Preparation, characterization and catalytic application of Cr-pillared clay for synthesis of octahydroxanthenes

A Dissertation
Submitted in partial fulfillment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy Of

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

By:

Sangeeta Adhikari

Under the Guidance of

Dr. B. G. Mishra

DEPARTMENT OF CHEMISTRY
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008
ORISSA

CERTIFICATE

Dr. Braja Gopal Mishra

Associate Professor
Dept. of Chemistry
National Institute of Technology,
Rourkela - 769008

This is to certify that the dissertation entitled "**Preparation, characterization and catalytic application of Cr-pillared clay for synthesis of octahydroxanthenes**" being submitted by **Sangeeta Adhikari** (Roll No. 409CY2001) to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by her under my supervision and guidance. I am satisfied that the dissertation has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

N.I.T. Rourkela — Dr. Braja Gopal Mishra

Date: **Supervisor**

Acknowledgement

I take this opportunity to express my deep sense of gratitude to my guide and supervisor Dr. Braja Gopal Mishra, Department of chemistry, N.I.T. Rourkela for his valuable guidance, motivation and full attention at all stages in my project work. Indeed, the experience of working under him is one of that I will cherish forever.

It is my great pleasure to sincerely thank our H.O.D., Dr. B. G. Mishra for giving us permission to carry out our research work anytime, without which I could hardly complete my project work.

I am indebted to all faculty and staff members of Department of Chemistry, N.I.T, Rourkela for their help.

I extend my thanks to Ph.D. Scholars Mr. Satish Samantaray and Ms. Purabi Kar who worked with me in every difficulty which I have faced and their constant efforts and encouragement was the tremendous sources of inspiration. I also thank my laboratory colleagues Mr. Anindya Sundar Patra & Mr. Pravat kumar Subuddhi for helping me everytime.

My heartfelt thanks to my family members, especially to my parents, and my friends for their love, affection, support and encouragement.

Last but never the least, I greatly acknowledge Department of Chemistry, National Institute of Technology, Rourkela for providing me infrastructure without which it was impossible to complete my project and making my stay a memorable one in the Institute.

Sangeeta Adhikari
Department of Chemistry
NIT, Rourkela

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CHAPTER-I

INTRODUCTION TO CLAY MATERIALS

Clays are the most common minerals on earth's surface. Clays are used in many area of application such as building ceramics, paper coating and filling, drilling muds, foundry moulds, and pharmaceuticals. Clays are also the most primitive materials to be used as catalysts and adsorbents for industrial applications [1]. The high surface area and polarity of the clay structures help in retaining the ionic species such as K^+, and Ca^{2+} which are vital for the plant growth [2]. The clay materials modified with salt, acid-treated and ion exchanged have been used as efficient catalysts for many organic transformations [3, 4].

Structure of clay materials: Clays are two dimensional layer silicates belonging to the phyllosillicate family [5]. The basic structure of clay consists of silicate layers designed from the condensation of the very stable SiO_4 tetrahedral units. The SiO_4 tetrahedra share three basal oxygen atoms by corner sharing to from the silicate layer. Condensations of silicate planes with octahedral planner units form different classes of clay materials. The octahedral layer is formed form the edge sharing of the MO_6 (M= Al, Mg etc.). The polymerization of MO_6 octahedra in the plane by sharing four of its edges forms the octahedral layer [5].

Montmorillonite is the most widely investigated clay in catalysis. The structure of montmorillonite consists of an alumina layer sandwiched between two-silicate layers. Then clay sheets are arranged in the z-direction to form the structure of montmorillonite. The structure of montmorillonite clay is shown in Fig. 1.

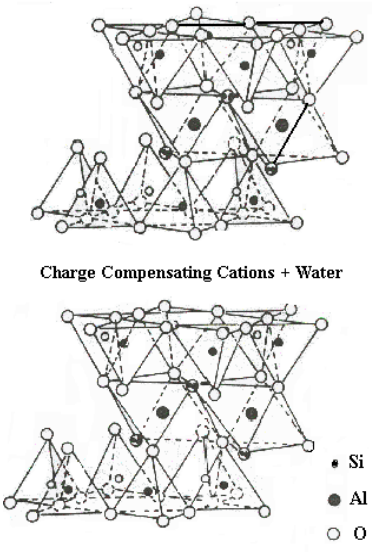


Fig. 1.1 Structure of 2:1 clay mineral montmorillonite

Pillaring of clay: Cationic clays have been used as solid acid catalyst for several acid catalyzed reactions. The acidity observed in the clay materials is mostly Brønsted in nature. However, it is possible to generate Lewis acidity by suitable thermal treatment. Although clays are used as solid acid catalysts, they possess certain inherent disadvantages, which limit their application in heterogeneous catalysis [6]. These limitations can be overcome by the process of pillaring. Pillaring of clay involve the insertion of inorganic polycations of nanodimension to the clay interlayer and subsequent thermal activation. Clay pillared with a variety of inorganic polycations of Al [7], Zr [8], Ti [9], Cr[10], Fe [11] etc. are reported in literature. These polycations are generally prepared by controlled hydrolysis of the corresponding metal cations in solutions. The result of pillaring includes the increase in thermal stability, microporosity, surface area and acidic properties of the parent clay.

Objective of the present work: The main objectives of the present study are to

1. Prepare Cr-Pillared clay by insertion of cationic nanoclusters of Chromium into the clay and explore its potential as a heterogeneous catalyst for synthesis of fine chemicals.

2. Characterize the synthesized Cr-Pillared clay materials by various analytical techniques such as XRD, TGA and UV-Vis to obtain information on the physicochemical characteristics of these materials.

3. Synthesize 1, 8-dioxo-octahydroxanthenes by condensation of aromatic aldehydes with dimedone in presence of the pillared clay materials under solvent free microwave conditions.

CHAPTER 2

MATERIALS AND METHODS

Preparation of Cr-pillared clay: The montmorillonite clay and chromium nitrate were used as such without any purification. The pillaring solution was prepared by mixing required amount of salt in distilled water followed by heating at 60^{o}C. The pillaring process was performed by suspending 2 gm of the clay in 200 ml of distilled water with drop wise addition of pillaring solution with continuous stirring. After the addition of the pillaring solution, the suspension was stirred for 12 h, washed repeatedly in distilled water, dried and calcined at 500^{0}C for 2 h to get Cr-pillared clay.

Characterization of the clay materials: The X-ray diffraction patterns of the pure clay, uncalcined and calcined Cr-pillared clay were recorded on Siemens D-500 diffractometer using Ni-filtered CuKα radiation. UV-Vis Spectra of clay and Cr-P calcined materials were recorded taken using barium sulphate as reference on a Shimadzu spectrophotometer (UV-2450) in the range of 200-900nm. Thermogravimetry analysis of the as prepared Cr-pillared clay was performed on Perkin-Elmer TGA-7 apparatus in air (30 ml per min) with linear heating rate (20^{o}C per min) from room temperature to 800^{o}C.

Synthesis of 1, 8-dioxo-octahydroxanthenes: A neat mixture of aryl aldehyde (1 mmol), dimedone (2 mmol) and 50 mg Cr-pillared clay were exposed to microwave radiation for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool and 10 ml of ethyl acetate was added. The catalyst was then separated by filtration and the filtrate solution was concentrated. The product obtained was purified by recrystallization. The final products were identified by comparing their physical and spectral properties with those reported in literature.

CHAPTER 3

RESULTS AND DISCUSSIONS

XRD study: The XRD patterns of the clay, along with the as synthesized Cr-pillared clay and Cr- pillared clay calcined at 500^0C is presented in figure 3.1. The parent clay shows relatively broader and intense reflections at $2\theta = 6.9^0$ with basal spacing of 12.8 Å corresponding to the reflection from (001) plane of the layered material. After the intercalation of the Cr-oxyhydroxy cluster into the clay layer the (001) peak has shifted to lower 2θ value indicating an expansion in the layer structure as a result of pillaring.

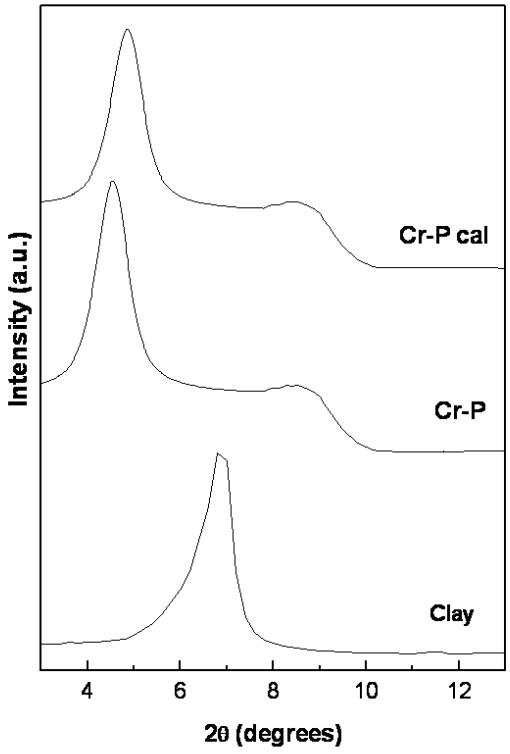


Figure 3.1. X-ray diffraction patterns of (a) clay, (b) Cr-P and (c) Cr-P calcined at 500^0C

The as prepared Cr-pillared clay shows a basal spacing of 19.8 Å with 2θ value of 4.5^0. The calcined Cr-P shows a slight decrease in basal spacing. The calcined Cr-P shows a basal spacing of 18.4 Å. Chromium salts are known to form oligomeric species in base hydrolyzed solutions.

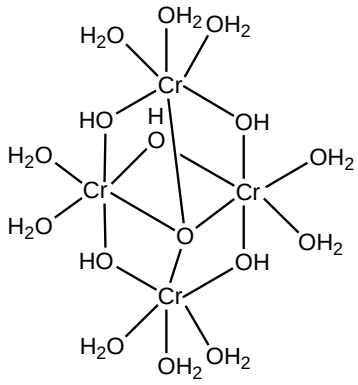


Fig 3 Structure of Cr-Pillaring species

The predominant species observed in a hydrolyzed salt solution of Chromium is $[Cr_4O(OH)_5(H_2O)_{10}]^{5+}$ (Figure 3) which is thoroughly characterized in literature [1, 6]. It is believed that this oligomeric species act as pillar in case of Cr-P material which is responsible for the expansion in the interlayer structure. The XRD study clearly indicates that the layer structure of the clay material is intact in the Cr-pillared clay and the thermal stability of the clay has been enhanced due to pillaring.

UV-Vis study: The UV-Visible spectra of the parent clay along with Cr-P are shown in (Fig. 3.2). The Montmorillonite clay shows characteristic absorption band at 247 nm (Fig. 3.2). This band is assigned to (Fe^{3+} O^{2-}, OH^- or OH_2) charge transfer band for the structural iron present in the octahedral layer of the clay mineral [12]. Intercalation of the chromium pillars into the clay structure results in a change in the absorption pattern and two new bands appeared at 425 nm and 595 nm (Fig 4). These two bands can be assigned to the d-d transitions arising out of the Cr^{3+}

species present in the clay interlayer. The band at 425 nm corresponds to the $A_{2g} \rightarrow T_{1g}$ and the band at 595 nm corresponds to the $A_{2g} \rightarrow T_{2g}$ transitions from the chromium (III) species present in the clay interlayer.

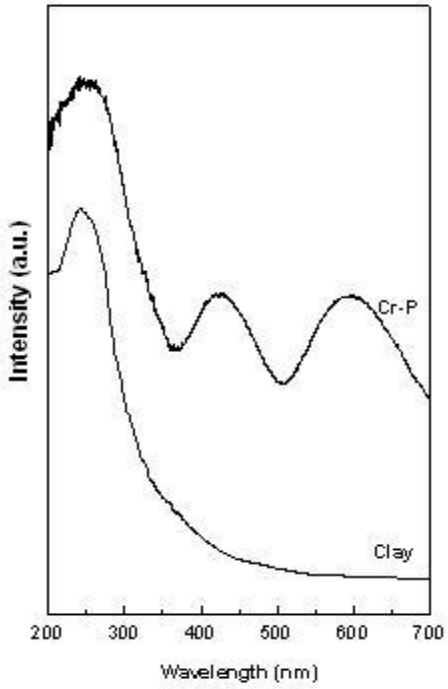


Figure 3.2. UV-Vis spectra of Clay and Cr-P materials.

TG study: The TG profile of the uncalcined Cr-pillared clay is presented in (Fig. 3.3). The pillared clay material shows three well defined weight loss regions between 50-150, 350-450 and 500-650^{o}C. These three weight loss region corresponds to various thermal transformations of the pillared clay materials.

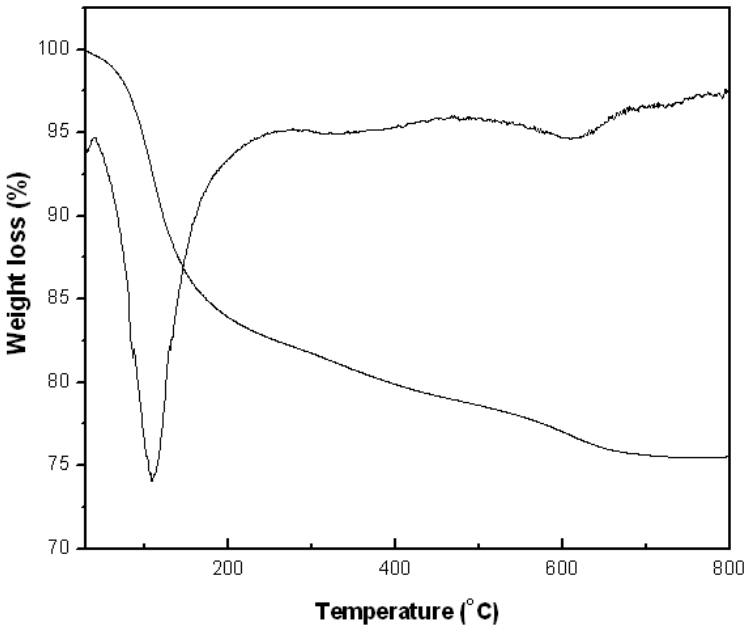
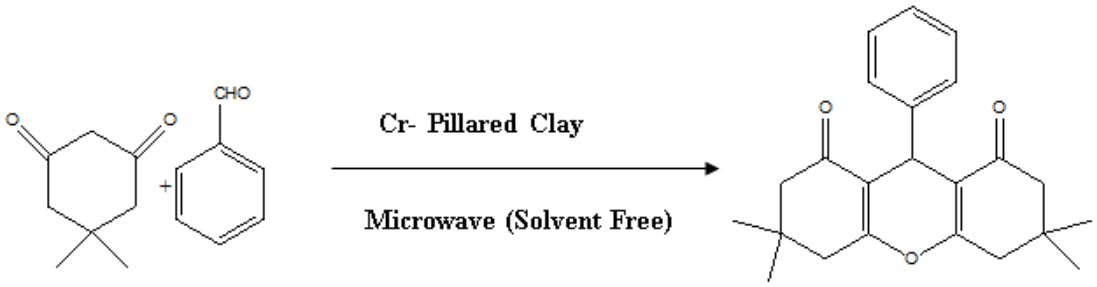


Figure 3.3. TG-DTA of Cr-Pillared clay.

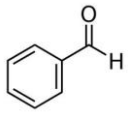
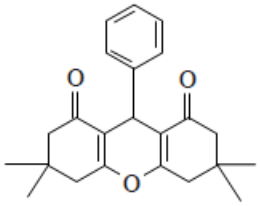
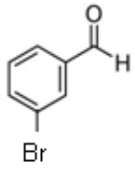
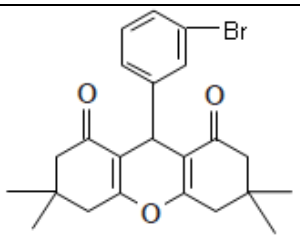
Synthesis of 1, 8-dioxo-octahydroxanthenes: The synthesis of xanthenes and its derivatives becomes the center of focus to organic chemists due to their wide applications in biological and therapeutics including antibacterial and antiviral properties [14, 15]. In this investigation, we have synthesized 1, 8-dioxo-octahydroxanthenes by condensation reaction of a variety of aromatic aldehydes and dimedone in presence of the Cr-P catalyst. Initially, the reaction of benzaldehyde, dimedone and 50 mg catalyst was taken as the model reaction (Scheme 3.1). In order to test the validity of the protocol a series of aryl aldehydes are used for the condensation reaction. The results obtained are presented in Table 3.1. A variety of aromatic aldehydes containing electron withdrawing and electron releasing group reacted in the optimized protocols to give the corresponding octahydroxanthenes in high yield and purity. The protocol

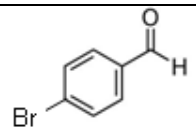
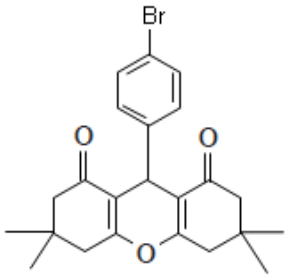
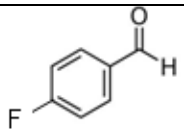
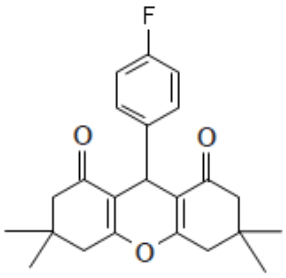
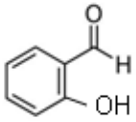
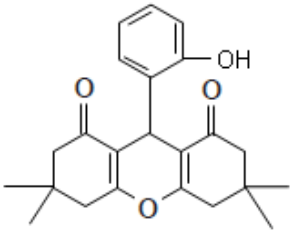
was found to be advantageous in terms of solvent free conditions, use of heterogeneous catalysts and high yield and purity of the products. .



Scheme 3.1. ***Synthesis of octahydroxanthenes catalyzed by Cr-P***

Table 3.1: **Cr-Pillared catalyzed synthesis of 1,8-dioxo-octahydroxanthenes**

Sl. No.	Aldehyde	Product	Time (mins.)	Yield (%)
1.			22	72
2.			28	78

3.			29	75
4.			30	81
5.			30	68

Conclusion:

We have performed interlayer modification of the clay materials to generate efficient heterogeneous catalytic materials for application in the field of organic synthesis. The XRD study of the materials indicates the expansion of the interlayer structure as a result of pillaring. The Cr-P material was used as an efficient catalyst for the synthesis of 1, 8-dioxo-octahydroxanthenes under microwave solventfree condition by condensation of aryl aldehyde and dimedone. The Cr-P material was found to give good yield and purity of the products for a variety of aromatic aldehydes.

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