Synthesis, characterization and catalytic applications of Al-Pillared clay towards environmentally benign synthesis of bis(indolyl)methanes

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CERTIFICATE

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This is to certify that the dissertation entitled "***Synthesis, Characterization and catalytic application off Al-pillared clay towards environmentally benign synthesis of bis(indolyl)methanes***" being submitted by **Anindya Sundar Patra** 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 him 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)*

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Anindya Sundar Patra

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CHAPTER 1

INTRODUCTION TO CLAY MATERIALS

1.1 Introduction

Clays are layered materials composed of polymeric sheets of SiO_4 tetrahedra linked to sheets of (Al, Mg, Fe) $(O,OH)_6$ octahedra belonging to the phyllosilicate or sheet silicate family of minerals. Today clay is the promising material because of wide variety of applications such as ceramics, liners for waste disposal, oil drilling, pharmaceutical and paper industry. Clays are also the most promising materials to be used as adsorbents and catalysts for various industrial applications [1-6].Clay materials are also known to be very good adsorbents for toxic organic chemicals such as chlorinated compounds, heavy metal ions (eg. Pb^{2+}, Hg^{2+}) and nuclear waste [3, 4]. Salt loaded, acid-treated and ion exchanged clays are the different modified form of clay materials evaluated as efficient catalysts for many organic reactions [1, 5 and 6]. Clays are divided into two main groups: cationic and anionic clays. The cationic clays are widely available in nature and contain negatively charged alumina-silicate layers. The negative charge in the layer is balanced by the presence of cations in the interlayer of these materials. These materials exhibit surface acidic properties due to the presence of structural hydroxyl groups. The present work in this thesis mainly concerned with the structural modification and catalytic application of the clay.

1.2 ACIDIC PROPERTIES OF CLAY MATERIALS

Cationic clays are used as solid heterogeneous catalysts for several acid catalyzed organic transformations. The acidity present in the clay materials is Brønsted in nature. However, it is likely to generate Lewis acidity by suitable thermal treatment. The origin and nature of Brønsted acidity in clay have been studied by several authors [9, 10]. The most important source of

Brønsted acidity in clay material is the dissociation of water molecules in the hydration sphere of the interlayer exchangeable cations. Several varieties of hydroxyl groups have been identified on the clay layers by FTIR spectroscopy [11, 12]. These hydroxyl groups differ in the chemical environment around them and consequently exhibit different acidic strength.

1.3 DISADVANTAGES OF CLAY MATERIALS AS CATALYSTS

Although clays have been used as solid heterogeneous acid catalysts for variety of organic reactions, they possess certain disadvantages, which limit their applications in heterogeneous catalysis [13]. Extensive dehydration of the clay sheets takes place at high temperatures leading to the loss in Brønsted acidity. The interlayer dimensions of the clays are typically between 3-5 Å, which results in diffusional constraints and decrease the catalytic activity.

1.4 MODIFICATION OF CLAY MATERIALS

In the recent years, the surfaces as well as interlayer modifications of clay materials have been done to increase the thermal stability, acidity and the catalytic properties. The important modifications employed in literature are the exchange of interlayer cations by inorganic and organic cationic species, pillaring by inorganic polycations, acid treatment, supporting active species on clay surface for catalysis [1, 6, 12-14]. The pillaring of clay by inorganic polycations provides multitude of advantages in terms of increasing surface area, thermal stability, microporosity, acidity and catalytic activity.

1.5 PILLARING OF CLAY BY INORGANIC POLYCATIONS

Exchange of interlayer cations of the clay materials by inorganic polyoxocationic nanoclusters results pillaring materials [6, 8, 13]. The intercalated polycations increase the basal spacing of the clays and upon heat treatment they are converted to stable metal oxide clusters. These oxide clusters called pillars hold the individual clay sheets and prevent them from collapsing during high temperature applications. Earlier reports on Clay pillaring includes a variety of inorganic polycations of Al [5], Zr [6], Ti [15], Cr [16], Fe [17] and Si [18]. These polycations are generally prepared by partial hydrolysis of the corresponding metal cations in solutions [8].

The process of pillaring is shown schematically in Fig. 1.7.

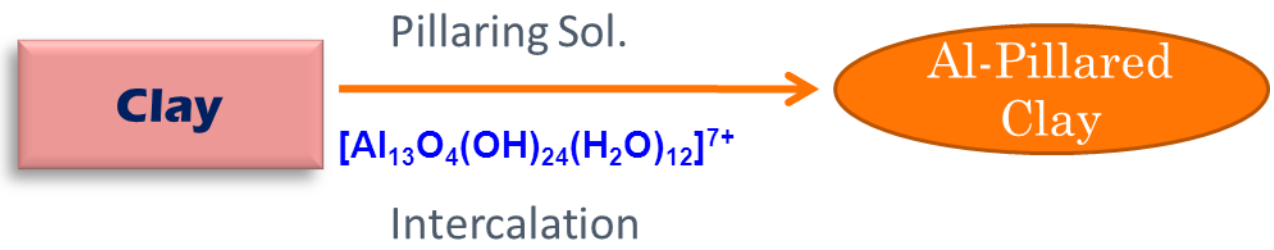


Fig. 1.1 Schematic representation of the process of pillaring of the clay sheets

The major changes that occur as a result of pillaring include increase in the higher thermal stability, surface area, microporosityand acidic properties of the parent clay.

1.6 OBJECTIVE OF THE PRESENT STUDY

The main objectives of the present study are

- ✓ To prepare interlayer modified aluminum pillared clay and to explore its potential as a heterogeneous catalyst.
- ✓ To characterize the synthesized Al-Pillared clay materials by various analytical techniques such as XRD, and FT-IR techniques to obtain information on the physicochemical characteristics of the synthesized material.
- ✓ To explore the potential of Al-pillared clay material as heterogeneous catalyst for synthesis of bis(indolyl)methanes under environmentally benign conditions.

CHAPTER 2

MATERIALS AND METHODS

2.1 PREPARATION OF CATALYST

2.1.1 PREPARATION OF PILLARED CLAY

The montmorillonite clay, NaOH, $AlCl_3.9H_2O$ were used as such without any purification. The 0.2 M $AlCl_3.9H_2O$ solution was prepared by dissolving the required quantity of salt in distilled water. The resulting solution was then allowed to heat at 50^oC for 12 h to prepare the pillaring solutions. Then, pillaring solutions were drop wise added to the clay suspension under stirring conditions and allowed to stirrer for 12 h. Filtered, washed thoroughly in double distilled water till free from chloride ions, dried and calcined at 400^0C for 2 h to get Al-Pillared clay (Al-P).

2.2 CHARACTERIZATION OF CATALYST MATERIALS:

2.2.1 X-RAY DIFFRACTION: The X-ray diffraction patterns of the clay materials were recorded on a Siemens D-500 diffractometer using Ni-filtered CuK_α radiation. The XRD measurements were carried out in the 2θ range of $4\text{-}20^o$ with a scan speed of 2 degrees per minute using Bragg-Brantano configuration.

2.2.2 INFRARED SPECTROSCOPY: The IR spectra of different clay samples (as KBr pellets) were obtained by using Perkin-Elmer infrared spectrometer with a resolution of 4 cm^{-1}, in the range of 400 cm^{-1} to 4000 cm^{-1}.

2.3 CATALYTIC STUDIES: synthesis of bis(indolyl) methanes

Synthesis of bis (indolyl) methanes was performed by taking 2 mmol of indole and 1 mmol of aromatic aldehyde in presence of Al-P catalyst (100 mg) (Scheme 1). The mixture was grinded by a mortar and pestle for the required time (Table 1). The completion of the reaction was confirmed by TLC. After completion of the reaction, the reaction mixture was dissolved in 10 ml of ethyl acetate and then the catalyst was filtered. The product were recovered from ethyl acetate solution by heating under reduced pressure to remove the ethyl acetate and then recrystallized. The products were known compound and identified by comparing their physical and spectral properties with those reported in literature.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 XRD study

The XRD patterns of clay, along with the as synthesized Al-Pillared clay and Al-Pillared clay clacined at 500^{o}C are presented in (**Fig. 3.1**). The parent clay shows relatively broader and intense reflections at 2θ = 6.8^{o} with basal spacing of 12.9 Å. This peak corresponds to the reflection from the (001) plane of the layered material. After the intercalation of the Al-oxyhydroxy cluster into the clay layer the (001) peak has shifted to lower 2θ value indicating indicating an expansion in the layer structure as a result of pillaring.

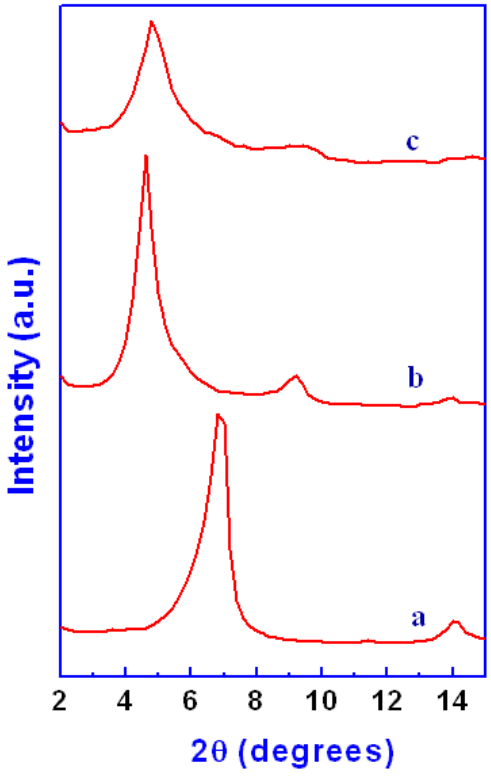


Fig. 3.1. ***X-ray diffraction patterns of*** **(a) clay, (b) Al-P (c) Al-P calcined at 500^{o}C**

The air dried Al-pillared clay shows a basal spacing of 21Å corresponding to interlayer spacing of 11.4 Å. The calcined Al-P shows a basal spacing of 19.2 Å with an interlayer spacing of ~ 9 .5 Å (**Fig. 3.1** c).

3.2 FTIR study

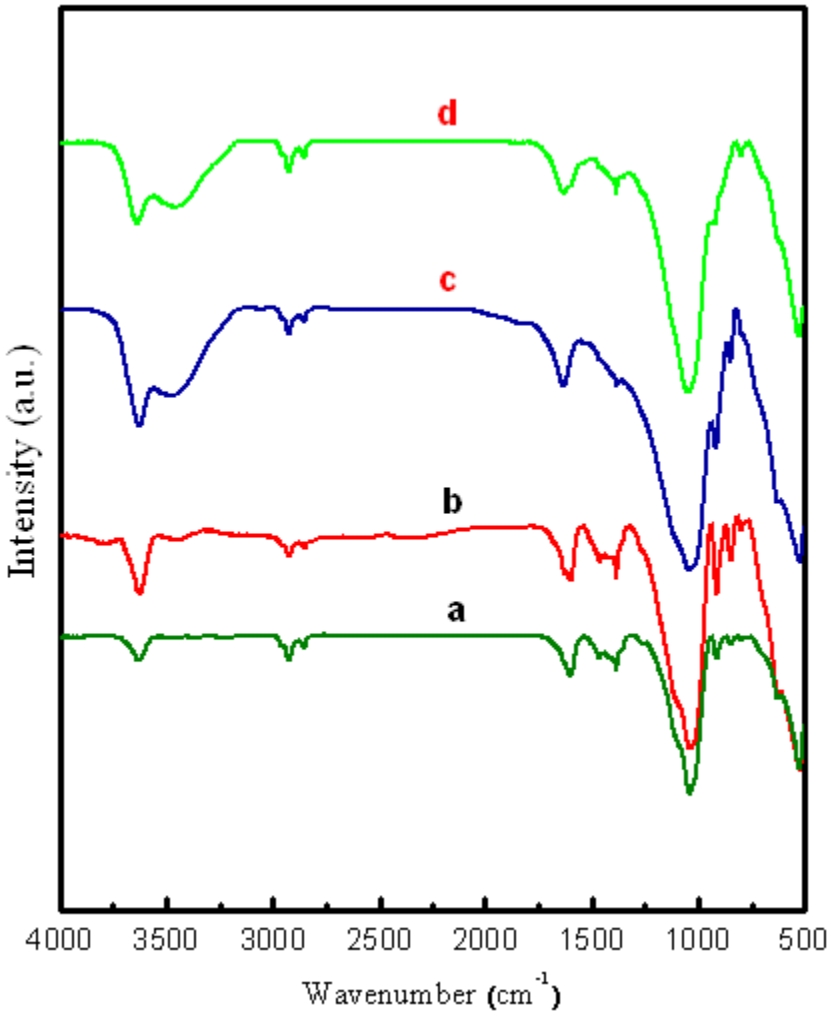


Fig. 3.2. ***FT-IR spectra of*** **(a) clay, (b) Clay at 500^{o}C (c) Al-P (d) Al-P calcined at 500^{o}C**

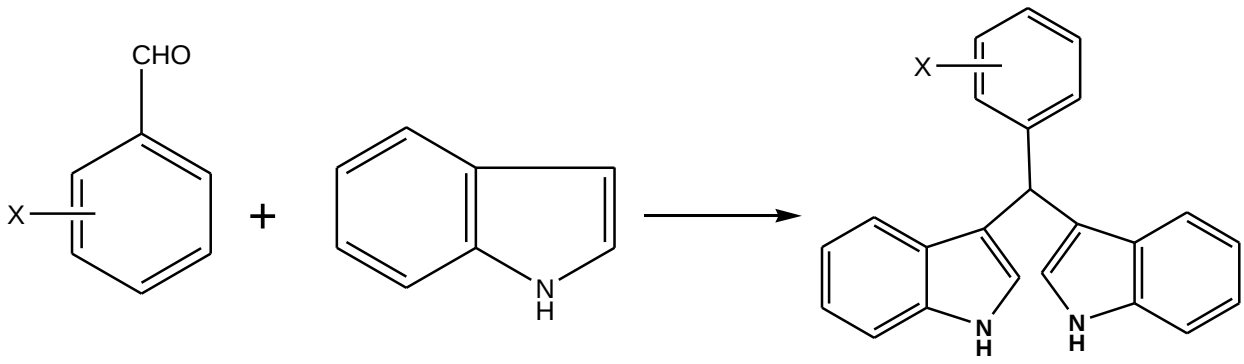
The IR spectra of the parent clay, as synthesized Al-Pillared clay and Al-Pillared clay clacined at 500^{o}C are shown in **Fig. 3.2**. At the O-H stretching frequency region, all the pillared clay materials show two intense IR band at 3640 cm^{-1} and 3420 cm^{-1} (**Fig. 3.2**). These two bands are assigned, respectively, to the O-H stretching vibration of the structural hydroxyl groups in the

clay sheets and the water molecules present in the interlayer [19]. The IR band observed at 1640 cm^{-1} (**Fig. 3.2**) is attributed to the bending vibration mode of coordinated interlayer OH groups. The structural OH-bending mode in montmorillonite absorbs IR radiation between 700 and 950 cm^{-1} and shows a series of discrete peaks depending upon the cation composition in the octahedral sheet [20]. In case of all the clay, three bands were observed at 915, 847 and 800 cm^{-1} which bands have been assigned to the bending vibration modes of Al-Al-OH, Al-Mg-OH and Mg-Mg-OH groups, respectively, in the octahedral layer of the clay.

3.4 Catalytic studies

In recent years, much attentation have been focused towards the synthesis of bis(indolyl)methanes which are the platforms in bioactive metabolites of terrestrial and marine origin [21-23]. Bis(indolyl)methanes have been isolated from natural sources, in cruciferous plants and are found to be pharmaceutically important [24, 25]. Most of the synthetic methods have been proposed in literature are the conventional synthesis process which associated with problems such as low yield, use of expensive and hazardous chemical material, handling and purification. Recently, improved protocols have been explored for the synthesis of this class of molecule which involves the one pot condensation of aromatic aldehyde and indole in presence acidic catalyst. The catalysts used for this one pot reaction includes K10, $AlPW_{12}O_{40}$, SO_4^{2-}/ ZrO_2, SO_4^{2-}/ TiO_2, SSA, morpholinium bisulfate and SO_3H-SBA 15 [26-32]. Hence, synthesis of this important class of molecule involving simple, cheap and environmentally acceptable protocol is highly desirable. In this work we have synthesized bis(indolyl)methanes under environmentally benign condition using Al-P as heterogeneous acid catalyst.

Intitally, the reaction conditions were optimized using the reaction of benzaldehyde and indole as a model reaction (scheme 1). It was observed that the reaction can be done conveniently by mechanical grinding of the reaction mixture along with the catalyst. It was also observed that 100 mg of the catalyst is ideally suited for the efficient condensation reaction and further increase in catalyst amount does not have a marked influence on the yield of the product. A series of aromatic aldehydes are used for the reaction. The reaction was found to be faster in case of aldehyde containing electron withdrawing groups. In certain cases mild heating for a period of 1-2 minutes is required for good yield of the product. The protocol developed using the Al-pillared clay material as catalyst for synthesis of bis (indolyl) methanes was found to be advantageous in terms of the solvent free synthesis, economical and recyclable catalyst and high yield and purity of the products.



(Scheme 1)

Table 1: Al-P catalyzed synthesis of Bis (indolyl) methanes

Entry	X	Time	Yield
1	H	15	70
2	o-NO_2	8	80
3	m-NO_2	14	78
4	p-NO_2	8	82
5	p-Br	12	74
6	p-F	15	74
7	o-Cl	8	76

Conclusion

In this thesis, we have reported the effective interlayer modification of clay by aluminum oxyhydroxy nanocluster. The expansion of the interlayer of clay was ascertained from XRD study because of pillaring with aluminum oxyhydroxy nanocluster. FTIR study indicated the presence of various functional groups responsible for the catalytic properties of the materials. Al-PILC material was demonstrated as an efficient heterogeneous solid acid catalyst for environmentally benign synthesis of bis (indolyl) methanes.

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