Journal of Chemistry, Vol. 48 (5), P. 648 - 652, 2010

PHENOL DEGRADATION BY HETEROGENEOUS FENTON PROCESS

Received 31 March 2010

NGUYEN THI DIEU CAM[1], NGUYEN VAN NOI[2], NGUYEN THU HANG[2], DAO THANH PHUONG[2], DO THI NGOC ANH[2], NGUYEN THI PHUONG LE CHI[1]

[1]*Faculty of Chemistry , Quy Nhon University*

[2]*Faculty of Chemistry, Hanoi University of Science - Vietnam National University, Hanoi*

ABSTRACT

The mixed Al-Fe pillared bentonite was tested as a heterogeneous catalyst for the photo-Fenton oxidation of phenol under solar light irradiation. The structural characteristics of the catalysts were examined by XRD and SEM. The results indicate that the heterogeneous photo-Fenton process employing the Al-Fe pillared bentonite as catalyst exhibits higher photo-catalytic activity compared to its corresponding homogeneous photo-Fenton process.

I - INTRODUCTION

Industrialization process has produced a large amount of organic substances. Many of them are persistent in aqueous environment and hard to biodegrade. This is the reason why there are many researches on treatment of these pollutants. Treating these substances is costly and it might also causes potential secondary pollution. One of the most popular solutions is using advanced oxidation process to completely degrade these organic pollutants into unharmful inorganic substances like CO_2 and H_2O [1]. Fenton reaction is known as a reaction that produces $OH^{\bullet}$ which is a strong oxidant [2, 3, 4] that can oxidize non – biodegradable pollutants. However, this reaction requires low pH, and reaction yield reduces rapidly when increasing pH. On contrast, pH of wastewater is about 6 to 8, so there is a need for researches on heterogeneous catalyst to decompose organic substances using H_2O_2 in higher pH range [5].

Ferric ion and ions of other transition metals have long been known as Fenton – like catalysts [6]. Moreover, after this process, there is no secondary pollution caused by metals if metal ions are immobilized on support. Bentonite support is widely known for its availability and cheapness; therefore its applicability in Vietnam is promising.

Pillared clay is material produced by calcinating modified clays. Clays is modified by exchanging cations which lies between layers with Keggin-like metal polyoxocations [7]. After adding metal polyhydroxy into layers of clay, it is calcined at high temperature to make stable pillars, keep clay layers away from each others. In this situation, oxide particles are in nano scale. In comparison with pillaring by only one metal, pillaring with mixture of metals can increase surface area, surface acidity of material and lead to increase catalytic activity [5].

II - EXPERIMENTAL

1. Materials

Bentonite from Thanh Hoa (CEC = 71 meq/100 g dry clay) is provided by Truong Thinh company (mineral composition is presented in table 1), $AlCl_3$, $FeCl_3$, NaOH, phenol, H_2O_2.

2. Al-Fe pillared clays

a) Polyoxocation solutions

Polyoxocation solution were prepared in ratio (Al+Fe):NaOH = 1:2. $AlCl_3$ and $FeCl_3$ solutions were kept at 65°C in 1h. Add gradually NaOH solution into these ($AlCl_3$ and $FeCl_3$) solutions, stir continuously at 65°C. Finally, solution was aged overnight at room temperature.

b) Al-Fe pillared clays preparation

A 2 wt% clay suspension was adjusted to pH 9.1 and swelled for 2 days. Polyoxocation solution was added into clay suspension until achieving 10 mmol Al-Fe/1g clay. The ratios of Al/Fe are 10/0; 9/1; 8.5/1.5; 4/1; 3/1; 1.5/1; 0/10. The suspension was stirred in 4h and aged for one day at room temperature. After that, the suspension was filtered and washed with deionized water repeatedly until completely eliminating chloride ions. Finally pillared clays were dry at 40, 70, 110°C in 12 h and calcined at 400°C in 3 h.

3. Analysis methods

Catalytic characterization was investigated by X- ray diffraction method using D8 ADVANCE instrument (Bruker - Germany), SEM (JEOS JSM - 5410 LV, Japan). Concentration of phenol was determined by spectrophotometric method using UV-VIS Novaspec II instrument (Germany) with 4-amino antipyrine as a color agent at 510 nm. Concentration of iron was measured using 1,10-phenanthroline as a color agent. Cation exchange capacity of clay was measured by methylene blue adsorption method according to American Petroleum Institute.

4. Photocatalytic experiments

The reaction was carried out in a sequencing batch reactor. 300 mL of 100 mg/L phenol solution was added to the 500 mL beaker, then 0.5 g pillared clay was added, and the suspension was stirred continuously to make uniform suspension. H_2O_2 was added to the suspension at the beginning of solar light irradiation. The pH of the solution was adjusted by HCl and NaOH solution. Phenol and iron concentration was determined.

III - RESULTS AND DISCUSSTION

1. Material characterization

Physicochemical properties of original bentonite and catalytic Al-Fe pillared clays are represented in tables 1 and 2.

Table 1: Mineral composition of enriched Thanh Hoa clay

Mineral	Concentration (wt %)
Monmorillonite	59-61
Illite	3-5
Zeolite(Heulandit +Chabazit)	3-5
Kaolinite + Clorite	12-14
Quartz	4-6
Felspat	4-6
Gotite	6-8
Lepidocrocite	Small
Gipxite	Small

Table 2: Interlayer distances of original Bentonite and modified Bentonite

Clay samples	d_{001}, Å
Bentonite	15.61
Bent-Al-Fe (10:0) (7)	18.14
Bent-Al-Fe (9:1) (6)	18.56
Bent-Al-Fe (8.5:1) (5)	18.88
Bent-Al-Fe(4:1) (4)	18.94
Bent-Al-Fe (3:1) (3)	18.48
Bent-Al-Fe (1.5:1) (2)	17.34
Bent-Al-Fe (0:10) (1)	15.32

The interlayer distances d_{001} are summarized in table 2. The basal space of Al-Fe pillared clay depends on the amount of Fe and Al in the pillaring solution. The higher the concentration of aluminium, the wider the interlayer distance; in contrast, the higher the concentration of iron, the narrower the interlayer distance. It is not well understood how aluminium species widen the interlayer distances while other metal species cause the opposite effect during pillaring process, though the scenario is often observed [8–10]. The widening probably results from the ability of aluminium to bridge the neighbouring silicate units between layers, in a way similar to the behaviour found with aluminium oxides inherently present in clays. XRD patterns (Fig. 1) show that maximum distance was achieved at ratio Al:Fe as 4:1.

2. Catalytic effect of Al-Fe pillared clays

Preliminary tests prove that phenol could not be degraded by H_2O_2 without Al – Fe pillared clay. Experimental data of phenol conversion degree is presented in Fig. 3.

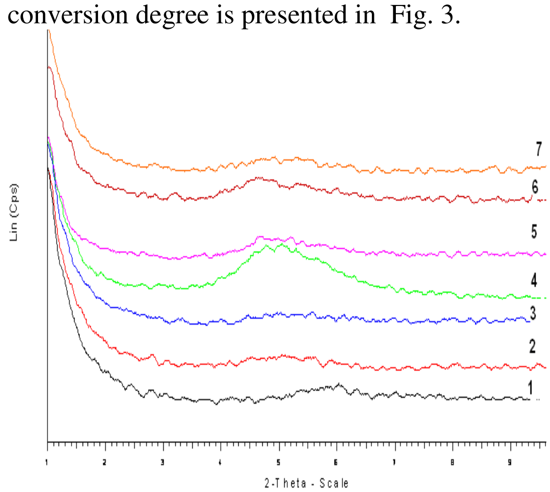

Figure 1: XRD pattern of Al-Fe pillared Bentonites

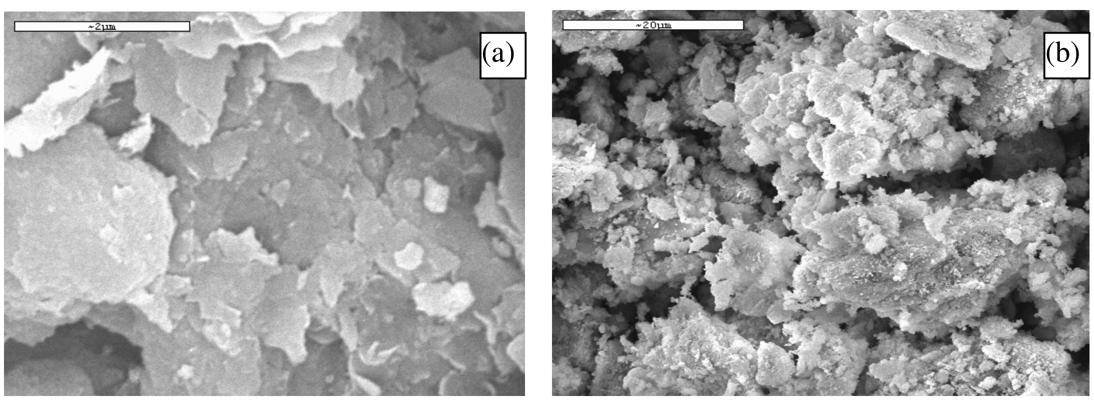

Figure 2: SEM pattern of (a) original bentonite (b) Al-Fe pillared bentonite

Results show that catalytic effect of Al – Fe pillared clays reaches its peak at molar ratio Al/Fe = 1.5/1 in pillared solution. Catalytic effect of pillared clays was low at higher iron amount. When clay is modified by only Al ions, the materials still have effect on phenol degradation [11]. However, original Bentonite does not have catalytic activity on phenol degradation [12].

This can be explained that there are two sources of iron: one from original Bentonite, one from pillared solution. These two sources are both in nano scale and can be considered as catalytic sites of Fenton reaction to oxidize phenol by H_2O_2. However, for original Bentonite, reactants (phenol and H_2O_2) is difficult to reach to iron ions because of smaller interlayer distance (15.6 Å) [13]. Bentonite modified by only Al can increase catalytic effect because of larger interlayer distance (data shown in Table 2), and reactants can disperse into layers of Bentonite [11]. This is why Al pillared clay has catalytic activity while original clay does not. If clay is pillared with only Fe, amount of Fe in clay increases but interlayer distance increases a little, so amount of reactants reaching iron ions is small, resulting at low catalytic activity. In case of pillaring by both Fe and Al, not only amount of Fe increases but also interlayer distance increase. Therefore the efficiency of dispersing reactants increases. Consequently, catalytic effect depends on amount of Al in pillared solution. In conclusion, both Al and Fe play important roles in synergetic catalytic effect. Al – Fe pillared clay has maximum catalytic effect at ratio Al:Fe = 1.5:1. This can be explained, although interlayer distance at this ratio is not maximum, it has competition between phenol and size of capillary. Moreover, increasing amount of Fe increases catalytic sites of the material. Therefore, pillared clay at this ratio is used for further researches.

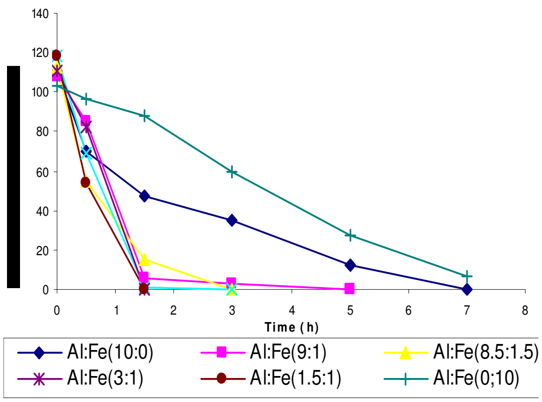

Figure 3: Phenol conversion efficiency versus time of different pillared clays

3. Test on the iron leaching

During reaction, iron from pillared clay is dissolved into solution. Results show that amount of iron leaching out is a function of time (Fig. 4). Consequently, material needs to be removed right after completion of reaction to limit the amount of iron leaching out.

4. Effect of H_2O_2 dosage

Changes in H_2O_2 concentrations led to significant changes in phenol decomposition process. Adition of H_2O_2 $1.6.10^{-2}$ M to 8.10^{-2} M, significally increases phenol conversion. Further increase of H_2O_2 above 6.10^{-2} M decreases the phenol degradation. It is resulted from the reassociation of $HO^{\bullet}$ radicals as shown in following reaction:

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$$

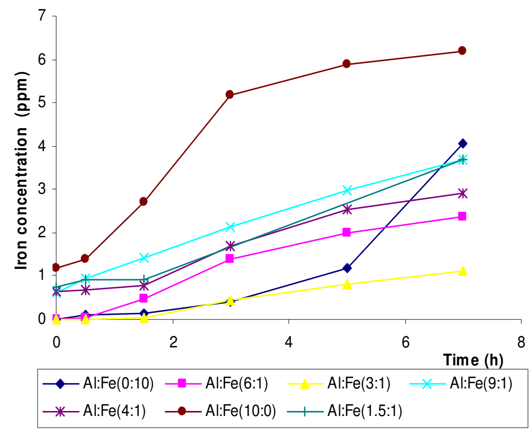

Figure 4: Iron concentration in solution

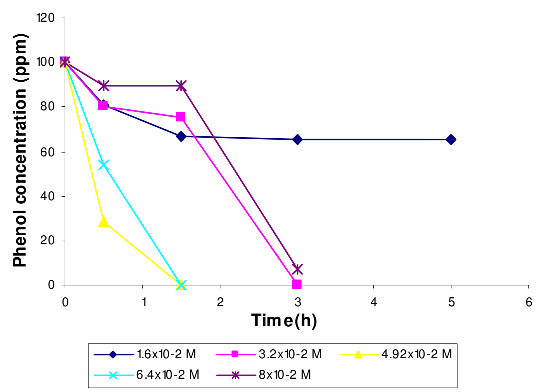

Figure 5. Effect of amount of H_2O_2 on phenol decomposition process

IV - CONCLUSION

Al-Fe pillared clay was successfully synthesized from Thanh Hoa bentonite and Al, Fe solutions. The material has highest catalytic activity at molar ratio of Al/Fe = 1.5/1. Al-Fe pillared clay has catalytic activity for completely degrading phenol at room temperature, sunlight irradiation, opening a new trend to treat persistent organic pollutants using this material.

Acknowledgments. *The support of this work by the National Foundation for Science and Technology Development (Project code 104. 99. 153. 09) is gratefully acknowledged.*

REFERENCES

1. Haiyang Li Yimin Li and Yang Jin React.Kinet.Catal.Lett. Vol. 85(2), 313 - 321 (2005).
2. Aposktolos Vlyssides, Elli Maria Barampouti, Sofia Mai and Anestis Vlyssides, Environmental Engineering Science, Vol. 25, (2008) p.3.
3. C. Walling, Acc. Chem. Res. 8, 125 - 131 (1975).
4. David H. Bremner, Arthur E. Burgess, Didier Houllemare, Kyu-Cheol Namkung, Applied Catalysis B: Environmental, 63, 15 - 19 (2006).
5. Xijun Hua, Frank L. Y. Lama, Lok M. Cheunga, Ka F. Chana, Xiu S. Zhaob, Gao Q. Lub. Catalysis Today, 68, 129 - 133 (2001).
6. M. Masarwa, H. Cohen, D. Meyerstein, D. L. Hickman, A. Bakac, J. H. Espenson. J. Am. Chem. Soc. 110 4293 (1988).
7. Ertl G., Knoziger H., Weitkamp J.,. Preparation of solid catalysts, Ed. Wilay-VCH, Weinkein–NewYork–Chickester - Brisbane-Singapore-Toronto (1999).
8. D. E. W. Vaughan. Catal. Today 2, 187 - 198 (1988).
9. E. Guelou, J. Barrault, J. Fournier, J.-M. Tatibouet. Appl. Catal. B 44, 1 - 8 (2003).
10. Y. Li, Y. Jin, H. Li, React. Kinet. Catal. Lett. 85, 313 - 321 (2005).
11. J. Carriazo, E. Guelou, J. Barrault, J.M. Tatibouet, R. Molina, S. Moreno, Water Res., 39, 3891 - 3899 (2005).
12. M. N. Timofeeva, S. T. Khankhasaeva, S. V. Badmaeva, A. L. Chuvilin, E. B. Burgina, A. B. Ayupov, V. N. Panchenko, A. V. Kulikova. Appl. Catal. B 59, 243 - 248 (2005).
13. J. Carriazo, E. Guelou, J. Barrault, J.M. Tatibouet, R. Molina, S. Moreno, Catal. Today 107 - 108, 126 - 132 (2005).

Corresponding author: **Nguyen Van Noi**
Faculty of Chemistry, Hanoi University of Science VNU-Hanoi
19 Le Thanh Tong Str., Hoan Kiem District, Hanoi, Vietnam.