products were separated by centrifugation. The liquid products were confirmed by GC–MS equipped with a DB-5 capillary column and a flame ionization detector (FID). Samples were taken periodically and analyzed by GC equipped with a BP-20 (wax) capillary column and a FID.

Results and discussion

Characterization studies

The XRD patterns of the samples are shown in Fig. 1. As shown in Fig. 1, the XRD patterns of the samples can be indexed to (111), (200), (220), (311), (222), and (400) reflections, which indicates the presence of fluorite cubic structured ceria in the synthesized samples [30–36]. Interestingly, no XRD peaks related to MoO₃, t-ZrO₂, and m-ZrO₂ phases were found for CeO₂–ZrO₂, MoO₃/CeO₂, and MoO₃/CeO₂–ZrO₂ samples. This observation may be due to either the amorphous nature of the respective metal oxides or incorporation of Zr and Mo into the CeO₂ lattice. The average crystallite sizes of CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ samples were found to be ~8.9, 4.7, 6.5, and 3.9 nm, respectively (Table 1). It is obvious that the addition of Mo and Zr to CeO₂ leads to a decrease in its crystallite size. This interesting observation reveals the existence of a strong interaction between the Ce and Mo/Zr in the final oxide matrix.

Raman analysis is an efficient method to understand the structural defects in the metal oxides because of its sensitive nature towards the M–O vibration of the metal oxides. Figure 2 shows Raman spectra of the samples. All the samples show a prominent Raman peak at around 460 cm⁻¹, which corresponds to the F_{2g} active mode of fluorite structured ceria [4, 37, 38]. This observation well supports the XRD results (Fig. 1). As observed in XRD studies, here also no Raman bands corresponding to MoO₃ and ZrO₂ phases were found for CeO₂–ZrO₂, MoO_x/CeO₂, and MoO_x/CeO₂–ZrO₂ samples. It is interesting to note that only the MoO_x/





Sample	$S (m^2 g^{-1})$	$D (nm)^a$	$V (\mathrm{cm}^3 \mathrm{g}^{-1})^\mathrm{b}$	$P (nm)^{b}$
CeO ₂	41	8.9	0.113	9.82
CeO ₂ -ZrO ₂	82	4.7	0.079	3.38
MoO _x /CeO ₂	50	6.5	0.083	4.37
MoO _x /CeO ₂ -ZrO ₂	87	3.9	0.084	3.69

Table 1 BET surface area (*S*), average crystallite size (*D*), pore volume (*V*), and pore size (*P*) of CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts

^a From XRD spectra

^b From BJH analysis

Fig. 2 Raman spectra of CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts



CeO₂–ZrO₂ sample exhibits a broad Raman band centred at ~642 cm⁻¹. This band reveals the presence of structural defects, such as oxygen vacancies in the MoO_x/ CeO₂–ZrO₂ sample [4, 28]. The formation of oxygen vacancies in MoO_x/ CeO₂–ZrO₂ catalyst can be explained by combined effect of two factors: (1) doping of Zr into the CeO₂ lattice, which can lead to generation of oxygen vacancies due to the difference in the ionic radii of dopant Zr⁴⁺ (0.084 nm) and host Ce⁴⁺ (0.111 nm) and (2) the existence of interaction between the MoO_x and CeO₂–ZrO₂, which can influence the Ce–O bond to create the oxygen vacancies in the CeO₂ lattice.

The obtained N₂ adsorption–desorption isotherms showed that all the samples exhibit type 4 isotherms with a H₁ hysteresis loop (Fig. 3) [39–41]. This observation reveals the mesoporous nature of the samples. The achieved pore diameters are ~ 0.113 , 0.079, 0.083, and 0.084 cm³ g⁻¹ for CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts, respectively (Table 1). As well, the pore volumes of the CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts are ~ 9.82 , 3.38, 4.37, and 3.69 nm, respectively (Table 1). Interestingly, the BET surface area of the cerium oxide was significantly improved after the addition of Mo and Zr, in line with the achieved crystallite sizes (Table 1). The BET surface areas are found



Fig. 3 $\rm N_2$ adsorption–desorption isotherms of CeO_2, CeO_2–ZrO_2, MoO_x/CeO_2 and MoO_x/CeO_2–ZrO_2 catalysts

to be ~41, 82, 50, and 87 m² g⁻¹, respectively, for CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts.

Figure 4 shows HRTEM images of CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts. It can see from HRTEM images that the synthesized catalysts are highly crystalline materials in the nanoscale range. The lattice fringes for all the samples are clearly visible with an estimated d-spacing of 0.31 nm, which is attributed to CeO₂ (111) plane [4]. Careful analysis of these figures disclosed that the particle sizes of CeO₂ and CeO₂–ZrO₂ were in the range of 6–12 nm. A careful observation of MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ samples revealed the existence of highly dispersed MoO₃ species with much smaller sized particles (~1–1.5 nm) on the surface of the supports.

XPS studies were performed to find the oxidation states of elements present in the synthesized catalysts. Figure 5 shows Ce 3d core level XP spectra of the prepared samples. It can be noted from Fig. 5 that the Ce 3d XP spectra are complex and composed of several peaks [37, 42, 43]. Hence, as per the literature, the peaks are labelled with u and v, which correspond to Ce $3d_{5/2}$ and Ce $3d_{3/2}$ contributions, respectively. The peaks denoted by u_0 , v_0 , u' and v' represent the Ce³⁺ and the bands labelled with u, u'', v, v'', and v''' indicate the Ce⁴⁺ [44, 45]. This observation confirms the coexistence of both Ce³⁺ and Ce⁴⁺ species in the synthesized samples. Interestingly, the XPS spectrum of the cerium oxide was significantly shifted to lower binding energies after the addition of Zr and Mo. This finding reveals that the Zr and Mo influence the chemical environment of ceria. The Mo 3d XP core level spectra of the MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ samples show two bands at about



Fig. 4 HRTEM images of CeO2, CeO2-ZrO2, MoOx/CeO2 and MoOx/CeO2-ZrO2 catalysts





~232.20 ($3d_{5/2}$) and 235.32 eV ($3d_{3/2}$) (Fig. S1 of supplementary material). The presence of these binding energies indicates the existence of Mo in +6 oxidation state [27]. The achieved Zr 3d XP spectra of CeO₂–ZrO₂ and MoO_x/CeO₂–ZrO₂ catalysts show two bands at around 181.65 ($3d_{5/2}$) and 184.03 eV ($3d_{3/2}$), indicating the presence of Zr⁴⁺ ions (Fig. S2 of supplementary material). A careful observation of O 1s spectra of the samples indicate the presence of two bands, corresponding to different oxygen species (Fig. S3 of the supplementary material). The band appears

Fig. 6 NH₃-TPD profiles of MoO_x/CeO₂ and MoO_x/ CeO₂-ZrO₂ catalysts



at a lower binding energy (\sim 529.5 eV) indicates lattice oxygen [46–49]. The band at the higher binding energy (532.2 eV) can be assigned to surface hydroxyl groups.

The NH₃-TPD analysis was performed to estimate the acidic properties of the catalysts because of the highly sensitive nature of NH₃ towards the acidic sites present on the surface of the catalysts [4, 27, 48, 49]. Figure 6 shows the NH₃-TPD profiles of the samples. The achieved profiles can be defined as low-temperature (LT) and high-temperature (HT) regions, corresponding to before and after 673 K, respectively. The LT region indicates the release of NH₃ from the weak acid sites, whereas the HT region reveals desorption of NH₃ from the strong acidic sites present on the catalyst surface. It is noted from Fig. 6 that the MoO_x/CeO₂-ZrO₂ sample shows a higher intensity HT peak compared with that of the MoO_x/CeO₂ sample. This significant result confirms the presence of more amounts of strong acidic sites in the MoO_x/CeO₂-ZrO₂ sample.

Catalytic activity studies

Benzylamine was chosen as a model substrate to perform the oxidative coupling of amines over CeO₂, CeO₂–ZrO₂, MoO_x/CeO₂ and MoO_x/CeO₂–ZrO₂ catalysts. The reaction was performed at 383 K for 6 h using O₂ as the oxidant under solvent-free conditions. The achieved results are shown in Fig. 7. The catalytic efficiency of ceria was remarkably improved after the addition of Zr and Mo. Amongst them, the MoO_x/CeO_2 –ZrO₂ catalyst exhibited the highest benzylamine conversion, which indicates the co-promoting effect of Mo and Zr on the catalytic efficiency of CeO₂–ZrO₂, MoO_x/CeO_2 , CeO_2 –ZrO₂ and CeO_2 catalysts, respectively (Fig. 7). On the other hand, low conversion of benzylamine (8 %) was found under blank conditions, which indicate the necessity of a catalyst in the oxidative coupling of benzylamine. Remarkably, a high selectivity of dibenzylimine (99.6–99.9 %) was found, along with negligible amounts of benzonitrile (0.1–0.4 %) for all the catalysts. This observation indicates the importance of the present study in selective oxidation catalysis.



Fig. 7 Aerobic oxidation of benzylamine over CeO₂ (C), CeO₂–ZrO₂ (CZ), MoO_x/CeO₂ (MC) and MoO_x/CeO₂–ZrO₂ (MCZ) catalysts. Reaction conditions: benzylamine (0.2 mmol), time (6 h), temperature (383 K), catalyst amount (0.1 g), and O₂ bubbling rate (20 mL min⁻¹)



 $Scheme \ 1 \ \ \text{Possible reaction mechanism for the aerobic oxidation of benzylamine over MoO_x/CeO_2-ZrO_2 catalyst}$

A possible mechanism for the aerobic oxidation of benzylamine to dibenzylimine is presented in Scheme 1 [4, 9, 24, 39, 50, 51]. As shown in Scheme 1, an imine intermediate (Ph-CH=NH) can be formed through the oxidative dehydrogenation of benzylamine. This imine intermediate (Ph-CH=NH) has a net positivity charge, thus there is a high possibility of the attack of available benzylamine (PhCH₂NH₂) on imine intermediate due to the presence of a lone pair of electrons on the nitrogen atom of the benzylamine. Then, the dibenzylimine product can be formed through the aminal formation followed by release of NH₃. As stated previously, a small amount of benzonitrile (0.1–0.4 %) was found in this study, which is due to the consecutive oxidative dehydrogenation of the imine intermediate (Scheme 1). It was



Fig. 8 Effect of reaction time on the oxidation of benzylamine with MoO_x/CeO_2 -ZrO₂ catalyst. Reaction conditions: benzylamine (0.2 mmol), temperature (383 K), catalyst amount (0.1 g), and O₂ bubbling rate (20 mL min⁻¹)

found that the acid catalysts exhibit higher efficiency in the amine oxidation through the activation of the imine intermediate as shown in Scheme 1 [4, 50, 51]. It is a well-known fact in the literature that high surface area catalysts exhibit a high catalytic performance due to the availability of more active sites on the catalyst surface. The presence of oxygen vacancies especially in MOO_x/CeO_2 – ZrO_2 catalyst (Fig. 2) is an additional advantage because the gas phase O_2 can be activated on these oxygen vacancies, which can play a key role in the oxidation of benzylamine. Therefore, the superior performance of MOO_x/CeO_2 – ZrO_2 catalyst can be attributed to the improved physicochemical properties, such as a high BET surface area (Table 1), abundant oxygen vacancy defects (Fig. 2), and high concentration of acidic sites (Fig. 6).

The effect of the amount of catalyst on the reaction was studied with the $MoO_x/$ CeO₂-ZrO₂ catalyst (Fig. S4 of supplementary material). The employed reaction conditions are as follows: benzylamine (0.2 mmol), temperature (383 K), reaction time (6 h), and O_2 bubbling rate (20 mL min⁻¹). It was found that the conversion of benzylamine gradually increases with the increase in the amount of catalyst . This observation could be attributed to the availability of more active sites at higher catalyst amounts. The benzylamine conversions were found to be $\sim 28, 54, 70, 89$, and 99 %, respectively, for 20, 40, 60, 80, and 100 mg of the catalyst. Interestingly, there was no considerable variation in the selectivity of imine product (99.6–99.9 %) with the variation in the catalyst amount. Figure 8 shows the effect of reaction time on benzylamine oxidation over MoO_x/CeO₂-ZrO₂ catalyst. Reactions were performed using 0.2 mmol of benzylamine at 383 K with 100 mg of catalyst amount and O_2 bubbling rate of 20 mL min⁻¹. The conversion of benzylamine was increased rapidly with the increase in the reaction time. The achieved benzylamine conversions for 1, 2, 3, 4, 5, and 6 reaction times were 15, 28, 65, 79, 95, and 99 %, respectively. It is noted that the selectivity of the imine product ($\sim 99.6-99.9$ %) almost remains the same at all reaction times, along with negligible amounts of nitrile by-product (0.1–0.4 %).

R	$M_{2} = \frac{M_{0}O_{x}/C_{0}}{O_{y}}$	eO_2-ZrO_2 [2 R	N R	+ R	N
R = CI, F,	Me, OMe		Imine	Nitri	le
Serial no.	Substrate	Time (h)	Amine conversion (%)	Selectivi	ty (%)
_				Imine	Nitrile
1	NH ₂	6	99	99.8	0.2
2	Cl NH ₂	6	96	99.8	0.2
3	Cl NH2	6	91	99.9	0.1
4	F NH2	6	90	99.7	0.3
5	Me NH ₂	6	98	99.7	0.3
6	Me NH2	6	89	99.9	0.1
7	MeO NH ₂	6	99	99.6	0.4
8	NH ₂	6	93	99.9	0.1
	OMe				

Table 2	Oxidative self-coupling of	substituted benzylamines	with MoO _x /CeO ₂ -ZrO ₂ catalyst
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Reaction conditions: temperature (383 K), time (6 h), amine (0.2 mmol), catalyst amount (0.1 g), and O_2 bubbling rate (20 mL min⁻¹)

We have further explored the catalytic efficiency of MoO_x/CeO_2-ZrO_2 catalyst for the oxidative coupling of various benzylamines bearing different substituent groups such as, F, Cl, Me, and OMe. The results obtained are presented in Table 2. Excellent amine conversions were found for all the substituted benzylamines irrespective of the nature of substituent present on the phenyl ring of benzylamine. On the other hand, steric hindrance nature of the substituent groups was found to play a role in the oxidation of benzylamine. For example, a higher conversion for para-substituted amines was found compared with that of meta- and orthosubstituted amines (Table 2, entries 3, 6, 8). The selectivity of the imine and nitrile

Serial no.	Amine	Conversion (%)	Selectivity (%)
1	N N	98	(100)
2	NH-	85	
3	NH	79	(100)

Table 3 Oxidation of various secondary benzylamines with MoOx/CeO2-ZrO2 catalyst

Reaction conditions: temperature (383 K), time (6 h), amine (0.2 mmol), catalyst mount (0.1 g), and O_2 bubbling rate (20 mL min⁻¹)

was found to be ~99.6–99.9 and 0.1–0.4 % for all the substituted benzylamines, respectively.

We have also investigated the oxidation of different secondary amines with MoO_x/CeO_2 –ZrO₂ catalyst (Table 3). The amine conversion was found to be low for all the secondary amines compared with that of the primary benzylamines (Fig. 7; Table 2). This observation clearly indicates the role of steric hindrance in the oxidation of secondary benzylamines. Interestingly, 100 % selectivity towards the imine product was found for all the secondary benzylamines. This observation is attributed to the lack of hydrogen attached to the N-benzylamine to give the nitrile product. Overall, the MoO_x/CeO_2 –ZrO₂ catalyst can be efficiently used for a number of oxidation reactions under eco-friendly conditions, such as O₂ as the oxidant and without the use of solvent.

We have finally studied the reusability efficiency of MoO_x/CeO_2 -ZrO₂ catalyst for the oxidation of benzylamine using O₂ under solvent-free conditions. The results obtained are presented in Fig. 9. The catalytic reaction parameters were fixed as



Fig. 9 Reusability of MoO_x/CeO_2 – ZrO_2 catalyst for benzylamine oxidation. Reaction conditions: benzylamine (0.2 mmol), temperature (383 K), reaction time (6 h), catalyst amount (0.1 g), and O_2 bubbling rate (20 mL min⁻¹)

follows: benzylamine (0.2 mmol), catalyst amount (100 mg), O₂ bubbling rate (20 mL min⁻¹), reaction time (6 h), and temperature (383 K). After completion of each cycle, the solid catalyst was recovered from the reaction mixture by means of centrifugation, washed several times with ethanol to remove reaction gradients and then dried at 423 K for 2 h. It was found that the MoO_x/CeO₂–ZrO₂ catalyst can be efficiently used up to five cycles without any significant variation in the benzylamine conversion. The achieved amine conversions are ~99, 97, 96, 94, and 89 % for the first, second, third, fourth, and fifth cycles, respectively. As well, no considerable variation in the selectivity of imine product was observed with the repeated use of the catalyst. This thorough activity investigation reveals that the MoO_x/CeO₂–ZrO₂ solid acid is a versatile catalyst for the oxidation of various benzylamines under eco-friendly reaction conditions.

Conclusions

In summary, the MoO_x/CeO_2 – ZrO_2 catalyst was found to exhibit an outstanding catalytic performance for the oxidation of benzylamine under eco-friendly reaction conditions. High surface area, abundant structural defects, and large amounts of acidic sites were found to be key factors for superior performance of the MoO_x/CeO_2 – ZrO_2 catalyst. The conversion of benzylamine is highly dependent on the catalyst amount and reaction time. It was found that the steric hindrance of the groups attached to benzylamine plays a key role, especially in the oxidation of secondary benzylamines. It is therefore suggested that the catalytic efficiency of ceria-based materials for the solvent-free aerobic oxidation reactions can be improved by modifying their unique textural, structural, and acid properties.

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