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Research Article

Recyclable Nanocrystalline Copper Based on MoO_3/SiO_2 as an Efficient Catalyst for Acylation of Amines

Jaymala M. Deshmukh, Sharda P. Dagade*

Department of Chemistry, Yashwantrao Mohite College Pune-411 038, Bharati Vidyapeeth Deemed University, Pune, India

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Abstract

Various loadings of copper supported on MoO_3/SiO_2 (CMS) were prepared by sol-gel method and used for the synthesis of substituted benzimidazole. Further it was characterized by using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), Transmission Electron Microscopy (TEM), and acidity measurement by potentiometric method. XRD results indicated that Cu is present on the support primarily as CuO. The SEM and TEM results showed dispersion of cubic CuO nanoparticles on the surface. These mixed oxides were studied for the acylation of *o*-phenylene diamine with acetic acid in liquid phase. 10 wt. % CMS gave best results at 110 °C with 94.81 % conversion of *o*-phenylene diamine and 100 % selectivity of substituted benzimidazole. Different parameters were studied for optimization of acylation, such as: temperature, acylating agents, solvents, amount of catalyst, and different catalysts. The CMS catalyst could also be recovered and reused at three times without any discernible decrease in its catalytic activity. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Acylation; *o*-Phenylene Diamine; Mixed Oxide; Benzimidazole; Sol-Gel

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1. Introduction

Solid acid catalysts are widely used in the chemical industry for various reactions such as esterification, acetalization, alkylation, and oligomerization [1-5]. Solid acid catalysts are very effective and some of them are known to exceed the acidity of concentrated acids, these catalysts hold their acidity internally and thus easy to handle and also reaction vessels or reactors are not corroded. Thus solid acid catalyst can allay concerns about safety and environmentally hazardous [6]. Supported or unsupported molybdenum oxide form is widely used as catalysts in a great number of reactions. A well known solid acid catalyst is molybdenum supported on silica which possesses both strong Lewis and Brönsted acidities [7,8]. Degree of dispersion and structure of the supported phase are the important factors which help to improve the catalytic activity of supported molybdenum oxide.

The main objective of green and sustainable chemistry is an efficient separation and recycling of catalysts. Hence heterogeneous catalysts are more superior over homogeneous as they are easily recoverable, reusable with minimum waste.

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* Corresponding Author.
E-mail: dagade@rediffmail.com (S.P. Dagade)

In pharmaceutical industry, benzimidazole is an important intermediate and it is a heterocyclic aromatic organic compound consisting of a fusion of benzene and imidazole. Benzimidazole is a privileged scaffold, having a variety of therapeutic uses including antitumor, antiulcer, antiviral [9-12], antibacterial [13-14], anti-inflammatory, anticonvulsant, analgesic [15], and ophthalmology [16]. Many workers have worked on condensation of *o*-phenylene diamine with carboxylic acid, aromatic aldehyde, acid anhydride, esters and urea under different reaction conditions. Recently, reported the synthesis of benzimidazole by using different carboxylic acids i.e acetic acid, salicylic acid and butanoic acid in presence of ρ-TsOH catalyst [17]. Few reactions were carried without catalyst in presence of different types of acids. Mohammad *et al.* [18] studied synthesis of 2-(phenoxymethyl)-1H-benzimidazole from condensation of o-phenylene diamine with phenoxyacetic acid in acidic medium, while Jubie *et al.* [19] were synthesized various benzimidazoles without catalyst from condensation of o-phenylene diamine with appropriate acid, was subjected to microwave irradiation.

From literature found that, condensation of *o*-phenylene diamine with acids or aldehydes over homogenous catalysts such as copper acetate and lead tetra acetate [20], zinc acetate [21], ammonium chloride [22], zinc chloride [23], ammonium bromide [24], copper hydroxide [25], fluoroboric acid [26], boric acid [27], zinc triflate [28], ceric ammonium nitrate [29], and nickel acetate [30] were studied. In acylation reaction transition metals used as catalyst namely palladium [31], rhodium [32], and ruthenium [33]. These conditions are not favourable from economic and industrial point of view.

To overcome the difficulties with homogeneous catalysts, many researchers were tried different heterogeneous catalysts [34]. Few mixed oxides have been reported for synthesis of benzimidazole derivatives as solid acid catalyst. From literature review heterogeneous mixed oxides were used as a catalyst, such as: RuO_2-MoO_3 [34], clay supported titanium [35], SiO_2-Pr-SO_3H [36], SBA-Pr-SO_3H [37], yttria-zirconia [38], ceria-yttria [39], polymer supported sulphanilic acid [40], Yb $(OTf)_3$ [41], and MoO_3/CeO_2-ZrO_2 [42], as a green heterogeneous catalyst with good catalytic activity for the synthesis of benzimidazole derivatives.

Synthesis of substituted benzimidazole were also carried out in ultrasonic and microwave irradiation by using $FeCl_3/Al_2O_3$ [43], ammonium nickel sulphate [44], montmorillonite KSF [45], $SnCl_2$ [46], and zeolite [47] as catalyst.

From literature, it was found that use of MoO_3/SiO_2 as support help to enhance the activity of the catalyst. Molybdenum possesses both types of acidity, due to which well known acid catalyzed reactions are reported in last few years. Therefore for synthesis of substituted benzimidazole, MoO_3/SiO_2 was used along with copper to increase the active sites. Also in literature, use of ternary mixed oxide catalyst for this reaction was not reported. Therefore, nano crystalline $Cu/M_OO_3/SiO_2$ (CMS) mixed oxide catalyst was prepared by sol gel method used for this reaction and characterized by XRD, SEM, EDX, TEM, and acidity measurement.

A series of some benzimidazole derivatives were synthesized from acetic acid in presence of ecofriendly novel $Cu/MoO_3/SiO_2$ (CMS) solid acid catalyst. Reaction conditions were optimized for the reaction by using different parameters. Moderate reaction conditions and lower amount of catalyst were more suitable to achieve higher conversion as well as selectivity of substituted benzimidazole.

2. Materials and Method

2.1 Material

All the reagent viz., tetraethyl orthosilicate (TEOS), ammonium molybdate (AHM), copper acetate, isopropyl alcohol, *o*-phenylene diamine, acetic acid, formic acid, chloroacetic acid, and benzoic acid, were of A.R grade and were obtained from Merck chemicals, India.

2.2 Method

To compare the catalytic activity of synthesized catalyst, catalysts prepared by two different methods, i.e. sol-gel method and impregnation method.

2.2.1 Sol-gel method

Copper supported on MoO_3/SiO_2 (CMS) catalyst was prepared with varying wt. % copper oxide concentration (1, 5, 10, 15, and 20 wt%) in a typical procedure. The 10 wt. % CMS catalyst was synthesized by dissolving equimolar quantity of AHM in 40 ml distilled water in sonicator for 30 min. This solution was added drop wise to the tetra ethyl orthosilicate (40 g) with constant stirring. To this mixture, aqueous solution of copper acetate was added. The resultant transparent bluish gel was obtained, further air dried and then heated in oven at 100 °C for 10 hour. Dried catalyst was calcined at 500 °C for 10 hours. Similarly, catalysts with

1, 5, 15, and 20 wt. % CMS were prepared [48]. MS catalysts were prepared without addition of copper acetate to the mixture.

2.2.2 Wet impregnation method

In a beaker, equimolar copper acetate solution was dissolved in distilled water and added to already synthesized 20 wt.% MS (Molybdenum supported on silica) by sol gel method and used as support for impregnation. The mixture was dried at room temperature then heated in oven and calcined in furnace.

2.3 Apparatus and Techniques

The synthesized catalysts obtained by the sol-gel process and were characterized by various spectroscopic and non-spectroscopic methods including X-ray diffraction (XRD), Scanning Electron microscope (SEM), Energy Dispersive Spectrometer (EDX), Transmission Electron Microscope (TEM), and surface acidity by potentiometric titration method.

The crystallite size of the synthesized samples was calculated by XRD using Rigaku Miniflex diffractometer equipped with a Ni filtered Cu-Kα line radiation source (λ=1.54178 Å) was used to record. Scanning Electron Microscope coupled with EDX (JEOL-JSM 6360A) was used for external surface of hybrid material. SEM and Energy dispersive X-ray analysis detector (EDX) were obtained at accelerating voltage 20 KeV. Sample were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. SEM images were made using a scanning electron microscope FEI Quanta 200 with EDX attachment. TEM measurements were performed on a JEOL model 1200EX instrument operating at an accelerating voltage at 120 kV and on a Tecnai G2-20 FEI instrument operating at an accelerating voltage at 200 kV. Before analysis, the powders were ultrasonically dispersed in ethanol, and two drops of ethanol containing the solid were deposited on a carbon coated copper grid.

Potentiometric titration was used for measurement of total acidity of solid samples [49, 50]. The solid acid catalyst (0.1 g) was suspended in 10 mL acetonitrile and stirred for 4 h. Then, the suspension was titrated with 0.1 N n-butylamine in acetonitrile at 0.1 mL.min^{-1}. The electrode potential (E_i) variation was measured using Seven Multi, METTLER-TOLEDO, GMBH, Switerl. A scale of acid strength measurement as follow: E_i <100 mV for very weak sites; 100 < E_i < 0 mV for weak sites; 0 < E_i < 100 mV for strong acid sites and finally E_i > 100 mV for very strong sites [51].

3. Results and Discussion

3.1 XRD Pattern

In Figure 1, the diffraction pattern of pure silica was amorphous in nature. XRD patterns of the MS and CMS materials, indicating characteristic reflections in the 2θ range of 20°-80°. XRD results showed that synthesized MoO_3/SiO_2 powder was mainly in α-MoO_3 phase. No β-MoO_3 phase was observed in the structure because the samples were calcined at 500 °C, a temperature at which β-MoO_3 phase was not stable. The XRD phase present in the

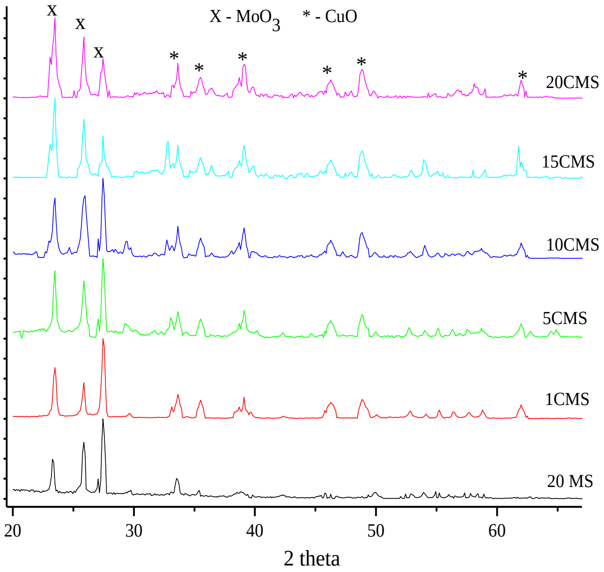


Figure 1. XRD patterns of the calcined copper supported mixed catalysts at 500 °C

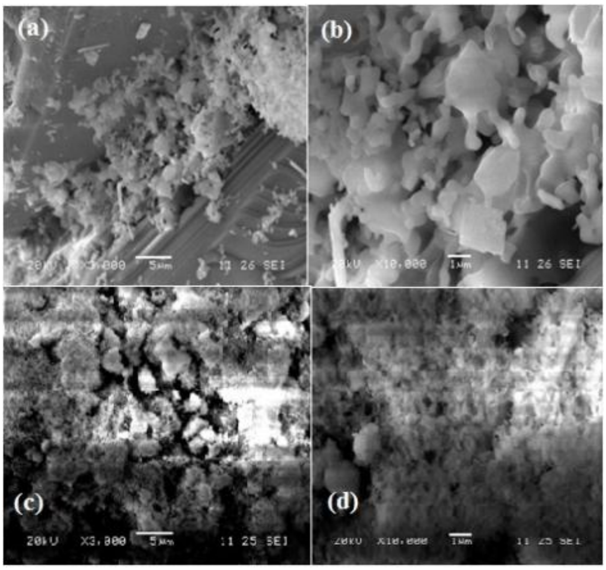


Figure 2. SEM images (a) 20 wt. % MS and (b) 10 wt. % CMS catalyst

prepared samples were identified with the help of JCPDS data files. The data was reported in earlier paper [52].

For all CMS catalyst, the diffraction peak of α-MoO_3 at 12.86°, 23.4° 25.8°, and 27.4° can be index to 001, 101, 002, 011 planes. In case of copper, CuO phase was found at 33.6°, 35.5°, 38.7°, 39.0°, 46.2°, 48.9°, and 61.98°, can be index at 110, 002, 111, 020, 133 (JCPDS-45-1548) lattice planes of CuO, indicating that Cu is present on the MoO_3/SiO_2 support primarily as the CuO phase are represented in Figure 1. Crystallite size of the CMS catalysts were calculated by using Scherrer equation from XRD found to be 48-89 nm.

3.2 SEM and EDX

SEM and TEM were used to examine the morphology of the solid acid catalyst. The above SEM data revealed that, all the catalysts were showed good dispersion of CuO on MoO_3/SiO_2 and EDX confirmed composition of the prepared catalysts.

3.3 TEM

TEM is commonly used for studying the size and nature of supported catalysts. Detection of supported particles is possible provided that there is sufficient contrast between particles of metal oxides and MS as support. Study the dispersion of supported oxides is the application of transmission electron microscopy. From images it was observed that, the agglomeration of nanoparticles has taken place. From the Figure 4, the TEM images of 1 wt.% CMS and 10 wt.% CMS indicated that, the catalysts were nano crystalline in nature.

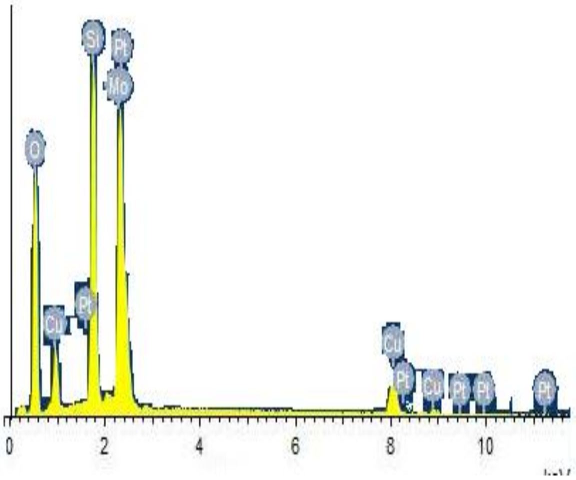


Figure 3. EDEX of 10 wt.% CMS catalyst

3.4 Surface Acidity

All calcined samples were measured for acidic properties using nonaqueous potentiometric titration of n-butylamine in acetonitrile [49]. Representative titration curves of calcined samples are shown in Figure 5. As it can be noted in the Table 1, for the same calcination products, both of acid amount and acid density increased with the increase of CuO on MoO_3 loading up to 10 wt.% and further it decreased slightly. This indicated that CuO content, the state of CuO species on the surface of MoO_3 and therefore it helps to enhance the acidic properties of the catalysts.

Potentiometric titration with 0.1 N n-butyl amine was used for the total number of acid sites and their relative strength, for the catalysts under investigation. Maximum acid strength of the sites was the initial electrode potential (E_i). The total number of acid sites indicated the value of meq amine/g solid, where the plateau was reached in titration curves [50, 51]. Table 1 showed the potentiometric titration results for all samples. From these results concluded that the all the CMS sample has weak acid sites and its maximum strength is 80 mV. Among all these catalysts, 10 wt. % CMS showed the higher acidic strength. Data was reported in earlier paper [52].

3.5 Catalytic Activity

Synthesized mixed oxide catalyst (CMS) were used in acylation reaction, to study the catalytic performance. The reaction between *o*-phenylene diamine with acetic acid to form substituted benzimidazole. The experimental procedure of acylation reaction as below:

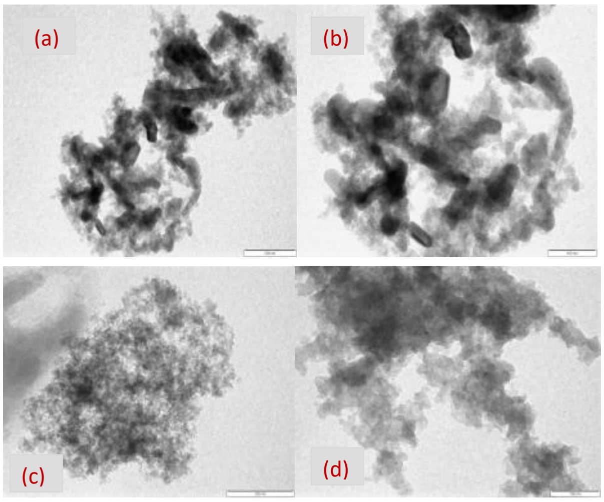


Figure 4. TEM images of 1 wt.% CMS and 10 wt.% CMS solid acid catalyst

Acylation reaction was carried out in a two necked round bottom flask fitted with water condenser. The catalyst (0.25 g) was activated at 200 °C and used for the reaction. To the mixture of *o*-phenylene diamine (1 mmol), acetic acid (1 mmol), and ethanol (10 mL), CMS catalyst was added in the flask. The reaction mixture was heated at temperature of 110 °C with constant stirred in oil bath. The progress of the reaction was monitored by TLC (n-hexane: ethyl acetate), and then by GC equipped with a flame ionization detector and capillary column (Shimadzu 2014 series). Samples of the reaction was withdrawn at regular time intervals and analyzed. Products were identified by comparing them with standard sample. After completion of the reaction, the heterogeneous solid acid catalyst was removed easily by simple filtration. The acid catalyst was reactivated by simple washing subsequently with water and acetone and then calcined at 500 °C temperature.

3.5.1 Effect of temperature

The effect of reaction temperature on the conversion of *o*-phenylene diamine and product selectivity was studied in this paper. The reaction temperature was an important operation parameter, which remarkably affected the acylation of organic compound. Hence, a series of experiments were performed at 60, 80, 110, and 120 °C temperature, the conversion of amine increased from 57.86 to 94.81 %. Results were shown in Table 2. Lower conversion of 61.93 % obtained at 60 °C with lower selectivity for substituted benzimidazole. The conversion increased considerably when temperature of reaction mixture was increased to 110 °C, it showed increase in selectivity to 100 % as well as conversion of *o*-phenylene diamine to 94.81 %. This may due to the rate of formation of carbocation was more at 110 °C than higher temperature. Therefore as the temperature increased further to 120 °C selectivity decreased. Overall reaction was optimized at 110 °C and for further study temperature was kept constant. Reaction was carried out up to 8 h but maximum conversion was obtained after 4 hours only.

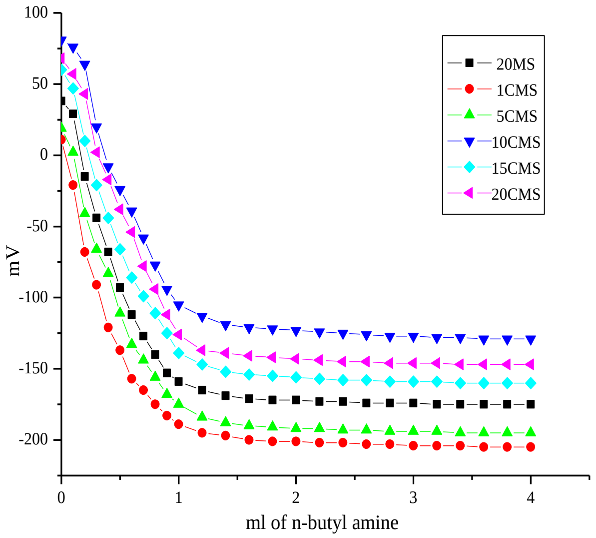


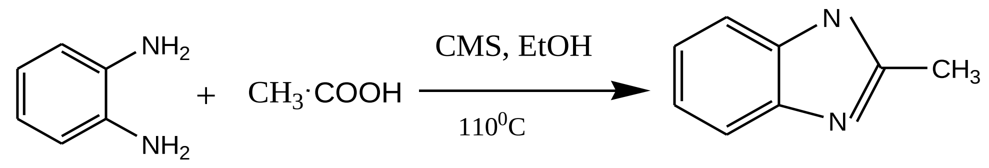
Figure 5. Potentiometric titration of n-butyl amine over calcined samples at 500 °C

3.5.2 Catalyst variation

To select the best catalyst for the optimization study, reaction were carried out on different loading of copper on molybdenum supported silica solid acid catalysts (20 wt.% MS, 1-20 wt.% CMS). Results were shown in Table 3 and compared with the reported reaction in the literature.

Table 1. Potentiometric titration data for the catalyst

Catalyst	(E_i mV) Maximum Acidic strength	Total acid sides
20 wt.%MS	38	0.12
1 wt.% CMS	12	0.14
5 wt.% CMS	17	0.22
10 wt.% CMS	80	0.30
15 wt.% CMS	60	0.16
20 wt.% CMS	68	0.25



o-phenylene diamine Acetic acid 2 methyl benzimidazole

Figure 6. Scheme of acylation of *o*- phenylene diamine with acetic acid

The reaction has been carried out at 110 °C for 4 h with molar ratio of 1:1 in the presence of 1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% CMS catalyst. In this work, it was found that the acylation reaction of *o*-phenylene diamine could proceed more effectively with 10 wt.% CMS. On increasing the catalyst concentration from 1 to 10 wt.%, conversion increased to 94.81 %. With 10 wt.% CMS catalyst gave maximum conversion, while at 15 wt.% and 20 wt.% CMS catalyst conversion as well as selectivity decreased. As per the acidity measurement study showed that 10 wt.% CMS was more acidic than 15 wt.% and 20 wt.% CMS catalysts. Therefore best results were obtained with 10 wt.% CMS catalyst.

These results were compared with literature (Table 3) as acylating agent acetic acid or benzaldehyde. Present result gave maximum conversion with 10 wt.% CMS catalyst at 110 °C within 4 hour, there was no need of microwave assembly to enhance the conversion.

Table 2. Effect of temperature on acylation of *o*-phenylene diamine

Temperature (°C)	% Conversion	% Selectivity
60	61.95	51.27
80	57.86	99.98
110	94.81	100

Reaction conditions: *o*-phenylene diamine: acetic acid- 1:1, solvent: ethanol, 4 h, 10 wt.% CMS-0.25 g

3.5.3 Effect of molar ratio

The reaction of *o*-phenylene diamine to substituted benzimidazole was carried out by keeping constant amount of *o*-phenylene diamine with varying amount of acylating agent acetic acid ratio from 1:0.5, 1:1, and 1:2. The result data clarified that the conversion of amine increased from 49 to 94 % (Figure 7). As the amount of acetic acid was increased with respect to ratio, there was decreased selectivity and also conversion of the product. Thus from

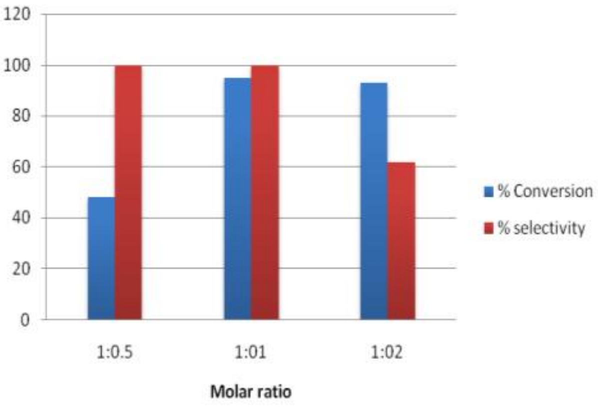


Figure 7. Study of Molar Ratio on acylation of *o*-phenylene diamine (Reaction conditions: 10 wt.% CMS-0.25 g, solvent: ethanol, catalyst-0.25 g, 4 h,110 °C)

Table 3. Effect of catalyst on conversion of *o*-phenylene diamine

Catalyst	Substitute	Condition	% Yield / Conversion	Reference
20 % MS	AA	EtOH, 4 h, 110 °C	30.62	Present work
1 % CMS	AA	EtOH, 4 h, 110 °C	68.12	Present work
5 % CMS	AA	EtOH, 4 h, 110 °C	81.57	Present work
10 % CMS	AA	EtOH, 4 h, 110 °C	94.81	Present work
15 % CMS	AA	EtOH, 4 h, 110 °C	72.00	Present work
20 % CMS	AA	EtOH, 4 h, 110 °C	85.31	Present work
p-TsOH	AA	Toluene, 3 h, reflux	72	[17]
WC	Phenoxy acetic acid	4N HCl, 110-120 °C, SF	84	[18]
WC	Acid	MW, 350 w, 25 min	48	[19]
10 % MoO_3/CeO_2-ZrO_2	Benzaldehyde	EtOH, 2 h, reflux	55	[41]
10 % Co_3O_4	Benzaldehyde	EtOH, RT, 6 h	78.9	[53]
Cu/TiO_2	octanol	Mesitylene, 24 h, 165 °C	65	[54]

Reaction conditions: *o*-phenylene diamine: acetic acid- 1:1, catalyst- 0.25 g, 110 °C the above observations, maximum conversion of *o*-phenylene diamine and selectivity of substituted benzimidazoles was obtained with 1:1 molar ratio. This indicated the exact amount of acetic acid required for the reaction to obtain the maximum conversion.

3.5.4 Effect of catalyst amount

This research also investigated the effect of the amount of catalyst on the reaction conversion. It was previously reported that for the Friedel-Crafts acylation using traditional catalysts, an excess over stoichiometric amounts of the Lewis acid can be required, for the formation of aryl products in significant amounts [55].

The catalyst concentration can be reduced by using solid catalysts for the reaction. The amount of catalyst was increased from 0.15 to 0.50 g by keeping other conditions constant. The selectivity for substituted benzimidazole was increased from 54.71 to 100 %. With increase in amount of catalyst there was slight decreased in conversion of amine. By comparing results, it concluded that the best results of acylation of *o*-phenylene diamine were obtained with 0.25 g of catalyst, may be due to the nanocrystalline size. Therefore more surface area help to enhance the catalytic activity. In absence of any catalyst showed conversion 22.28 % and also selectivity was lowered as compared to the solid acid catalyst.

3.5.5 Effect of acylating agent

The study was then extended to the Friedel-Crafts acylation of *o*-phenylene diamine with different acylating reagents, including acetic acid, formic acid, monochloroacetic acid, benzoic acid, 2-chloro benzoic acid, salicylic acid and cinnamic acid. The reaction was carried out for 4 h at 110 °C using 10 wt.% CMS catalyst with the molar ratio of 1:1. Posternak and coworkers [56] previously reported a positive effect of electron-withdrawing groups present in the acylating reagent for Friedel-Crafts acylation. Here we examined substituted acid and aldehydes including aliphatic and aromatic groups which underwent smooth conversion to afford a wide range of benzimidazole aromatic acid containing both electron withdrawing and electron donating groups worked in this reaction.

It indicated that maximum conversion was obtained with acetic acid with maximum selectivity. After changing the acylating agent, it gave less conversion as compared to acetic acid shown in Table 4.

3.5.6 Effect of various solvents

It is interesting to note that ethanol; a weak dipolar aprotic solvent that is immiscible with *o*-phenylene diamine afforded a much higher selectivity with a total conversion of 94.81 %. In comparison to the given in table strong solvents, ethanol enhanced the selectivity of substituted benzimidazole. Besides, different solvents affect the reactant or product through H-bonding, dipole-dipole interactions, van der Waals interactions, etc. [57]. The effect of solvents affecting the catalytic activity of CMS catalysts was investigated under the optimized reaction conditions. Among the solvent like ethanol, water, acetonitrile, carbon tetrachloride and water: ethanol used for this reaction, ethanol showed the highest yield for 4 h and

Table 4. Effect of amount of catalyst on conversion of *o*-phenylene diamine

Amount of catalyst (g)	% Conversion	% Selectivity
Without catalyst	22.28	49.56
0.15	97.90	54.71
0.25	94.81	100
0.50	93.95	99.98

Reaction conditions: *o*-phenylene diamine: acetic acid- 1:1, solvent: ethanol, 4 h, 110 °C

Table 5. Effect of acylating agent on conversion of *o*-phenylene diamine

Acylating agent	% Conversion	% Selectivity
CH_3-COOH	94.81	99.98
H-COOH	92.56	61.10
Cl-CH_2-COOH	99.09	71.87
	94.77	31.75
	95.80	94.36
	96.48	90.61
	98.20	52.74

Reaction conditions: *o*-phenylene diamine: Acid- 1:1, 10 wt.% CMS-0.25 g, 4 h,110 °C was found best solvent. Acetonitrile and water showed almost same activity. Water:ethanol gave poor activity. A compromise between polarities a little hydrophobicity might result in the best performance for ethanol as solvent. Maximum conversion was observed with polar solvent, i.e. ethanol.

3.5.7 Effect of method of preparation of catalyst on conversion

The reaction of *o*-phenylene diamine to substituted benzimidazole was carried out by using two kinds of preparation of catalyst was used i.e. sol-gel method and another wet impregnation method. It indicated that catalyst prepared by sol gel method showed excellent results other than the catalyst used for the wet impregnation method. Observed results were given in Figure 9. Sol-gel method used for the preparation of catalyst showed maximum conversion 94.81 %. Lower conversion (53.87 %) was observed by using wet impregnated catalyst. Catalyst prepared by sol gel method was homogeneous and nanocrystalline with uniform particle size. Therefore due to homogeneity nature with nano form of the catalyst, gave maximum conversion. The advantage of sol-gel process has been recognized for its versatility, which allows control of the texture, composition, homogeneity and structural properties of the finished solids [58-59]. As CuO was impregnated on surface of MoO_3, so active sites of MoO_3 was overlapped by CuO. This can be seen from XRD also. So it proved that CuO and MoO_3 played a major role in acylation reaction. Hence sol gel synthesized catalyst gave higher conversion.

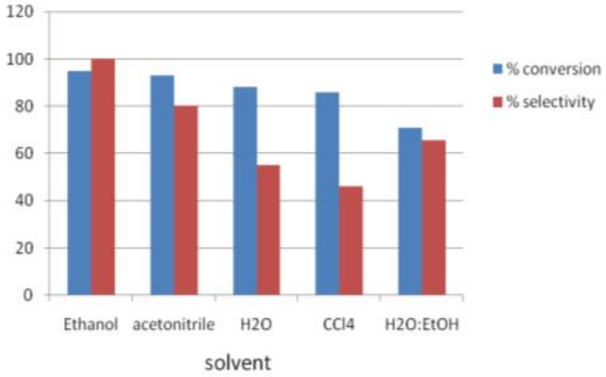


Figure 8. Effect of various solvent on acylation of *o*-phenylene diamine to benzimidazole (Reaction condition: *o*-phenylene diamine: acetic acid- 1:1, 10 wt.% CMS-0.25 g, 4 h, 110 °C)

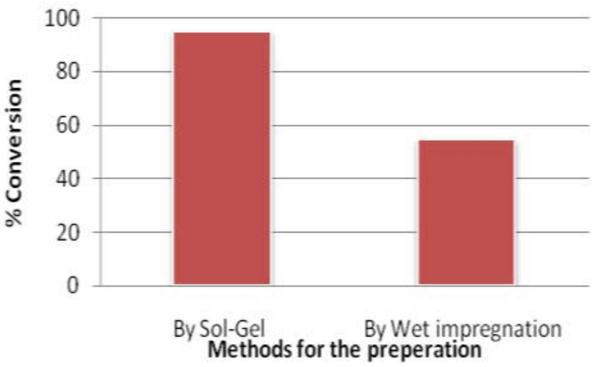


Figure 9. Effect of preparation method of catalyst on acylation of *o*-phenylene diamine (Reaction conditions: diamine: Acid- 1:1, 4 h, Catalyst- 0.25 g, temp-110 °C)

3.5.8 Types of reactant

The effect of different reactant on the conversion of reactant and selectivity of substituted benzimidazole was studied. Two kinds of reactant was used one aromatic amine and another one was aliphatic amine i.e. *o*-phenylene diamine and ethylene diamine. Best results ob-

Table 6. Effect of reactant on conversion of *o*-phenylene diamine

Types of reactant	% Conversion	% Selectivity
	94.81	100
	82.61	26.61

Reaction conditions: diamine: Acid- 1:1, 10 wt.% CMS-0.25 g, 4 h, 110 °C

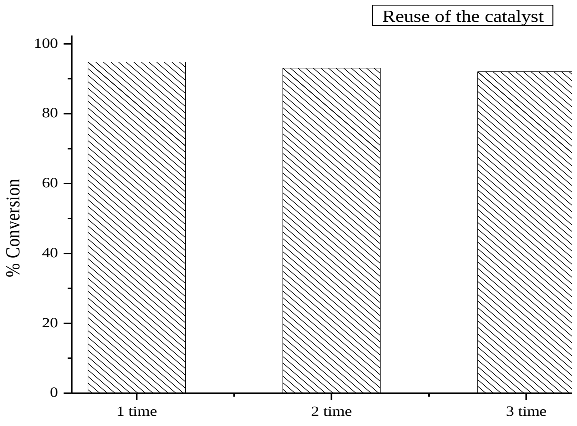


Figure 10. Study of recycle and reuse of catalyst on acylation of *o*-phenylene diamine (Reaction conditions: diamine: Acid- 1:1, Time-4 h, 10 wt.% CMS-0.25 g, temp-110 °)

tained using reactant by aromatic amine (table 5). It indicated that maximum conversion of *o*-phenylene diamine was obtained with maximum selectivity due to resonance effect.

3.5.9 Recycle and reuse of the catalyst

To examine the recyclability of the catalyst, the CMS was recovered from the reaction media and re-used. Following each use, the catalyst was separated from the reaction mixture by simple filtration, washed sequentially with acetone and water, dried at 100 °C for 2 h, and then activated at 500 °C for 5 h. Reaction with fresh catalyst showed conversion of benzimidazole was 94.81 % after second and third recycle of the catalyst gave the conversion 91.07 and 88.08 % respectively. The slight loss in activity indicated by the catalysts. Therefore it concluded that the catalyst can be reused for more runs with slight loss in activity.

3.6 Reaction Mechanism

The proposed mechanism of acylation of *o*-phenylene diamine with acetic acid is given in Figure 11. As earlier mentioned, Friedel-Crafts acylation reaction is electrophilic substitution reaction in which formation of carbocation species takesplace by complexation of acylating agent in presence of catalyst. In acylation reaction, the carbocation species generated attack on aromatic species. Therefore, formation of this carbocation was most important during acylation reaction.

5. Conclusion

By using sol gel method CMS catalyst with various loading were synthesized and characterized by XRD, SEM and EDX, TEM, and acidity measurement. The results showed that CuO species were dispersed on the MoO_3/SiO_2 primarily as the CuO phase. SEM and TEM data revealed that all catalyst was in nano form, it was also confirmed from XRD results. Acidity measurement result showed 10 wt.% CMS has higher acidic strength than other.

Acylation of *o*-phenylene diamine was carried over synthesized catalysts gave higher conversion as well as selectivity. The optimized conditions for the reaction were *o*-phenylene diamine (1 mmol), acetic acid (1 mmol), 10

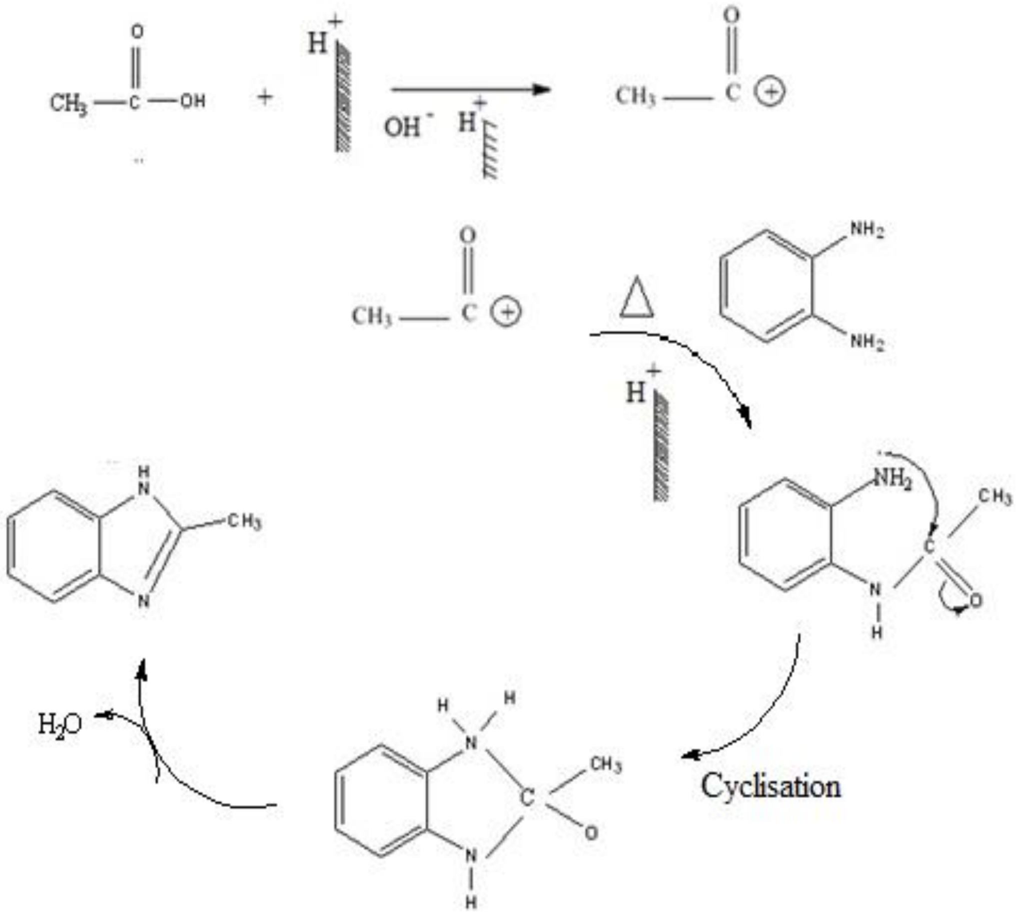


Figure 11. Proposed mechanism of acylation reaction by CMS mixed oxide catalyst

wt.% CMS catalyst, and ethanol (10 mL) at 110 °C for 4 h. 10 wt.% CMS catalyst gave maximum results due to nano crystallite size as well as presence of maximum acid sites. Copper supported MoO_3/SiO_2 catalyst was inexpensive, noncorrosive, environmental benign catalysts and can be reused by filtration method without significant degradation in catalytic activity and gave excellent product yields and a simple workup procedure resulting from the heterogeneous conditions.

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