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

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Table S1 Specific surface area and Brønsted acidity of fresh and spent montmorillonite K10, halloysite, and kaolinite

Entry	Catalyst	Specific surface area / $m^2 \cdot g^{-1}$	Brønsted acidity / $mmol \cdot g^{-1}$
1[a]	Montmorillonite K10	251.7	0.378
2	Montmorillonite K10 after the fourth run	249.1	0.369
3[a]	Halloysite	60.5	0.181
4[a]	Kaolinite	7.0	0.093

[a]Results obtained from [1].

Table S2 Methyl levulinate uptake rate using montmorillonite K10, halloysite, and kaolinite[a]

Entry	Catalyst	Methyl levulinate uptake rate / %
1	Montmorillonite K10	15.0
2	Halloysite	3.4
3	Kaolinite	2.1

[a]Reaction conditions: catalyst, 50 mg; *n*-dodecane, 0.30 mmol; methyl levulinate, 1.0 mmol; 1,4-dioxane, 3.0 mL; N_2 pressure, 1.0 MPa; temperature, 423 K; time, 1.5 h.

Table S3 Esterification of levulinic acid with methanol, 1-propanol, and 1-butanol over montmorillonite K10[a]

Entry	Alkyl alcohol	Yield / %[b]
1	Methanol	71.7
2	1-Propanol	52.8
3	1-Butanol	57.2

[a]Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; alkyl alcohol, 3.0 mL; N_2 pressure, 0.6 MPa; temperature, 423 K; time, 1.5 h. [b]Yield of the corresponding alkyl levulinates.

Table S4 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]	Wells-Dawson HPA	351 K, 10 h	76.0
3[c]	Sulfated ZrO_2	343 K, 10 h	27.5
4[d]	UiO-66-$NHSO_3H$	433 K, 4 h	74.5

[a]Yield of ethyl levulinate. [b]Result obtained from [2]. [c]Result obtained from [3]. [d]Result obtained from [4]. The catalytic results shown in Table S4, entries 2-4, were obtained by other groups.

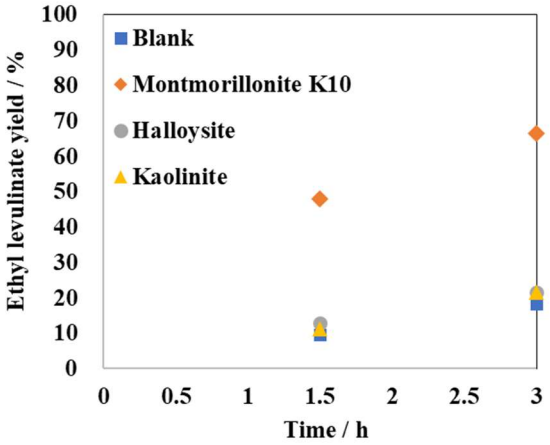


Fig. S1 Time profile of the esterification of levulinic acid with ethanol over montmorillonite K10, halloysite, and kaolinite. Reaction conditions: catalyst, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; ethanol, 3.0 mL; N_2 pressure, 1.0 MPa; temperature, 423 K.

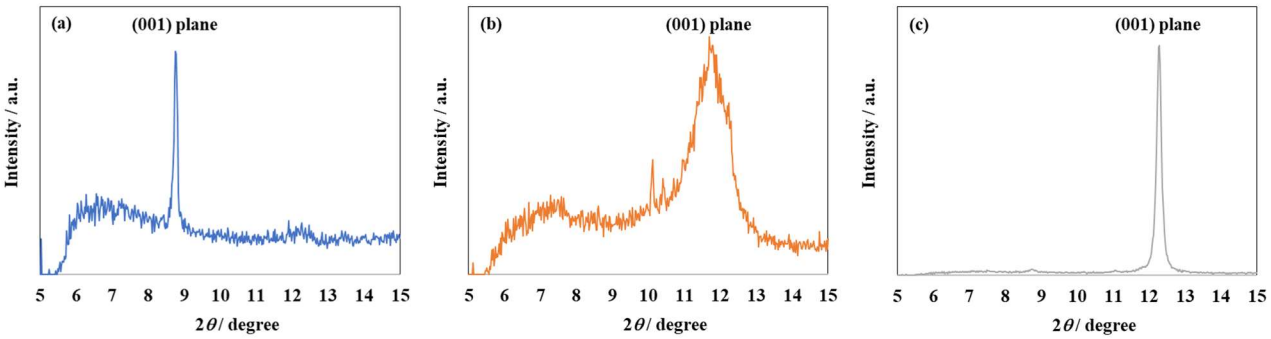


Fig. S2 XRD patterns of (a) montmorillonite K10, (b) halloysite, and (c) kaolinite. Adapted with slight modification from [5] with permission from the Royal Society of Chemistry, copyright 2024. The peaks at $2\theta = 8.8°$, 11.7°, and 12.3° correspond to the (001) planes of montmorillonite, halloysite, and kaolinite, respectively [6-8].

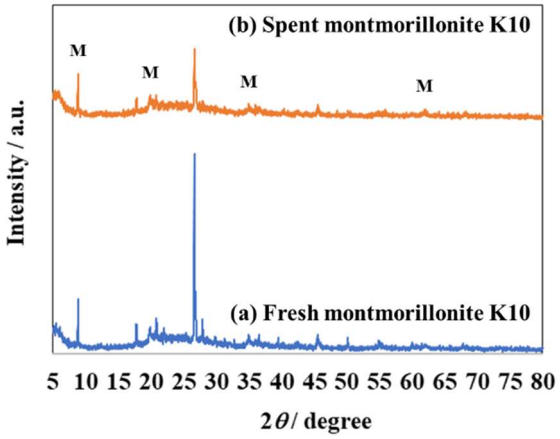


Fig. S3 XRD patterns of montmorillonite K10 (a) before and (b) after the fourth run; M: Montmorillonite (COD 00-901-0957). The peak at $2\theta = 8.8°$ corresponds to the (001) plane of montmorillonite [6].

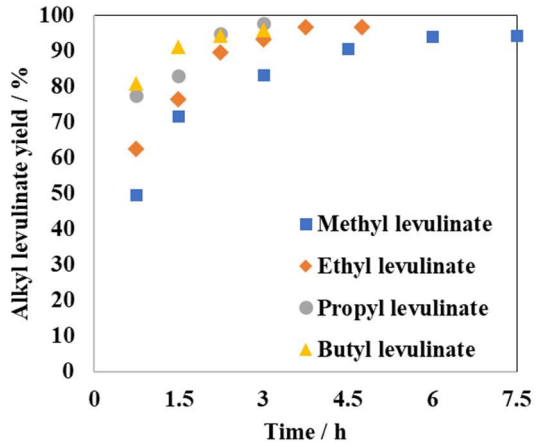


Fig. S4 Time profile of the esterification of levulinic acid with methanol, ethanol, 1-propanol, and 1-butanol over montmorillonite K10. Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; levulinic acid, 1.0 mmol; alkyl alcohol, 1.5 mL; N_2 pressure, 0.6 MPa; temperature, 443 K. The esterification of levulinic acid with methanol was conducted under different reaction conditions (methanol, 3.0 mL; temperature, 423 K) while the other reaction parameters remained constant.

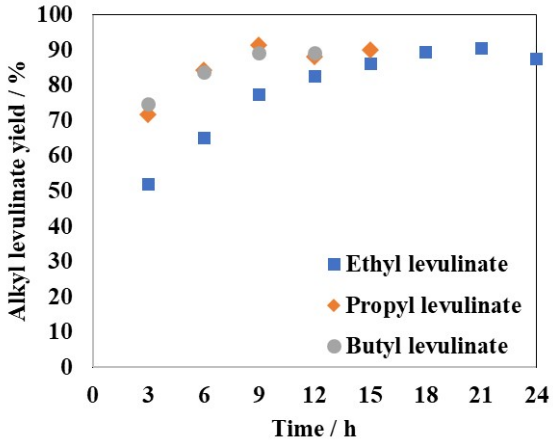
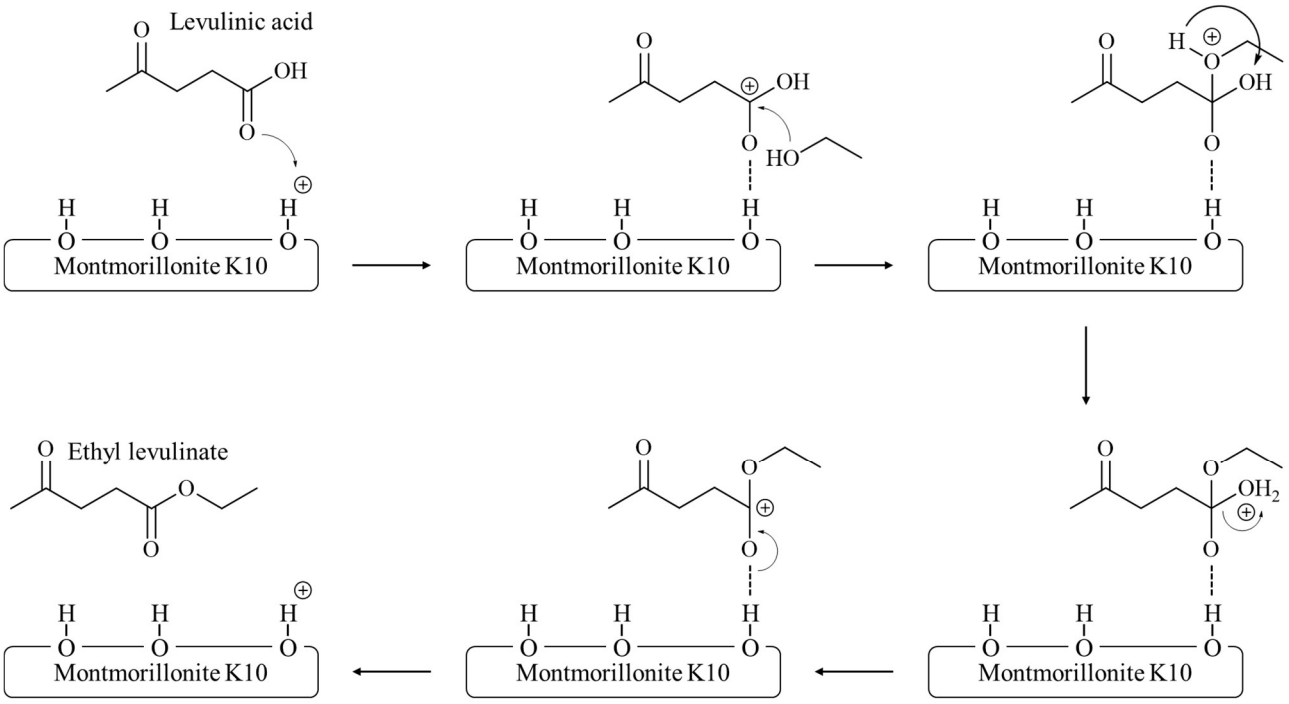


Fig. S5 Time profile of the transesterification of methyl levulinate with ethanol, 1-propanol, and 1-butanol over montmorillonite K10. Reaction conditions: montmorillonite K10, 50 mg; *n*-dodecane, 0.30 mmol; methyl levulinate, 1.0 mmol; alkyl alcohol, 1.5 mL; N_2 pressure, 0.6 MPa; temperature, 443 K.



Scheme S1 A plausible reaction mechanism for the esterification of levulinic acid with ethanol over montmorillonite K10. This reaction mechanism is based on [9].

References

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