

# Photocatalytic Synthesis of Phenol by Direct Hydroxylation of Benzene by a Modified Nanoporous Silica (LUS-1) under Sunlight

Ghasem SHIRAVAND<sup>1</sup>, Alireza BADIEI<sup>1,\*</sup>, Ghodsi Mohammadi ZIARANI<sup>2</sup>, Morteza JAFARABADI<sup>1</sup>, Majid HAMZEHLOO<sup>1</sup>

<sup>1</sup>School of Chemistry, College of Science, University of Tehran, Tehran, Iran

<sup>2</sup>Department of Chemistry, Faculty of Science, Alzahra University, Tehran, Iran

**Abstract:** Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1 was prepared by the thermal decomposition of dicyandiamide inside the pores of LUS-1 under an inert atmosphere. It was used as a photocatalyst for the hydroxylation of benzene to phenol in sunlight. The catalysts were characterized by Fourier transform infrared spectroscopy, N<sub>2</sub> adsorption-desorption, X-ray diffraction, and scanning electron microscopy. In Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1, a single layer of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was formed on the surface of LUS-1. The photocatalytic activity of the iron containing g-C<sub>3</sub>N<sub>4</sub> based catalysts was investigated, and the catalytic activity was remarkably enhanced when the reaction condition was changed from dark to sunlight. The best result was obtained with 20%Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1 in sunlight.

**Key words:** mesoporous silica; photocatalyst; phenol; benzene hydroxylation; sunlight; nanoporous silica; carbon nitride

There is increasing interest in the photocatalytic technology in catalytic processes for hydrogen production from splitting water, self-cleaning coatings, high efficiency solar cells, and dye degradation [1–8]. These processes need considerable energy, and providing the energy is one of the most important issues. Many attempts have been made to find photocatalytic processes that utilize a renewable low cost irradiation source, such as sunlight, instead of expensive artificial irradiation sources [8–12]. Since visible light comprises a large portion of the solar energy reaching the surface of the earth, the utilization of visible light will give a more efficient solar energy usage. To achieve this, a material with a suitable band gap for absorbing visible light and that acts as an oxidative material is needed. Several materials, e.g., Bi<sub>38</sub>ZnO<sub>58</sub> [13], CuO [14], Au/TiO<sub>2</sub> [15], NiO/InTaO<sub>4</sub> [16], BiVO<sub>4</sub> [17], and g-C<sub>3</sub>N<sub>4</sub> [3,18], have a suitable band gap for use in photocatalytic processes under visible light irradiation and in sunlight. The band gap of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was estimated to be 2.7 eV from its UV-Vis diffuse reflectance spectrum [19], which is equal to 460 nm wavelength. As a result, g-C<sub>3</sub>N<sub>4</sub> can be used as

a photocatalyst in the visible light region. There are several models for the structure of these compounds. The tri-s-triazine based model is the predicted most stable structure of g-C<sub>3</sub>N<sub>4</sub> [20,21].

Several methods have been used to synthesize g-C<sub>3</sub>N<sub>4</sub>, e.g., by solid state reaction [21,22], solvothermal reaction [23,24], thermal decomposition [25], ionothermal reaction [26], and other methods [27–29]. Several precursors such as cyanamide, dicyandiamide, melamine, and cyanuric chloride have been used to get the g-C<sub>3</sub>N<sub>4</sub> solid [28–31]. The easy sublimation of melamine is a serious issue in thermolysis. Dicyandiamide is recommended as a precursor to suppress this sublimation [20].

g-C<sub>3</sub>N<sub>4</sub> has been used as a photocatalyst in several reactions [18,32,33]. Chen et al. investigated the catalytic performance of graphitic carbon nitride for the direct hydroxylation of benzene to phenol [18]. They reported that benzene is adsorbed and activated on g-C<sub>3</sub>N<sub>4</sub>, and therefore, this catalyst is a promising catalyst for the hydroxylation of benzene to phenol. In this work, graphitic carbon nitride was prepared and loaded on the surface of mesoporous Type LUS-1 silica. Due to its

Received 21 January 2012. Accepted 30 May 2012.

\*Corresponding author. Tel: +98-2161112614; Fax: +98-2161113301; E-mail: abadiei@khayam.ut.ac.ir

This work was supported by University of Tehran.

Copyright © 2012, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier BV. All rights reserved.

DOI: 10.1016/S1872-2067(11)60422-1

high surface area (800 cm<sup>2</sup>/g), long range ordered pores (average pore diameter 3 nm) and hydrothermal stability, LUS-1 is a good support for catalytic reactions such as the hydroxylation of benzene [34]. The hydroxylation of benzene to phenol over Fe-loaded mesoporous silica, such as SBA-15 or MCM-41, with different iron contents had been investigated previously [35,36]. In this study, the properties and applications of *x*Fe-g-C<sub>3</sub>N<sub>4</sub> and *x*Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1 in the direct hydroxylation of benzene were studied. These reactions were carried in just under sunlight to study if they can be used to reduce cost.

## 1 Experimental

### 1.1 Materials

Silica gel (column chromatography), sodium hydroxide, dicyandiamide, iron(III) chloride hexahydrate, acetonitrile, benzene, toluene, hydrogen peroxide (30%), and cetyltrimethylammonium bromide (Merck) and *p*-toluenesulfonic acid monohydrate (Aldrich) of analytical grade were used without further purification.

### 1.2 Characterization

The catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and N<sub>2</sub> adsorption-desorption. SEM was carried out on a Hitachi (model S-4160) apparatus after gold plating of the samples. XRD patterns were recorded with a Bruker D8-Advance diffractometer at  $2\theta = 2^\circ\text{--}70^\circ$  with monochromatized  $K_\alpha$  radiation ( $\lambda = 0.1541874$  nm) from a Cu source operated at 40 kV/30 mA. FT-IR spectra were obtained with an EQUINOX 55BRUKER. N<sub>2</sub> adsorption-desorption isotherms were obtained using a BELSORP-mini II at  $-196^\circ\text{C}$ . All samples were degassed at  $100^\circ\text{C}$  for 3 h under an inert gas flow before measurement. The BET equation was used to calculate specific surface area and the BJH equation was used to calculate the pore size distribution and total pore volume.

### 1.3 Synthesis of catalysts

#### 1.3.1 Synthesis of g-C<sub>3</sub>N<sub>4</sub> and Fe-g-C<sub>3</sub>N<sub>4</sub>

g-C<sub>3</sub>N<sub>4</sub> was prepared using the method reported by Wang et al. [18]. In a typical reaction, dicyandiamide (1 g) was mixed with distilled water (10 ml) and heated to remove the solvent. The resulting mixture was heated at  $600^\circ\text{C}$  for 4 h under flowing argon, followed by cooling to room temperature under the inert atmosphere. For the synthesis of Fe-g-C<sub>3</sub>N<sub>4</sub>, different amounts of FeCl<sub>3</sub>·6H<sub>2</sub>O (0.1, 0.2, 0.3 g) were added to the mixture of dicyandiamide (1 g) and distilled water (10 ml), and then this solution was heated until a dry product was obtained.

Different amounts of FeCl<sub>3</sub> were loaded on g-C<sub>3</sub>N<sub>4</sub> to obtain *x*Fe-g-C<sub>3</sub>N<sub>4</sub> ( $x = 10\%, 20\%, 30\%$ ).

#### 1.3.2 Synthesis of *x*Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1

In a typical synthesis, LUS-1 (1 g, prepared using the method reported by Badiei et al. [37]) was dispersed in distilled water (30 ml) with vigorous stirring (named mixture A). An amount of FeCl<sub>3</sub>·6H<sub>2</sub>O and dicyandiamide were dissolved in distilled water (30 ml) (iron(III) chloride/dicyandiamide = 0.1), which was named solution B. Solution B was gradually added to mixture A to prepare *x*Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1 ( $x$  (wt%) = [dicyandiamide/LUS-1] × 100%). The mixture of solution A and solution B was heated at  $100^\circ\text{C}$  to remove water until a reddish mixture was obtained. Finally, the product was obtained by heating the reddish material at  $600^\circ\text{C}$  under an inert atmosphere for 4 h.

#### 1.3.3 Catalytic test

Catalytic experiments were done to investigate the activity of the catalysts for the conversion of benzene to phenol. Solvent (4 ml acetonitrile) was poured into a 50 ml round bottom flask equipped with a condenser and the temperature was raised to  $60^\circ\text{C}$ . Benzene (1 ml, 11.3 mmol) and well milled catalyst (50 mg) were added to the flask. After 0.5 h stirring, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 30 wt%, 0.5 ml, 16.5 mmol) was added to the mixture and the reaction mixture was stirred for 4 h. Then, 5 ml ethanol was poured into the flask to stop the reaction by capturing remaining hydroxyl radicals (OH·) and convert the biphasic mixture into a single phase [38]. All reactions were carried out in dark and in sunlight (the sunlight reactions were done on sunny days with an intensity of about 80000 LUX) to evaluate the effect of light on the catalytic activity of g-C<sub>3</sub>N<sub>4</sub>. In addition, the photocatalytic activities of these catalysts were investigated using an artificial visible light source (125 W mercury lamp with an intensity about 67000 LUX with colored filter). The quantitative analysis of the product was done with a Perkin-Elmer 8500 GC with an FID detector and toluene as the internal standard.

## 2 Result and discussion

### 2.1 XRD results

Wide angle XRD patterns were used to characterize the structures of Fe-g-C<sub>3</sub>N<sub>4</sub>, LUS-1, and Fe-g-C<sub>3</sub>N<sub>4</sub>-LUS-1. The results are shown in Fig. 1. The predicted structure of g-C<sub>3</sub>N<sub>4</sub> based on tri-*s*-triazine building blocks (Franklin's model) would exhibit two major diffraction peaks in the XRD pattern corresponding to the (100) and (002) reflection planes [20,26,33]. Here, these peaks were observed in the XRD patterns of the synthesized materials (Fig. 1). This result proved

Download English Version:

<https://daneshyari.com/en/article/59254>

Download Persian Version:

<https://daneshyari.com/article/59254>

[Daneshyari.com](https://daneshyari.com)