

## Mild Temperature Oxidation of Phenol over Rare Earth Exchanged Aluminum Pillared Montmorillonites

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**ABSTRACT:** Wastewater treatment and re-use of industrial process water are critical issues for the development of human activities and environment conservation. The present study was undertaken to evaluate the degradation of organic pollutants taking phenol as the model compound over aluminium pillared montmorillonite and the rare earth exchanged analogues, underlining the use of environ friendly clay catalysts for the effective removal of water pollutants. From the study it was noted that for reaction variables like temperature, peroxide load, catalyst load, phenol concentration etc, optimal values exist that must be taken into account for obtaining best results. The catalysts used were aluminium pillared montmorillonite prepared by partial hydrolysis method exchanged with La, Ce and Th metal salts at room temperature. Characterisation of the prepared systems were done using X-ray diffraction and surface area and pore volume measurements. The pillared montmorillonite showed considerable increase in basal spacing and BET surface area compared to parent montmorillonite.

**Key words:** Wet, Peroxide, Oxidation, Phenol, Metal exchange

### INTRODUCTION

Phenol and its derivatives are considered as Persistent Organic Pollutants (POP's). Currently phenol is produced at a rate of about 6 million ton/year worldwide. Though phenol has sterilizing activity due to its protein denaturing ability, it can affect liver, kidneys, lungs and can cause comas, convulsions and cyanosis. Phenol is highly relevant in the field of environmental research, because it is often chosen as a model compound since its presence can lead to the formation of substituted compounds during disinfection and oxidation processes (Busca *et al.*, 2008).

A great variety of different methods have been considered in order to remove a specific compound from water (Arshad *et al.*, 2011; Vohra *et al.*, 2011; Uemura *et al.*, 2011; Rameshraj and Suresh, 2011; Subramanyam and Ashutosh, 2012; Shafieiyoun *et al.*, 2012). Wet oxidation, also known as hydrothermal treatment, refers to the process of oxidizing materials suspended or dissolved in liquid water with dissolved oxygen at elevated temperature. Wet Peroxide Oxidation (WPO) uses a liquid oxidizing agent (hydrogen peroxide) since the oxidizing properties of hydrogen peroxide are stronger than those of molecular oxygen allowing to perform the reaction at conditions close to the ambient ones. Aqueous  $H_2O_2$  is a stable reagent, if

handled and stored in a proper manner. Water is the only by product formed and the oxidant is inexpensive. Phenol oxidation by  $H_2O_2$  initially results in hydroquinone and catechol formation and subsequently results in polymer formation. Catechol and hydroquinone are also used as photographic developers and antioxidants. Catechol is the major product formed, but it is rapidly oxidized to the polymer, particularly in the presence of phenol. Hydroquinone is also involved in polymer formation. The conventional Fenton reaction uses hydrogen peroxide in conjunction with an iron(II) salt to produce high fluxes of hydroxyl radicals but its application is limited due to the problems typical of homogenous catalysis such as catalyst separation, regeneration, control of pH etc (Namkung *et al.*, 2008, Nevens *et al.*, 2003). Thus, Fenton like heterogenous catalysts, i.e., solids containing transition metal cations (mostly iron ions) have been developed and tested (Calleja *et al.*, 2005, Timofeeva *et al.*, 2007). Non-iron catalysts also work to enhance water peroxide oxidation reaction rate (Zrnecic *et al.*, 2005).

Intercalation of clays via exchange of cations located in their interlayer space with hydroxy metal cations, followed by thermal treatment is an effective approach to obtain catalysts, catalyst supports,

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sensors and adsorbents. The materials thus prepared are referred to as pillar interlayered clays (PILCs). By varying the size, charge and shape of the entering ions, a homogenous network of micropores can be obtained with pore openings ranging in size from 16- 30 Å. Pillared clays have been the subject of recurrent research owing to interesting properties like high surface area, regular porous structure, appreciable thermal stability and substantial Lewis and Brønsted acidity. Pillars constituted of stable oxides of metals like aluminium, iron, zirconium, titanium, chromium, vanadium, gallium etc as well as their mixed oxides have been reported (Pinnavia *et al.*, 1983, Gil *et al.*, 2000). Traditionally, pillared clays have been treated as solid acid catalysts owing to the presence of a well characterised network of Lewis and Brønsted acid sites and several acid catalysed reactions like Friedel Crafts alkylations, acylations etc have been reported to occur efficiently and selectively over these catalysts (Manju *et al.*, 2006). However, stable pillars of metals of redox nature immediately suggest potential oxidation activity and only a modest literature is set aside on this fact (Carriazo *et al.*, 2003, Carriazo *et al.*, 2005). Presence of elements with variable oxidation states like rare earth metals can further increase the oxidation capacity of pillared catalysts which makes the oxidation activity worth investigating. In this report we present a detailed study of the wet peroxide oxidation of phenol over rare earth metal exchanged aluminium pillared montmorillonite catalysts underlining the use of environ friendly clay catalysts in green chemistry. Catalytic activities of the prepared systems towards Wet Peroxide Oxidation of phenol have been evaluated in detail using aluminium pillared montmorillonite as the reference. The pillared clays prepared by partial hydrolysis method have been characterized thoroughly using instrumental methods like XRD and NMR spectroscopies, surface area and pore volume analysis and EDAX.

## MATERIALS & METHODS

Aluminium pillared montmorillonite was synthesised by partial hydrolysis method. 0.1 M solution of the aluminium nitrate was hydrolysed by the drop wise addition of 0.2 M Na<sub>2</sub>CO<sub>3</sub> solution under vigorous stirring for 3 hours. This solution was agitated for another hour. The pillaring solution was aged for 24 hours at room temperature. In the meantime, a suspension of the clay in distilled water was swollen for 24 hours. Intercalation of the pillaring species into the montmorillonite layers was done by treating the pillaring solution with the clay suspension for 25 hours

[OH / Al ratio of 2 and Al / clay ratio of 20 mmol / g clay]. The temperature for the preparation of the pillaring solution as well as the intercalation process was 80°C. The clay after pillaring was washed several times with distilled water, filtered and dried in the air oven at 110°C overnight. The sample was calcined for 6 hours at 450°C in the muffle furnace. Exchange with La and Th was done using 0.1M aqueous solutions of the corresponding metal nitrate and for Ce, 0.1M ammonium ceric sulphate solution was used. The pillared clay was stirred mechanically with the salt solutions for 24 hours at room temperature. The clay after exchange was washed 5-6 times with distilled water. This was filtered and dried in the air oven at 110°C overnight and calcined for 6 hours at 500°C. The pillared sample was designated Al PM and the exchanged systems as M/Al PM where M is La, Ce or Th.

Wet Peroxide Oxidation of phenol was carried out in liquid phase at the specified conditions in a 50 mL RB flask immersed in an oil bath (attached to a dimmerstat), magnetic stirrer and water condenser. At specified intervals, the reaction mixture filtered off from catalyst was subjected to HPLC (Waters 7 Dual Model) using 30% methanol and 70% water as solvent at a flow rate of 0.4 mL/minute. Surface area and pore volume measurements were done in Micromeritics Gemini analyser at liquid N<sub>2</sub> temperature. The diffractometer traces of the catalyst samples were taken in RIGAKU D/MAX-C instrument using Cu K $\alpha$  radiation ( $\lambda = 1.5405\text{\AA}$ ).

## RESULTS & DISCUSSION

Phenol is a major water pollutant. The catalytic performance of various aluminium pillared systems towards hydroxylation of phenol with hydrogen peroxide is given in Table 1. Almost 76% of the phenol gets converted over Al PM within 30 minutes with 34.1% selectivity towards hydroquinone. Aluminium pillared clays perform well for the reaction. As the aluminium oxide cluster prop the clay layer, a micro porous structure with high surface area is created. This facilitates the easy diffusion of reactants in and products out of the catalyst active sites. High selectivity for hydroquinone can be ascribed to the shape selective nature of pillared clay. Incorporation of rare earth metals except Ce into the porous network reduces the activity of pillared clay, which may be due to deposition of these metals in the pores as evidenced by surface area and pore volume measurements. The product selectivity however remains almost same as in the case of parent pillared clay.

**Table 1. Catalytic activity of rare earth metal exchanged aluminium pillared montmorillonite**

Catalyst	Conversion (%)	Selectivity of catechol (%)	Selectivity of hydroquinone (%)
Al PM	76.3	65.9	34.1
Th/Al PM	69.9	58.5	41.5
Ce/Al PM	79.9	69.2	30.8
La/Al PM	70.3	64.5	35.5

Reaction Conditions: Phenol:H<sub>2</sub>O:H<sub>2</sub>O<sub>2</sub> (molar ratio), 1:5:5; Catalyst, 0.1g; Temperature, 80°C; Time, 30min

Hydroxylation of phenol is extremely sensitive to reaction conditions as well as quality of the catalyst. Hence the influence of various reaction variables like time, temperature, phenol concentration, oxidant concentration, solvent concentration and catalyst concentration was extensively studied using Al PM as reference catalyst. The effect of temperature was checked in a range of 60-80°C at an interval of 10°C (Fig. 1). At room temperature, reaction does not occur even after 3 hours. As the temperature is increased, there is a drastic change in reaction rate. Maximum conversion is observed at 80°C. Regarding selectivity pattern, low temperature conditions favour high yields of hydroquinone. Another remarkable point is that at low temperatures, hydroquinone selectivity decreases with time. As the temperature is raised, hydroquinone selectivity suffers but increases with time at a particular temperature.

The effect of time on wet peroxide oxidation of phenol was studied at a range of 90 minutes (Fig. 2). From the figure it can be deduced that excellent conversion occurs at 30 minutes. The conversion % does not alter much with increase in duration of run. After 30 minutes, the activity of the catalyst drops slightly which may be attributed to tar, produced by over oxidation of diphenol which can act as a major poison for surface sites. The hydroquinone selectivity increases with time. In zeolites and molecular sieve catalysts, catechol is formed in the external surface of the catalyst, whereas hydroquinone is formed inside pores. Since pillared clays possess a porous network, as time goes by, more and more reactants diffuse in and out of pores leading to increased hydroquinone selectivity.

The influence of the amount of phenol in reaction mixture was studied by keeping the amount of water and hydrogen peroxide constant and altering the amount of phenol. From fig. 3, it can be noticed that a minimum phenol concentration is required for good conversions. The amount of phenol oxidized is directly dependant on the amount of phenol originally present in the reaction mixture. With increase in phenol concentration, the conversion % drops. In the selectivity pattern, one can notice that hydroquinone selectivity almost improves with increase in the amount

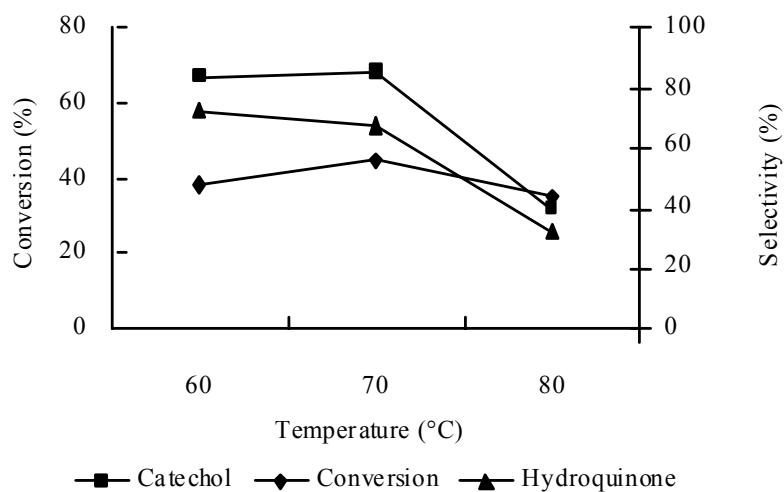
of phenol. At lower concentrations due to solvent effects, phenol molecules may be experiencing difficulty in approaching active sites and hence the reduced activity. Increase in phenol concentration increases the rate of diffusion of reactants into the pores and hence the increase in hydroquinone selectivity.

The amount of oxidant used is an essential parameter for oxidation reactions. The influence of phenol to hydrogen peroxide molar ratio is given in fig. 4. Oxidant present even in trace quantities can bring about oxidation of phenol to diphenols over pillared clay catalysts. Increase in amount of peroxide increases the activity. Maximum conversion of phenol to diphenols was observed at peroxide to phenol molar ratio of 1:5. The increase in oxidant concentration increases the deep oxidation of produced diphenol to tar and hence conversion decreases. ie, after an optimum amount of oxidant, the conversion % decreases. The hydroquinone selectivity also increases with increase in hydrogen peroxide concentration. The high concentration of H<sub>2</sub>O<sub>2</sub> can also accelerate self decomposition of the oxidant, reducing the conversion of phenol.

Oxidation of phenol is a means for removing the organic pollutant from water streams. Thus, the amount of water in system becomes critical. Hence influence of water concentration was studied by varying the amount of water used, keeping the amount of phenol, oxidant and catalyst constant (Fig. 5). Phenol conversion increases with increase in the amount of water and after an optimum phenol to water molar ratio of 1:5, it drops. The influence of water concentration has been studied using organic peroxides in hydrocarbon oxidation. The active water species interact with peroxy radicals. The propagation and termination steps are influenced by water via hydrogen bond interaction of peroxy radicals. The interaction of active water species with peroxy radicals increases with water concentration and hence the increased conversions at high amounts of solvent.

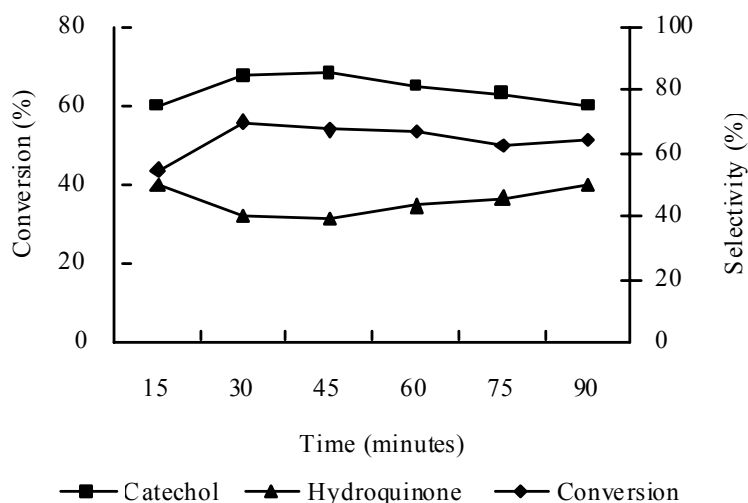
The catalyst amount required for maximum conversion of phenol was found out in the specified reaction condition (Fig. 6). From the figure, it can be noted that phenol oxidation increases with catalyst

*Oxidation of Phenol*



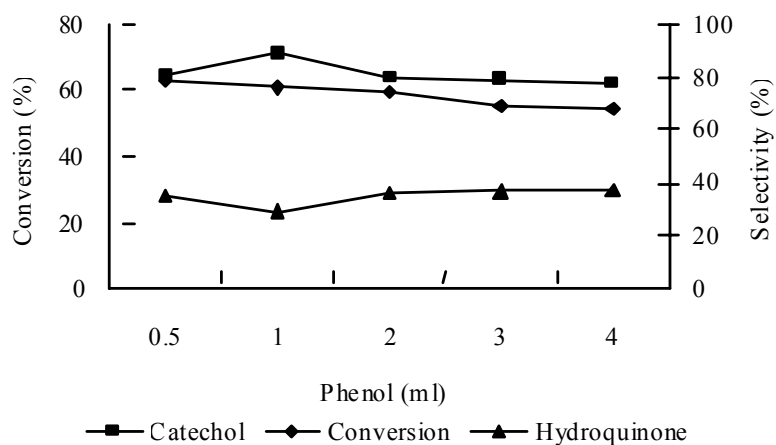
**Fig. 1. Effect of temperature**

Reaction conditions: Phenol:H<sub>2</sub>O<sub>2</sub>: H<sub>2</sub>O (molar ratio), 1:5:5; Catalyst, 0.1g; Time, 45 minutes



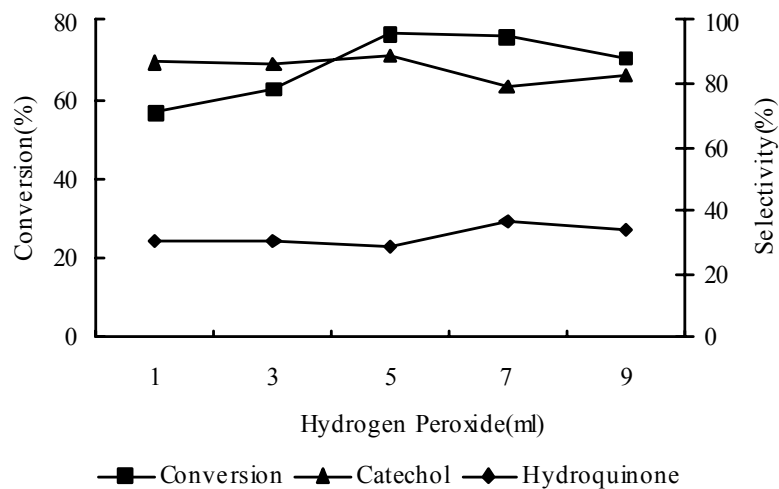
**Fig. 2. Effect of time**

Reaction conditions: Phenol:H<sub>2</sub>O<sub>2</sub>: H<sub>2</sub>O (molar ratio), 1:5:5; Catalyst, 0.1g; Temperature, 70°C



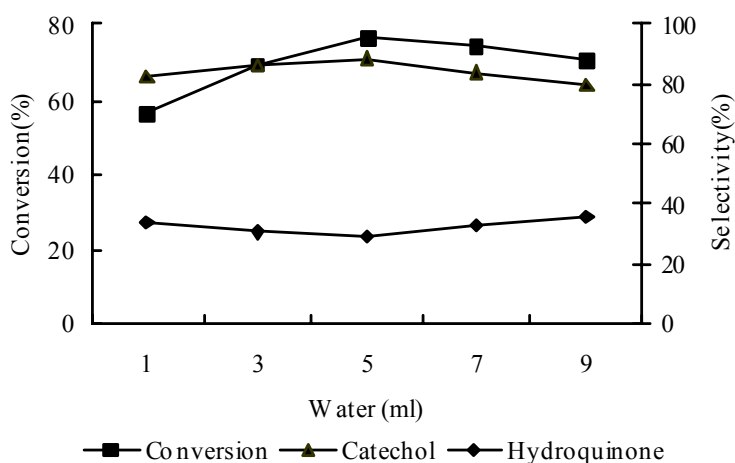
**Fig. 3. Effect of phenol concentration**

Reaction conditions: H<sub>2</sub>O: H<sub>2</sub>O<sub>2</sub>(molar ratio), 1:1; Catalyst ,0.1g; Temperature, 80°C; Time, 30 minutes



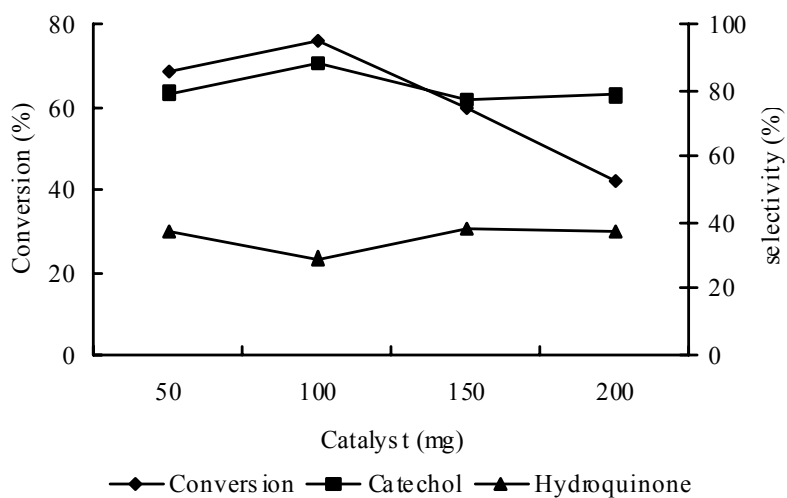
**Fig. 4. Effect of oxidant concentration**

Reaction conditions: Phenol: H<sub>2</sub>O (molar ratio), 1:5; Catalyst, 0.1g; Temperature, 80°C; Time, 30 minutes



**Fig. 5. Effect of solvent concentration**

Reaction conditions: Phenol:H<sub>2</sub>O<sub>2</sub> (molar ratio), 1:5; Catalyst, 0.1g; Temperature, 80°C; Time, 30 minutes



**Fig. 6. Effect of catalyst concentration**

Reaction conditions: Phenol:H<sub>2</sub>O:H<sub>2</sub>O<sub>2</sub> (molar ratio), 1:5:5; Temperature, 80°C; Time, 30 minutes

concentration. However, after an optimum amount of catalyst, the activity falls. From this, it can be concluded that a minimum amount of catalyst sites is required for the easy occurrence of the reaction. Decrease in reaction rate with increase in catalyst concentration can be due to manifold reasons. Increase in catalyst concentration can accelerate the decomposition of hydrogen peroxide. Also, the increased amounts of active sites in concurrence with increase in catalyst concentration can also lead to readsorption of products to active sites.

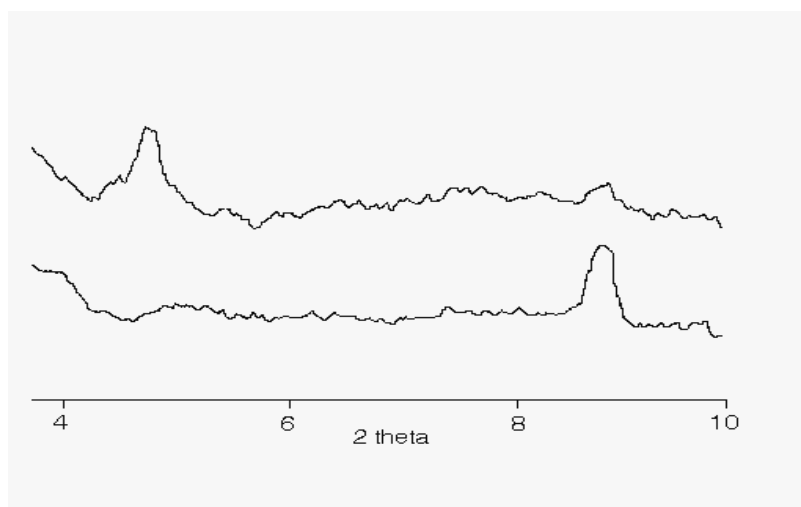
The most convenient approach to the textural characterisation of pillared clays is to obtain the adsorption isotherm at a temperature lower than or equal to the critical adsorbate temperature.  $N_2$  (at 77.2 K) is traditionally used as the adsorbate. In the present study, the BET and Langmuir surface areas of the various systems obtained directly are tabulated. The external and microporous surface areas were calculated from  $t$ -plot. Table 2 furnishes the surface area and pore volumes of the various aluminium pillared systems. The surface area and pore volume of the montmorillonite increases drastically as a result of

pillaring. Aluminium pillaring increases the BET surface area to 229.1  $m^2/g$  and Langmuir surface area to 302.8  $m^2/g$ . The pore volume increases to 0.2502  $cc/g$ . About one third of the area can be attributed to the external surface. As a result of rare earth metal exchange, surface area and pore volume decreases. This decrease can be correlated well with the amount of the metal oxide incorporated into the pillared system. Rare earth metal exchange deposits the metal oxides nearby the pillars and hence the lower percentage of external surface for these systems.

Fig.7 depicts the XRD patterns of the parent montmorillonite and aluminium pillared clay. Pillared clays are semi crystalline in nature. The broad bands obtained in the XRD spectrum, instead of sharp peaks can be attributed to the semi crystalline nature of clays. The characteristic  $d_{001}$  spacing of the parent montmorillonite is seen at  $2\theta$  value of 9.8 Å. For Al PM, this value increased to 20.11Å. Shifting of  $2\theta$  values clearly suggest the expansion of the clay layer during the pillaring process. The major intercalated species giving rise to the stable basal spacing in the aluminium pillared clay is the so called  $Al_{13}$

**Table 2. Surface and pore volume of aluminium pillared series**

Catalyst	Surface Area ( $m^2/g$ )				Pore volume ( $cc/g$ )
	BET	Langmuir	Microporous	External	
La/Al PM	205.2	274.3	131.2	74.0	0.2412
Ce/Al PM	210.7	283.9	134.6	76.1	0.2473
Th/Al PM	215.2	291.8	133.8	81.4	0.2489
Al PM	229.1	302.8	143.7	85.4	0.2502
M	7.1	11.1	2.2	4.9	0.0072



**Fig. 7. XRD profile of montmorillonite and aluminium pillared montmorillonite**

polyhydroxy polymer or Keggin cation which has been characterised by small angle X-ray scattering and  $^{27}\text{Al}$  NMR. This polymer with the structural formula,  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$  is a tri-decamer composed of one aluminium tetrahedra surrounded by 12 aluminium octahedra. It contains the four layers of superimposed oxygen atoms needed for expanding the clay basal spacings to 18 Å. The expansion of the (001) plane of the clay layer near this value suggests that the intercalated species is the  $\text{Al}_{13}$  polymer in Al PM.

The effect of exchange with rare earth metals on the XRD pattern of the pillared system was studied for representative samples. The XRD patterns were exactly identical to that of the parent pillared sample. Thus, it can be concluded that insertion of the second metal after the formation of stable pillars does not destabilise the porous network. Additional peaks corresponding to the exchanged metal oxides were not noticed. This may be due to the diminutive amounts (2-3%) of the exchanged metal in these samples.

#### CONCLUSION

- Aluminium pillared clays and their rare earth metal exchanged analogues are good oxidation catalysts.
- Time has a promotional effect on the hydroxylation of phenol. Oxidation of phenol increases with temperature and maximum conversion is observed at 80°C and 30 minutes, after which it drops. Hydroquinone selectivity decreases with temperature.
- Reaction rate increases linearly with solvent concentration. After an optimum value of solvent, the conversion % levels off.
- Phenol conversion decreases with increase in concentration of phenol. However, hydroquinone selectivity increases at higher concentrations of phenol.
- After an initial increase, the conversion % decreases with increase in catalyst concentration. Selectivity is independent of the amount of catalyst.
- Hydrogen peroxide concentration plays a promotional role on hydroxylation of phenol. After an optimum concentration of the oxidant, the activity levels off. Hydroquinone selectivity is independent of oxidant taken.

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