

Wet peroxide oxidation of phenol over mixed pillared montmorillonites

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Abstract

Wet peroxide oxidation (WPO) of phenol is an effective means for the production of diphenols, which are of great industrial importance. An added advantage of this method is the removal of phenol from wastewater effluents. Hydroxylation of phenol occurs efficiently over mixed iron aluminium pillared montmorillonites. An initial induction period is noticed in all cases. A thorough study on the reaction variables suggests free radical mechanism for the reaction.

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1. Introduction

Phenol is a major water pollutant. The presence of phenol even in trace amounts has been proven fatal to living beings. Among catalysed wet oxidations, oxidation with hydrogen peroxide is preferred because the active oxygen content of hydrogen peroxide is much higher than other oxidants. Wet peroxide oxidation (WPO) with hydrogen peroxide can bring about removal of phenol from effluents. Water is the only by product formed and the oxidant is inexpensive. Also, aqueous hydrogen peroxide is a stable reagent, provided it is handled and stored in the proper manner [1]. An added advantage of the reaction is that oxidation of phenol produces catechol and hydroquinone, two important intermediates in agrochemical and fine chemical industries. Catechol and hydroquinone are also used as photographic developers and antioxidants. Conventionally, HClO_4 - H_3PO_4 and Fe(III)/Co(II) catalysts were used for oxidation of phenol [2,3]. But obvious shortcomings of these homogeneous catalysts prevent their wide use in diphenol production. Titanium silicalite-1 (TS-I), a titanium containing zeolite was found superior to other catalysts for phenol hydroxylation, due to decreased formation of tar and polluting by products and subsequently the method was commercialised. Extensive study of the reaction has been conducted using this catalyst [4,5]. Though TS-I is

an excellent catalyst for phenol hydroxylation, lack of thermal stability and somewhat complex preparation method have led researchers to develop other cheaper catalysts for the hydroxylation of phenol. Since peroxide is used, free radical mechanism can be expected for the reaction and hence various iron and copper containing catalysts have been employed [6–9].

Pillar interlayered clays constitute a novel class of microporous materials with good thermal stability, high surface area and pronounced Brønsted and Lewis acidity. These materials result from a two step modification of naturally occurring swelling clay minerals; the propping apart of clay layers by intercalation with oligo or polymeric cationic metal complexes and calcination of the intercalated clays transforming the inserted complexes into nanosized pillars of metal oxides cross linked to the clay layers. Several processes of industrial importance have been reported over pillared clays [10–13]. Here we report the use of iron aluminium mixed pillared montmorillonite and its transition metal exchanged analogues for the hydroxylation of phenol.

2. Experimental

The mixed pillared clay was synthesised by partial hydrolysis of 0.1 M $\text{Fe(NO}_3)_3$ and $\text{Al(NO}_3)_3$ solution (equimolar ratio) by drop wise addition of 0.3 M Na_2CO_3 solution under vigorous stirring. Intercalation of pillaring species into the clay layers was done by treating the pillaring solution with a previously swollen clay suspension at 80 °C [OH/metal ratio, 2

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and metal/clay ratio, 20 mmol/g clay]. The clay after exchange was washed several times with distilled water and filtered. This was dried in air oven at 110 °C overnight, followed by calcination for 6 h at 450 °C in muffle furnace. Exchange with transition metals was done using 0.1 molar aqueous solutions of the corresponding metal nitrate. The clay after exchange was washed five to six times with distilled water. This was filtered and dried in air oven at 110 °C overnight and calcined for 5 h at 500 °C. The pillared clays synthesised for the present study are notated as X/FeAl PM, where X is the transition metal exchanged. The diffractometer traces of the catalyst samples were taken in RIGAKU D/MAX-C instrument using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The simultaneous determination of surface areas and pore volumes of the catalyst samples was done on a Micromeritics Gemini analyser. NMR spectra of samples were recorded by a 300 DSX Bruker spectrometer. Cumene cracking was carried out in vapour phase at atmospheric pressure. The products were analysed using Chemito 8610 Gas Chromatograph equipped with flame ionisation detector and FFAP column.

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, preactivated at 500 °C for 2 h was added to calculated amounts of phenol and solvent. Required amounts of 30% H₂O₂ was added drop wise to the reaction medium and reaction ensued at specified temperatures. Reaction mixture was periodically analysed using gas chromatography. Benzoquinone was not detected in any case. Tarry products were observed in all runs. Quantitative estimation of tarry products was not pursued and conversion of phenol refers to conversion to diphenols. Thus, percentage conversion (wt.%) of phenol is the total percentage of phenol transformed into diphenols.

3. Results and discussion

3.1. Surface area and pore volume measurements

The surface area and pore volume of the prepared systems are given in Table 1. Montmorillonite has a BET surface area of 14.3 m² g⁻¹ and Langmuir surface area of 27.9 m² g⁻¹. As a result of pillaring, surface area and pore volume increases dras-

Table 1
Surface area and pore volume of the systems

Catalyst	Surface area (m ² g ⁻¹)		Pore volume ^a (cc g ⁻¹)
	BET	Langmuir	
V/FeAl PM	158.3	229.9	0.1753
Mn/FeAl PM	156.0	219.2	0.1703
Co/FeAl PM	164.9	229.5	0.1871
Ni/FeAl PM	142.2	203.9	0.1673
Cu/FeAl PM	144.5	207.6	0.1658
Zn/FeAl PM	147.2	233.6	0.1635
FeAl PM	170.6	253.7	0.1894
M ^b	14.3	27.9	0.0058

^a Pore volume measured at 0.9976 P/P₀.

^b Montmorillonite KSF.

tically. Transition metal exchange decreases the surface area and pore volume, mainly in external surface. Pillaring is the process by which stable metal oxide clusters are incorporated into inter-layer space of swellable clays. As a result, a three dimensional porous network is created. Hence surface area and pore volume increases extensively, especially the microporous surface area. The external surface area in pillared clays arises from mesopores, which are mainly interparticle voids. Transition metal exchange deposits the metal oxides inside the porous network and hence the decrease in surface area (especially the external surface) and pore volume.

3.2. X-ray diffraction

With the exception of surface area and pore volume measurements, the easiest way to determine whether pillar intercalation is successful is to record the X-ray diffraction pattern of an oriented film of the product. Fig. 1 depicts XRD patterns of montmorillonite and FeAl PM. Pillared clays are semi crystalline in nature. The broad bands obtained in the XRD spectrum, instead of sharp peaks can be attributed to semi crystalline nature of clays. Hence indexing of the spectrum is not possible for this type of solid acids. The only data that can be obtained is the *d* spacing of (001) plane, which indicates the extent of propping apart of clay layers. The characteristic *d*₀₀₁ spacing of montmorillonite increased from 9.8 Å to 17.8 Å for FeAl PM. Shifting of 2 θ values clearly suggests expansion of clay layer during pillaring process. The increase in *d* spacing of (001) plane to 17.8 Å is indicative of the presence of Al₁₃ like polymers. This polymer with structural formula, [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺ is a tri-decamer composed of one aluminium tetrahedra surrounded by 12 aluminium octahedra. It contains four layers of superimposed oxygen atoms needed for expanding clay basal spacings to 18 Å. Formation of mixed Al_{13-x}Fe_x pillars, based on the Fe content of the pillared solids was reported by Bergaya et al. [14]. The effect of exchange with transition metals on the XRD patterns was studied for representative samples. The XRD patterns were exactly identical to that of montmorillonite. 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

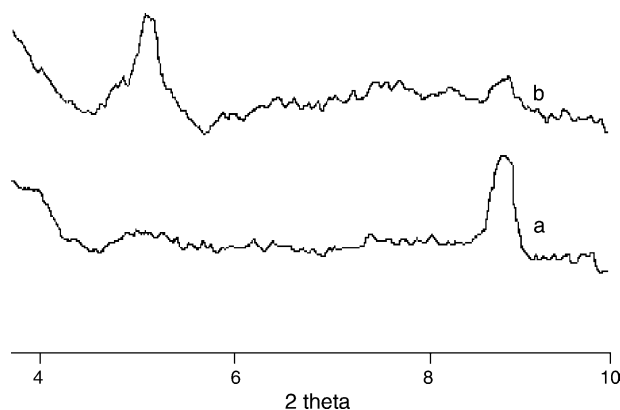


Fig. 1. XRD profile: (a) M; (b) FeAl PM.

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