Article

Facile synthesis of Fe-containing graphitic carbon nitride materials and their catalytic application in direct hydroxylation of benzene to phenol

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ABSTRACT

Fe-containing graphitic carbon nitride (Fe-g-C_3N_4) materials were synthesized via one-step pyrolysis of $FeCl_3$ and dicyandiamide. The physicochemical properties of the synthesized Fe-g-C_3N_4 samples were characterized by N_2 adsorption-desorption, X-ray diffraction, thermal gravimetric, Fourier transform infrared, UV-vis diffuse reflectance, X-ray photoelectron spectroscopy, and transmission electron microscopy. The Fe cations were anchored by nitrogen-rich g-C_3N_4, whereas the graphitic structures of g-C_3N_4 were retained after the introduction of Fe. As heterogeneous catalysts, Fe-g-C_3N_4 exhibited good catalytic activity in the direct hydroxylation of benzene to phenol with H_2O_2, affording a maximum yield of phenol of up to 17.5%. Compared with other Fe- and V-containing g-C_3N_4 materials, Fe-g-C_3N_4 features a more convenient preparation procedure and higher catalytic productivity of phenol.

1. Introduction

As an important commodity chemical, phenol is extensively used for the manufacture of phenol resins, caprolactam, adipic acid, dyestuffs, pesticides [1,2], etc. The three-step cumene process is the main approach for the synthesis of phenol and contributes with more than 90% of the global output of phenol. However, the conventional industrial synthetic route suffers from several drawbacks including high-energy consumption, low one-pass yield of phenol (~5%, based on the initial benzene quantity), and dependence on the market of acetone [3–5]. In the past decade, several new synthetic strategies have been proposed for the production of phenol. Among them, the direct hydroxylation of benzene, featuring an environmentally benign procedure, has been commonly proposed as the catalytic process with the most potential for the manufacture of phenol [3,6].

A series of oxidant agents including air, oxygen, N_2O, and H_2O_2 have been employed for the direct hydroxylation of benzene [7,8]. Although either air or oxygen is very cheap and widely available, the catalytic activity in such a process is very low and far from industrial implementation [9]. Furthermore, the main restriction for the industrial implementation of N_2O is its complicated operational technology [3]. In contrast, the use

of H_2O_2 as an oxidant for the transformation from benzene to phenol demands milder reaction conditions together with a simpler process than its counterparts. Simultaneously, water is, ideally, the sole co-product [10]. Therefore, the direct hydroxylation of benzene under H_2O_2 has received tremendous attention in the field of phenol synthesis. Nevertheless, phenol can be over-oxidized to produce hydroquinone and benzoquinone. In this sense, it is still a hot topic to develop a robust catalyst that can provide excellent activity along with high selectivity to the target molecule.

A variety of heterogeneous catalysts, including titanium silicalite sieves (TS-1) [11,12], heteropolyacids (HPAs) [2,5,6], metal oxides supported on mesoporous materials [1,2,13], and transition metals incorporated into molecular sieves [7], have been extensively employed for the direct hydroxylation of benzene. In the past decade, graphitic carbon nitride (g-C_3N_4) has attracted tremendous attention as a new type of catalyst in both thermal catalysis [14,15] and photocatalysis [16,17]. In particular, because of its unique capacity to activate the benzene molecule, g-C_3N_4 (especially mesoporous g-C_3N_4) has demonstrated potential catalysis in several benzene-involved reactions, including alkylation [18], acylation [19,20], and oxidation of benzene [21–23]. Recently, our group has synthesized mesoporous g-C_3N_4 materials, which were then loaded with vanadyl(IV) acetylacetonate [VO(acac)$_2$] [24] and vanadia [8]. The results showed that such g-C_3N_4-based composites were able to promote the direct hydroxylation of benzene under H_2O_2, with a maximum yield of phenol of about 18%.

Although mesoporous g-C_3N_4 catalysts possessed high surface areas and exhibited promising catalysis in benzene-activating reactions, all the reported mesoporous g-C_3N_4 supports have been prepared by a nanocasting method, with silica materials as hard templates [19,25,26]. This preparation demanded a silica-etching procedure with a volatile and toxic HF or NH_4HF_2 solution, which was time-consuming and not environmentally friendly [15,27,28]. To circumvent these issues we, very recently, developed vanadia catalysts supported on exfoliated g-C_3N_4 nanosheets, which were more conveniently synthesized than mesoporous g-C_3N_4 [29]. However, the final catalytic activity of such catalysts in the hydroxylation of benzene is still not satisfactory. On the other hand, the transition metal halides represented by FeCl$_3$, are the typical Lewis acids which are extensively used in benzene-activating reactions [30,31]. In this work, a facile and rapid method to prepare Fe-containing g-C_3N_4 materials was developed via one-step pyrolysis of FeCl$_3$ and dicyandiamide. As heterogeneous catalysts, the Fe-g-C_3N_4 materials catalyzed the direct hydroxylation of benzene under H_2O_2 with good catalytic activities, affording a maximum yield of phenol of as much as 17.5% at a reaction time of 2 h.

2. Experimental

2.1. Catalyst preparation

FeCl$_3$ (0.15 g) and dicyandiamide (DCDA, 4.00 g) were added into 100 mL of ethanol, and then refluxed at 80 °C for 3 h.

The solution was dried at 60 °C until removal of ethanol and formation of a dark yellow solid. After being ground, the yellow powder was calcined under N_2 atmosphere at 550 °C for 4 h, and the resultant solid was designated as mFe/g-C_3N_4 catalyst, where m indicated the weight percentage of Fe of g-C_3N_4.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a D8 Advance (Bruker) X-ray diffractometer equipped with a graphite monochromator (40 kV, 40 mA) using Ni-filtered Cu-K_α radiation (λ = 1.5418 Å).

Nitrogen adsorption and desorption measurements were carried out at –196 °C using an ASAP 2020 (Micromeritics) porosimeter. Before the measurement, the samples were degassed (1.33 × 10^{-2} Pa) at 150 °C for 4 h. The specific surface areas were calculated using the Brunauer–Emmet–Teller (BET) method, and the pore size distributions were determined by the Barret–Joyner–Halenda (BJH) model, from the desorption branches.

Fourier transform infrared (FT-IR) spectra in transmission mode were analyzed on a Tensor 27 (Bruker) spectrometer with the aid of KBr pellets. Each spectrum was measured with a resolution of 4 cm^{-1} and recorded at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI 5000C (Perkin–Elmer) spectrometer recording in the constant energy mode (Mg K_α radiation as the excitation source).

UV–vis diffuse reflectance spectra (DRS) were recorded in a UV-3600 (Shimizu) spectrophotometer. The UV-vis spectra used BaSO$_4$ as the standard reference.

Thermal gravimetric (TG) tests were performed on a TGA 7 (Perkin–Elmer) thermogravimetric analyzer. The specimens were heated, under a flow of air, from 50 to 800 °C with a ramping rate of 20 °C min^{-1}.

Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F20 S-TWIN microscope operated at 200 kV. Energy dispersive X-ray spectra (EDS) and elemental mapping were performed on the equipped Oxford X-Max 80T detector.

2.3. Catalytic evaluation

The catalytic reactions were evaluated in a round-bottom flask. Benzene (1 mL, 11.2 mmol) and solvent (5 mL of acetonitrile and 1 mL of acetic acid) were mixed well, followed by the addition of the catalyst. After the temperature of the mixture reached 60 °C, 3 mL of H_2O_2 (a.q., 30 wt%) were continuously fed into the flask through a peristaltic pump (the addition of H_2O_2 lasted for ∼30 min). During the reaction, a small amount of reaction mixture (< 0.15 mL) was periodically collected and centrifuged. The liquid phase was analyzed by gas chromatography using an SE-54 capillary column. The conversion (Conv.) of benzene and selectivity (Sel.) for phenol were calculated by means of an area-normalization method, and the detailed calculation equations were as follows: