



## Ultrasound Promoted Synthesis of Organic Compounds using K-10 Montmorillonite Clay

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### ABSTRACT

The power of ultrasonic waves plays the most important role in the size and morphology of the products. Montmorillonite K-10 found to be highly efficient, environmentally friendly and recyclable heterogeneous catalysts and also found to play the role in the size and morphology of the products. In order to find the combined effect of both ultrasonic waves and montmorillonite K-10 clay, aspirin, m-dinitrobenzene and glucosazone were synthesised under ultrasound irradiation (sonication method) using montmorillonite K-10 clay. This new methodology provides excellent yields in short reaction times (5–20 min). The reaction work-up is very simple and the catalysts can be easily separated from the reaction mixture and reused several times in subsequent reactions. The compounds synthesized confirmed by FT-IR. The size and morphology of products characterized by XRD and SEM compared with products obtained by (i) conventional method (ii) conventional method with clay. Similarly the percentage yield obtained and the time factor also compared between the three methods.

### 1. Introduction

Recent advances in nanostructured materials have been led by the development of new synthetic methods that provide control over size, morphology, and nano microstructure. The utilization of high intensity ultrasound offers a facile, versatile synthetic tool for nanostructured materials that are often unavailable by conventional methods [1].

High intensity ultrasound can be used for the production of novel materials and provides an unusual route to known materials without bulk high temperatures, high pressures, or long reaction times. Several phenomena are responsible for sonochemistry and specifically the production or modification of nanomaterial during ultrasonic irradiation [2].

The primary physical phenomena associated with ultrasound that are relevant to materials synthesis are cavitation and nebulization. Acoustic cavitation (the formation, growth, and implosive collapse of bubbles in a liquid) creates extreme conditions inside the collapsing bubble and serves as the origin of most sonochemical phenomena in liquids or liquid-solid slurries. Nebulization (the creation of mist from ultrasound passing through a liquid and impinging on a liquid-gas interface) is the basis for ultrasonic spray pyrolysis (USP) with subsequent reactions occurring in the heated droplets of the mist [1]. According to the “hot-spot” theory, extreme temperatures (> 5000 K) and high pressures (> 1000 atm) occur within the bubbles during cavitation collapse [3-6].

Moreover, the other benefit in using ultrasonic waves in reactions is believed to be providing highly-intensive mixing especially in viscous media. This would lead to an acceleration effect in chemical dynamics and rates of the reactions. Therefore, by this circumstance, different properties of the final products such as particle size, shape and its purity would be controlled by as sonication output power, temperature, the solvent, the chemical species and their concentrations in the reaction mixture [7].

As concern for the environment continues to shape the way chemists think about the construction of physiologically active compounds, the development of synthetic methodologies that promote greener reactions is essential. Environmentally benign clays are ideally suited for the

‘greening’ of modern synthetic chemistry—they are naturally abundant, inexpensive, nontoxic, chemically versatile, and recyclable [8].

K-10 montmorillonite clay has been widely used as catalyst in a large variety of organic reactions [9-12] and it has also received considerable attention in different areas of organic synthesis [13-18]. Many clay based catalysts such as claycop, clayzinc, clayfen, envirocat, etc., are commercially available, the two most common modified clays applied in organic synthesis are the K-10 and KSF montmorillonites. Both are synthetic clays produced from natural montmorillonites and are available from many suppliers in large quantities. While the physicochemical properties are similar, their BET surface areas are quite different. K-10 has a higher surface area (about 250 m<sup>2</sup>g<sup>-1</sup>) compared to that of KSF (10 m<sup>2</sup>g<sup>-1</sup>). The remarkable surface area of K-10 usually leads to faster reaction, since more active sites are exposed to the reaction mixture. This feature led to several recent studies to apply K-10 montmorillonite in organic synthesis [19].

The clay catalysts and montmorillonite in particular, have received considerable attention for different organic syntheses because of their environmental harmlessness, low cost, high selectivity, reusability and operational simplicity [20]. The reactions catalyzed by montmorillonite are generally carried out under mild conditions, the separation of the spent catalyst is achieved by filtration, and the product is recovered by mere evaporation of the solvent [21].

Nanoparticles are synthesized into the nanopores of Montmorillonite K-10. The clay prevented the agglomeration of nanoparticles without any external stabilizer [22]. Chen et al studies reveal that ultrasound decrease the reaction time and increase the yields [23].

### 2. Experimental Methods

All reagents were purchased commercially and used without further purification. The X-ray diffraction (XRD) patterns of compounds were obtained using a Bruker AXS D8 Advance, Inst ID: OCPL/ARD/26-002 X-ray diffractometer. Fourier transform infrared spectra (FT-IR) were recorded using Nicolet 6700, Thermo Electronic Corporation, USA made spectrophotometer. The scanning electron microscopy (SEM) analysis performed using a Philips XL-20 electron microscope. Computations were made using Microcal Origin (Version 6.0) software.

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## 2.1 Preparation of Aspirin

### 2.1.1 Conventional Method (CM)

Exactly 1 g of salicylic acid, 1.4 mL of acetic anhydride and 2 drops of concentrated sulphuric acid were taken in a conical flask. The flask was rotated to ensure thorough mixing. It was warmed on a water bath to about 50-60 °C, with stirring for about 15 minutes. The mixture was allowed to cool and stirred occasionally. 30 mL of water were added to it and stirred well. The solids were filtered at the pump. The recollected clay was washed thoroughly with distilled water and reused for the subsequent synthesizes. The above procedure was repeated using montmorillonite clay (CCM – conventional method with clay).

### 2.1.2 Sonication Method (USCM – Ultrasonic Method with Clay)

Accurately 1 g of salicylic acid, 1.4 mL of acetic anhydride and 2 drops of concentrated sulphuric acid were taken in a boiling tube. To this 2 g of K-10 montmorillonite clay were added. The tube was kept in a sonicator and set the time for 5 minutes. The mixture obtained was cooled and stirred occasionally with 30 mL of water and filtered at the pump, dried. The precipitate was dissolved in 1:1 acetic acid, stirred well and filtered. The filtrate was collected. This procedure was repeated for 2 or 3 times. The collected filtrates were evaporated to get the product.

## 2.2 Preparation of *m*-Dinitrobenzene

### 2.2.1 Conventional Method (CM)

Precisely 2 mL of nitrobenzene were dissolved in 2 mL of concentrated sulphuric acid contained in an RB flask. 4 mL of nitrating mixture (2 mL of conc. sulphuric acid and 2 mL of conc. nitric acid) were slowly added with shaking. After the addition was over, it was fitted with an air condenser. The reaction mixture was heated for about an hour on a boiling water bath till a test portion of the reaction mixture with cold water gave a solid. It was cooled and then poured into about 150 mL of cold water. The solid was filtered at the pump, washed thoroughly with water to remove traces of acid. The above procedure was repeated using montmorillonite clay (CCM).

### 2.2.2 Sonication Method (USCM)

Exactly 2 mL of nitrobenzene were dissolved in 2 mL of concentrated sulphuric acid contained in a boiling tube. 4 mL of nitrating mixture (2 mL of conc. sulphuric acid and 2 mL of conc. nitric acid) were slowly added with shaking. 2 g of K-10 montmorillonite clay were added. The tube was kept in a sonicator and set the time for 15 minutes. After the reaction was over, the mixture was cooled and then poured into about 150 mL of cold water. The solid was filtered at the pump, washed thoroughly with water to remove traces of acid and dried. The precipitate was dissolved in alcohol, stirred well and filtered. The filtrate was collected. This procedure was repeated for 2 or 3 times and the filtrates were collected. The collected filtrates were evaporated to get the product.

## 2.3 Preparation of Glucosazone

### 2.3.1 Conventional Method (CM)

Accurately 0.5 g of glucose was dissolved in 2.5 mL of water in a boiling tube. In another tube 1 mL of acetic acid, 2.5 mL of water and 1 mL of phenyl hydrazine were shaken well. This was to ensure the formation of phenyl hydrazine acetate. Then it was added to sugar solution, stirred well and placed in a boiling water bath. In about 15 minutes, the yellow osazone began to crystallize out. It was further heated for about 30 minutes and then cooled in cold water. The osazone was filtered at the pump, initially washed with water and then methylated spirit. The above procedure was repeated using montmorillonite clay (CCM).

### 2.3.2 Sonication Method (USCM)

Exactly 0.5 g of glucose was dissolved in 2.5 mL of water in a boiling tube. In another tube 1 mL of acetic acid, 2.5 mL of water and 1 mL of phenyl hydrazine were shaken well. This was to ensure the formation of phenyl hydrazine acetate. Then it was added to sugar solution, stirred well. 1 g of K-10 montmorillonite clay were added to this and kept in a sonicator. Set the time for about 20 minutes and then the reaction mixture was cooled in cold water. The mixture was filtered at the pump, initially washed with water and then methylated spirit. It was dried, dissolved in dilute alcohol and filtered. This procedure was repeated for 2 or 3 times and the filtrates were collected. The collected filtrates were evaporated to get the product. The clay obtained after filtrating the conventional method was washed thoroughly with water, dried and reused for the corresponding ultrasonic method IR, XRD and SEM analysis confirmed the identities of the products.

## 3. Results and Discussion

### 3.1 Characterization of Compounds

The FT-IR spectras of compounds viz aspirin, *m*-dinitrobenzene and glucosazone, which have been synthesized by USCM, are shown in Figs. 1-3. There is an observation from Fig. 1 the FT-IR peaks showing the characteristics nature of aspirin. The presence of stretching frequencies, at 3200-3680  $\text{cm}^{-1}$  (broad) corresponds to O-H stretching, at 2700-3300  $\text{cm}^{-1}$  corresponds to aromatic C-H stretching, at 1550-1850  $\text{cm}^{-1}$  corresponds to C=O stretching, at 1085-1300  $\text{cm}^{-1}$  corresponds to C-O stretching and the peak at 2975-2950  $\text{cm}^{-1}$  corresponds to  $\text{CH}_3$  stretching, strongly confirmed that the compound synthesized using sonication is aspirin.

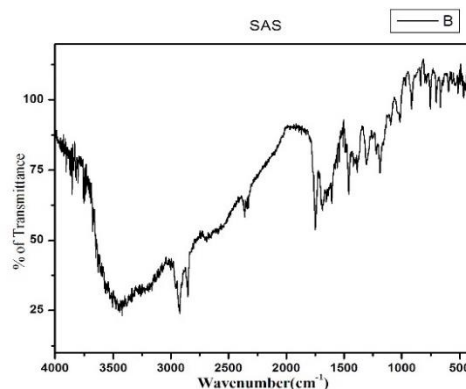


Fig. 1 FT-IR spectrum of aspirin synthesized by USCM

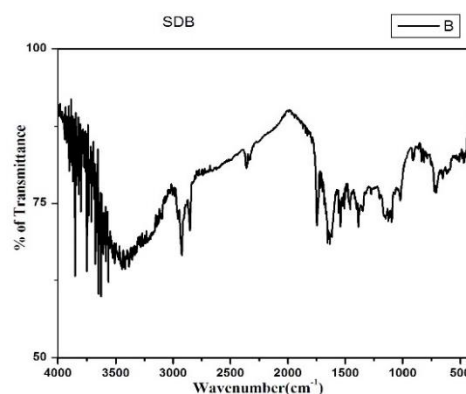


Fig. 2 FT-IR spectrum of *m*-dinitrobenzene synthesized by USCM

The Fig. 2 shows the characteristic frequencies of *m*-dinitrobenzene. The presence of bands at 2700-3300  $\text{cm}^{-1}$ , 1020-1250  $\text{cm}^{-1}$  and 1530-1510  $\text{cm}^{-1}$  are corresponds to the C-H stretching, C-N stretching and  $\text{NO}_2$  stretching of *m*-dinitrobenzene respectively.

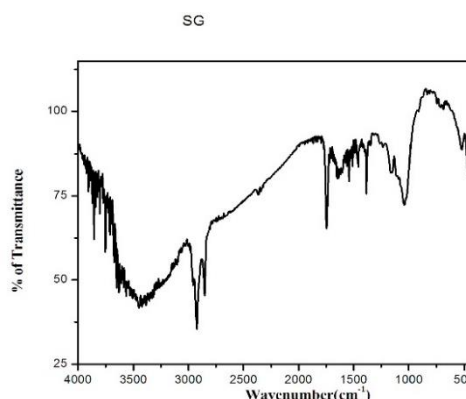


Fig. 3 FT-IR spectrum of glucosazone synthesized by USCM

The Fig. 3 shows the stretching frequencies, at 3300-3500  $\text{cm}^{-1}$  corresponds to N-H stretching, at 2700- 3300  $\text{cm}^{-1}$  corresponds to aromatic C-H stretching, at 1020-1250  $\text{cm}^{-1}$  corresponds to C-N stretching, at 1670  $\text{cm}^{-1}$  corresponds to C=N stretching and the peak at 3200 - 3680  $\text{cm}^{-1}$  (broad) corresponds to O-H stretching and the peak at 2940-2915  $\text{cm}^{-1}$  corresponds to  $\text{CH}_2$  stretching. The above observed frequencies are corresponds to the glucosazone.

### 3.2 Reduction of Time and Raise in Yield

The Figs. 4 and 5 explains that the sonication method showing very fast reactivity and higher in yield percentage when compared with CM as well as CCM preparations. The yield of sonication method was 77.23% of aspirin which is 29.06% higher than CCM and 55.82% higher than CM. When time is concerned, the reaction was completed by 5 minutes whereas other two methods required 15 minutes. In total, time saving is 10 minutes. In the case of m-dinitrobenzene, increase in yield was found to be 28.04% and 43.10% in USCM when compared with CCM and CM respectively. In USCM m-dinitrobenzene could be synthesized by 15 minutes which is 45 minutes faster than CCM and CM. The percentage difference in yield was 15.34 between USCM and CCM and 34.10 between USCM and CM for the synthesis of glucosazone. The time reduction observed in synthesis of glucosazone was 25 minutes.

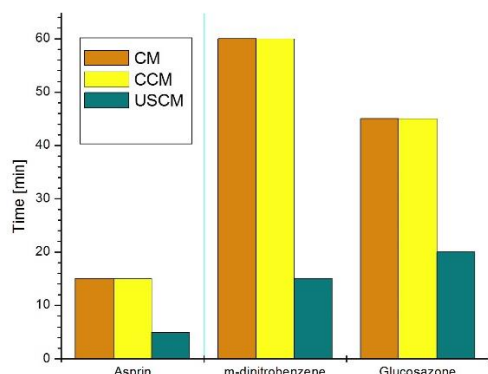


Fig. 4 Comparison of reaction time of CM, CCM and USCM

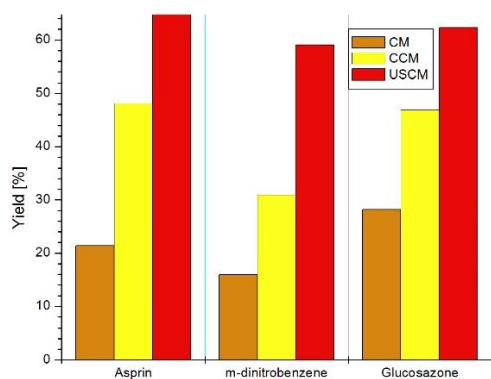


Fig. 5 Percentage yield variation of CM, CCM and USCM

### 3.3 Effects on Size and Morphology

The XRD patterns in Figs. 6-8 reveals that the combined effect of both the ultrasound and clay (USCM) on particle size is found to be more in all the three samples (Table 1). The effect is maximum in glucosazone (22.09 nm) and minimum in aspirin (66.64 nm). The clay also has some effect on particle size. But the effect of clay is found to be more in the case of aspirin and very less in the case of glucosazone. The effect of clay is lesser than the combined effect. SEM images in Figs. 9-11 and Table 2 representing the clear distinction between morphologies of the compounds prepared by USCM, CCM and CM.

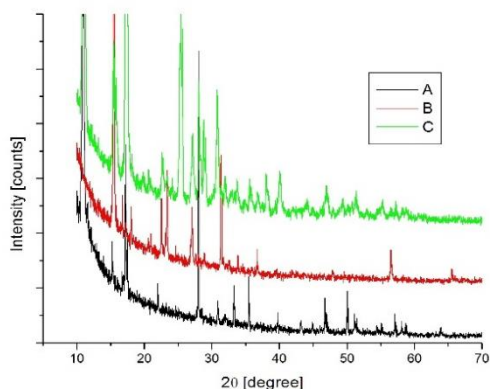


Fig. 6 XRD patterns of aspirin synthesized by a) CM b) CCM c) USCM

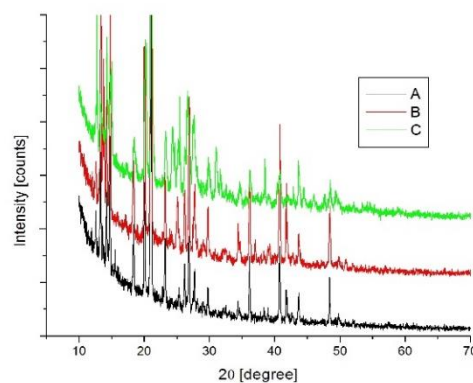


Fig. 7 XRD patterns of m-dinitrobenzene synthesized by a) CM b) CCM c) USCM

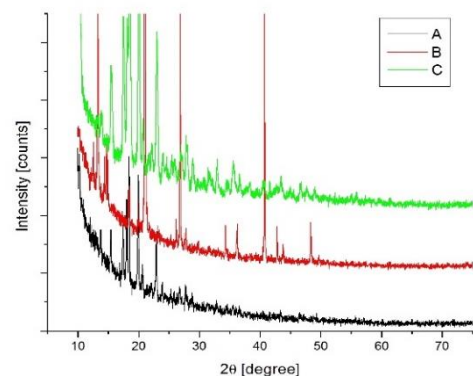


Fig. 8 XRD patterns of glucosazone synthesized by a) CM b) CCM c) USCM

Table 1 The range of Particle size (nm) of compounds synthesized by CM, CCM and USCM

Sample	CM	CCM	USCM
Aspirin	88.39 – 176.80	75.79 – 136.9	66.64 – 89.72
m-dinitrobenzene	89.50 – 177.07	80.48 – 134.11	53.49 – 76.73
Glucosazone	66.86 – 107.29	59.39 – 89.34	22.09 – 88.70

Table 2 Morphological observation of compounds from SEM images

Sample	CM	CCM	USCM
Aspirin	Broad Rods	Branched Rods	Narrow Rods
m-dinitrobenzene	Cluster Rod	Netlike	Fiber
Glucosazone	Wire	Thin Rods	Fiber Rods

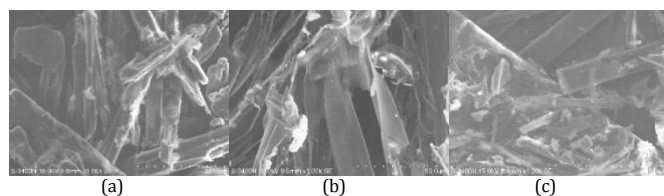


Fig. 9 SEM images of aspirin synthesized by a) CM b) CCM c) USCM

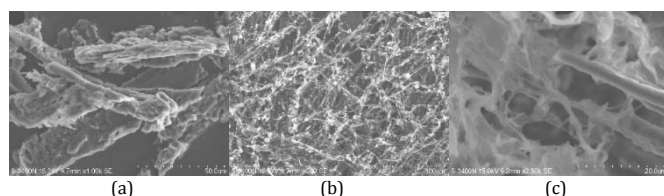


Fig. 10 SEM images of m-dinitrobenzene synthesized by a) CM b) CCM c) USCM

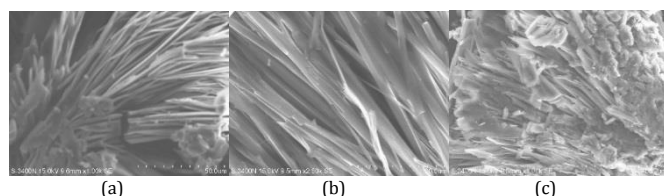


Fig. 11 SEM images of glucosazone synthesized by a) CM b) CCM c) USCM

#### 4. Conclusion

The role of ultrasound waves as a catalyst increases the yield extremely in all the three compounds synthesized and also reduces the reaction time significantly. Notable morphological changes observed in ultrasonic mediated synthesized compounds and the particle size also reduced drastically to the minimum. These remarkable changes in morphology and size are due to the combined effect of ultrasound and nanopores of montmorillonite K-10 clay. The above results reveal that the dual nature of both ultrasound and montmorillonite K-10 as the catalyst and as size reducing agent can be applied to the organic synthesis.

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#### About the Conference...

“National Conference on Advanced Materials and Their Applications” has been convened by Dr. C. Vedhi, Assistant Professor, PG and Research Department of Chemistry, V.O.Chidambaram College, Thoothukudi at his designated venue on 21<sup>st</sup> & 22<sup>nd</sup> January 2016, sponsored by Department of Science and Technology, Govt. of India, and V. O. Chidambaram College, Thoothukudi.