

Synthesis and Characterization of a Green Catalyst – Fe-Pillared Montmorillonite Clay and Study of Its Catalytic Activity

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Abstract:

High-surface-area iron pillared clay (PILC) was prepared from the source montmorillonite clay by exchanging the interlayer ions (e.g. Na, Ca, etc.) to iron. The pillared clay was characterized by XRD, TGA and FT-IR. The catalytic activity was studied in the hydroxylation of phenol. The product formed in the hydroxylation reaction was identified by GC-MS.

Index Terms : Na-montmorillonite clay, FeCl₃, Phenol, H₂O₂,

I. INTRODUCTION :

The crystal structures of clay minerals consist of negatively charged hydrous aluminosilicate layers that are weakly bonded by interlayer cations which are easily exchangeable in the smectite mineral group [1,2]. Metal oxide pillared smectites derived from the intercalation of polyoxocations of Al, Zr, Cr and other metals as well as mixed pillared materials have been studied for their utility as selective catalysts [3]. Now a days pillared interlayered clays (PILCs) take much interest for the scientist. They constitute one of the families of new microporous materials prepared by a multi-step synthesis, viz., (i) preparation of bulky inorganic polyoxocations by polymerization of cations of some metallic elements; (ii) exchange of the exchangeable charge balancing cations of smectite clays by these polyoxocations, forming intercalated solids; (iii) stabilization of the intercalated solids by calcinations. The intercalation produces a large increase in the basal spacing of the clays, and the calcination transforms the intercalated polycations into metal oxide clusters by dehydration and dehydroxylation processes. These metal oxide clusters, called pillars, are inserted between the clay layers, maintaining them apart for a relatively large distance thus avoiding their collapse and developing a porous network with molecular range dimensions.

The catalytic properties of PILCs depend on nature of both the clay skeleton and the intra-gallery pillars that determines their textural and surface reactivity characteristics. The presence of transition metals as iron and other elements, associated or structurally included into clay minerals, has proven to be useful to promote different organic reactions [4]. The Fe containing pillared clays have been studied for Fisher- Tropsch processes [5]. The presence of redox sites in materials simultaneously exhibiting acid environment shows great interest too promote catalytic conversion of phenol to hydroquinone and catechol. These compounds are important intermediates for fine chemicals thoroughly used in photography and polymer industries. The classical route to hydroquinone was initially from aniline, sulfuric acid and manganese oxide and produced high amounts of waste (mainly ammonium and manganese sulfates). More recently, this reaction has been carried out in the presence of hydrogen peroxide giving water as the main waste product. The oxidation catalysts enhance the effectiveness of the reactions because they increase the production of OH* radicals. In addition, these heterogeneous conditions allow the recovery of the catalyst and the easy separation of the reaction products.

We have reported the preparation of Fe pillared montmorillonite clay, its acidic study, and the hydroxylation reaction of phenol using this catalyst.

II. EXPERIMENTAL SECTION-1:

II.1. MATERIALS :

The materials used are:

1. Wyoming montmorillonite clay obtained from Source clay, USA.,
2. FeCl_3 obtained from Merck
3. Na_2CO_3 obtained from Merck
4. Phenol obtained from Merck
5. H_2O_2 obtained from Merck.

II.2. SYNTHESIS OF THE CATALYST :

An iron polyoxocation solution was prepared by hydrolyzing 0.002M FeCl_3 solution (2mmol/g of clay) with Na_2CO_3 . 2.0 equivalent of Na_2CO_3 per mole of iron was added and the solution stirred for about 20hr with simultaneous flushing with N_2 gas to evolved CO_2 gas during hydrolysis. Then ethylene glycol expanded clay was added to the polycation solution and stirred for 2hr. The product was centrifuged and washed with distilled water to remove excess chloride ions. The washing and centrifugation were continued till the pH remains constant at 4. The product was centrifuged and then make slide for XRD.

Now the above slide was heated at 100°C for 1hr and XRD was taken.

II.3. CHARACTERIZATION OF THE CATALYST :

The XRD pattern of the synthesized iron pillared clay is shown in the Fig.1, Fig.2 and Table-1

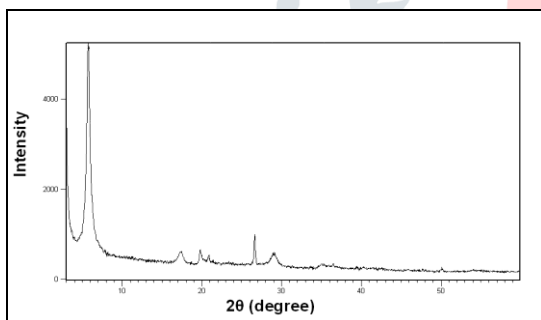


Fig.1: XRD pattern of Fe-mont clay

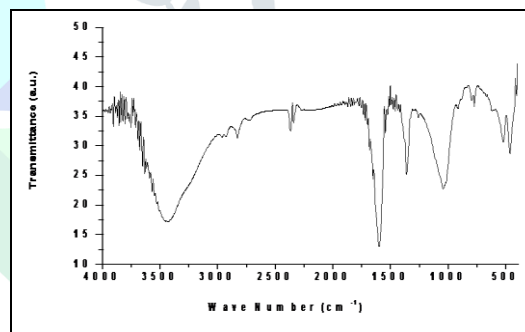


Fig.2: FT-IR of Fe-mont clay

Table-1 : XRD analysis

Angle (2θ)	d-value (Å)	Rel. Intensity
5.764	15.333	100
17.369	5.105	5.48
19.791	4.485	6.94
20.838	4.263	3.97
26.618	3.345	15.31
29.044	3.074	5.88
35.132	2.554	1.52
50.038	1.821	0.84

FT-IR shows the following bands [6] :

Bands (cm ⁻¹)	Vibration modes
3449	H-O-H vibration of adsorbed water
1601	OH bending vibration
915	Al ₂ -OH bending vibration
524	Si-O-Al (octahedral Al) bending vibration
464	Si-O-Si bending vibration
797	Presence of amorphous SiO ₂

The TGA of the synthesized pillared clay is shown in the Fig.3. The TGA shows three weight losses in the range of 75-150 °C, 300-350 °C and 454-500 °C. The first weight loss is due to the loss of moisture adsorbed on the surface of Na-Mont clay, while the second weight loss is due to the dihydroxylation from interlayer hydroxide sheet and the third weight loss is because of decarboxylation.

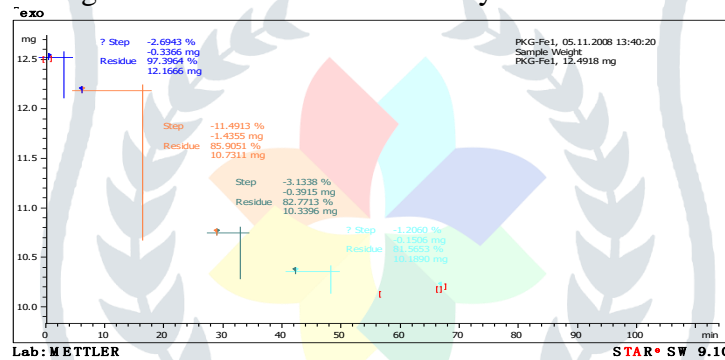


Fig.3 : TGA of Fe-Mont clay

II.4. DETERMINATION OF THE ACID SITES OF THE Fe-PILLARED CLAY USING FT-IR :

Acidity of Fe pillared clay was analyzed using FT-IR and is shown in Fig.4.

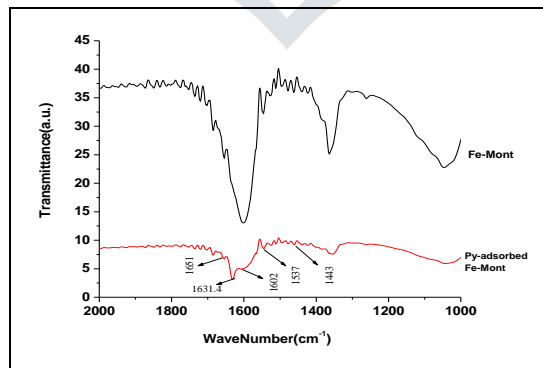


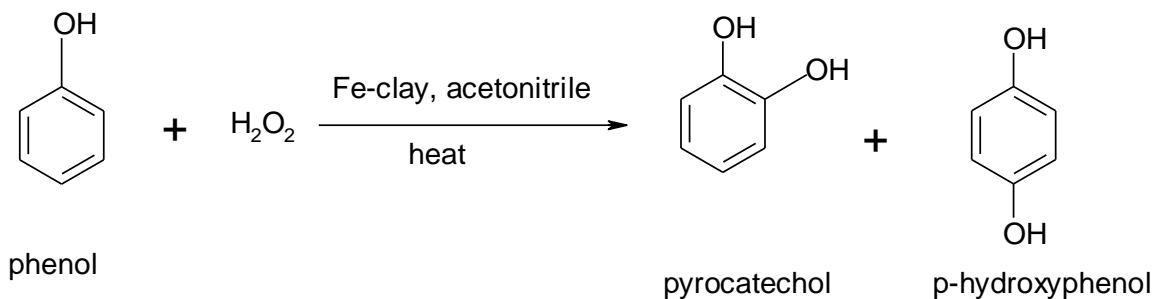
Fig.4 : FT-IT of pyridine adsorbed Fe-pillared clay

In comparison to the Fe-Mont spectra, the Pyridine adsorbed Fe-Mont shows a new band at 1631cm⁻¹. The Fe-Polyoxocationic clay does not show well resolved Lewis acid band at around 1450cm⁻¹. But the combined Lewis and Bronsted acid site band appears at 1631cm⁻¹.

III. EXPERIMENTAL SECTION-2 :

III.1. STUDY OF CATALYTIC ACTIVITY :

The reaction is shown in the scheme-1 below :



Scheme-1 : Hydroxylation of phenol

0.2g of the catalyst was taken in a 50 mL RB flask and to it, 1 mole : 1.5 mole = phenol (1.67g) : H_2O_2 (30% V/V) were added followed by 5 mL of acetonitrile as solvent. The reaction mixture was then refluxed at 353K and the reaction was monitored for different intervals of time. The results were shown in Table-2. The GC-Mass spectra characterization were also shown in Fig. 5 and 6.

Table-2 : The % conversion and selectivity of the products

Reaction time (min)	% of conversion	Selectivity	
		Pyrocatechol (%)	p-hydroxyphenol (%)
0	0.00	0	0
15	52.97	51	49
20	54.00	53	47
25	58.44	53	47
30	59.00	50	50
45	59.31	51	49

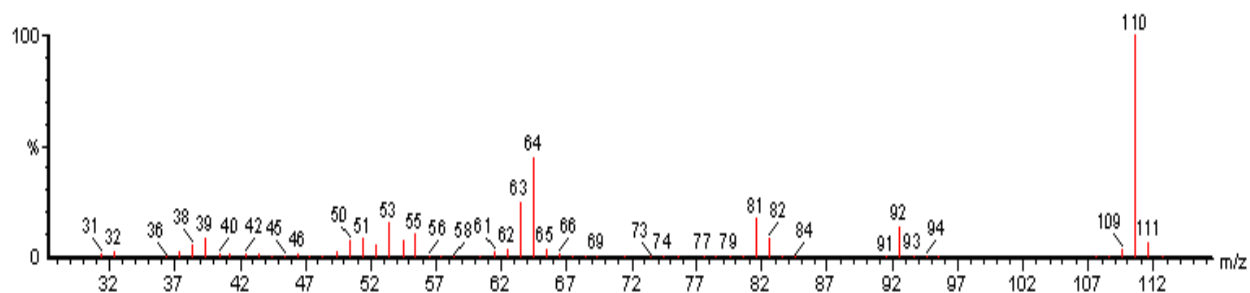


Fig. 5 : The MASS spectra of pyrocatechol

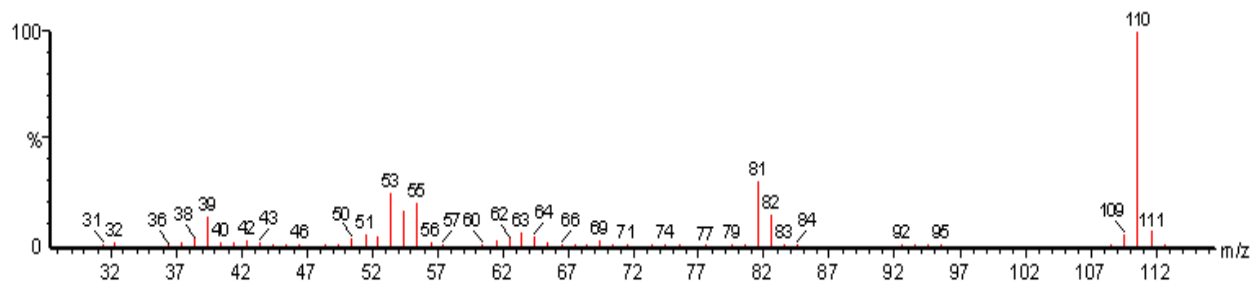


Fig. 6 : The MASS spectra of p-hydroxyphenol

IV. CONCLUSION :

The Montmorillonite clay can be pillared using Fe metal which can be used for the hydroxylation of phenol. The catalyst is stable at air and can be recycled for several times without leaching of metal. The method of synthesis for both the catalyst and the reaction products are quite eco-friendly.

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