



## Short Communication

## Catalytic activity enhancement by thermal treatment and re-swelling process of natural containing iron-clay for Fenton oxidation

Artit Ausavasukhi<sup>a,\*</sup>, Tawan Sooknoi<sup>b</sup><sup>a</sup> Program in Applied Chemistry, Faculty of Sciences and Liberal Arts, Rajamangala University of Technology Isan, Nakhon Ratchasima 30000, Thailand<sup>b</sup> Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

## ARTICLE INFO

## Article history:

Received 29 April 2014

Accepted 15 August 2014

Available online 4 September 2014

## Keywords:

Thermal treatment

Re-swelling

Natural containing Fe-clay

Fenton oxidation

## ABSTRACT

In this research, catalytic activity of the modified natural containing Fe-clay, Fenton-like catalyst, toward successful decolorization of methylene blue (MB) and degradation of phenol (PhOH) was demonstrated. Among the natural containing Fe-clay prepared only by thermal treatment, the sample treated at 500 °C provides a high Fenton oxidation activity presumably due to high number of available Fe active sites. However, the efficient use of treated natural containing Fe-clay is restricted due to the loss in BET surface area during thermal treatment process. Interestingly, modification by the thermal treatment and subsequent re-swelling cannot only generate the active Fe species, but also enhance the basal space that facilitates diffusion of the reagents toward the active sites within the clay layers. It is expected that the active Fe species formed and retained by thermal treatment and re-swelling process which is on the surface of the catalyst reacts with hydrogen peroxide and leads to the formation of active oxidant that remove the MB and PhOH.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Clay is ubiquitous in nature, with nanoscopic size, anisotropic shape, apparently nontoxic nature, and low cost. However, the efficient use of clay is restricted by their low porosity and poor thermal stability [1]. Thermal treatment of clays generally results in the dehydroxylation of the clay minerals in the temperature range 500–800 °C, depending on the type of the clay mineral and on the structure of the octahedral sheet [2]. The dehydroxylation may well promote a transformation of crystalline mineral phases into metastable, nearly amorphous phases [3]. The introduction of inorganic pillars in the natural clay improves its resistance and stability, increases its micro porosity and provides larger surface area [4]. Recently, metal oxide pillars, especially Fe<sub>2</sub>O<sub>3</sub>, have been successfully introduced between the silicate layers [5]. Collaborated efforts have been made to evaluate such modified clay for the Fenton oxidation for the treatment of industrial wastewater containing non-biodegradable organic pollutants.

Although iron-pillared clay has been widely used as Fenton catalyst, the reports of natural containing Fe-clay used as heterogeneous Fenton catalyst are still rare in wastewater treatment. Natural containing Fe-clay could also be used as heterogeneous

catalysts in the Fenton-like reaction. In fact, the natural clay generally possesses a high iron content, which make it ideal as Fenton catalyst. The presence of iron may include the following; (i) iron oxide species distributing onto the surface of clay and/or (ii) iron oxide species present in the interlayer. However, the active Fe species present in natural clay possesses relatively less available active sites for Fenton oxidation, as compared to Fe-pillared clay. Zhang [6] reports that the structure of the activate iron species in the pillared clay was an amorphous FeO(OH)-like species generated after calcining at 500 °C. The activities of the pillared clay catalysts can be particularly increased by intercalating larger iron clusters. Accordingly, it would be interesting to study on the catalytic activity enhancement of natural containing Fe-clay developed by thermal treatment process. It was expected that the active iron species formed by thermal treatment can be greatly accelerated the oxidation, which was due to the formation of active oxidant on the catalyst surface. However, the activation of Fe species present in the natural clay at high temperature can also remove the water molecules by desorption of physisorbed water and dehydroxylation. This leads to the shrinkage and loss in surface area of natural containing Fe-clay catalyst. Interestingly, the swelling of the clay layers could be simply achieved by introducing cations into the clay structure [7]. The clay that is immersed into the solution of cations can freely exchange its interlayer cations for other metal cations in solution. This process is the so-called

\* Corresponding author. Fax: +66 4 4233 072.

E-mail address: ausavasukhi@gmail.com (A. Ausavasukhi).

shrinkage-swelling reversibility, which can be observed over the treated clay. The most interesting features of the clay are their reversibility behavior which can improve diffusion rate and hence the catalytic properties.

In this research, heterogeneous Fenton systems using natural containing Fe-clay catalysts have recently been developed by both thermal treatment and re-swelling process. The Fenton-like processes including decolorization of methylene blue (MB) and degradation of phenol (PhOH), were tested as models using such modified natural containing Fe-clay catalysts. The potential to apply natural containing Fe-clay before and after thermal treatment and re-swelling process as heterogeneous Fenton type catalyst was discussed.

## 2. Experimental section

### 2.1. Chemicals

All chemicals used here are of reagent grade and used without further purification. Methylene blue (MB) and phenol (PhOH) were purchased from Merck. Hydrogen peroxide ( $H_2O_2$ ) (50 wt.%) was obtained from Sigma–Aldrich. The pH of the solution was adjusted to a desired value using dilute solutions of  $H_2SO_4$  or NaOH. The required concentration of the MB and PhOH solutions was made using deionized water.

### 2.2. Catalyst preparation and characterization

Natural containing Fe-clay was obtained from the SCG Chemicals. The clay samples were calcined at 100–700 °C for 5 h. Hereafter, the catalysts will be designated as Clay-100, Clay-300, Clay-500 and Clay-700 according to their thermal treatment. Re-swelling process employed for catalytic activity enhancement was performed by stirring treated natural containing Fe-clay with 0.1 M NaCl solution at room temperature. The samples were dried at 60 °C for 24 h. In the case of the sample that was re-swelling, the prefix “re-” will be used to refer to it, such as re-Clay-500.

Atomic absorption spectroscopy (AAS) was carried out for determining the iron content of clay sample. Powder X-ray diffraction (XRD) was employed for determining phase formation and crystallographic state (Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm)).

### 2.3. Catalytic activity for Fenton oxidation

The activity of the catalyst to decolorize MB was tested in a batch reactor. The reaction conditions were as follows: pH solution, 3.0; 50 wt.%  $H_2O_2$  volume, 0.5 mL; reaction time, 30 min; reaction temperature, 50 °C; MB concentration, 60 mg/L; catalyst content, 50 mg; solution volume, 250 mL. The color removal of dye solutions was analyzed by measuring the absorbance with UV–Vis spectrophotometer at  $\lambda_{max} = 665$  nm.

The activity of the catalyst to degrade PhOH was tested in a batch reactor. The reaction conditions were as follows: pH solution, 5.0; 50 wt.%  $H_2O_2$  volume, 0.5 mL; reaction time, 30 min; reaction temperature, 50 °C; PhOH concentration, 50 mg/L; catalyst content, 50 mg; solution volume, 250 mL. High performance liquid chromatography was used to measure the phenol conversion as well as the products formed by the reaction.

## 3. Results and Discussion

### 3.1. Characterization of natural containing Fe-clay

The characteristics of the natural containing Fe-clay samples are shown in Table 1.

**Table 1**  
Surface area and chemical composition of natural containing Fe-clay.

Type of catalyst	BET surface area ( $m^2/g$ )	Fe content (wt.%)
Clay-100	85	5.4
Clay-300	84	5.3
Clay-500	72	5.1
Clay-700	43	5.1
re-Clay-100	86	5.2
re-Clay-300	84	5.1
re-Clay-500	83	4.9

The observed drop in BET surface area with increasing treatment temperature is very pronounced, particularly at 700 °C, indicating the poor thermal stability of natural containing Fe-Clay. In clays, the tetrahedral sheets are always bonded to octahedral sheets via the Coulombic interaction with the counter cations. When clays are heated, the interlayered cations can move into the hexagonal cavities of the tetrahedral sheet and even into the vacant octahedral positions [8–14]. These migration processes reduce the apparent negative layer charge leading destruction of the layer structure and hence a decrease in surface area.

However, the BET surface area of re-Clay-500 is increased, as compared to that of Clay-500. This indicates that when Clay-500 is immersed into the solution of sodium cations, both the intercalation of water molecule and swelling occur. Moreover, the BET surface area of re-Clay-100, re-Clay-300, and re-Clay-500 is similar to that of Clay-100 after the re-swelling process. This is because, beside the degree of dehydroxylation, the chemical composition of the treated clay does not significantly change with the treatment temperature (namely 300 or 500 °C). Therefore, the treated clay (at any treatment temperature) would carry a similar extent of negative surface charges that interact with the sodium cations introduced upon swelling process. This also leads to a similar extent of water adsorption and hence the layers expansion. Accordingly, recoverable surface area of the treated sample is somewhat similar. However, the clay shall lose its swelling capacity if severe thermal treatment that causes a completed phase change is applied [15]. Hence, the increase in the BET surface area of re-Clay-700 was not expected after re-swelling process.

In addition, the treated clay can also freely exchange its interlayer cations for other sodium cations in solution. This leads to a slightly decrease in iron content in clay sample. In addition, the natural containing Fe-clay possesses a relatively high wt.% of Fe (~5%), which make it ideal as Fenton catalyst.

The XRD patterns of the clay sample after thermal treatment at different temperatures and the clay sample after thermal treatment at 500 °C and subsequent re-swelling (re-Clay-500) are shown in Fig. 1.

The Clay-100 shows a strong diffraction peak at 5.9°, 17.6°, 19.9° and 35.6° corresponding to montmorillonite phase [16]. While, the diffraction peaks at 29.5° and 35.6° are assigned to the magnetite ( $Fe_3O_4$  or  $FeO \cdot Fe_2O_3$ ) crystallite [17]. The peak intensity of  $Fe_3O_4$  crystallite is accordingly low as some iron species may well be dispersed. After thermal treatment (>300 °C), the treated-clay shows the shift peak at 5.9–9.1° and peak at 17.6–18.3° (lower d-spacing). This is presumably due to a removal of interlayer water molecules. The peak at 9.1° and 18.3° indicates the formation of illite [18], as a result of thermal treatment. Moreover, the magnetite structure was altered after thermal treatment (>300 °C) as a new peak at 27.8° was appeared indicating the formation of hematite ( $Fe_2O_3$ ) [19]. However, no significant change of XRD pattern can be observed after treating at temperature greater than 500 °C. This result indicates that the thermal treatment may well promote a phase transformation of both iron species and clay. It is generally seen from the TGA data of parent clay samples (not

Download English Version:

<https://daneshyari.com/en/article/606936>

Download Persian Version:

<https://daneshyari.com/article/606936>

[Daneshyari.com](https://daneshyari.com)