Diatomite as high performance and environmental friendly catalysts for phenol hydroxylation with H$_2$O$_2$

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Abstract

A series of diatomite catalysts were treated and characterized. For the first time, the resulting materials were used in catalysis for the hydroxylation of phenol with H$_2$O$_2$ and showed very high hydroxylation activity due to the Fe species in the diatomite. The effect of HCl treatment, contents of catalysts and H$_2$O$_2$ were investigated and the active components of diatomite were discussed. The results show that diatomite is the promising candidate for industrial output due to their high catalytic activity, easy physical separation and very low costs.

Keywords: Diatomite; Phenol hydroxylation; H$_2$O$_2$

1. Introduction

Diatoms are tiny single-celled plants that live inside a hard shell. They occur in great quantities in both salt and fresh water. When the plant dies, the shell sinks to the bottom. Over time, large quantities of these shells accumulate, eventually forming the materials called diatomaceous earth or the more lightweight rock called diatomite. The component of diatomite was silica and various impurities such as certain minerals and chemicals (especially the form of iron, a major impurity) [1].

Diatomite has been widely used in sound and heat insulation as filters, abrasives and in the manufacture of explosives. Besides, the diatomite has been tested as a support in the reactions such as hydrogenation [2,3], oxidation [4], Fischer–Tropsch synthesis [5] and CO$_2$ reduction to alkanes [6]. However, the catalytic performance of sole diatomite was never reported.

In this paper, we reported that the diatomite exhibited high catalytic performance in phenol hydroxylation with H$_2$O$_2$. The effect of HCl treatment, contents of catalysts and H$_2$O$_2$ were investigated and the active components of diatomite were discussed.

2. Experimental

The initial diatomite (i-diatom) was obtained from Aldrich (Celatom FW80). All the reagents are AR and used as received. The water was deionized and twice distilled. The diatomite was soaked with HCl aqueous solution (1 and, 5 M, respectively) for 24 h followed by filtration, washed with water until pH = 7, then dried at 100°C overnight. The samples were denoted as diatom 1 and diatom 5, respectively.

The hydroxylation of phenol was carried out in a 50 ml flask fitted with a water-cooled condenser. In a typical reaction, an aqueous solution of 30% H$_2$O$_2$ and phenol were mixed in H$_2$O, and the reaction mixture was heated at 80°C with continuous stirring in an oil bath. An appropriate catalyst was added to the reaction mixture, and with this the reaction was considered to begin. During the reaction, the concentrations of products were analyzed.

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by the HP-6890 gas chromatograph with the flame ionization detector and the hp-5 capillary column after a specific interval of time by withdrawing small aliquot out. The column temperature was 120 °C, and the injector temperature was 280 °C. The concentration of residual H₂O₂ was determined by iodometric titration.

The conversion of phenol and H₂O₂, the selectivity and yield of products are defined as follows:

\[ X_{\text{phenol}} = \frac{n^0_{\text{phenol}} - n_{\text{phenol}}}{n^0_{\text{phenol}}} \],

\[ X_{\text{H}_2\text{O}_2} = \frac{n^0_{\text{H}_2\text{O}_2} - n_{\text{H}_2\text{O}_2}}{n^0_{\text{H}_2\text{O}_2}} \],

\[ S_{\text{DHB}} = \frac{n_{\text{cat}} - n_{\text{HQ}}}{n_{\text{cat}} + n_{\text{HQ}} + n_{\text{PBQ}}} \].

\( X_{\text{phenol}}, X_{\text{H}_2\text{O}_2} \) and \( S_{\text{DHB}} \) denote the conversions of phenol, H₂O₂ and the selectivity of dihydroxybenzene, respectively. \( n^0 \) and \( n \) denote the initial molar amount and the final molar amount, respectively. CAT, HQ and PBQ represent catechol, hydroquinone and p-benzoquinone, respectively.

The catalysts were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrum (EDS), UV–Vis diffuse reflectance spectra (UV-VIS DRS), atomic absorption spectra (AAS) and powder X-ray diffraction (XRD).

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the SEM image and XRD pattern for initial diatomite. The initial diatoms show a cylindrical structure with a length of ca. 15–20 μm internal pore diameter of about 4 μm. There is a nearly regular array of submicron pores in a diameter of 500 nm in the wall. Because of the macroporosity and the micron scales, it is very facile for reactants diffusion and physical separation. The AAS measurements of the initial diatomite revealed that they consisted of about 0.94% Fe, 0.70% Al, 1.58% Na and silica. XRD pattern of the initial diatomite (Fig. 2) is consistent with the crystalline silica.

UV–Vis DRS (Fig. 3(a)) was used to characterize the nature and coordination of Fe³⁺ ions in diatomite and HCl-treated samples. A broad band between 200 and 300 nm centered at 260 nm is observed in all samples (Fig. 3(b)). This band has been assigned to a low-energy charge transfer between the oxygen ligands and the central Fe³⁺ ion in tetrahedral symmetry. Moreover, the weak broad absorption bands centered in the visible region (Fig. 3(c)) are detected probably due to the presence of octa-coordinated extra-framework species and Fe₂O₃ species [7]. The information collected so far supports the assumption that the majority of the iron atoms exist tetrahedrally coordinated within the diatomite. The intensity of
the bands near the visible region decreases monotonically with the increasing HCl concentration used, which could be contributed to the decreasing extra-framework species content; however, the intensity of the band near 245 nm remains almost unchanged. It can be concluded that extra-framework Fe species and Fe$_2$O$_3$ are more favorably dissolve than framework Fe species with HCl treatment.

3.2. Catalytic activity

The performances of the catalysts were evaluated at 80°C with H$_2$O as solvent. The reaction results are presented in Table 1. In another separate test, a blank reaction was performed under the same condition with reaction (4). No catalytic activity was observed after 6 h. The main products are catechol and hydroquinone with a small amount of p-benzoquinone. All the samples show considerable activity. AAS results show that Fe impurity in the diatomite is probably the active component. As is well known, iron oxide and iron-containing molecular sieves have been widely used in selective oxidation [8–12].

Phenol conversion and dihydroxybenzene selectivity depend strongly on the Fe content in the diatomite, the amount of H$_2$O$_2$ and the catalyst. It is observed that phenol conversion decreases with decreasing Fe content. For example, sample i-diatom has a phenol conversion of 21.05% and dihydroxybenzene selectivity of 95.15% in reaction 1. After 6 h reaction, the catalyst (denoted as r-diatom) was recovered by filtering, washing with deionized water and drying at 60°C overnight followed by calcinations at 500°C for 6 h. The EDS results show that i-diatom and r-diatom have the similar Fe/Si ratio, 0.0283 for i-diatom and 0.0265 for r-diatom, respectively. The r-diatom sample was also characterized by XRD (Fig. 2). The XRD pattern of the r-diatom was same with the i-diatom. From these tests, it is concluded that the phenol hydroxylations are catalyzed by diatomite.

Compared to the samples diatom1 (reaction (2)) and diatom5 (reaction (3)), the relatively higher conversion and selectivity was obtained over the catalyst of i-diatom. However, catechol selectivity increases with the decreasing of Fe content. According to the UV–Vis DRS results, HCl treatment prefers to remove extra-framework Fe species. One of the possible reasons is that catechol tends to generate on the tetrahedrally coordinated Fe sites and hydroquinone tends to generate on the extra-framework Fe sites. Actually, with Fe$_2$O$_3$ as catalyst, the $n_{\text{CAT}}/n_{\text{HQ}}$ ratio was less than 1.5 [13]. Besides, because the decomposition

![Fig. 2. XRD pattern of i-diatom and r-diatom.](image)

![Fig. 3. UV-vis DRS of i-diatom, diatom1 and diatom5. a. the full scale view; b. the enlarged view between 200–300 nm; c. the enlarged view between 380–500 nm.](image)
of H\textsubscript{2}O\textsubscript{2} was accelerated by the presence of extra-framework Fe species [14], the conversion of H\textsubscript{2}O\textsubscript{2} decreases with the decreasing of the amount of extra-framework Fe species. When decreasing the phenol/H\textsubscript{2}O\textsubscript{2} ratio from 3 (reaction (1)) to 1 (reaction (4)) with i-diatom as catalyst, the conversion of phenol increases from 21.05% to 40.09%. It is also interesting that the selectivity of dihydroxybenzene decreases from 95.15% to 88.74% with the increasing phenol/H\textsubscript{2}O\textsubscript{2} ratio. This could be due to the high concentration of H\textsubscript{2}O\textsubscript{2} facilitating the generation of tar [15]. The amount of catalyst also strongly affects the products’ distribution. When increasing the amount of catalyst from 5% (reaction (4)) to 50% (reaction (5)) in the unit of phenol, the conversion of phenol and selectivity of dihydroxybenzene increase from 40.09% and 88.74% to 54.19% and 99.34%, respectively. This result could be accounted for the more active sites when more catalysts are added.

4. Conclusion

For the first time, the diatomites were used as catalyst for hydroxylation of phenol with H\textsubscript{2}O\textsubscript{2} and showed very high hydroxylation activity due to the Fe species in the diatomite. UV–Vis DRS and AAS studies confirm that the majority of the Fe atoms in the diatomite exist in a tetrahedral coordination environment. Analyzing the effects of Fe content in the diatomite, the amount of H\textsubscript{2}O\textsubscript{2} and the amount of catalyst on the catalytic activity of the resulting materials, we found that the coordination environment of Fe plays an important role in phenol hydroxylation with H\textsubscript{2}O\textsubscript{2}. The diatomite is a promising candidate for industrial output due to its high catalytic activity, easy physical separation and very low costs.

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Table 1

| Reaction No. | Catalyst | $X_{\text{phenol}}$ | $X_{\text{H}_2\text{O}_2}$ | $SDHB$ | $n_{\text{CAT/NIHQ}}$ |
|--------------|----------|---------------------|--------------------------|--------|---------------------|
| 1            | i-diatom\textsuperscript{a} | 21.05 | 100 | 95.15 | 2.09 |
| 2            | diatom1\textsuperscript{a} | 19.44 | ~99 | 91.29 | 2.52 |
| 3            | diatom5\textsuperscript{a} | 16.97 | 93.76 | 90.12 | 2.67 |
| 4            | i-diatom\textsuperscript{b} | 40.09 | 100 | 88.74 | 3.50 |
| 5            | i-diatom\textsuperscript{c} | 54.19 | 100 | 99.34 | 1.62 |

Reaction conditions: Temperature 80°C; Time 6h; Phenol 1 g; H\textsubscript{2}O\textsubscript{1} 15 g
\textsuperscript{a} catalyst 0.05 g, phenol/H\textsubscript{2}O\textsubscript{2} = 3
\textsuperscript{b} catalyst 0.05 g, phenol/H\textsubscript{2}O\textsubscript{2} = 1
\textsuperscript{c} catalyst 0.5 g, phenol/H\textsubscript{2}O\textsubscript{2} = 1