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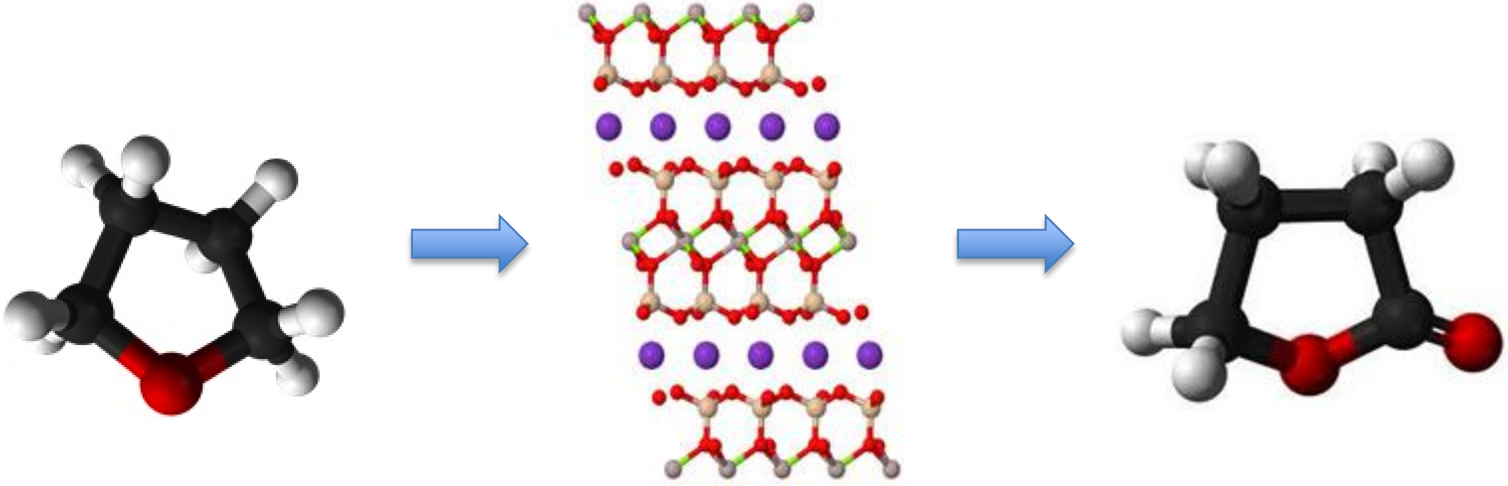

Earth-abundant iron-containing clay can be applicable as an oxidation catalyst for butyrolactone production from biomass-derived tetrahydrofuran using hydrogen peroxide as oxidant at mild condition.

Oxidation of tetrahydrofuran to butyrolactone catalyzed by iron-containing clay

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Abstract

The thermally treated iron-containing clay was used as a greener oxidation catalyst for the conversion of tetrahydrofuran (THF) to butyrolactone (BTL). Mild liquid phase reactions were tested at 50-66 ^oC using hydrogen peroxide (H_2O_2) as oxidizing agent. XRD, TGA, ESR, DR-UV, and FTIR revealed the dislodged iron oxide species formed by treating at ≥ 500 ^oC become active oxidizing species on the surface upon contacting with H_2O_2. Such active species can promote oxidation of THF giving high yield and selectivity of BTL. While the iron-containing clay treated at lower temperature (< 500 ^oC) perform Fenton-like oxidation with lower THF conversion and non-selective product. 2-Hydroxy tetrahydrofuran (THF-2-ol) was primarily produced and further oxidized to BTL with small amount of 4-hydroxybutyric acid as minor products. Minimal H_2O_2/THF ratio as 1.0 is sufficient for production of BTL. Deactivation can be observed presumably due to deposition of the products despite of a slight leaching of active iron species.

Keywords: Greener oxidation, Iron-containing clay, Tetrahydrofuran, Thermal treatment

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1. Introduction

Because of factors such as the finite reserves of petroleum, their unequal geographic distributions, and the environmentally motivated desire to decrease CO_2 emissions, renewable feedstocks, such as lingo-cellulosic biomass, have become promising candidates for the production of renewable fuels and chemicals. One of an attractive biomass-derived chemical feedstock is butyrolactone (BTL). Its demand is steadily growing due to the major use as an important intermediate for biodegradable polymer and a direct use as a dielectric material or a solvent. BTL is typically produced using two processes: (i) Davy McKee process based on the hydrogenation of diethyl or dimethyl maleate and (ii) Reppe process based on acetylene and formaldehyde.[1] Alternatively, oxidation of tetrahydrofuran (THF) can be applied for the production of BTL. The THF can be simply obtained by decarbonylation and hydrogenation of the furfural derivatives[2] found mainly in biomass pyrolysis oil.

Selective oxidation[3-10] is one of the key approaches for production of BTL from THF. The earlier reports describe the synthesis of BTL by the organometallic-catalyzed oxidation of THF, which was performed homogeneously with BTL selectivity of 22-100% depending on the oxidant types.[11-14] Although molecular oxygen (O_2) is a cheap oxidant with no waste, its oxidation potential is limited due to a long reaction time (> 24 hours). Even though H_2O_2 is more expensive than the molecular oxygen, it can be the oxidant of choice for fine chemicals because of its simplicity of operation.[11-12] Salavati-Niasari *et.al.*[9] reports that bis(macrocyclic) copper(II) complexes containing aromatic linkers can catalyze the oxidation of THF to give BTL under mild conditions. However, the homogeneous process has some disadvantages, such as expensive catalyst. As a comparison, heterogeneous catalytic processes serve as an environmentally benign alternative for easy catalyst separation, regeneration, and relatively low process cost.

Encapsulated complexes ($[Cu(R_2[16]aneN_6)]^{2+}$/Zeolite Y)[14] is example of early attempt for heterogeneously catalytic system for this approach. However, it yields mainly 2-hydroxytetrahydrofuran (THF-2-ol) and insignificant amount of BTL while, with their homogeneous counterparts, selectivity to BTL are higher.[14] Titanosilicates (TS-1) can be used as heterogeneous catalyst for the oxidation of THF to BTL in moderate to good yields in the presence of dilute aqueous H_2O_2 as oxidant.[10] However, such catalysts in use today are based on expensive, and methods of preparing catalysts continue to be complicated, and laborious. Iron is the element of choice that performs a number of chemically challenging oxidative processes. Fenton's reagent[15-16], a mixture of Fe(II) ions and H_2O_2, is widely applied to oxidize organic substrates. In the last decade, several systems based on heterogeneous Fenton-like catalyst (Fe-supported solids), such as iron oxides, zeolites, pillared clays, and alumina, have been investigated for use in environmental remediation processes.[15-18] Some preliminary studies using iron-containing clay based catalysts have shown the promising possibilities of this kind of catalysts because they are natural, abundant, inexpensive, and environmental friendly.

In this research, greener oxidation using earth-abundant iron-containing clay as catalyst and H_2O_2 as oxidizing agent is investigated for BTL production under mild condition. The heterogeneous oxidizing sites can be generated by simple thermal treatment at high temperature. The ESR, DR-UV and FTIR study permits us to detect the active oxidizing iron species. Effects of thermal treatment and role of the oxidizing iron species on BTL production from THF are discussed. Reaction pathway for the selective oxidation is also generalized.

2. Experimental

2.1. Catalyst preparation and characterization

The iron-containing clay was obtained from the SCG Chemicals. The sample was brown color and used as received. Such parent clay possesses a relatively high wt.% of Fe (~ 5 %), which makes it ideal as oxidation catalyst. The sample was treated at 100-700 ^{o}C for 5 hours and designated as Clay-Temperature according to their treatment temperature. XRD and TGA provided information on the catalyst structure and phase transformation upon thermal treatment. BET surface areas of the all samples were also determined. The ESR spectra was taken in the X-band at 20 ^{o}C and registered at 1 mW microwave power in the field range of 10-810 mT (one scan with a sweep time of 4 min). The diffuse reflectance UV-VIS spectra of the clay samples in the form of self-supporting pellets were recorded with $BaSO_4$ coated integration sphere. FTIR spectra was acquired in the transmission mode at room temperature over the wavenumber range of 4000-650 cm^{-1}.

2.2. Catalytic testing

In a typical procedure for oxidation of THF; a mixture of iron-containing clay as catalyst (0.05-0.20 g) and THF (0.05 mol) was stirred for 30 min in a 100 mL round bottom three-necked flask equipped with a condenser. Then 0.05 mol of the H_2O_2 (30% in H_2O) was added via the dropping funnel. The mixture was then heated under reaction temperature (50 ^{o}C and 66 ^{o}C) for 1-8 hours. At the end of reaction, the mixture was quenched in an ice bath and the solid catalyst was separated from the solution by cold-filtration. The remaining H_2O_2 residual was analyzed using iodometric titration method.[19] The cold mixture was promptly analyzed by GC-FID to avoid further oxidation and the products are identified using GC-MS. The products containing H_2O_2 residual was disposed according to literature.[20]

3. Results and discussion

3.1. Catalytic characterization

The parent iron-containing clay shows a strong diffraction peak corresponding to montmorillonite and magnetite (Fe_3O_4 or $FeO{\cdot}Fe_2O_3$) crystallite (Fig. 1). As being a mineral, it is expected that these two phases are separately aggregated and existed as a physical mixture. Under thermal treatment ≥ 500 ^{o}C, such iron-containing clay catalyst was completely transformed into illite and hematite (Fe_2O_3). The TGA and DTG profile of the catalyst sample showed the major weight-loss at 60-180 ^{o}C, corresponded to desorption of the physisorbed water and the minor weight-loss at 450-700 ^{o}C, denoted the dehydroxylation of iron hydroxide and/or clay layer (Fig. 2a). In consistent with TGA, a noticeable decrease in the terminal hydroxyl group (Si-OH, Al-OH) is observed by FTIR at ~3630 cm^{-1}, together with a lower intensity of bands at ~3500-3250 cm^{-1} (Fig. 2b) and ~ 1630 cm^{-1} (Fig. 2c) corresponded to the adsorbed water. A significant change in BET surface area is in line with the observed phase change by thermal treatment. While Fe content remains similar for all samples (Table 1).

As phase transformation take place upon calcination at ≥ 500 ^{o}C, DR-UV reveals different coordination of the Fe species as shown in Fig. 3a. It can be seen that Clay-100 and Clay-300 exhibit only two absorption edges at about λ ~263 nm and 525 nm, corresponding to octahedral Fe(III) substituted for Al(III)[21], and larger particles of Fe_2O_3 aggregates[22], respectively. This suggests that certain amount of Fe is also present in the clay structure, not only as separated magnetite aggregates. However, the additional signal of the 425 nm band ascribed to the oligomeric octahedrally coordinated Fe(III) species[22], can be observed on the Clay-500. This Fe species is presumably formed by dislodgement of the substituted Fe(III) in the clay structure upon dehydroxylation, and then segregated within the clay layer. The presence of this oligomeric Fe species is also evidenced as a series of ESR signals superimposed on the major resonance of Fe oxides clusters at g = 2.3[23-24] as shown in Fig. 3b. Experimentally, the intensity of the ESR line at g = 2.3 increased significantly when the parent clay was thermally treated due to the transformation of Fe_3O_4 to Fe_2O_3. However, such a series of the superimposed signals are only pronounced when the sample was treated at 500 ^oC, in consistence with an additionally observed UV signal at 425 nm, as discussed above.

It is worth noting that the weak ESR signal at g = 4.2 assigned to the presence of isolated Fe(III)[23-24] in the tetrahedral or octahedral coordination is observed for all sample. For the clay minerals, this corresponds to the Fe located in the interior of the clay sheets (iron substituting aluminum in the octahedral layers).

3.2. Oxidation of tetrahydrofuran

Table 2 shows the activity of various thermally treated iron-containing clay catalyst in the oxidation of THF to BTL. The Clay-500 exhibits relatively higher activity, as compared to those from the Clay-100, Clay-300, and Clay-700. It is clear that the oxidation activity is generally increased with treating temperature. However, the lower activity observed in the reaction using Clay-700 as the catalyst is presumably due to the significant loss of catalyst surface area (Table 1) by further dehydroxylation at 700 ^oC. This is consistent with the TGA/DTG, and FTIR results (Fig. 2) that show the dehydroxylation of clay layer.

With respect to the same range of catalyst surface area (72-85 m^2/g), the increase in activity with the treatment temperature can be accounted for the degree of dehydroxylation and hence the formation of oligomeric octahedrally coordinated Fe(III) species formed by dislodgement of the substituted Fe(III) in the clay structure, as evidenced by TGA, FTIR, DR-UV, and ESR. This is speculated from a linear relationship between the catalyst activity (conversion) and the UV absorbance at 425 nm that corresponded to such Fe(III) species as shown in Fig. 4. It is expected that the dislodged Fe(III) oxide species would possess higher degree of coordinative unsaturation, as compared to those in the bulk oxide. Hence, H_2O_2 can readily react with such Fe(III) species forming high valence iron-oxo, peroxo or superoxo species (Surface-Fe=O, Surface-Fe(O-O) or Surface-$FeOO^{\cdot -}$)[25-28] that acts as oxidizing species. As higher extent of dehydroxylation was observed when treated at 500 °C, higher fraction of dislodged Fe(III) oxide species and hence higher activity could be expected.

The presence of active oxidizing species generated by reaction of H_2O_2 and the dislodged Fe(III) oxide can be further supported by FTIR spectroscopy. From Fig. 5, the band at ~1000 cm^{-1} were assigned to Fe-O-H overlapped with Si-O-Al in montmorillonite[29], while the signal at and 916 cm^{-1} can be referred to Al_2-OH.[30] Interestingly, a new signal at 1050 cm^{-1} become pronounced when H_2O_2 is introduced into Clay-500. This relatively high frequency signal is generally attributed to O-O stretching of end-on superoxo or peroxo complexes.[31-34] Hence, it is proposed in this work to be derived from the formation of high-valence iron-superoxo or peroxo species (Fe-O-$O^{\cdot -}$ or Fe(O-O)) on the surface of dislodged Fe oxide via surface oxidation by H_2O_2. This species may well be an active oxidizing species, or may also be a precursor of a hydroxylhydroperoxyl Fe species (Fe(OH)(OOH))[28, 35] that promote oxidation of THF. It is important to emphasize that this additional signal at 1050 cm^{-1} is particularly obtained only for the clay treated at high temperature (Clay-500 and Clay-700). Without a certain degree of dehydroxylation and hence the presence of dislodged Fe oxide species, the bulk Fe oxide and substituted Fe in the clay structure may be too stable to interact with H_2O_2 to form such Fe superoxo or peroxo species. The formation of the active site can be proposed as follows;

Fe(III) oxide in the framework $\rightarrow$ Surface-Fe(III) (Dislodged species) Eq. (1)
Surface-Fe(III) + H_2O_2 $\rightarrow$ Surface-Fe(III)-$O_2^{\cdot-}$ Eq. (2)
Surface-Fe(III)-$O_2^{\cdot-}$ + H_2O $\rightarrow$ Surface-Fe(IV)(OH)(OOH) Eq. (3)

One could expect that the Fenton-type oxidation[36-37] would be also responsible for the observed activity. This may be true in the case of iron-containing clay treated at low temperature (Clay-100 or Clay-300) since a larger fraction of Fe(II) oxide species is present in these samples. However, a relative lower conversion of THF was obtained from the reaction over Clay-100 or Clay-300. This is because the Fenton process involves the reaction of Fe(II) with H_2O_2, giving rise to hydroxyl radicals ($^{\bullet}OH$) (Eq. (4)). This catalytic cycle can be completed by the reduction of Fe(III) to Fe(II) (Eq. (5)).[37]

Surface-Fe(II) + H_2O_2 $\rightarrow$ Surface-Fe(III) + $^{\bullet}OH$ + OH^- Eq. (4)
Surface-Fe(III) + H_2O_2 $\rightarrow$ Surface-Fe(II) + $^{\bullet}OOH$ + H^+ Eq. (5)

Since the reduction of Fe(III) to Fe(II) by H_2O_2 is extremely slow[38-40], the Fe(III) would be accumulated in the system and that would result in a low activity.[41] Therefore, the observed higher activity for the catalyst treated at higher temperature (Clay-500) suggests that the active oxidizing center would be derived from the high-valence iron-oxo species that is formed by interaction of H_2O_2 with the dislodged Fe(III) oxides, rather than the Fenton-type species. For all catalysts, butyrolactone (BTL) is the main product from THF oxidation. Major co-products include 2-hydroxytetrahydrofuran (THF-2-ol) and 4-hydroxybutyric acid (4-HBA). Furanone and polyhydroxy derivatives of the aboves are also observed. It is clear from Fig. 6 that the conversion is increased together with yields of all products when both catalyst content and reaction time is increased, suggesting that the reaction is catalytically controlled. As BTL and THF-2-ol appears to form in parallel, these products may well be derived from the decomposition of the parent hydroperoxide intermediate (in a manner similar to ketone-alcohol from the decomposition of alkyl hydroperoxide). However, it is noticed that THF-2-ol yield start to level off while yields of BTL and 4-HBA are steadily increased with conversion. This also suggests that THF-2-ol may well be primarily produced from the oxidation of THF and become a precursor of BTL and 4-HBA (Scheme 1). In the mechanistic point of view, the H-abstraction at from the carbon adjacent to the oxygen in THF can be most likely promoted and hydroxylation at this position readily leads to formation of THF-2-ol. This product is prone to be further oxidized to BTL. It is possible that the BTL is formed either by (i) direct oxidation of THF-2-ol while the ring is kept intact or by (ii) ring opening of THF-2-ol to 4-hydroxybutanal that is subsequently oxidized to 4-HBA. This ω-hydroxy acid can also undergo self-esterification to form BTL. Although 4-HBA is actually found as evidence for the ring opening-oxidation (ii), it is unlikely that self-esterification of 4-HBA to form BTL is the case in the reaction with large amount of water present. Moreover, selectivity of 4-HBA is relatively small and it is increased together with BTL selectivity while THF-2-ol selectivity is reduced with increased conversion (Fig. 7). This suggests that BTL and 4-HBA may be produced in paralleled, presumably from the oxidation of THF-2-ol. It is also worth noting that BTL is relatively stable under the reaction condition and no hydrolysis of BTL to 4-HBA was observed when BTL was used as feed in a separate test (not shown). The overall reaction pathway can be proposed as shown in Scheme 1.

As also seen in Fig. 7, small amounts of other products, such as 2-furanone and 3,4-dihydroxytetrahydrofuran were obtained with increased catalyst content and time. However, no significant change in the selectivity can be observed at lower temperature (Table 2). These co-products may be the result of further oxidation of C-H bond at different positions on the major products. However, the selectivity of these products is particularly high in the reaction using Clay-100 and Clay-300 as catalysts despite lower conversions were obtained (Table 2). This is presumably because there is much less amount of dislodged Fe(III) oxide present in these samples, and hence less number of active Fe superoxo or peroxo species as discussed earlier. Nevertheless, the oxidation of THF can be somewhat facilitated via •OH radical mechanism that is promoted by decomposition of H_2O_2 over Fe(II) oxide surface. Although, they are less active as compared to the Clay-500, the •OH radical initiates a radical chain reaction by randomly abstracting hydrogen atom from THF. This leads to the generation of carbon radicals that undergo oxidation to various oxygenated products.

From Fig. 6b, it can be seen that the activity is gradually declined over the course of the reaction. This can be accounted either for (i) limit of the oxidant, H_2O_2 or (ii) deactivation of the catalysts. Accordingly, the effect of H_2O_2/THF ratio was investigated and it is clear that the decline activity observed in Fig. 6b is not due to the limit of H_2O_2. As seen from Fig. 8, no significant increase in activity is obtained when H_2O_2/THF ratio was raised to 2. This suggested that H_2O_2/THF ratio of 1 is sufficient for the oxidation of THF to BTL and shall not restrain the activity as observed in Fig. 6b. Although the excess H_2O_2 does not strongly effect the conversion, selectivity of 4-HBA and other products are slightly increased with H_2O_2/THF ratio while THF-2-ol selectivity is decreased. This indicates that further oxidation of THF-2-ol can be promoted when H_2O_2 is in excess.

According to the study on the effect of H_2O_2, it appears that the observed decline in activity after 4 hours would be resulted from the catalyst deactivation. This may be due to adsorption of products on the catalyst surface or leaching of the active iron species. However, it is clear from Fig. 9 that severe catalyst leaching is not the case. This is because, as the catalyst recovered from THF oxidation experiment was tested under similar condition for another three cycles, the catalytic activity is reproducible in consecutive experiments without a remarkable drop in the efficiency. This again indicates the absence of significant deactivation of the catalyst due to iron leaching, but presumably due to the adsorption of products and the washing with THF or appropriate solvent, can easily regenerate the catalyst.

Conclusions

Butyrolactone can be successfully produced via a greener oxidation of THF using earth-abundant iron-containing clay as catalysts. The active oxidizing species can be obtained by thermal treatment at temperature ≥500 ^{o}C. The dehydroxylation of the clay structure leads to partial dislodgement of the iron oxide species that can react with hydrogen peroxide. Spectroscopic evidences suggest the formation of Fe superoxo or peroxo upon contacting hydrogen peroxide with the dislodged Fe oxide species, which is also well correlated with the observed activity. It appears that 2-hydroxytetrahydrofuran (THF-2-ol) is a primarily product from THF oxidation. This product is further oxidation of butyrolactone (BTL), 4-hydroxy butyric acid (4-HBA) and other oxidized products. Up to 70% selectivity of BTL is obtained over Clay-500 catalyst. H_2O_2/THF ratio of 1.0 is sufficient for BTL production and no significant leaching of the active species can be observed. The catalyst can be simply regenerated by washing with the feed, THF, and re-used at least 4 cycles without significant drop in activity.

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