J MATER SCI **41** (2006) 3001–3006

Iron supported clay as catalysts for oxidation of cyclooctane

W. TRAKARNPRUK*, P. DUMRONGPONG
Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: twimonra@chula.ac.th

Iron supported bentonite clay catalysts have been prepared by the ion exchange of bentonite with iron^{2+} and iron^{3+} solution and immobilization with iron compounds using ligands: acetylacetonate, picolinate, pyrazinate and bipyridine. The catalysts were characterized by FT-IR spectroscopy, X-ray diffraction, X-ray fluorescence analysis and scanning electron microscopy. They were used as catalyst in the oxidation reaction of cyclooctane with *tert*-butyl hydroperoxide as oxidant. The experimental results show that activity of the catalysts is influenced by ligand, it decreases in the following order: acetylacetonate > picolinate > pyrazinate ~ bipyridine. Bentonite supported with iron^{3+} acetylacetonate gave 17% yield with 80% selectivity to cyclooctanone at 70°C for 24 h. The mechanism of the cyclooctane oxidation with *tert*-butyl hydroperoxide was proposed to occur *via* alkyl hydroperoxide intermediate in radical pathway.

---

1. Introduction

Catalytic oxidation reactions generally involve the use of soluble salts or transition metal complexes in combination with oxidants like O_2, H_2O_2 or RO_2H ($R =$ alkyl, aryl). The industrial process for oxidation of cyclohexane uses oxygen as an oxygen donor in the presence of traces of transition metals, e.g. cobalt salts, at temperatures above 150°C with conversion around 4% and selectivities of 85% [1]. Saturated hydrocarbon oxidation using iron^{3+} and copper^{2+} with hydrogen peroxide as oxidant was reported to give high conversion and selectivity [2]. *Tert*-butyl hydroperoxide can also be used in the oxidation of hydrocarbons [3]. Even though homogeneous catalyst gave high yield but its disadvantage is separation of catalyst. Therefore the current tendency is to replace the homogeneous catalysts by their immobilized counterparts. Such catalysts combine the high selectivity of a homogeneous catalyst and the ease of separation of a heterogeneous one. Examples are by incorporation of metals into the framework of zeolites [4], microporous silicates [5] and silica [6]. As a result of the site isolation of the transition metal complexes into or on the support, any bimolecular reaction, leading to a oxidative destruction, is prevented. However, the problem associated with the use of these catalysts is metal leaching. Clays are interesting support as they possess a unique combination of intercalation, swelling and exchange properties, which endows them with the ability to imbibe into their interlayers various cationic species or complexes [7]. Iron is a widely studied metal for catalysts mimicking cytochrome *P*-450 monooxygenase [8], which is capable of oxygenating hydrocarbon in a catalytic way. It is also contained in new biomimetic systems, the Gif IV system (catalyst: $FeCl_2{\cdot}4H_2O$, oxidant, air, electron source: zinc powder) and GoAgg II (catalyst: $FeCl_3 \cdot 6H_2O$, combined oxidant and electron source: hydrogen peroxide) [9, 10].

Therefore, in this work, we report the preparation and catalytic activity of iron supported bentonite clay in the oxidation reaction of cyclooctane.

2. Experimental

2.1. Reagents

All reagents were of analytical grade. Cyclooctane, *tert*-butyl hydroperoxide (TBHP, 70% aqueous) was supplied by Merck. Bentonite was obtained from source in Thailand (Cernic International Co. Ltd). The chemical composition (wt%) was: SiO_2 63.6%, $A1_2O_3$ 17.6%, CaO 3.0%, Fe_2O_3 3.1%, Na_2O 3.4%, K_2O 0.5%, loss on ignition 5.8%, surface area measured by nitrogen adsorption method (BET) is 59 m^2/g and its cation exchange capacity

---

*Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-006-6767-5

determined by the copper bis(ethylenediamine) method [11] is 76 meq/100 g.

2.2. Preparation of catalysts

The general procedure used for the iron exchange into clay was the following: Bentonite (10.0 g) was dispersed in acetone (30 mL) for 24 h and added varying amount of 1 M $FeSO_4$, $FeCl_3$ or $Fe(NO_3)_3$ solution and stirred for 24 h. The solid was centrifuged and washed with deionized water to remove excess iron compound. It was dried at 100°C overnight. These iron exchanged clays were tested for oxidation of cyclooctane, a calcined one (at 300°C for 5 h) was also compared the activity.

Further samples of immobilized clay were prepared as following: Bentonite (5.0 g) was slowly added to 0.06 M solution of $FeCl_3$ in 100 mL methanol to exchange cation of clay with Fe^{3+}. The suspension was stirred at room temperature for 24 h. The solid was filtered, washed with methanol and dried at 50°C under vacuum. Then 1.0 g of dried solid was added to a dichloromethane solution of ligand (2.18 mmol): acetylacetone (acac), picolinic acid (pic), pyrazine-2-carboxylic acid (pyraz) or 2,2′-bipyridine (bipy). In the case of acac ligand, higher amount of ligand was also loaded onto the clay. The suspension was heated under reflux condition for 24 h, filtered and washed with dichloromethane to remove unreacted ligand and dried under vacuum at 50°C. Then the oxidation activities of these catalysts were tested, compared with a calcined one (at 300°C for 5 h).

2.3. Characterization of catalysts

Powder X-ray diffractograms of catalysts were obtained by Rigaku, DMAX 2002/Ultima Plus diffractometer equipped with a rotating anode using Ni filtered Cu–Kα radiation between 2 and 30° (2θ) with a scanning rate of 2°/min. Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer. SEM micrographs of the catalyst were obtained in a Jeol JSM T-300 Scanning Electron Microscopy operated at 20 kV. The iron contents in the catalyst were determined using a SISONS X-ray fluorescence spectrometer ARL 8410 and Varian Spectra-AA300 atomic absorption spectrometer with air/acetylene flame. UV-Visible spectra were recorded on Diode Array Spectrophotometer on Varian 8452 A. The specific areas of the clays were determined by the BET method using the adsorption of nitrogen measured with Quantachrome Autosorb-1 nitrogen adsorptometer. Cation exchange capacity determined by the copper bis(ethylenediamine) method.

2.4. Catalytic reactions

Oxidation of cyclooctane was carried out in a three-necked flask, placed in a temperature equilibrated bath and fitted with a reflux condenser. Typically, a mixture of cyclooctane, solvent (if any) and the catalyst were mixed. Then the *tert*-butyl hydroperoxide (TBHP, 70% aqueous) was added dropwise into the reaction mixture at 10°C. The mole ratio of substrate/oxidant was 2. The temperature was raised to 70°C and the mixture was stirred for 24 h. The reaction mixture was taken, acidified with 25% H_2SO_4 and extracted with diethyl ether, neutralized with saturated solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4. The reaction mixture was analyzed by gas chromatography (GC). A Shimadzu GC-14B gas chromatograph equipped with a DB-1 capillary column (30 m × 0.25 mm × 0.25 μm film thickness) coupled to a flame ionization detector (FID) was used. Detector and injection temperature was set at 220°C, the temperature was increased from 40–180°C at a rate of 5°C/min and nitrogen gas was used as carrier gas. The identity of products were established by comparing the retention times to those of commercially compounds. Product quantification was carried out using ethylbenzene as internal standard. Since cyclooctyl hydroperoxide decomposes in part during chromatographic analysis, its contents were determined by decomposition with triphenylphosphine (PPh_3) and quantification of the additionally formed cyclooctanol by GC [12]. The increase in the quantity of cyclooctanol corresponds to the amount of cyclooctyl hydroperoxide in the sample before the reduction.

2.5. Test of iron leaching

The catalyst (0.4 g) was suspended in selected solvent (10 mL). A 70% *tert*-butyl hydroperoxide (0.7 mL) was subsequently added. The mixture was stirred at 70°C for 24 h. The iron leached out was determined by atomic absorption spectrometer.

2.6. Recycling of the catalysts

As a test of the recycling, the iron supported bentonite catalyst was used for three successive reactions. After each reaction, the catalyst was removed from the reaction mixture by filtration, washed with diethyl ether and dried at 100°C. Then it was subjected to the next catalytic run.

3. Results and discussion

3.1. Catalyst characterization

The catalysts were prepared by ion exchange of bentonite clay with $FeSO_4$, $FeCl_3$ and $Fe(NO_3)_3$ solution and then reacted with ligand: acetylacetone (acac), picolinic acid (pic), pyrazine-2-carboxylic acid (pyraz) or 2,2′-bipyridine (bipy) to immobilize iron compounds. They were characterized by XRD and FTIR. Iron content in the catalysts was determined by AAS (also confirmed by XRF). Cation exchange capacity (CEC) was measured. The data of the catalysts are summarized in Table I.

The X-ray diffractogram of bentonite showed that it contains mainly montmorillonite, d_{001} (11.8 A) was observed at $2\theta = 6.1°$ with some quartz impurity, d_{101} was observed at $2\theta = 26.5°$ [13]. Fig. 1 shows XRD of some

TABLE I. Some physical data of iron-bentonite catalysts

	Ben	Ben/$FeSO_4$ $FeCl_3$ $Fe(NO_3)_3$	Ben/Fe(acac)$_3$	Ben/Fe(acac)$_3$	Ben/Fe(pic)$_2$Cl$_3$	Ben/Fe(pyraz)$_2$Cl$_3$	Ben/Fe(bipy)$_2$Cl$_3$
%Fe_2O_3	3.0	9.0	4.4	8.3	3.8	3.8	3.8
d_{001}	11.8	13.7	13.6	15.3	13.7	13.6	13.6
SE	59	59	60	52	57	58	55
CEC	76	70	63	61	65	64	62

%Fe_2O_3 determined by AAS (values determined by XRF give about 10% higher).
SE = surface area (m^2/g), CEC = cation exchange capacity (meq/100 g).

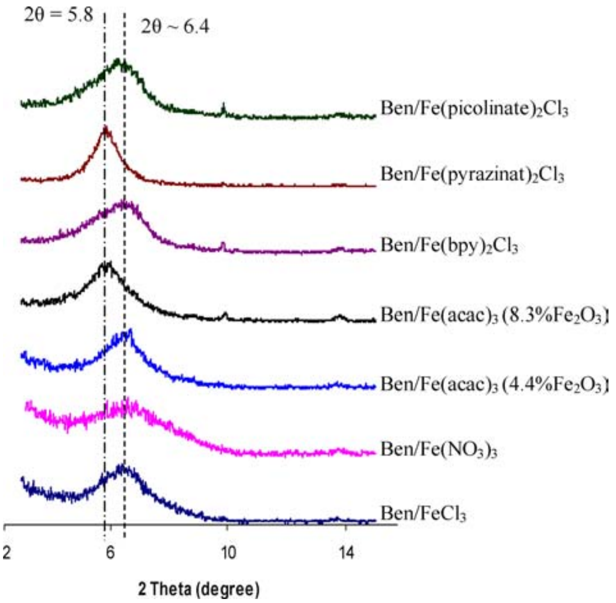

Figure 1 XRD patterns of iron supported bentonite catalysts.

representative bentonites loaded with iron. When the bentonite was loaded with iron, the d_{001} spacing shifted from 11.8 to 13.7 A, For the high iron content loaded catalyst, Ben/Fe(acac)$_3$ (8.3% Fe_2O_3), the XRD shows a remarkable change ($d_{001} = 15.3$ A), indicating intercalation of the iron complexes into the clay interlayers [14].

The specific surface areas of the catalysts were decreased when iron immobilized complex was increased, which can be seen in Ben/Fe(acac)$_3$ (4.4% vs 8.3% Fe_2C_3). This might be explained by agglomeration of iron species on the clay surface [15].

It was observed that the iron exchanged catalysts (Ben/$FeSO_4$/$FeCl_3$/$Fe(NO_3)_3$) had comparable CEC to the starting clay. For the catalysts containing iron complex, their CEC values are smaller compared to the starting clay. This indicated the coagulation of iron and iron cluster on the clay surface [16].

FT-IR spectra of bentonite and iron supported bentonite catalysts were quite similar. They showed O–H stretching at 3624 cm^{-1}, O–H bending at 1400 cm^{-1}. Nevertheless, the shift of Si–O stretching to higher value (from 1026 cm^{-1} in bentonite to 1040 cm^{-1} in iron supported bentonite catalysts) suggests that there is a contribution of Si–O–Fe bonds [17]. For Ben/Fe(acac)$_3$ catalyst, it was observed absorption peak of the acetylacetonate ligand, C=O stretching at 1565 cm^{-1}. It should be noted that after the catalyst calcination, FT-IR spectra revealed the disappearance of this peak as shown in Fig. 2. For Ben/Fe(pic)$_3$Cl$_3$ and Ben/Fe(pyraz)$_3$Cl$_3$ catalysts, they show C=O stretching absorption peak of the picolinate and pyrazinate ligand at 1742 and 1747 cm^{-1}, respectively.

Scanning electron microscopy (SEM) of the bentonite reveals its layer structure. For the supported catalysts, they show the presence of iron aggregate (in Fig. 3), which was also revealed by the qualitative EDX (energy dispersive X-ray technique, Fig. 4).

3.2. Catalytic results

The results of the oxidation of cyclooctane with *tert*-butyl hydroperoxide catalyzed by iron supported bentonite catalysts are given in Table II.

It can be seen that the iron exchanged catalysts: Ben/$FeSO_4$, Ben/$FeCl_3$ and Ben/$Fe(NO_3)_3$ (entries 1, 4 and 6) gave comparable yield. But for the selectivity, Ben/$FeSO_4$ shows higher %on/ol than those in $FeCl_3$ and Ben/$Fe(NO_3)_3$, this might be due to the different oxidation state of iron. It was also mentioned in the other work that $FeCl_2$ gave higher selectivity ratio (ketone/alcohol) than $FeCl_3$ [18].

It should be pointed out that in this work the oxidation reaction was also performed similarly to entry 1 but using mixed solvent (acetonitrile/pyridine = 3:1), it resulted in only 3% yield with %selectivity on/ol = 75/25. This shows that solvent has an effect on both activity and selectivity of the reaction.

When iron content in the catalyst was increased (in entry 1 vs 3 or 4 vs 5), the catalytic results show that the activity for oxidation was decreased. This might be due to the aggregation of iron species in the catalyst which makes them less active or become inactive [19]. A similar result was reported for iron/silica support [20]. The results obtained in this work indicate that for iron exchanged bentonite catalysts, % Fe_2O_3 in the bentonite should be around 9.

For the immobilized catalysts, (entry 7 vs 8) amount of iron in the catalyst also affected the yield. Higher amount

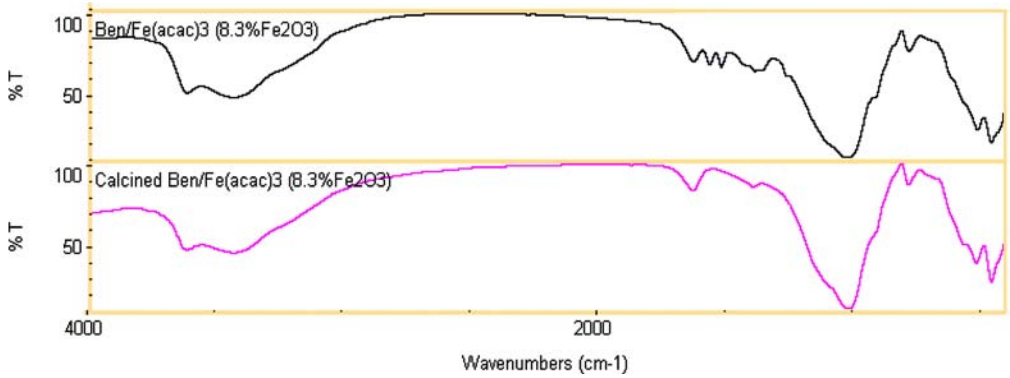

Figure 2 IR spectra of Ben/Fe(acac)$_3$ (above) and calcined Ben/Fe(acac)$_3$ (below).

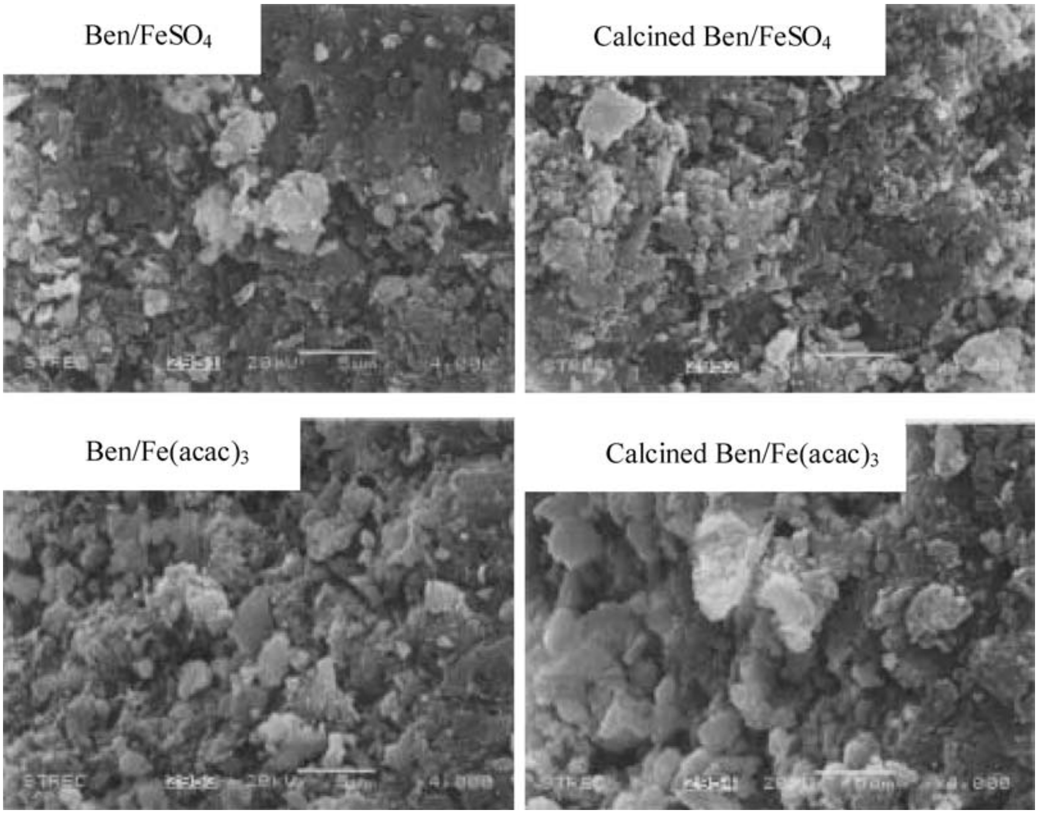

Figure 3 SEM photographs of the catalysts.

of loaded iron resulted in decreasing yield. Even though the amount of iron was not optimized in this work, but it can be seen that for immobilized catalysts, less amount of iron (∼4% Fe_2O_3) can give higher yield than that of exchanged iron catalysts.

It should be noted that reaction performed with added molecular sieve to remove water (entry 9) resulted in a little decreasing yield. This result is similar to the report using montmorillonite/potassium ferrate in the oxidation of benzyl alcohol which showed higher activity in the presence of water [21]. In the case of selectivity, the selectivity to cyclooctanone was decreased when water was removed by adding molecular sieve. This change in selectivity might be explained that in the presence of water, clay surface has high hydrophilicity therefore cyclooctanol which is polar will favor to reside longer time on the surface of clay and reacted further to produce cyclooctanone [22].

Comparison between the calcined and uncalcined Ben/Fe(acac)$_3$ catalysts (entry 7 vs 10), it can be seen that the calcined catalyst shows lower % yield, this can be explained by the loss of the acetylacetonate ligand from the catalyst. It was reported that acetylacetonate ligand increased rate of reaction [23].

For the iron compound immobilized catalysts tested in this work it was found that the ligand affects both the catalyst activity and the selectivity. The order of catalytic activity according to the ligand is: acetylacetonate > picolinate > pyrazinate ∼ bypyridine. It is believed that the presence of ligand, especially bidentate ligand which

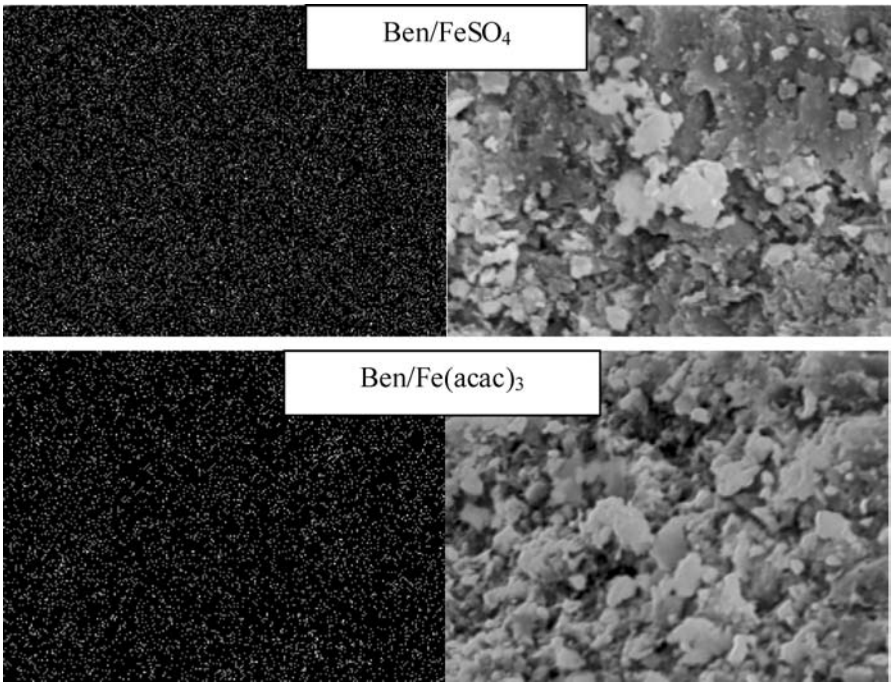

Figure 4 Iron distributions on surface of catalysts.

TABLE 2. Oxidation of cyclooctane with iron supported bentonite catalysts

Entry	Catalyst	%Fe_2O_3 in catalyst	CEC (meq/l00 g)	mmol Fe in reaction	% Yield	%Selectivity on/ol
1	Ben/$FeSO_4$	9.0	70	0.45	13	89/11
2	Cal-Ben/$FeSO_4$	9.0	58	0.45	6	73/27
3	Ben/$FeSO_4$	13.2	66	0.66	3	90/10
4	Ben/$FeCl_3$	9.0	70	0.45	11	78/22
5	Ben/$FeCl_3$	10.5	66	0.52	5	80/20
6	Ben/$Fe(NO_3)_3$	9.1	70	0.45	13	76/24
7	Ben/$Fe(acac)_3$	4.4	63	0.22	17	80/20
8	Ben/$Fe(acac)_3$	8.3	61	0.42	5	78/22
9	Ben/$Fe(acac)_3$*	4.4	63	0.22	14	64/36
10	Cal-Ben/$Fe(acac)_3$	4.4	62	0.22	9	68/32
11	Ben/$Fe(pic)_3Cl_3$	3.8	65	0.18	11	81/19
12	Ben/$Fe(pyraz)_3Cl_3$	3.8	64	0.18	7	75/25
13	Ben/$Fe(bpy)_3Cl_3$	3.8	62	0.18	7	75/25

Cyclooctane 20 mmol, catalyst 0.4 g, TBHP (70% aqueous) 10 mmol, 24 h, 70°C.
Cal- = The catalyst was calcined at 300°C for 5 h.
%Yield (determined by GC) based on cyclooctane.
*added with molecular sieve.

actively coordinates iron atoms that are bound to clay are oriented to the inorganic support, makes the active centers of the catalyst accessible to a substrate. As previously reported for benzene oxidation with hydrogen peroxide, homogeneous iron complex with N,O-ligand is more active than those containing N, N-ligand [24].

In order to check that the catalytic activity is not resulted from iron oxide hydroxide which was detected by XRD to form on the Ben/Fe(acac)$_3$ catalyst which was calcined at 300°C for 5 h, in this work iron oxide (goethite, α-FeO(OH)) was synthesized [25] and tested for the oxidation reaction of cyclooctane, with amount of 1 mmol Fe, under the same condition. It showed a much lower activity, 3% yield with%selectivity on/ol = 70/30. There was also a report that Fe_2O_3 catalyzed oxidation of cyclohexane using oxygen 1 atm gave 16.5% yield with %selectivity on/ol = 40/60 [26]. In addition, it was reported that Fe_2O_3 and Fe_3O_4 catalyzed oxidation of cyclohexane in Gif-KRICT system (pyridine, acetic acid, zinc), gave 4.86% and 5.55% conversion with%selectivity on/ol = 84/16 and 90/10, respectively [18]. Therefore, we believed that the layered structure and hydrophilicity of clay is responsible for the observed results.

3.3. Recycling of the catalyst

Catalyst recycling experiments were carried out with repeated use of the catalyst. After each reaction, the catalyst was removed by filtration, washed and reused. It still showed the similar catalytic activity after 3 cycles.

3.4. Test of iron leaching

The strong metal ion-surface binding is illustrated by leaching studies with dichloromethane and acetonitrile. The results showed that iron was not removed from the support ($<1\%$ leached).

3.5. Reaction pathway

There is a general agreement that *tert*-butyl hydroperoxide (TBHP) chemistry is radical chemistry [27]. The radical pathway was proved by treatment of reaction solution with PPh_3, from the GC analysis, %yield determined before the PPh_3 addition was noticeably lower than that after added [28]. Therefore, it can be proposed that the Fe^{3+} compound was transformed to high valent $Fe^{IV}=O$ species and *t*BuO• initiator radical was formed. In the next step, hydrogen was transfered between *t*BuO• and cyclooctane and c-C_8H_{15}• radical was formed. Then dioxygen from the decomposition of TBHP reacted with c-C_8H_{15}• radical and produced cyclooctylperoxide radical (c-$C_8H_{15}OO$•) that was then converted to cyclooctanone and cyclooctanol in the final step.

4. Conclusions

The layered aluminosilicate like bentonite is shown to be a good support for immobilizing iron as its layered structure enables the intercalation of iron complexes and the specific orientation of a substrate in the course of oxidation. The iron supported bentonite catalysts prepared in this work are efficient in oxidizing cyclooctane with low amount of oxidant under mild condition, resulting in good yield and high selectivity to cyclooctanone. The advantages of these catalysts are the inexpensiveness and easy preparation of the catalysts.

Acknowledgements

The authors thank Graduate School, Chulalongkorn University for financial support on this work.

References

1. G. W. PARSHALL and S. D. ITTEL, in Homogeneous Catalysis 2nd edn. (John Wiley & Sons, New York, 1992) p. 242.
2. D. H. R. BARTON, S. D. BÉVIÈRE, W. CHAVASIRI, E. CSUHAI and D. DOLLER, *Tetrahedron* **48** (1992) 2895.
3. U. SCHUCHARDT, R. PEREIRA and M. RUFO, *J. Mol. Catal. A: Chemical* **135** (1998) 257.
4. W. A. CARVALHO, M. WALLUA and U. SCHUCHARDT, *J. Mol. Catal. A: Chemical* **144** (1999) 91.
5. R. CRUZ, J. SILVA, U. ARNOLD, M. SERCHELI and U. SCHUCHARDT, *J. Braz. Chem. Soc.* **13** (2002) 170.
6. H. H. MONFARED and M. GHORBANI, *Monatshefte för Chemie* **132** (2001) 989.
7. J. KONTA, *J. Appl. Clay Sci.* **10** (1995) 275.
8. J. B. VINCENT, G. L. OLIVIER-LILLEY and B. A. AVERILL, *Chem. Rev.* **90** (1990) 1447.
9. D. H. R. BARTON, K. W. LEE, W. MEHL, N. OZBALIC, L. ZHAN, *Tetrahedron* **46** (1990) 3753.
10. D. H. R. BARTON, D. DOLLER, Y. U. GELETH and E. CSUHAI, *Tetrahedron* **47** (1991) 6561.
11. F. BERGAYA and M. VAYER, *Appl. Clay Sci.* **12** (1997) 275.
12. P. A. JACOB, P. G. ROUXHET, M. I. GENET, D. E. VOS and D. L. VANNOPEN, *Angew. Chem. Int. Ed. Engl.* **34** (1995) 56.
13. E. R. GRIM, in Clay Mineralogy (McGraw-Hill, New York, 1962).
14. D. GOURNIS, M. LOULOUDI, M. KARAKASSIDES, C. KOLOKYTHA, K. MITOPOULOU and N. HADJILIADIS, *Mat. Sci. Eng.* **22** (2002) 113.
15. A. PARMALIANA, F. ARENA, F. FRUSTERI, A. MARTÍNEZ-ARIAS, M. L. GRANADOS and J. L. FIERRO, *Appl. Catal. A: General* **226** (2002) 163.
16. E. GUÉLOU, J. BARRAULT, J. FOURNIER and J.-M. TATIBOUËT, *Appl. Catal. B: Environ.* **1346** (2003) 1.
17. S. ROSENIRA, M. JULIANA, A. ULRICH, A. S. D. MAURICIO and S. ULF, *J. Brazil Chem. Soc.* **13** (2002) 170.
18. O.-S. PARK, S.-S. NAM, S.-B. KIM and K.-W. LEE, *Bull. Korean Chem. Soc.* **20** (1999) 49.
19. N. GROOTBOOM and T. NYOKONG, *J. Mol. Catal. A: Chem.* **179** (2002) 113.
20. Y. IAMAMOTO, Y. M. IDEMORI and S. NAKAGAKI, *J. Mol. Catal. A: Chem.* **99** (1995) 187.
21. L. DULAUDE, P. LASZIO and P. LEHANCE, *Tetrahedron Letters* **36** (1995) 8505.
22. E. PARDO, F. LLORET, R. CARRASCO, M. C. MUÑOZ, T. TEMPARAL-SÁNCHEZ and R. RUIZ-GARCÍA, *Inorg. Chim. Acta* **357** (2004) 2713.
23. W. CHAVASIRI and D. O. JANG, *Bull. Korean Chem. Soc.* **18** (1997) 362.
24. D. BIANCHI, R. BORTOLO, R. TASSINARI, M. RICCI and R. VIGNOLA, *Angew. Chem. Int. Ed.* **39** (2000) 4321.
25. M. KOSMULSKI, E. MACZKA, E. JARYCH and J. B. ROSENHOLM, *Adv. Colloid Interface Sci.* **103** (2003) 57.
26. N. PERKAS, Y. KOLTYPIN, O. PALCHDC, A. GEDAKEN and S. CHADRASEKARAN, *Appl. Catal. A: Gen.* **209** (2001) 125.
27. F. MINISCI, F. FONTANA, S. ARANEO, F. RECUPERO and L. ZHAO, *Catalysis. Synlett* (1996) 119.
28. G. V. NIZOVA, B. KREBS, G. SÜSS-FINK, S. SCHINDLER, L. WESTERHEIDE, L. G. CUERVO, G. B. SHUL'PIN, *Tetrahedron* **58** (2002) 9231.

Received 7 May
and accepted 13 September 2005