Encapsulation of The Iron Oxide Nanoparticles as a Photocatalyst in The Zeolite Structure by Ion Exchange Method

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Abstract
Encapsulation of the iron oxide nanoparticles in the zeolite cages by ion exchange method which is accompanied by characterization and examination of the photocatalytic activity for phenol photodegradation are reported. The largest Fe exchanged and the lowest zeolite structural damaged can be obtained when the ion exchange was carried out at pH 7. The iron uptake by the zeolite may be formed as nanoparticles encapsulated in the zeolite cages and as iron oxide fine particles dispersed on the external surface that can be easily removed by EDTA solution. It is provided evident that the encapsulation of the iron oxide in the zeolite can increase their band gap energy (Eg) as a character of a photocatalyst and so their photocatalytic activity in the phenol photodegradation.

1 Introduction
Recently, iron oxide nanoparticles encapsulated in the zeolite structure have got considerable attention because of interest in their characteristic catalytic and photocatalytic activities.[1-2] The encapsulation can be carried out in many ways including by adsorption and decomposition of volatile organometallic compounds,[3] impregnation,[4] and aqueous ion exchange of Fe(II) ions.[5-7] Although the aqueous ion exchange method is in favor, the zeolite partially structural damaged was always observed due to the low pH of the solution. The zeolite structural damaged and the fact that Fe(II) is easily air oxidized to form large Fe (III) species lead to the iron oxide, in addition to be encapsulated in the zeolite cages, also to be formed on the zeolite external surface. The presence of the iron oxide located on the zeolite external surface can reduce their photocatalytic activity, which is unexpected.

This research deals with attempts to minimize the zeolite structural damaged with maximally iron oxide encapsulated in the zeolite cages, and to remove the iron oxide located on the zeolite external surface selectively. The first attempt was carried out by evaluating the influence of the pH solution on the amount of iron exchanged by zeolite and on the zeolite structural damaged, and the second one was carried out by using EDTA solution. Characterization by means of electron spin resonance (ESR) and diffuse reflectance UV-Visible (DRUV) spectrophotometers were carried out to determine the types and their band gap energy (Eg) as
a character of photocatalysts of the iron oxide formed, respectively. The effect of the encapsulation on the photocatalytic activity of the iron oxide was examined by using phenol photo-degradation as a model.

2 Experiment

2.1 Materials

Zeolite-Y was used for encapsulation host, Fe(II) solution 0.05 M (M = mol dm$^{-3}$) prepared by dissolving Fe(NH$_4$)$_2$(SO$_4$)$_2$ in the deionized water was employed as a starting material, and borax buffer solutions possessing pH 5, 6, and 7, were prepared from Na$_2$B$_4$O$_7$ adjusted with HCl solutions.

2.2 Ion Exchange Process

Ion exchange process was carried out as follow. Into 240 cm$^3$ solutions containing Fe(II) ions 0.05 M and borax buffer having pH 5, 6, and 7, which have been saturated with N$_2$ gas, were added 2 gram zeolite-Y. The mixtures were magnetically stirred for 45 min (as the equilibrium state) along with N$_2$ gas flowing. After being filtered, each filtrate was analyzed by AAS to measure Fe(II) concentration, while the solid phase (noted as FeO-Z) was calcined at 200°C. A part of FeO-Z prepared at pH 7 was washed with EDTA solution, then dried at 200°C, which was noted as FeO-Z aw (after washing). The solid samples were ready to be characterized and photo-examined.

2.3 Characterization

The X-RD patterns were recorded on a 6000-Shimadzu diffractometer using Cu K$\alpha$ irradiation from: 4-40 of 2$\theta$ angles. The ESR spectra were measured by using Bruker ESP 300 spectrometer. The DRUV spectra were collected on Jasco-550 spectrophotometer from 700-200 nm of the wavelength.

2.4 Photocatalysis phenol degradation

The reaction was carried out in a closed reactor set with UV lamp with $\lambda$ : 200-350 nm. About 50 mg of photocatalyst was added into 100 cm$^3$ phenol solution. The suspension was flown with O$_2$ gas along with magnetically stirring for 30 min, then was irradiated for various of time period. The solution was analyzed by GC to determine the concentration of the residual phenol.

3 Results and Discussion

3.1 Ion exchange result

In the study of the pH effect, solutions with pH 5, 6, and 7 were selected because in such pH, the structure of the zeolite-Y is relatively stable, as obtained in the previous study, and Fe(II) species exists as small cationic form [8] The effect of the solution pH on the loading of Fe in FeO-Z and on % relative zeolite crystallinity are presented in Table 1. The latter was determined by comparing the intensities of the XRD patterns of FeO-Z samples to that of the zeolite parent.

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Loading of Fe (%w)</th>
<th>The relative zeolite crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.03</td>
<td>60.03</td>
</tr>
<tr>
<td>6</td>
<td>3.25</td>
<td>64.80</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>67.44</td>
</tr>
</tbody>
</table>
Table 1 shows that the increase of pH from 5 to 7 has increased the loading of Fe and reduced the zeolite structural damaged. This is because, in the higher pH, the density of the negative charge at the zeolite structure is higher that results in the high affinity toward Fe (II) ion, and the acidity of the Fe(II) species is lower leading to the weak interaction between Fe(II) and the zeolite framework and generating smaller zeolite structural damaged. It is clear that the ion exchange carried out at pH 7 gives the lowest zeolite structural damaged and the highest iron loading in the zeolite. The results suggest that the encapsulation of the iron oxide should be carried out at pH 7.

3.2 Characterization results

ESR spectra of FeO-Z prepared in pH 7 before and after washing is presented as Fig. 1. Two signals at $g = 2.3$ and 2.0 are observed assigning the iron oxide fine particles and the iron nanoparticles attached with the framework oxygen atoms as the zeolite exchange sites, respectively.[9] The former is most possible to be formed on the zeolite external surface, while the latter is encapsulated inside the zeolite cages. Based on their intensities, it is clear that the number of iron oxide encapsulated inside the zeolite cages is much larger than that of the iron oxide located on the external surface. Moreover, after FeO-Z being washed with EDTA, the $g$ at $= 2.3$ has nearly disappeared implying that iron oxide fine particles on the zeolite external surface have been removed.

The DRUV spectra of the FeO-Z prepared in pH 7 before and after washing together with that of Fe$_2$O$_3$ are depicted as Fig. 2. The figure shows that the absorption bands ($\lambda_g$) of FeO-Z, whether before and after washing, were shifted into UV radiation that is so-called a blue shift due to the quantum size effect (QSE). The QSE is an indication of the presence of the nanoparticles (1-10 nm),[10] resulted by confinement of the oxide particle growth in the zeolite cages. The washing of FeO-Z with EDTA leads to the absorption band shift into shorter wavelength, inferring that the iron left has smaller particle size. It is indicated that the washing has removed the larger iron oxide particles located on the external surface, which is in good agreement with the ESR data.

The $E_g$ of the respective oxides can be calculated following $E_g = 1240/\lambda_g$, as seen in Table 2. It can be seen that the iron oxide prepared in the zeolite host shows higher $E_g$ than its bulk form (Fe$_2$O$_3$) due to the smaller particle size. The removal of the iron oxide on the external surface by using EDTA solution can further increase its $E_g$ value. The value of $E_g$ represents the strenght of photocatalyst in the light absorption as
a driving force to promote photoredox reactions. It is inferred that the driving force of the photocatalyst are in the descending order as FeO-Z after washing, FeO-Z before washing, and Fe₂O₃.

### Table 2 Eg of some photocatalysts

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Fe₂O₃</th>
<th>FeO-Z before washing</th>
<th>FeO-Z after washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg(eV)</td>
<td>2.19</td>
<td>4.13</td>
<td>4.43</td>
</tr>
</tbody>
</table>

#### 3.3 Photocatalytic activity

The three photocatalysts have been examined for catalysing the phenol photo degradation, and the results presented as % phenol disappearance are illustrated as Fig. 3. The figure shows the phenol photodegradation results, which were uncatalyzed as well catalyzed by Fe₂O₃, FeO-Z bw and FeO-Z aw.

It is seen in the figure that the use of the iron oxide photocatalyst has considerably increased the rate of the phenol photodegradation due to the OH radicals provided by the iron oxide. Preparing iron oxide in the zeolite structure (FeO-Zbw) can clearly improve its photocatalytic activity and further improvement of the activity is observed after FeO-Z being washed in EDTA solution (FeO-Zaw). It may be inferred that the removal of the iron oxide on the external surface allows more phenol molecules to reach the iron oxide nanoparticles in the zeolite cages, that will increase the photocatalysis rate. It is also found that the photocatalytic activities of the photocatalysts are well correlated with their Eg values: a photocatalyst with higher Eg shows higher photo activity. The higher Eg enables the photocatalyst to absorb the light (photon energy) more strongly, resulting in the larger photoactivated surface or the larger number of OH radicals as an oxidator [11].

![Fig. 3 The phenol photodegradation results which were a) uncatalyzed, b) catalyzed by Fe₂O₃, c) by FeO-Z bw and d) by FeO-Z aw](image)

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**References**