

**Preparation of zeolite-based porous materials via
photopolymerization and applied in 3D printing and gas storage**

Yijun Zhang^{†,‡}, Yuanyuan Gao^{†,‡}, Ludovic Josien^{†,‡}, Cyril Vaultot^{†,‡}, Angélique Simon-Masseron^{†,‡},
and Jacques Lalevée^{†,‡*}*

[†] Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

[‡] Université de Strasbourg, France

Experimental Section

Materials

The monomer, Ebecryl 605, was purchased from Allnex, and 2-benzyl-2(dimethylamino)-4-morpholinobutyrophenone (BDMK) used as photoinitiator was supplied by Sigma-Aldrich. Polyethylene glycol-200 (PEG-200, molecular weight = 200 g/mol) and the dispersant MELIORAN P312L (abbreviation: D) were purchased from Sigma-Aldrich and ARKEMA respectively. LTA-5A zeolite powder (abbreviation: Z) and Al₂O₃ powder (abbreviation: A) were purchased from ACROS ORGANICS and CONDEA respectively. The LTA-5A beads (4-8 mesh) was obtained from ACROS. Characteristics of LTA-5A, powder and commercial beads, were listed in Table S1.

Composite preparation *via* photopolymerization

Firstly, Ebecryl 605, BDMK, PEG-200 and MELIORAN P312L were mixed homogenously in order to obtain monomer mixture liquid. PEG-200 and dispersant were both used to modified the viscosity and dispersibility of formulations. Then, monomer mixture liquid, LTA-5A and Al₂O₃ were mixed at different ratios to prepare different formulations for photopolymerization (see Table S2). All mixing processes were performed through Speedmixer (DAC 150.1 FVZ-K) with rotation speed around 2000 rpm.

For photopolymerization, a mold filled with investigated formulation was placed under irradiation of LED@405nm for 30 s. Then, the sample in the mold was taken out and cleaned by acetone to remove the uncured monomer.

3D Printing

A homemade 3D printer (a layer-by-layer method to deposit materials) was used to obtain 3D objects. The air pressure for injection was controlled around 1 MPa, and the deposit rate for X-axis and Y-axis was set at 1 mm.s⁻¹. The 3D printed structured composites are shown in Figure 3.

Calcination

Composites after photopolymerization were calcined at 750 °C under air (heating rate at 1 K.min⁻¹, without air flow) for 1 h, 2 h, 4 h, and 8 h. After calcination process,

the shape and structure of calcined samples can remain intact, compared to their corresponding composites without calcination.

Characterization

The rheology measurements were carried out by a rotational rheometer HAAKE MARS (Thermo Scientific) with a shear rate from 0.01 to 1000 s⁻¹ at 25 °C. Thermogravimetric analysis (TGA) was performed with a METTER-TOLEDO TGA/DSC3+ thermoanalyzer (heating rate at 10 K.min⁻¹, from 30 °C to 750 °C, air flow 150 L.min⁻¹). For dynamic thermomechanical analysis (DMA), composites after photopolymerization were polished to obtain pellets with a thickness of 0.1 cm, and then analysis were carried out on a Viscoanalyser METTLER DMAA861 at a frequency of 1.0 HZ. The crystalline structures of fillers were identified by X-ray diffraction (XRD) measurements through a PANalytical MPD X'Pert Pro diffractometer. Bear-loading tests were performed on calcined samples (diameter= 9 mm, thickness=1 mm) by using different weights (100 g, 200 g and 300 g).

N₂ adsorption-desorption isotherms were performed at -196 °C with Micromeritics ASAP 2420 Instrument on calcined samples, pure powder and commercial LTA-5A beads to determine their micro- and mesoporous characteristics. All samples were outgassed to a residual pressure of less than 0.8 Pa at 90 °C for 1 h and 300 °C for 15 h. Specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method (0.01 < p/p⁰ less than 0.03). The *t*-plot method was used to calculate microporous volume (V_{micro}) and microporous surface area (S_{micro}). The external surface (S_{ext}) was obtained by subtracting S_{micro} from the total surface. Mesopore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method on the desorption branch of the isotherm. CO₂ adsorption capacities of calcined samples were performed with a Micromeritics ASAP 2420 instrument at 0 °C under 105 KPa. Before measurement, samples were outgassed to a residual pressure of less than 0.8 Pa at 90 °C for 1 h and 300 °C for 15 h.

Table S1. Characteristics of zeolites used in this work

Filler	Framework Type	Si/Al	Na/Al	Crystal Size (av diam.)
	Code			Or beads size (diam.)
LTA-5A powder	LTA	0.9	0.3	(Crystals) 2.6 μm
LTA-5A commercial beads	LTA	1.3	0.2	(Beads) 2.4-4.8 mm (Crystals) n.d.

Table S2. Formulations for photopolymerization

Filler (60 wt%)		Eberycl 605 (wt%)	PEG-200 (wt%)	Dispersant (wt%)	BDMK (wt%)
Al ₂ O ₃ (wt%)	LTA-50 (wt%)				
30	30	30.73	9.03	0	0.24
15	45	30.73	9.03	0	0.24
0	60	30.73	9.03	0	0.24
30	30	29.5	8.66	1.6	0.24
15	45	29.5	8.66	1.6	0.24
0	60	29.5	8.66	1.6	0.24
30	30	28.16	8.28	3.32	0.24
15	45	28.16	8.28	3.32	0.24
0	60	28.16	8.28	3.32	0.24
30	30	27.01	7.95	4.8	0.24
15	45	27.01	7.95	4.8	0.24
0	60	27.01	7.95	4.8	0.24
30	30	26.12	7.00	6.64	0.24
15	45	26.12	7.00	6.64	0.24
0	60	26.12	7.00	6.64	0.24

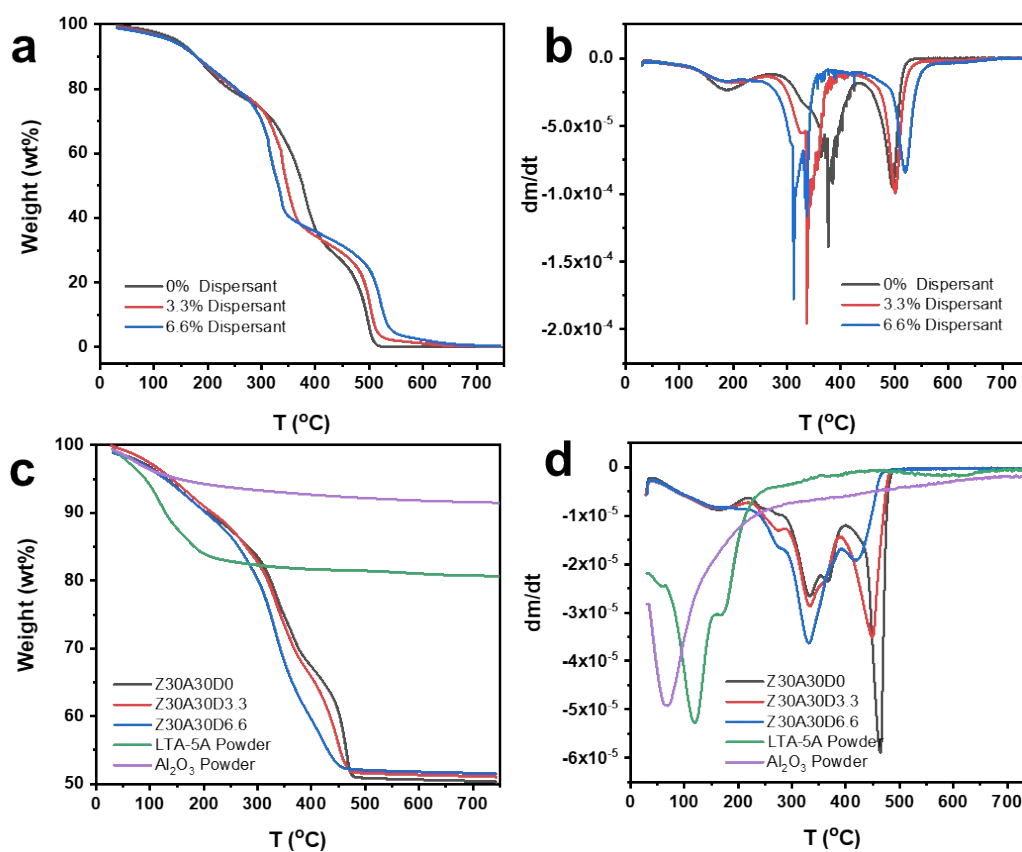


Figure S1. TGA and DTG (derivative of TGA) curves for (a, b) Z0A0D0, Z0A0D3.3 and Z0A0D6.6; (c, d) Z30A30D0, Z30A30D3.3, Z30A30D6.6, LTA-5A powder and Al₂O₃ powder.

Table S3. Weight loss values highlighted by TGA for LTA-5A, Al₂O₃ and related composite materials.

	Z0A0D	Z0A0D	Z0A0D	Z30A30	Z30A30	Z30A30	LTA-5A	Al ₂ O ₃
	0	3.3	6.6	D0	D3.3	D6.6	Powder	powder
T max (°C)	181, 376, 493	181, 337, 513	181, 311, 519	166, 333, 364, 464	166, 273 333, 449	167, 273, 330, 420	58, 119, 169	68
ML-1 (wt%)^a (50-250 °C)	21.1	19.9	19.50	12.6	12.3	13.5	17.2	6.3
ML-2 (wt%)^b (250-750 °C)	78.9	79.9	80.0	37.1	36.7	35.0	2.2	2.3
FW (wt%)^c	Ca. 0	0.28	0.51	50.3	51.0	51.5	80.7	91.5
FWC (wt%)^d	-	-	-	51.6	51.8	51.9	-	-

^a ML-1: the first step of mass loss for water desorption;

^b ML-2: the second step of mass loss for PEGDA carbonization;

^c FW: Final weight at 750 °C;

^d FWC: Theoretical final weight taking into account the water content of fillers

Table S4. Bear-loading test results on calcined samples. Weight supported by the pellets without cracks.

	Calcination Time		
	2h	4h	8h
Z30A30D0	N.M.	100 g	300 g
Z30A30D1.6	N.M.	N.M.	300 g
Z30A30D3.3	200 g	200 g	300 g
Z30A30D4.8	N.M.	N.M.	300 g
Z30A30D6.6	N.M.	200 g	300 g
Z45A15D0	N.M.	200 g	300 g
Z45A15D1.6	N.M.	N.M.	300 g
Z45A15D3.3	200 g	200 g	300 g
Z45A15D4.8	N.M.	N.M.	300 g
Z45A15D6.6	N.M.	200 g	300 g
Z60A0D0	N.M.	100 g	300 g
Z60A0D1.6	N.M.	N.M.	300 g
Z60A0D3.3	100 g	200 g	300 g
Z60A0D4.8	N.M.	N.M.	300 g
Z60A0D6.6	N.M.	200 g	300 g

N.M.: The measurement was not performed.

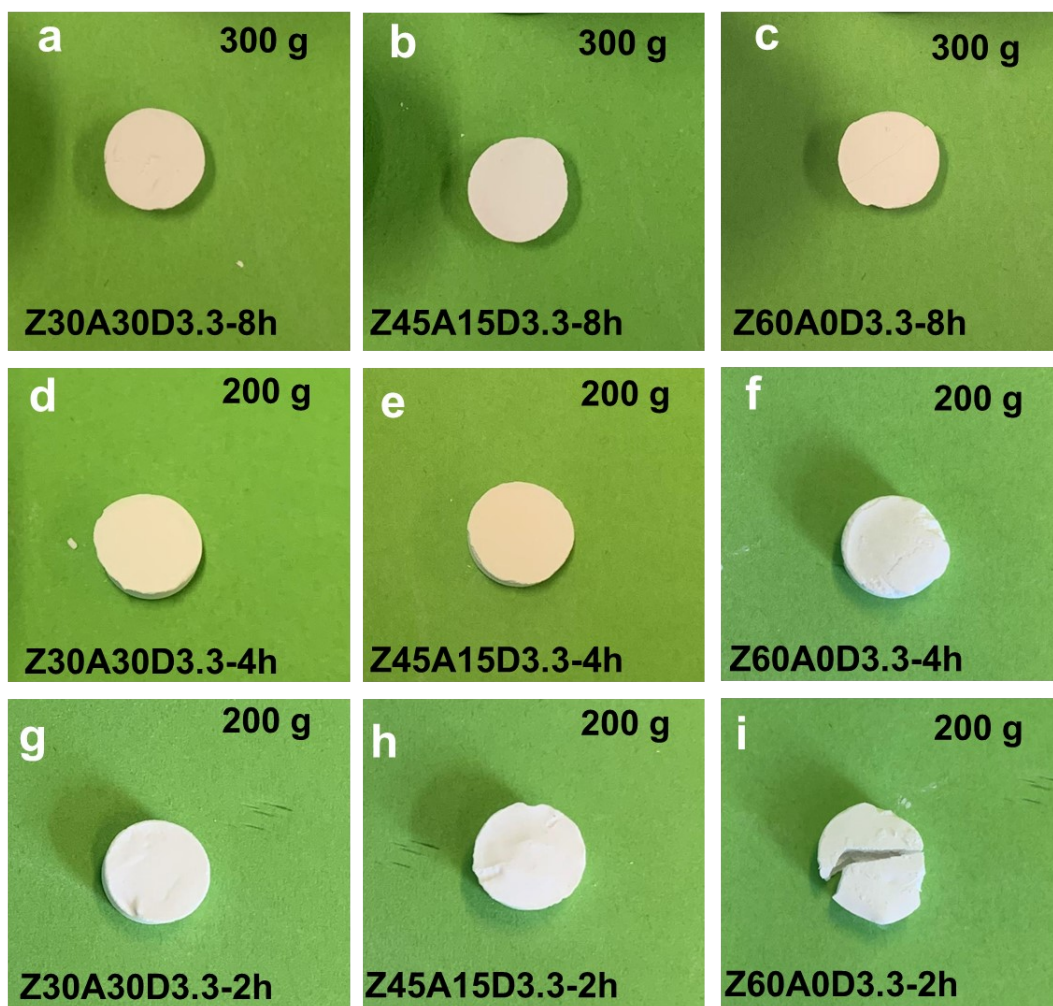


Figure S2. Bear-loading test on calcined samples (a) Z30A30D3.3-8h, (b) Z45A15D3.3-8h, (c) Z60A0D3.3-8h, (d) Z30A30D3.3-4h, (e) Z45A15D3.3-4h, (f) Z60A0D3.3-4h, (g) Z30A30D3.3-2h, (h) Z45A15D3.3-2h, (i) Z60A0D3.3-2h.

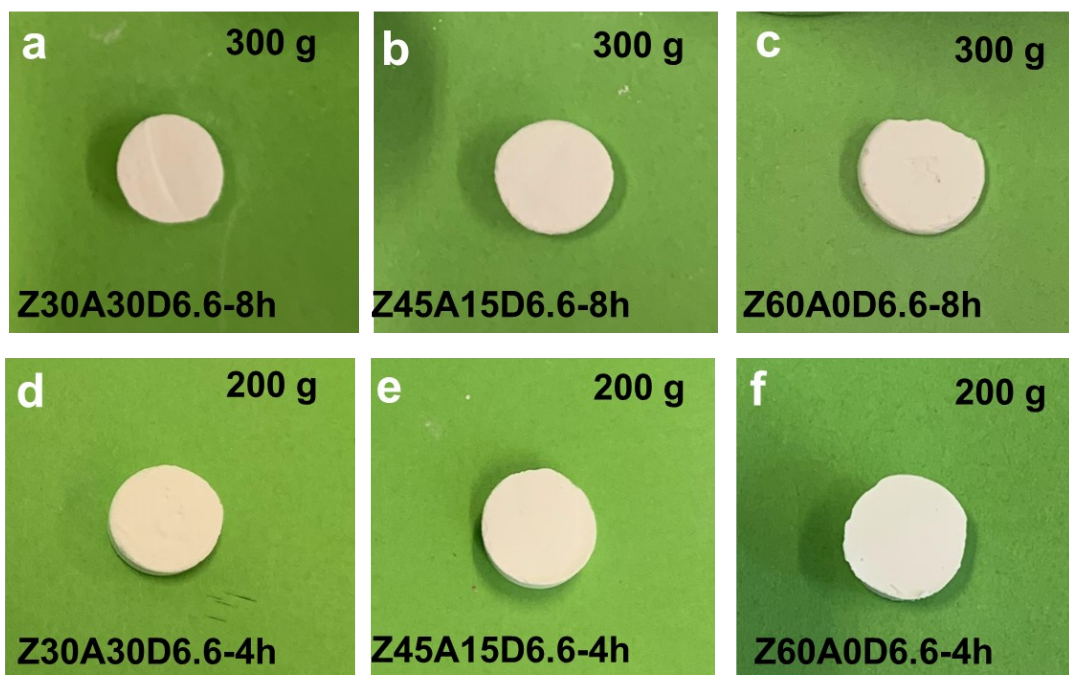


Figure S3. Bear-loading test on calcined samples (a) Z30A30D6.6-8h, (b) Z45A15D6.6-8h, (c) Z60A0D6.6-8h, (d) Z30A30D6.6-4h, (e) Z45A15D6.6-4h, (f) Z60A0D6.6-4h.

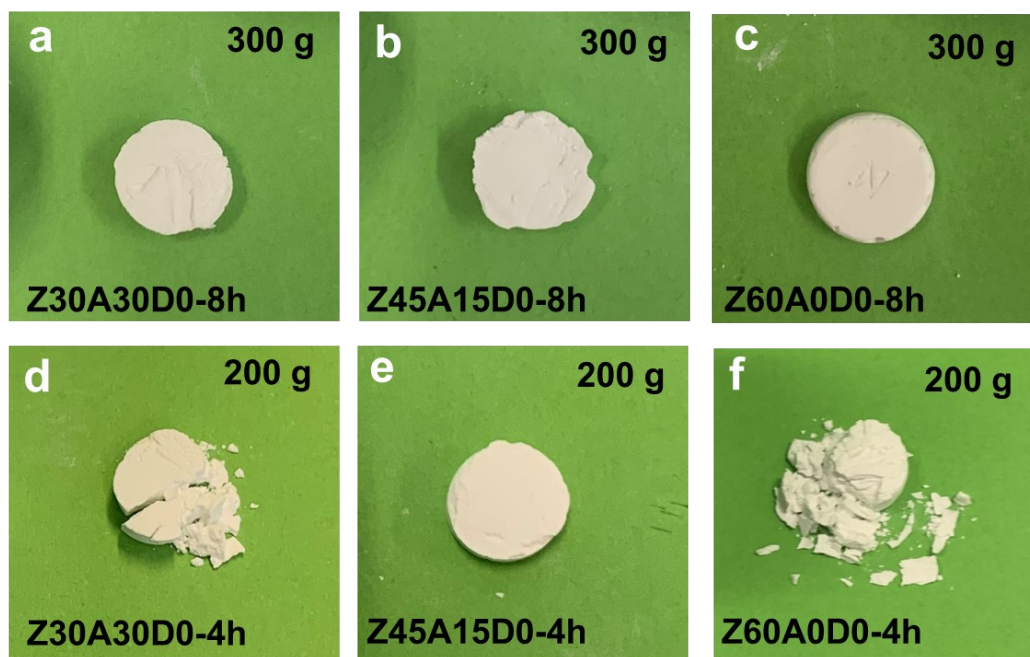


Figure S4. Bear-loading test on calcined samples (a) Z30A30D0-8h, (b) Z45A15D0-8h, (c) Z60A0D0-8h, (d) Z30A30D0-4h, (e) Z45A15D0-4h, (f) Z60A0D0-4h.

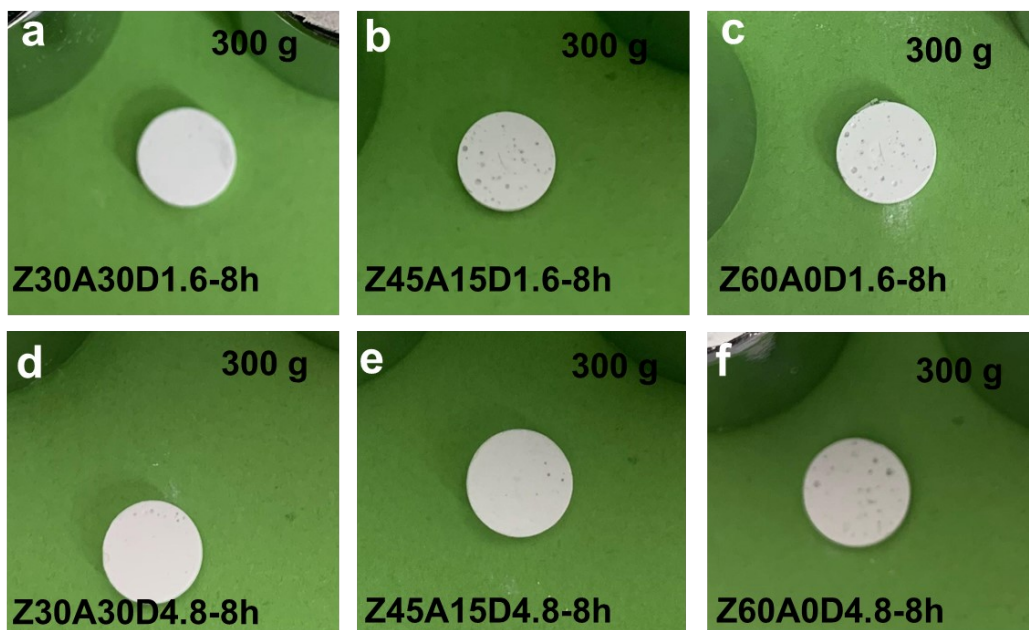


Figure S5. Bear-loading test on calcined samples (a) Z30A30D1.6-8h, (b) Z45A15D1.6-8h, (c) Z60A0D1.6-8h, (d) Z30A30D4.8-8h, (e) Z45A15D4.8-8h, (f) Z60A0D4.8-8h.

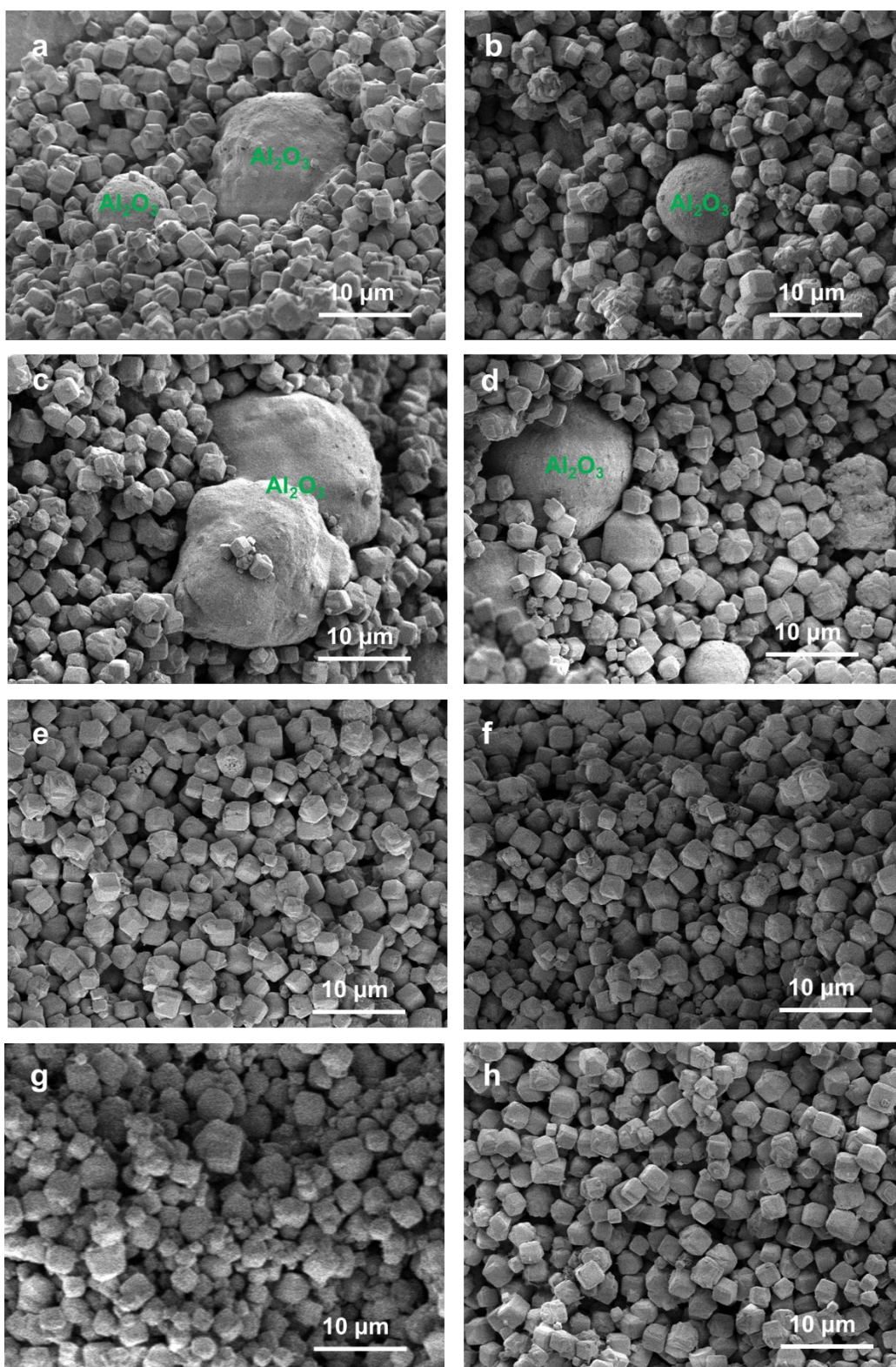


Figure S6. SEM images for the cross-section of calcinated samples: (a) Z45A15D3.3-1h; (b) Z45A15D3.3-2h; (c) Z45A15D3.3-4h; (d) Z45A15D3.3-8h; (e) Z60A0D3.3-1h; (f) Z60A0D3.3-2h; (g) Z60A0D3.3-4h; (h) Z60A0D3.3-8h.