Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2018, 10(7): 118-123

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Modified Montmorillonite: An Active Heterogeneous Catalyst for the Synthesis of Benzimidazoles

Subrat Jyoti Borah and Diganta Kumar Das*
Department of Chemistry, Gauhati University, Guwahati-781014, Assam, India

ABSTRACT

Acid treated modified montmorillonite clay was used as catalyst precursors for the synthesis of benzimidazoles through the room temperature stirring of aromatic aldehyde and o-phenylene- diamine. The modification of the clay was done by treating the clay with HCl to under controlled conditions to produce a porous matrix with high surface area. The modified clay was characterized by powder XRD, N2 adsorption-desorption and SEM-EDX analysis. The recyclability of the catalyst was also investigated and showed efficient catalytic activity for several catalytic run.

Keywords: Modified montmorillonite; Heterogeneous catalyst; Benzimidazole

INTRODUCTION

The development of environmentally benign, efficient and green synthetic methods has become the major current challenge to the chemists to address industrial and environmental concerns [1-2]. Due to growing environmental regulations, the chemical industry has to use manufacturing processes that do not cause any permanent damage to the environment or disturb the ecological balance [3-4]. The researchers also try to minimize the consumption of energy and raw materials required in synthesis so that optimal value of resources could be realized. Thus, development of clean technology for both material synthesis and organic synthesis is a great challenge for the researchers. In this context, the use of environmentally benign, easily available, robust and cheap materials as catalyst has gained interest in recent years [5-6]. Among the different materials, clays are widespread, easily available and cheap materials which show activities in both in their native state and numerous modified forms [7-8]. Now a day, clays are important materials with a large variety of applications in ceramics, oil drilling, and the metal and paper industry. Clays are furthermore used as adsorbents, decoloration agents, ion exchangers and molecular sieve catalysts [9-10]. Clays are lamellar aluminosilicates showing a large variety of physicochemical properties such as swelling, adsorption, surface acidity, ion exchange etc. Clays can be modified very easily by simple acid treatment and this provides the scope for altering their properties like surface area, pore size, acidity and other characteristics [5-8]. These properties make them attractive for utilization as catalysts or support materials for the development of metal nanocatalysts for organic synthesis. Montmorillonite clay, which is included in the Smectite group, has enjoyed a great deal of attention because of its useful cation exchanged, intercalation and adsorption properties [10-20]. In this work, we have reported modification of montmorillonite K10 by treatment with HCl under refluxing conditions to get a high surface area and porous matrix. The modified clay has been utilized as an efficient heterogeneous catalyst for the heterocyclic condensation between different aromatic aldehydes and arene-1,2-diamines to give benzimidazoles under mild reaction conditions.

Benzimidazoles are important synthetic intermediates in organic synthesis and are considered to be privileged sub-structure for drug design [21-22]. Benzimidazole derivatives have shown different pharmaceutical activities such as antiviral, antihypertension, anticancer and some other properties [23-26]. Thus, they are important building blocks in organic synthesis. The conventional method for the synthesis of benzimidazole involved condensation reaction between 1,2-diaminobenzene and carboxylic acid or acid derivative under acidic condition at high temperature [27-28]. In recent years, a lot of methods have been developed to synthesize benzimidazole derivatives. Some of the examples are intramolecular condensation, condensation of o-phenylenediamine with carboxylic acid or its halide derivative and condensation of o-phenylenediamine and aldehyde etc [29-34]. Although much progress has been made in this reaction, it is still highly desirable to develop efficient and green synthetic methods for the synthesis of benzimidazoles. Herein, we have reported a procedure for the synthesis of benzimidazole through the room temperature stirring of different aromatic aldehyde and o-phenylenediamine using modified montmorillonite clay as catalyst and toluene as a solvent.

MATERIALS AND METHODS

Material

Montmorillonite K-10 was purchased from M/S Sigma Aldrich, USA. All aldehydes and O-phenylenediamine were purchased from M/S Sigma Aldrich.

Modification of Clay

An amount of 10 g of Montmorillonite K10 (10 g) was dispersed in 200 ml 2M HCl and refluxed for 2 h. After cooling, the supernatant liquid was discarded and the activated montmorillonite was repeatedly washed with deionised water until no Cl¬ ions could be detected by the AgNO3 test. The activated clays were dried in air oven at 50oC over for 12 h and the solid products were designated as modified montmorillonite.

General Procedure for the One-Pot Synthesis of Benzimidazoles

Aldehyde (1 mmol), o-phenylenediamine (1.2 mmol), 20 mg catalyst (modified montmorillonite) and 5 ml toluene were taken in a 25 ml round bottom flask and the reaction mixture was stirred for stipulated time period (3 h). The progress of the reactions was monitored by TLC. After completion of the reaction, the solid catalyst was separated from the reaction mixture by filtration through a sintered funnel (G3) and the solvent was removed under low pressure in a rotary evaporator. The recovered catalyst was washed with acetone, dried in a desiccator and stored for another consecutive reaction run. The crude product obtained was then purified by silica gel column chromatography using ethyl acetate and hexane as eluents. The products were characterized by 1H and 13C NMR spectrometry.

RESULTS AND DISCUSSION

The parent montmorillonite K10 exhibited an intense basal reflection at 7.10o 2θ corresponding to a basal spacing of 12.7 Å (Fig. 1). The reflection intensity of the basal peak decreased with time during acid treatment and no basal reflection was seen after 2 h. It was due to the fact that acid treatment modified the layered structure of the clay by leaching out aluminium from octahedral sites and developed a porous amorphous silica phase.

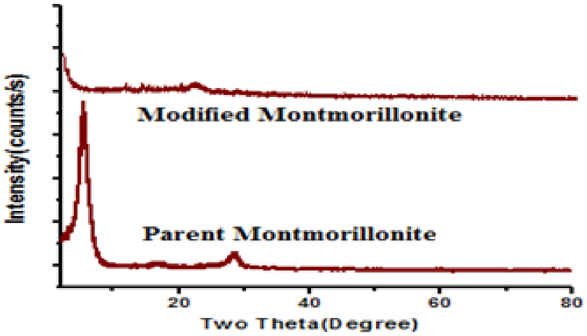


Figure 1: Powder XRD pattern of parent and modified clay

The specific surface area and pore size distribution of modified montmorillonite determined by N2-adsorption study revealed that the clay matrix contained mesopores (> 2 nm). The adsorption-desorption isotherms (Fig. 2) were of the type-IV with a H3 hysteresis loop at P/Po ~ 0.4-0.9, indicating mesoporous solid. The specific surface area of parent montmorillonite K10 was found to be 192 m2/g with pore volume ~0.30 cm3/g. After acid modification, the surface area of the clay was found to be 416 m2/g with large specific pore volume 0.65 cm3/g. The increase in surface area might be due to the formation of mesopores during acid treatment which leached out aluminum from octahedral sites.

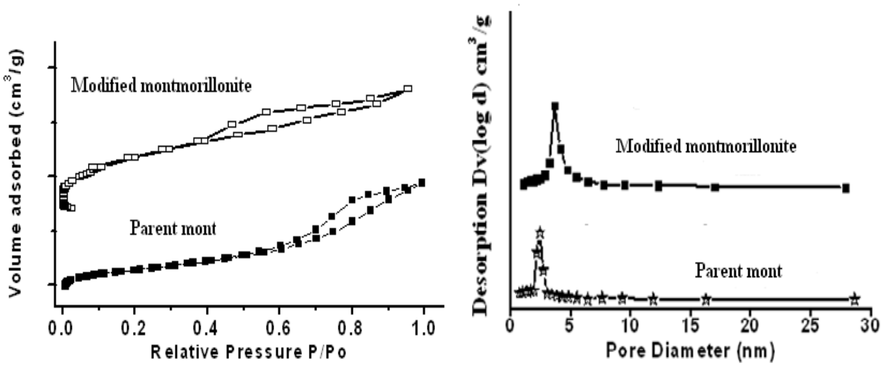


Figure 2: N2 adsorption/desorption isotherms and pore size distribution curves of Parent Mont and modified montmorillonite

The SEM analysis of parent and modified montmorillonite showed the formation of porous matrix on the surface of montmorillonite after acid treatment which was not observed on unmodified clay [Fig. 3. (a) and (c)]. The unmodified parent clay showed the uniform layered structure of the clay in the SEM image. EDX analysis showed a decrease in Al content after acid treatment which was due to the leaching of aluminium from the clay structure [Fig. 3. (b) and (d)]. Na, Mg present in the parent clay also disappeared from the EDX spectra of modified montmorillonite as they were leached out during acid treatment.

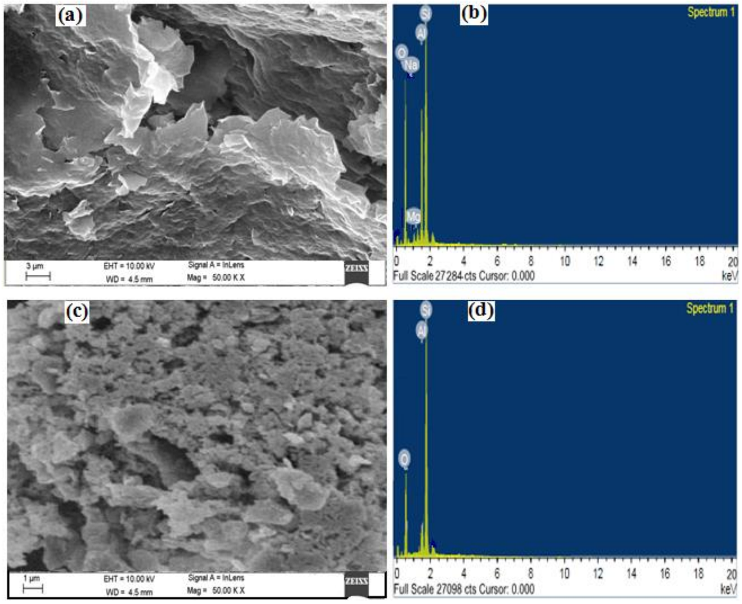
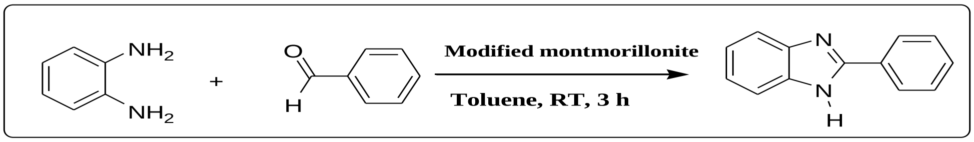


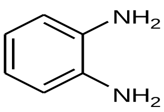
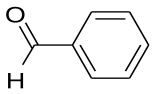
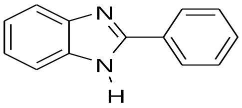
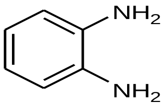
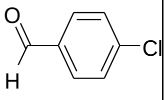
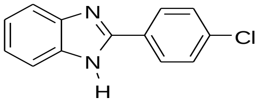
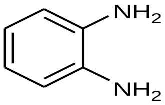
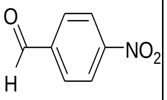
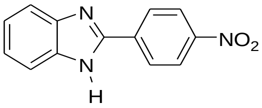
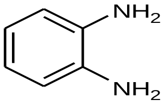
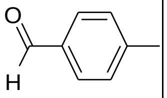
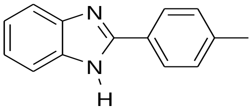
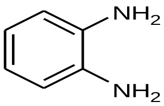
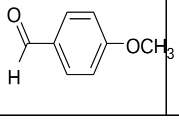
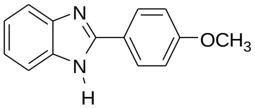
Figure 3: (a) SEM image of parent mont K10, (b) EDX analysis of Parent Mont, (c) SEM image of modified montmorillonite, (d) EDX analysis of modified montmorillonite

Catalytic Activity

The conditions for the synthesis of benzimidazoles were optimized by using the model substrates benzaldehyde and o-phenylenediamine. After screening a wide range of reactions, we have found that our catalytic system i.e. modified montmorillonite is most efficient at room temperature in toluene as solvent for the of benzimidazole synthesis. The model reaction with modified montmorillonite catalyst gave 86% yield of the desired product. The reaction mixture was also stirred without catalyst to test its requirement for the reaction and we obtained only 12% yield of the desired product in 3 h. The use of unmodified montmorillonite as catalyst gave 48% yield in 3 h in the model reaction. Thus, the catalytic synthesis of benzimidazole was carried out with modified montmorillonite catalyst. The higher catalytic activity of modified montmorillonite might be due to its higher surface area compared to the raw mont catalyst. A variation in the reaction was done by using different aldehydes with o-phenylenediamine and all these gave the expected benzimidazoles with excellent yield and selectivity. The various substrates and products were represented in table 1. In this study, it was observed that the aldehydes with electron withdrawing substituent gave slightly higher yield of product than the aldehydes with electron donating substituent. This might be due to the fact that the presence of electron withdrawing substituent on aldehyde made the carbonyl group more positive and this increased its reactivity.

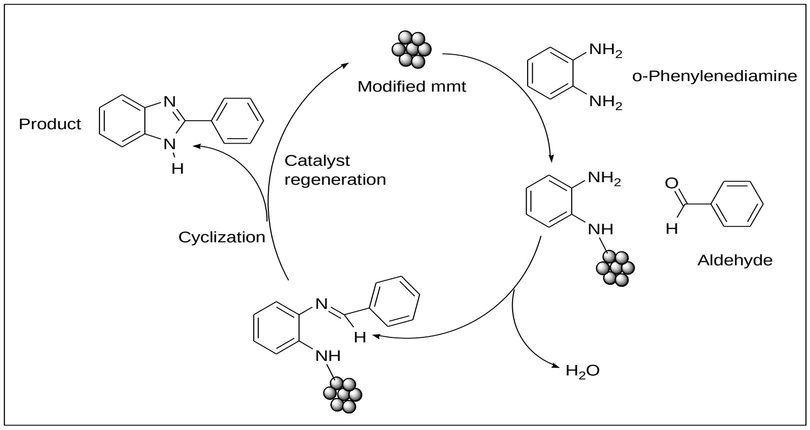
Table 1: Modified montmorillonite catalysed synthesis of benzimidazoles



Entry	Arene-1,2-diamine	Aldehyde	Products	Yield*(%)
S1				86 84(2nd run) 81(3rd run)
S2				88 86(2nd run) 84(3rd run)
S3				87
S4				82
S5				84

*Yields are isolated products based on aldehyde after silica-gel column chromatography. **Reaction conditions: Aldehyde (1 mmol), o-Phenylenediamine (1.2 mmol), Catalyst (20 mg), Solvent: Toluene, Room Temperature, Time: 3 h.

A plausible mechanism for the synthesis of benzimidazole catalysed modified mmt is proposed (Scheme 1). First, the arene-1,2-diamine and aldehyde are adsorbed on the catalyst surface. Then arene-1,2-diamine and aldehyde undergo dehydration to give the intermediate imine. The imine undergoes cyclization to give the product and the catalyst is regenerated.



Scheme 1: Proposed mechanism for the synthesis of benzimidazole

CONCLUSION

Modification of montmorillonite was carried out with 2M HCl for 2 h. The modified clays was characterized by Powder-XRD, N2 adsorption-desorption and SEM-EDX analysis. The modified clay was evaluated as a heterogeneous catalyst for the synthesis of benzimidazoles under mild reaction condition. The used modified clay catalyst was recovered and reused upto 3rd catalytic run without any significant loss in activity.

REFERENCES

[1] Chen WW, Nguyen RV, Li CJ. *Tetrahedron Lett*. **2009,** 50, 2895.
[2] Stern R, Jedrzejas MJ. *Chem Rev*. **2008,** 108, 5061.
[3] Nagendrappaa G. *Resonance*. **2002,** 64.
[4] Kaur N, Kishore D. *J Chem Pharm Res.* **2012,** 4(2), 991.
[5] Rout L, Jammi S, Punniyamurthy T. *Org Lett.* **2007,** 9, 3397.
[6] Saladino R, Crestini C. *Chem Bio Chem*. **2004,** 5, 1558.
[7] Nagendrappaa G. *Appl Clay Sci.* **2011,** 53, 106.
[8] Vogels RJMJ, Kloprogge JT, Geus JW, Catal J. **2005,** 231, 443.
[9] Fowden L, Barrer RM, Tinker RB. (Eds.), Clay Minerals: Their Structure, Behaviour and Use. Philosophical Transactions of the Royal Society of London, Series A, Mathematical and Physical Sciences, **1984,** 311, 219.
[10] Carretero MI. *Appl Clay Sci.* **2002,** 21, 155.
[11] Lachar M, Lahav N, Yariv S. *J Therm Anal.* **1993,** 40, 41.
[12] Fusi M. *Soil Biochem.* **1989,** 21, 911.
[13] Schoonheydt RA. *Clays and Clay Minerals*. **1979,** 27, 269.
[14] Moronta A. *Appl Catal A Gen*. **2008,** 334, 173-178.
[15] Waterlot C, Couturier D, Rigo B. *Tetrahedron Lett*. **2000,** 41, 317.
[16] Troast DM, Yuan J, Porco JA. *Adv Synth Catal.* **2008,** 350, 1701.
[17] Li JT, Xing CY, Li TS. *J Chem Tech Biotech*. **2004,** 79, 1275.
[18] Thomas B, Prathapan S, Sugunan S. *J Chem Res*. **2005,** 79, 21.
[19] Dintzner MR. *Tetrahedron Lett.* **2004,** 45, 79.
[20] Dutta D. *Appl Clay Sci.* **2011,** 53, 650.
[21] Horton DA, Bourne GT, ML. *Smythe Chem Rev.* **2003,** 103, 893.
[22] Zhang C, Zhanga L, Jiao N. *Green Chem*. **2012,** 14, 3273.
[23] Payne JE. *J Med Chem.* **2010,** 53, 7739.
[24] Tebbe MJ. *J Med Chem.* **1997,** 40, 3937.
[25] Palmer AM. *J Med Chem.* **2010,** 53, 3645.
[26] Mukhopadhyay C. *RSC Adv.* **2011,** 1, 1033.
[27] Ebenezer WJ. *Tetrahedron Lett.* **2007,** 48, 1641.
[28] Ansari KF, Lal C. *Eur J Med Chem.* **2009,** 44, 4028.
[29] Peng J. *J Org Chem.* **2011,** 76, 716.

[30] Gupta S, Agarwal PK, Kundu B. *Tetrahedron Lett*. 2010, 51, 1887.
[31] Shen M, Driver TG. *Org Lett*. **2008,** 10, 3367.
[32] Heravi MM. *Catal Commun*. **2007,** 9, 504.
[33] Raghavendra GM. *Tetrahedron Lett*. **2011,** 52, 5571.
[34] Willis MC. *Chem Rev*. **2010,** 110, 725.