Electronic Supplementary Information (ESI)

Sustainable Manufacturing of CALF-20 via a ZnO-Based Route Eliminating the Washing Step

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Experimental details

Materials

All commercially available chemicals were used without further purification. Zinc oxide (ZnO, ≥98%), zinc oxalate dihydrate ($ZnC_2O_4 \cdot 2H_2O$), oxalic acid ($H_2C_2O_4$, ≥99.5%), sodium oxalate ($Na_2C_2O_4$), and methanol (≥99.5%) were purchased from Fujifilm Wako Pure Chemical Corporation. Zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$)was purchased from Sigma-Aldrich. 1,2,4-Triazole ($H_3C_2N_3$, >99.0%) was purchased from Tokyo Chemical Industry Co. Oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) was also obtained from Fujifilm Wako Pure Chemical Corporation.

Wash-free Synthesis of CALF-20 using ZnO (This study)

First, 4.07 mmol of ZnO was added to an aqueous methanol solution (total volume: 20 mL; H_2O/methanol = 16/4 mL) and stirred for 30 min using a magnetic stirrer. Separately, 4.07 mmol of 1,2,4-triazole and 2.04 mmol of oxalic acid were dissolved in another identical solvent mixture and stirred for 30 min. The two solutions were then combined and stirred for *x* hours (*x* = 1, 2, 3, 4, 5, 6, 24). The resulting solid was collected by centrifugation without any washing step. The product was dried in air at 100 °C and 101.3 kPa, followed by drying at 130 °C overnight under vacuum. The product is denoted as *wf*-CALF-20.

Solvothermal Synthesis of CALF-20

According to the procedure reported in reference [1], zinc oxalate dihydrate (2.50 mmol) and 1,2,4-triazole (4.21 mmol) were added to a Teflon-lined vessel containing 3.75 mL of methanol. The mixture was heated at 180 °C for 48 h. After synthesis, the solid was isolated by centrifugation at 6000 rpm for 6 min. The product was dried in air at 100 °C and 101.3 kPa, followed by drying at 130 °C overnight under vacuum. The product is denoted as *st*-CALF-20.

Room Temperature Synthesis of CALF-20

According to the procedure reported in reference [2], 4.07 mmol of zinc acetate dihydrate was added to an aqueous methanol solution and stirred for 5 min, yielding a clear solution. Next, 2.04 mmol of sodium oxalate was added to this solution, followed by stirring the solution for 5 min, yielding a Zn-oxalate suspension. Subsequently, 8.14 mmol of 1,2,4-triazole was added to the suspension (total volume: 40 mL; H_2O/methanol = 32/8 mL), followed by stirring for 60 min. The product was collected by centrifugation at 6000 rpm for 6 min and then dried in air at 100 °C and 101.3 kPa, followed by drying at 130 °C overnight under vacuum. The product is denoted as *rt*-CALF-20.

Mechanochemical (Liquid-assisted Grinding) Synthesis of CALF-20

According to the procedure reported in reference [3], 4.07 mmol of zinc oxide and 2.04 mmol of oxalic acid were mixed in deionized water for 1 h. The product was collected by centrifugation at 6000 rpm for 6 min and dried in air and under vacuum. Subsequently, 4.00 mmol of the resulting zinc oxalate, 6.74 mmol of 1,2,4-triazole, and 1.36 mL of methanol were

placed into a milling vessel together with thirty 10 mm zirconia balls. The mixture was milled at 150 rpm for 1 h. After milling, the product was collected by centrifugation at 6000 rpm for 6 min, dried in air at 100 °C and 101.3 kPa, followed by drying at 130 °C overnight under vacuum. The product is denoted as *lag*-CALF-20.

Mechanochemical (Neat Grinding) Synthesis of CALF-20

According to the procedure reported in reference [4], 4.07 mmol of zinc acetate dihydrate, 4.07 mmol of 1,2,4-triazole, and 2.04 mmol of oxalic acid dihydrate were placed into a milling vessel. Twelve 5 mm zirconia balls and seven 10 mm zirconia balls were added, and the mixture was milled at 150 rpm for 15 min. The product was dispersed once in methanol and collected by centrifugation at 6000 rpm for 6 min. The product was dried in air at 100 °C and 101.3 kPa, followed by drying at 130 °C overnight under vacuum. The product is denoted as *ng*-CALF-20.

Table S1. Summary of the starting materials used in this study and in previously reported syntheses.

Synthesis Method	Zn / mmol	Tz / mmol	Ox / mmol	ref
Wash-free	ZnO / 4.07	$H_3C_2N_3$ / 4.07	$H_2C_2O_4$ / 2.04	This work
Solvothermal	$ZnC_2O_4 \cdot 2H_2O$ / 2.5	$H_3C_2N_3$ / 4.21	–	[1]
Room Temperature	$Zn(CH_3CO_2)_2 \cdot 2H_2O$ / 4.07	$H_3C_2N_3$ / 4.07	$Na_2C_2O_4$ / 2.04	[2]
Mechanochemical (Liquid-assisted grinding)	ZnC_2O_4 (prepared) / 4.07	$H_3C_2N_3$ / 4.07	–	[3]
Mechanochemical (Neat grinding)	$Zn(CH_3CO_2)_2 \cdot 2H_2O$ / 4.07	$H_3C_2N_3$ / 4.07	$H_2C_2O_4 \cdot 2H_2O$ / 2.04	[4]

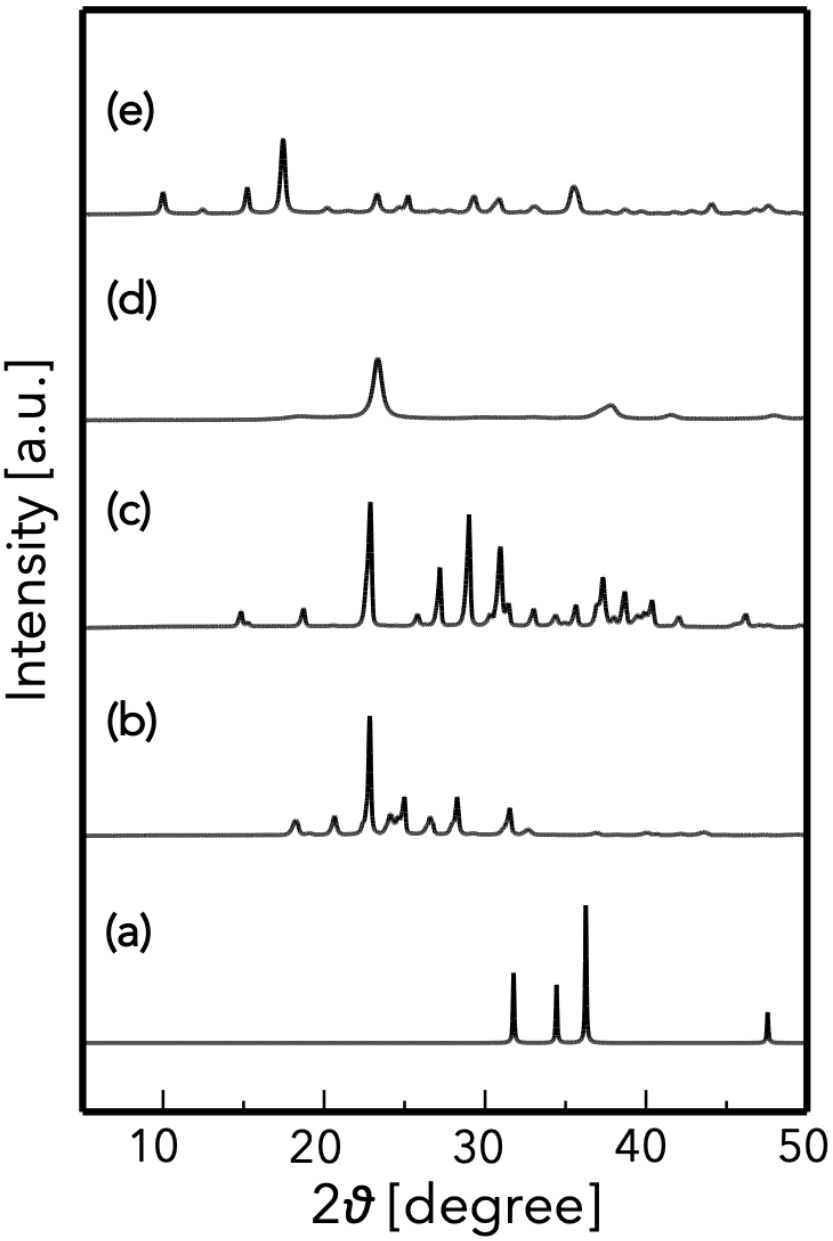

Fig. S1 PXRD patterns of the starting materials and the possible intermediate products formed from them: (a) zinc oxide, (b) 1,2,4-triazole, (c) oxalic acid, (d) Zn–Ox, and (e) Zn–Tz.

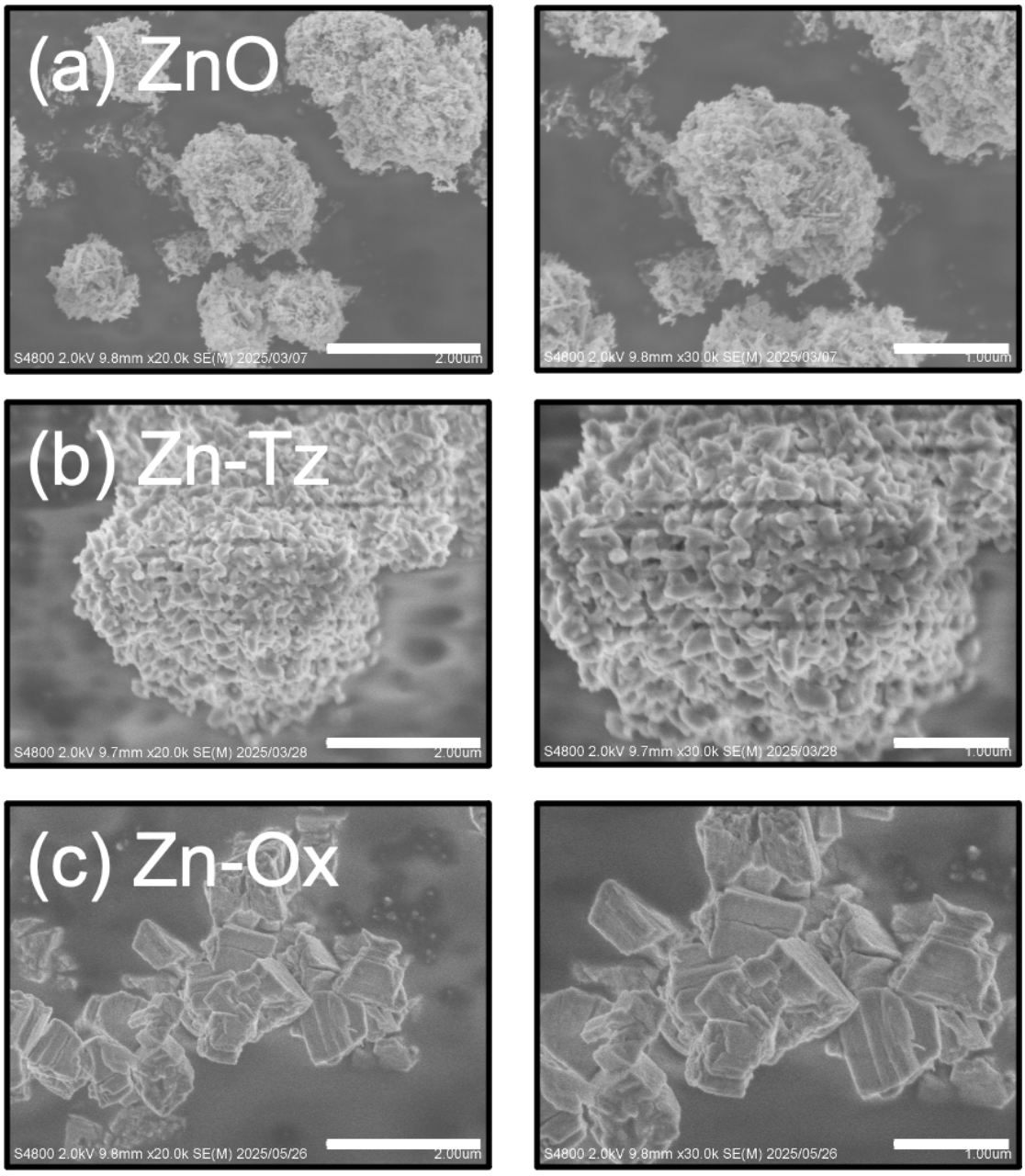

Fig. S2 FE-SEM images of (a) zinc oxide, (b) Zn–Ox intermediate, and (c) Zn–Tz intermediate. Scale bar: (left) 2 μm, (right) 1 μm.

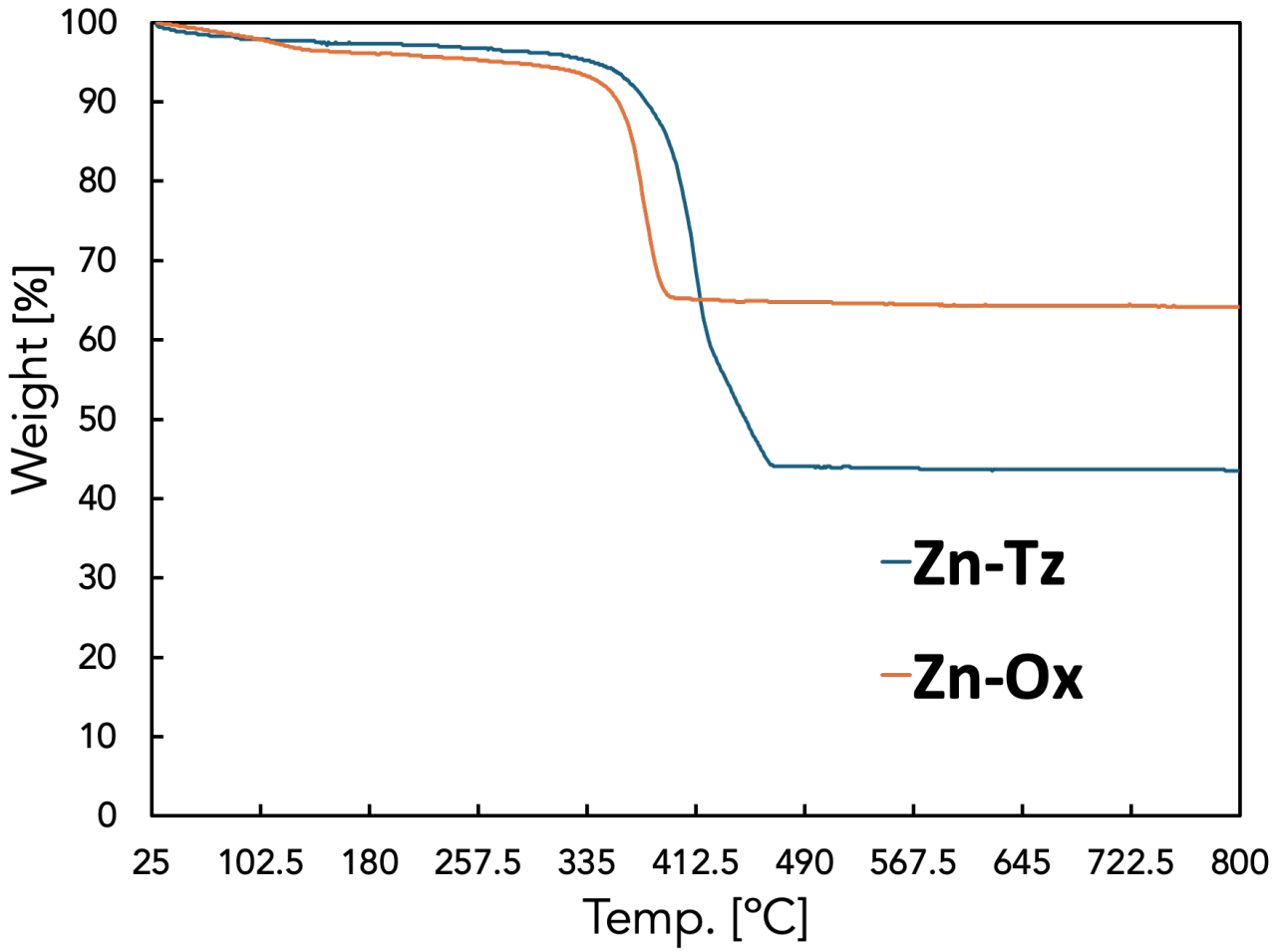

Fig. S3 TG curves of intermediate products. (2°C/min)

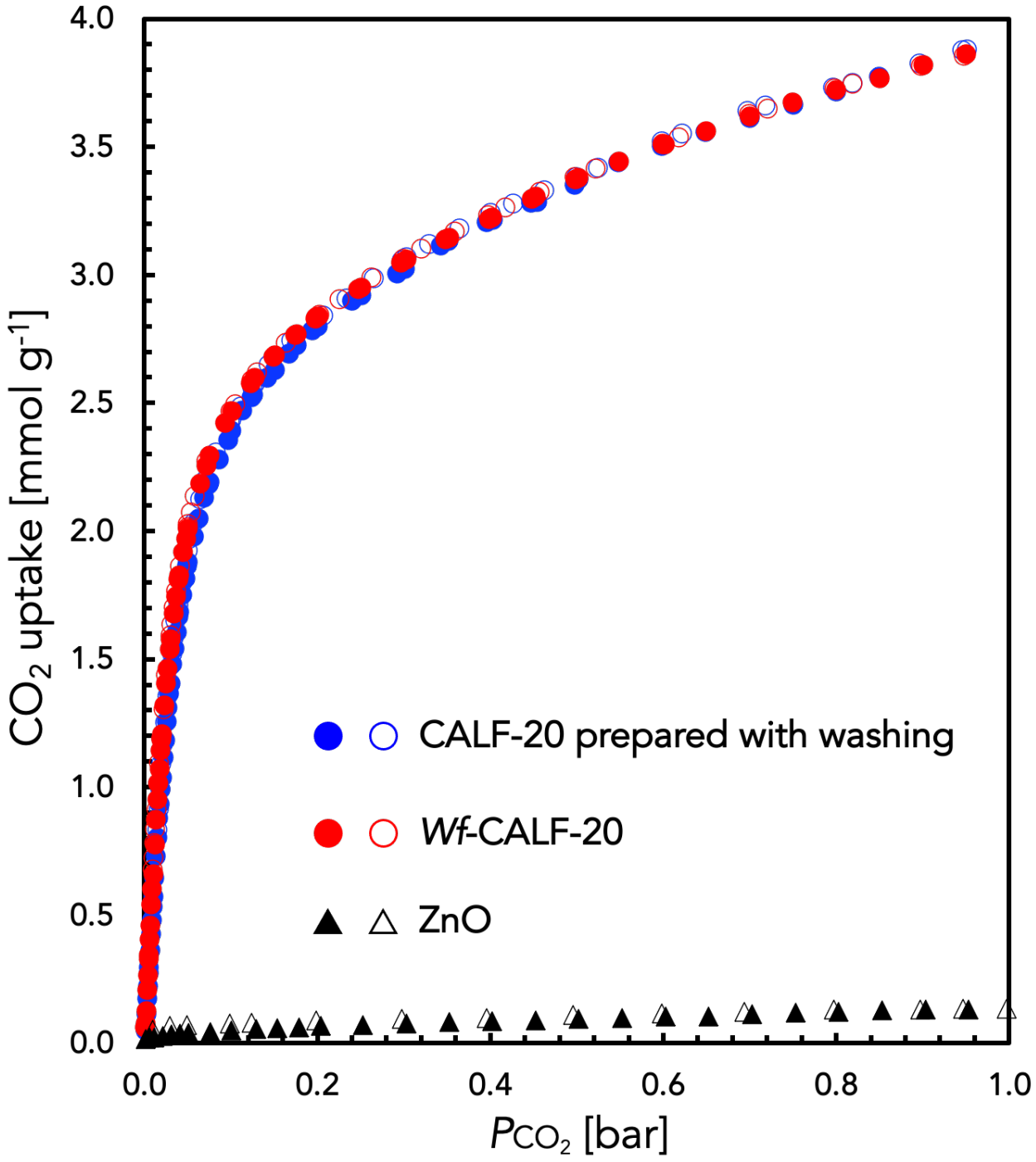

Fig. S4 CO_2 adsorption–desorption isotherms at 298 K for CALF-20 prepared from ZnO (24 h) with and without the washing, showing the effect of washing on CO_2 uptake. (open symbol : adsorption, closed symbol : disadsorption)

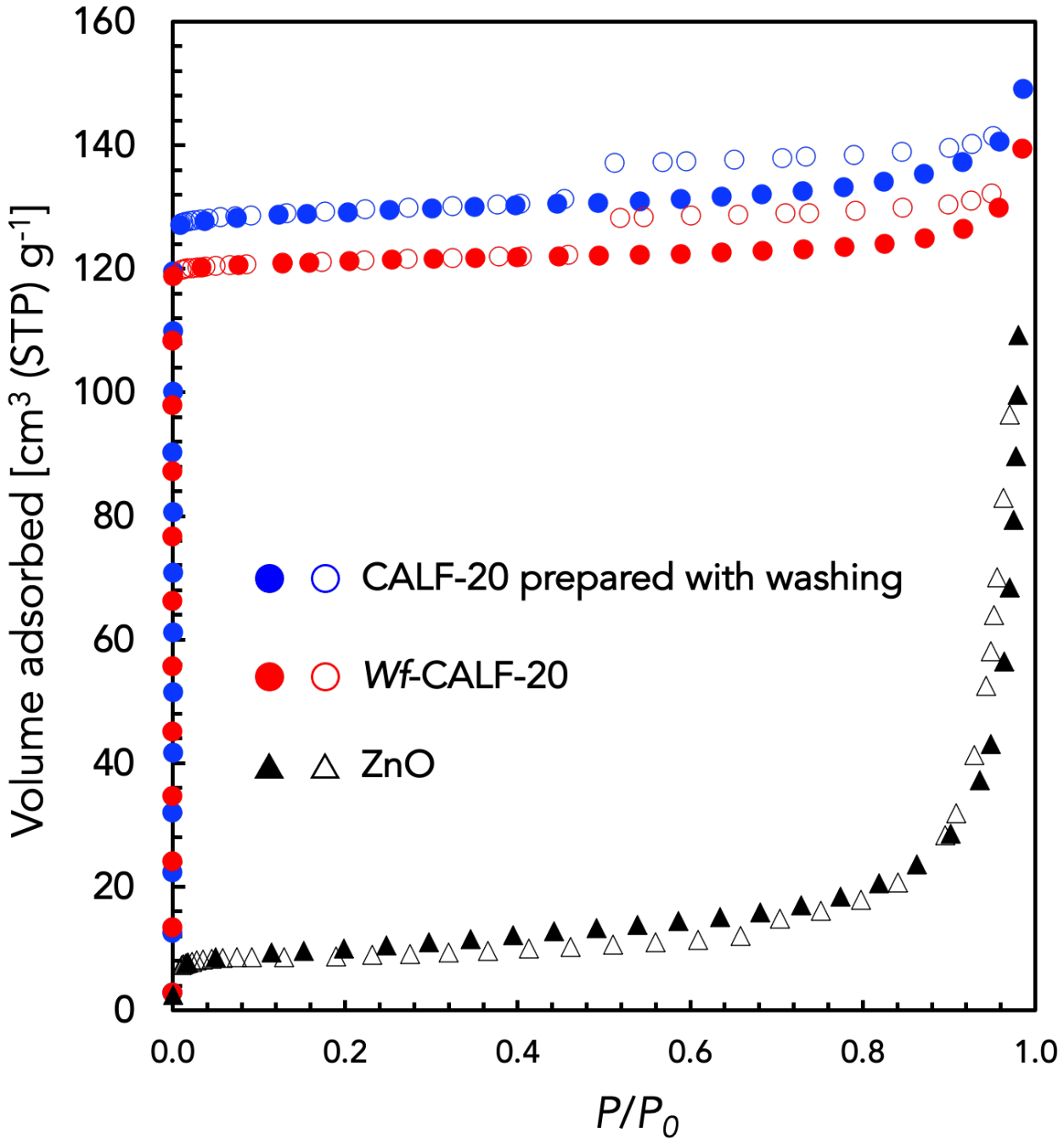

Fig. S5 N_2 adsorption–desorption isotherms at 77 K for CALF-20 prepared from ZnO (24 h) with and without the washing, showing the effect of washing on the microporous characteristics. (open symbol : adsorption, closed symbol : desorption)

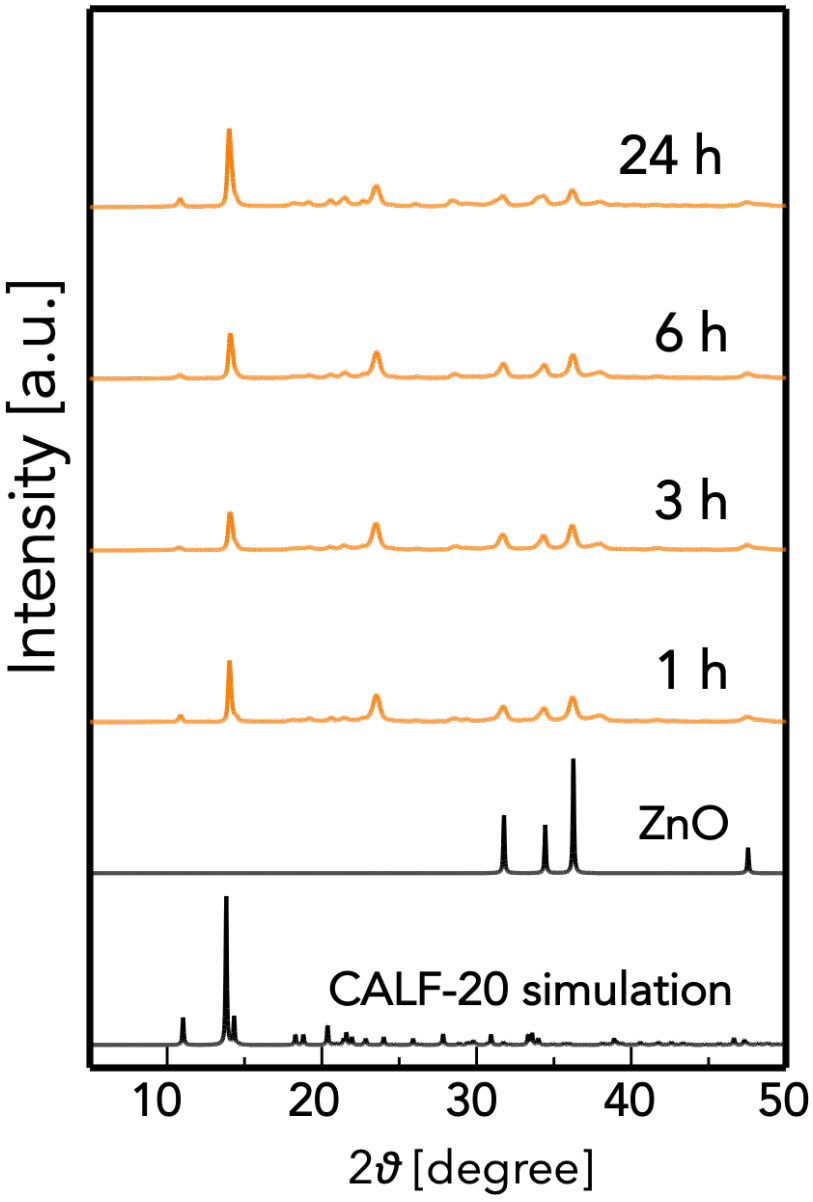

Fig. S6 PXRD patterns of products prepared from ZnO under static conditions with different reaction times.

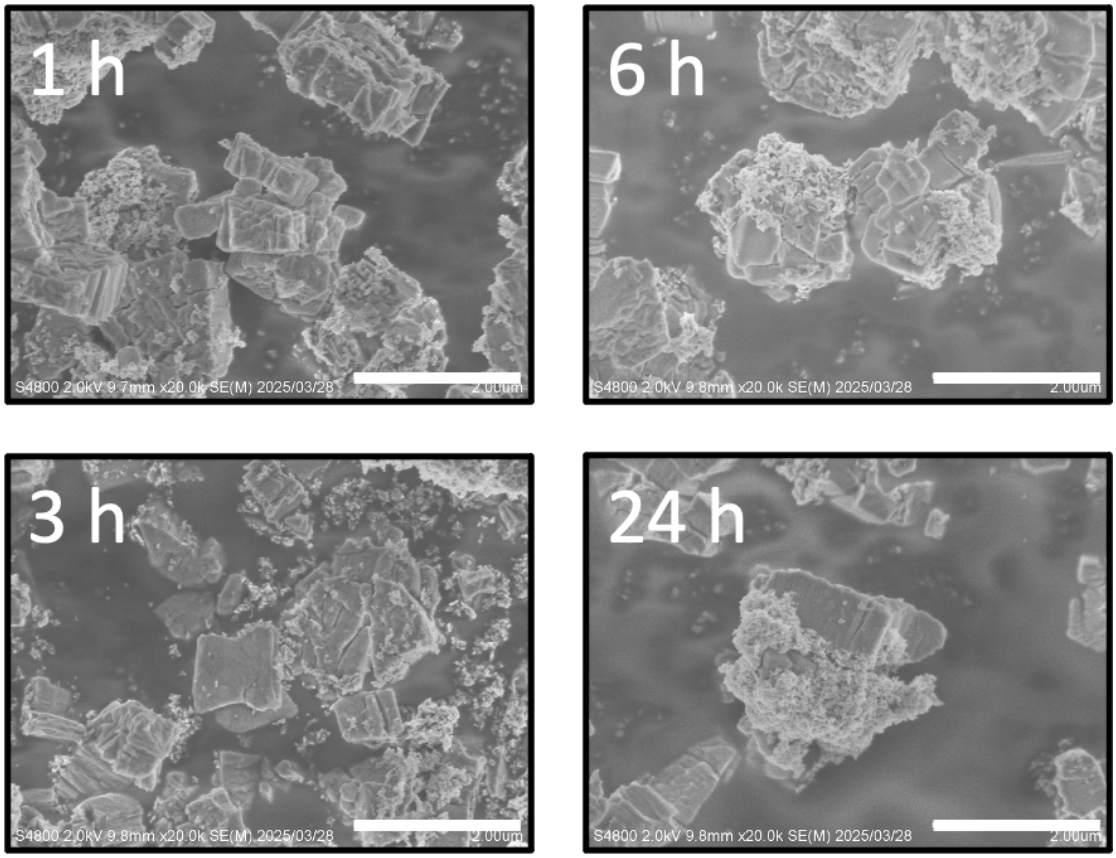

Fig. S7 FE-SEM images of products prepared from ZnO under static conditions with different reaction times. Scale bar: 2 μm.

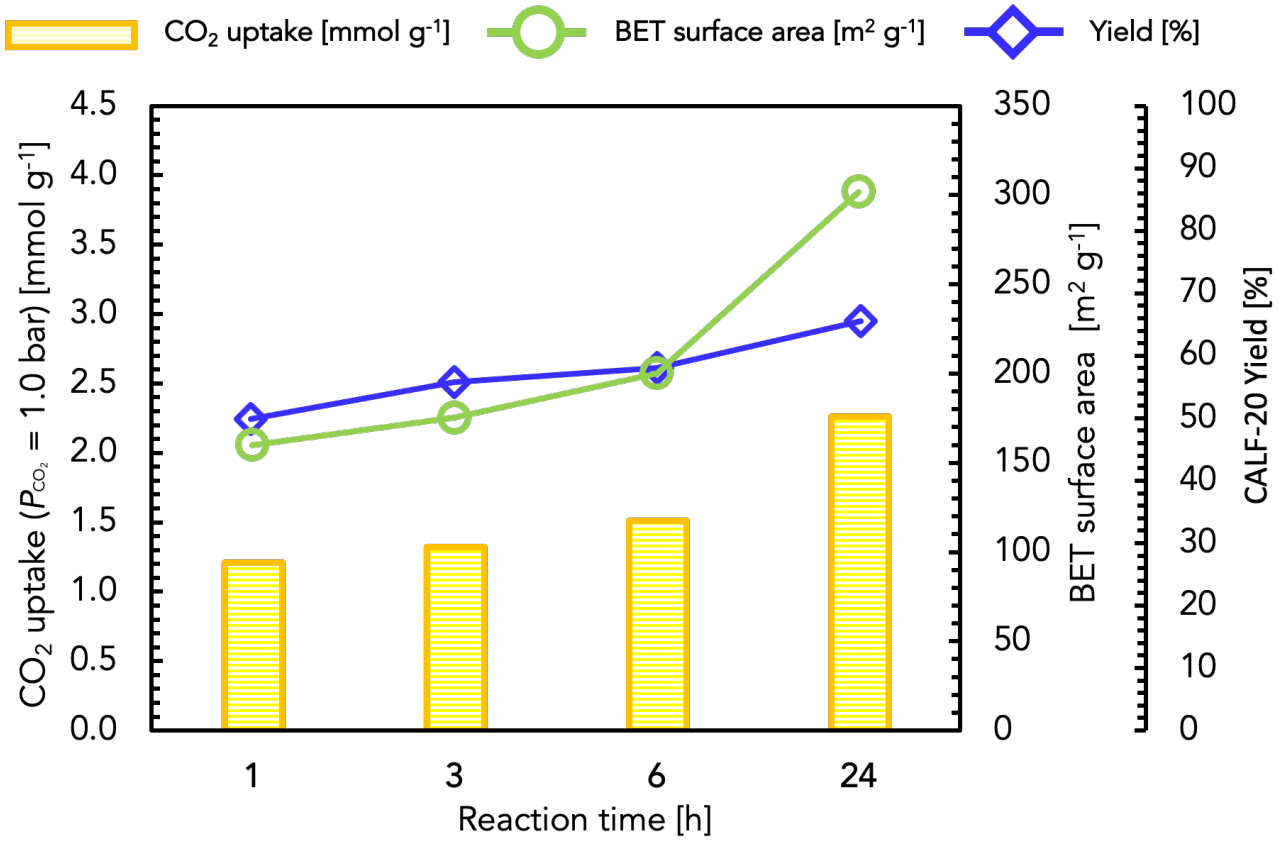

Fig. S8 Relationship between CO_2 uptake at 298 K and 1.0 bar, BET surface area, and CALF-20 yield for products obtained under static conditions as a function of reaction time.

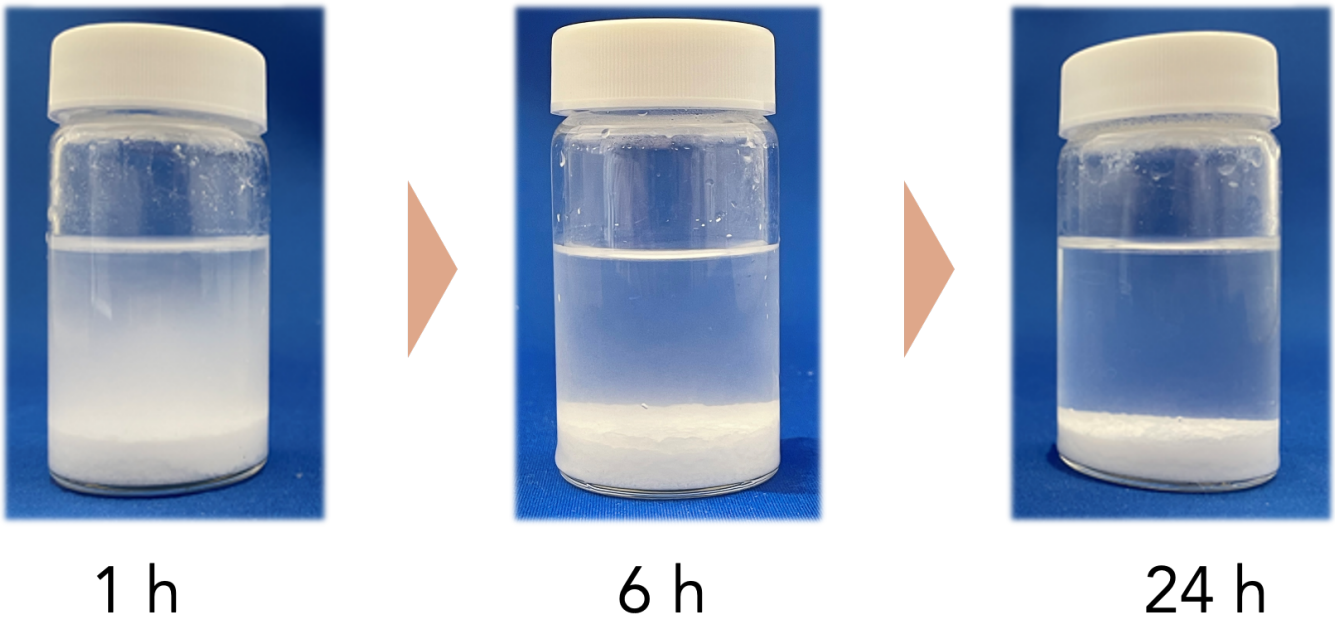

Fig. S9 Photographs of the reaction mixture under static conditions monitored at different reaction times.

References

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