



Optimization and mechanistic study of the liquid-phase oxidation of naphthalene over biomass-derived iron catalyst



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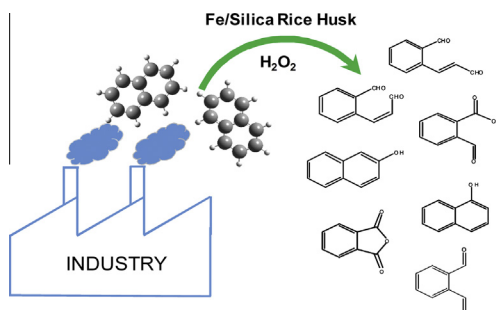
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HIGHLIGHTS

- Ferric ions are the active centre responsible for the oxidation activity.
- RH-10Fe was the best catalyst in oxidizing naphthalene into benign products.
- Textural properties and surface morphology influenced the catalytic activity.
- Free-radical mechanism was occurring for this catalyst system.
- Occurrence of loosely bounded ferric ions was minimal under the studied condition.

GRAPHICAL ABSTRACT

Iron supported silica catalysts were efficient in breaking naphthalene ring into aldehyde and anhydrides under ambient condition.



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ABSTRACT

Iron supported silica catalysts were synthesized from rice husk using sol–gel route at room temperature. FT-Raman spectroscopy and XRD analysis confirmed that the iron catalysts were free from iron oxide while pyridine adsorption–desorption analysis proved the presence of both Brønsted and Lewis acid sites. NH₃-TPD analysis showed the total acidity was maximum for 10 wt.% iron catalyst and declined with further incorporation of iron content. The morphology and topography of the iron catalysts changed at different iron concentration. The performance of the iron catalysts was evaluated in the liquid-phase oxidation of naphthalene with H₂O₂ as an oxygen source. The highest activity of 48.2% was registered over catalyst loaded with 10 wt.% Fe³⁺ after 4 h reaction time. Free-radical mechanism was postulated based on the GC–MS analysis. Leaching of ferric ion was minimal under the studied reaction condition. The catalyst retained its performance and stability even after four consecutive cycles.

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1. Introduction

Building and sustaining a safer environment has been an immense challenge to the environmentalist. For the past decade,

human has exploited the world for industrialization, economic development and globalization. These activities emit extensive amount of atmospheric contaminants such as polyaromatic hydrocarbon (PAH). PAH are produced from various industries, i.e. petrochemical, coal, wood and power generation plant. These noxious pollutants have been classified by WHO as mutagenic, teratogenic and carcinogenic [1].

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Naphthalene (NAP), the simplest form of PAH family, is viewed as a target compound and commonly studied in research laboratories. NAP pollution of 46,000 mg kg⁻¹ is reported to occur in soils and sediments [2]. High level of exposure to NAP can lead to cataract and laryngeal tumors among the workers [2]. Thus, NAP has been listed as one of the leading pollutants among other 16 PAHs by the United States Environmental Protection Agency (US-EPA) [3].

NAP is a very stable compound due to its aromatic ring. Hence, it has always been a difficult and challenging task to remove it from the environment. For decades, NAP removal is known to happen via biodegradation, catalytic oxidation, adsorption, photolysis and ozonation [4]. However, each of these remediation method exhibits several restrictions such as being very slow, require prolonged treatment [5] and needs high temperature and pressure [6]. These limitations hinder their application in the destruction of NAP.

Thus, there is a pressing need to create a safe and cheap method to remove NAP from the environment. Undoubtedly, this could be achieved by a simple liquid-phase oxidation of NAP with H₂O₂. NAP oxidation in the presence of H₂O₂ allows the conversion of this toxic compound into major valuable products such as 1-naphthol (1-NAP), 2-naphthol (2-NAP), 1,4-naphthaquinone (1,4-NQ) and phthalic anhydride (PTA). Naphthols are used as an intermediate in the synthesis of dyes, medicines, plastics and rubber [7]. Vitamin K₃ is produced from the oxidation reaction between 1-NAP and methanol. PTA is used in the production of phthaleins, phthalates, benzoic acid, indigo and glyptal [8]. Industrially, PTA is produced with H₂SO₄ and Hg as catalyst which gave a yield of only 25%.

So far, only a few reports exist on the liquid-phase oxidation of NAP by H₂O₂ and, hitherto these works yielded only low conversions. For example, Khavasi et al. [9] reported no measurable conversion over iron(III) porphyrins as catalyst and imidazole as co-catalyst. In another research, Shylesh and Singh [10] reported a lower conversion of only 13.5% after 24 h reaction time over vanadium mesoporous catalyst synthesized by hydrothermal method. Besides, leaching of vanadium species was noticed during the reaction which confirms the non-heterogeneity of the catalyst system. Monfared and Amouei [11] reported that the NAP oxidation in the presence of Fe³⁺-Al₂O₃ for 6 h was unsuccessful as no activity was observed. In another study, NAP conversions of only ~0.05% and 5.1% were registered over Fe-SBA-15 and Fe-MCM-41 at 353 K for 5 h. No leaching or regeneration studies were reported in this work [12]. Therefore, most catalysts studied in literature gave low activity in the oxidation of NAP with fewer studies conducted on catalyst regeneration. Thus, it is important to design a cheaper, active and stable catalyst towards achieving higher catalytic activity.

Biomass such as wood, saw dust, animal waste, vegetable oil, farming crop and their by-products offer a great alternative against non-renewable energy sources. Numerous explorations on the conversion of biomass in diverse fields had been reported. For example, in fuel production [13], energy storage [14], degradation of toxic pollutants [15] and air pollution control [16]. Among the well-known biomass, Rice husk (RH) appears as an important class of agricultural waste due to its high silica source (20 wt.%). This biogenic silica has been used as an inert support for various applications [17,18]. However, most of the work reported, deal with rice husk ash (RHA). Generally, RHA is obtained from the combustion of RH at high temperature; i.e. 923 K for 1 h [19]. Since pyrolysis involves uncontrolled burning, the preparation of silica through a benign and low energy procedure is required and this could be achieved by a simple acid–base treatment leading to the formation of sodium silicate. Recovery of silica from RH without calcination conforms to green technology. Moreover, the availability of –OH group in RH silica enables the binding with metal cations.

Thus, in this research, iron was incorporated into RH silica and the resulting catalyst was investigated in the oxidation of NAP. We believe this is the first communication on metal supported RH silica catalyst for the oxidation of NAP. In addition, the earlier studies reported only the identification of products from the oxidation of NAP, but did not provide information on reaction pathway. Thus, in this communication, a reaction mechanism was postulated by analyzing the products formed during the liquid-phase oxidation of NAP.

2. Experimental

2.1. Materials

Ferric nitrate nonahydrate, Fe(NO₃)₃·9H₂O (Bendosen, 98.5%) was used as the metal precursor. Other analytical reagents used were acetonitrile (QReC, >99.9%), acetone (QReC, 99.5%), acetophenone (guaranteed reagent), acetic acid (System, 99.5%), dimethylformamide (QReC, 99.5%), hydrogen peroxide (H₂O₂, J.T. Baker, 30.0%), naphthalene (Bendosen, 99.0%) and tetrahydrofuran (Lab-Scan Asia Co. Ltd, 99.7%). The chemicals were used as received without further purification.

2.2. Preparation of the catalysts

RH was chosen as the silica source. The extraction of silica in the form of sodium silicate was done according to the previous method [20]. The detailed preparation routes of the control silica and iron modified silica catalysts with various iron concentrations (5–20 wt.%) were published earlier [21]. In brief, the prepared sodium silicate solution was titrated to pH 3, under a constant stirring (500 rpm), with 130 mL of 3.0 M HNO₃ or 3.0 M HNO₃ containing the requisite amount of 5, 10, 15 and 20 wt.% Fe³⁺ to get RH-silica or iron modified catalysts. After aging at room temperature for 48 h, the gel was centrifuged (4000 rpm), washed with distilled water followed by acetone and suction filtered. The resulting soft gel was dried at 383 K for 18 h and ground into fine powder. The iron modified xerogels were designated as RH-xFe, where x = 5, 10, 15 and 20 wt.% Fe³⁺.

2.3. Catalyst characterizations

The prepared catalysts were characterized by several physico-chemical techniques such as N₂-sorption porosimetry, FT-IR spectroscopy, X-ray diffractometry, ²⁹Si MAS NMR, AAS and UV-Vis diffuse spectroscopy. The details on these spectroscopic methods were reported in our previous work [21]. In addition, the FT-Raman spectrum of selected catalyst was recorded in the 200–1100 cm⁻¹ region through excitation with a He–Ne laser of wavelength 633 nm (model INVIA REFLEX). The acidity of the iron catalysts was evaluated by FT-IR using pyridine as the probe molecule. Ammonia temperature programmed desorption profile and acidity measurement of the catalysts was recorded on a Thermo Finnigan TPDRO 1100 apparatus equipped with a thermal conductivity detector. A Phillips CM12 TEM at 80 kV accelerating voltage was employed to examine the morphology of the catalysts. The topography and roughness of the samples were determined by AFM (ULTRAObjective) employing a non-contact acquisition mode.

2.4. Catalytic evaluations in the oxidation of NAP

The oxidation of NAP was conducted in a 50 mL two-necked round bottom flask fitted with a water-cooled reflux condenser. In a typical reaction, a mixture of NAP (1.28 g, 10 mmol) dissolved in 15 mL acetonitrile was added into the flask containing 70 mg

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