Direct Hydroxylation of Benzene to Phenol over Fe_3O_4 Supported on Nanoporous Carbon

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Abstract: $\text{Fe}_3\text{O}_4/\text{CMK-3}$ was prepared by impregnation and used as a catalyst for the direct hydroxylation of benzene to phenol with hydrogen peroxide. The iron species in the prepared catalyst was Fe_3O_4 because of the partial reduction of iron(III) to iron(II) on the surface of CMK-3. The high catalytic activity of the catalyst arises from the formation of Fe_3O_4 on the surface of CMK-3 and the high selectivity for phenol is attributed to the consumption of excess hydroxyl radicals by CMK-3. The effect of temperature, reaction time, volume of H_2O_2 , and amount of catalyst on the catalytic performance of the prepared catalyst were investigated. Under optimized conditions, the catalyst showed excellent catalytic performance for the hydroxylation of benzene to phenol and 18% benzene conversion was achieved with 92% selectivity for phenol and with a TOF value of 8.7 h^{-1} . The stability of catalyst was investigated by determining its activity after the fourth run and it was found to have decreased to 80% of the fresh catalyst's activity.

Key words: nanoporous carbon; ferroferric oxide; hydroxylation of benzene; phenol

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Phenol is one of the most valuable intermediates for manufacturers and it is still being produced by the cumene process. However, the reaction pathway is a multistep process and it is environmentally unfriendly. In addition, the production of phenol by the cumene process depends on the market price of acetone, which is a by-product of this procedure. These disadvantages limit the efficiency and profitability of this process. Therefore, plenty of research has been devoted to realizing an economical and environmentally friendly process for the conversion of benzene to phenol [1,2]. However, the oxidation of benzene to phenol is challenging because the benzene ring is chemically stable and the oxidation of phenol is much easier than the oxidation of benzene [3]. Recently, much effort has been devoted to finding a suitable catalyst for the selective oxidation of benzene to phenol under mild conditions with clean oxidants such as O_2 and H_2O_2 [4–16]. Various supported metal oxides have been studied for the one-step oxidation of benzene to phenol using hydrogen peroxide but the self-decomposition of hydrogen peroxide in these reactions has limited its application [17]. The excellent dispersion of metal ions on high surface-area supports can overcome this disadvantage [17]. As a result, porous materials have been extensively used as supports for the conversion of benzene to phenol because of their high surface areas and large pore volumes, which results in the high dispersion of metal ions

[18–21]. Because of the relatively low cost of iron salts, suitable iron-containing catalysts for the hydroxylation of benzene to phenol have been sought [22–24]. The catalytic performance of Fe_2O_3 -containing and Fe_3O_4 -containing catalysts in the hydroxylation of benzene to phenol has been investigated [22,25]. The use of Fe_2O_3 -containing catalysts results in a low benzene conversion as well as a low selectivity for phenol. Although the catalytic performance of Fe_3O_4 -containing catalysts is higher than that of Fe_2O_3 -containing catalysts, the application of Fe_3O_4 -containing catalysts have been limited because of the difficulty in preventing the further oxidation of phenol in these systems [25]. Therefore, overcoming the disadvantages of Fe_3O_4 -containing catalysts is an interesting challenge for the hydroxylation of benzene to phenol. Choi et al. [18] investigated the catalytic performance of transition metals supported on activated carbon and MCM-41 for the hydroxylation of benzene to phenol. They reported that the hydrophobic nature of activated carbon enhances the catalytic performance of transition metals during the hydroxylation of benzene to phenol.

Considering the above factors, we prepared an efficient catalyst by loading Fe_3O_4 onto the surface of CMK-3, which is a highly ordered nanoporous carbon and investigated its catalytic performance for the hydroxylation of benzene to phenol using hydrogen peroxide.

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1 Experimental

1.1 Materials

The triblock copolymer poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) (P123), tetraethyl orthosilicate (TEOS), hydrochloric acid (37%), sulfuric acid (98%), sucrose, iron(III) nitrate nonahydrate, acetonitrile, benzene, hydrogen peroxide (30%), and toluene were purchased from Merck. Hydrofluoric acid (48%) was purchased from Aldrich.

1.2 Preparation of Fe₃O₄/CMK-3

The synthesis of CMK-3 was performed according to Ref. [26] using SBA-15 as the hard template and sucrose as the carbon source. The SBA-15 sample was prepared according to the procedure reported by Zhao et al. [27].

The preparation of Fe₃O₄/CMK-3 was carried out as follows: 1 g of CMK-3 was suspended in a solution obtained by dissolving 0.4 g of Fe(NO₃)₃·9H₂O in ethanol. The solvent was then evaporated off at 243 K with continuous stirring. Finally, the resulting mixture was heated in a quartz reactor at 523 K for 4 h under an Ar flow. The resulting mixture was denoted Fe₃O₄/CMK-3.

1.3 Characterization

N₂ adsorption-desorption isotherms were obtained using a BELSORP-miniII at 77 K. All the samples were degassed at 473 K for 3 h under inert gas flow before measurement. The Brunauer-Emmett-Teller (BET) equation was used to calculate specific areas and the Barret-Joyner-Halenda (BJH) equation was used to evaluate the pore size distributions and the total pore volumes. Scanning electron microscopy (SEM) images of CMK-3 were obtained using a Hitachi S-4160 scanning electron microscope. Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-Advance diffractometer in a 2θ range from 4°–70° using monochromatized Cu K_α radiation (λ = 0.1541874 nm) operated at 40 kV/30 mA. X-ray fluorescence (XRF) analysis was carried out using an ARL ADVANT'X IntelliPower 3600. Fourier transform infrared (FT-IR) spectra were obtained using a Bruker EQUINOX 55. The cyclic voltammogram (CV) for CMK-3 was obtained using an Autolab PGSTAT302N. A conventional three-electrode system was used in the experiment. The working electrode was manufactured as follows: CMK-3 was mixed with paraffin oil at a mass ratio of 10:1. The obtained mixture was packed into a polypropylene syringe and a copper wire was inserted into it. NaNO₃ (0.5 mol/L) was chosen as the electrolyte and a graphite rod as well as a standard Ag/AgCl electrode

(SSCE) were used as the counter and reference electrodes, respectively. Cyclic voltammetry was carried out over a potential range from –0.1 to 1.7 V and at a scan rate of 0.1 V/s.

1.4 Catalytic investigation and product analysis

The hydroxylation of benzene with 30% aq. H₂O₂ was performed in a 50 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer. In a typical reaction, 0.40 g of Fe₃O₄/CMK-3 was dispersed in 6 ml of acetonitrile. After the mixture was heated to the desired reaction temperature using a water bath, 1 ml of benzene was added to the mixture. The desired amount of 30% aq. H₂O₂ was then added dropwise within 15 min and the reaction was carried out under stirring for 1–6 h. Ethanol, a well-known reagent for capturing hydroxyl radicals, was then added to the liquid product to quench the reaction and to obtain a homogenous phase for GC analysis. Finally, the resulting mixture was allowed to cool to room temperature and the catalyst particles were separated by centrifugation. The reaction products were analyzed with a Perkin-Elmer 8500 GC containing an FID detector. A quantitative analysis of the resultant solution was done using calibration curves with toluene as the internal standard. Before loading Fe₃O₄ onto the CMK-3 we investigated the catalytic performance of CMK-3 for the hydroxylation of benzene to phenol and no benzene conversion was observed.

The reaction performance parameters are defined as follows:

$$\begin{aligned}\text{Benzene conversion} &= \frac{\text{mole of benzene reacted}}{\text{initial mole of benzene}} \\ \text{Phenol selectivity} &= \frac{\text{mole of phenol produced}}{\text{mole of benzene reacted}} \\ \text{Turn over frequency (TOF)} &= \frac{\text{mole of phenol produced}}{\text{mole of metal catalyst} \times \text{reaction time (h)}}\end{aligned}$$

2 Results and discussion

2.1 Characterization

Figure 1 shows N₂ adsorption-desorption isotherms for SBA-15, CMK-3, and Fe₃O₄/CMK-3. The isotherms for all the samples are similar to type IV standard isotherms indicating their mesoporous structure. By loading iron species onto the surface of CMK-3 the specific surface area (*A*_{BET}), pore radius, and total pore volume of CMK-3 decreased, as shown in Table 1.

SEM was used to investigate the morphology of CMK-3. The SEM images shown in Fig. 2 indicate that CMK-3 consists of column-like particles, which are made up of nanorod

Fig. 1. Adsorption-desorption isotherms of SBA-15, CMK-3, and $\text{Fe}_3\text{O}_4/\text{CMK}$.

Table 1 Specific surface area, pore radius, and total pore volume of SBA-15, CMK-3, and $\text{Fe}_3\text{O}_4/\text{CMK}$ -3

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Pore radius (nm)	Total pore volume (cm^3/g)
SBA-15	660	3.53	0.7766
CMK-3	1162	1.65	1.1120
$\text{Fe}_3\text{O}_4/\text{CMK}$ -3	955	1.63	0.7427

bundles.

XRF and XRD were used to characterize the $\text{Fe}_3\text{O}_4/\text{CMK}$ -3. XRF showed that the amount of loaded Fe in the prepared catalyst was 0.897 mmol/g. Figure 3 shows the XRD patterns of CMK-3 and $\text{Fe}_3\text{O}_4/\text{CMK}$ -3. Five new peaks were present at 30.05° , 35.4° , 42.99° , 56.90° , and 62.49° in the XRD pattern of $\text{Fe}_3\text{O}_4/\text{CMK}$ -3 suggesting that Fe_3O_4 formed on the surface of CMK-3 (JCPDS 19-0629). The formation of Fe_3O_4 is attributed to the partial reduction of iron(III) to iron(II) by CMK-3. To show that CMK-3 is able to reduce iron(III) to iron(II), CV was used to determine the standard reduction potential for CMK-3. Figure 4 shows the CV of CMK-3. Using the position of the peaks on the potential axis we conclude that the standard reduction

Fig. 3. XRD patterns of CMK-3 (1) and $\text{Fe}_3\text{O}_4/\text{CMK}$ -3 (2).

Fig. 4. Cyclic voltammogram of CMK-3.

potential for CMK-3 is about +0.49 V [28]. Since the standard reduction potentials for Fe(III)/Fe(II) and Fe(II)/Fe are +0.771 and -0.44 V, respectively, CMK-3 can reduce iron(III) to iron(II) but a further reduction of Fe(II) to Fe does not occur.

2.2 Optimization of the reaction conditions

2.2.1 Influence of temperature

The influence of reaction temperature on the catalytic activity was investigated by several separate reactions under

Fig. 2. SEM images of CMK-3. (a) Low-magnification; (b) High-magnification.

Fig. 5. Effect of reaction temperature on the catalytic activity of $\text{Fe}_3\text{O}_4/\text{CMK-3}$. Reaction conditions: 1 ml benzene, 1 ml 30% aq. H_2O_2 , 6 ml acetonitrile, 0.04 g $\text{Fe}_3\text{O}_4/\text{CMK-3}$, reaction time 3 h.

the same reaction conditions. As shown in Fig. 5, the conversion of benzene increased by increasing the temperature to 343 K and then it decreased at higher temperatures because of the spontaneous decomposition of H_2O_2 to O_2 and H_2O at high temperatures [29]. Figure 5 shows that selectivity for phenol decreases with an increase in the reaction temperature because of the further oxidation of phenol at high temperatures. Therefore, in this narrow temperature range, 333 K appears to be the optimum reaction temperature.

2.2.2 Influence of reaction time

Figure 6 shows a plot of benzene conversion and phenol selectivity as a function of reaction time. Figure 6 also indicates that higher benzene conversions may be achieved over long reaction time. However, long reaction times result in a drop in selectivity for phenol. Therefore, 4 h was found to be the optimum reaction time.

Fig. 6. Effect of reaction time on the catalytic activity of $\text{Fe}_3\text{O}_4/\text{CMK-3}$. Reaction conditions: 1 ml benzene, 1 ml 30% aq. H_2O_2 , 6 ml acetonitrile, 0.04 g $\text{Fe}_3\text{O}_4/\text{CMK-3}$, reaction temperature 333 K.

2.2.3 Influence of H_2O_2 amount

The influence of H_2O_2 quantity on the catalytic activity is shown in Fig. 7. Benzene conversion increases with an increase in the amount of H_2O_2 . However, the selectivity for phenol decreases by an increase in the amount of H_2O_2 because of the further oxidation of phenol with excess H_2O_2 . We found that 2 ml of 30% aq. H_2O_2 is the optimum volume.

Fig. 7. Effect of H_2O_2 volume on the catalytic activity of $\text{Fe}_3\text{O}_4/\text{CMK-3}$. Reaction conditions: 1 ml benzene, 6 ml acetonitrile, 0.04 g $\text{Fe}_3\text{O}_4/\text{CMK-3}$, reaction temperature 333 K, reaction time 4 h.

2.2.4 Influence of the catalyst amount

Figure 8 shows a plot of benzene conversion and phenol selectivity as a function of the amount of $\text{Fe}_3\text{O}_4/\text{CMK-3}$. An increase in the amount of catalyst from 0.02 to 0.1 g leads to an increase in benzene conversion from 5.7% to 23.4% because of the formation of a large amount of hydroxyl radicals. Figure 8 shows that phenol selectivity decreases with an increase in the amount of catalyst because of the further oxidation of phenol by excess hydroxyl radicals. Consider-

Fig. 8. The effect of amount of $\text{Fe}_3\text{O}_4/\text{CMK-3}$ on the hydroxylation of benzene to phenol. Reaction conditions: 1 ml benzene, 2 ml 30% aq. H_2O_2 , 6 ml acetonitrile, reaction temperature 333 K, reaction time 4 h.

ing the above results, 0.06 g seems to be the optimum amount of catalyst. Under the optimized conditions, the catalyst showed an excellent catalytic performance of 18% benzene conversion and 92% selectivity for phenol with a TOF value of 8.7 h^{-1} .

2.3 Effect of hydroxyl radicals on the catalyst

Defect sites in CMK-3 play an important role in maintaining high selectivity for phenol. The reaction between excess hydroxyl radicals and the defect sites in CMK-3 prevents the further oxidation of phenol. This assumption is confirmed by the FT-IR. Figure 9 shows FT-IR spectra of $\text{Fe}_3\text{O}_4/\text{CMK-3}$ before and after use as a catalyst for the hydroxylation of benzene. Despite the strong absorption effect of black carbon materials, considerable changes were observed in the FT-IR spectrum of $\text{Fe}_3\text{O}_4/\text{CMK-3}$ indicating that new groups are introduced to the surface of CMK-3 during the hydroxylation of benzene to phenol. The peak appearing around 1735 cm^{-1} is assigned to a C=O stretching vibration in the carboxyl groups. The weak peak at around 1630 cm^{-1} originates from the C=O stretching vibration in quinone. The band around 1565 cm^{-1} has been observed by many authors and can be attributed to the stretching vibration of the keto groups [30]. The peak around 1255 cm^{-1} is assigned to C–O stretching vibrations in the carboxyl and ether groups. The new peak around 1160 cm^{-1} is attributed to C–O stretching in hydroxyl groups indicating that some hydroxyl groups are created on the surface of CMK-3. Two new peaks appeared around 2842 and 2922 cm^{-1} and these are due to C–H stretching vibrations. The peak appearing around 1460 cm^{-1} is assigned to C–H bending vibrations and the new peak at 1375 cm^{-1} is attributed to methyl rock vibrations. The above results reveal that hydroxyl radicals attack unsaturated bonds and defect sites in CMK-3 and create new groups on the surface of CMK-3 by oxidation or

by electrophilic addition. The peaks that originate from C–H vibrations might be related to the mechanism of interaction between the hydroxyl radicals and CMK-3 but this is still unclear.

2.4 Stability of the catalyst

The stability of $\text{Fe}_3\text{O}_4/\text{CMK-3}$ was investigated by reusing the catalyst several times. After each run, the catalyst was separated by centrifugation, washed with acetonitrile, and used for a next run. After the fourth run, the activity of the catalyst decreased to 80% of the fresh catalyst's activity. As mentioned previously, hydrogen peroxide can react with CMK-3 and this reaction can lead to the structural collapse of CMK-3, which leads to a decrease in the catalytic activity of $\text{Fe}_3\text{O}_4/\text{CMK-3}$.

3 Conclusions

$\text{Fe}_3\text{O}_4/\text{CMK-3}$ showed good catalytic performance for the hydroxylation of benzene to phenol with hydrogen peroxide. The defect sites in CMK-3 play a key role in the catalytic performance of $\text{Fe}_3\text{O}_4/\text{CMK-3}$. The formation of Fe_3O_4 on the surface of CMK-3, which is due to the partial reduction of iron(III) to iron(II) at the defect sites of CMK-3, leads to the high catalytic activity of $\text{Fe}_3\text{O}_4/\text{CMK-3}$. In addition, the defect sites in CMK-3 can react with excess hydroxyl radicals and thus prevent the further oxidation of phenol. However, the reaction between the hydroxyl radicals and CMK-3 can lead to a decrease in the catalytic activity of $\text{Fe}_3\text{O}_4/\text{CMK-3}$ after a few runs.

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Fig. 9. FT-IR spectra of $\text{Fe}_3\text{O}_4/\text{CMK-3}$ before (1) and after (2) using as a catalyst for the hydroxylation of benzene.

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