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Short communication

Fast catalytic oxidation of phenol over iron modified zeolite L nanocrystals

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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 H₂O₂ 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 H₂O₂ to form peracetic acid which served as a better oxidant.

ABSTRACT

Iron modified zeolite L nanocrystals (Fe/KL) were synthesized hydrothermally by the incorporation of Fe³⁺ in zeolite L lattice. XRD results showed an increase in the inter-planar spacing and lattice parameters. Transition characteristic of the tetrahedral Fe³⁺ 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.

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 titanosilicates [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
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 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

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 10SiO₂:Al₂O₃:FeO₂:K₂O:10H₂O. Iron(III) nitrate nonohydrate (0.5387 g) was added into the potassium aluminate 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, AAAnalyst 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. 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 H₂O₂ (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 H₂O₂ 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 Fe₃O₄ (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, \(a = 18.55\, \text{Å}, c = 7.55\, \text{Å}, V = 2245.75\, \text{Å}^3\), and \(a = 18.50\, \text{Å}, c = 7.51\, \text{Å}, V = 2152.13\, \text{Å}^3\), 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 Fe³⁺ species. The absorption bands located in the 385–485 nm regions are assigned to forbidden d–d transitions of Fe³⁺ 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 ~0.76 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 (~6 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 Bronsted acidity in Fe/KL nanocrystals. The adsorption band at 1487 cm⁻¹ corresponds to the physisorbed pyridine attributed to both Bronsted 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-
tion was observed over pure zeolite L at the same reaction conditions. The oxidation activity of phenol over Fe/KL catalyst was significantly enhanced by adding three drops of acetic acid into the reaction mixture, as portrayed in Fig. 5. In the presence of acetic acid, the oxidation of phenol gave 93.40% conversion in 30 min. Meanwhile, only 33.13% conversion was observed when acetic acid was absent. This observation suggested that the acetic acid was oxidized by H₂O₂ to form peracetic acid in situ, which served as a better oxidant [26]. To investigate this possibility, the formation of peracetic acid was examined in the absence and presence of the catalyst by volumetric titrations with sodium thiosulfate solution. The results (Supplementary) clearly show that the presence of the catalyst has no effect on the production of peracetic acid. This study was found to give catechol (CAT) and hydroquinone (HQ) as the only products. The effect of reaction temperature, catalyst mass and molar ratio of reactant was studied, to optimize the reaction conditions.

The oxidation of phenol was studied over the temperature range of 30–80 °C, as presented in Fig. 6. The phenol conversion increased from 34.92% to 86.48% when the temperature was increased from 30 to 70 °C. No significant change was observed when the reaction temperature was increased to 80 °C. This was due to the rapid decomposition of H₂O₂ at the higher temperature [27,28]. The results suggested that the optimum reaction temperature for oxidation of phenol was 70 °C.

The influence of the mass of catalyst was investigated by varying the catalyst mass from 30 to 100 mg. Fig. 7 shows the phenol conversion with respect to the mass of catalyst at 70 °C. It is seen that the conversion increased from 75.30% to 87.10% as the catalyst mass was increased from 30 to 50 mg. No significant change was observed with further increase in catalyst mass to 100 mg (82.42%). Many researchers had reported a similar phenomenon and the rationale for this was explained in terms of mass transfer limitations [8,29]. It was thus concluded that 50 mg of catalyst was optimal for this catalytic system.

The effect of the molar ratio of phenol to H₂O₂ on the rate of oxidation was examined and the results are presented in Fig. 8. The conversion was found to increase from 64.61% to 93.40% for 1:1 and 1:3 M ratios respectively. However, the conversion decreased...
slightly to 90.66% at a molar ratio of 1:4. Nevertheless, increasing the molar ratio from 1:1 to 1:4 did not show significant variation in the CAT selectivity (ca. 77.47%). Thus, a molar ratio of 1:3 was found to be the optimum ratio to achieve highest phenol conversion. The use of excess H₂O₂ was due to the self-decomposition of the peroxide and the exothermic nature of the reaction [28,30].

Optimization of the reaction parameters gave 93.40% phenol conversion in 30 min with selective formation of 77.47% CAT and 22.53% HQ. Maurya et al. had prepared several zeolite-encapsulated transition metal complexes and their catalytic activities were tested similarly, in the oxidation of phenol [7]. Although the catalysts gave fairly high selectivity towards CAT (68.30%), the conversion was only about 50.00% in 6 h. The preparation of these catalysts also required several tedious procedures. Mesoporous titanosilicates [3] were also used in the oxidation of phenol. However, the phenol conversion was relatively low (e.g. 9.10% conversion for Ti-HMS in 4 h).

The reusability of Fe/KL nanocrystals was tested over four consecutive runs and the results are illustrated in Fig. 9. The used catalyst was recovered and rinsed with copious amount of distilled water and acetone after each catalytic run. The washed catalyst was dried at 110°C for 24 h before reuse. The catalytic activity was found to decrease by 6.83% after four consecutive runs. This result suggested that the catalyst was sufficiently stable and reusable with minimal loss of reactivity.

The heterogeneity of the catalyst was determined by leaching test (hot filtration method). The leaching test was carried out according to the method described in our previous publication [6,18] with a slight modification. The catalyst was filtered after 3 min and the reaction was continued up to 30 min (without the catalyst) by using the filtrate at the same conditions. It was found that the phenol conversion was increased by ca. 18.00% after catalyst removal. The increase in the conversion might be due to the leached iron. To further confirm the leached iron, the filtrate was subjected for AAS analysis. The results showed that 11.27% of iron was leached out from the Fe/KL catalyst. Another reaction was carried out using iron(III) nitrate as a homogeneous catalyst under optimized condition. It was noted that the use of this metal salt gave 87.38% of phenol conversion. Since the leached iron only results in an increase of 18% conversion as compared to the ca. 87.4% conversion due to the homogeneous iron(III) nitrate, it can safely be concluded that the leached iron(III) did not have a significant effect in the reaction.
4. Conclusion

This study describes an improved catalytic system for the fast oxidation of phenol over Fe/KL catalyst. The oxidation of phenol can be significantly enhanced by the addition of acetic acid. It was found that the acetic acid was oxidized by H₂O₂ to form per-acetic acid, which served as a better oxidant. The Fe/KL catalyst showed much better product selectivity compared to other catalyst reported in the literature. Besides, the prepared catalyst was found to be stable and reusable although it suffered from minor leaching.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.10.017.

References