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Use of Montmorillonites in organic reactions

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Introduction

An important family of catalysts that has received considerable attention of the synthetic chemist in recent times is derived from the soil, the most noteworthy one being clays [1]. Clay catalysts have been shown to contain both Brönsted and Lewis acid sites with the Bronsted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites [2,3].

Montmorillonite clays are layered silicates. The crystalline structure of Montmorillonite consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets (Scheme 1) [4].

In Montmorillonite clay both Bronsted and Lewis acidic catalytic sites are available hence its natural occurrence as well as ion exchange properties allow it to function efficiently as a catalyst. The interlayer cations are exchangeable, thus allowing alteration of the acidic nature of the material by simple ionexchange procedure [5].

The major current challenges before chemists are to



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.



develop synthetic methods that are less polluting, i.e., to design clean or 'green' chemical transformations [6]. Clays are widely used due to their ecofriendly nature, these are non-toxic, non-corrosive, economical and recyclable, and thus are efficiently used for a variety of organic reactions [7-9].

reactions which catalyzed The are by montmorillonite clays are usually carried out under mild conditions with high vields and high selectivity and the work up of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent required. are Montmorillonite clays are easily recovered and reused [10].

Abstracts

(A) Sulfonic acid-functionalized ordered nanoporous Na^+ -montmorillonite (SANM), is easily prepared by the reaction of Na^+ -montmorillonite with chlorosulfonic acid. This reagent acts as a highly efficient and reusable catalyst for the chemoselective trimethylsilylation of alcohols and phenols and deprotection of silyl ethers under mild and completely heterogeneous reaction conditions [11].

(B) Primary and secondary benzylic alcohols were oxidized to the corresponding carbonyl compounds in good to high yields by using an environmentally friendly and green oxidant (H_2O_2) in the presence of Montmorillonite-K10 supported manganese (II) chloride [12].

(C) Various indan-1,3-dione derivatives were synthesized from the reaction of different phthalic anhydrides with diethylmalonate using montmorillonite KSF clay as a recyclable heterogeneous acidic catalyst and microwave irradiation in good yields and short reaction times[13].

(**D**) An efficient green protocol for the preparation of amidoalkyl naphthols, employing a three-component one-pot condensation reaction of β -naphthol, aromatic aldehydes and amides or urea in the presence of montmorillonite K10 clay under solvent free conditions has been described [14].

(E) Aryl imines, formed in situ from aldehydes and amines undergo smoothly nucleophilic addition with trimethylsilyl cyanide on the surface of montmorillonite KSF clay under mild reaction conditions to afford the corresponding α aminonitriles in excellent yields. The solid acid can be recovered and recycled in subsequent reactions with a gradual decrease of activity [15].

ROH HMDS (0.75 mmol), SANM (20mg), CH₃CN, r.t. SANM (20mg), MeOH, r.t. ROSiMe₃

$$\underset{R'}{\overset{R}{\longrightarrow}} OH \xrightarrow{MnCl_2.6 H_2O / Montmorillonite-K10} \underset{H_2O_2 / DMF, 60 °C}{\overset{\circ}C} \underset{R'}{\overset{R}{\longrightarrow}} O$$







(**F**) Indoles and carbazoles on treatment with ammonium thiocyanate on montmorillonite K10 clay at 80°C furnished the corresponding 3-thiocyanato derivatives in good to high yields [16].

References

- [1] P. Lasszlo, Science 235 (1987) 1473-1477.
- [2] L.P. Aldridge, J.R. McLaughlin, C. G. Pope, J. Catal. 30 (1973) 409-416.
- [3] L. Forni, Catal. Rev. Sci. Eng. 8 (1973) 65-115.
- [4] E. G. Ralph, Clay Mineralogy, 2nd edition, McGraw-Hill, New York (1968) 39-41.
- [5] Ch. Zhou, X. Li, Z. Ge, Q. Li, D. Tong, Catal. Today 93-95 (2004) 607-613.
- [6] N. Kaur, D. Kishore, J. Chem. Pharm. Res. 4 (2012) 991-1015.
- [7] T.S. Li, T. S. Jin, Youji Huaxue 16 (1996) 385-402.
- [8] R.K. Ramchandani, B.S. Uphade, M.P. Vinod, R.D. Wakharkar, V.R. Choudhary, A. Sudalai, Chem. Commun. 21 (1997) 2071-2072.



- [9] P.C. LeBaron, Z. Wang, T.J. Pinnavaia, Appl. Clay Sci. 15 (1999) 11-29.
- [10] L.J. Krsti, S. Sukdolak, S. Soluji, J. Serb. Chem. Soc. 67 (2002) 325-329.
- [11] F. Shirini, M. Mamaghani, V. Atghia, Appl. Clay Sci. 58 (2012) 67-72.
- [12] G.R. Najafi, Chin. Chem. Lett. 21 (2010) 1162-1164.
- [13] O. Marvi, M. Giahi, Bull. Korean Chem. Soc. 30 (2009) 2918-2920.
- [14] S. Kantevari, S.V.N. Vuppalapati, L. Nagarapu, Catal. Commun. 8 (2007) 1857-1862.
- [15] J.S. Yadav, B.V.S. Reddy, B. Eeshwaraiah, M. Srinivas, Tetrahedron 60 (2004) 1767-1771.
- [16] M. Chakrabarty, S. Sarkar, Tetrahedron Lett. 44 (2003) 8131-8133.