Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Pelagia Research Library

Advances in Applied Science Research, 2015, 6(6):167-170

Advances in Applied Science Research
Pelagia Research Library
ISSN: 0976-8610
CODEN (USA): AASRFC

An efficient and ecofriendly RuO_2-MoO_3 solid heterogeneous catalyst for the synthesis of benzimidazole from aldehydes

Kaluram N. Vidhate* and Rahul A. Waghmare

Department of Chemistry, Milind College of Science, Aurangabad, M.S. India

---

ABSTRACT

An ecofriendly and recyclable solid RuO_2-MoO_3 mixed oxide was used as catalyst for the synthesis of benzimidazole derivatives. This method provides several advantages such as short reaction times, high yields, simple work-up procedure, environmental friendliness and catalyst was successfully reused for four cycles without significant loss of activity.

Keywords: Solid RuO_2-MoO_3, Benzimidazoles, Aldehydes.

INTRODUCTION

The heterogeneous solid acid catalyst plays vital role in organic synthesis and transformation reactions. Many organic reactions like alkylation, acylation, nitration, esterification and rearrangements such as pinacol, Beckmann etc., are carried out by using acid catalyst. All these acid catalyzed reactions are mostly carried out by using conventional mineral acids like H_2SO_4, HNO_3 and HF or Lewis acids such as $AlCl_3$ and BF_3. For the environmental reasons there is an ongoing effort to replace the conventional catalyst with newer solid acid catalyst. Solid acid catalyst has some advantages such as non-toxicity, non-corrosiveness, less expensive, ease of handling and easy to recover and reuse [1-5]. Accordingly, various solid acid catalysts, such as, zeolites, clays, hetropolyacids, and ion exchange resins were investigated [6-8]. The disadvantages of zeolites and clays are that they are quite reliable and activities of this material are much lower than the conventional homogeneous acids due to pore blocking and hydration. The main disadvantage of hetropolyacids is that they are fairly soluble in polar solvents and loose their activity at higher temperature by loosing structural integrity. Although ion exchange resins like Amberlyst and Nafllon-H exhibit poor thermal stability and low surface area. [5]. For this purpose, there is ongoing effort to develop stronger solid acid which are water tolerant, stable at high temperature and suitable for both liquid and vapor phase conditions. The metal oxides based catalysts are active over a wide range of temperatures and more resistant to thermal excursions.

Metal oxide and mixed metal oxide have been extensively as a catalyst for wide variety of reactions such as [9-14], By observing such a wide applicability of mixed metal in catalytic reactions and their potential uses, we are encourage preparing a mixed metal oxide and utilized in the synthesis of benzimidazoles derivatives by the condensation of 1, 2 diaminobenzene and various aldehydes. The benzimidazoles moiety is found in various synthetic pharmaceuticals displaying a broad spectrum of biological activity including anti-ulcer, anti-tumor and anti-viral effects [15-17]. The numbers of methods have been reported for the synthesis of benzimidazoles [18-21]. Many of the synthesis protocol reported so far suffer from disadvantages such as needing anhydrous conditions, use of organic solvents, harsh reaction condition and prolonged reaction time. Therefore the development of most effective, safe and environment friendly reagent system is desirable. We report here, a series of some benzimidazoles derivatives were synthesized from various aldehydes and 1, 2 diamines in the presence of an ecofriendly RuO_2-MoO_3 solid acid catalyst.

MATERIALS AND METHODS

Catalyst preparation

The RuO_2-MoO_3 solid acid catalyst was prepared by simple co-precipitation method. Analytical reagent grade ruthenium trichloride and ammonium molybdate were used as precursor. Stichiometric amounts of ruthenium trichloride and ammonium molybdate were dissolved double distilled water at room temperature with constant stirring in a separate 100 ml standard flask. the molar ratio of Ru^{+3} and Mo^{+6} = 2:8. Their solution was mixed and 20 ml of 2% polyethylene glycol as structure directing agent was added. The solution was constantly stirred for a half an hour and then required amounts of aqueous ammonia solution (1:1) was added dropwise until all the metal form hydroxide (pH = 11). Precipitate was stirred for 1 hr and its ageing was done for 1 hr at 50-60^{0}C in electric oven. After the ageing it was filter, dried at 373 K for 12 hand calcined at 500^{0}C in air for an hour in high temperature muffle furnace. The catalyst was stored in vacuum desiccators and was activated at 100^{0}C for an hour before catalytic run.

Catalyst characterization

The synthesized sample was characterized by using XRD, FTIR, SEM and EDS. The RuO_2-MoO_3 catalyst was prepared by simple co-precipitation method. The resulting sample was heated at 500^{0}C in high temperature muffle furnace (SONAR) for 1hour at rate 3^{0}C per minute and naturally cooled. These material were characterized by XRD using model D8.Bruker AXS, with monochromatic Cu-Kα radiation (40 Kv and 30 mA) at room temperature. The XRD spectra are shown in fig.1. The broad peak observed due to orthorhombic structure.

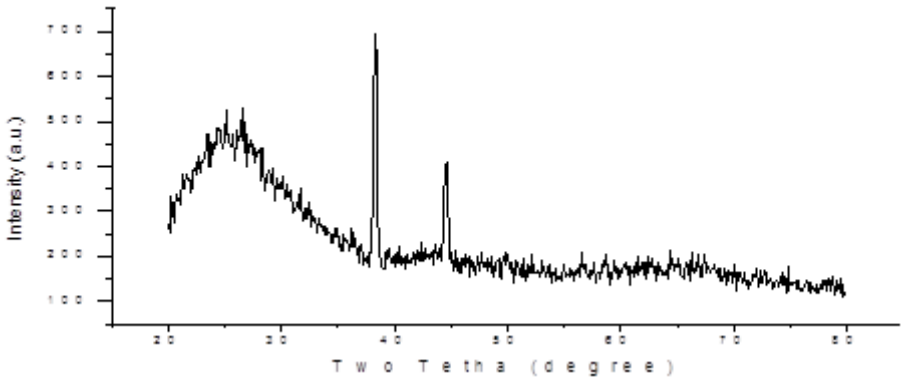


Fig.1 XRD pattern of RuO_2- MoO_3 mixed oxide

Infrared spectroscopy

The IR spectra were recorded on FT-IR spectrometer (JASCO FTIR/4100) Japan, using dry KBr as standard reference in the range of 4000-400 cm^{-1} are shown in fig.2. The peak at 560.22 cm^{-1} due to Ru-O vibration indicating formation of RuO_2. The peak at 1034.62 cm^{-1} characteristics the vibration of Mo-O terminal bond. The weak vibration also detected on 1640.16 cm^{-1} associated with vibration mode of Mo-OH bond and bending mode of absorbed water.

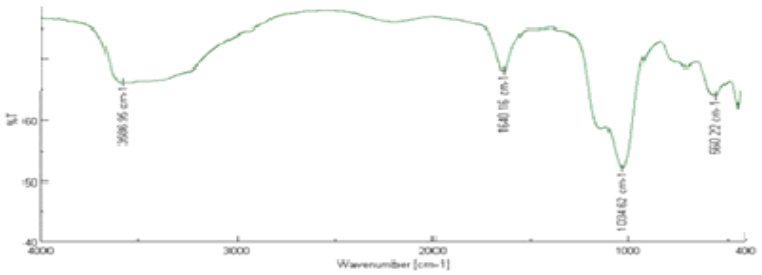


Fig.2 FT-IR spectra of RuO_2- MoO_3 mixed oxide

Scanning Electron Microscope (SEM) analysis with Energy dispersive X-ray spectroscopy (EDS)

The morphology of RuO_2-MoO_3 catalyst as shown in fig.3. The SEM micrograph of CMZO catalyst shows homogeneous agglomeration of particles and was irregular in shape and agglomerated, with an average primary particle size > 1µm.It was also observed that there is a generation of some porosity, that may be due to addition of 2% PEG as structure directing agent. A scan be noted from the micrograph of all the two metal oxides is strongly

interacted and highly dispersed on their surface. EDS analysis of RuO_2-MoO_3 oxide gives 2 mass % ruthenium and 8 mass % molybdenum.

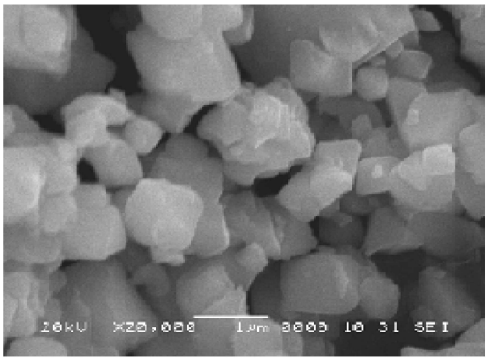


Fig.3. SEM image of RuO_2- MoO_3 mixed oxide

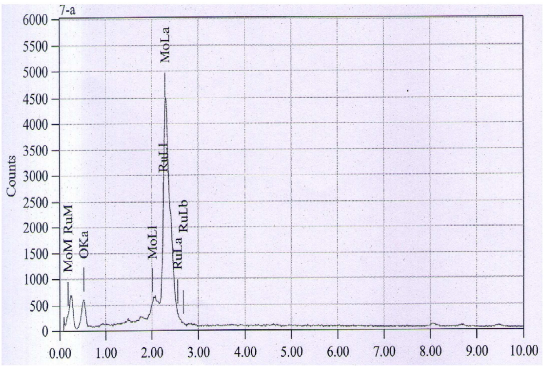
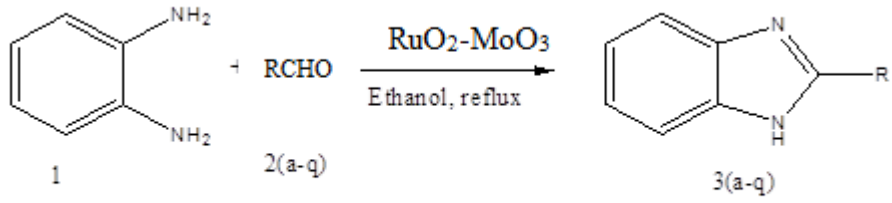


Fig.4. EDS spectrum of RuO_2- MoO_3 mixed oxide

General Procedure

Aldehydes (0.5 mmol) and 1, 2-diaminobenzene (0.5 mmol) were thoroughly mixed in ethanol (10 ml) then RuO2-MoO_3 mixed oxide (3 wt % with respect to initial concentration of reactant) was added, and the solution was refluxed for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the resulting solid was collected by filtration. After evaporation of the solvent, the resulting solid product was recrystallized from ethanol to obtain pure product. The catalyst was recovered by filtration and washing with n-hexane and subjected to further reaction after heating it at 110^0C in oven for one hour.



R = alkyl or Aryl

Fig.5 Reaction between 1,2-diaminobenzene and aldehyde that yielded benzimidazole

RESULTS AND DISCUSSION

In order to find the optimum reaction conditions for ecofriendly synthesis of benzimidazole derivatives by condensation of 1,2-diaminobenzene and 4-chlorobenzaldehyde in presence of various amounts of RuO_2-MoO_3. **(Table 1)**. The condensation reaction was carried out using 1:1 molar ratio of reactants in ethanol medium and the results of this synthetic route are found to be inspiring when the catalyst amount was 3 wt% with respective to initial concentration of reactants. In a similar fashion, a variety of benzimidazole derivatives were synthesized with optimized condition using various aldehydes and in each case it was observed that the time period for condensation was reduced considerably and the yield of the products changed to excellent yields **(Table 2).** This indicates that the present catalyst efficiently makes the condensation reaction much faster with increased yields.

Although water is a desirable solvent for chemical reactions for reasons of cost, safety and environmental concerns, use of water in this reaction gave only moderate yield (63%) of product. Aldehyde compounds which have electron donating or electron withdrawing groups were used and as expected, in all the cases benzimidazole derivatives were obtained in good yields. In this reaction the catalyst can be recovered by filtration and washing with n-hexane and subjected to further reaction after heating it at 110^0C in oven for an hour. The recovery and reusability of the catalyst was tested by performing same condensation reaction using recovered catalyst and observed that the percentage yield remains almost same. This indicates that the catalyst could be recycled without much loss of catalytic activity.

Table 1: Study of catalyst in condensation of 1,2-diaminobenzene and 4-chlorobenzaldehyde acid in ethanol

Weight of Catalyst(%)	Time(hr)	Yield[a] (%)
No catalyst	3	57
1	1	71
2	1	82
3	1	94
4	1	94

[a] *Yield refer to isolated products.*

Table 2: RuO_2- MoO_3 catalyzed synthesis of benzimidazole derivatives

Entry	R	Time (min)	Yield(%)	MP/^{0}C	
				Found	Reference
1	C_6H_5	55	90	292-293	290-293
2	2-$NO_2C_6H_4$	60	89	261-263	264-265
3	2-ClC_6H_4	55	93	234-235	234
4	2-$OCH_3C_6H_4$	60	94	291-292	288-291
5	3-$OCH_3C_6H_4$	65	92	236-238	238
6	4-$NO_2C_6H_4$	55	87	179-180	179-180
7	3-$NO_2C_6H_4$	50	88	205-206	204-206
8	2-BrC_6H_4	65	90	247	246
9	4-$CH_3C_6H_4$	70	91	263-265	264-265
10	C_6H_5CH=CH	55	90	200	199-200
11	2-OHC_6H_4	45	85	240	242
12	4-$OCH_3C_6H_4$	55	81	225	223-226

CONCLUSION

The present synthetic protocol for the synthesis of benzimidazole derivatives is advantageous over the earlier reported methods as

i) The reaction performed effectively and ecofriendly with RuO_2-MoO_3 catalyst.
ii)It provides a good yield of product.
iii) The reaction occurs more rapidly.
iv) The catalyst was easily separated from the reaction mixture.
v) Efficiency of catalyst remains almost same in recycling process.

Acknowledgment
The authors thanks to the Prof. M. K. Lande, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada university, Aurangabad -431004 (MS), India, for his help and inspiration in the research work.

REFERENCES

[1] Corma A, *Chem Rev*, **1995**, 95, 559.
[2] Clark J H, *Acc Chem Res*, **2002**, 35, 791.
[3]. Corma A, Garcia H, *Chem Rev*, **2003**, 103, 4307.
[4] Okuhara T, *Chem Rev*, **2002**, 102, 3641.
[5] Hamer M A, Sun Q, *Appl Catal A: Gen*, **1985,** 221, 45.
[6] Olah G A, Takashi K, Devid M, *Synthesis*, **1978**, 929.
[7]. Guttmann A T, Grasselli R K, *Appl Catal*, **1983**, 9, 57.
[8] Dupont P, Vedrine JC, Paumard E, Hecquit G, Lefebvre F, *Appl Catal A: Gen*, **1995**, 129 217.
[9] Reddy B M, Patil M K, *Curr Org Chem*, **2008**, 12, 118.
[10] Reddy BM, Patil MK, Rao K N, Reddy G K, *J Mol Catal A:Chem*, **2006**, 258, 302.
[11] Reddy BM, Sreeknath PM, Lakshmann P, *Mol Catal A:Chem*, **2005**, 237, 93.
[12] Yadav G D, Nair JJ, *Microporous Mesoporous Mater*, **1999**, 33, 1.
[13] Gillesppie R J, Peel TE, *J Am Chem Soc*. **1973, 95**, 5173.
[14] Arata K, Matsuhashi H, Hino M, Nakamura H, *Catal Today*, **2003** 81, 17.
[15] Spasov A A, Yozhista IN, Bugaeva LI,. Anisimova VA, *Pharma Chem*, 1999, 33, 232.
[16] Porcari A R, Devivar RV, Kucera LS,. Drach JC, Townsend LB, *J. Med Chem*,**1998,** 12, 1251.
[17] Roth M, Morningstar ML, Boyer PL, Hughes SH, Bukheit RW, Michejda CJ, *J Med Chem*, **1997**, 40, 4199.
[18] Yadagiri B, Lown JW, *Synth Commun* **1990**, 20, 955.
[19] Sun Q, Yan Bioorg B, *Med Chem Lett*, **1998,** 8, 361.
[20] Bahrami K, Khodaei MM, Kavianima I, *Synthesis*, **2007,** 4, 547.
[21] Sharghi N, Asemani O, Khalifeh R, *Synth Commun*, **2008,** 38, 1128.