

Supporting Information

Catalytic Oxidation of Phenol Analogues in Aqueous Medium Over Fe/SBA-15

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Synthesis of Fe/SBA-15

SBA-15 was synthesized by a hydrothermal crystallization method as described previously.¹⁻³ Briefly, 4.0 g P123 was dispersed in 30 g of distilled water and stirred for 3 h, to the resulting solution 120 g of 2N HCl was added under stirring and finally 9.5 mL of TEOS was added drop wise as silica source. The mixture was continuously stirred at 313 K for 24 h, then transferred into a teflon-lined autoclave and aged for 48 h at 313 K. The product was filtered, washed and dried at 383 K in air. The obtained sample was calcined at 823 K in air for 6 h. **Fe/SBA-15** sample was prepared by wet impregnation using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as iron precursor. Equal amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and SBA-15 were dissolved in minimum volume of deionized water under stirring condition for 60 min. The mixture was dried at 353 K, calcined in air at 823 K for 3 h, and obtained Fe/SBA-15. The characterization of SBA-15 and Fe/SBA-15 were accomplished by powder X-ray diffraction (PXRD), FTIR, thermo-gravimetric analysis (TGA), N_2 adsorption-desorption isotherm, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and inductive coupled plasma (ICP) analysis. The dried material was ground well and sieved using 400 mesh (0.037 mm) size test sieves. FTIR (KBr) 457, 695, 790, 960, 1079, 1229, 1380, 1446, 1635, 1638, 2340, 3436 cm^{-1} . ICP analysis of **Fe/SBA-15** catalyst showed 11.8 wt % iron metal.

Mechanism for Oxidative Destruction of Phenol Analogues

A mechanism for the oxidation of phenol analogue is suggested based on

- (i) GC-MS identification of some products after the reaction,
- (ii) Known products of degradation obtained from literature,
- (iii) Probable products of degradation from the suggested reaction pathways and observed kinetics of the reaction

Catalytic Oxidation of 2-Chlorophenol (2-CP). A mechanism for wet oxidation of 2-CP by Fe/SBA-15 has been proposed taking cue from the mechanism given by Ilisz *et al.*⁴ for photocatalytic oxidation of 2-CP with TiO_2 . In the

simplified mechanism for the catalytic degradation of 2-CP (I) can be presented as consisting of the steps (Scheme S1): (i) The attack by $\bullet\text{OH}$ radicals converts the aromatic ring leading to the formation of chlorodihydroxycyclo-hexadienyl radical (CIDHCHD, II), (ii) Compound (II) disproportionates into 2-CP and chlorohydroquinone (III), or (iii) Compound (II) simply converts itself to chlorohydroquinone (III) if the addition is at *p*-position, or (iv) Compound (II) yields pyrocatechol (IV) if the addition is at *o*-position (v) In the alternative route, CIDHCHD (II) is converted to 2-chloro-1,4-benzoquinone (V) through water elimination/ H^+ abstraction (vi) Further oxidation of the aromatic intermediates leads to ring opening and formation of carboxylic acids and hydroxylated carboxylic acids.

Catalytic Oxidation of 4-Chlorophenol (4-CP). The mechanism for 4-CP proceeds through the steps (Scheme S2)⁵: (i) An electrophilic $\bullet\text{OH}$ radical adds onto 4-chlorophenol ring (I) at ortho or para position, leading to the formation of chlorocatechol (II) and hydroquinone (III), (ii) On further oxidation, chlorocatechol (II) is likely to be converted to aliphatic acids and hydroquinone (III) to *p*-benzoquinone (IV), (iii) *p*-benzoquinone (IV) is easily oxidized to the corresponding dicarboxylic acid, 2,5-dioxo-3-hexenedioic acid (V), (iv) This acid (V) produces maleic acid (VI), which decomposes to oxalic acid (VII), formic acid (VIII), acrylic acid (IX), malonic acid (X) and acetic acid (XI). These low molecular organic acids can gradually be mineralized to carbon dioxide and water, the ultimate oxidation product by further interaction with the OH radicals.

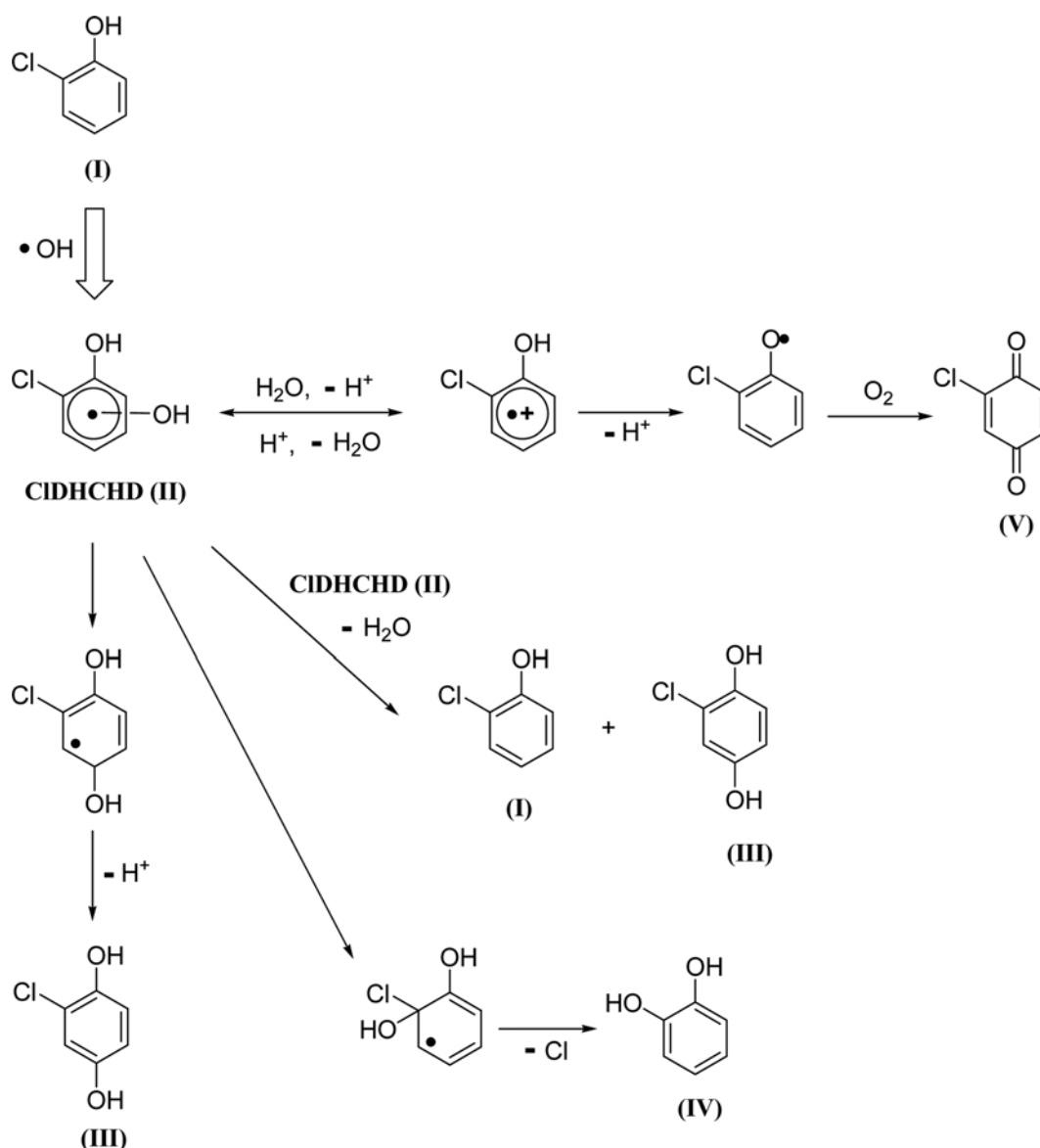
Catalytic Oxidation of 2-Nitrophenol (2-NP). The probable pathway for oxidative destruction of 2-NP (I) initiated by the catalysts could be proposed to have proceeded via the hydroxyl radicals as the steps (Scheme S3): (i) The radicals will add to 2-NP (I) at the para-position of the cyclic ring to give 2-nitrohydroquinone (II), (ii) This product (II) is converted by more hydroxyl radicals to 2-nitro-1,4-benzoquinone (III), (iii) 2-nitro-1,4-benzoquinone (III) undergoes further transformation through ring cleavage and subsequent degradation to simple aliphatic compounds, which will eventually decompose to CO_2 , H_2O , HNO_2 , and HNO_3 . Najjar *et al.*⁶ have suggested an identical scheme for degradation of 2-NP by photodegradation on Aluminum

pillared montmorillonite doped with copper.

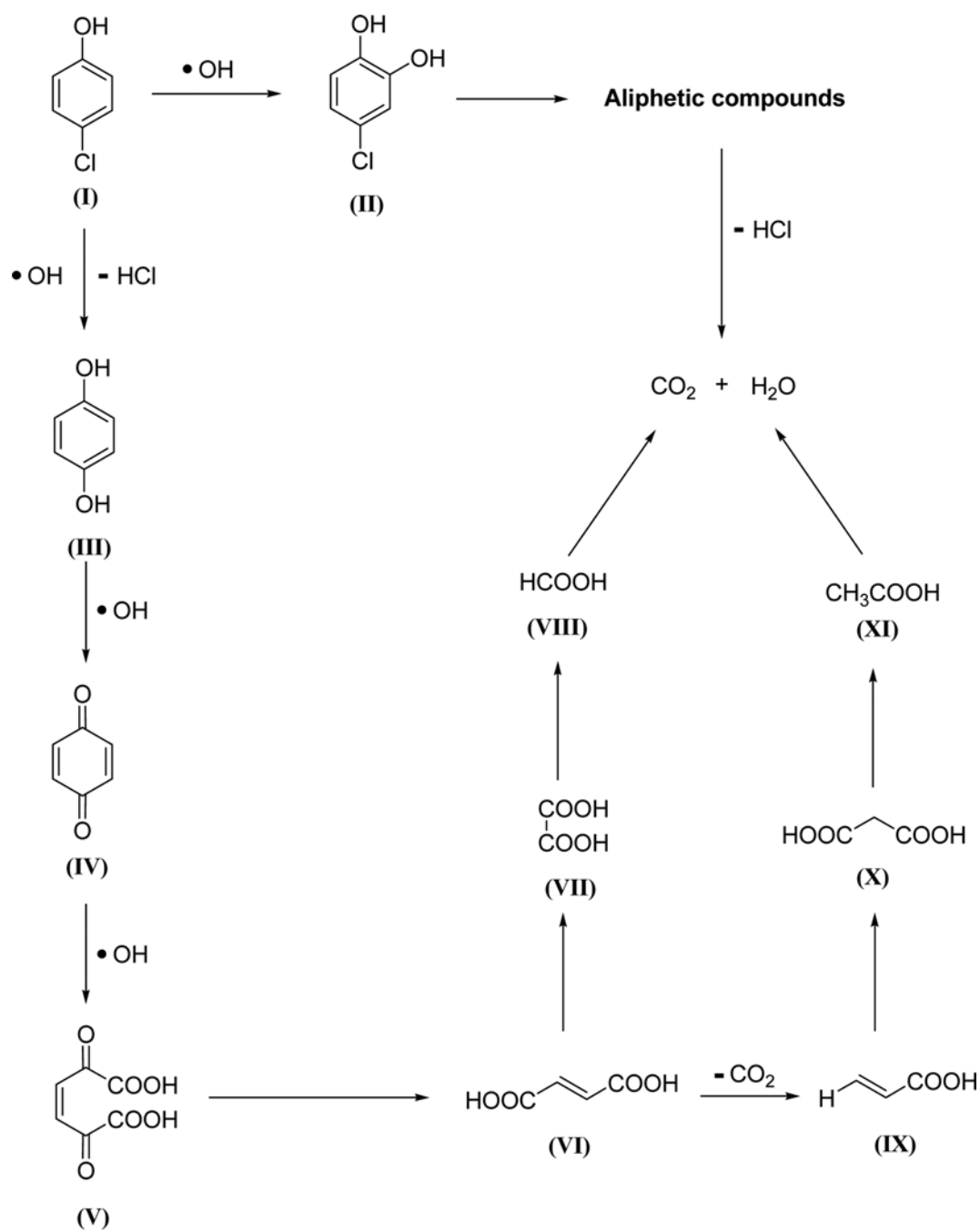
Catalytic Oxidation of 4-Nitrophenol (4-NP). The probable pathway in oxidative destruction of 4-NP initiated by Fe(III)-, incorporated SBA-15 is presented in Scheme S4.⁷ The steps are: (i) The OH radicals will add to 4-NP (I) at the ortho-position of the cyclic ring to give 4-nitrocatechol (II), (ii) This product (II) will take up more OH radicals to form 4-nitropyrogallol (III) or 1,2,4-trihydroxybenzene (IV), (iii) The products (III) and (IV) may undergo further transformation through ring cleavage and subsequent degradation to simple aliphatic compounds, which eventually decompose to CO₂, H₂O, HNO₂, and HNO₃, (iv) The OH radicals may also displace NO₂ group at para position giving hydroquinone (V), which is again converted to aliphatic compounds

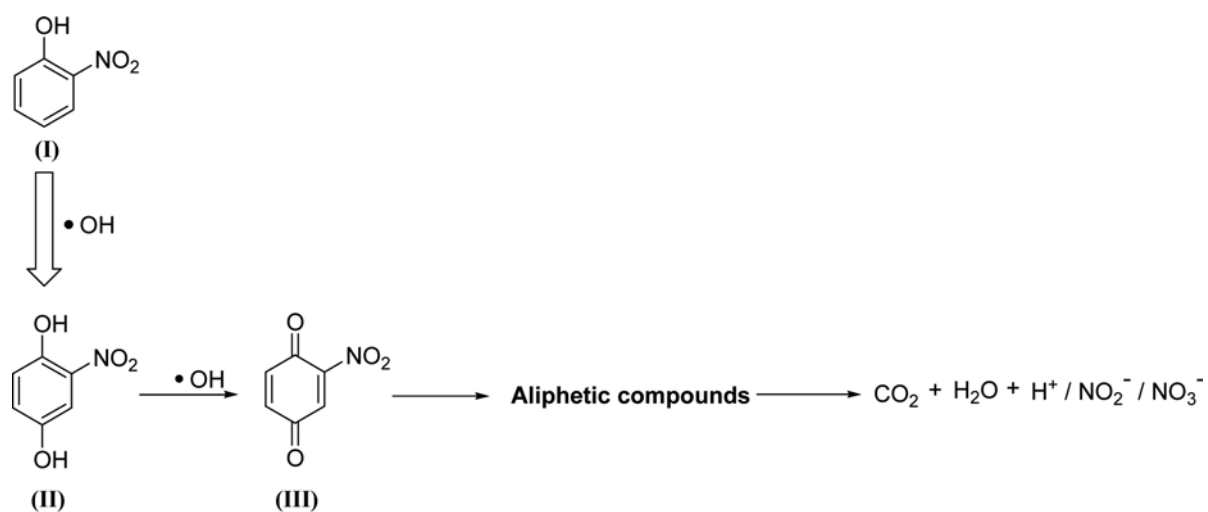
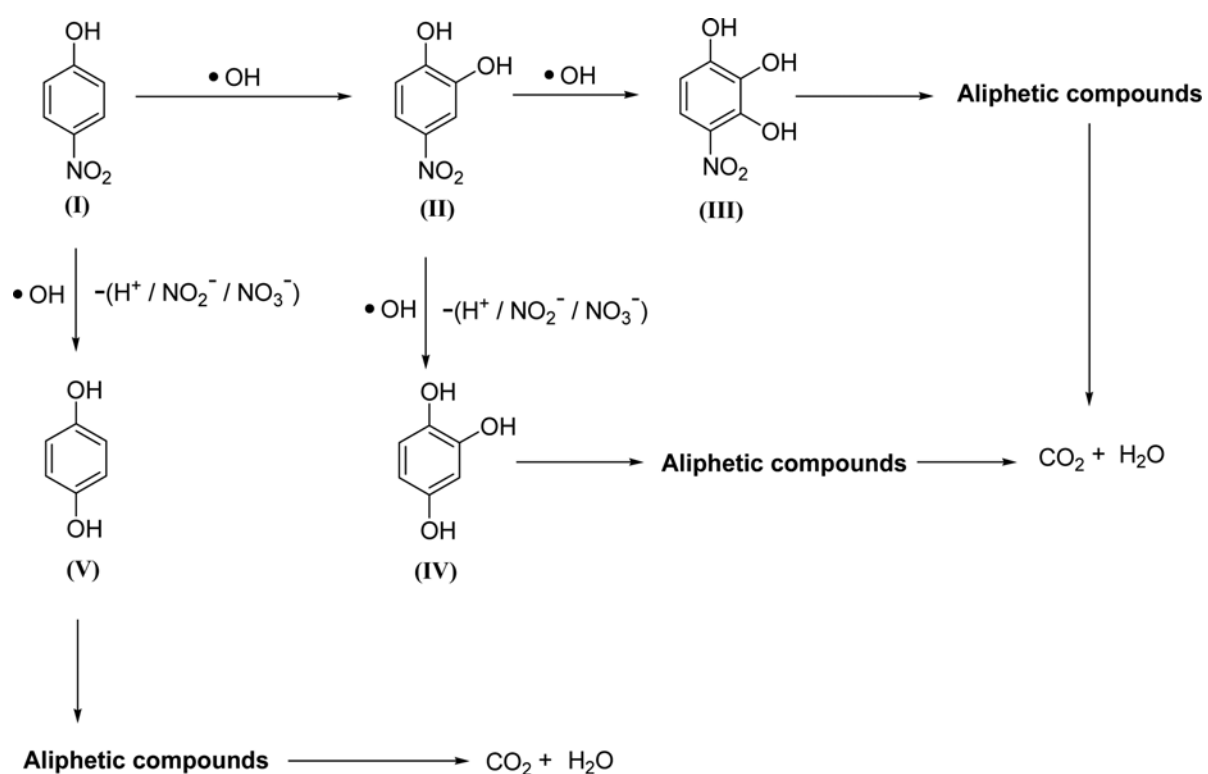
and further to CO₂ and H₂O.

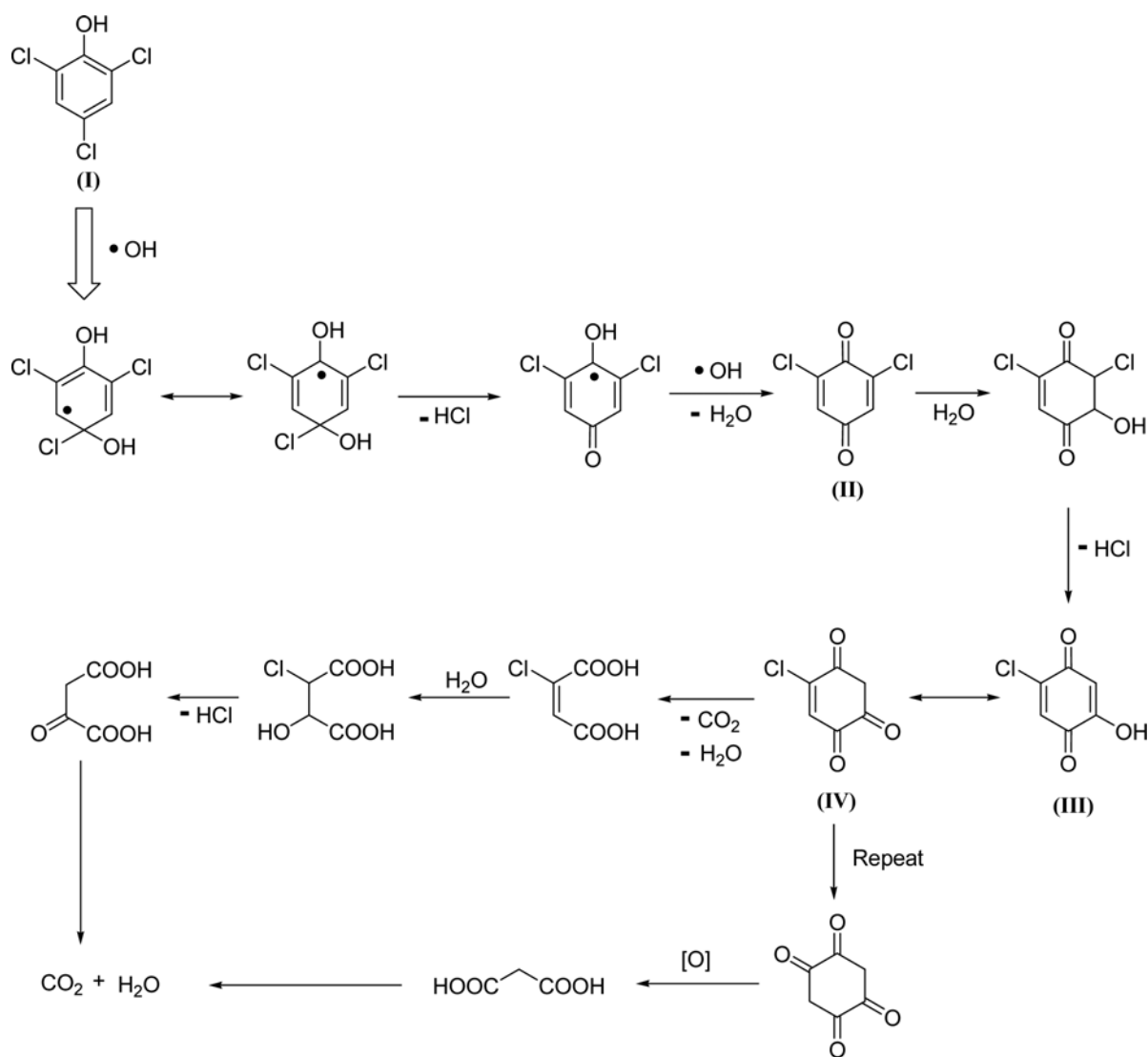
Catalytic Oxidation of 2,4,6-Trichlorophenol (2,4,6-TCP). A mechanism of oxidative destruction of 2,4,6-TCP is proposed (Scheme S5) having the pathway⁸: (i) The oxidation of 2,4,6-TCP (I) initiated proceeds with OH groups successively replacing the electron-withdrawing Cl-atoms to give 2,6-dichloro-1,4-benzoquinone (II), (ii) The compound (II) adds on more OH groups to give 5-chloro-2-hydroxy-1,4-benzoquinone (III), (iii) The product (III) converts to another product (IV) and undergoes further transformation in either of the two parallel pathways through ring cleavage and subsequent degradation to simple carboxylic acids, eventually mineralizing to CO₂ and H₂O.

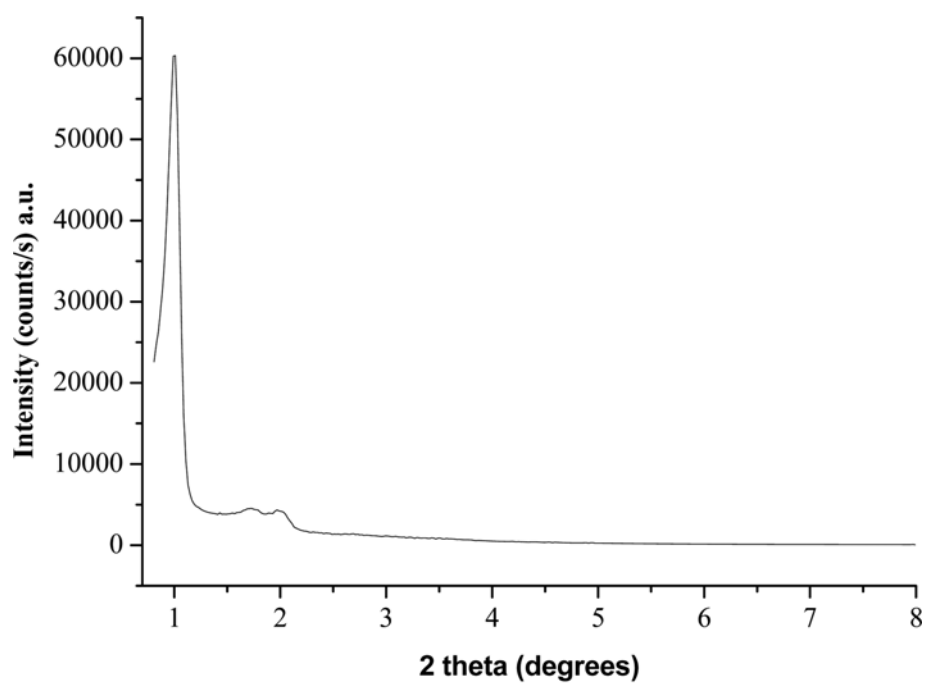
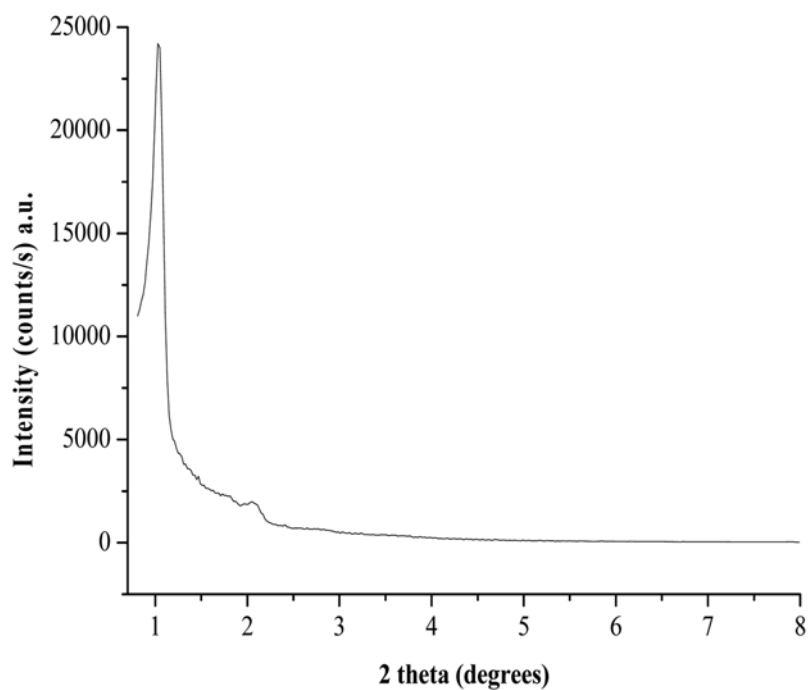


Scheme S1. Catalytic oxidation of 2-CP

**Scheme S2.** Catalytic oxidation of 4-CP

**Scheme S3.** Catalytic oxidation of 2-NP**Scheme S4.** Catalytic oxidation of 4-NP

**Scheme S5.** Catalytic oxidation of 2,4,6-TCP

**Figure S1.** Powder XRD of SBA-15**Figure S2.** Powder XRD of Fe/SBA-15

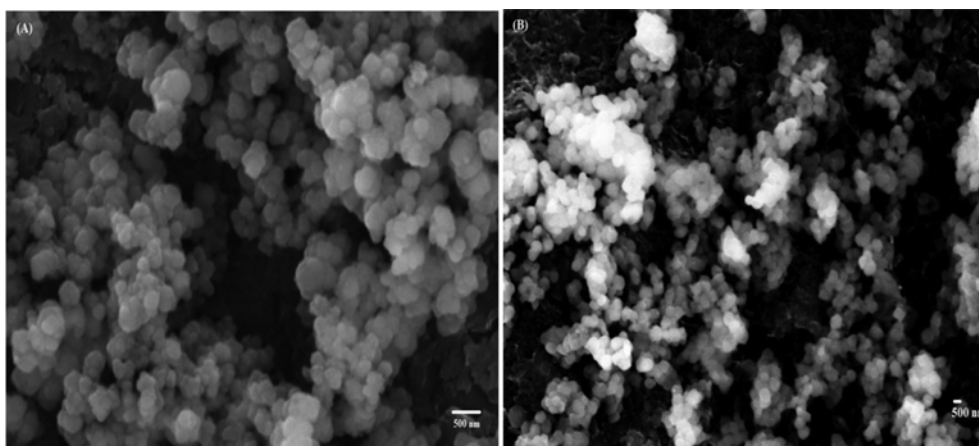


Figure S3. SEM images of SBA-15 (A) and Fe/SBA-15 (B)

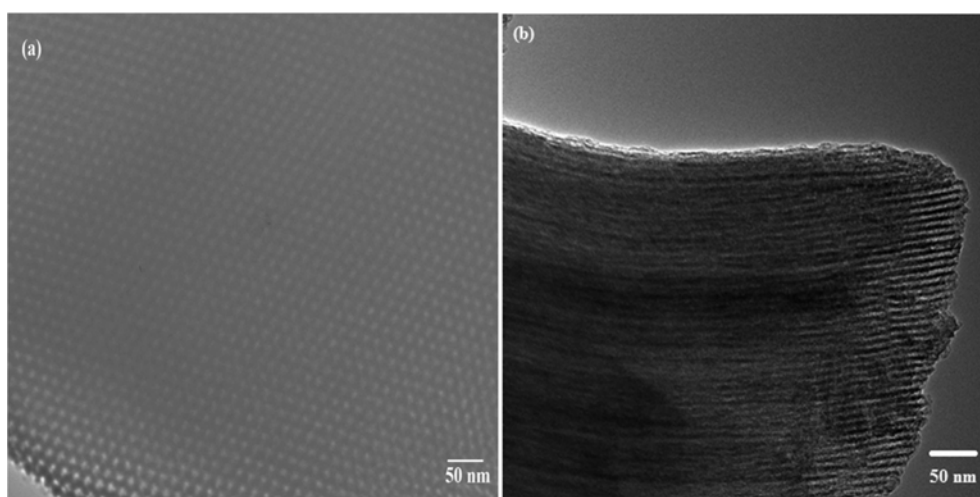


Figure S4. TEM images of SBA-15 (a) and Fe/SBA-15 (b)

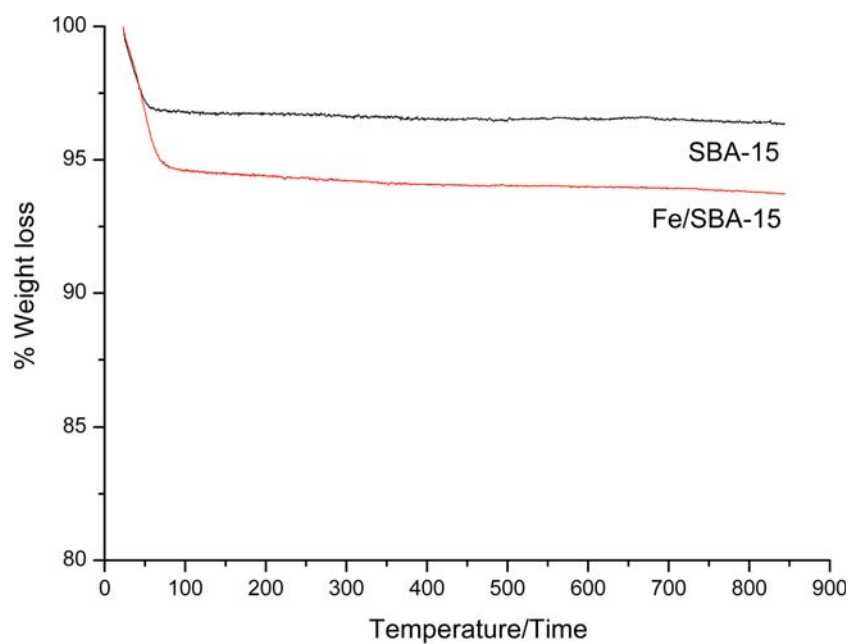


Figure S5. TGA curves of SBA-15 and Fe/SBA-15

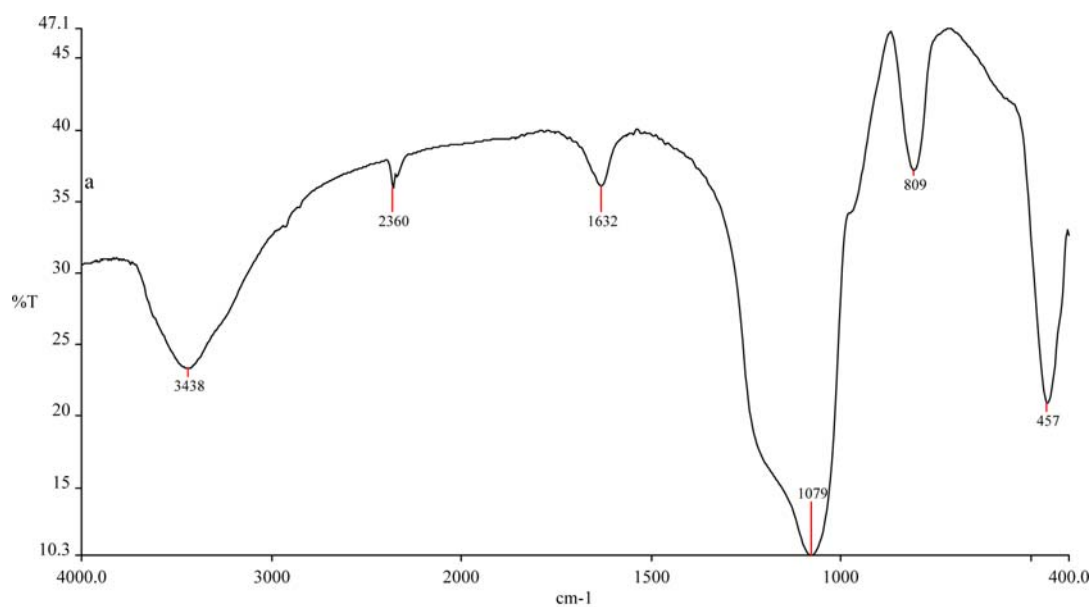
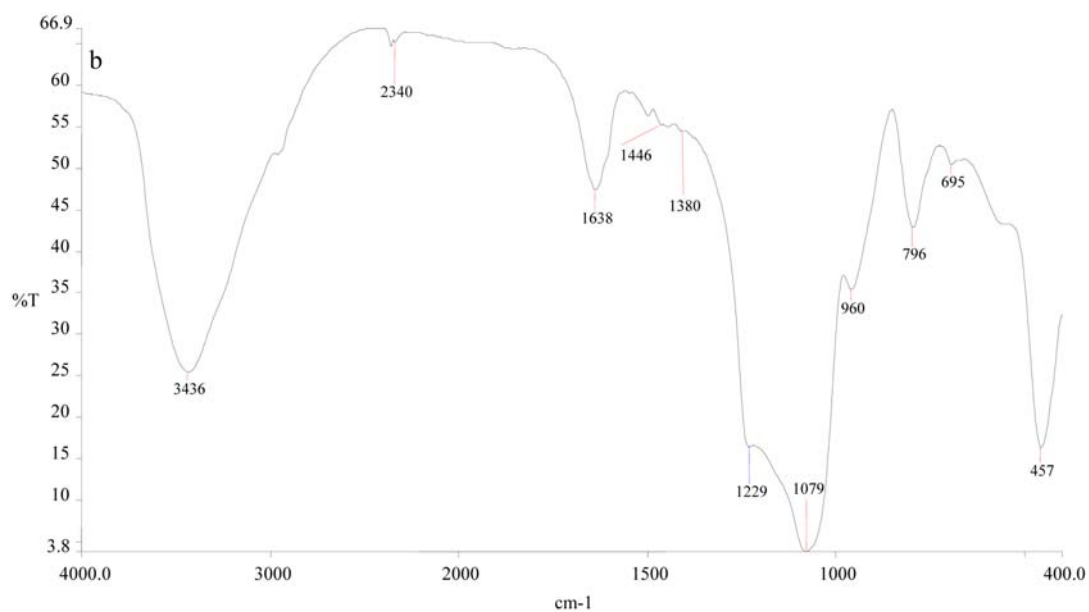
**Figure S6.** FTIR spectra of calcined SBA-15 (a)**Figure S7.** FTIR spectra of Fe-SBA-15 (b)

Table S1. Surface and pore characteristics of SBA-15 and Fe/SBA-15

Compound	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	BJH pore diameter (Å)
SBA-15	795	1.289	78.9
Fe-SBA-15	512	0.925	73.8

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