


 Cite this: *RSC Adv.*, 2025, 15, 14152

Synthesis of alkyl levulinates *via* the esterification of levulinic acid and transesterification of methyl levulinate with alkyl alcohols over montmorillonite K10†

 Nobutaka Yamanaka, * Koji Nishi, Kenji Yasunaga and Hiroshi Yamada

Alkyl levulinates are bio-based chemicals with great potential for application in the fields of energy and fine chemical synthesis. They are synthesized *via* the esterification of levulinic acid with the corresponding alkyl alcohols over Brønsted acid catalysts. Here, three types of commercially available, low-cost, and environmentally friendly layered clay minerals (montmorillonite K10, halloysite, and kaolinite) were applied to the esterification of levulinic acid with ethanol as heterogeneous Brønsted acid catalysts. This is because of their surface hydroxyl groups, which can function as Brønsted acid sites. The catalytic activity followed the order of montmorillonite K10 \gg halloysite \approx kaolinite \approx blank (no catalyst). This was most likely attributable to the difference in the thickness of a layer with one interlayer space. The most effective clay mineral, montmorillonite K10, was used to synthesize the target product (ethyl levulinate) at an excellent yield of 96.5% under optimized reaction conditions (N₂ pressure, 0.6 MPa; temperature, 443 K; time, 3.75 h). The clay mineral was observed to be reusable at least thrice for the esterification reaction without any significant decrease in its catalytic activity. Furthermore, it could be used to synthesize various alkyl levulinates in excellent yields by varying the selection of alkyl alcohols used. In addition, it was applied to the transesterification of methyl levulinate with various alkyl alcohols, producing the corresponding alkyl levulinates in extremely good yields. This study provides an environmentally friendly, economical, and effective route to biomass utilization.

 Received 26th January 2025
Accepted 20th April 2025

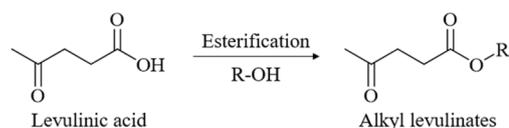
 DOI: 10.1039/d5ra00615e
rsc.li/rsc-advances

Introduction

Owing to the depletion of nonrenewable fossil fuel reserves and the increasing concern regarding global climate change, tremendous efforts have been devoted toward converting renewable biomass resources into fuels and valuable chemicals.^{1–4} The most abundant and renewable biomass on Earth is lignocellulose, which mainly comprises cellulose (30–50 wt%), hemicellulose (20–35 wt%), and lignin (15–30 wt%).^{3–5} Levulinic acid, formed from the hydrolysis of cellulose, has been highlighted by the United States Department of Energy in 2004 and 2010 as a promising building block for chemistry; it is used to synthesize various value-added chemicals.^{3,5–9} Among levulinic acid derivatives, alkyl levulinates have attracted attention because of their numerous potential industrial applications as flavoring agents, fragrances, green solvents, and precursors for synthesizing valuable γ -valerolactone.^{1,3,9,10} Their physicochemical properties are similar to those of biodiesel

fatty acid methyl esters, but they do not exhibit the principal drawbacks of cold flow properties and gum formation.^{1,3,10,11} The addition of alkyl levulinates to biodiesel is expected to be beneficial owing to their favorable properties of low toxicity, high lubricity, flash point stability, and moderate flow properties at low temperatures.^{1,3,12–14}

Alkyl levulinates can be obtained *via* the esterification of levulinic acid with the corresponding alkyl alcohols in the presence of mineral acids, such as HCl, H₂SO₄, and H₃PO₄ (Scheme 1).^{9,10,15} Although effective for the esterification reaction, the homogeneous Brønsted acid catalysts present certain severe drawbacks such as product separation, catalyst recycling, and environmental problems.^{10,15,16} The limitations of homogeneous catalysts can be surmounted through the use of heterogeneous catalysts. Thus, heterogeneous Brønsted acid



Scheme 1 Synthesis of alkyl levulinates *via* the esterification of levulinic acid with alkyl alcohols.

Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan. E-mail: yamanaka@nda.ac.jp

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5ra00615e>



catalysts that are environmentally friendly and effective for the esterification of levulinic acid to alkyl levulinates are required.

Clay minerals, such as kaolinite, halloysite, and montmorillonite K10, are abundant, easily available, and environmentally friendly mineral solids made of layered silicates.^{17–20} They have been applied in various chemical processes mainly as supports for complex and metal nanoparticles because of their favorable properties of high thermal stability (kaolinite and halloysite) and high specific surface area (montmorillonite K10).¹ These three clay minerals bear surface hydroxyl groups that function as Brønsted acid sites.¹ Thus, we first applied them as heterogeneous Brønsted acid catalysts for the esterification of levulinic acid with ethanol. Thereafter, the reaction conditions were optimized using the most effective clay mineral, and the reusability of this mineral was evaluated. Finally, the esterification of levulinic acid over the best catalyst was conducted in the presence of various alkyl alcohols. Here, the catalyst was further applied to the transesterification of methyl levulinate to expand its substrate scope. The proposed catalyst improved the production of alkyl levulinates in terms of product separation, cost, and performance.

Experimental details

Materials

Levulinic acid, methyl levulinate, ethyl levulinate, propyl levulinate, and butyl levulinate were purchased from Tokyo Chemical Industry Co., Ltd. *n*-Dodecane, methanol, ethanol, 1-propanol, 1-butanol, 1,4-dioxane, sodium chloride, and phenolphthalein were purchased from Wako Pure Chemical Industries, Ltd. All the organic chemicals were used as received without further purification. Montmorillonite K10, halloysite, and kaolinite were purchased from Sigma-Aldrich.

Catalyst characterization

Powder X-ray diffractograms (XRD) were recorded on a Bruker D8 ADVANCE diffractometer operated at 40 kV and 40 mA using CuK_α radiation ($\lambda = 0.15418$ nm) and identified by using Crystallography Open Database (COD).²¹ Fresh and spent montmorillonite K10 were scanned at a step width of 0.02° and a speed of 6° min⁻¹ over the range 5° ≤ 2θ ≤ 80°. Nitrogen adsorption and desorption isotherm was measured at 77 K (*i.e.*, liquid-nitrogen boiling temperature) using Belsorp Max (BEL Japan). To remove the physisorbed gases prior to the measurement, the spent montmorillonite K10 was degassed at 423 K for 2 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. The Brønsted acidity of the spent montmorillonite K10 was calculated using acid–base titration. The procedure is described below. The spent montmorillonite K10 (50 mg) was dispersed in 0.10 M NaCl aqueous solution (50 mL) for 24 h and then titrated with 0.01 M NaOH aqueous solution in the presence of phenolphthalein.

Typical experimental procedures

The esterification of levulinic acid with alkyl alcohols over the clay minerals was conducted in a high-pressure autoclave using

a magnetic stirrer, a pressure gauge, and an automatic temperature controller. In a typical procedure, the clay mineral (50 mg), *n*-dodecane (0.30 mmol) as an internal standard material, levulinic acid (1.0 mmol), and ethanol (3.0 mL) were charged into the autoclave. The autoclave was purged with N₂ to remove air and maintained at 1.0 MPa at room temperature. The autoclave was placed in a preheated oil bath at 423 K for 1.5 h. After the reaction, the autoclave was removed from the oil bath and rapidly cooled in a water bath to stop the reaction. The autoclave was left in the water bath for at least 0.5 h until the catalyst settled to the bottom of the autoclave.²² The remaining N₂ was discharged, and the supernatant solution was analyzed using a gas chromatograph (Nexis GC-2030, Shimadzu, with a flame ionization detector) equipped with a capillary column (Rxi-5ms, 30 m × 0.25 mm). The yield of the target product (ethyl levulinate) was calculated using the internal standard method.

Results and discussion

The esterification of levulinic acid with ethanol has been reported to occur even in the absence of Brønsted acid catalysts because of the acidity of levulinic acid itself.^{15,23} Thus, a thermal reaction first occurred under N₂ (1.0 MPa) at 423 K for 1.5 h. Tables 1 and Fig. S1† show the results. The esterification reaction proceeded, and ethyl levulinate was obtained at 9.6% yield (Table 1, entry 1). Thereafter, montmorillonite K10, halloysite, and kaolinite were applied to the esterification reaction as heterogeneous Brønsted acid catalysts under the same reaction conditions. The results are also shown in Table 1 and Fig. S1.† Montmorillonite K10 exhibited a significantly higher yield of ethyl levulinate (47.9%) compared with the thermal reaction (Table 1, entries 1 and 2). Using halloysite and kaolinite for the esterification reaction, the target product was obtained at yields of 12.8% and 11.4%, respectively, which were similar to that obtained in the thermal reaction (Table 1, entries 1, 3, and 4). Even at a longer reaction time of 3 h, the latter two clay minerals showed almost no difference in the yield of ethyl levulinate obtained from the thermal reaction (Fig. S1†). The reaction results indicate that halloysite and kaolinite hardly promoted the esterification reaction.

Table 1 Esterification of levulinic acid with ethanol over montmorillonite K10, halloysite, and kaolinite^a

Entry	Catalyst	Yield ^b /%	<i>d</i> ₀₀₁ ^c /nm
1	Blank	9.6	—
2	Montmorillonite K10	47.9	1.01
3	Halloysite	12.8	0.76
4	Kaolinite	11.4	0.72

^a Reaction conditions: catalyst, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; ethanol, 3.0 mL; N₂ pressure, 1.0 MPa; temperature, 423 K; time, 1.5 h. ^b Yield of ethyl levulinate. ^c Determined based on 2θ = 8.8°, 11.7°, and 12.3° corresponding to the (001) planes of montmorillonite, halloysite, and kaolinite, respectively (Fig. S2).



We attempted to identify the factor responsible for the difference in the catalytic activities of montmorillonite K10 and the other two clay minerals. First, the catalytic activities, specific surface areas, and Brønsted acidities of the three clay minerals were compared (Table 1 and S1†). However, no relationship was observed between their catalytic activities and physicochemical properties. Montmorillonite K10, halloysite, and kaolinite are layered silicates, and their hydroxyl groups, which function as Brønsted acid sites, are located between the layers.^{24–27} Thus, we calculated the thickness of a layer with one interlayer space, which is referred to as the *d*-spacing (d_{001}) or basal spacing.²⁸ The d_{001} values of montmorillonite K10, halloysite, and kaolinite were calculated using Bragg's equation based on the 2θ positions of the (001) diffraction peaks, and the results are shown in Table 1. Montmorillonite K10 exhibited a d_{001} of 1.01 nm, whereas halloysite and kaolinite exhibited smaller and similar d_{001} values of 0.76 and 0.72 nm, respectively (Table 1, entries 2–4). Thus, it can be concluded that the d_{001} is a key factor controlling the catalytic activity of the layered clay minerals for the esterification of levulinic acid with ethanol. To support this assumption, we calculated the rate of the uptake of methyl levulinate (instead of levulinic acid) using the clay minerals because we could not create a calibration curve for levulinic acid with the capillary column. As shown in Table S2,† the uptake rate followed the order of montmorillonite K10 \gg halloysite \approx kaolinite, consistent with that of the d_{001} values (Table 1), thereby reinforcing the aforementioned conclusion.

We optimized the reaction conditions for the esterification of levulinic acid with ethanol using the most effective clay mineral (montmorillonite K10).

First, the effect of the volume of ethanol was investigated using ethanol (approximately 3.0 mL), keeping the other reaction parameters constant. Table 2 presents the results. The ethanol volume was observed to significantly impact the yield of ethyl levulinate. When the esterification of levulinic acid with ethanol over montmorillonite K10 was conducted using less than 3.0 mL of ethanol, the yield significantly increased to 70.0% (Table 2, entries 1 and 2). When more than 3.0 mL of ethanol was used, the yield decreased to 40.0% (Table 2, entries 2 and 3). Thus, an ethanol volume of 1.5 mL was determined as optimal for the subsequent experiments.

Next, the effect of the N_2 pressure was investigated by decreasing the N_2 pressure from 1.0 to 0.2 MPa. To evaluate the initial activity of montmorillonite K10, the esterification of levulinic acid with ethanol was performed for a shorter reaction

Table 3 Effect of N_2 pressure on the esterification of levulinic acid with ethanol over montmorillonite K10^a

Entry	N_2 pressure/MPa	Yield ^b /%
1	1.0	46.5
2	0.8	47.3
3	0.6	45.3
4	0.4	37.6
5	0.2	34.4

^a Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; ethanol, 1.5 mL; temperature, 423 K; time, 0.75 h. ^b Yield of ethyl levulinate.

time of 0.75 h. Table 3 presents the results. A decrease in the N_2 pressure to 0.6 MPa only slightly influenced the ethyl levulinate yield (45.3%) (Table 3, entries 1–3), and a further decrease in the N_2 pressure to 0.4 and 0.2 MPa decreased the yield to 37.6% and 34.4%, respectively (Table 3, entries 4 and 5). A similar behavior has been reported.^{16,29} Thus, an N_2 pressure of 0.6 MPa was determined as optimal for the subsequent experiments.

Thereafter, the effect of the reaction temperature range of 403–443 K was investigated, and Table 4 presents the results. Although ethyl levulinate was obtained at a yield of 23.5% at 403 K, the yield increased to 62.5% at 443 K (Table 4, entries 1–3). Thus, 443 K was determined as optimal for the subsequent experiments.

Finally, the effect of the reaction time was investigated, and Fig. 1 shows the results. The ethyl levulinate yield was 62.5% at a reaction time of 0.75 h. The yield gradually increased with an increase in the reaction time, reaching 96.5% after 3.75 h. However, prolonging the reaction time to 4.75 h did not cause a further increase in the yield. Thus, a reaction time of 3.75 h was determined to be optimal.

The reusability of montmorillonite K10 for the esterification of levulinic acid with ethanol was tested under the optimized reaction conditions (N_2 pressure, 0.6 MPa; temperature, 443 K; time, 3.75 h). Fig. 2 shows the results. After the reaction, the spent catalyst was separated from the reaction solution by centrifugation, washed with acetone, dried in a vacuum overnight, and reused for the next run under the same reaction conditions. After the first run, ethyl levulinate was formed at a yield of 90.5%. A similar yield of 87.8% was obtained in the second run. Although the yield slightly decreased during the third run, a sufficiently high yield of 80.9% was still obtained in the fourth run. Thus, it was concluded that montmorillonite

Table 2 Effect of ethanol volume on the esterification of levulinic acid with ethanol over montmorillonite K10^a

Entry	Ethanol volume/mL	Yield ^b /%
1	1.5	70.0
2	3.0	47.9
3	4.5	40.0

^a Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; N_2 pressure, 1.0 MPa; temperature, 423 K; time, 1.5 h. ^b Yield of ethyl levulinate.

Table 4 Effect of reaction temperature on the esterification of levulinic acid with ethanol over montmorillonite K10^a

Entry	Reaction temperature/K	Yield ^b /%
1	403	23.5
2	423	45.3
3	443	62.5

^a Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; ethanol, 1.5 mL; N_2 pressure, 0.6 MPa; time, 0.75 h. ^b Yield of ethyl levulinate.



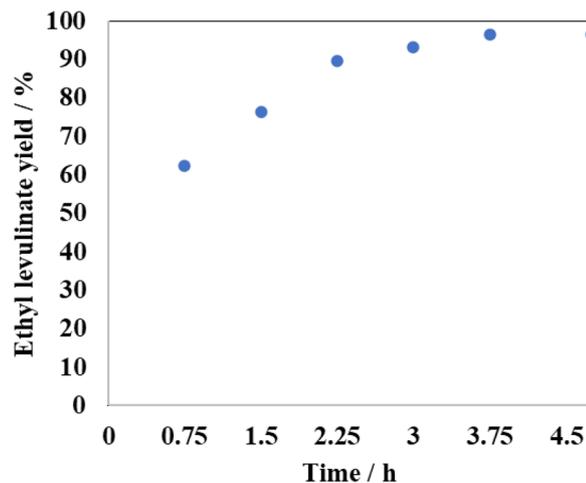


Fig. 1 Time profile of the esterification of levulinic acid with ethanol over montmorillonite K10. Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; ethanol, 1.5 mL; N₂ pressure, 0.6 MPa; temperature, 443 K.

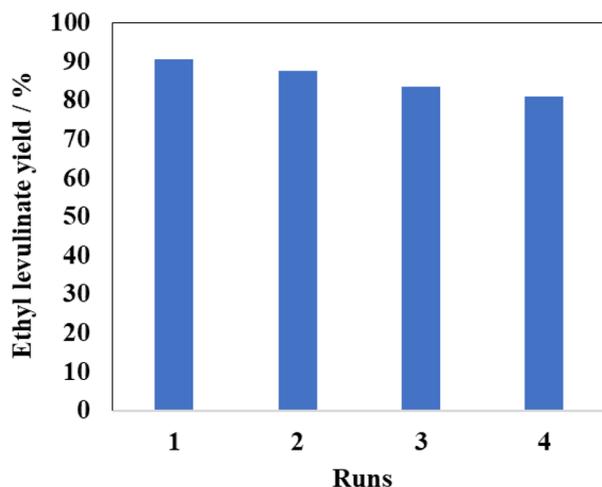


Fig. 2 Reusability of montmorillonite K10 for the esterification of levulinic acid with ethanol. Reaction conditions: montmorillonite K10, 100 mg; *n*-dodecane, 0.60 mmol; levulinic acid, 2.0 mmol; ethanol, 3.0 mL; temperature, 443 K; time, 3.75 h.

K10 is reusable at least thrice for the esterification of levulinic acid with ethanol without a significant decrease in its catalytic activity. To determine the reason for the deactivation of montmorillonite K10, montmorillonite K10 recovered after the fourth run was characterized by XRD, BET, and acid–base titration. Fig. S3† shows the XRD patterns of the catalysts before and after the fourth run. No appreciable changes were observed. In addition, the spent catalyst showed similar specific surface area and Brønsted acidity to the fresh catalyst (Table S1,† entries 1 and 2). These results indicate that the physicochemical properties of the catalysts before and after the fourth run remained almost unchanged. Finally, the rates of decrease in the ethyl levulinate yield and catalyst weight in the fourth run compared with the first run were calculated. The rates of

decrease in the yield and weight were similar at 89.4% and 91.0%, respectively. Thus, it was concluded that the catalyst deactivation was primarily due to the loss of the catalyst during the recycling process.

Montmorillonite K10 was applied to the esterification of levulinic acid with other alkyl alcohols (*i.e.*, methanol, 1-propanol, and 1-butanol) to expand its substrate scope. The esterification of levulinic acid with methanol was conducted under different reaction conditions (methanol, 3.0 mL; temperature, 423 K) while keeping the other reaction parameters constant. As shown in Table 5 and Fig. S4,† regardless of the alkyl alcohols used, the corresponding alkyl levulinates were synthesized at excellent yields. Here, 1-propanol and 1-butanol exhibited higher activity for the production of the corresponding alkyl levulinates than ethanol under identical reaction conditions (Fig. S4†). When the esterification of levulinic acid with 1-propanol and 1-butanol was conducted under the same reaction conditions as that of levulinic acid with methanol, methanol exhibited a significantly higher initial activity than 1-propanol and 1-butanol (Table S3†). A plausible mechanism for the esterification of levulinic acid with an alkyl alcohol involves the nucleophilic attack of the oxygen of the alcohol toward the carbonyl carbon of the protonated levulinic acid intermediate (Scheme S1†).^{23,30} Thus, the notably higher reactivity of methanol was most likely due to its higher nucleophilicity.^{31,32}

The catalyst was further applied in the transesterification of methyl levulinate with ethanol, 1-propanol, and 1-butanol to broaden its substrate scope. To the best of our knowledge, this is the first report on the transesterification of methyl levulinate with ethanol and 1-propanol. Table 6 and Fig. S5† show the results. Regardless of the alkyl alcohols used, the corresponding alkyl levulinates were synthesized at extremely good yields of approximately 90%.

Finally, the catalytic result of montmorillonite K10 for the esterification of levulinic acid with ethanol was compared with those of certain heterogeneous Brønsted acid catalysts (Table 7). Montmorillonite K10 was observed to be considerably more efficient for the production of ethyl levulinate than ZrO₂/SBA-15 because it formed ethyl levulinate at a considerably higher yield of 62.5% at a significantly lower temperature of 443 K and a shorter time of 0.75 h (Fig. 1 and Table 7, entry 2). Compared with desilicated HZSM-5 and Micro/Meso-HZ-5, montmorillonite K10 required a higher reaction temperature but synthesized ethyl levulinate at a similar yield at a shorter reaction time

Table 5 Esterification of levulinic acid with various alkyl alcohols over montmorillonite K10^a

Entry	Alkyl alcohol	Time/h	Yield ^b /%
1 ^c	Methanol	6	93.9
2	Ethanol	3.75	96.5
3	1-Propanol	2.25	95.1
4	1-Butanol	2.25	96.6

^a Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; alkyl alcohol, 1.5 mL; N₂ pressure, 0.6 MPa; temperature, 443 K. ^b Yield of the corresponding alkyl levulinates. ^c Methanol, 3.0 mL; temperature, 423 K.



Table 6 Transesterification of methyl levulinate with various alkyl alcohols over montmorillonite K10^a

Entry	Alkyl alcohol	Time/h	Yield ^b /%
1	Ethanol	18	89.5
2	1-Propanol	9	91.3
3	1-Butanol	9	89.3

^a Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; methyl levulinate, 1.0 mmol; alkyl alcohol, 1.5 mL; N₂ pressure, 0.6 MPa; temperature, 443 K. ^b Yield of the corresponding alkyl levulinates.

Table 7 Comparison of the esterification of levulinic acid with ethanol over montmorillonite K10 and other heterogeneous Brønsted acid catalysts

Entry	Catalyst	Reaction conditions	Yield ^a /%
1	Montmorillonite K10	443 K, 3.75 h	96.5
2 ^b	ZrO ₂ /SBA-15	523 K, 1 h	50
3 ^c	Desilicated HZSM-5	403 K, 5 h	95
4 ^c	Micro/Meso-HZ-5	403 K, 5 h	95

^a Yield of ethyl levulinate. ^b Result of a previous study.³⁰ ^c Results of a previous study.³³ The catalytic results shown in Table 7, entries 2–4, were obtained by other groups.

(Table 7, entries 1, 3, and 4). Table 8 compares the catalytic result of montmorillonite K10 for the transesterification of methyl levulinate with 1-butanol with those of other heterogeneous Brønsted acid catalysts. Compared with catalytic systems using sulfated SnO₂ and Amberlyst-15, the proposed catalytic system required a higher reaction temperature but did not use toluene, a volatile organic compound that is harmful to human health and the environment (Table 8, entries 1–3).^{34,35} In addition, montmorillonite K10 can synthesize butyl levulinate at a significantly higher yield and shorter reaction time. Montmorillonite K10 is commercially available, low-cost, and environmentally friendly compared with the other heterogeneous catalysts listed in Tables 7 and 8. Thus, the proposed catalytic system substantially improves the production of alkyl levulinates from levulinic acid or methyl levulinate and alkyl alcohols in terms of product separation, cost, and performance, thereby providing an environmentally friendly, economical, and effective route to biomass utilization.

Table 8 Comparison of the transesterification of methyl levulinate with 1-butanol over montmorillonite K10 and other heterogeneous Brønsted acid catalysts

Entry	Catalyst	Reaction conditions	Yield ^a /%
1	Montmorillonite K10	443 K, 9 h	89.3
2 ^b	Sulfated SnO ₂	Toluene, 383 K, 10 h	45
3 ^b	Amberlyst-15	Toluene, 383 K, 10 h	54

^a Yield of butyl levulinate. ^b Results of a previous study.²³ The catalytic results shown in Table 8, entries 2 and 3, were obtained by other groups.

Conclusions

Here, we demonstrated that commercially available, low-cost, and environmentally friendly montmorillonite K10 is an effective heterogeneous Brønsted acid catalyst in the synthesis of alkyl levulinates *via* the esterification reactions. In the esterification of levulinic acid with ethanol, montmorillonite K10 exhibited a significantly higher catalytic activity than halloysite and kaolinite, most likely attributable to the difference in their basal spacings. This finding offers valuable insight into the design of layered compounds that are effective for organic synthesis reactions, including biomass valorization. Under the optimized reaction conditions, montmorillonite K10 generated the target product (ethyl levulinate) at an excellent yield of 96.5%. Montmorillonite K10 was observed to be reusable at least thrice for the esterification reaction without any significant loss in its catalytic activity. Montmorillonite K10 was applied in the esterification of levulinic acid and transesterification of methyl levulinate with various alkyl alcohols, and the corresponding alkyl levulinates were synthesized in extremely good to excellent yields.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Author contributions

Nobutaka Yamanaka: conceptualization, methodology, validation, formal analysis, investigation, resources, writing – original draft, visualization, project administration, funding acquisition. Koji Nishi: methodology, formal analysis, investigation, data curation, writing – review & editing. Kenji Yasunaga and Hiroshi Yamada: data curation, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by JSPS KAKENHI (Grant Numbers 23K13787 and 23K03705).

References

- N. Yamanaka, D. Abe, M. Miwaka-Saiga, K. Yasunaga, H. Yamada and S. Shimazu, *Sustainable Energy Fuels*, 2022, **6**, 5153.
- G. Wang, Z. Zhang and L. Song, *Green Chem.*, 2014, **16**, 1436.
- N. Yamanaka and S. Shimazu, *Reactions*, 2023, **4**, 667.
- S. Zhu, Y. Cen, J. Guo, J. Chai, J. Wang and W. Fan, *Green Chem.*, 2016, **18**, 5667.
- A. Démolis, N. Essayem and F. Rataboul, *ACS Sustain. Chem. Eng.*, 2014, **2**, 1338.



- 6 B. Girisuta, L. P. B. M. Janssen and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2007, **46**, 1696.
- 7 J. Yang, G. Li, L. Zhang and S. Zhang, *Catalysts*, 2018, **8**, 14.
- 8 S. Dharne and V. V. Bokade, *J. Nat. Gas Chem.*, 2011, **20**, 18.
- 9 W. Zhao, H. Ding, J. Zhu, X. Liu, Q. Xu and D. Yin, *J. Bioresour. Bioprod.*, 2020, **5**, 291.
- 10 J. Zhang, S. Wu, B. Li and H. Zhang, *ChemCatChem*, 2012, **4**, 1230.
- 11 D. J. Hayes, *Catal. Today*, 2009, **145**, 138.
- 12 M. M. Aguilar, X. Duret, T. Ghislain, D. P. Minh, A. Nzihou and J.-M. Lavoie, *Fuel*, 2020, **264**, 116702.
- 13 V. Trombettoni, L. Bianchi, A. Zupanic, A. Porciello, M. Cuomo, O. Piermatti, A. Marrocchi and L. Vaccaro, *Catalysts*, 2017, **7**, 235.
- 14 F. G. Cirujano, A. Corma and F. X. Llabrés i Xamena, *Chem. Eng. Sci.*, 2015, **124**, 52.
- 15 K. Y. Nandiwale, S. K. Sonar, P. S. Niphadkar, P. N. Joshi, S. S. Deshpande, V. S. Patil and V. V. Bokade, *Appl. Catal., A*, 2013, **460–461**, 90.
- 16 N. Yamanaka, K. Nishi, K. Yasunaga and H. Yamada, *RSC Adv.*, 2024, **14**, 25221.
- 17 B. Zeynizadeh, S. Rahmani and S. Ilkhanizadeh, *Polyhedron*, 2019, **168**, 48.
- 18 A. Jha, A. C. Garade, M. Shirai and C. V. Rode, *Appl. Clay Sci.*, 2013, **74**, 141.
- 19 P. Pasbakhsh, G. J. Churchman and J. L. Keeling, *Appl. Clay Sci.*, 2013, **74**, 47.
- 20 D. Tong, X. Chen, Y. Dong, Z. Fang, H. Zhang, C. Zhou and W. Yu, *Biomass Convers. Biorefin.*, 2024, **14**, 5295.
- 21 A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni and R. Rizzi, *J. Appl. Crystallogr.*, 2015, **48**, 598.
- 22 Q. Cao, W. Zhang, S. Luo, R. Guo and D. Xu, *Energy Fuels*, 2021, **35**, 12725.
- 23 M. Melchiorre, R. Amendola, V. Benessere, M. E. Cucciolo, F. Ruffo and R. Esposito, *Mol. Catal.*, 2020, **483**, 110777.
- 24 M. N. Norhayati, T. I. Tuan Noor Maznee, S. S. Hoong, H. Nurul Ain, A. Srihanum, P. P. Kosheela Devi, S. Mohd Norhisham, S. K. Yeong and A. H. Hazimah, *J. Oil Palm Res.*, 2016, **28**, 114.
- 25 H. Nanao, H. Amanuma, K. Yoshida, O. Sato, A. Yamaguchi and M. Shirai, *Clay Sci.*, 2017, **21**, 35.
- 26 J. González-Rivera, A. Spepi, C. Ferrari, I. Longo, J. T. Rodriguez, E. Fantechi, C. Innocenti, F. Pineider, M. A. Vera-Ramírez, M. R. Tiné and C. Duce, *Appl. Clay Sci.*, 2020, **196**, 10572.
- 27 I. Yellapurkar, S. Shaikh, G. Pavale, S. Bhabal and M. M. V. Ramana, *Res. Chem. Intermed.*, 2021, **47**, 4067.
- 28 Clay Mineral – An Overview, <https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/clay-mineral>, accessed November 2024.
- 29 T. A. Natsir, T. Hara, N. Ichikuni and S. Shimazu, *ACS Appl. Energy Mater.*, 2018, **1**, 2460.
- 30 N. A. S. Ramli, D. Sivasubramaniam and N. A. S. Amin, *BioEnergy Res.*, 2017, **10**, 1105.
- 31 M. J. da Silva and M. T. Cordeiro, *Processes*, 2024, **12**, 1802.
- 32 F. P. Martins, F. A. Rodrigues and M. J. Silva, *Energies*, 2018, **11**, 1263.
- 33 E. Ahmad, M. I. Alam, K. K. Pant and M. A. Haider, *Green Chem.*, 2016, **18**, 4804.
- 34 J. Y. Hong, S. Y. Yu, S. Y. Kim, J. J. Ahn, Y. Kim, G. W. Kim, S. W. Son, J.-T. Park and S. Y. Hwang, *Environ. Res.*, 2016, **146**, 59.
- 35 X. Wang, Y. Luo, Y. Gao, D. Han, Z. Wang, B. Shen and X. Wang, *Chemosphere*, 2024, **368**, 143720.

