



Short communication

Fast catalytic oxidation of phenol over iron modified zeolite L nanocrystals

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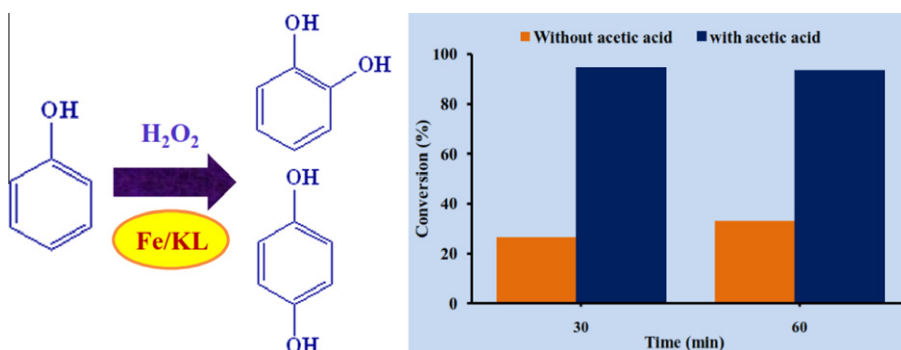
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HIGHLIGHTS

- ▶ Iron modified nanozeolite L was synthesized and tested in the oxidation of phenol.
- ▶ The oxidation was significantly enhanced by the addition of acetic acid.
- ▶ 93.40% of phenol conversion was achieved in 30 min.
- ▶ Acetic acid was oxidized by H_2O_2 to form peracetic acid.

GRAPHICAL ABSTRACT

Oxidation of phenol in the presence of acetic acid was carried out over iron-modified nanozeolite L. The oxidation activity of phenol was significantly enhanced by the addition of acetic acid. It was found that the acetic acid was oxidized by H_2O_2 to form peracetic acid which served as a better oxidant.



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ABSTRACT

Iron modified zeolite L nanocrystals (Fe/KL) were synthesized hydrothermally by the incorporation of Fe^{3+} in zeolite L lattice. XRD results showed an increase in the inter-planar spacing and lattice parameters. Transition characteristic of the tetrahedral Fe^{3+} species were observed in the UV–Vis spectrum. The oxidation of phenol in the presence of acetic acid over Fe/KL gave 93.40% conversion in 30 min with selective formation of 77.47% catechol and 22.53% hydroquinone. The catalytic activity was significantly enhanced by the addition of acetic acid. It was found that the acetic acid was oxidized by hydrogen peroxide to form peracetic acid, which served as a better oxidizing agent.

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1. Introduction

Oxidation of phenol has been given much attention in industries over the past few decades as mild oxidation of phenol produces benzenediols. Benzenediols, viz., catechol (CAT) and hydroquinone (HQ) are important precursors in the production of many valuable chemical products [1,2]. For example, catechol is used in the production of pesticides, perfumes and pharmaceutical

products; hydroquinone is used as a major ingredient in rubber antioxidants, herbicides, and dyestuffs.

In recent years, many studies have been conducted for the oxidation of phenol using various heterogeneous catalysts such as titanasilicates [2–4], copper alginate [5], iron silica [6], zeolite-Y encapsulated metal complexes [7,8], and polymer-supported transition metal complexes [9]. Among the oxidants, hydrogen peroxide is often used for the oxidation of phenol, due to its clean and eco-friendly nature [10,11]. These catalysts showed good catalytic activity with good recyclability. However, most of the catalysts available for the production of CAT and HQ take ~6 h for the

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reaction [7,12], not selective [3] or give low yield [3,8]. Thus, there is good scope for the development of new catalytic systems for the liquid-phase oxidation of phenol.

Nanozeolites are widely known as highly selective catalyst for many reactions [13–15]. To the best of our knowledge, there is no published report on the oxidation of phenol by using transition metal modified nanozeolite L catalyst. Nanometer size Zeolite L with uniform micropores was thought to be an advantage if used as a catalyst support due to its large external surface area and shorter diffusion pathway to the active sites which result in increasing catalytic activity [16,17]. Herein we report an improved catalytic system for the liquid-phase oxidation of phenol over iron modified zeolite L nanocrystals (Fe/KL) in the presence of acetic acid.

2. Experimental

2.1. Synthesis and characterization

Rice husk ash (RHA) was used as an alternative silica source as it is abundant in Malaysia [18]. The preparation of RHA and Fe/KL were carried out following the procedures similar to our previous publication [19]. The initial gel composition of the mixture was $10\text{SiO}_2: \text{Al}_2\text{O}_3: 0.1\text{Fe}_2\text{O}_3: 4\text{K}_2\text{O}: 100\text{H}_2\text{O}$. Iron(III) nitrate nonahydrate (0.5387 g) was added into the potassium aluminates solution and stirred for 1 h. The resulting dark brown solution was then introduced into the silicate solution under vigorous stirring. The solution was autoclaved and heated at 170 °C for 3 days under static condition. Finally, the solid product was filtered and washed with distilled water. It was dried in an oven at 110 °C for 24 h. The resulting powder was labeled as Fe/KL.

The solid Fe/KL was characterized by X-ray diffractometry (XRD, Siemens Diffractometer D5000, Kristalloflex), transmission electron microscopy (TEM, FEI, CM12), scanning electron microscopy (SEM, Leo Supra 50 VP, Field Emission), diffuse reflectance UV–Vis spectrometry (DR UV–Vis, Lambda 35, Perkin–Elmer) and atomic absorption spectroscopy (AAS, AAnalyst-200, Perkin–Elmer). The surface acidity of the sample was determined by *in situ* pyridine–IR spectroscopy. The FTIR spectra were recorded at 25, 100, 200 and 300 °C after pyridine desorption for 1 h using an *in situ* adsorption–desorption system [20].

2.2. Liquid phase oxidation of phenol

Oxidation of phenol was performed using water as the solvent [21]. In a typical run, phenol (0.94 g, 10 mmol) was dissolved in 10 mL of water and transferred into a round-bottom flask containing 50 mg of Fe/KL catalyst. Three drops of acetic acid was added into the mixture and refluxed at 70 °C. The H_2O_2 (2.28 g, 20 mmol, 30%) was added drop-wise into the reaction vessel within 15 min with stirring at 750 rpm. The products were analyzed by GC (Clarus 500, Perkin Elmer) and identified using GC–MS (Clarus 600, Perkin Elmer) equipped with a capillary wax column. Permanganometric and iodometric titrations were performed to determine the H_2O_2 and peracetic acid content in the mixture.

3. Results and discussion

3.1. Characterization of the catalyst

The crystalline Fe/KL obtained was white in color, indicating the absence of any occluded Fe_2O_3 (brown color). Fig. 1b shows the XRD pattern of the Fe/KL compared to that of zeolite L (Fig. 1a) obtained from our previous study [19]. Virtually identical XRD patterns of LTL-type zeolite were observed regardless of the iron content in the sample. It is noted that the XRD diffraction bands are shifted slightly to higher d values (inter-planar spacing) for

the iron-substituted samples. This is accompanied by an increase in the lattice parameters for Fe/KL. The cell dimensions of Fe/KL and pure zeolite L are, $a = 18.55 \text{ \AA}$, $c = 7.55 \text{ \AA}$, $V = 2245.75 \text{ \AA}^3$, and $a = 18.50 \text{ \AA}$, $c = 7.51 \text{ \AA}$, $V = 2152.13 \text{ \AA}^3$, respectively. These results indicated that the iron was successfully incorporated into the LTL framework [22]. To further confirm this, atomic absorption analysis was carried out and the result showed that the amount of iron incorporated was 1.15 wt.%.

The DR UV–Vis spectrum of the as-synthesized Fe/KL nanocrystals is shown in Fig. 2. The spectrum is in good agreement with the previously reported results, with absorption bands located at 245, 385, 423, 444, and 485 nm [23]. The intense absorption band centred at 245 nm is a ligand-to-metal charge transfer (LMCT) transition of tetrahedral Fe^{3+} species. The absorption bands located in the 385–485 nm regions are assigned to forbidden $d-d$ transitions of Fe^{3+} in tetrahedral symmetry, which broaden the DR UV–Vis spectrum of Fe/KL [24].

TEM and SEM were used to study the surface morphologies of the catalyst. This is shown in Fig. 3. The TEM image (Fig. 3a) shows the Fe/KL has one-dimensional channels of $\sim 0.76 \text{ nm}$ width with tablet-like structure. The particle size distribution (Fig. 3b) was obtained by using the measurement method described in our earlier publication [19]. The results show that the average particle size of the catalyst is 121 nm.

Surface acidity plays an important role in the oxidation reaction. Fig. 4 depicts the stepwise pyridine desorption spectra of iron-substituted zeolite L at 25, 100, 200 and 300 °C under vacuum ($\sim 6 \text{ mmHg}$). The bands centred at 1437 cm^{-1} and 1585 cm^{-1} are attributed to pyridine adsorption on Lewis acid sites [25]. The intensity of the bands at the Lewis acid site decreased with increasing evacuation temperature up to 300 °C. The incomplete desorption of pyridine after evacuation at 300 °C confirms the high strength of Lewis acid sites. No IR absorption band was detected at 1545 cm^{-1} , indicating the absence of Brønsted acidity in Fe/KL nanocrystals. The adsorption band at 1487 cm^{-1} corresponds to the physisorbed pyridine attributed to both Brønsted and Lewis acid sites [25]. The band intensity gradually decreased and almost disappeared at 300 °C. These observations show that only Lewis acid sites are present on the catalyst.

3.2. The oxidation of phenol

The as-synthesized Fe/KL catalyst was evaluated for the liquid phase oxidation of phenol in the presence of acetic acid. No reac-

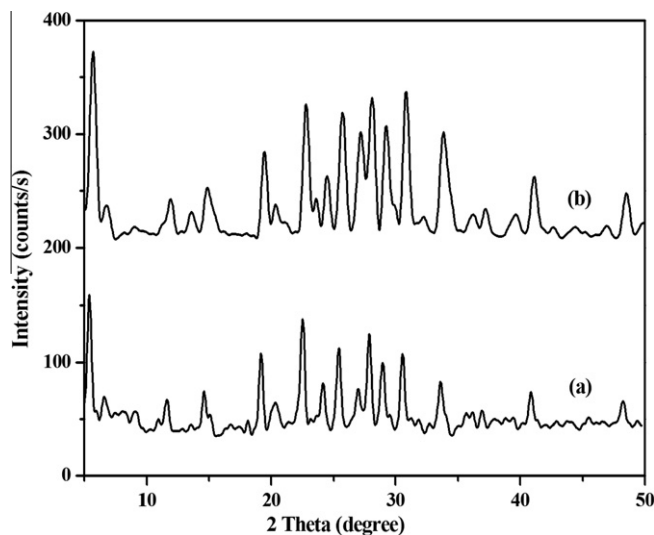


Fig. 1. The XRD patterns of (a) L-type zeolite and (b) Fe/KL.

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