Highly active heterogeneous Fenton catalyst using iron oxide nanoparticles immobilized in alumina coated mesoporous silica†

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A highly active heterogeneous Fenton catalyst was fabricated by impregnating iron oxide nanoparticles in alumina coated mesoporous SBA-15 silica.

Conventional environmental technologies focus on separating pollutants from the environment, and this has resulted in the production of concentrated and toxic residues. Since the disposal of such residues is becoming more stringent these days, degradation techniques have attracted considerable attention.1 Advanced oxidation technologies (AOTs), which involve the in-situ generation of highly potent chemical oxidants such as the hydroxyl radical, represent an important class of environmental technologies.2 Among the various AOTs, the Fenton process is an especially powerful method, because it does not require any special equipment or energy input and can oxidatively degrade various organic pollutants with the high oxidation potential of the hydroxyl radical which is produced in the Fenton reaction, as described below.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{HO}^- \tag{1}
\]

However, the homogeneous Fenton process which is conventionally employed is usable only at pH 2–3, and produces iron sludge. Therefore, it is necessary to adjust the pH before and after the process and to dispose of the sludge and, consequently, additional cost and labour are required. In order to overcome these drawbacks of the homogeneous Fenton process, various heterogeneous Fenton catalysts have been developed. Nafion,3 polyethylene film,4 alginate gel beads,5 Nafion/glass fibre,6 silica fabrics7 and layered clays8 were used as the solid matrix for immobilizing iron, and the corresponding catalysts were tested in the heterogeneous Fenton process. These heterogeneous Fenton catalysts were demonstrated to be useful to treat various organic pollutants in an aqueous environment. However, the heterogeneous Fenton reaction itself is too slow to be used by itself for the treatment of wastewater. Thus, most of the heterogeneous Fenton catalysts which have been developed so far rely on UV irradiation for the acceleration of the reaction. This requirement results in the need for specific equipment at additional cost, besides which the accessibility of light at the surface of the solid catalyst might be limited in certain practical applications.

In this context, it is necessary to investigate the possibility of facilitating the heterogeneous Fenton reaction without any external energy input. In this study, two possible approaches to accomplishing this were examined; the first involved the increasing of the active sites by using nanosized iron oxide particles (nanoparticles), and the second involved changing the chemical environment of iron by using alumina coated mesoporous silica support.

To investigate these approaches, two kinds of heterogeneous Fenton catalysts were synthesized. FeSi was prepared by the direct impregnation of iron oxide nanoparticles on mesoporous SBA-15 silica, and FeAlSi was prepared by the impregnation of iron oxide nanoparticles on alumina coated mesoporous SBA-15 silica. The usefulness of mesoporous silica as an insoluble matrix for introducing the desired active sites has previously been reported.9 SBA-15 silica was prepared following the reported procedure.10 Briefly, 4 g of P123 was dissolved in a solution composed of 130 ml of deionized water and 20 ml of hydrochloric acid (37 wt%), and the temperature of the solution was raised to 40 °C. 9.2 ml of tetraethoxysilane (TEOS) was added to the solution, which was stirred vigorously and kept at 40 °C for 20 h, followed by aging at 100 °C for 24 h. The resulting white precipitate was filtered, dried at room temperature, and finally calcined at 550 °C to remove the P123. To obtain the alumina coated SBA-15 silica (hereafter referred to as AlSi), mesoporous SBA-15 silica was dispersed in a solution containing the desired amount of AlCl3·6H2O, stirred for more than 30 min, and finally dried in an oven at 85 °C overnight. The impregnation process was repeated three times, allowing for AlSi with an Si/Al ratio of 3 to be obtained. This stepwise incorporation of the aluminium source into the mesopores of SBA-15 prevented the agglomeration of the alumina. The aluminium chloride impregnated SBA-15 was heat-treated at 550 °C for 4 h in air. AlSi (or pure silica SBA-15) was impregnated with a solution containing the desired amount of FeCl3·6H2O and dried completely in an oven at 85 °C. The iron chloride impregnated AlSi (or pure silica SBA-15) was heated to 300 °C in air for 30 min. For the sake of brevity, the products are hereafter referred to as FeSi for the iron oxide impregnated SBA-15 silica and FeAlSi for the iron oxide impregnated on alumina coated SBA-15 silica. The Fe content of the final products (FeSi and FeAlSi) which were used in this study was 12 wt% as Fe unless otherwise specified.

The catalytic ability of FeSi and FeAlSi for the decomposition of H2O2 and the degradation of a reactive dye, Reactive Black 5 (RB5, from Aldrich Co.) was examined. The H2O2 decomposition
experiments were conducted at 25 °C in the presence of 0.2 g l\(^{-1}\) of FeSi and FeAlSi particles. The initial concentration of \(\text{H}_2\text{O}_2\) was 5 mM. The solution pH was adjusted to 4.1 and kept within 0.2 pH units of this value with \(\text{HClO}_4\) and NaOH during the experiments. This pH condition was selected to avoid any possible iron leaching into the bulk phase and, consequently, the amount of iron leaching was negligible throughout the entire set of experiments. The degradation of 100 mg l\(^{-1}\) of RB5 was investigated under the same conditions as those used for the \(\text{H}_2\text{O}_2\) decomposition experiments. RB5 was selected as a model wastewater component, because vast amounts of wastewater containing dyestuffs are produced annually and reactive dyes make up a large proportion of these dyestuffs. Hematite and magnetite were used as the control, because the iron oxide formed in FeSi and FeAlSi was determined to be hematite, and magnetite is known to be the most effective catalyst as compared to the other iron oxides.\(^{11}\)

Fig. 1 shows the catalytic ability of FeSi and FeAlSi; Fig. 1a is for the decomposition of \(\text{H}_2\text{O}_2\) and Fig. 1b is for the degradation of RB5. In both data, the heterogeneous Fenton reaction was much faster in the FeAlSi system than in the FeSi system. Considering that the amount of iron oxides was similar in both catalysts, this remarkable enhancement in the rate of the heterogeneous Fenton reaction afforded by the use of FeAlSi as compared to that of FeSi is interesting. In addition, it is noted that commercial hematite and magnetite powders did not show any significant activity for the degradation of RB5, even when RB5 was totally degraded in the FeAlSi system. Since the iron content of these control iron oxides is about six times higher than that of FeAlSi, the actual difference in the catalytic activity between the control iron oxides and FeAlSi is larger than that shown in Fig. 1b. Fig. 1a and Fig. 1b show that \(\text{H}_2\text{O}_2\) produces \('\text{OH}\) as a result of its decomposition in this system, which contributes to the oxidation of RB5. This interpretation was further supported by a separate experiment involving the degradation of \(p\)-chlorobenzoic acid (\(p\text{CBA}\)), which is a well known reaction involving \('\text{OH}\) (see ESI\(^{\dagger}\)). It is noted that pure SBA-15 silica and AlSi in themselves did not show any catalytic activity with \(\text{H}_2\text{O}_2\).

The decomposition of \(\text{H}_2\text{O}_2\) was examined while varying the composition in FeAlSi (the Si/Al ratio and Fe content (wt%)), and the observed first-order rate constants are summarized in Table 1. For the same Fe content (12 wt%), a high proportion of Al (Si/Al = 3) caused \(k_{\text{obs, H}_2\text{O}_2}\) to be about two times as high as that for a low proportion of Al (Si/Al = 8). With a fixed Si/Al ratio of 3, \(k_{\text{obs, H}_2\text{O}_2}\) increased in the Fe content range of 3 wt% to 6 wt%, and then decreased as the Fe content was further increased to 24 wt%. In addition, as the alumina content was low (Si/Al = 8), the increasing the Fe content from 3 to 24 wt% hardly affected the degradation rates for \(p\text{CBA}\) (see ESI\(^{\dagger}\)). These results appear to indicate that the iron oxide which is directly associated with alumina (the active iron oxide) plays a more important role in the enhancement of the catalytic activity than the iron content itself.

The role of the alumina incorporated with iron oxide in enhancing the heterogeneous Fenton reaction is discussed in more detail in the discussion of the physical properties below (Fig. 2 and Table 2).

Table 1 Effect of composition of FeAlSi on the decomposition of \(\text{H}_2\text{O}_2\)

<table>
<thead>
<tr>
<th>Si/Al ratio</th>
<th>Fe content (wt%)</th>
<th>(k_{\text{obs, H}_2\text{O}_2})/min(^{-1})</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td>12</td>
<td>(4.15 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>(4.97 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>(7.82 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>(7.31 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>(4.24 \times 10^{-4})</td>
</tr>
</tbody>
</table>

Fig. 2 shows the X-ray diffraction (XRD) patterns of the FeSi and FeAlSi particles. Fig. 3 and Table 2 show the scanning transmission electron microscopy (TEM) images and pore characteristics of the SBA-15, AlSi, FeSi and FeAlSi. In Fig. 2, there are several characteristic peaks for hematite (\(\alpha\text{-Fe}_2\text{O}_3\)) in the
resulted in the production of small particle sized iron oxide nanoparticles in AlSi, because the large amount of seeds generally
infiltrated throughout the pores of AlSi. In the present study, these Fe\textsubscript{3+} ions were homogeneously dispersed on the pore walls of SBA-15 silica. As shown in Fig. 3, the well developed hexagonal porous silica structure of SBA-15 was retained during the coating of alumina or impregnation of iron oxide. In Fig. 3b, there is no aggregated alumina phase in AlSi, despite the high loading of aluminium oxide. This indicates that the aluminium oxide layers were homogeneously coated on the pore walls of SBA-15 silica. In Fig. 3c, iron oxide nanowires were formed inside the pores of SBA-15, and aggregated large particles with diameters of 20–60 nm were found on the outer surface of SBA-15 silica. This result indicates that the iron oxide particles were not well-dispersed, rather they were severely aggregated to form large particles in FeSi. However, there are no observable iron oxide nanoparticles in FeAlSi, demonstrating that the small sized iron oxide nanoparticles were homogeneously dispersed on the pore walls of AlSi (Fig. 3d).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Surface area/m\textsuperscript{2} g\textsuperscript{-1}\textsuperscript{a}</th>
<th>Pore volume/ml g\textsuperscript{-1}\textsuperscript{a}</th>
<th>Pore size/nm</th>
<th>Wall thickness/nm</th>
<th>a Obtained by BET measurement. b Calculated by BJH method using N\textsubscript{2} adsorption isotherms. c Obtained by SAXS measurement.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>661</td>
<td>0.80</td>
<td>8.54</td>
<td>1.85</td>
<td></td>
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<tr>
<td>AlSi</td>
<td>231</td>
<td>0.40</td>
<td>6.33</td>
<td>3.86</td>
<td></td>
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<tr>
<td>FeSi</td>
<td>624</td>
<td>0.79</td>
<td>8.46</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>FeAlSi</td>
<td>143</td>
<td>0.17</td>
<td>6.02</td>
<td>2.32</td>
<td></td>
</tr>
</tbody>
</table>

XRD patterns for FeSi and FeAlSi, both of which have the same Fe loading. While the peaks for FeSi are sharp and intense, those for FeAlSi are not. This means that much smaller and well-dispersed hematite particles were formed on AlSi than on pure SBA-15 silica. This observation was further supported by Fig. 3. As shown in Fig. 3, the well developed hexagonal porous silica structure of SBA-15 was retained during the coating of alumina or impregnation of iron oxide. In Fig. 3b, there is no aggregated alumina phase in AlSi, despite the high loading of aluminium oxide. This indicates that the aluminium oxide layers were homogeneously coated on the pore walls of SBA-15 silica. In Fig. 3c, iron oxide nanowires were formed inside the pores of SBA-15, and aggregated large particles with diameters of 20–60 nm were found on the outer surface of SBA-15 silica. This result indicates that the iron oxide particles were not well-dispersed, rather they were severely aggregated to form large particles in FeSi. However, there are no observable iron oxide nanoparticles in FeAlSi, demonstrating that the small sized iron oxide nanoparticles were homogeneously dispersed on the pore walls of AlSi (Fig. 3d). As shown in Table 2, direct iron oxide impregnation (FeSi) on pure SBA-15 silica only slightly changed the pore properties, while alumina coating (AlSi) on SBA-15 silica and iron oxide impregnation (FeAlSi) on AlSi changed the pore properties considerably. It can be explained using the above observations in XRD patterns and TEM images. In SBA-15, iron oxide formed as nanowires and aggregated particles inside pores without covering the surface of silica, so only slightly changed the pore characteristics. On the other hand, in AlSi, iron oxide formed on the pore with a covering on the alumina surface of AlSi, contributing to the decrease in pore characteristics. All of these observations are consistent with the explanation that alumina allows the iron oxide nanoparticles to be well dispersed over the matrix, thereby contributing to the enhancement of the heterogeneous Fenton reaction in the FeAlSi system. One explanation for the high dispersion of iron oxide on AlSi can be described as follows. The state of aluminium in mesoporous silica with a high aluminium loading can be classified into two types, tetrahedral aluminium and octahedral aluminium.\textsuperscript{1,2} Octahedral aluminium has a Lewis acid character\textsuperscript{12b} and tetrahedral aluminium embedded in silica walls has an ion-exchange capacity. During the impregnation processing of AlSi, part of the Fe\textsuperscript{3+} ions were exchanged with H\textsuperscript{+} ions present within the tetrahedral aluminium. These ion-exchanged Fe\textsuperscript{3+} ions are homogeneously distributed throughout the pores of AlSi. In the present study, these Fe\textsuperscript{3+} ions acted as seeds for the growth of iron oxide nanoparticles, which resulted in the production of small particle sized iron oxide nanoparticles in AlSi, because the large amount of seeds generally led to the generation of small sized nanoparticles during the synthesis of the nanoparticles in the solution phase.\textsuperscript{13} The formation of highly dispersed iron oxide nanoparticles led to an increase in the number of active sites for the heterogeneous Fenton reaction.

Moreover, aluminium is thought to play another role in addition to the dispersion of iron oxide. We also paid attention to the characteristic Lewis acidity of alumina. In the Lin & Gurol mechanism\textsuperscript{14} proposed for the decomposition of H\textsubscript{2}O\textsubscript{2} on the surface of iron oxide, the valence states of the surface iron are interconverted between 2\textsuperscript{+} and 3\textsuperscript{+} in the reaction with H\textsubscript{2}O\textsubscript{2}. Since the production of \textsuperscript{18}OH accompanying the oxidation of the ferrous iron by H\textsubscript{2}O\textsubscript{2} is known to be much faster than the reduction of the ferric iron by H\textsubscript{2}O\textsubscript{2}, the enhancement of this redox cycle should focus on facilitating the reduction of the ferric iron by H\textsubscript{2}O\textsubscript{2}. It is already known that \textsuperscript{18}OH bound to Fe\textsuperscript{3+} can enhance its oxidation via the transfer of electron density through both the \pi and \sigma systems, which stabilizes the Fe\textsuperscript{3+} formed during the oxidation.\textsuperscript{15} Therefore, it can be supposed that a Lewis acid which is associated with iron could facilitate the reduction of the ferric ion by H\textsubscript{2}O\textsubscript{2} by attracting the electron density from the iron centre and destabilizing the Fe\textsuperscript{3+} state. This explanation seems to be plausible based on the limited amount of data obtained in this study, but more evidence needs to be garnered to confirm this hypothesis, thus requiring further research.

In conclusion, iron oxide nanoparticles immobilized in alumina coated mesoporous silica exhibited very high catalytic activity for heterogeneous Fenton reactions. The alumina coating on mesoporous SBA-15 silica played a crucial role in the high activity, by increasing the dispersion of the iron oxide nanoparticles and facilitating the redox cycle of iron species.

Notes and references