修士学位論文

Development of Aluminium-exchanged Montmorillonite as a Solid Acid Catalyst for Triose Transformation

トリオース変換反応に向けた固体酸触媒としてのアルミニウム交換モンモリロナイト触媒の開発

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CONTENTS

Chapter 1. General Introduction

Chapter 2. A Highly Efficient Synthesis of Alkyl Lactates from Triose Using Reusable Aluminium-exchanged Montmorillonite Catalyst

General Conclusion

Acknowledgement

Chapter 1.

General Introduction

1. Background

Green chemistry is a demanding but richly promising field. It underlies chemistry and increasingly biology, engineering, and medicine as well as in developing highly valuable materials. It is an essential application for chemical engineering, materials science, environmental science, and biophysical chemistry. In this era of diminishing petroleum reserve, our society should find an alternative ways to utilize the abundant and renewable biomass resources effectively to produce new sources of energy and highly-demand chemical intermediate [1].

In the future, the author believes science and technology will be focused to meet the requirement for clean and environmentally benign technologies in chemical process engineering. For instance, the establishments of environmentally-friendly catalytic processes in solving environmental problems caused by industrial plants are likely in reducing the production of green house gases, developing highly efficient catalyst, converting waste product to become commercially valuable products, minimization of by-product formations, simplification of workup procedures, and removal of toxic reagents [2].

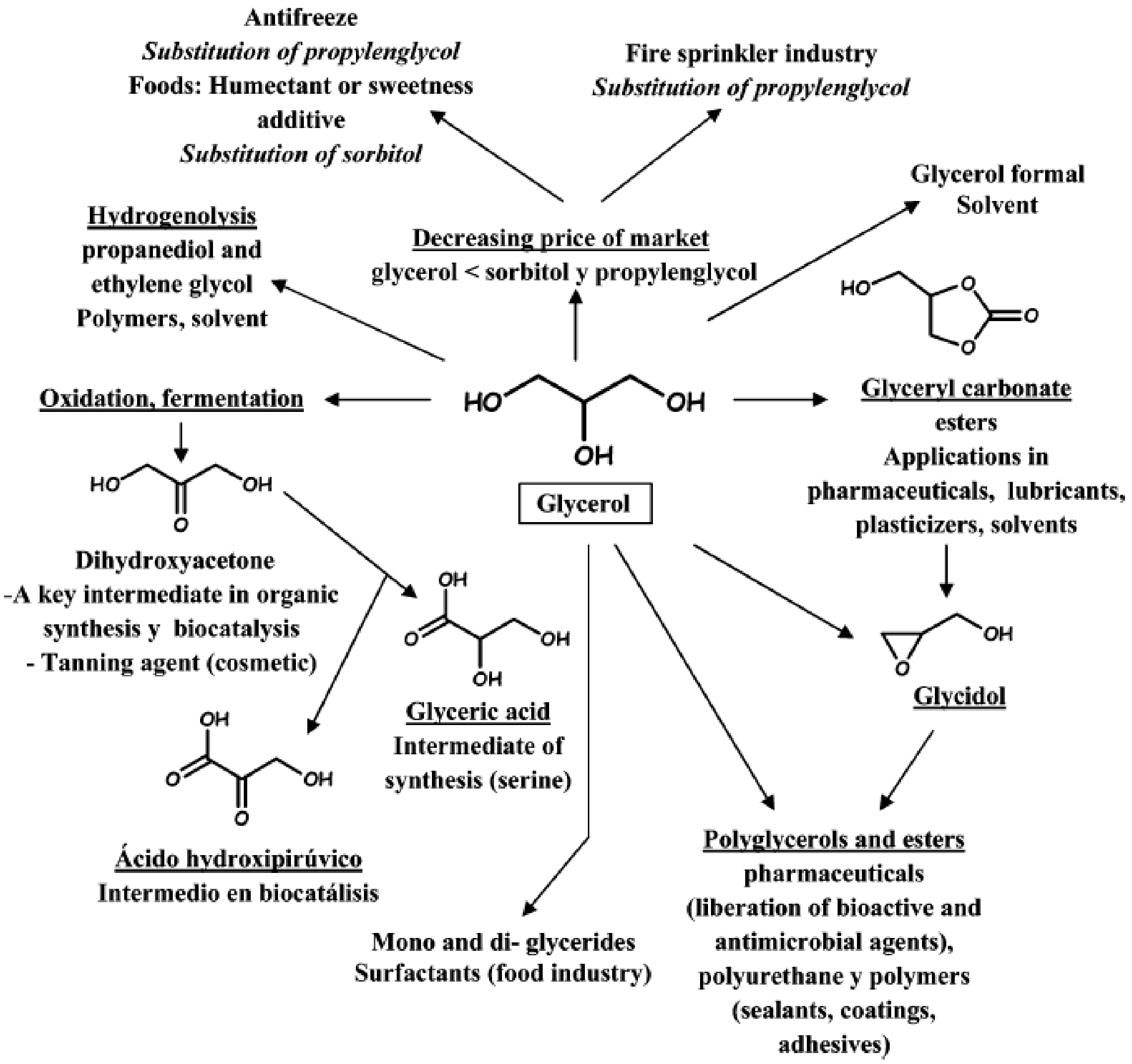
By converting inexpensive materials to highly valuable compounds under mild conditions with high atom efficiency and lowering the activation energy of the chemical reaction, catalyst will play a decisive role in developing a sustainable society, because catalysts have the potential to solve the problems concerning energy, resources, and health [3]. The current trend of research mainly directed towards the development of high-performance heterogeneous catalysts for environmentally-friendly chemical processes. The development of well-defined active metal sites on a solid will aids an understanding of the molecular basis of heterogeneous catalysis, especially the path and mechanism of catalyzed reaction [4].

1-1. Biomass Derivatives as Chemical Sources

Over the years, biodiesel has emerged as a viable fuel and fossil fuel additive to replace sulfur according to strict environmental policy, thereby reducing emission and conserving fossil fuels. As biodiesel production soars, so does glycerol. Unfortunately, high production cost made biodiesel profitless without government subsidies [5]. However, its increasing production is predicted to spread and increase, hence provides advantages to merit subsidy as the conversion of glycerol are likely to absorb the high cost of biodiesel by 6% by lowering the dependence on natural-gas-derived methanol. The production of methanol from glycerol for example, could reduce the burden due to low-value waste glycerol.

Until July 2006, pure glycerol was sold at 600–800 € per ton while crude glycerol of high quality obtained by biodiesel production was sold at 600–700 € per ton with glycerol currently priced at around 850 USD per ton. Even at prices approaching 770 USD per ton, glycerol becomes a major platform chemical. If biodiesel production grows to 3.23 million tons worldwide, an extra 323000 tons of glycerol would reach the market thus rendering glycerol as a readily available commodity [6]. Meanwhile, the US biodiesel industry is expected to 1 billion pounds of glycerol into a worldwide market which is currently around 600 million pounds. Again, the economics of biodiesel depend heavily on the utilization of glycerol because it can absorb the production cost of biodiesel.

There are number of research have been done in converting glycerol to commercially valued products through selective chemical processes [6]. Still, selectivity and catalytic activity are the main constraint. The development of heterogeneous systems is preferable because of the simplicity of catalyst and product to be isolated from the reaction mixture, beside the possibility of the reaction to operate continuously in heterogeneous systems. The potential of glycerol in future biorefineries must not be forgotten as its derivatives are very useful in fuels, chemicals, pharmaceutical, and other promising industries. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic bio-based industry. Its concept is similar to current petroleum refineries where it produces various types of fuel and petroleum-based products [7].



Scheme 1. Potential Application from Glycerol as Chemical Feedstock

One of the products that can be obtained from glycerol is dihydroxyacetone (DHA), a type of triose [8]. DHA is used in the manufacture of tanning products. It reacts with the amino acids contained in the surface cells of the skin, which then develop a darkening or tanned effect. It is a nontoxic ingredient and has been approved by the U.S. FDA for application in cosmetics. The main source of DHA is raw sugar cane fermentation with glycerine. Today, DHA is commercially produced by the fermentation route by Merck and Daicel [9].

1-2. Transformation of Triose to Lactate Derivatives

A triose is a class of monosaccharide which consist three carbon atoms in its structure. There are only two types of trioses which is an aldotriose (glyceraldehydes) and a ketotriose (dihydroxyacetone). These trioses are essential for respiration. Biologically, lactic acid and pyruvic acid can be produced by glyoxalase enzyme system from dihydroxyacetone phosphate (DHAP), which catalyzes an intramolecular methylglyoxal rearrangement system in our body [10].

Industrially, the production of lactic acid is carried out through the fermentation of dextrose by using lactic acid bacilli [11]. However, the biological processes always suffer from severe drawbacks. For instance, this process is time-consuming because of the slow rate of reaction. Besides that, low concentration of products and needs for product separation make this process unpractical in term of cost and green chemical synthesis standpoints.

Therefore, chemical methods are likely to meet these requirements and have been reported recently. For example, R. Kelly has patented the production of n-butyl lactate from DHA in butanol solution, catalyzed by $CrCl_3.6H_2O$ [12]. This homogeneous catalyst is known for its toxicity and difficult separation. Moreover, limited scope of substrate in which, lower catalytic activity is observed in case of alcohol solutions other than butanol.

Then, Sasaki and Hayashi reported that better activity can be performed by $SnCl_4.5H_2O$ [13]. This catalyst gave correspond alkyl lactates for 82, 84, and 91 % yields in methanol, ethanol, and butanol solutions while the formation of by-products is detected. They proposed the formation of pyruvic aldehyde as an intermediate, followed by esterification to afford alkyl lactate. This catalyst system also can be applied if using pyruvic aldehyde as a substrate to give 88, 74, and 78 % in methanol, ethanol, and butanol solution, respectively.

Mønsted and co-worker also developed a mechanism of lactic acid formation catalyzed by tetraamine macrocyclic Chromium and Rhodium complexes [14, 15]. Their observation revealed that the transformation pyruvic aldehyde to lactic acid involve bidentate substrate coordination followed by protonation, dehydration, and carbocation formation. Hence, intramolecular 1,2-hydride shift and deprotonation were occured to complete reaction mechanism. This argument was related to the Zinc-containing glyoxalase I enzyme which perform similar transformation in natural system. In the case of trioses as a substrate, the mechanism is more complicated and ^{1}H NMR study showed that one of hydrogen atom in the methyl group is originated from water solvent.

An attempt to utilize solid catalyst was pioneered by Janssen and co-workers [16]. They found that Y-type zeolite can be considered as a functional biomimics of glyoxalase enzyme. In this reaction, they use DHA dimer as a substrate in ethanol solution. They also suggested the formation of pyruvic aldehyde as an intermediate. The existence of Brønsted acid site in zeolite structure favour the formation of pyruvic aldehyde diethyl acetals while steam-treated zeolite which expected to contain high amounts of extra framework aluminium (EFAL) species show tendency to form ethyl lactate. The behaviour of EFAL species as Lewis acid which remains unclear is believed to influence the selectivity towards ethyl lactate or pyruvic aldehyde diethyl acetals.

Very recently, Christensen and his group utilize Sn-beta as strong Lewic acid to convert DHA in water and methanol solutions into lactic acid and methyl lactate [17]. As a result, Sn-beta is smoothly catalyzed this reaction efficiently to give quantitative yield of methyl lactate and 90 % of lactic acid. The incorporation if Sn species into the zeolite framework as a singlesite heterogeneous catalyst improve the catalytic activity because from the IR spectra, the shifted carbonyl stretching frequency for Sn-beta (49 cm^{-1}) was found to be the highest compare to Zr-beta (28 cm^{-1}) and Ti-beta (22 cm^{-1}). Therefore, these trends can explain why stronger acid strength will exhibit higher catalytic activity.

They also found that Lewis acid catalysts are selective towards methyl lactate formation while Brønsted acid catalysts such as Al-beta and acidic resin are selective for the formation of pyruvic aldehyde dimethyl acetal. They proposed the reaction mechanism initially by dehydration of DHA to afford pyruvic aldehyde. Finally, it undergoes MPVO-type redox reaction of pyruvic aldehyde hemiacetal in which 1,2-hydride shift take place to produce methyl lactate.

1-3. Montmorillonite

Montmorillonites, abbreviated as mont, are layered smectite clay minerals, consisting of alumina octahedral sheets and sandwiched by two silica tetrahedral layers as shown below [18, 19]. The partial replacement of aluminium atoms in the center of the octahedral sheets by magnesium or iron atoms caused the cation deficiency in the whole structure. Typically, sodium ions exist in the interlayer spaces in order to compensate the cation deficiency.

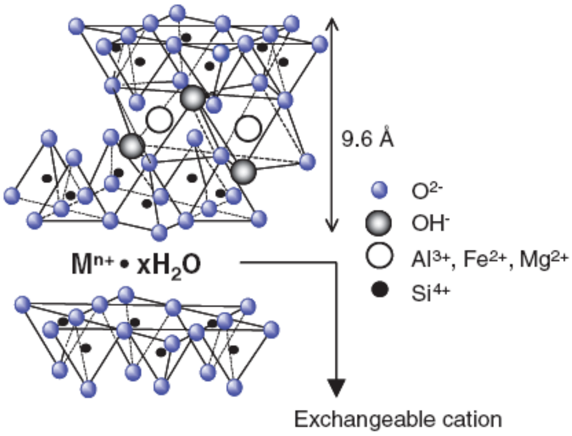


Figure 1. Crystal structure of montmorillonite.

Various types of metal cation can be introduced into the interlayer spaces of mont via cation exchange with sodium ions, hence creating the altered acid site as active species for organic synthesis [20]. There are four types of well-defined cation-exchanged montmorillonite (M^{n+}-mont) that have been developed [21]: 1) a chain-like metal species (Ti^{4+} and Fe^{3+}), 2) a monomeric dioxo complex (V^{5+}), 3) a monomeric aqua complex (Cu^{2+} and Sc^{3+}), and 4) proton (H^+). As shown below, The Brønsted acid sites are originated on oxygen species of the chain-like structure while Cu^{2+} and Sc^{3+} acted as Lewis acid sites. All these catalysts showed outstanding catalytic activity in heterogeneous organic synthesis [22]. Moreover, it offers significant advantages such as facile preparation, easy separation, and can be reused without appreciable loss of their catalytic activities and selectivities.

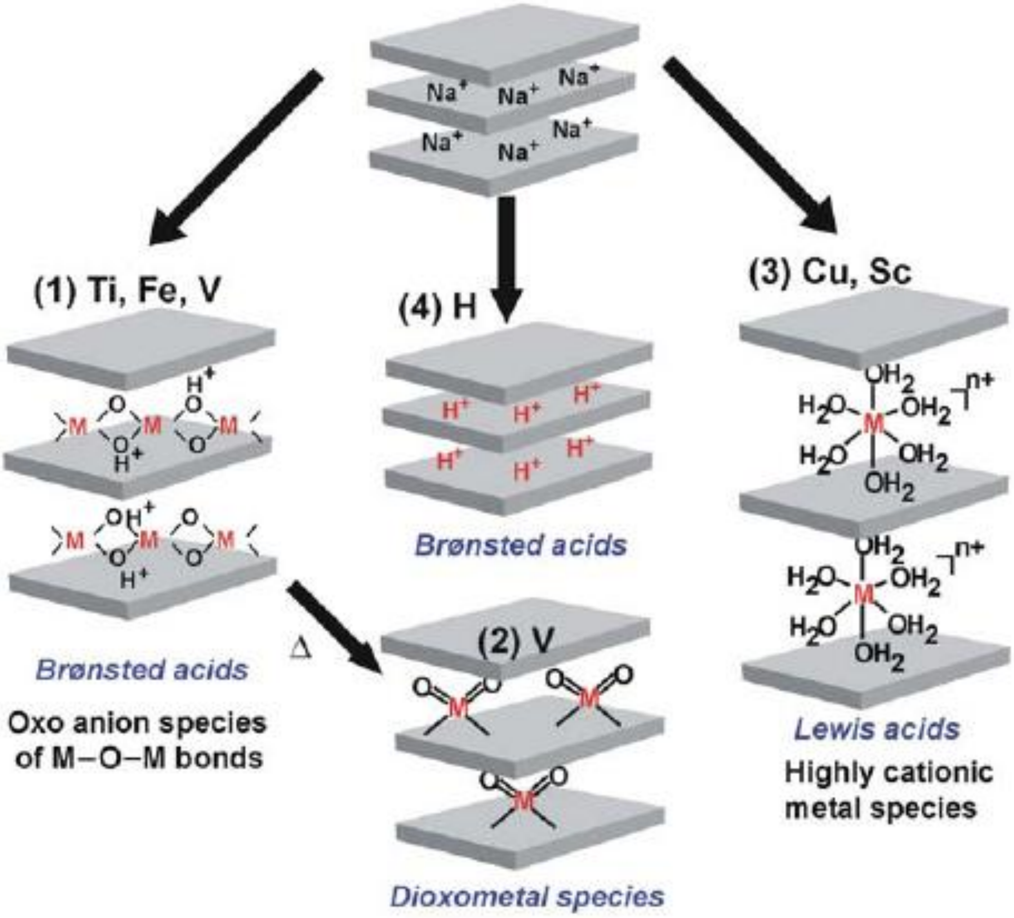
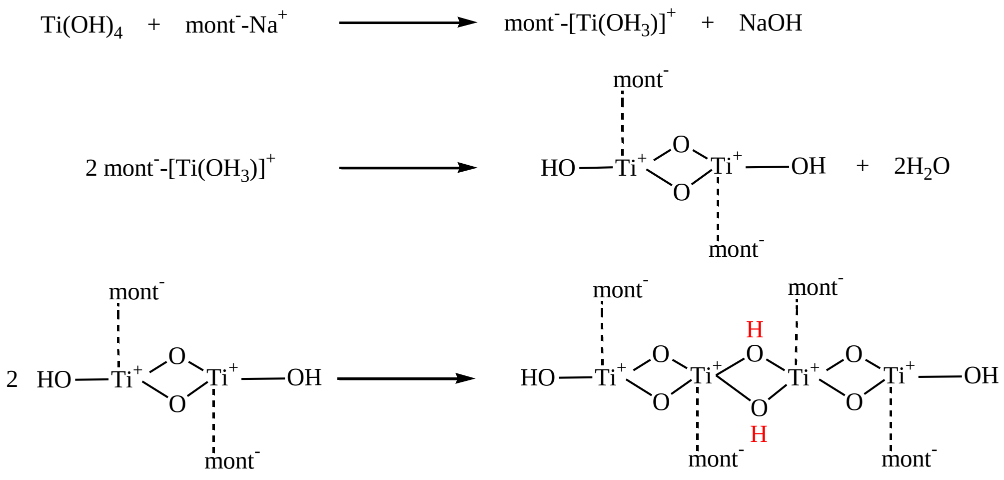


Figure 2. Heterogenization of metal species using montmorillonites

1-3-1. Ti^{4+}-mont

Ti^{4+}-mont was prepared by ion-exchanged treatment of an aqueous $TiCl_4$ solution with Na^+-mont [22a-d]. The Ti K-edge XANES of Ti^{4+}-mont revealed the analogue spectrum of the anatase TiO_2, which is different with an isolated Ti^{4+}[23]. Sodium ions are replaced by $Ti(OH)_4$, formed from the hydrolysis of $TiCl_4$ with water. The successive dehydration of two neighbouring $Ti(OH)_4$ will generate titanium oxide species hence it can be concluded that a two-dimensional titanium oxide is formed in the interlayer of montmorillonite **(Scheme 2).**

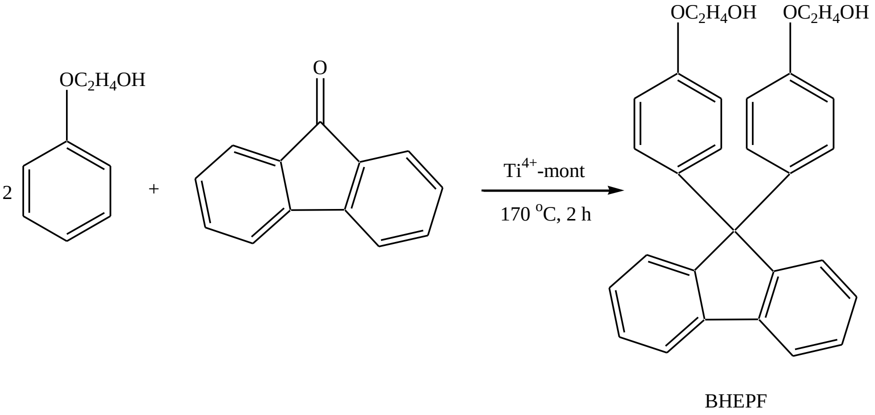


Scheme 2

The acidity of Ti^{4+}-mont can be used in the aromatic alkylation of phenoxyethanol with fluoren-9-one to produce 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene (BHEPF), a highly stable and valuable chemicals for highly functionalized polymers for optical application [24]. Conventionally, it can be obtained by multi-step procedure or homogeneous acid-catalyzed reaction [25, 26]. However, the toxicity of strong acid and producing large amount of waste render this synthetic method unattractive.

With the present of Ti^{4+}-mont, the reaction of phenoxyethanol and fluren-9-one gave 82 % yield of BHEPF **(Scheme 3)**. The parent Na^+-mont totally had no catalytic activity. Among tested catalyst, the higher amount of adsorbed NH_3 will give higher yield of BHEPF.

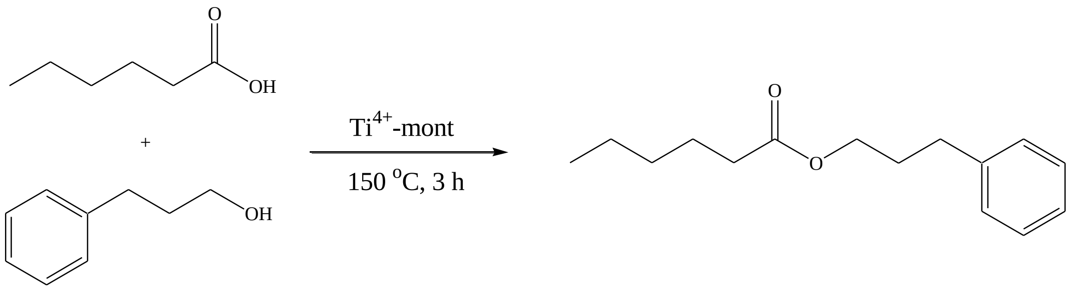
The acid site might be located on the oxygen anion of the Ti-O-Ti bonds and interaction through the oxygen anion between Ti^{4+} and Si^{4+} strengthen the acidity of proton sites [27]. Moreover, the interlayer space of Ti^{4+}-mont was expanded from 2.7 Å to 8.4 Å in phenoxyethanol which allow smooth entrance of substrate to react with active sites.



Scheme 3

These properties of Ti^{4+}-mont can be further explored for typical acid-catalyzed reaction such as acetalization [22c], deacetalization [22b], and esterification [22a] in order to replace traditional homogeneous acid catalyst. As expected, Ti^{4+}-mont exhibits excellent performances catalystic activity. For instance, acetalization of bulky ketone 1,3-diphenyl-2-propanone gave quantitative yield of correspond acetal while Ti^{4+}-mont also catalyzed efficiently deacetalization of various acetals.

Another advancement is we reported the novel esterification of carboxylic acid (hexanoic acid) with alcohols (3-phenyl-1-propanol) using equimolar amount of both substrates (100 mmol) under solvent-free condition, affording 93 % yield of 3-phenyl-1-propyl hexanoate **(Scheme 4)**. It should be noted that the separation of this catalyst from reaction mixture for all these reactions can be done easily by simple filtration and it can be reused without any significant loss of catalytic activity.



Scheme 4

1-3-2. Fe^{3+}-mont

Fe^{3+}-mont was prepared by treatment of Na^{+}-mont in Fe(NO$_3$)$_3$.9H$_2$O [22e]. The interlayer space was 2.2 Å, smaller than Na^{+}-mont (2.9 Å). XPS and Fe K-edge XANES spectra analysis confirmed the trivalent Fe species in the interlayer and the structure of an active species is similar to α-iron(III) hydroxide oxide (α-FeOOH). Therefore, the proposed structure of Fe^{3+}-mont might be two Fe cations linked by hydroxide anions along in the interlayer space as a chain-like structure **(Figure 3)**.

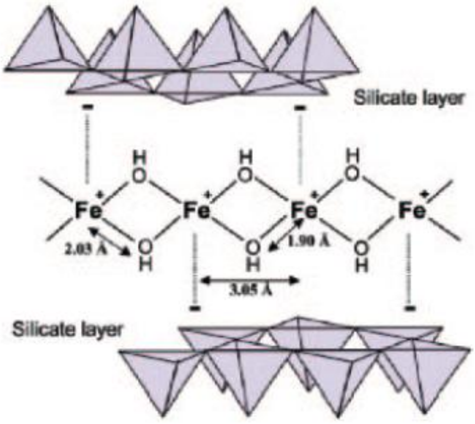
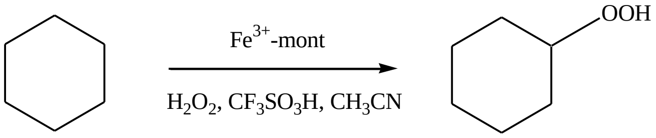
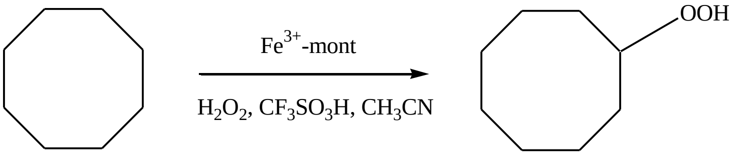


Figure 3

Fe^{3+}-mont was found to have potential in catalyzing liquid-phase oxygenation of cyclohexane to give cyclohexyl hydroperoxide, with the present of trifluoromethane sulfonic acid (TFSA) **(Scheme 5)**. A TON based in Fe ions reached 23200 after 60 hours. XRD analysis showed that the interlayer space was expanded from 2.2 to 10.6 Å when soaked in acetonitrile. The enlargement of interlayer distance in polar solvent enhances the performance of montmorillonite [28]. Fe^{3+}-mont was also capable to oxidize cyclooctane to yield cyclooctyl hydroperoxide with TON of 21000 after 60 hours **(Scheme 6)**. This catalyst can be reused while maintaining its high reaction rate and selectivity.



Scheme 5

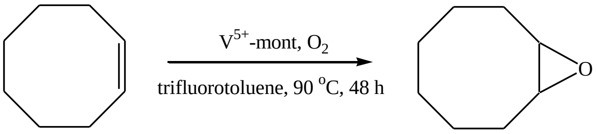


Scheme 6

1-3-3. V^{5+}-mont

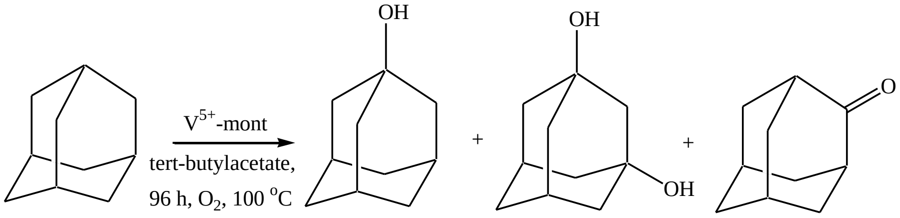
V^{5+}-mont was prepared by stirring Na^+-mont in aqueous solution of VCl_3, before calcined at 800 °C [22h]. Upon calcinations, the structure transformed from chain-like structure to card-house structure, as confirmed by XRD analysis. The V K-edge XANES spectrum of V^{5+}-mont is similar to Na_3VO_4, but not $VOSO_4$ [29]. This result suggested that the vanadium species existed in a tetrahedral-like geometry with oxidation state of pentavalent. It can be concluded that monomeric dioxovanadium (V) species surrounded by four oxygen atoms are existed in the interlayer of montmorillonite.

One of the interesting reactions over V^{5+}-mont is epoxidation of cyclic alkanes under ambient pressure of O_2 without reducing reagents **(Scheme 7)**. However, only a few efforts have been reported [30]. This reaction was carried out in α,α,α-trifluorotoluene solvent. As a result, cyclooctene was converted to cyclooctene oxide by V^{5+}-mont to afford 80 % yield and >99 % selectivity. Other zeolite-supported vanadium catalysts gave lower results.



Scheme 7

V^{5+}-mont also found to be active for oxygenation of adamantane in tert-butyl acetate solvent under ambient pressure of O_2 to produce various oxygenated products; 1-adamantanol, 1,3-adamantanediol, and 2-adamantanone with total yields of 93 % for 96 hours.

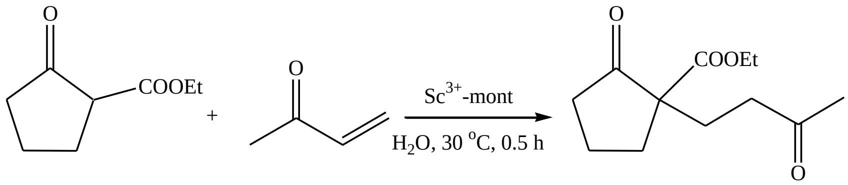


Scheme 8

1-3-4. Sc^{3+}-mont

Triflate of rare earth (RE) metals are known for their water-compatibility and can act as Lewis acids [31]. Unfortunately, they posses low activity and long reaction times. The treatment of Na^+-mont in $Sc(OTf)_3$ afforded Sc^{3+}-mont with basal spacing of 3.6 Å. The existence of trivalent Sc species was revealed by XPS analysis. Elemental analysis showed that three Na ions were replaced by one Sc ion. Sc K-edge EXAFS proved the formation of monomeric Sc species without hydrolyzing to the M-O-M moiety.

Sc^{3+}-mont exhibited good catalytic activity for Michael reaction under aqueous condition [22f]. As a model reaction, 2-oxocyclopentanecarboxylate with 3-buten-2-one were smoothly converted to correspond adduct quantitatively **(Scheme 9)**, which is higher than homogeneous $Sc(OTf)_3$ [32]. The scope of donours can be expanded to 1,3dicarbonyl compounds without requiring activated donours such as silyl enol ether. Importantly, after three reused experiments, no appreciable loss of catalytic activity was observed.

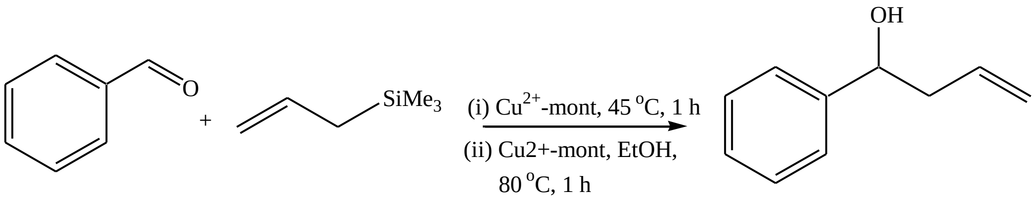


Scheme 9

1-3-5. Cu^{2+}-mont

By treating Na^+-mont with an aqueous solution of $Cu(NO_3)_2.3H_2O$, Cu^{2+}-mont can be synthesized in which the basal spacing is similar to Na^+-mont [22g]. From elemental analysis, one Cu ion will be exchanged with two Na ions. UV analysis and Cu K-edge XANES spectra showed that Cu species is divalent and exist as distorted octahedral coordination environment. Meanwhile, EXAFS analysis provide the information that monomeric Cu species in montmorillonite is similar to $[Cu(H_2O)_6]^{2+}$, also have been reported for X-type zeolite [33].

Despite catalyzing Michael reaction efficiently, the versatility of Cu^{2+}-mont also can be applied to Sakurai-Hosomi reaction to produce homoallylic alcohols. For example, this catalyst active to convert benzaldehyde and allyltrimethylsilane followed by addition of ethanol to 4-phenyl-1-buten-4-ol with quantitative yield **(Scheme 10)**. Various aldehydes and ketones compounds can react smoothly with allyltrimethylsilane to afford correspond homoallyl alcohols with excellent yields. As expected, this catalyst can be reused at least three times with appreciable loss and also can be utilized for 100 mmol-scale reaction.

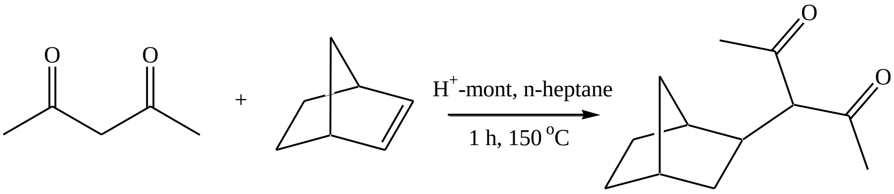


Scheme 10

1-3-6. H^+-mont

By treating Na^+-mont in the HCl aqueous solutions, we managed to afford H^+-mont [34]. From NH_3-TPD measurements, an acid amount and acid strength were found to be 0.86 mmol/g and 111 kJ/mol, respectively. XRD analysis confirmed the retention of layered structure after the treatment in HCl solutions. IR spectra showed the existence of Brønsted acid site from pyridine adsorption methods.

Nucleophilic additions to alkenes or alcohols instead of alkyl halides are attractive salt-free methods since simple alkenes are readily available but addition of 1,3-dicarbonyl compounds to alkenes remain challenging. Homogeneous catalysis systems have been developed but it requires expensive reagents and halogenated solvents [35, 36]. Recently, we managed to develop simpler synthetic method in which H$^+$-mont can acted as an efficient heterogeneous catalyst to catalyze 1,3-dicarbonyl addition to simple olefins in good yield, based on dual activation of the olefinic double bond and the reacting C-H bond of the nucleophile. For instance, the reaction of acetyl acetone with norbornene gave 90 % of adduct **(Scheme 11)**. Other solid catalysts as well as homogeneous acid catalyst were not superior compare to H$^+$-mont. This catalyst is reusable despite maintaining its high catalytic activity.



Scheme 11

2. Purpose of This Thesis

Much attention have been given to the development of multifunctional heterogeneous catalyst in converting biomass with high selectivity and catalytic activity, because of the opportunities has not been explored entirely as a multipurpose low-cost feedstock in fine chemicals, pharmaceuticals, detergents, chemical intermediates, textiles, and others. For instance, in the case of acid catalyzed reaction, montmorillonite catalyst proved to be highly efficient solid acid catalyst since both Brønsted acid and Lewis acidic sites are available in the interlayer of montmorillonite.

Moreover, its ion-exchange properties render montmorillonite to act as a catalyst. Therefore, metals ions can be introduced hence it becomes possible to alter the acidic nature by simple ion-exchange treatment. In fact, precise design of active site to allow one-pot synthesis is beneficial in term of cost and environmental aspect. Since the price and demands of fossil fuels keep on increasing every year to fulfil worldwide needs, the roles of biomass as bio-feedstock for biorefineries to produce various types of organic compounds will become reality. Hopefully, by listing some of practical limitation, it will give a new breath to find an alternative effort to alleviate these problems, especially when employing inefficiency conventional catalytic reactions.

3. Outline of This Thesis

This thesis focuses on the development of solid acid in triose transformation by using montmorillonite as a catalyst support. In this reaction, zeolite-based catalysts have been widely used and some of them exhibit good catalytic performances. However, their intricate preparation and rigid pore size contribute to the reproducibility and limitation for using larger molecules. To overcome these problems, montmorillonite can be an alternative solid acid support since it is commercially-available and expansibility in polar solvents. By introducing metal species in the interlayer space of montmorillonite, it can create the acidic site which is essentials in this transformation.

In this study, the author describes the simple preparation and catalysis of Aluminium-exchanged montmorillonite (Al^{3+}-mont) as an efficient heterogeneous catalyst for triose transformation to alkyl lactates in high yield and good selectivity. The existence of acidic site nature was determined by pyridine-adsorption IR spectra. The acid amounts and acid strength were confirmed by NH_3-TPD measurements. The proposed mechanism involves the cooperative contribution from Lewis and Brønsted acid sites. Moreover, the syntheses of other alkyl lactates were also demonstrated just by changing the solvents. In fact, this catalyst can be reused at least five times without any significant loss of its catalytic activity and applicable to the large-scale reaction.

Finally, the author summarized his thesis and mentions the future works dealing with montmorillonite catalyst for biomass transformation.

4. References

[1] Klass, D. L. *Biomass for Renewable Energy, Fuels, and Chemicals*; Academic Press: San Diego, 1998.

[2] Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford Press: Oxford, 1998.

[3] a) Trost, B. M. *Science* **1991**, *254*, 1471. b) Sheldon, R. A. *CHEMTECH* **1994**, 38.

[4] Mizuno, N.; Masano, M. *Chem. Rev*. **1998**, *98*, 199.

[5] Hill, J.; Nelson, E.; Tilman, D.; Polasky, S.; Tiffany, D. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 11206.

[6] Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Pina, C. D. *Angew. Chem. Int. Ed*. **2007**, *46*, 4434.

[7] Clark, J. H.; Budarin, V.; Deswarte, F. E. I.; Hardy, J. J. E.; Kerton, F. M.; Hunt, A. J.; Luque, R.; Macquarrie, D. J.; Milkowski, K.; Rodriguez, A.; Samuel, O.; Tavener, S. J.; White, R. J.; Wilson, A. J. *Green Chem*. **2006**, *8*, 853.

[8] a) Kimura, H.; Tsuto, K. *Appl. Catal. A* **1993**, *96*, 217. b) Kimura, H. *Appl. Catal. A* **1993**, *105*, 147.

[9] Corma, A.; Iborra, S.; Velty, A. *Chem. Rev*. **2007**, *107*, 2411.

[10] a) Weber, J.; Kayser, A.; Rinas, U. *Microbiology* **2005**, *151*, 707.

[11] a) Wee, Y.-J.; Kim, J.-N.; Ryu, H.-W. *Food Technol. Biotechnol*. **2006**, *44*, 163. b) Datta, R.; Henry, M. *J. Chem. Technol. Biotechnol*. **2006**, *81*, 1119.

[12] Kelly, R. EU Patent 0460831A2, **1991**.

[13] Hayashi, Y.; Sasaki, Y. *Chem. Commun*. **2005**, 2716.

[14] Bang, E.; Eriksen, J.; Mønsted, L.; Mønsted, O. *Acta Chem. Scand*. **1994**, *48*, 12.

[15] Eriksen, J.; Mønsted, O. *Transition Met. Chem*. **1998**, *23*, 783.

[16] Janssen, K. F.; Paul, J. S.; Sels, B. F.; Jacobs, P. A. *Stud. Surf. Sci. Catal*. **2007**, *170*, 1222.

[17] Taarning, E.; Saravanamurugan, S.; Holm, M. S.; Xiong, J.; West, R. M.; Christensen, C. H. *ChemSusChem*. **2009**, *2* 625.

[18] Pinnavaia, T. J. *Science* **1983**, *220*, 365.

[19] Laszlo, P. S*cience* **1987**, *235*, 1473.

[20] a) Laszlo, P. *Acc. Chem. Res*. **1986**, *19*, 121. b) Clark, J. H.; Macquarrie, D. J. *Chem. Soc. Rev*. **1996**, *25*, 303. c) Izumi, Y.; Onaka, M. *Adv. Catal*. **1992**, *38*, 245.

[21] Kaneda, K. *Synlett*. **2007,** *7*, 999.

[22] Ti: (a) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2003**, *44*, 9205. (b) Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Lett.* **2003**, *32*, 648. (c) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2001**, *42*, 8329. (d) Ebitani, K.; Kawabata, T.; Nagashima, K.; Mizugaki, T.; Kaneda, K. *Green Chem.* **2000**, *2*, 157. Fe: (e) Ebitani, K.; Ide, M.; Mitsudome, T.; Mizugaki, T.; Kaneda, K. *Chem. Commun.* **2002**, 690. Sc: (f) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2003**, *125*, 10486. Cu: (g) Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Eur. J.* **2005**, *11*, 288. V: (h) Mitsudome, T.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Lett.* **2005**, *34*, 1626.

[23] Bordiga, S.; Collucia, S.; Lamberti, C.; Marchese, L.; Zecchina, A.; Boscherini, F.; Buffa, F.; Genoni, F.; Leofanti, G.; Petrini, G.; Vlaic, G. *J. Phys. Chem*. **1994**, *98*, 4125.

[24] Chen, C. S.; Bulkin, B. J.; Pearce, E. M. *J. Appl. Polym. Sci*. **1982**, *27*, 1177.

[25] Papava, G. S.; Maisuradze, N. A.; Zarkua, Z. L.; Dokhturishvili, N. S.; Razmadze, G. B.; Vinogradova, S. V.; Korshak, V. V. *Acta Polym*. **1988**, *8*, 445.

[26] Yamada, M.; Sun, J.; Suda, Y.; Nakaya, T. *Chem. Lett*. **1988**, 1055.

[27] Bodoardo, S.; Chiappetta, R.; Onida, B.; Figueras, F.; Garrone, E. *Microporous Mesoporous Mater*. **1998**, *20*, 187.

[28] Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir*, **1996**, *12*, 3038.

[29] Wong, J.; Lytle, F. W.; Messmer, R. P.; Haylotte, D. H. *Phys. Rev. B* **1984**, *30*, 5596.

[30] a) Tang, Q.; Wang, Y.; Liang, J.; Wang, P.; Zhang, Q.; Wan, H. *Chem. Commun*. **2004**, 440. b) Yin, C.-X.; Finke, R. G.; *Inorg. Chem*. **2005**, *44*, 4175. c) Nishiyama, Y.; Nakagawa, Y.; Mizuno, N.; *Angew. Chem., Int. Ed*. **2001**, *40*, 3639. d) Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Am. Chem. Soc*. **1994**, *116*, 2424. e) Khan, M. M. T.; Rao, A. P. *J. Mol. Catal*. **1987**, *39*, 331. f) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc*. **1985**, *107*, 5790.

[31] Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev*. **2002**, *102*, 2227.

[32] Kobayashi, S. *Eur. J. Org. Chem*. **1999**, 15.

[33] Ebitani, K.; Nagashima, K.; Mizugaki, T.; Kaneda, K. *Chem. Commun*. **2000**, 869.

[34] Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2605.

[35] a) Pei, T.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 11290. b) Pei, T.; Widenhoefer, R. A. *Chem. Commun.* **2002**, 650. c) Wang, X.; Pei, T.; Han, X.; Widenhoefer, R. A. *Org. Lett*. **2003**, *5*, 2699. d) Yang, D.; Li, J.-H.; Gao, Q.; Yan, Y.-L. *Org. Lett.* **2003**, *5*, 2869. e) Leitner, A.; Larsen, J.; Steffens, C.; Hartwig, J. F. *J. Org. Chem.* **2004**, *69*, 7552; for oxidative additions, see: f) Pei, T.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 648. g) Wang, X.; Widenhoefer, R. A. *Chem. Commun*. **2004**, 660.

[36] a) Yao, X.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884. b) Nguyen, R.-V.; Yao, X.-Q.; Bohle, D. S.; Li, C.-J. *Org. Lett.* **2005**, *7*, 673 c) Yao, X.; Li, C.-J. *J. Org. Chem.* **2005**, *70*, 5752.

Chapter 2.

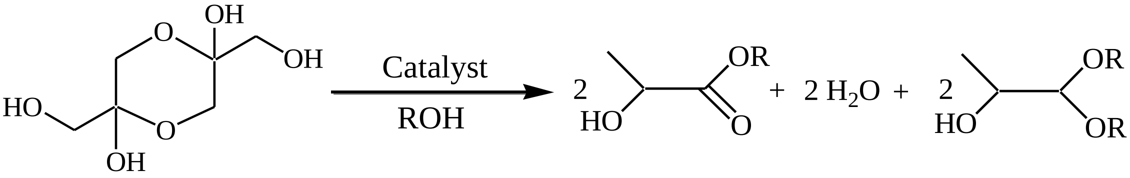
A Highly Efficient Synthesis of Alkyl Lactates from Triose using Reusable Aluminium-exchanged Montmorillonite Catalyst

1. Introduction

The demands of polylactide based-polymers as biodegradable materials are soaring due to the environmental concern. Polylactide has received great interest because of its unique physical and biological properties which can be used for commercial plastics and biomedical materials [1]. In addition, the production of alkyl lactates as a precursor for the synthesis of polylactide can be obtained from abundant and renewable resources such as sugar cane and sugar beet through the oxidation of glycerol, allowing this process attractive for a long term [2]. The fermentation of dextrose by lactic acid bacilli is currently conducted through biological processes [3-5]. However, the method suffers from low catalytic yield despite tedious preparation and separation.

Recently, Sasaki *et. al* found that homogeneous tin chlorides, $SnCl_2$ and $SnCl_4.5H_2O$ are excellent catalysts for the synthesis of alkyl lactates from trioses (dihydroxyacetone and glyceraldehydes) [6]. However, the serious drawbacks such as tedious separation and thermal instability are inevitable when utilizing homogeneous catalysis system. Also, some heterogeneous catalysts such as zeolite-Y [7], USY zeolite [8], and Sn-beta [9] have been reported.

Montmorillonites of smectite clays with layered structure exhibit excellent catalytic activities and have been widely used as environment-friendly Brønsted and Lewis acid catalysts for organic synthesis [10]. We have developed various metal-exchanged montmorillonites as solid acid catalysts [11]. Their simple preparation, facile separation, and recyclability are vital towards Green and Sustainable Chemistry (GSC). Moreover, we have demonstrated that Al^{3+}-mont catalyst displays high catalytic activity and selectivity due to the cooperative catalysis between a Brønsted acid site and a Lewis acidic Al^{3+} species in its interlayer spaces [12]. Herein, we found that Al^{3+}-mont efficiently catalyzed the conversion of dihydroxyacetone dimer (DHAD) to alkyl lactate (Scheme 1).



Scheme 1. Conversion of DHAD in alcohol solutions to alkyl lactate (major product), pyruvic aldehyde dialkyl acetal (major by-product) and water (co-product).

2. Experimental

2-1. General

Infrared spectra were obtained with a JASCO FTIR-410. Analytical GLC and GLC-Mass were performed by Shimadzu GC-8A PF with flame ionization detector equipped with KOCL 3000T, Silicon SE-30, and OV-17 columns. JEOL JMS-700 mass spectrometer was used for HRMS analyses. Powder X-ray diffraction patterns were recorded using Philips X'Pert –MPD with Cu Kα radiation. NH_3-TPD of the samples was carried out in a flow-type fixed bed reactor using Japan BELCAT-A instrument.

2-2. Material

Unless otherwise noted, materials were purchased from Wako Pure Chemicals, Tokyo Kasei Company, Nacalai tesque, and Aldrich Inc., and were used after appropriate purification.

2-3. Solid Acid

Na^+-montmorillonite (Na-mont; Na 2.73; Al 10.3; Fe 1.35; Mg 1.97 %) was purchased from Kunimine Industry Co. Ltd., Japan as Kunipia F.

2-4. Preparation of Al^{3+}-mont

A mixture of parent Na^+-mont (1.0 g) and 100 mL of aqueous $AlCl_3.6H_2O$ (5.0 mM) was stirred at 50°C for 12 h. The slurry obtained was filtered and washed with 1 L of distilled water, followed by drying at 110°C in air to afford the Al^{3+}-mont as a whitish gray powder. Elemental analysis: Na 0.05; Al 10.5; Fe 1.25; Mg 1.78 %. The mont-enwrapped metal cations, Sn^{4+} and Ce^{4+} were prepared by treating the Na^{+}-mont with an aqueous solution of the appropriate metal chloride and nitrate with similar experimental procedure. For Zn^{2+}, Sc^{3+}, and Cu^{2+} [11] were prepared according to the literature given.

2-5. NH_3-TPD Measurement

Acid amounts and strengths (change of enthalpy upon desorption of NH_3: ΔH) of the Al^{3+}-mont was determined by NH_3-TPD measurement. The sample was first treated for 1 h at 373 K under He flow, and ammonia was adsorbed at 373 K by 5 % NH_3/He gas flow, followed by exposure of the sample to water vapor (ca. 20 Torr, 60 min) to remove *l*-peak. [12] The temperature of the cell is increased linearly at a rate of 10 K min^{-1} from 373 K to 1073 K while flowing the carrier He with the pressure in the catalyst bed at 100 Torr. The desorbed NH_3 was detected by a quadruple mass spectrometer. After the measurement, a known concentration of NH_3 was fed to the mass spectrometer in order to calibrate the desorption peak intensity.

ΔH (kJ mol^{-1}) was determined by Niwa and Katada's method [12, 13] according to eq 1, where F (flow rate: $cm^3\ s^{-1}$), W (catalyst weight: g), A_0 (acid concentration: mmol g-1), T_m (peak maximum temperature: K).

$$\ln T_m - \ln(A_0W/F) = \Delta H/(RT_m) + \ln\left[\beta(1-\theta_m)^2(\Delta H-RT_m)/P_0\exp(\Delta S/R)\right] \qquad (1)$$

2-6. Typical example for the conversion of trioses dimer to alkyl lactate

Al^{3+}-mont (0.05 g), methanol (5 mL), and DHAD (0.625 mmol) were placed into a pressure tube. The mixture was vigorously stirred at 150 °C for 17 hours. After that, the catalyst was separated by centrifugation and GC analysis of filtrate showed 97 % yield of methyl lactate. The recovered catalyst was washed by methanol followed by drying in oven at 110 °C and could be reused at least for five times without significant loss of catalytic activity and selectivity.

2-7. IR measurement of Pyridine-adsorbed Al^{3+}-mont Catalyst

Into a Schlenck tube were placed Al^{3+}-mont catalyst (0.1 g) and pyridine (1 mmol). The resulting mixture was stirred at room temperature for 3 hours. After the adsorption of pyridine, the excess pyridine was removed by evacuating the samples at 150 °C for 12 hours. The IR spectrum was obtained from self-supported wafer containing 30 mg of sample.

3. Results and Discussion

Elemental analysis showed that the degree of sodium exchange in Al^{3+}-mont was 98.2% (Na; 0.05%, Al; 10.5%, Fe; 1.25%, Mg; 1.78%). From NH_3-TPD, acid amount and acid strength were 0.348 mmol g^{-1} and 252 kJ mol^{-1}, respectively. After cation-exchange treatment, the structure of montmorillonite is retained and the interlayer space increase from 2.6 Å to 3.5 Å, as confirmed by XRD analysis.

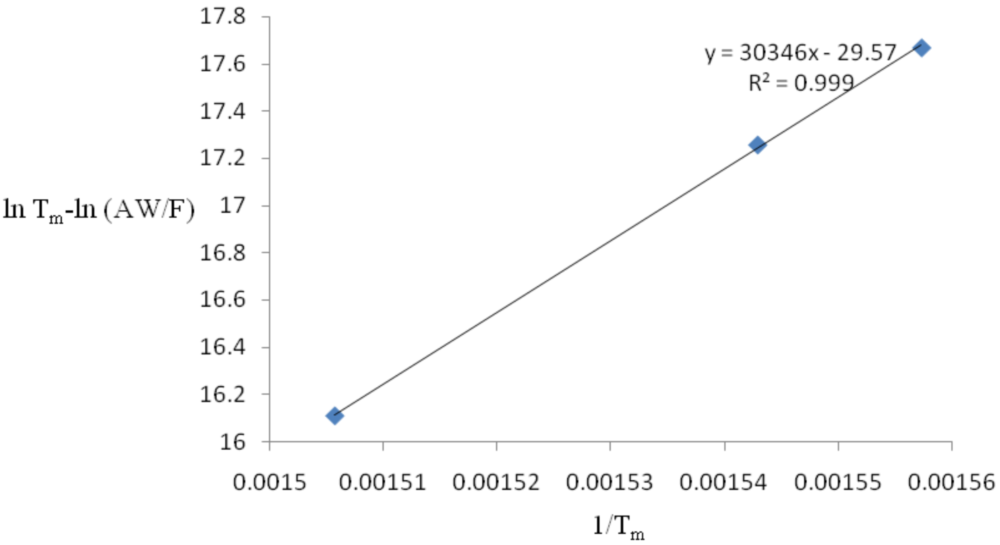
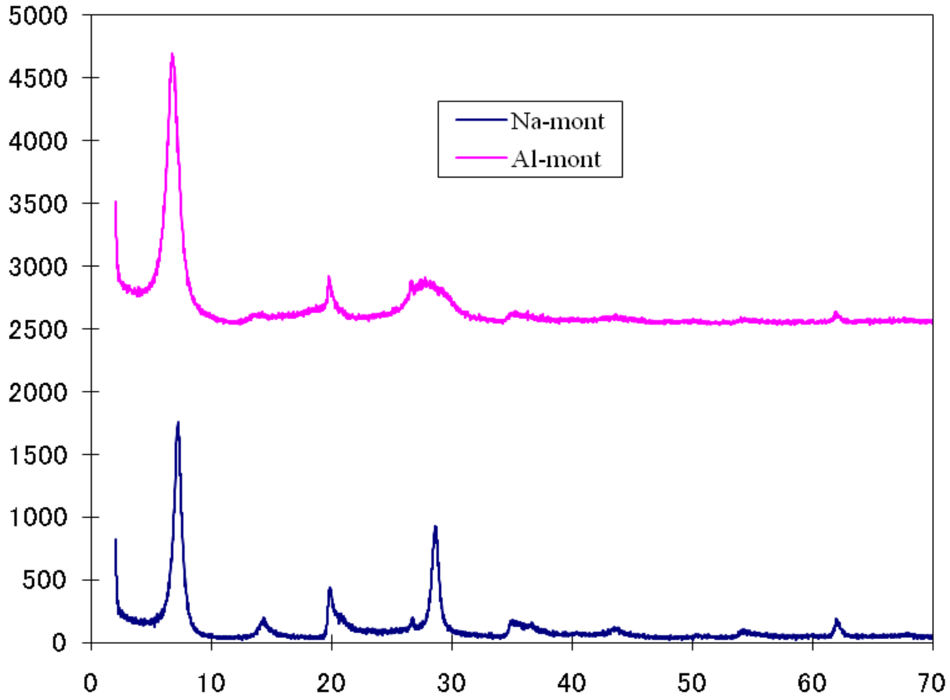


Figure 1. Plot of the left-hand side of the equation (1) against $1/T_m$



The existence of Brønsted and Lewis acid sites were proved by IR spectra [14]. By using pyridine-adsorption method, the IR peak around 1545 cm^{-1}, correspond to protonated pyridine (marked as **O**) and 1440 cm^{-1}, assigned to adsorbed-pyridine to Lewis acid site (marked as **X**) were observed. The existence of Brønsted acid might be originated from water polarization's ability by particular atoms and enhanced by the adjacent hydrophilic clay surface [15].

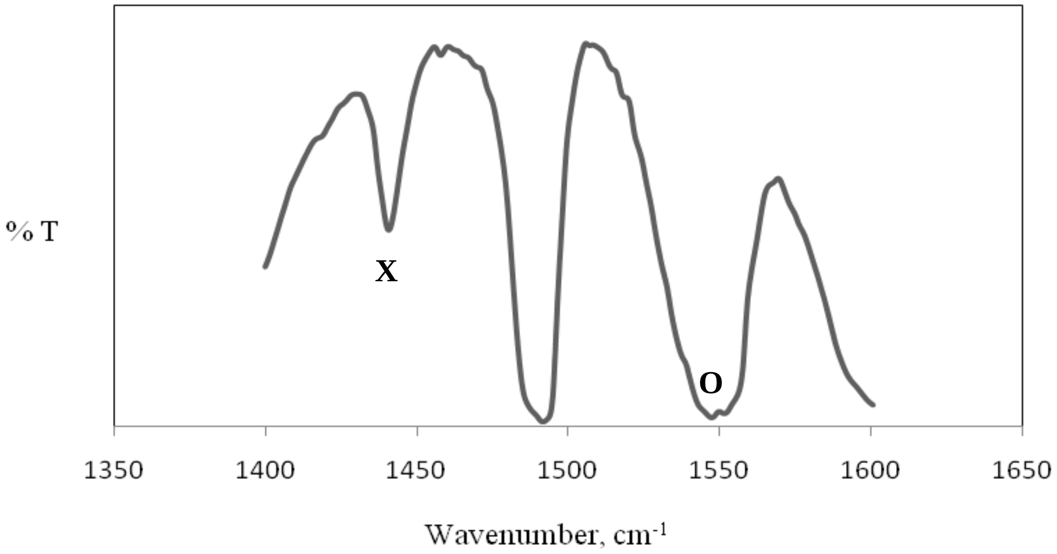


Figure 3. IR spectrum for Al^{3+}-mont after the treatment with pyridine

For the model reaction, the reactivity of dihydroxyacetone dimer (DHAD) in methanol solution was examined with the presence of several acid catalysts in Table 1.

Table 1. The results for the conversion of DHAD to methyl lactate in methanol solution using various type of M^{n+}-mont.

Entry	Catalyst	Yield of Methyl Lactate (%) [b]	TON [c]
1	Al^{3+}-mont	76 (15)	256
2	Sn^{4+}-mont	75 (25)	43
3	H^{+}-mont	72 (18)	21
4	Cu^{2+}-mont	61 (24)	34
5	Sc^{3+}-mont	50 (26)	42
6	Ce^{4+}-mont	27 (31)	29
7	Zn^{2+}-mont	0 (0)	0
8	Na^{+}-mont	0 (0)	0
9	No catalyst	0 (0)	0

[a] Reaction conditions: Catalyst (0.05 g), DHAD (0.625 mmol = 1.25 mmol of DHA), methanol (5 mL), 150 °C, 1 hour. [b] Determined by GC analysis using internal standard technique. Yields in parenthese correspond to pyruvic aldehyde dimethyl acetal. [c] Based on metal amounts.

As shown in Table 1, among metal-exchanged montmorillonite tested, Al^{3+}-mont was found to be the most active catalyst for the synthesis of methyl lactate from DHAD to afford 76% yield. The calculation of TON based on metal amounts showed that Al^{3+}-mont achieved the highest TON among metal-exchanged montmorillonites. Although Sn^{4+}-mont and H^{+}-mont displayed almost similar performances, the values of TON were lower than Al^{3+}-mont. Others acid catalyst such as Cu^{2+}-mont, Sc^{3+}-mont, Ce^{4+}-mont, and Zn^{2+}-mont gave moderate to poor yield (Entries 4-7). Neither Na^{+}-mont nor the catalyst-free system was effective for this reaction (Entries 8 and 9).

Table 2. The results for the conversion of DHAD to methyl lactate in methanol solution using various type of Al catalysts.

Entry	Catalyst	Yield of Methyl Lactate (%) [b]
1	Al^{3+}-mont	76 (15)
2	SiO_2-Al_2O_3[c]	44 (3)
3	SiO_2-Al_2O_3[d]	36 (2)
4	Al_2O_3	8 (0)
5	Al-HAP	6 (7)
6	$AlCl_3.6H_2O$[e]	68 (13)
7	$Al(acac)_3$[e]	16 (0)
8	$Al(NO_3)_3.9H_2O$[e]	3 (8)
9	$Al(OH)_3$[e]	0 (0)

[a] Reaction conditions: Catalyst (0.05 g), DHAD (0.625 mmol = 1.25 mmol of DHA), methanol (5 mL), 150 °C, 1 hour. [b] Determined by GC analysis using internal standard technique. Yields in parenthese correspond to pyruvic aldehyde dimethyl acetal. [c] JRC-SAL-2. [d] JRC-SAH-1. [e] 0.0025 mmol.

Another type of Al catalysts were tested. Notably, other Al heterogeneous catalysts such as alumina, silica-alumina, and aluminium-hydroxyapatite (Al-HAP) were inferior to Al^{3+}-mont (Entries 2-5). Furthermore, the homogeneous Al catalysts were also not as efficient as Al^{3+}-mont (Entries 6-9). It can be concluded that the combination of Al species and Na^+-mont is essential to achieve this transformation.

The effects of solvents for the transformation of DHAD to methyl lactate were conducted. By utilizing methanol as a solvent, it affords an excellent yield of methyl lactate (Entry 1). In contrast, by using 1,4-dioxane, acetonitrile, and acetone gave poor yield of methyl lactate. (Entries 18-20). Other solvents such as *t*-butyl acetate, DMSO, DMF, and DMA were totally ineffective for this reaction (Entries 21-24). The use of non polar solvent such as heptane makes DHAD insoluble, render catalytic reaction could not be proceeded smoothly. Therefore, methanol can be used as a substrate and suitable solvent for this reaction.

It is due to the ability of DHAD to dissociate in methanol solution even at 5 °C to form DHA, hence gradually converted to methyl lactate [6].

Table 3. The results for the solvent effect of DHAD to methyl lactate

Entry	Catalyst	Solvent	Yield of Methyl Lactate (%) [b]
1	Al^{3+}-mont	Methanol	76 (15)
2	Al^{3+}-mont	Acetone	10 (5)
3	Al^{3+}-mont	1,4-dioxane	6 (0)
4	Al^{3+}-mont	Acetonirile	trace (0)
5	Al^{3+}-mont	*t*-butyl acetate	0 (2)
6	Al^{3+}-mont	DMSO	0 (0)
7	Al^{3+}-mont	DMF	0 (0)
8	Al^{3+}-mont	DMA	0 (0)

[a] Reaction conditions: Catalyst (0.05 g), DHAD (0.625 mmol = 1.25 mmol of DHA), solvent (4.94 mL), methanol (0.06 mL), 150 °C, 1 hour. [b] Determined by GC analysis using internal standard technique. Yields in parenthese correspond to pyruvic aldehyde dimethyl acetal.

This catalyst exhibit high activity in which nearly quantitative yield of methyl lactate can be obtained without the formation of pyruvic aldehyde dimethyl acetal when the reaction time was extended to 17 hours (Figure 2). In contrast, although some zeolite catalysts had good performance, it requires intricate preparation [9], long reaction time [8], and moderate catalytic performance [7]. In the case of homogeneous catalysts [6], tedious separation is unavoidable and formation of by-product was observed.

In order to confirm this reaction proceeded only with the presence of Al^{3+}-mont, the catalyst was separated after about 70% conversion to methyl lactate. Further production of methyl lactate did not occur after continuous stirring the filtrate under similar reaction conditions. It clearly shows the Al^{3+}-mont acts as a truly heterogeneous catalyst and rule out any contribution from leached Al species to catalyze this reaction.

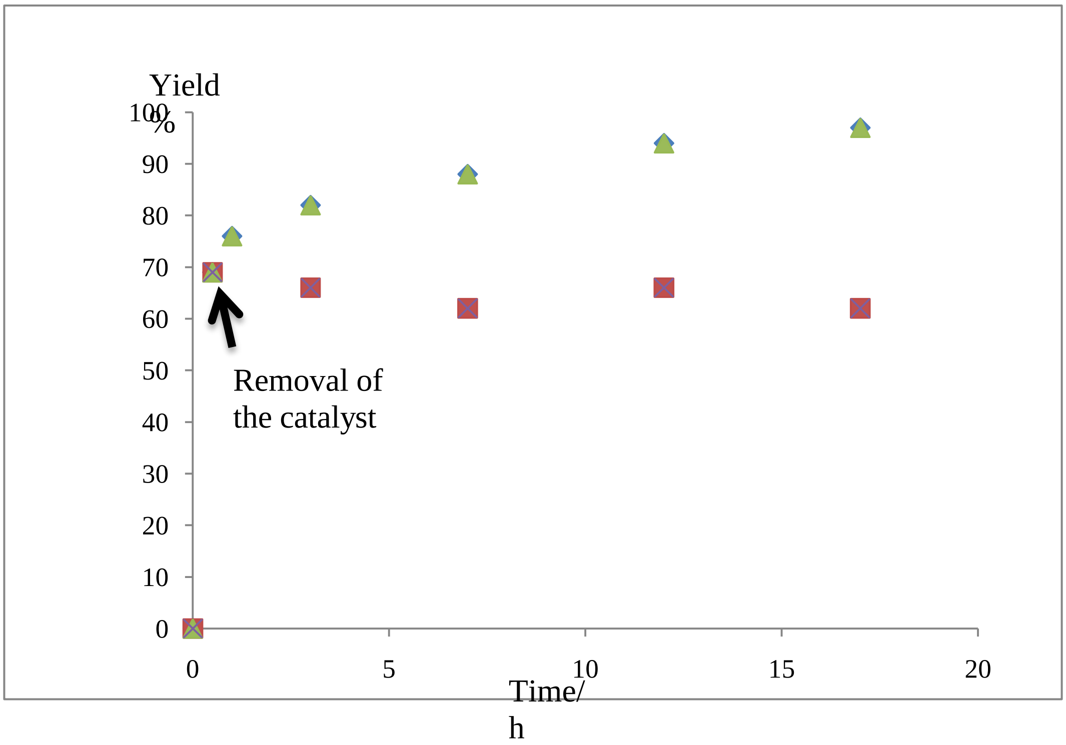


Figure 2. The time-course of methyl lactate v.s reaction time

The reusability of Al^{3+}-mont in this transformation is shown in Figure 3. Al^{3+}-mont is proved to be an efficient and durable catalyst since it can be reused for at least five times without any significant loss of catalytic activity under similar conditions. The yields were kept over 92% during five recycling experiments.

Even though the reaction mechanism is still arguable, DHAD was believed to monomerize by heat and/or Al^{3+}-mont to give DHA [6]. Strong interaction between Lewis acidic Al^{3+} species with hydroxyl group to form cyclic intermediate consisting of Al-OH bond and Al-O=C, as well as cooperative catalysis of Brønsted acid site to promote isomerisation to its enediol derivative by dehydration of primary hydroxyl group [16]. The enediol derivative would be converted to enol-pyruvic aldehyde [17].

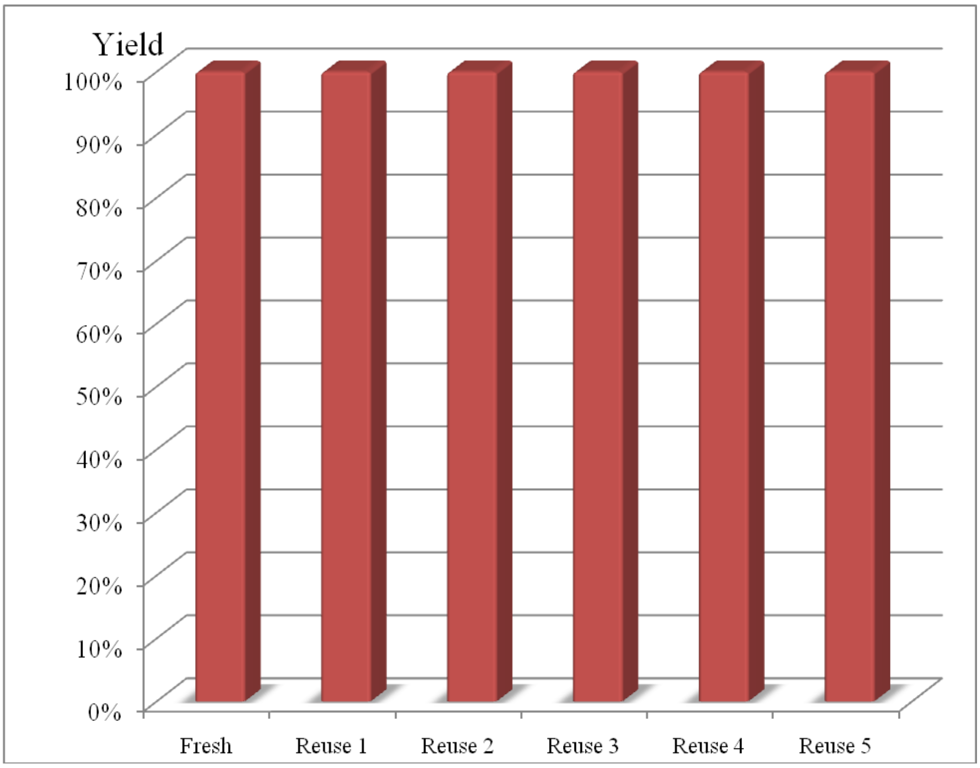


Figure 3. The reusability of Al^{3+}-mont for this transformation

The presence of pyruvic aldehyde dimethyl acetal proves the formation of pyruvic aldehyde since metal species simply act as Lewis acid to promote acetalization of carbonyl compound with alcohol [18]. On the other hand, Al^{3+}-mont might also interact uniquely to form specific intermediate to give methyl lactate [19] and also promote deacetalization of pyruvic aldehyde dimethyl acetal as well. It can be seen from the yield of pyruvic aldehyde dimethyl acetal which gradually decreased as the reaction time was prolonged (Figure 4).

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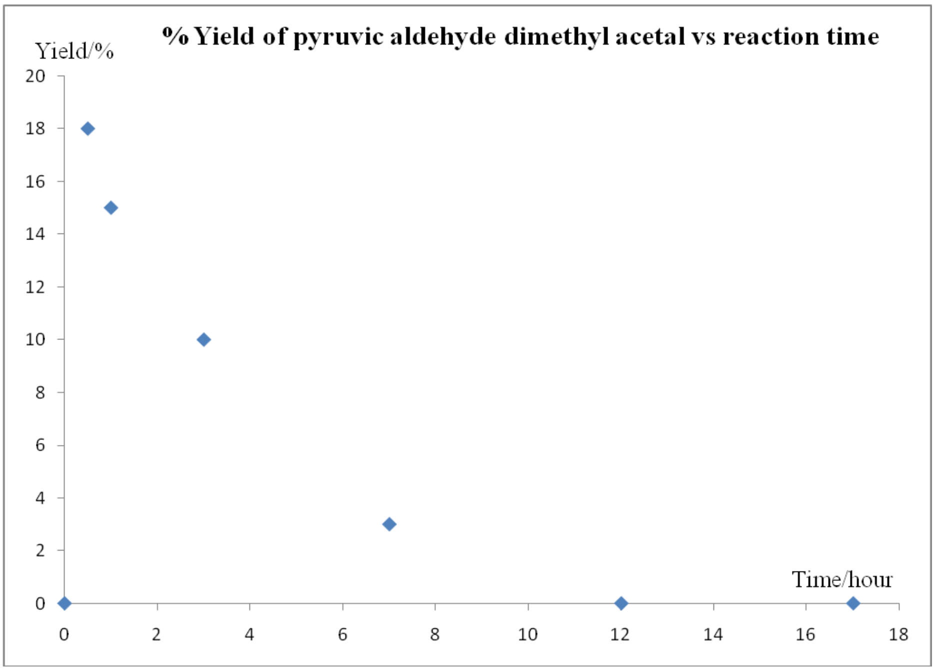
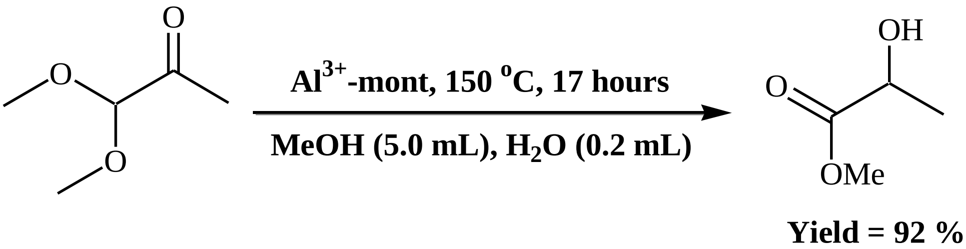
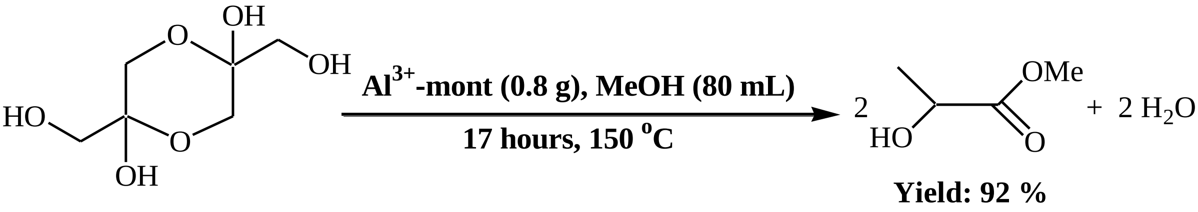


Figure 4. The time-course of pyruvic aldehyde dimethyl acetal v.s reaction time



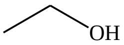
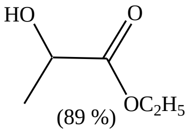
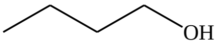
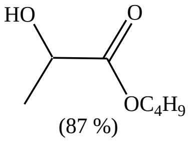
Scheme 2. Direct transformation of pyruvic aldehyde dimethyl acetal to methyl lactate

In order to prove the plausible reaction pathway of methyl lactate from pyruvic aldehyde dimethyl acetal, direct conversion was carried out by utilizing pyruvic aldehyde dimethyl acetal as a substrate under above condition (Scheme 2). As a result, 92% of methyl lactate can be obtained and directly prove the pyruvic aldehyde as an intermediate for this reaction. For 20 mmol-scale reaction, DHAD was smoothly catalyzed by Al^{3+}-mont to afford 92% yield of methyl lactate (Scheme 3).



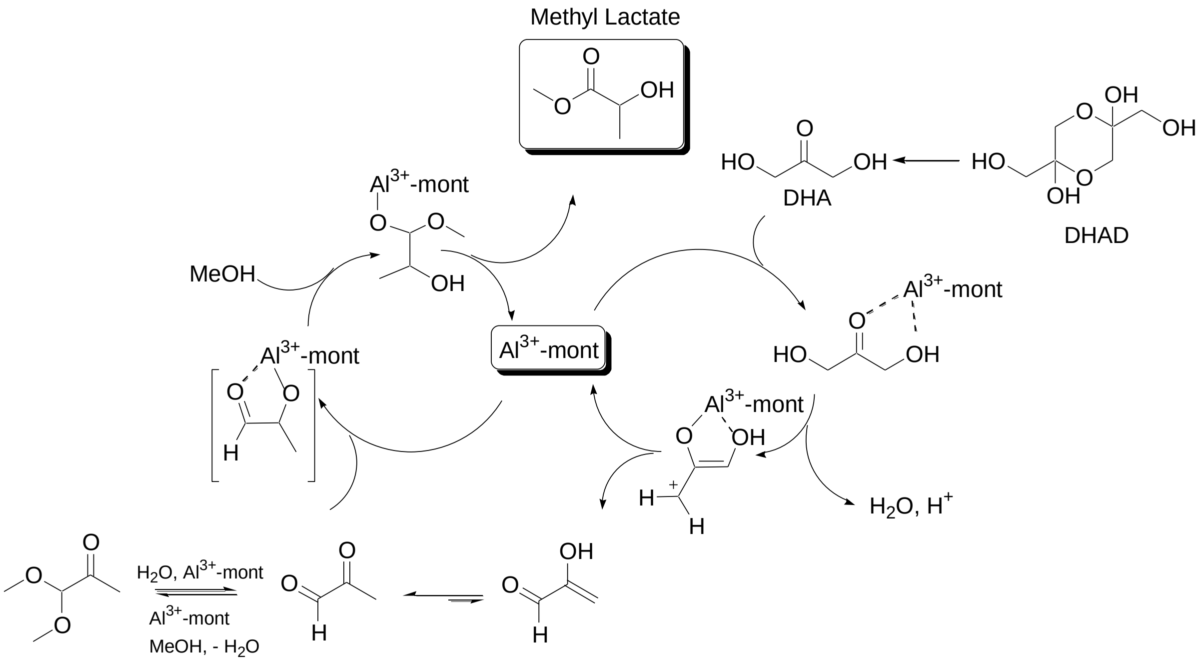
Scheme 3. 20 mmol-scale reaction of DHAD with methanol.

Table 4. Conversion to alkyl lactate under correspond alkyl alcohol solutions

Entry	Alcohol	Yield (%) [b]
1[c]		 (89 %)
2[d]		 (87 %)

[a] Reaction conditions: Catalyst (0.05 g), DHAD (0.625 mmol = 1.25 mmol of DHA), alcohol solution (5 mL), solvent,150 °C. [b] Determined by GC analysis using internal standard technique. [c] 24 hours. [d] 0.2 mL of water was added.

As shown in Table 4, the versatility of Al^{3+}-mont can be expanded for other alcohol solutions. For instance, by using ethanol and *n*-butanol solutions, DHAD can also be converted to ethyl lactate and butyl lactate for 89 % and 87 % yield, respectively.



Scheme 4. The proposed mechanism of Al^{3+}-mont catalyzed conversion of DHAD to methyl lactate.

4. Conclusion

In conclusion, we demonstrated that the Al^{3+}-mont efficiently catalyzed the transformation of DHAD to alkyl lactates in alcohol solution. The cooperative catalysis between a Brønsted acid site and a Lewis acidic Al^{3+} species in the interlayer spaces of montmorillonite allow smooth conversion of DHAD to alkyl lactate. This catalyst possesses significant advantages; 1) high catalytic activity, 2) facile preparation, 3) easy separation from the reaction mixture, and 4) high reusability without any significant loss of the catalytic activity.

5. References

[1] Vink, E. T. H.; Rabago, K. R.; Glassner, D. A.; Springs, B.; O'Connor, R. P.; Kolstad, J.; Gruber, P. R. *Macromol. Biosci.,* **2004**, *4*, 551.

[2] For excellent review of glycerol as chemical feedstock: a) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Pina, C. D. *Angew. Chem. Int. Ed.* **2007**, *46*, 4434. b) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411.

[3] Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.

[4] Lunt, J. *Polym. Degrad. Stab.* **1998**, *59*, 145.

[5] Vink, E. T. H.; Rabago, K. R.; Glassner, D. A.; Springs, B.; O'Connor, R. P.; Kolstad, J.; Gruber, P. R. *Polym. Degrad. Stab.* **2003**, *80*, 403.

[6] Hayashi, Y.; Sasaki, Y. *Chem Comm.,* 2005, 2716.

[7] (a) Taarning, E.; Saravanamurugan, S.; Holm, M. S.; Xiong, J.; West, R. M.; Christensen, C. H. *ChemSusChem*. **2009**, *2* 625. b) Janssen, K. F.; Paul, J. S.; Sels, B. F.; Jacobs, P. A. *Stud. Surf. Sci. Catal*. **2007**, *170*, 1222.

[8] Laszlo, P. *Acc. Chem. Res*. **1986**, *19*, 121.

[9] Ti: (a) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2003**, *44*, 9205. (b) Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Lett.* **2003**, *32*, 648. (c) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2001**, *42*, 8329. (d) Ebitani, K.; Kawabata, T.; Nagashima, K.; Mizugaki, T.; Kaneda, K. *Green Chem.* **2000**, *2*, 157. Fe: (e) Ebitani, K.; Ide, M.; Mitsudome, T.; Mizugaki, T.; Kaneda, K. *Chem. Commun.* **2002**, 690. Sc: (f) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2003**, *125*, 10486. Cu: (g) Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Eur. J.* **2005**, *11*, 288. V: (h) Mitsudome, T.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Lett.* **2005**, *34*, 1626.

[10] Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.*, **2007**, *72*, 6006.

[11] Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Eur. J.* **2005**, *11*, 288.

[12] Niwa, M.; Katada, N.; Sawa, M.; Murakami, Y. *J. Phys. Chem.* **1995**, *99*, 8812.

[13] Niwa, M.; Katada, N. *Catal. Surv. Jpn.* **1997**, *1*, 215.

[14] (a) Daniell, W.; Topsøe, N.-Y.; Knözinger, H. *Langmuir.* **2001**, *17*, 6233. (b) Parry, E. P. *J. Catal.* **1963**, *2*, 371.

[15] M. Frenkel, *ClaysClay Miner*. **1974,** *22*, 435.

[16] The Brønsted acid site is also capable to form cyclic intermediate to promote enolization of carbonyl group. See ref. [10].

[17] Enol-pyruvic aldehyde is a transient intermediate of the decomposition of DHA-phosphate to pyruvic aldehyde via its methylglyoxal synthase: Rose, I. A.; Nowick, J. S. *J. Am. Chem. Soc*. **2002**, *124*, 13047.

[18] Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; John Wiley & Sons: New York, 1999.

[19] 1,2-hydride shift from the terminal to the central carbon might occurred to afford alkyl lactate: a) Bang, E.; Eriksen, J.; Mønsted, L.; Mønsted O. *Acta Chem. Scand*. **1994**, *48*, 12. b) Eriksen, J.; Mønsted, O. *Transition Met. Chem*. **1998**, *23*, 783.

General Conclusion

This thesis shows the fundamental, preparation, characterization, and catalysis of Al^{3+}-mont as an excellent heterogeneous catalyst for the transformation of triose into alkyl lactates. Only a few report concerning of biomass transformation by using montmorillonite catalyst. Biologically, the synthesis of lactic acid from dihydroxyacetone phosphate (DHAP) deals with glyoxalase enzyme system in our body. Therefore, this catalyst can be considered as functional biomimetics of this enzyme system.

In Chapter 1, the author gives some overview regarding the potential of biomass as chemicals feedstock, including the background study of glycerol and its derivatives. The potential of triose, which can be obtained from the glycerol oxidation have been highlighted. The utilization of montmorillonite as solid acid catalyst for organic reactions was demonstrated. The unique characteristics and properties of montmorillonite that contribute to the high catalytic performance were discussed briefly.

The discussion of triose transformation by using Al^{3+}-mont catalyst was described in Chapter 2. This characterization was carried out by using XRD, IR, and NH_3-TPD to gain insight the properties of Al^{3+}-mont. The ability of montmorillonite catalyst to expand in polar solvent was reported to be essential to catalyze efficiently by allowing smooth entrance of substrate to the active site in the interlayer of montmorillonite.

Compare to other solid acid catalysts, this catalyst features strikingly simple preparation and was reusable in recycling experiments. Moreover, it can be applied for large-scale reaction without the formation of any by-product other than water. In addition, the versatility was proved in which the scope of products can be extended to other alkyl lactates such as ethyl lactate and butyl lactate with high yields. The plausible mechanism has been proposed based on cooperative catalysis of Brønsted and Lewis acid sites.

In the future, the main focus is converting waste materials into fine chemicals by using green synthetic methods. For instance, the transformation of pentoses and hexoses, known as the most abundant sugar sources to date have not been explore entirely. The potential of these sugars especially in acid-catalyzed reaction will be studied in order to reduce the dependency on petroleum as chemicals feedstock. Utilization of montmorillonite as macroligand for metal species seems to be fruitful considering its advantages to achieve environment-friendly organic synthesis.