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MONTMORILLONITE: A MILD AND EFFICIENT RECYCLABLE HETEROGENEOUS CATALYST FOR DECARBOXYLATION OF 3, 4-DIALKOXYTHIOPHENE-2, 5-DICARBOXYLIC ACIDS OR ITS SALTS.

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ABSTRACT

Proton and metal ion-exchanged Montmorillonite catalyzes the decarboxylation of 3, 4-alkylene dioxythiophenedicaboxylic acid or its salts or 3, 4- dialkoxythiophenedicarboxylic acid or its salts respectively, in presence of less expensive and reusable heterogeneous catalyst. The main objective of the present invention is to provide an improved process for the preparation of 3, 4-alkylenedioxythiophenes or 3, 4-dialkoxythiophenes which is simple, high purity and industrially applicable. The main objective is to generate a process for 3, 4-alkylenedioxythiophenes or 3, 4 - dialkoxythiophenes which is ecofriendly, commercially viable and easily adoptable in plant scale.

KEY WORDS: Montmorillonite, decarboxylation, 3, 4- alkylenedioxythiophenedicarboxylic acid or its salts, 3, 4-alkylenedioxythiophene.

INTRODUCTION

The process according to the present invention is particularly for the preparation of 3, 4-alkylenedioxythiophene or 3,4-dialkoxythiophene by decarboxylation of 3,4- alkylenedioxy thiophenedicarboxylic acids or its salts or 3,4- dialkoxythiophenedicarboxylicacids or its salts respectively, using reusable heterogeneous catalysts such as montmorillonite clays, hydro talcites,hydroxyapatites and nano metal oxides.Clays are a class of soil with a particle size of

<2 mm in diameter and with a surface area of about 23000 cm' per gram. Their characteristic physical features are sticky and plastic when moist, but hard and cohesive when dry. Structurally, they are crystalline hydrous aluminosilicates and also contain various other cations.Their chemical composition and crystal structure is divided into four main groups such as illite, smectite, vermiculite, and kaolinite. Among these, subgroup of the smectite clay, called montmorillonite, is the most useful catalyst to the synthetic organic chemist, which is the main constituent of bentonites and Fuller's earth. 3, 4-Alkylenedioxythiophenes and 3, 4-dialkoxythiophenes are starting compounds for the preparation of electrically condu ctive polymers which may be transparent in thin layers and have recently been finding a wide range of uses. These polymers are used, for example, as electrodes, sensors, for producing capacitors or electro- luminescent displays and other electro optic components, for producing photovoltaic devices, as electro chromic layers, as auxiliaryes for the production of metal coatings, as thin films for dissipating static charges, in gel electrolytes or ion-exchange membranes. A particularly important monomer 3,4-alkylenedioxythiophene is 3,4-ethylene dioxythiophene(EDOT:IUPAC Name 2,3-dihydrothieno[3,4-b]-1,4-dioxin).

PROPERTIES OF MONTMORILLONITE CLAY

The montmorillonite lattice is composed of a sheet of octahedrally coordinated gibbsite $[Al_2(OH)_6]$ sandwiched between two sheets of tetrahedrally coordinated silicate $[SiO_4]^{4-}$sheets. The three-sheet layer repeats itself, and the interlayer space holds the key to the chemical and the physical properties of the clay (vide infra).An important and useful property of montmorillonite stems from its high degree of efficiency for M^+ cation exchange. This happens because of charge imbalances in its structure caused by exchange of Al^{3+} for Si^{4+} in the tetrahedral sheets, and of Mg^{2+} for Al^{3+} cations in the octahedral sheets. The defects at the edges of crystals also add to this imbalance. If approximately 20% of $A1^{3+}$ positions are replaced by Mg^{2+} montmorillonite will gain a cation exchange capacity of 100 millimoles of M^+ per 100 grams of clay. These balancing cations are presumably situated between the lattice layers. On wetting, the layers move apart by the entry of water molecules, thereby the clay swells and the existing interlayer cations become easily exchangeable.Chemically modified clays are considered to be potentially the most cost-effective nano materials.A variety of organic reactions have been carried out with great success using such clays as catalysts.The interlayer in montmorillonite clay normally contains Na^+, Ca^{2+} and Mg^{2+} as compensatory cations for the charge imbalance. When the clay is dry these cations reside in the hexagonal cavities of the silica sheets. However, when it is treated with water, the cations relocate themselves in the interlamellar region and become exchangeable by a variety of both metallic and nonmetallic cations, for example, H_3O^+, NH^{4+}, Al^{3+}, Fe^{3+} etc. One of the most useful properties of clay minerals lies in this fact. Various types of metal cations and protons can be readily introduced into the interlayer spaces of the Mont via cation exchange with the sodium, thus creating the acidic nature. The cation-exchanged montmorillonite (Mn+-Mont) catalysts along with the local structure of the Metal cations exhibited excellent catalytic performance in various heterogeneous organic transformations, which bring about the advantage of easy handling, eliminate waste production and simplify the workup procedure. Furthermore, the Mont catalysts are reusable without appreciable loss of their high activities and selectivities. Because of these reasons, and the fact that the catalyst can be reused or regenerated, the entire synthetic activity is not only economical but also environmentally benign.

Hydrotalcite, $[Mg_6 Al_2 (OH)_{16}] (CO_3).4H_2O$, is one of few naturally occurring clays capable of anion exchange. These materials can be thought of as comprised of brucite-like $Mg (OH)_2$ layers, in which each Mg^{2+} cation is 6-fold bonded to hydroxyl groups in an octahedral arrangement. These octahedral share edges to form infinite sheets. When some Mg^{2+} are replaced by Al^{3+} the layer gains a positive charge, originating in the trivalent cation, which is neutralized by interlamellar anions. Charge-balancing anions (usually CO_3^{2-}) and water molecules are present in the inerlayers. A wide variety of synthetic hydrotalcite-like materials can be obtained by the substitution of both cations in the layer and anions in the interlayer region. Hydrotalcite-like materials can be represented by general formulae, $[M (II) x M (III)_X (OH)_2]$ X+ [An-x'n] x- mH_2O where M (II) and M (III) are divalent and trivalent metal ions, respectively . The activity of this inorganic compound can be easily tuned up by the set of hetero elements M(II)/M(III) and changing their ratio for brucite sheets and or by incorpora ting different anions in the interlayer of brucite from a wide range of multiple options, where M(II) = Mg^{2+} Ni^{2+} Cu^{2+} Zn^{2+}, etc., M(III) = Al^{3+} Fe^{3+} Cr^{3+}, etc., An-= $[CO3]^{2-}$, Cl", $[NO_3]$. Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLCs) have recently received much attention in view of their potential usefulness as adsorbents, anion exchangers and catalysts.

RESULTS AND DISCUSSION

The reaction can be carried out in presence of suitable solvent selected from a group consist ing of DME, DMA, NMP, DMF, DMSO, ethylene glycol, sulfolane or mixtures thereof. The reaction is carried out at temperature ranging from 100°C to about reflux temperature of the solvent, more preferably 140-180°C. The reaction time varies from 1 hour to about 50 hours, more preferably from 6 hours to about 36 hours. After completion of the reaction, the catalyst is separated by simple filtration. The filtrate is diluted with organic solvent and the organic layer was washed with water. The organic layer is separated after removal of solvent and the product is distilled under vacuum to afford 3,4-alkylenedioxythiophene or 3,4-dialkoxythiophene. Organic solvents used for dilution or extraction are selected from a group consisting of aromatic solvents, ethers, ketones, esters, dihalides, preferably dihalides selected from alkyl dihalides such as ethylene dichloride, methylene dichloride and so on, aromatic solvents such as toluene, xylene and so on, esters such as ethyl acetate, methyl acetate, butyl acetate and so on, most preferably ethylenedichloride. In a particular embodiment, 3, 4-alkylenedioxythiophene is preferably 3, 4- ethylenedicarboxylicacids or its salts (Table1).

Table1. Effect of solvent on the decarboxylation of 3, 4-alkylenedioxythiophene-2, 5-dicarboxylic acids or its salts.

Entry	Solvent	Yield (%)
1	DMF	96
2	DMA	45
3	ETHYLENE GLYCOL	50
4	DMSO	35

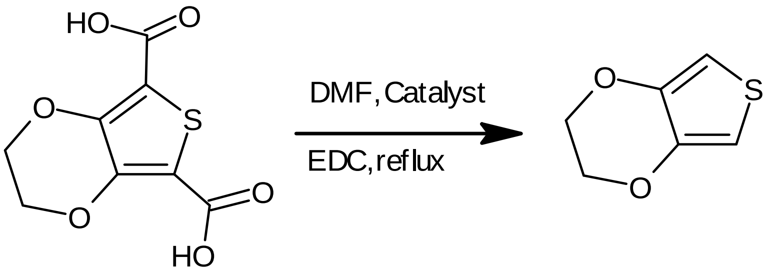
In particular embodiment, the invention involves process for the preparation of 3,4- alkylene dioxythiophene or 3,4-dialkoxythiophene by using reusable heterogeneous catalysts such as montmorillonite clays, hydrotalcites, hydroxyapatites and nano metal Oxides.The heterogene ous catalyst is selected from montmorillonite clays, metal enwrapped montmorillonite clays, metal doped hydroxy apatite catalyst or metal hydrotalcite catalyst or nano metal oxides (Table2).

Table 2. Decarboxylation of 3, 4- alkylenedioxythiophene-2, 5-dicarboxylic acids or its salts.

Entry	Catalyst	Yield (%)
1	H^{+}-mont	92
2	Zn^{2+}-mont	96
3	Cu^{2+} -mont	96
4	Zn/Al- HT	90
5	Cu/Al-HT	80

6	Zn-HAP	87
7	Cu-HAP	89
8	ZnO	80
9	CuO	90

Reaction Scheme



montmorillonite clay is selected from H+-montmorillonite clay or metal doped montmorillonite clay is selected from Iron montmorillonite, Copper montmorillonite, Aluminum montmorillionite, Zinc montmorillonite etc., preferably Copper montmorillonite or Zinc montmorillonite; metal doped hydroxy apatite is selected from CuHAP, ZnHAP,SnHAP,AlHAP, FeHAP, etc., preferably, CuHAP or ZnHAP; metal hydrotalcite is selected from Mg/Al HT, Cu/Al HT, Zn/Al HT, Ni/Al HT, Sn/A1 HT etc., preferably Cu/Al HT or Zn/Al HT;nano metal oxide is selected from nano Zinc Oxide, nono Cupper Oxeide, nano Titanium Oxide, preferably Zinc Oxide.

EXPERMENTS

Example 1. Preparation of Na$^+$- Mont

To a round bottomed flask containing 1g of K-10 montmorillonite clay was added 25 ml of IM NaCl solution and kept for stirring for 3 days and then filtered, and washed repeatedly with water to remove excess sodium chloride. It was then dried overnight in an oven at 90^{o}C.

Example 2. Preparation of H$^+$-Mont

A mixture of parent Na$^+$-mont (3.0 g) and 200 ml of aqueous HCl (1.1 wt%) was stirred at 90 °C for 24 h. The slurry obtained was filtered and washed with 1L of distilled water to remove chlorine, followed by drying at 110 °C in air to afford the H-mont as a whitish grey powder.

Example 3. Preparation of Cu-Montmorillonite catalyst

The Na$^+$-mont (3.0 g) was stirred in aqueous Cu $(N0_3)_2.3H_20$ (8.3x10-3 M, 200 ml) at 50°C for 24 h. The resulting suspension was filtered and the solid was washed repeatedly with deionized water and dried at 110 °C to yield a light blue powder. The basal spacing for the Cu-

Montmorillonite was estimated to be 2.9 A, which was comparable to that of the parent Na^+-mont. Elemental analysis confirmed that two Na^+ ions are replaced by one Cu^{2+} ion during ionexchange (Cu 3.21; Na 0.09%).

Example 4. Preparation of Zn-Montmorillonite catalyst

To a solution of 2M Zinc chloride (100 ml), 1% slurry of Na-Mont (100 ml) in water was added and stirred for a period of 12 h and then set aside for settling. The supernant salt solution was removed and again 2 M Zinc chloride solutions (100 ml) was added and kept for stirring for another 12h. Stirring and removal of supernant solution was repeated and then distilled water was added, stirred, settled and decanted off the large excess of salt was removed by this process. The Zn cation-exchanged Mont (Zn11-Mont) composites thus obtained were dried at 50±5 °C in air oven to obtain the solid products.

Example 5. Preparation of Zn/Al Hydrotalcite catalyst

A solution of 3:1 molar ratio of zinc chloride and aluminum chloride was prepared. To this a 2M solution of sodium hydroxide was added until the original pH of the chloride solution had been increased from around 3 to pH 10-11. This resulted in the formation of a white gel-like precipitate which was separated by centrifuging. The precipitate was then washed by suspen sion in demineralised water followed by centrifuging. This washing process was repeated several times.

Example 6. Preparation of Cu/Al Hydrotalcite catalyst

A mixture of $CuCl_2.6H_2O$ (50 g, 0.293 mol) and $AlCl_3.6H_2O$ (30 g, 0.225 mol) was dissolved in 200 ml deionized water. To this aqueous solution was slowly added IM NaOH (100 ml) solution at 25 °C, and a further amount of IM NaOH solution was added to maintain a pH of 10 under nitrogen flow. The resulting suspension was stirred overnight at room temperature. The solid at product was isolated by filtration, washed thoroughly with deionized water, and dried overnight 80 °C. All of the synthetic steps were carried out using deionized water.

Example 7. Preparation of Hydroxyapatite [HAP, $Ca_{10} (PO_4)_6(OH)_2$]

$Ca (NO_3)_2.4H_20$ (15.576 g, 0.066 mol) dissolved in water (60 ml) was brought to pH 11-12 with concentrated NH_4OH and thereafter diluted to 120 ml. A solution of $(NH_4)_2HP0_4$ (5.28 g, 0.04 mol) in 100 ml water was brought to pH 11-12 with concentrated NH_4OH and thereafter diluted to 160 ml. The calcium solution was vigorously stirred at room temperature, and the phosphate solution was added drop wise over a period of 30 min to produce a milky, somewhat gelatinous precipitate which was then stirred and boiled for 10 min. The precipitate was filtered, washed, dried at 80˚C overnight and calcined at 500°C for 3h. All the above steps were carried out using doubly distilled water.

Example 8. Preparation of Cu exchanged HAP

HAP (1g) was stirred with aqueous Cu $(OAc)_2$ (0.400 g, 2 mmol) in 25 ml water at 60 °C for a period of 10 h. The obtained slurry were filtered, washed with deionized water and dried over night at 110 °C yielding copper exchanged hydroxyapatite (CuHAP) as a light blue powder (Cu content by means of ICP-Ms: CuHAP - 0.66 mmolg-).

Example 9. Preparation of Zn exchanged HAP

HAP (1g) was stirred with aqueous Zn $(OAc)_2.2H_2O$ (0.439 g, 2 mmol) in 25 ml water at 80 °C for a period of 10 h. The obtained slurries were filtered, washed with deionized water and dried over night at 110 °C yielding copper exchanged hydroxyapatite (ZnHAP) as a white powder (Zn content by means of ICP-Ms: 1.15 mmolg-).

CONCLUSION

Proton and metal ion-exchanged Montmorillonite catalyzes the decarboxylation of 3, 4-alkylene dioxythiophene dicaboxylic acid or its salts or 3, 4- dialkoxythiophenedicarboxylic acid or its salts respectively, in presence of less expensive and reusable heterogeneous cata - lyst. The catalyst can be reused or regenerated; the entire synthetic activity is not only economical but also environmentally benign.

SPECTRAL DATA

^{1}H NMR (300 MHz, CDCl3):4 δ 2(s, 4H), 6.31(s, 2H).

^{13}C NMR (MHz, CDCl3): δ 67.5, 121.8, 143.5.

IR (KBr): 2981, 2872, 1053, 933, 889, 833, 677 cm^{-1}.

Mass: *m/z* 143 (M+1).

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REFERENCES

1. O. Hinsberg et al, (Ber. Dt. Chem. Ges. 43, 1910, 901-906 and 45, 1912, 2413- 2418).
2. M. Coffey et al., (Synthetic Communications, 1996; 26 (11): 2205-2212.

3. M. colfey et al., [Synlh Commun., 1996; 26; 2205412]
4. E. Fager [.I. Am. Chem. Soc, 1951; 2956457]
5. Murashima et al.; Tetrahedron Letters, 1996; 37 (18): 3133-3136.
6. Zong et al.; J. Org. Chem., 2001; 66: 6873-6882.
7. D. L. Hughes, Org. React., 1992; 42:335–656.
8. F. Dallacker and V. Mues, Chem. Ber., 1975; 108: 569–575;
9. F.Dallacker and V. Mues, Chem. Ber., 1975; 108:576–581.
10. 10.V. N. Gogte, L. G. Shah, B. D. Tilak, K. N. Gadekar and M. B.
11. Sahasrabudhe, Tetrahedron, 1967; 23: 2437–2441.
12. P. Schottland, O. Stephan, P.-Y. Le Gall and C. Chevrot, J. Chim. Phys.
13. Phys.-Chim. Biol., 1998; 95: 1258–1261.