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Montmorillonite Clay : An Efficient Heterogeneous Catalyst in Organic Synthesis: A Review

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ABSTRACT

Montmorillonite is a very soft phyllosilicate group of mineral that develop when minute crystal of clay precipitate from aqueous solution. A variety of organic reaction that are catalyzed by Montmorillonite clay under mild condition, with greater selectivity, better yield and short reaction time. Therefore, organic chemists are interested in such type of heterogeneous catalyst in organic synthesis. The present review focus on the recent development in the catalytic application of Montmorillonite clay catalyst for organic transformation. This review article describes the literature report of various synthetic methods that are catalyzed by Montmorillonite clay catalyst published in 2010 to 2020. This could be useful to organic chemist, researcher and students for the utilization of Montmorillonite clay catalyst in chemical reactions.

Keywords : Montmorillonite, Heterogeneous Catalyst, Organic Synthesis.

I. INTRODUCTION

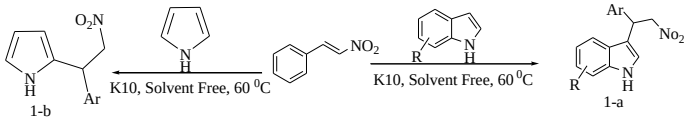
Catalyst plays an important role in developing clean or green synthetic method which is a significant challenge for organic chemist. Clays and modified/supported clay catalyst have received considerable attention of the synthetic chemist and widely used as catalyst in variety of organic transformation because of their easy structural modification and activation, low cost, eco-friendly nature, ready availability, ability to acts as acidic and basic catalyst without being corrosive[1]. Montmorillonite is very soft phyllosilicate group of mineral has chemical formula $(Na, Ca)_{0.3}$ $(Al, Mg)_2$ Si_4O_{10} $(OH)_{2n}$ (H_2O). Montmorillonite as a member of smectites group is 2:1 clay with central octahedral sheet of alumina sandwiched by two tetrahedral sheets of silica [2].Montmorillonite clay possesses both Bronsted and Lewis acid characteristics in their natural and ion exchange form and used as solid acid catalyst for a number of organic reactions [3]. The main objective of this review is to provide an

overview on the catalytic application of montmorillonite K10, KSF, modified or supported clay catalyst in various organic transformations. In this short review, we describe the literature report on the recent and representative organic synthesis catalyzed by montmorillonite clay catalyst published in the year 2010-2020.

II. MONTMORILLONITE: APPLICATION IN DIFFERENT ORGANIC SYNTHESIS AS CATALYST

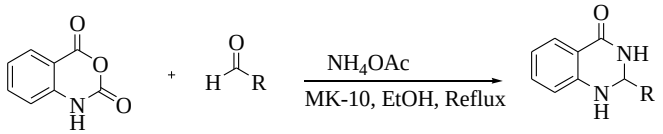
Montmorillonite clay has been found to effectively catalyze broad range of chemical reaction. Some of them are discussed below.

Li-Tao An and co-worker [4] have used the Montmorillonite K10 as green catalyst for the Michael addition of indoles and pyrrole with nitro alkene under solvent free condition (**Scheme-1**). The advantages of this method are high yield of product, simple workup procedure, green and reusable catalyst, dry reaction condition and short reaction time.



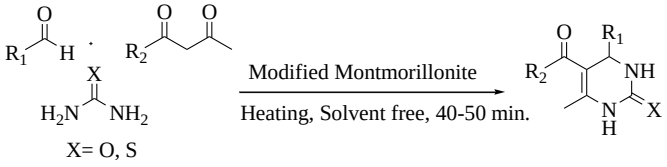
Scheme-1

S. M. Roopan et al [5] have described the one pot synthesis of 2-substituted -2, 3-dihydroquinazolin-4(1H)-one derivatives by the cyclocondensation reaction of isatoic anhydride, NH4OAc and aromatic/heteroaromatic aldehyde under ambient condition catalyzed by Montmorillonite K10 catalyst (Scheme-2). The authors reported the biologically active 2-heterosubstituted-2, 3 dihydroquinazolin-4(3H)-one first time using Montmorillonite K10 catalyst. This methodology offer several advantages such as short reaction time, high yield, economic viability and reusability of catalyst.



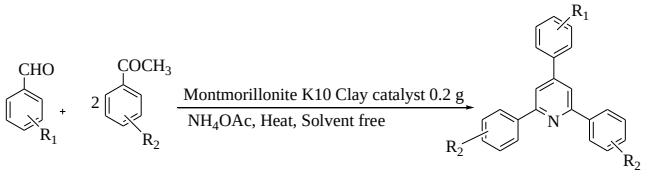
Scheme-2

An efficient synthesis of 3,4-dihyropyrimidine-2(1H) one derivative via one pot three component reaction of aldehyde,1,3,dicarbonyl compound, urea or thiourea under solvent free condition catalyzed by Montmorillonite modified catalyst was described by S. M. Sodegh Hosseini and Co-worker [6] (Scheme-3). The authors reported that montmorillonite modified was prepared by acid activation and TiO2-pillaring treatment method and characterized by XRD, SEM and FT-IR. High yield of product, short reaction time, inexpensive catalyst and environmental friendly procedure are the advantages of this method.



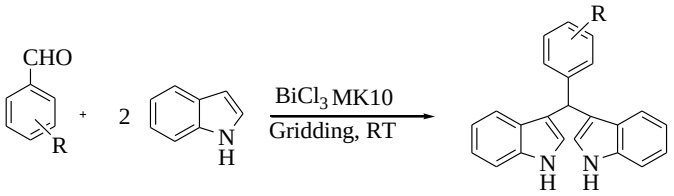
Scheme-3

V. Kannan and K. Sreekumar [7] have reported montmorillonite K10 catalyzed synthesis of 2, 4, 6 trisubstituted pyridine using aromatic aldehyde, aromatic ketone and ammonium acetate under solvent free condition (Scheme-4). This protocol has several advantages such as use of non-corrosive catalyst, solvent free condition and easy workup procedure.



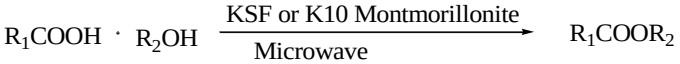
Scheme-4

K. Ravi et al [8] have described the new solid acid catalyst $BiCl_3$-loaded MK10 was prepared by solid dispersion method and characterized by SEM, EDS and BET surface area analysis. The prepared catalyst shows the excellent activity for the synthesis of bis(indolyl) methane derivative using various aromatic aldehyde and indole under solvent free condition (**Scheme-5**). This novel method offer several advantages such as mild reaction condition, excellent yield of product, short reaction time, recovery and reusability of catalyst.



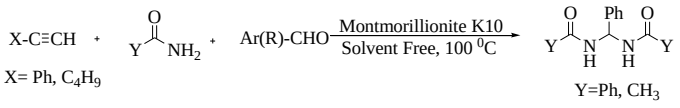
Scheme-5

O. Marvi and Co-worker [9] have reported the esterification of phenol and alcohol under microwave irradiation and solvent free condition using montmorillonite K10 and KSF clay catalyst **(Scheme-6).** Mild reaction condition, high reaction rate, inexpensive and non-toxic catalyst and solvent free condition are the advantages of this protocol.



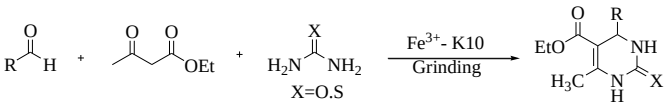
Scheme-6

Synthesis of N, N'-alkylidene bisamide derivative via one pot reaction of phenyl acetylene/1-hexyne, aromatic aldehyde and benzamide/acetamide under solvent free condition using montmorillonite K10 as efficient and green catalyst was pointed out by T. L. Lambat et al [10] **(Scheme-7)**. Advantages of this green protocol are short reaction time, simple workup procedure, environmentally benign, excellent yield, cost effective, recovery and reusability of catalyst.



Scheme-7

L. Z. Fekri, and co-worker [11] used Fe^{3+} montmorillonite K10 as efficient catalyst for the synthesis of 3, 4-dihydro pyrimidin-2(1H)-one and thiones derivatives by the reaction of various benzaldehyde, urea or thiourea and ethyl acetoacetate **(Scheme-8)**. The authors reported that various aromatic aldehyde having electron donating or electron withdrawing group at ortho and para position were used in this reaction. Simple workup procedure, solvent free condition, environmentally friendly, short reaction time and high yield of product are the advantages of this methodology.

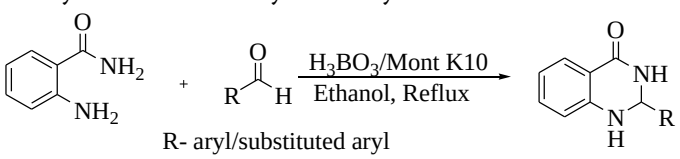


Scheme-8

One pot synthesis of 5-substituted 1H-tetrazole through [3+2] cycloaddition of sodium azide with various nitrile catalyzed by montmorillonite KSF as efficient heterogeneous catalyst was described by R. Hosseinzadeh et al [12] (**Scheme-9**). This green procedure has many advantages which include high yield, simple experimental procedure, short reaction time, use of various substrates, easy work up, non-toxic, easy recovery and reusability of catalyst.

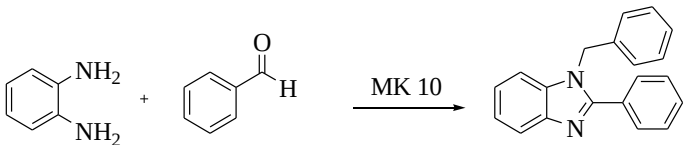
Scheme-9

K. Mahesh and coworker [13] have reported that H_3BO_3/ montmorillonite K10 catalyzed synthesis of 2, 3 dihydrouinazolin-4(1H)-one derivative by the reaction of anthranilamide and benzaldehyde (**Scheme-10**). The authors described that H_3BO_3/ montmorillonite K10 and H_3BO_3/ montmorillonite K30 was prepared and characterized by XRD, IR, BET surface area analysis, TGA, SEM and DRIFTS. The prepared catalyst shows good catalytic activity for the synthesis of 2, 3 dihydrouinazolin-4(1H)-one derivative. This method has advantages such as use of inexpensive reagent, easy separation of product and catalyst and reusability of catalyst.



Scheme-10

The synthesis of 1, 2 di-substituted and 2-substituted Benzimidazole using o-phenylenediamine and benzaldehyde under microwave heating at 60 ^{0}C catalyzed by montmorillonite K10 as efficient heterogeneous catalyst was pointed out by M. Nardi et al [14] (**Scheme-11**). The easy workup procedure, solvent free condition, short reaction time, reusable, inexpensive and environmentally friendly catalysts are the advantages of this procedure.



Scheme-11

III. CONCLUSIONS

Montmorillonite, an important clay type has received growing interest in utilization as a heterogeneous catalyst or used as unique support material to integrate catalysis for efficient organic transformation. In this review article Montmorillonite K-10 and KSF catalyzed various synthetic methods were discussed. This review article is helpful for further research work on the catalytic activity of Montmorillonite for the synthesis of organic compounds.

IV. ACKNOWLEDGEMENT

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