

Wet peroxide oxidation of phenol over Cerium impregnated Aluminium and Iron- Aluminium Pillared Clays

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I. Introduction.

Hydroxylation of phenol to dihydroxy products is an industrially important reaction as the products found immense application in various fields. The products, hydroquinone and catechol have been used in large scale as photographic film developer, antioxidant, polymerization inhibitor and used as synthetic intermediate for the production of medicines, perfumes etc [1]. The quinone derivatives play an important role in bio-systems and find many miscellaneous industrial applications. More over phenol is considered as one of the most toxic water pollutants, harmful to human health and to water life [2,6]. It is classified as a teratogenic and carcinogenic agent listed in water hazard class two in several countries. Hydroxyl radicals have been effectively applied in the field of environmental remediation of pollutants because of their strong oxidation potential capable of degrading wide range of products. Different Advanced Oxidation Processes (AOPs) have been used to generate the $\bullet\text{OH}$ radicals. Among them, the classic Fenton and Fenton-like reagents which contain Fe(II) or Fe (III) in combination with H_2O_2 remain attractive alternatives for the treatment of non biodegradable contaminants such as phenol [3-6]. However, these systems are seriously affected by the typical drawback of homogeneous catalysis such as separation, regeneration and also by ineffective consumption of oxidant H_2O_2 . Thus, different Fenton-like heterogeneous catalysts have been developed by immobilizing transition metal cations on adequate supports such as silica, zeolites, pillared clays, activated carbon, polymers, resins etc

Fe-containing molecular sieves, such as Fe-containing zeolite, Fe-ZSM-5[7] ferrisilicate [8], Fe-containing mesoporous silica such as Fe-MCM-41 [8], Fe-MCM-48 [10], Fe-SBA-15[11], Fe_2O_3 supported alumina[12] and FeALPO [13] were recently reported in literature which showed high catalytic performance for the oxidation of phenol using H_2O_2 as oxidant. Pillared clay containing iron oxide pillars such as Iron pillared clay[14] and mixed pillared clay such as Fe-Al pillared clays[15-18] were successfully employed for the removal of phenolic compounds in water combining good catalytic activity with high stability against iron leaching.

Pillared clays are a class of porous material prepared by the propping apart of natural clay layers by the intercalation of bulky inorganic polyoxo-hydroxo cations followed by the calcinations. The robust metal oxide pillars formed after calcination step increases basal spacing of clays and potential catalytic material with high acidity, surface area and activity were produced [19]. Several process of industrial importance such as Friedel's craft alkylation, acylation, oxidations have been reported over pillared clays[20]. Here we report oxidation of phenol over cerium impregnated Aluminium and Iron-Aluminium pillared clays in aqueous media. The promoting effect of cerium is also investigated. Our interest was conversion of phenol in to useful product than complete oxidation.

II. Experimental.

Catalyst preparation.

Pillared clays were prepared from Montmorillonite (KSF) clay by ion exchange method. Montmorillonite clay (M) is refluxed with 0.2M NaNO_3 solution to produce Na-Montmorillonite (NaM). The pillaring agents of Aluminium and Iron were prepared by the partial hydrolysis of 0.2M $\text{Al}(\text{NO}_3)_3$ and $\text{Fe}(\text{NO}_3)_3$ solution respectively by the drop wise addition of 0.4 M NaOH solution under vigorous stirring (OH/M ratio is maintained as 2). The intercalation of pillaring species was done by refluxing aluminium polyoxycation solution to the pre swelled 1% Na-montmorillonite clay suspension maintained at 80°C keeping Al/clay ratio 10mmol/g. The suspension was aged for 24 hours and then filtered and washed and dried at 110°C for six hours followed by calcinations at 450°C for 4 hours to get the Aluminium Pillared Clay (AIPC). For the preparation of Iron-Aluminium mixed pillared Clay (Fe-AIPC) aluminium and iron pillaring agents were taken in the molar ratio 5:1 and pillaring agents were added to the clay suspension maintained at 90°C and the remaining procedure was done as same above. Cerium is loaded in pillared clay by wet impregnation method. Required amount of cerium nitrate is dissolved in water. It was then added to the calcined pillared clay and stirred for six hours. The water was then evaporated off by maintaining the mixture at 70°C . The samples then dried at 110°C for six hours and finally calcined at 450°C for 4 hours to get cerium impregnated pillared

clay. Cerium impregnated aluminium and iron aluminium pillared clay were denoted as Ce/AlPC and Ce/Fe-AlPC respectively.

Characterization

Elemental analyses of the catalyst were done by ICP- AES analysis using GBS plasmalab 8440 instrument. EDX analysis of the catalyst was done in a JOEL JSM-840 with resolution of 1.3 eV. XRD analysis of samples were done using Rigaku Dmax Ni filtered CuK α radiation in 2 to 70 $^{\circ}$ at a scan rate of 2 $^{\circ}$ /min. Surface area and pore volume measurements of catalysts were simultaneously done by Micrometrics Tristar 3000 using N $_2$ gas adsorption/desorption at 77 K and by the application of BET equation. Samples were activated at 90 $^{\circ}$ C for 30 minutes and then degassed at 300 $^{\circ}$ C for three hours. FTIR spectra of the samples were recorded using JASCO FT-IR spectrometer using KBr pellets in the range of 400-4000 cm $^{-1}$ in the transmission mode. TG analysis were done by Perkin Elmer Pyris Diamond TGA-DTA analyzer with dried samples in nitrogen atmosphere with a heating rate of 10 $^{\circ}$ C/min. UV-Vis DR spectra of the prepared samples were taken in 200-800 nm on Labomed UV-Vis Double beam UVD-500. Acidity and acid site distribution of catalysts were done by Temperature programmed Desorption of Ammonia. TPD of ammonia was done over prepared catalysts as the procedure described below. The pelletized samples are housed in a quartz reactor and preheated in a flow of N $_2$ atmosphere at 300 $^{\circ}$ C and cooled to room temperature. Ammonia is injected to the samples and saturated for 30 minutes. The excess physisorbed ammonia was then flushed off. The adsorbed ammonia is desorbed in a programmed manner. The desorbed ammonia is passed through 100 ml H $_2$ SO $_4$ (0.0125N) solution. The excess H $_2$ SO $_4$ is back titrated with NaOH for quantitative determination of acid sites. The amount desorbed at 35-200 $^{\circ}$ C, 200-400 $^{\circ}$ C, 400-600 $^{\circ}$ C were assigned as weak, medium and strong acid sites respectively.

The liquid phase hydroxylation of phenol was carried out in a 50 mL round bottomed flask equipped with air condenser and magnetic stirrer, 0.1 g of the catalyst was added to calculated amounts of phenol and solvent. Required amounts of 30 % H $_2$ O $_2$ were added drop wise to the reaction medium and reaction ensued at specified temperature. The products were analyzed using Chemito 8610 Gas Chromatograph equipped with flame ionization detector and OV-17 column. Quantitative estimation of tarry products was not pursued and conversion of phenol refers conversion to dihydroxy phenols. Thus the percent conversion (wt%) of phenol is the total percentage of phenol transformed in to diphenols.

III. Result and discussion

3.1 Elemental Analysis

The results of Elemental analysis of the catalysts are given in table 1. It can be seen that appreciable amount of metal is incorporated as metal oxide during the pillaring process. Initial clay have 20.74 % weight as aluminum. After the aluminium pillaring it is increased to 35.8. In Iron- Aluminium pillared clay the weight % of aluminium and iron are 30.5 and 16.52 respectively. The weight % of cerium is calculated from EDX analysis. The weight % of cerium in Ce/AlPC and in Ce/Fe-AlPC is found to be 1.82 and 1.65 respectively. The EDX spectrum of Ce/Fe-AlPC is given in Fig.1

Table - 1: Elemental analysis of prepared catalysts

Catalyst	SiO $_2$	Al $_2$ O $_3$	Fe $_2$ O $_3$	Na $_2$ O	K $_2$ O	MgO	CaO
M	56.47	20.74	12.10	2.67	2.81	2.61	2.60
NaM	55.44	19.52	11.88	7.58	2.48	2.64	0.46
AlPC	47.92	35.8	11.16	0.45	1.93	2.1	0.87
FeAlPC	47.58	30.5	16.52	0.36	2.07	2.17	0.80

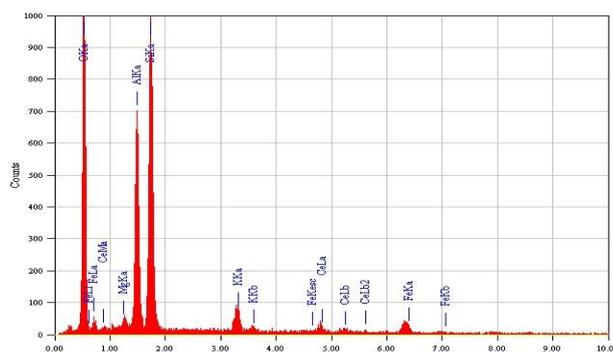


Fig: 1 EDX spectrum of Ce/Fe-AlPC

3.2 XRD

The broad bands obtained in the XRD spectrum instead of sharp peaks can be attributed the semi crystalline nature of clays. The success of pillaring process can readily understood from XRD analysis. The XRD pattern of pillared clays are shown in Fig 2. The parent clay shows peak at 2θ value 8.9 corresponds to the basal (001) spacing of 9.8Å . After the pillaring process this value is shifted to lower 2θ values which indicate the increase in basal spacing of clay by the expansion of clay due the incorporation of metal oxide pillars in between clay layers. The d spacing was shifted to 19.2Å for Aluminium pillared clay and it was shifted to 21.5Å for Iron-Aluminium pillared clay. Bergaya et al [21] reported the formation of mixed $\text{Al}_{13-x}\text{Fe}_x$ pillars, based on the Fe content of the pillared solids. The wide angle XRD patterns of catalysts are given in Fig 3. Peaks at 2θ value 19.6 and 35.1 corresponds to the reflection from (110) and (130) planes respectively of 2:1 phyllosilicate clay. The peak at 26.7 corresponds to quartz impurity. The absence of peaks corresponds to cerium indicate that cerium is uniformly distributed on catalyst surface.

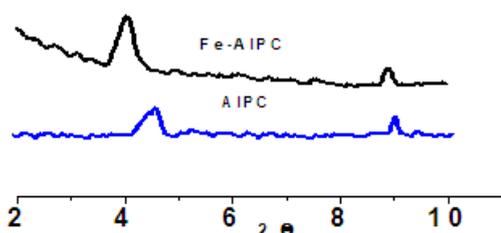


Fig 2 : XRD Of Pillared clays

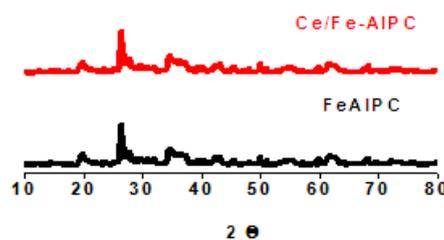


Fig 3: Wide angle XRD of Pillared clays

3.3 Surface area measurements

The surface area and pore volume of catalysts are given on the table 2. The starting parent clay has a lower surface area of $17\text{ m}^2/\text{g}$ only. The increase in surface area of in sodium montmorillonite is attributed to the dealumination of octahedral aluminium during exchange process which may present in interlayer region. As result of pillaring, surface area and pore volume increased drastically since metal oxide pillars are inserted in between the two dimensional gallery of clay layers to produce a three dimensional porous network. The active surface of clays is now more accessible. In cerium impregnated Aluminium pillared clay the surface area is lowered due to pore blocking. But the surface area of Ce/Fe-AIPC is higher than that of Fe-AIPC. This may be due to the additional surface area provided by ceria mesopores.

Table 2: Textural and acidic properties of catalysts.

Catalysts	Surface Area (m^2/g) S_{BET}	Pore volume (cc/g)	Weak (mmol/g)	Medium (mmol/g)	Strong (mmol/g)	Cumulative (mmol/g)
NaM	70	0.0253	0.249	0.137	0.034	0.420
AIPC	128	0.1689	0.443	0.308	0.132	0.883
Fe-AIPC	132	0.1713	0.383	0.265	0.103	0.751
Ce/AIPC	119	0.1582	0.416	0.342	0.148	0.906
Ce/Fe-AIPC	143	0.1728	0.368	0.293	0.108	0.769

The adsorption isotherms of pillared clays are shown in Figs 4& 5. The adsorption isotherm is both the blend of type I and and Type IV with hysteresis loop H4 (according to IUPAC) characteristics of mesoporous materials with some micropores containing slit like pores. At lower P/P_0 value the shape is of type I characteristics of microporous material. But at higher P/P_0 values it shows hysteresis loop due to the capillary condensation.

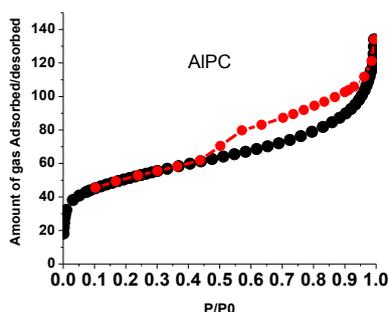


Fig 4: Adsorption isotherm of AIPC

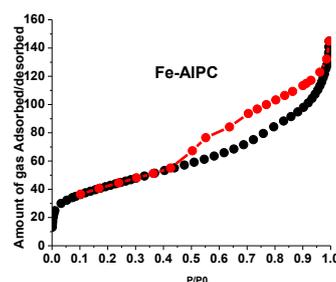


Fig 5: Adsorption isotherm of Fe- AIPC

3.3. Acidity measurements

The results of acidity measurements using TPD of ammonia are given in Table 2. As a result of pillaring a dramatic increase in acidity in weak, medium and strong acidic region is observed. During the pillaring process the desegregation of clay layer helps in exposing more number of acidic sites and the expansion in layer structure in pillared clays increases the accessibility of interlayer protons which otherwise obscure to reactant molecules in parent clay due to smaller interlayer distance. In addition metal oxide pillars formed in the interlayer can contribute to the overall acidity of pillared material. Upon cerium loading the medium and strong acid sites were increased at the expense of weak acid sites.

3.4. FT-IR Analysis

Fig 6. shows the infrared (IR) spectra of sodium Montmorillonite and pillared samples. Broad band near 3500 cm^{-1} corresponds to the stretching vibration of -OH group. For Sodium montmorillonite, this was a very intense peak. The intensity of this peak considerably reduced for the pillared samples showing the loss of hydroxyl groups upon pillaring during calcination at higher temperature.

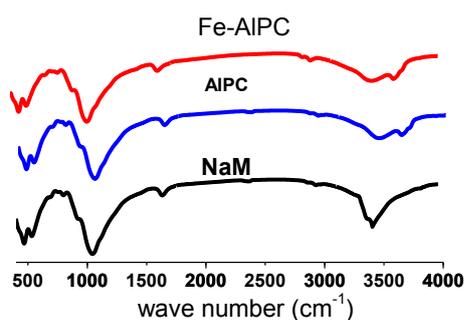


Fig 6: IR spectrum of catalysts

For the pillared samples two bands were observed corresponding to the hydroxyl groups. One probably assigned to the pillar OH group and the other assigned to layer hydroxyl groups. Peak at around 1600 cm^{-1} is due to bending vibrations of water. The decrease in the intensity of -OH peaks is observed after the pillaring process as the pillaring process replaces a large amount of interlayer cations that generally exists as hydrated forms. The band around 1060 cm^{-1} is due to asymmetric stretching vibrations of SiO_2 tetrahedra. A band around 800 cm^{-1} is due to stretching vibrations of Al tetrahedra and absorption at 526-471 cm^{-1} is due to bending vibration of Si-O [22].

3.5. Thermogravimetric Analysis.

The heat changes associated with the preparation process and the thermal stability of the prepared catalysts can be understood from thermo gravimetric analysis (Fig 7). The weight loss up to 200 $^{\circ}\text{C}$ corresponds to the loss of physisorbed water. The weight loss above 200 $^{\circ}\text{C}$ in sodium montmorillonite is as result of removal of water originates from dehydration of the layers. This structural collapse continues up to 800 $^{\circ}\text{C}$.

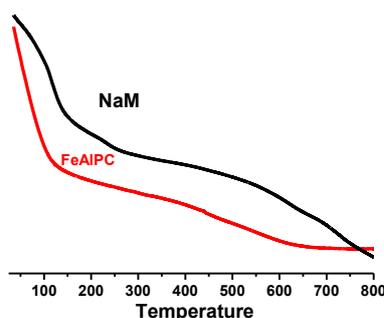


Fig 7: TG profile of NaM and FeAIPC

In intercalated samples the weight loss from 200 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ is due to the water removal from the surface, micro pores and the dehydroxylation of hydroxy metal oligomer or polymers. The new deflections at

400⁰C is due to the transformation of metal hydroxide in to metal oxide pillars .The weight loss above 500⁰C is absent in pillared clays indicate the additional stability due to the pillaring process.

3.6. UV-VIS DRS analysis

The UV-VIS DR spectrum of cerium impregnated catalysts are shown in fig 8.For cerium impregnated Iron-Aluminium pillared clay the broad adsorption peak detected in the range of 250–450nm is related to Fe³⁺ ← O²⁻ charge transfer[23]. The bands in the region of 300–400nm are characteristics of Fe³⁺ in octahedral coordination. The peak around 290 nm corresponds to Ce⁴⁺ ← O²⁻ charge transfer transitions can be seen in both catalysts [24].

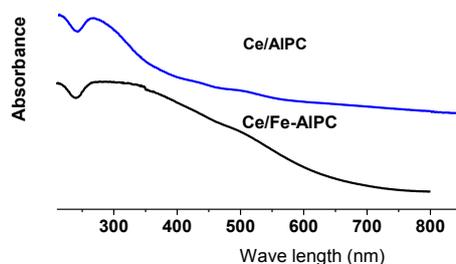


Fig 8: UV DR Spectrum of Ce/AIPC and Ce/Fe-AIPC

IV. Activity studies :-Hydroxylation of phenol

The hydroxylation of phenol was done over prepared catalysts in aqueous media and the results are given in Table.3 .As it can be seen, conversion increased to more than two times after the pillaring process. This may be due to increase in surface area, pore volume and acidity after the pillaring process. Phenol hydroxylation is strongly diffusion limited and it was believed that hydroquinone is formed inside the pores and catechol and other products were formed in external surface[25] .Fe-AIPC got higher conversion than AIPC due to higher iron content and higher surface area and pore volume. The incorporation of cerium in pillared clays leads to enhancement in conversion of phenol and selectivity of hydroquinone. Cerium impregnated iron Aluminium pillared clay got more than 80 % conversion of phenol obtained within 45 minutes. This may be due to the promoting effect of ceria ,its redox property and additional surface area provided by the ceria mesopores. Prolong reaction time leads to further oxidation of diphenols and tarry products are formed. We limit our study to 45 minnutes and we are interested in converting phenol in to useful products than complete oxidation. Since the reactions are done in aqueous media the prepared catalyst can be effectively used for the abatement of phenol in waste water. Even though there were reports that the conversion depends on acidity, in this present case Iron-Aluminium mixed pillared clay which has less acidity than Aluminium pillared clay have got higher conversion probably due to the higher redox property of iron .

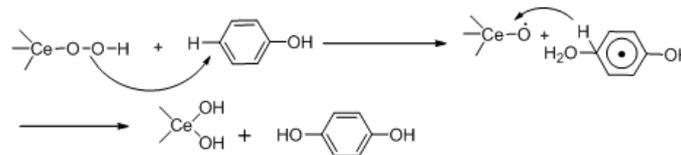
Table 3: Hydroxylation of phenol over various pillared clays

Catalysts	Conversion of phenol (%)	Selectivity	
		Catechol	Hydroquinone
NaM	36.2	78.8	21.2
AIPC	63.4	66.6	33.4
Fe-AIPC	68.8	67.1	32.9
Ce/AIPC	72.8	64.3	35.7
Ce/Fe-AIPC	82.2	60.9	39.1

Temperature -70⁰C, phenol :water: H₂O₂ =1:5:5 (volume ratio) , catalyst-100mg, time-45 min

Even though we have not done any mechanistic studies a free radical mechanism can be envisaged as in our earlier reports[18].The suggested mechanism involves the formation of phenoxy radical on catalyst surface, which then reacts with peroxide giving OH radical and biphenol.The produced free radical propagates the chain by attacking phenol molecule ,forming diphenol.

Fig 9: mechanism of hydroquinone formation with metaloxo peroxide species



The Fenton type behavior of ceria and the promoting role of cerium in iron based catalysts systems were studied by various researchers [26]. Cerium species played two roles in this model reaction. First, as a widely used promoter in redox reactions, the introduction of ceria could efficiently improve the diphenol distribution. Hydroquinone selectivity is slightly raised after the incorporation of cerium. Cerium forms a metaloxo peroxide species [27] which react with phenol to form hydroquinone rather than catechol as the scheme in figure 9 .

V. Conclusions

Aluminium pillared clay and Iron-Aluminium pillared clays were prepared by ion exchange method and cerium was loaded in pillared clays by wet impregnation method. The prepared catalysts were characterized by various physico- chemical methods. The shift in 2θ value and increase in d spacing indicates the successful pillaring of the clay. The adsorption isotherm of pillared clay is a blend of both type I and type IV with hysteresis loop H4 corresponds to slit like pores characteristics of mesoporous material with some micropores. A large increase in surface area, pore volume and acidity were observed as a result of pillaring. The nature and oxidation state of iron and cerium is confirmed from UV-VIS DRS analysis. The catalytic activities of the prepared catalysts were evaluated for the hydroxylation of phenol in aqueous media. Incorporation of ceria provides promoting effect towards the oxidation of phenol. Cerium impregnated Iron- Aluminium pillared clay is found to be promising catalyst with more than 80% conversion in 45 minutes owing to redox property and additional surface area provided by ceria mesopores. Incorporation of cerium enhances the selectivity of hydroquinone by the formation of metaloxo peroxide intermediate. These catalysts can be effectively used as green catalyst for the abatement of phenol in waste water.

Acknowledgement

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