CHEMICAL ENGINEERING TRANSACTIONS

VOL. 99, 2023

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Flavio Manenti
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ISBN 978-88-95608-98-3; **ISSN** 2283-9216

DOI: 10.3303/CET2399079

Selective Oxidation of Benzene to Phenol using Fe-N-codoped TiO_2 Embedded in Monolithic Syndiotactic Polystyrene Aerogel

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A polymeric composite consisting of Fe-N-codoped TiO_2 (Fe-N-TiO_2) dispersed into a monolithic syndiotactic polystyrene (sPS) aerogel (Fe-N-TiO2/sPS, 10/90 w/w) was used for the photocatalytic hydroxylation of benzene to phenol in presence of H_2O_2 to enhance the phenol selectivity and yield compared to Fe-N-TiO_2 in powder form. Under UV light, Fe-N-TiO_2/sPS composite aerogel showed selectivity to phenol of 43%, one order of magnitude more than the selectivity showed by Fe-N-TiO_2 in powder form (4%). Under visible light irradiation Fe-N-TiO_2 in powder form did not produce phenol, whereas selectivity to phenol of Fe-N-TiO_2/sPS was 16%. The polymeric composite was recycled and reused up to five times without a significant decrease in photocatalytic oxidation activity in terms of benzene conversion and phenol yield, indicating the stability of the catalytic composite. Therefore, it was proved that the obtained photoreactive polymer composite could allow the development of innovative sustainable processes able to realize the selective oxidation reactions of aromatic hydrocarbons under mild conditions.

1. Introduction

Phenol is an important chemical intermediate normally used as a precursor for the production of resin plastics, drugs and pesticides (Furukawa and Takeichi, 2012). Nowadays, the industrial phenol production from benzene is based on the three-stage cumene process with high energy consumption due to the extreme operative conditions, the generation of highly hazardous explosive (cumene hydroperoxide) and the production of an equal amount of acetone as a byproduct (Zakoshansky, 2007, Yadav and Asthana, 2003).

To overcome the disadvantages related to the industrial synthesis of phenol, it would be essential to find efficient and environmentally friendly alternatives. Heterogeneous photocatalysis could represent a promising technology for phenol production based on semiconducting material activated by a suitable light source at room temperature and pressure. In this perspective, many efforts of researchers were devoted to the hydroxylation of benzene to phenol in a single reaction step using different photocatalytic formulations (Hosseini et al., 2018, Verma et al., 2017, Xu et al., 2017, Xiong and Tang, 2021) However, the main issue of the synthesis of phenol from benzene is the higher reactivity of phenol with respect to benzene. Indeed, the produced phenol is further converted into hydroquinone, p-benzoquinone, or even oxidized to carbon dioxide. For the photocatalytic oxidation of benzene to phenol (where the reactant is hydrophobic and the product hydrophilic) the affinity of benzene towards non-polar supports has been exploited to favor both the adsorption of benzene and the desorption of phenol from the photocatalytic surface. In this regard, Zhang et al. entrapped undoped TiO_2 in a silica foam with modified hydrophobicity to facilitate both the adsorption of benzene and the desorption of phenol preventing further oxidation reactions and enhancing the selectivity to desired product (about 35 %) (Zhang et al., 2011). Based on these considerations, among the substrates with hydrophobic properties, syndiotactic polystyrene (sPS) monolithic aerogels were used for their ability to reversibly adsorb

Paper Received: 12 December 2022; Revised: 3 March 2023; Accepted: 7 May 2023
Please cite this article as: Mancuso A., Sacco O., Antico P., Venditto V., Vaiano V., 2023, Selective Oxidation of Benzene to Phenol using Fe-N-codoped TiO_2 Embedded in Monolithic Syndiotactic Polystyrene Aerogel, Chemical Engineering Transactions, 99, 469-474 DOI:10.3303/CET2399079

non-polar organic molecules and low or no affinity towards polar compounds. Fe-N codoped TiO_2 photocatalyst, activated both by UV and visible light, was used as catalyst for benzene oxidation reaction. Therefore, in this work, visible light active Fe-N TiO_2 particles, commonly used for water pollutant degradation (Mancuso et al., 2020, Mancuso et al., 2021), were dispersed in sPS monolithic aerogel (Vaiano et al., 2014) and the photoreactive composite (Fe-N-TiO_2/sPS) was tested in the hydroxylation of benzene to phenol under UV and visible light to increase phenol production while maintaining high benzene conversion.

2. Materials and Methods

2.1 Chemicals and reagents

Syndiotactic polystyrene (sPS) used for aerogels preparation was manufactured by Idemitsu Kosan Co., Ltd. under the trademark XAREC© 90ZC. Benzene (purity>99.7%) and phenol (purity>99) were purchased from Sigma Aldrich. Distilled water and acetonitrile (purity>99.9%) were acquired from Carlo Erba. Hydrogen peroxide solution, used as an oxidant, was purchased from Sigma Aldrich (30 wt%).

2.2 Fe-N-TiO_2 preparation

Fe-N-codoped TiO_2 (Fe-N-TiO_2) photocatalyst was prepared by sol-gel method using urea and iron(II) acetylacetonate as nitrogen and iron precursors, respectively, and titanium isopropoxide as TiO_2 source, according to the procedure reported by Mancuso et al. (Mancuso et al., 2020). The N/Ti and Fe/Ti molar ratio in the final photocatalyst was equal to 0.97 and 0.0017, respectively (Mancuso et al., 2020).

2.3 Fe-N-TiO_2/sPS composite aerogel preparation and characterization

sPS polymer and Fe-N-TiO_2 photocatalyst were dispersed in chloroform inside a hermetically sealed test tube at 100°C until the complete polymer dissolution. The obtained suspension was then cooled at room temperature under sonication until to produce a gel. The monolithic composite aerogel (D.I.=5.6 mm and a h= 3 cm) was obtained by treating the gel with supercritical carbon dioxide (by using an ISCO SFX 220 extractor), for 4 h at T=40 °C and P= 20 MPa, to extract the solvent (Vaiano et al., 2014). The amount of Fe-N-TiO_2 incorporated into the aerogel structure, previously optimized, was 10 wt% (Sacco et al., 2018). X-Ray diffraction (XRD) patterns were acquired with a Brucker D8 diffractometer, employing Cu Ka radiation. The values of specific surface area (S_{BET}) were determined by dynamic N_2 adsorption at low temperature (-196 C) using a Costech Sorptometer 1042 instrument.

2.4 Photocatalytic activity tests

35 mL of an aqueous solution containing benzene (initial concentration: 25.6 mmol/L) and acetonitrile (2.3 mL) as a co-solvent with 0.1 g/L of Fe-N-TiO_2 photocatalyst in powder form or 3 g/L of Fe-N-TiO_2/sPS aerogel was used for photocatalytic oxidation reactions. The system was first maintained in dark (without any light irradiation) at room temperature for 60 min or for 1280 min to obtain sorption equilibrium of benzene on photocatalyst powder or Fe-N-TiO_2/sPS aerogel, respectively, under continuous stirring. Before irradiating the reactor, 2.8 mL of H_2O_2 (30 wt% in H_2O) was added to the reaction mixture. The pyrex reactor was subsequently irradiated for 600 min by a UV-A (emission: 365 nm; irradiance: 13 W/m^2) and visible LEDs strip (emission range: 400–800 nm; irradiance: 16 W/m^2) placed around and in contact with the external surface and was cooled down by a fan during photoirradiation time. Solution aliquots were withdrawn from the reactor at different times by a 1mL syringe, filtered through a 0.22 μ CA filter (SIMPLEPURE) to remove solid particles for the tests with Fe-N-TiO_2 photocatalyst in powder form and immediately analyzed quantitatively by an Agilent gas chromatograph (model 7820 A) equipped with a flame ionization detector (FID) to evaluate the benzene and phenol concentration (Mancuso et al., 2022). Hydroquinone, resorcinol, p-benzoquinone and catechol were determined quantitatively by HPLC using a Dionex UltiMate 3000 Thermo Scientific system equipped with DAD detector, column thermostat and automatic sample injector with 100μL loop. Separations were carried out on a Phenomenex Luna C-18 column (150 x 4.6 mm i.d.; 5μm) eluted with a mixture of water (solvent A) and acetonitrile (solvent B) (Mancuso et al., 2022). The following mathematical formulas for the determination of benzene conversion, phenol yield and selectivity to phenol were used:

$$benzene\ conversion\ (Bz_{conv}) = \left(1 - \frac{C}{C_0}\right) x\ 100 \tag{1}$$

$$Phenol\ yield\ \ (Y_P) = \left(\frac{S}{Q_0}\right) x\ 100 \tag{2}$$

$$Phenol\ selectivity\ \ (S_P)\ = \left(\frac{S}{S_{TOT}}\right) x\ 100 \tag{3}$$

Where:
C_0 = benzene concentration after the dark period (mmol/L);
C = benzene concentration at the generic irradiation time (mmol/L);
Q_0 = moles of benzene in solution after the dark period (mmol);
P = reaction product (phenol);
S = moles of phenol in liquid phase (mmol);S_{TOT} = total moles of the reaction products in liquid phase detected by HPLC (mmol);

3. Experimental Results

3.1 Characterization results

X-ray diffraction analysis (Figure 1) of Fe-N-TiO_2 photocatalyst in powder form showed that the anatase is the principal crystalline phase (Mancuso et al., 2021, Mancuso et al., 2020) while the spectra of Fe-N-TiO_2/sPS aerogel evidenced the typical peaks of sPS in delta form (Vaiano et al., 2014) together with peaks of Fe-N-TiO_2 (the most intense at about 25.5°). Specific surface area of Fe-N-TiO_2, determined by Brunauer Emmet Teller method, was equal to 117 m^2/g. The incorporation of Fe-N-TiO_2 into the sPS caused an increase of specific surface area, that is equal to 340 m^2/g with respect to 260 m^2/g for bare sPS.

3.2 Photocatalytic activity results

The benzene oxidation result under visible light, using Fe-N-TiO_2/sPS as photoreactive composite aerogel, is shown in Figure 2.

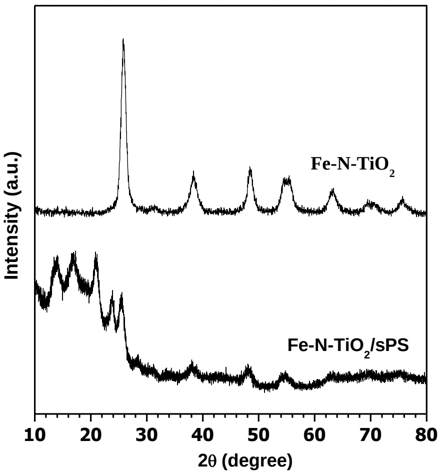

Figure 1: X-Ray diffraction patterns of Fe-N-TiO_2 photocatalyst in powder form and Fe-N-TiO_2/sPS aerogel.

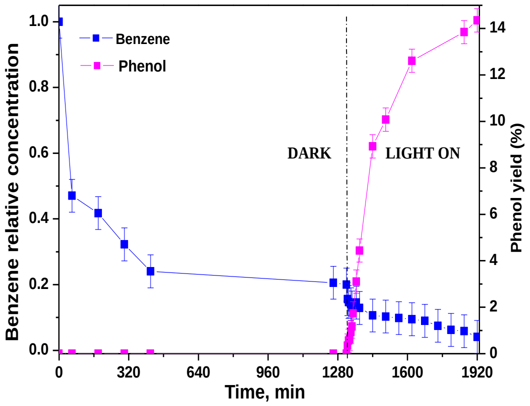

Figure 2: Benzene relative concentration and phenol yield as a function of run time using Fe-N-TiO_2/sPS photoreactive solid phase.

Fe-N-TiO_2/sPS absorbed almost 80% of benzene after 1280 min without irradiation (dark conditions) and no phenol formation was observed, demonstrating that the presence of light is necessary to obtain the desired reaction.

When visible LEDs were switched on, benzene is converted to phenol and its relative concentration decreased with run time (Figure 2). It is pointed out that the photoreactive composite favors the phenol formation via benzene hydroxylation in presence of visible light. In fact, the phenol yield gradually increased during the irradiation time, reaching a value of about 14% after 600 min of visible irradiation.

The oxidation activity of Fe-N-TiO_2 photocatalyst in powder form and Fe-N-TiO_2/sPS photoreactive composite, under UV and visible light irradiation, was compared in Figure 3.

After 600 min of UV light irradiation, benzene conversion was 70 and 53 % using Fe-N-TiO_2 and Fe-N-TiO_2/sPS, respectively (Figure 3a), while the phenol yield was 4 and 23 % with FeN-TiO_2 and Fe-N-TiO_2/sPS, respectively (Figure 3b). It is worth noting that the Fe-N-TiO_2 photocatalyst dispersion in the sPS aerogel leads to a phenol yield about 5 times higher than the value obtained with the powder under UV light. However, after 600 min of visible light irradiation, benzene conversion was about 30 and 80 % with Fe-N-TiO_2 powder and Fe-N-TiO_2/sPS aerogel, respectively (Figure 3c), while the phenol production was not observed using Fe-N-TiO_2 and a phenol yield of 14 % was obtained using Fe-N-TiO_2/sPS (Figure 3d). Under both irradiation conditions, the Fe-N-TiO_2/sPS composite aerogel can enhance the selective formation of phenol from benzene oxidation. Indeed, under UV light, the phenol selectivity was 43 and 4 % (Table 1) with Fe-N-TiO_2/sPS and Fe-N-TiO_2 powder. Under visible light, the phenol selectivity achieved in presence of Fe-N-TiO_2/sPS was 16%, whereas Fe-N-TiO_2 powder form was not able to produce phenol.

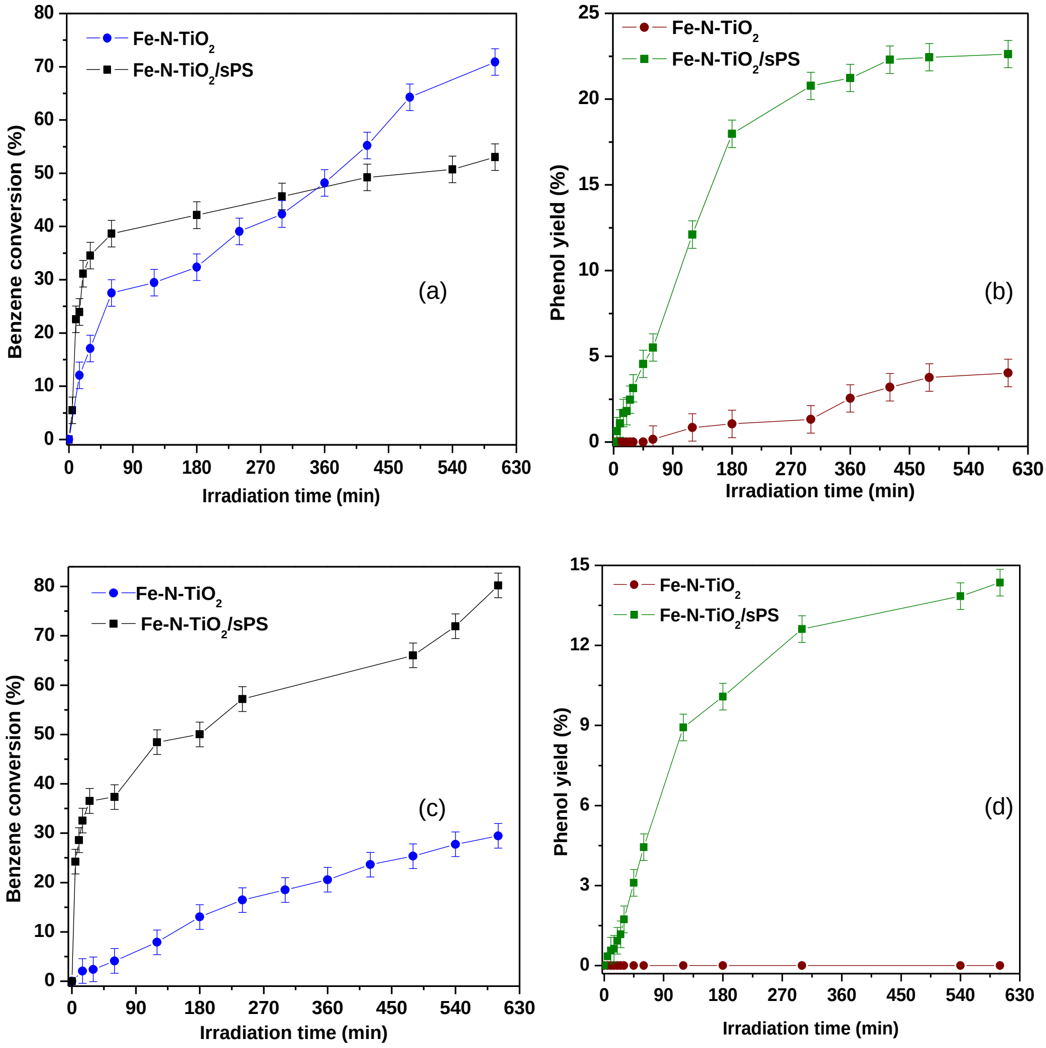

Figure 3: Benzene conversion and phenol yield as a function of irradiation time using Fe-N-TiO_2 in powder form and Fe-N-TiO_2/sPS photoreactive composite. a) Benzene conversion under UV light; b) phenol yield under UV light; c) benzene conversion under visible light; d) phenol yield under visible light.

Table 1: Benzene conversion (Bz_{conv}), phenol yield (Y_p), selectivity to phenol (S_p) using Fe-N-TiO_2 and Fe-N-TiO_2/sPS, under UV and visible light irradiation.

Sample	light	Bz_{conv}	Y_p	S_p
Fe-N-TiO_2	UV	70 %	4%	6%
Fe-N-TiO_2/sPS	UV	53%	23%	43%
Fe-N-TiO_2	visible	30%	n.d.	n.d.
Fe-N-TiO_2/sPS	visible	80%	14%	16%

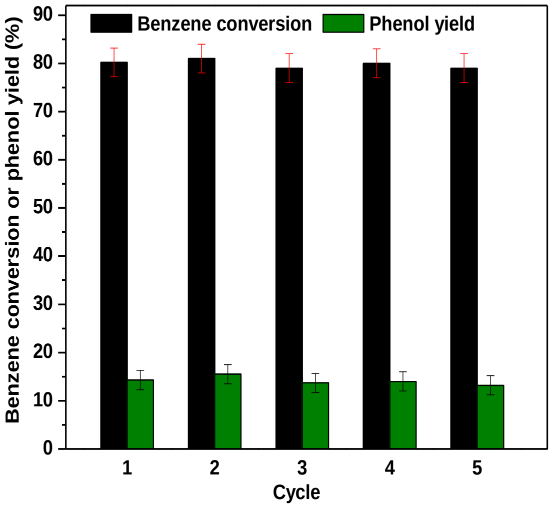

Figure 4: Benzene conversion and phenol yield after 600 min of visible LEDs irradiation for five reuse cycles.

Recycling oxidation tests under visible light were carried out to evaluate the stability of Fe-N-TiO_2/sPS aerogel. At the end of the oxidation reaction cycle, the composite aerogel was taken out of the liquid phase and dried at room temperature for 24 hours and subsequently reused. The procedure was performed five times. As shown in Figure 4, any significant decrease both in benzene conversion and phenol yield was observed, proving the stability of the catalytic material.

4. Conclusions

A polymeric photoreactive composite based on Fe-N-codoped TiO_2 powder embedded into syndiotactic polystyrene monolithic aerogel was prepared and tested in the selective synthesis of phenol from benzene oxidation in presence of UV and visible light. Under UV light, a very high benzene conversion (70 %) was achieved with Fe-N-TiO_2 but with low phenol selectivity (4 %), while Fe-N-TiO_2/sPS composite aerogel allowed an enhancement of selectivity to phenol (43 %), obtaining a high value of benzene conversion (53 %). In presence of visible light, Fe-N-TiO_2 in powder form is not selective to phenol because phenol formation was not observed, achieving a low benzene conversion (30 %). The activity improvement under visible light was obtained using Fe-N-TiO_2/sPS with phenol selectivity (16 %) and a significant benzene conversion (80 %).

Moreover, the photoreactive composite was recovered from the aqueous solution containing the reaction products and reused up to five times without any notable decrease both in benzene conversion and phenol yield.

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