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Sequential oxidation and condensation of alcohols to benzimidazoles/benzodiazepines by MoO₃–SiO₂ as a heterogeneous bifunctional catalyst

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1. Introduction

Benzimidazole structural motifs have attracted much interest in diverse areas of medicinal chemistry. These heterocycles have shown various pharmacological activities such as anti HIV [1], poli(ADPribose)phosphorilase inhibitors [2], Histamine H₄ receptor binders [3], antiparasitic [4], cardiovascular [5], anticancers [6], and antihypertensives [7]. In view of the tremendous biological activities of benzimidazoles, their preparation has gained considerable attention in recent years. Similarly, benzodiazepines are also used as intermediates for the synthesis of fused ring compounds such as triazolo-3.5-oxadiazolo- [8], oxazino- [9], and furano-benzadiazepines [10]. Despite their wide range of pharmacological, industrial and synthetic applications, the synthesis of 1,5-benzodiazepines has received little attention. Benzodiazepines have been synthesized by the condensation of *o*-phenylenediamine (OPDA) with α , β -unsaturated carbonyl compounds, β-haloketones or with ketones. Many reagents have been reported in the literature for this condensation, including BF₃etherate [11], polyphosphoric acid [12], SiO₂ [13], MgO/POCl₃ [14], Yb(OTf)₃ [15], acetic acid under microwave conditions [16] and in ionic liquids [17]. Many of these processes suffer from one or more limitations, such as long reaction time, occurrence of several side reactions, drastic reaction conditions, low yield of desired products and tedious work-up procedures.

ABSTRACT

Sequential oxidation of alcohols to their corresponding aldehydes/ketones using H_2O_2 as a green oxidant and its further condensation with diamines to yield benzimidazoles/benzodiazepines with minimum side product formation under mild reaction conditions has been described. MoO_3 -SiO₂ is explored as a heterogeneous bifunctional catalyst for both oxidation as well as condensation reaction thus making it a versatile catalyst. The prepared catalysts were characterized using FT-IR, Raman spectroscopy, XRD, SEM and NH₃-TPD to study its surface properties. MoO_3 -SiO₂ shows good catalytic activity and reusability for both the reaction systems giving high yields of the desired products.

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However, the traditional synthesis of benzimidazoles involves reaction between OPDA and carboxylic acid or its derivatives (nitriles, amidates, and orthoesters) under harsh dehydrating conditions [18–23]. Some other strategies for their synthesis utilise *o*-nitroanilines as intermediates or resort to direct *N*-alkylation of an unsubstituted benzimidazole [24]. Condensation of OPDA with aldehyde in the presence of oxidative reagents such as $I_2/KI/K_2CO_3/H_2O$ [25], sodium metabisulfite [26], $Na_2S_2O_5$ under microwave irradiation [27], silica sulfuric acid [28], iodobenzene diacetate (IBD) [29], HCl/H_2O_ [30], air in dioxane [31], bromodimethylsulfonium bromide (BDMS) [32], and CAN/H_2O_ [33] have also been reported.

Very recently, Corma et al. [34] have reported a new route for synthesis of benzimidazole wherein the starting reactant alcohol is oxidized to generate aldehyde *in situ* and then the diamines are added to yield the corresponding benzimidazoles using Au/CeO₂ and Pd/MgO as bifunctional catalyst. Although this methodology shows utilization of bifunctional catalysts to couple both the steps of oxidation and cyclization there is enough scope to improve this route as it suffers from drawbacks such as use of oxidant (O₂) under pressure conditions, long reaction time, use of expensive Au or Pd based catalyst and complex reaction procedure.

In continuation of our endeavour to develop new synthetic methodologies using bifunctional catalysts herein we report, MoO_3 -SiO₂ as a heterogeneous bifunctional catalyst for sequential oxidation of alcohols to their corresponding aldehydes/ketones using H_2O_2 as a green oxidant and its sequential condensation with OPDA to yield benzimidazoles/benzodiazepines with minimum side product formation under mild reaction conditions (Scheme 1).

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2. Experimental

2.1. Materials

All chemicals were procured from firms of repute. Various alcohols were purchased from Sigma-Aldrich. All solvents used were purchased from S. D. Fine Chem. India Ltd. All the chemicals were used without any further purification.

2.2. Catalyst preparation

MoO₃/SiO₂ catalysts with varying molybdenum oxide molar concentrations (5, 10, 15, 20, 25) were prepared. Ammonium heptamolybdate (AHM) and tetraethyl orthosilicate (TEOS) were used as molybdenum and silica sources, respectively. In a typical procedure 20 mol% MoO₃/SiO₂ catalyst was synthesized by dissolving 14.11 g AHM in 40 mL distilled water at 80 °C. This hot solution was added drop wise to the dry isopropyl alcohol solution of TEOS (48.0 g) with constant stirring. The resultant transparent greenish gel was air dried and calcined at 500 °C in air in a muffle furnace for 12 h. Similarly catalysts with 5, 10, 15 mol% Mo loadings were prepared. The prepared catalysts are further named as 5MoO₃-SiO₂, 10MoO₃-SiO₂, 15MoO₃-SiO₂ and 20MoO₃-SiO₂. Pure high surface area silica catalyst was prepared for comparison by adding 52 g TEOS to 30 g dry isopropyl alcohol; to this mixture 0.02 g ammonia solution (25%) was slowly added with constant stirring. The transparent white gel thus obtained was air dried and calcined in a muffle furnace at 500 °C for 12 h [35].

2.3. Characterization techniques

The FT-IR spectra were recorded using a Perkin Elmer (Spectra 100) spectrometer by KBr pellet technique. The laser Raman spectrum was obtained on a Jobvin-Yvon-Horiba (HR800UV) Raman spectrometer at ambient conditions equipped with laser supplying the excitation line at 514.5 nm with 1-10 mW. Powder X-ray diffraction (XRD) of the catalyst was recorded with a (Philips 1050) diffractometer using graphite monochromatized Cu-K α radiation over a 2 θ range of 10–90°. SEM images were recorded using a Tungsten source on JEOL model JSM-6390 instrument. NH₃-TPD technique was used to assess the acidic strength of the catalyst using a conventional flow reactor on Micrometrics microbalance using 20 mg sample of the catalyst and a commercial 10% NH₃ in He gas mixture. Gas Chromatogram were recorded on Thermofisher GC-1000 equipped with capillary column (30 m×0.32 mm1D–0.25 μ m BP-10). GC–MS spectra were recorded on Shimadzu (GCMS-QP 2010). ¹H and ¹³C NMR spectra were recorded on Joel-300 MHz NMR spectrometer using TMS as an internal standard.



Scheme 1. Sequential oxidation and condensation for synthesis of benzimidazole and benzodiazepine.

2.4. Typical experimental procedure

2.4.1. Synthesis of benzimidazoles

2 mmol of primary aromatic alcohol was added to the mixture of 6 mmol of 30% H₂O₂ and 20 wt.% of the catalyst in a 25 mL round bottom flask fitted with a distillation condenser and were heated at 70 °C for 7 h. The reaction mixture was further cooled till room temperature, to this 2 mmol of OPDA (in aliquots) and 2 mL ethanol was added. The intermediate (aldehyde) was monitored by TLC/gas chromatography. After completion of the reaction ethyl acetate (10 mL) was added, and the organic solution was separated from catalyst by filtration. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography over silica gel eluting with hexane/ ethyl acetate 9:1 mixture, yielding the products. The products were identified by GC–MS and confirmed by NMR.

2.4.2. Synthesis of benzodiazepines

2 mmol of secondary alcohol was added to the mixture of 6 mmol of 30% H_2O_2 and 20 wt.% of the catalyst in a 25 mL round bottom flask fitted with a distillation condenser and were heated at 70 °C for 7 h. The reaction progress was monitored by TLC/gas chromatography analysis. The reaction mixture was further cooled till room temperature and to this 1 mmol OPDA (in aliquots) and 2 mL of ethanol was added. After completion of the reaction ethyl acetate (10 mL) was added, and the organic solution was separated from catalyst by filtration. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography over silica gel eluting with hexane/ethyl acetate 9:1 mixture, yielding the products. The products were identified by GC–MS and confirmed by NMR.

2.4.3. Reusability of catalyst

After completion of reaction, reaction mixture was filtered under vacuum and the catalyst was washed with acetone (3 times) and then kept for drying at 100 °C for 2 h, after which the catalyst was reused for next cycle. The catalyst reusability was checked for first step of oxidation and also for the sequential protocol.

3. Results and discussion

3.1. Characterization of MoO₃-SiO₂

3.1.1. FT-IR analysis

The FT-IR spectra of all the catalyst samples prepared by sol-gel technique are presented in Fig. 1. The intensive bands at around 1090, 800 and 460 cm⁻¹ are ascribed to Si–O vibration of SiO₂, and the broad band centered at about 960 cm⁻¹ with a shoulder at about 920 cm⁻¹ for all the samples is the sign of supported molybdenum species. All the above mentioned peaks were observed for Mo loaded catalysts however, peaks at 960 and 920 cm⁻¹ were not observed for MoO₃ (Fig. 1e) [36].

3.1.2. Raman spectral analysis

Raman spectrum for $15MoO_3$ –SiO₂ catalyst is shown in Fig. 2. The spectrum shows presence of Mo species anchored to silica surface. Bands for SiO₂ matrix can be seen at 440–550 cm⁻¹ and 609–615 cm⁻¹ attributed to strained trisiloxane rings; Si–O stretches appear at 880–925 cm⁻¹, assigned to symmetrical stretching of the Si–O bonds of geminal silanols and to the siloxane bridges (Si–O–Si). Raman spectrum shows bands at 993, 820 and 630 cm⁻¹ which may be assigned to the stretching mode of terminal Mo=O groups, the asymmetric and symmetric modes of Mo–O–Mo bridges in α -MoO₃ respectively. Signal at 960–970 cm⁻¹ may be attributed to the symmetric stretching mode of terminal Mo=O bonds with a possible contribution of Si–O stretching of SiOH–OMo and of Si–O–Mo moieties. However, typical bands at 851 and 781 cm⁻¹ ascribed for β -MoO₃ were not present [37].



Fig. 1. FT-IR spectra of a) SiO_2 , b) $5 MoO_3$ -Si O_2 , c) $10 MoO_3$ -Si O_2 , d) $15 MoO_3$ -Si O_2 , and e) $20 MoO_3$ -Si O_2 .

3.1.3. XRD studies

The XRD patterns of all the catalysts prepared by sol-gel are shown in Fig. 3. For comparison, the XRD pattern of pure silica is also included (Fig. 3). The patterns show the amorphous nature of the material at low Mo loadings (Fig. 3b-d) indicating a very high dispersion of amorphous molybdenum oxo species on amorphous silica support up to 15 mol% loading of Mo. The XRD patterns of 20% Mo loaded catalyst (Fig. 3e) exhibit sharp peaks on the broad underlying peaks characteristic of the amorphous silica at $2\theta = 24^\circ$. These intense peaks observed at $2\theta = 12.9$, 23.4, 25.8 and 27.4° are characteristic of the α -MoO₃ orthorhombic phase [38]. It is interesting to note that even though the MoO_3 is in the crystalline form at higher Mo loading, the silica support still retains its amorphous nature leading to the high surface area of the catalysts [39]. It appears from the XRD results that up to 15 mol% MoO₃ loading there is a uniform dispersion of amorphous molvbdenum oxo species on silica support, however at higher loading; MoO₃ crystalline bulk phase is formed on amorphous silica support (Fig. 3).

3.1.4. SEM analysis

The scanning electron microscope study provides an insight on the morphological changes in MoO_3 –SiO₂. SEM image of SiO₂ shows presence of smooth surface without any pores, however micrographs for MoO_3 –SiO₂ clearly shows marked difference in the morphology from that of SiO₂. The differences in SEM images thus, illustrate that incorporation of MoO_3 changes the morphological structure of SiO₂ surface considerably (Fig. 4).



Fig. 2. Raman spectrum of 15MoO₃-SiO₂.



Fig. 3. X-ray diffraction of a) SiO₂, b) 5 MoO₃–SiO₂, c) 10 MoO₃–SiO₂, d) 15 MoO₃–SiO₂, and e) 20 MoO₃–SiO₂.

3.1.5. NH₃-TPD analysis

Acidity measurements were carried out using NH₃-TPD analysis (Table 1), it was found that the acidity of SiO₂ (entry 1) was very less compared to the Mo loaded SiO₂. This showed that the acidity of the catalyst is majorly due to Mo species. It was observed that as the percentage of Mo loading was increased acidity of the catalyst was also increased (entries 2–4). However, the best results were obtained with 15 mol% Mo loadings (entry 4) although 20% Mo loading had higher acidity. Similar results were obtained by Wang et al. [40] where the decreased activity of the MoO₃–SiO₂ catalyst at higher MoO₃ loading was attributed to the aggregation of MoO₃ particles on SiO₂ surface. The aggregation of MoO₃ at higher loading can also be observed in XRD results in Fig. 3.

3.2. Influence of MoO₃-SiO₂ with different Mo loading

In order to study various reaction parameters for sequential oxidation and condensation we chose sequential oxidation of benzyl alcohol and condensation of the formed benzaldehyde with OPDA as a test reaction. We started our investigation by using individual component oxides SiO₂ and MoO₃ as the catalyst (Table 1; entries 1, 2). As expected SiO₂ showed no product formation, however, MoO₃ provided low yield of the desired 2-phenyl benzimidazole. Next, MoO₃–SiO₂ with different Mo loadings were used and it was observed that as Mo loading increased from 5–15 mol% the yield of 2-phenyl benzimidazole also increased (entries 3–5). However, on further increasing the Mo loading till 25 mol% the yield decreased to 72%. Thus 15MoO₃–SiO₂ was used as the preferred catalyst for further studies.

3.3. Influence of catalyst concentration

The effect of catalyst concentration on the given reaction protocol was studied. It was found that as the concentration of $15MoO_3$ -SiO₂ was increased from 5 wt% to 20 wt% (Table 1; entries 5, 8–11) yield of the desired benzimidazole also increased. On further increasing the concentration to 25 wt% no change in yield was observed and hence 20 wt% of MoO_3 -SiO₂ catalyst was chosen as the optimum concentration.



Fig. 4. SEM images of a) SiO₂ and b)15MoO₃-SiO₂.

3.4. Influence of solvent for oxidation of alcohols

As first step is crucial in sequential synthesis, it was very important to check the influence of solvent on reaction outcome. Generally, chlorinated solvents are used for oxidation of alcohols to aldehydes which limits their application from an environment point of view and hence we intended to use an alternate solvent system and compare it with effect of chlorinated solvent medium (Table 2). When CH₂Cl₂ and CHCl₃ (entries 1, 2) were used as a solvent the yield of benzaldehyde was found to be . reaction using acetonitrile as a solvent yielded desired product in 90% (entry 3). However, reaction without any solvent provided excellent yield of the desired product (entry 5) hence solvent free conditions were applied for further studies.

In the second step i.e. condensation of formed benzaldehyde with OPDA, solvent free conditions gave by products of bis-anils and 1,2disubstituted benzimidazoles. Thus in order to increase the yield of our desired 2-phenyl benzimidazole solvent effect was studied where solvent was added along with OPDA. Amongst the screened solvents ethanol was used as the solvent of choice as it gave the maximum yield of desired benzimidazole.

Table 1

Influence of $\mathsf{MoO}_3\text{-}\mathsf{SiO}_2$ and its component oxides on sequential oxidation and condensation.^a

Entry	Catalyst	Catalyst amount (wt.%)	NH ₃ desorbed (mmol/g)	Yield ^b (%)
Effect of	Mo loading			
1	SiO ₂	20	0.02	-
2	MoO ₃	20	0.13	28
3	5 MoO ₃ -SiO ₂	20	0.47	42
4	10 MoO ₃ -SiO ₂	20	0.62	63
5	15 MoO ₃ -SiO ₂	20	0.77	77
6	20 MoO ₃ -SiO ₂	20	0.82	73
7	25 MoO ₃ -SiO ₂	20	0.80	72
Effect of catalyst loading				
8	15 MoO ₃ -SiO ₂	5	-	38
9	15 MoO ₃ -SiO ₂	10	-	63
10	15 MoO ₃ -SiO ₂	15	-	72
11	15 MoO ₃ -SiO ₂	25	-	77

^a Reaction conditions: benzyl alcohol (2 mmol), catalyst, H_2O_2 (6 mmol), 7 h at 70 °C. OPDA (2 mmol) and ethanol (2 mL) added after 7 h and stirred at room temperature further for 3.5 h. ^b Isolated yield.

3.5. MoO₃-SiO₂ catalyzed sequential oxidation and condensation

To test the general scope and versatility of this procedure for synthesis of variety of substituted benzimidazoles, we examined various substituted aryl alcohols. Thus, for the initial step of oxidation benzyl alcohol (2 mmol) and 30% H_2O_2 (6 mmol) were heated to 70 °C for 7 h which is then followed by addition of OPDA (2 mmol) and ethanol (2 mL) and allow it to stir for next 3.5 h at room temperature (Table 4). We were pleased to find high yields for the initial oxidation reaction as it was a prerequisite for our sequential reaction protocol. As Table 3 shows, benzyl alcohol and substituted benzyl alcohols bearing electrondonating group such as $-CH_3$ and $-OCH_3$ provided good yields of the desired benzimidazoles (entries1–3). However, when electron-withdrawing substituents like Cl⁻ and Br⁻ was attached to benzyl alcohol marked difference was observed and yields of benzimidazoles were decreased (entries 4, 5).

To extend the scope of this methodology, we also examined sequential oxidation of secondary alcohols to ketones and its condensation with OPDA to give their corresponding 1, 5-benzodiazepine derivatives under same reaction conditions. To effect this transformation, phenethyl alcohol and substituted phenethyl alcohols were studied (Table 3, entries 6–10) and were found to give high yields of benzodiazepines. Phenethyl alcohol reacted effectively giving 94% of acetophenone which on further condensation with diamine gave 82% of the desired benzodiazepine. Phenethyl alcohol with electron-donating substituents like $-CH_3$, $-OCH_3$ and electron-withdrawing group like Cl^- gave good yields of their respective benzodiazepines between 84–72% (entries 7–9).

Cyclic alcohol like cyclohexanol (entry 10) also reacted smoothly to give high yields up to 74% of the corresponding fused ring benzodiazepines.

Table 2Influence of solvent for oxidation of alcohols.^a

Entry	Solvent	Yield ^b (%)
1	CH ₂ Cl ₂	84
2	CHCl ₃	85
3	CH₃CN	90
4	C ₂ H ₅ OH	72
5	-	91

 $^a\,$ Reaction conditions: benzyl alcohol (2 mmol), 15 MoO_3–SiO_2 (20 wt%), 30% H_2O_2 (6 mmol), solvent (2 mL), 7 h at 70 °C. $^b\,$ GC yield.

Table 3

Sequential oxidation and condensation for synthesis of benzimidazoles and benzodiazepines.^a

Entry	Alcohol	Aldehyde/ketone ^b	Benzimidazol/benzodiazepine ^c	Yield ^{b/c} (%)
1	ОН	ОН		91/77
2	Н3С ОН	H ₄ C		94/80
3	Н3СО ОН	H ₂ CO	N N H OCH ₃	96/85
4	СІ	CI H		86/54
5	Вг	Br		85/52
6	OH		$ \underset{N}{\overset{H}{\underset{N}{\overset{Ph}{\underset{N}{\overset{Ph}{\underset{Ph}{\overset{Ph}{\underset{Ph}{Ph}{\underset{Ph}{\underset{Ph}{\underset{Ph}{\underset{Ph}{\underset{Ph}{\underset{Ph}{P}{Ph}{Ph}{Ph}{Ph}{Ph}{Ph}{Ph}{Ph}{$	94/82
7	он н _э с	H ₃ C	$ \begin{array}{c} $	94/84
8	Н3СО	H ₃ CO	$ \underset{N}{\overset{H}{\longrightarrow}} \underset{PhOCH_{3}}{\overset{PhOCH_{3}}{\longrightarrow}} $	95/83
9	CI OH		$ \begin{array}{c} H \\ N \\ N \\ N \\ PhCl \\ PhCl \\ \end{array} $	88/72
10	OH	Ů	H	90/74
	\bigcirc	\bigcirc		

^a Reaction conditions: alcohol (2 mmol), 15 MoO₃-SiO₂ (20 wt%), H₂O₂ (6 mmol), 7 h at 70 ^oC. OPDA (2 mmol) and ethanol (2 mL) added after 7 h and stirred at room temperature further for 3.5 h. ^b G.C yield.

^c Isolated yield.

Table 4

Reusability study of MoO₃–SiO₂ for oxidation and condensation reactions.^{a,b}

Run	Yield ^{a,c} (%)	Yield ^{b,d} (%)
1	91	77
2	88	74
3	87	74
4	86	72
5	86	72

 $^a\,$ Reaction conditions: benzyl alcohol (2 mmol), 15 MoO_3–SiO_2, 30% H_2O_2 (6 mmol), 7 h at 70 °C.

 $^{\rm b}$ Reaction conditions: benzyl alcohol (2 mmol), 15 MoO₃–SiO₂, 30% H₂O₂ (6 mmol), 7 h at 70 °C. OPDA (2 mmol) and ethanol (2 mL) added after 7 h and stirred at room temperature further for 3.5 h.

^c GC yield.

^d Isolated yield.

3.6. Catalyst reusability

Reusability was initially studied for the first step of oxidation as that would give us an insight whether the active catalytic sites were available for the second step of condensation. From Table 4, it is clearly observed that the catalyst was successfully reused several times after the first step i.e. oxidation of alcohol to aldehyde without any appreciable loss of its activity. Similarly, reusability for sequential reaction was also carried out and catalyst was found to be reusable for five cycles.

4. Conclusion

In conclusion, we have developed a efficient catalytic protocol wherein MoO_3 –SiO₂ is explored as a heterogeneous bifunctional catalyst for sequential oxidation and condensation reaction of alcohols with *o*-phenelene diamine to give to their corresponding benzimidazoles/benzodiazepines. Environmentally viable H₂O₂ was used as an oxidant for oxidation of alcohols. The protocol offers minimum side product formation and works under mild reaction conditions. Easy work-up procedure and reusability of the catalyst makes the catalytic system highly attractive.

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