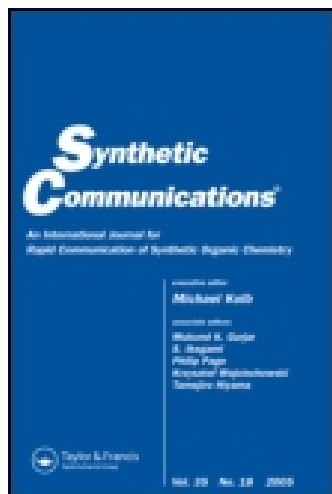


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### A Novel Montmorillonite - $\text{KMnO}_4$ System for the Oxidation of Alkenes Under Triphase Conditions

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A NOVEL MONTMORILLONITE -  $\text{KMnO}_4$  SYSTEM  
FOR THE OXIDATION OF ALKENES  
UNDER TRIPHASE CONDITIONS<sup>†</sup>

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**Abstract**

A very simple oxidation of alkenes to dicarboxylic acids using H-montmorillonite- $\text{KMnO}_4$  system has been described for the first time.

Mimicking of enzymes at the industrial level is possible only through natural clays, which are micro-reactors. These micro-reactors has the ability to store organic matter between their interlayers and compelling the reaction to take place in fascinating way on a single plane<sup>1-4</sup>. Clayey micro-reactors attract ions to the proximity of their interface, there by accelerating the course of the

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<sup>†</sup> IICT Communication : 2313

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reaction. Intralamellar silicate sheets of montmorillonite are the versatile hosts for the Brønsted and Lewis acid catalyzed organic reactions namely, protonation of alkenes, esterification, Diels-Alder, Friedel-Craft reaction etc. and redox reactions such as nitration of phenols, polymerization of benzene and photo cleavage of water<sup>5,6</sup>. This striking reactivity of montmorillonite is due to the electrical double layer formed between the delocalised negative charge on the basal surface oxygens and counter-ions used to counter balance the surface charge. The unit cell of montmorillonite carries most of the times the negative charge in fraction (less than unit) on its basal oxygens. During counter balancing with cations, surplus positive charge, developed is again counterbalanced by associated anions. This constitutes a polyelectrolyte system which is in the highly polarisable state and stabilises pairs of ions due to columbian attraction.

This intrinsic property of montmorillonite prompted us to explore it as phase transfer catalyst. We describe in this communication a new system, comprising of H-montmorillonite and  $\text{KMnO}_4$  for the oxidation of alkenes to dicarboxylic acids. As explained in the preceding lines, H-montmorillonite generates a highly reactive, free  $\text{MnO}_4^-$  ion from  $\text{KMnO}_4$  in the interlayers of montmorillonite, which can effectively oxidise olefins to dicarboxylic acids in benzene and water system by a very simple and easily adoptable method under triphase catalysis. Thus oxidation of alkenes (Table-I) proceeds very rapidly to give acids in high yields at moderate temperatures

**Table - 1**  
**Oxidation of alkenes by H-Montmorillonite / KMnO<sub>4</sub><sup>a</sup>**

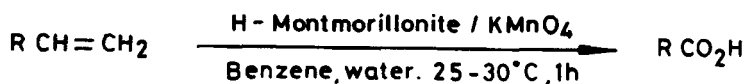
Entry No.	Substrate	Product <sup>b</sup>	Yield <sup>c</sup> (%)
1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	93
2	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	87
3	PhCH=CH <sub>2</sub>	PhCOOH	91
4		PhCOOH	94
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CH·CH <sub>2</sub> OH	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> H	92
6			90
7			92
8			88
9		No reaction	—

a. Temperature 25°-30°C, Time 1h

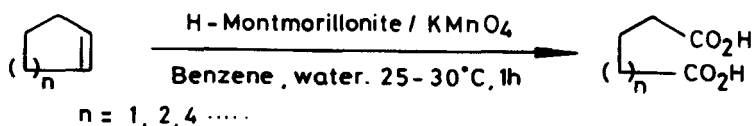
b. Characterized by IR, <sup>1</sup>H NMR and Mass

c. Isolated yields.

(25–30°C) within an hour. Controlled experiments conducted with neutral/acidic  $\text{KMnO}_4$  and without H-montmorillonite afforded poor yields (5–10%) under identical conditions. These results demonstrated the efficacy of H-montmorillonite in this oxidation.



R = alkyl, aryl



Thus oxidation of terminal olefins with the present system gave the aliphatic carboxylic acids, while the monocyclic olefins under the similar conditions afforded dicarboxylic acids in almost quantitative yield. When bicyclic olefin, Norbornene subjected to the oxidation reaction with H-montmorillonite -  $\text{KMnO}_4$  system, the starting material was recovered as such even after prolonged reaction times. This can be attributed to the restricted interlayer space of H-montmorillonite, which is unable to accommodate the bicyclic ring requiring more interlayer space than the available space.

The striking feature of the present work envisages the use of H-montmorillonite prepared easily from the commercially and cheaply available  $\text{K}_{10}$ -montmorillonite and the yields are comparable to the conventional crowns and tetra alkyl ammonium salts<sup>7</sup>. Further crown ethers and tetra alkyl ammonium salts are expensive and

require tedious workup procedures. Further, the present method is superior over the KMnO<sub>4</sub> impregnated solid supports, especially K<sub>10</sub> - montmorillonite<sup>8</sup> which requires longer reaction times (76 h) and higher temperatures (70°C) with almost same yields. In addition, the inherent advantage of the instantaneous separation of the reaction product from the reactant during reaction to avoid secondary reactions and easy separation of the product after reaction, present in the phase-transfer catalysts still exists in our triphase catalysis.

Another interesting feature of the present work is the use of sub-stoichiometric amounts of KMnO<sub>4</sub> (substrate/KMnO<sub>4</sub> = 2/3) than the required stoichiometric one for the oxidation of alkene (substrate/KMnO<sub>4</sub> = 3/8) was used<sup>9</sup>. However, the reaction, when conducted with total exclusion of oxygen/air from the system by flushing with nitrogen, proceeded to completion with stoichiometry quantities of KMnO<sub>4</sub> only. This may lead to the conclusion that the H-montmorillonite used may be reoxidising the manganese species by utilising oxygen present in the reaction medium during the course of the reaction. Further work to understand the mechanism and to make the system totally catalytic are under progress.

Therefore, the simple and convenient reactions described above, provided a practical alternative to other methods and expand the scope of utilisation of montmorillonite in useful organic transformation.

## Experimental

Materials and Methods : Commercial montmorillonite (Fluka,  $K_{10}$ ) was allowed to sediment for 24 h as a 1 wt.% aqueous slurry to remove dense impurities. Montmorillonite was then treated with excess saturated aqueous NaCl solution to get Na-montmorillonite. Thus, the sodium saturated montmorillonite was treated with 0.1 N HCl to replace the sodium ions and H-montmorillonite was washed with deionised water. A supercentrifuge was used to separate the clay. The H-montmorillonite was dispersed in 95% ethanol in a waring blender and washed three times with absolute ethanol and three times with absolute ether to remove the adsorbed water.

Model oxidation reaction : Freshly prepared H-montmorillonite (0.5g), and  $KMnO_4$  (0.03 mol) were taken in benzene (5 ml) and water (10 ml) in a round bottom flask and subjected to vigorous stirring for 1 h. The suspension was then treated with styrene (0.02 mol) over a period of 0.5 h under vigorous stirring. The high exothermic reaction was controlled by cooling the flask with cold water to maintain the temperature at about 25-30°C. The overall contents were further stirred for half an hour more. After addition of sodium sulphite to destroy the excess  $KMnO_4$  present, the reaction mixture was filtered and acidified with dilute HCl. The solid residue was thoroughly washed with benzene which can also be used to wash with aqueous layer. The combined benzene layers were shaken with 10% NaOH solution. The aqueous layer was then washed with ether and acidified with dilute HCl. The carboxylic acid was extracted



into ether, dried (anhydrous Na<sub>2</sub>SO<sub>4</sub>) and on evaporation yielded benzoic acid (91%).

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