Alginate-supported L-arginine as biobased heterogeneous catalyst for the conversion of glycidol and CO_2 into glycerol carbonate

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ELECTRONIC SUPPORTING INFORMATION

Content

S1 General information and experimental procedures

Drying glycidol to investigate catalyst deactivation

Traces of water in glycidol may have a detrimental effect on the stability of Arg-NaAlg and lead to the formation of glycerol as a by-product. To investigate this hypothesis, glycidol was dried and distilled before use. Glycidol was kept overnight over 4Å molecular sieves (activated at 150 °C under vacuum overnight) before distillation under reduced pressure at 80 °C, 20 mbar (only the middle fraction was collected). The obtained dried and distilled glycidol was kept under N_2 in a closed, refrigerated bottle until use.

Table S1: The measured water content in glycidol (GD) was reported by Karl Fischer titration, with each sample carried out in triplicate. All samples are kept under N_2 in a closed, refrigerated bottle until use.

Sample	**Water content**
Commercial/Undried GD	0.44%
Dried GD_1[a]	0.20%
Dried GD_2[a]	0.16%

[a] Both samples were dried under identical conditions and subsequently stored in separate containers.

Calculation of the active sites of the applied catalysts

The nature of the active sites differs among the catalysts. To reflect such complexity, we chose to define two types of TON, which are $TON_{active\ sites}$ (defined as number of moles of glycerol carbonate produced within the reaction time, divided by the total moles of all active sites in each catalyst) and TON_{Arg} (defined as number of moles of glycerol carbonate produced within the reaction time, divided by the moles of arginine units).

Each of the two provides different information, as it becomes apparent when considering that there are 2 amino active sites per arginine in Arg-COOMe; 1 amino active site and 1 carboxylate active site per grafted arginine unit and 1 carboxylate active site per ungrafted NaAlg unit in Arg-NaAlg; 1 carboxylate active site per monomer unit in NaAlg.

1. Arg-COOMe: Arginine contains two active sites per molecule, represented by the α-amino group and by the guanidino group. Since arginine is commercially available in the chloride salt of its methyl ester (Arg-COOMe·2HCl), the active sites might be in the form of the basic α-amino and guanidino groups but might also be the chloride anions if the α-amino and guanidino groups are in their protonated form. The moles of Arg and the moles of active sites were calculated using the molecular mass of Arg-COOMe (MM = 261.15 g/mol):

$$mol_{Arg} = \frac{mass_{cat.}\,(g)}{261.15\ g/mol}$$

$$mol_{active\ sites} = \frac{2 \cdot mass_{cat.}\,(g)}{261.15\ g/mol}$$

2. Guanidine: The active site is the guanidine group, which means one active site per molecule of guanidine (as guanidine hydrochloride, MM = 95.53 g/mol). Therefore:

$$mol_{active\ sites} = \frac{mass_{cat.}\,(g)}{95.53\ g/mol}$$

3. Arg-NaAlg: The active sites of the synthesized Arg-NaAlg catalyst are the guanidino groups (as shown in Scheme 1c) and the sodium carboxylate groups present in the grafted arginine and in the alginate backbone. The guanidino groups can act as basic sites, either in their dehydrated amino form, or by providing OH^- in their protonated form.
From elemental analysis, the N wt% in Arg-NaAlg is 9.56 wt%. Based on this and on the MM of the NaAlg repeating unit (198.11 g/mol) and of the one with Arg grafted onto NaAlg

(354.30 g/mol), we can calculate the Degree of Substitution (n in Schemes 3-4) using the following equation (where m + n = 1):

$$Fraction\ of\ N\ in\ ArgNaAlg = \frac{n \cdot (4 \cdot 14.01 \frac{g}{mol})}{m \cdot 198.11 \frac{g}{mol} + n \cdot 354.30 \frac{g}{mol}} = 0.0956$$

Solving this system of two equations in m and n, we obtained n = 0.46, which means a degree of substitution of 46%.

This means that in m·198.11 g/mol + n·354.30 g/mol = 0.54·198.11 g/mol + 0.46·354.30 g/mol = 269.96 g/mol, there are 0.46 Arg units and 1 Na carboxylate unit (0.54 from the NaAlg and 0.46 from the Arg). Therefore:

$$mol_{Arg} = \frac{0.46 \cdot mass_{cat.}\,(g)}{269.96\ g/mol}$$

$$mol_{active\ sites} = \frac{1.46 \cdot mass_{cat.}\,(g)}{269.96\ g/mol}$$

4. NaAlg monomer unit: The active sites of NaAlg were the Na carboxylate groups, which means one active site per NaAlg repeating unit (MM = 198.11 g/mol). Therefore:

$$mol_{ative\ sites} = \frac{mass_{cat.}\,(g)}{198.11\ g/mol}$$

Calculation of the turnover number (TON)

$$TON_{Arg} = \frac{mol_{GLC}}{mol_{Arg}}$$

$$TON_{active\ sites} = \frac{mol_{GLC}}{mol_{active\ sites}}$$

S2 Investigation of Amino-Acid Immobilization on Alginate

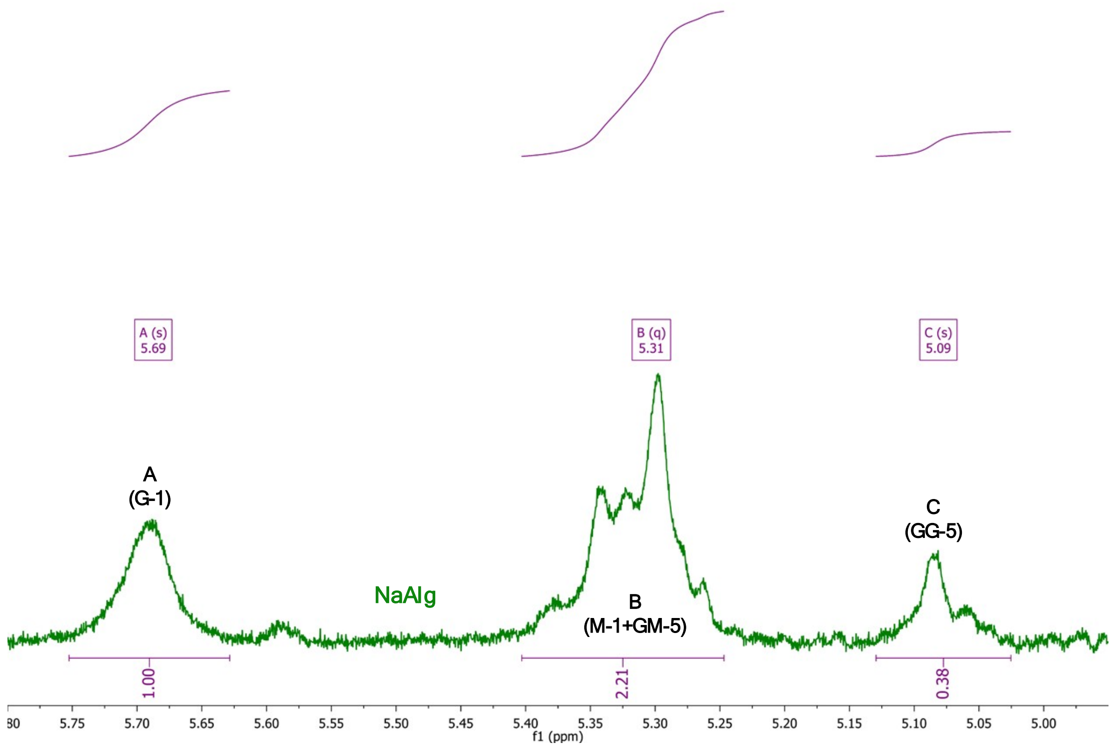

Figure S1. H^1-NMR spectrum (in D_2O) of sodium alginate (NaAlg) measured at 90 °C.

Peak A (5.69 ppm) represents the anomeric proton of guluronate (G-1) monomer. Multiplet B (5.25-5.40 ppm) represents an overlapping of anomeric protons of mannuronate (M-1) monomer and protons of alternating blocks of guluronate and mannuronate (GM-5). Peak C (5.09 ppm) represents the proton of the guluronate residues in the homopolymeric G blocks (GG-5).[1,2]

$$F_G = \frac{I_A}{I_B + I_C} = \frac{1}{(2.21 + 0.38)} = \frac{1}{2.59} = 0.39$$

F_G is the fraction of guluronate monomer units. I_A, I_B, and I_C represent the integration of the corresponding NMR peaks. The total fraction of the two monomers would add up to 1 ($F_G + F_M = 1$).

$$M/G = \frac{(1 - F_G)}{F_G} = \frac{(1 - 0.39)}{0.39} = 1.56$$

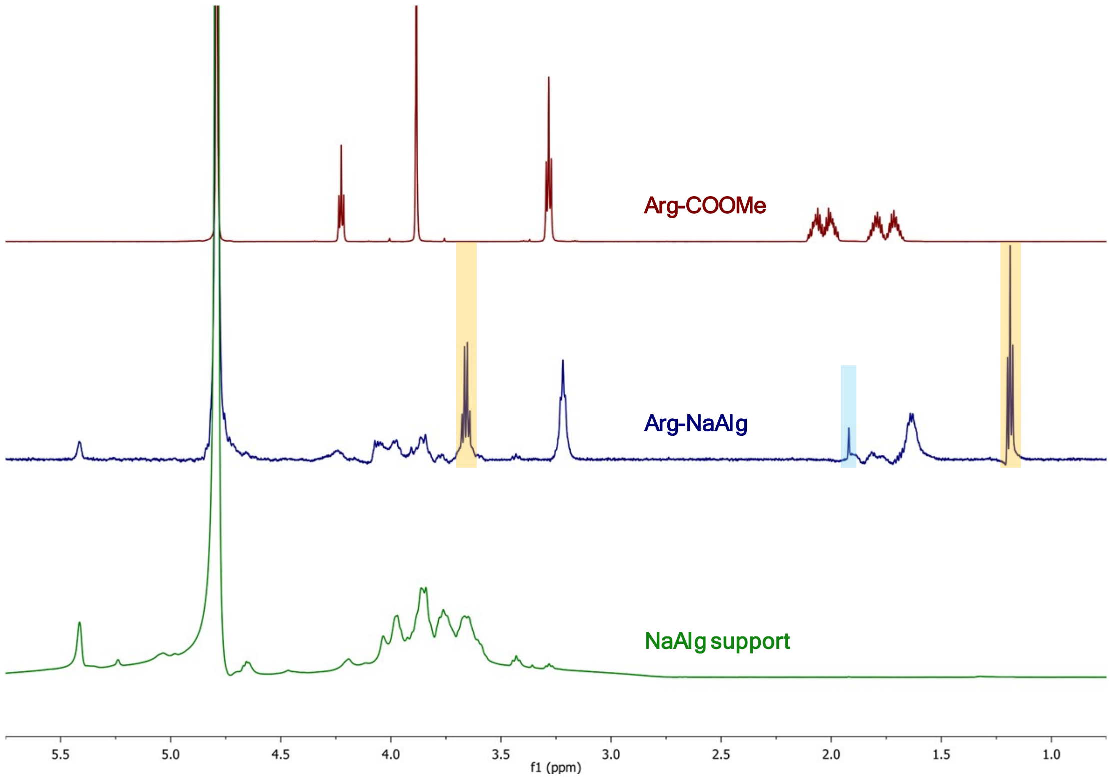

Figure S2. ^{1}H-NMR spectrum of Arg-NaAlg at a small scale[3] compared to those of Arg-COOMe and NaAlg. The highlighted peaks represent residue solvents: yellow is ethanol from the synthesis, and blue is possible contamination from drying in a shared vacuum oven.

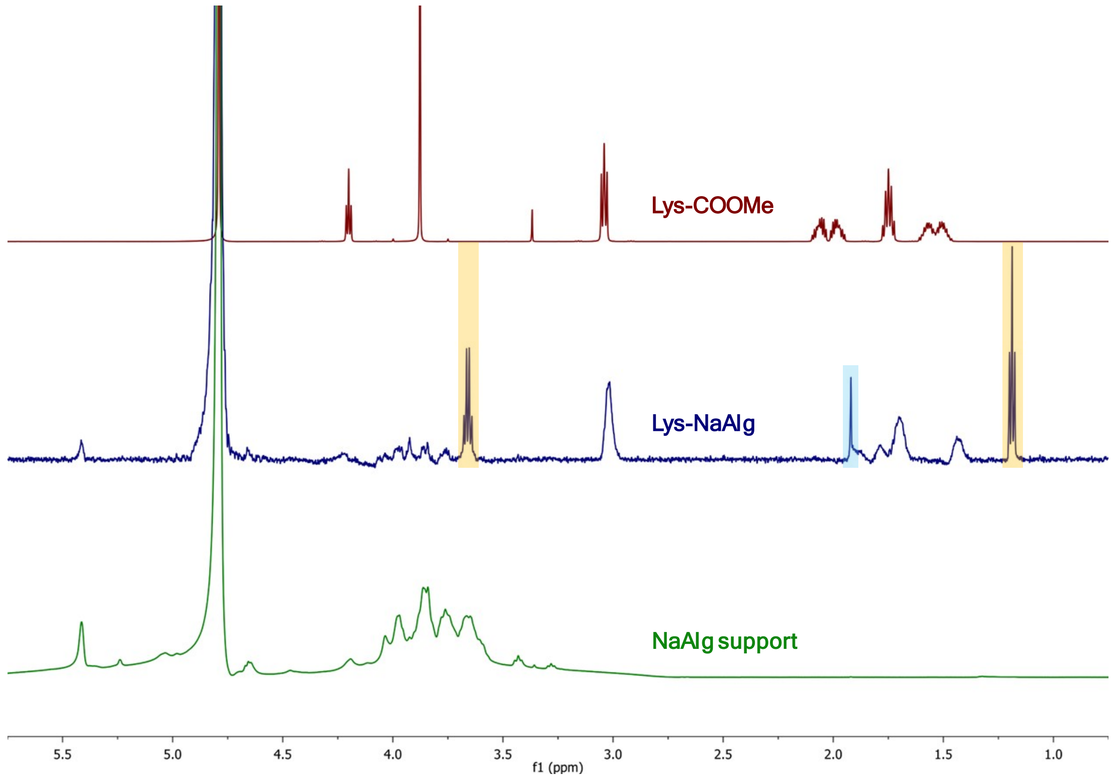

Figure S3. ^{1}H-NMR spectrum of Lys-NaAlg at a small scale[3] compared to those of Lys-COOMe and NaAlg. The highlighted peaks represent residue solvents: yellow is ethanol from the synthesis, and blue is possible contamination from drying in a shared vacuum oven.

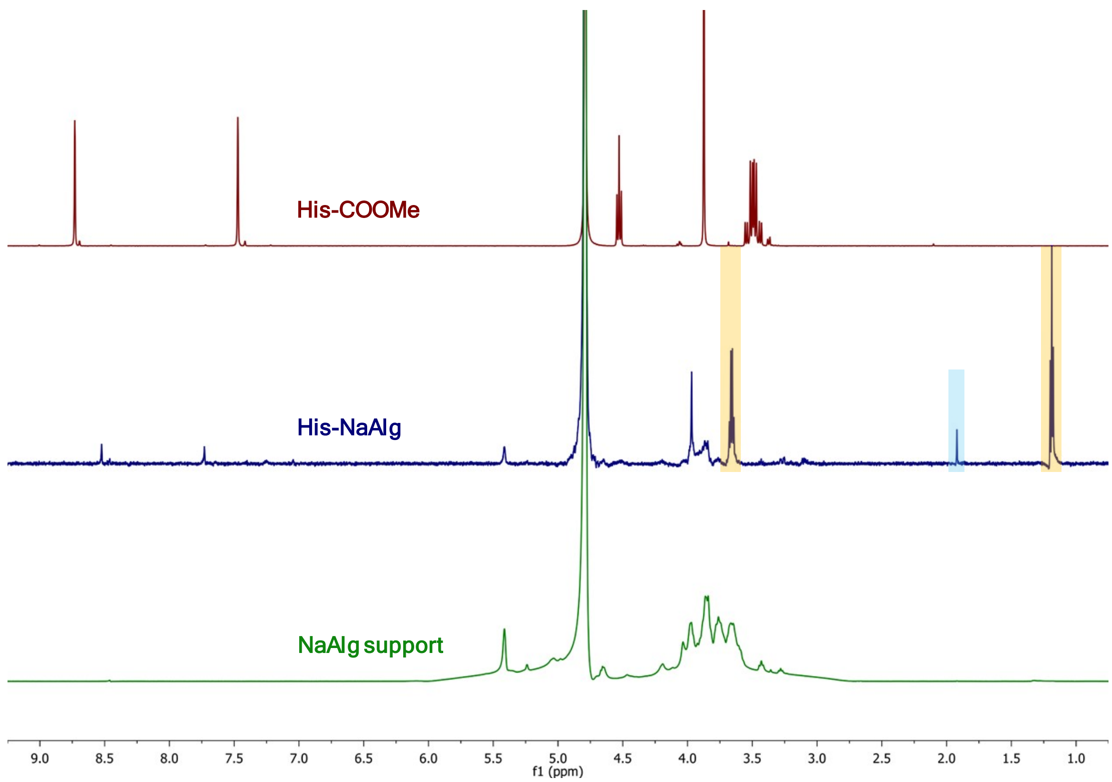

Figure S4. ^{1}H-NMR spectrum of His-NaAlg at a small scale[3] compared to those of His-COOMe and NaAlg. The highlighted peaks represent residue solvents: yellow is ethanol from the synthesis, and blue is possible contamination from drying in a shared vacuum oven. The peaks observed in the 7.5–8.5 ppm region of His-NaAlg remain unidentified.

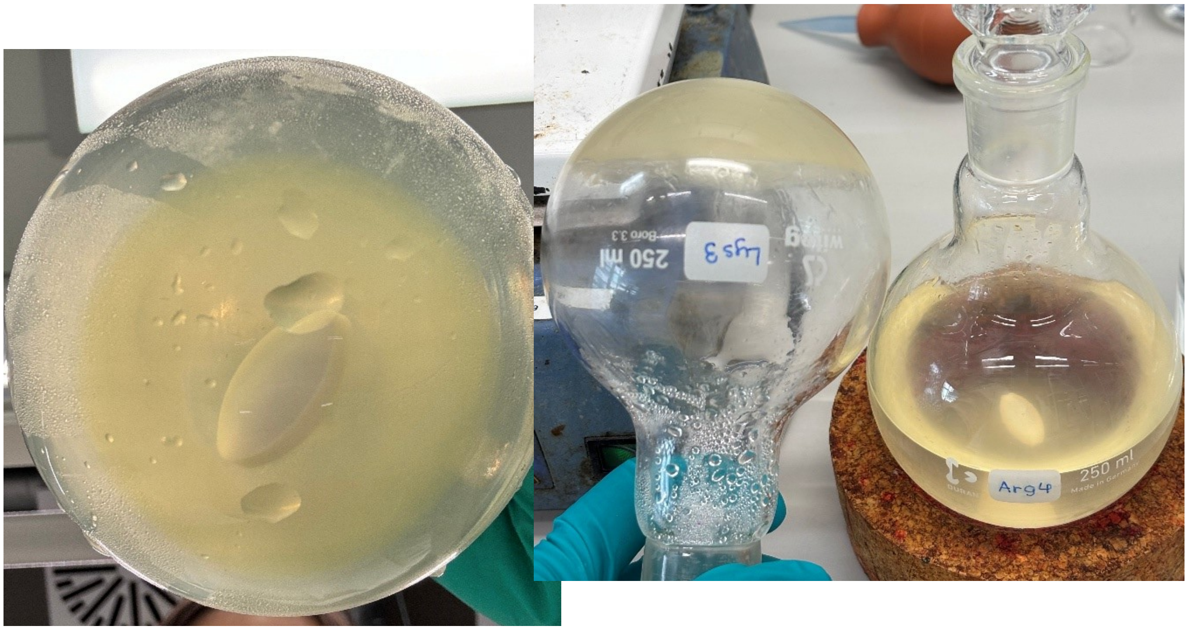

Figure S5. The gel-like material that formed from the first (left, partial gelation) and second (right, complete gelation) attempts at upscaling the synthesis of Lys-NaAlg.

Table S2: Catalytic performance of Lys-NaAlg at different catalyst loading under 10 bar CO_2 for 3 h.

Entry	Catalyst	Loading (wt%)	T (° C)	NMR Yield (%)	Selectivity (%)
1	Lys-NaAlg	3	80	90	95
2	Lys-NaAlg	1.5	80	80	97

S3 Reproducibility and upscalability of the synthesis of Arg-NaAlg

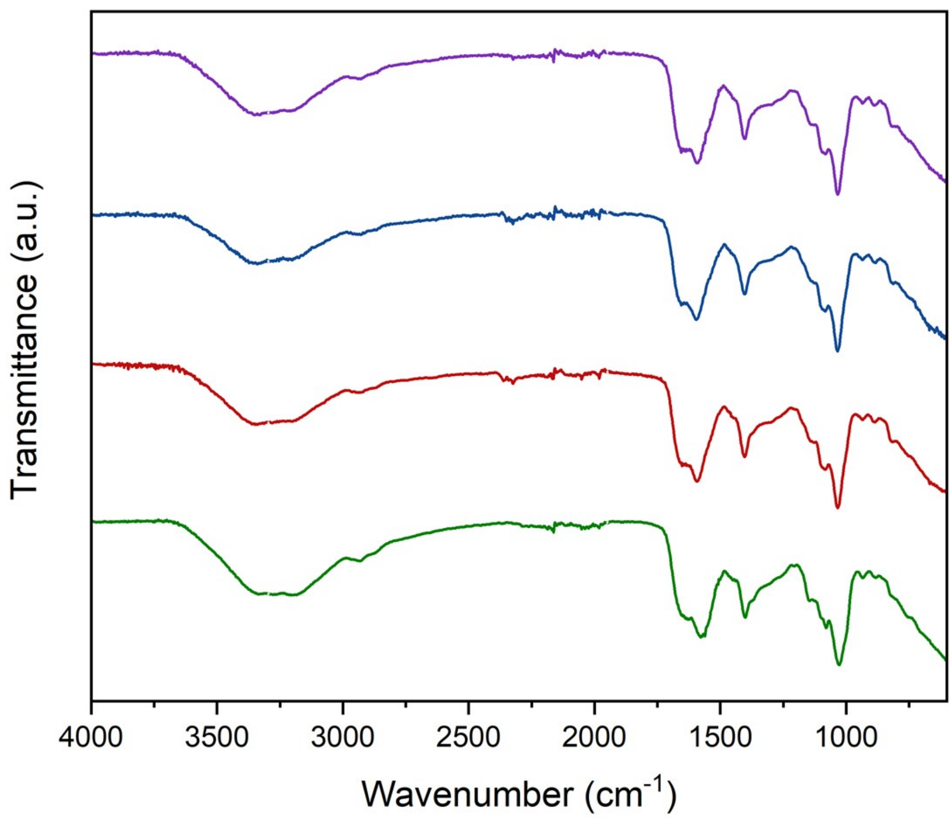

Figure S6. Normalized FTIR spectra of 4 batches of Arg-NaAlg synthesized in the original scale (green) based on a procedure developed by Labre et al.,[3] upscaled by 9 (red), and upscaled by 10 (blue and purple).

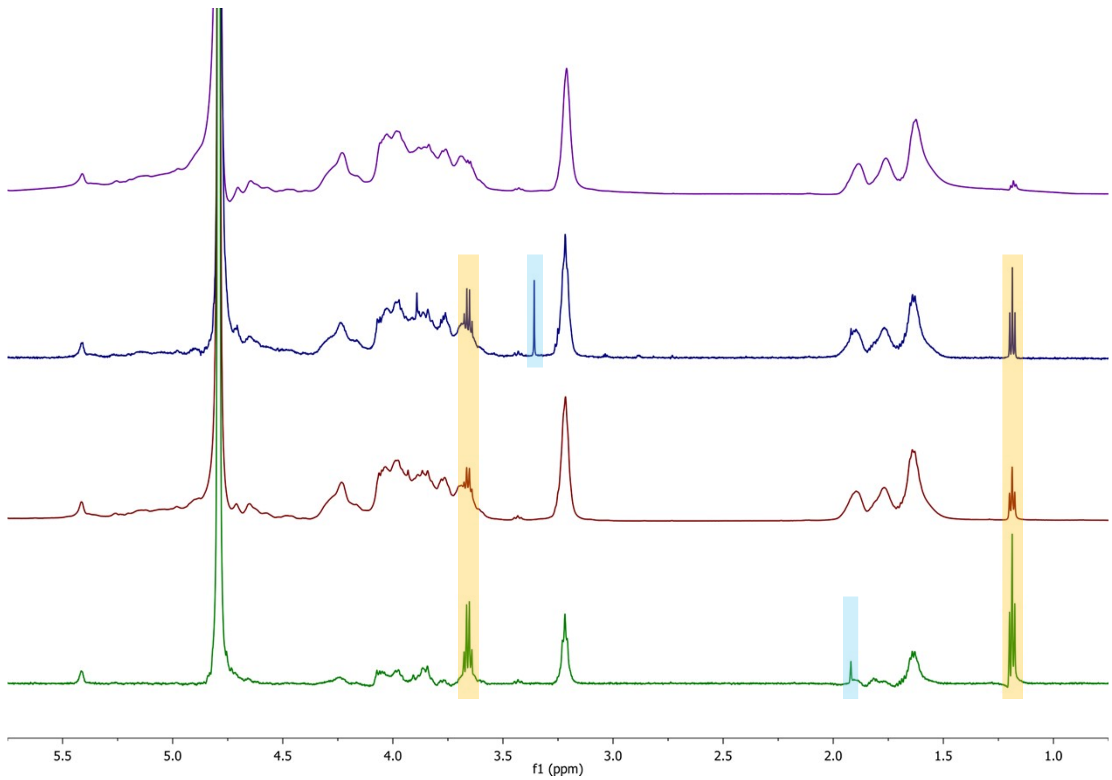

Figure S7. Normalized NMR spectra of 4 batches of Arg-NaAlg synthesized in the original scale (green) based on a procedure developed by Labre et al.,[3] upscaled by 9 (red), and upscaled by 10 (blue and purple). The highlighted peaks represent solvent residues: yellow is ethanol from the synthesis, and blue is possible contamination from drying in a shared vacuum oven.

S4 Characterization of fresh and spent Arg-NaAlg catalysts

Table S3: Elemental analysis of pristine Arg-NaAlg (3 different batches) and used Arg-NaAlg_1a-u, Arg-NaAlg_1b-d and Arg-NaAlg_2a-d.

Sample	% C[a]	% N[a]	N/C (mass)	N/C (mol)	DS (%)[c]
Arg-NaAlg_1 (scaled up x9)	34.50	9.10	0.264	0.226	43
Arg-NaAlg_2 (scaled up x10)	35.57	9.56	0.269	0.230	46
Arg-NaAlg_3 (scaled up x10)	35.59	9.94	0.279	0.239	49
Arg-NaAlg_1a-u[b]	40.42	6.08	0.150	0.129	26[d]
Arg-NaAlg_1b-d[b]	41.53	6.16	0.148	0.127	26[d]
Arg-NaAlg_2a-d[b]	39.01	7.75	0.199	0.170	35[d]

[a] These values were obtained via elemental analysis and are reported as mass percentages.

[b] The sample analyzed corresponds to Arg-NaAlg_2 following its use in recyclability experiments under the conditions abbreviated.

[c] The formula for DS calculation is explained under the section "Calculation of the active sites of the applied catalysts" in the main text.

[d] The calculation is based on the same DS formula, disregarding any potential changes to the spent catalyst after the recyclability tests, which could slightly alter the molecular weight. This approach allows for a rough comparison.

Table S4: Pristine NaAlg and Arg-NaAlg

	C 1s (1)	**C 1s (2)**	**C 1s (3)**	**C 1s (4)**	**O 1s (1)**	**O 1s (2)**	**O 1s (3)**	**N 1s (1)**	**N 1s (2)**	**Na 1s**
B.E. (eV)	284.8 284.6[a]	286.3 286.0[a]	287.4 287.6[a]	288.4 288.3[a]	531.1	532.6	533.5	399.8	398.2	1071.5
% At.	32.78	13.92	8.51	8.07	7.12	16.37	2.42	7.05	1.28	2.48
moiety	*C*-*C*	*C*-O, *C*-N	-O-*C*-O-guanidine[b]	-O-*C*=O-, -N-*C*=O-	C*OO*Na, *O*=C-OH	C-*O*-H, C-*O*-C	O_{ads}	*N*-C=O, guanidinium	C=*N*H	COO*Na*

[a] Refers to NaAlg, taken from reference.[4]; [b] HN=*C*-(NH, NH_2).

Table S5: Spent Arg-NaAlg_1a-u after the recyclability tests

	C 1s (1)	**C 1s (2)**	**C 1s (3)**	**C 1s (4)**	**O 1s (1)**	**O 1s (2)**	**O 1s (3)**	**N 1s (1)**	**N 1s (2)**
B.E. (eV)	284.8	286.4	287.3	288.6	532.2	533.4	534.3	400.2	398.5
% At.	58.94	8.35	2.44	8.17	14.84	4.95	1.00	1.09	0.22
moiety	*C*-*C*	*C*-O, *C*-N	-O-*C*-O-guanidine[b]	-O-*C*=O-, -N-*C*=O-	C*OO*Na, *O*=C-OH	C-*O*-H, C-*O*-C	O_{ads}	*N*-C=O, guanidinium	C=*N*H

[b] HN=*C*-(NH, NH_2).

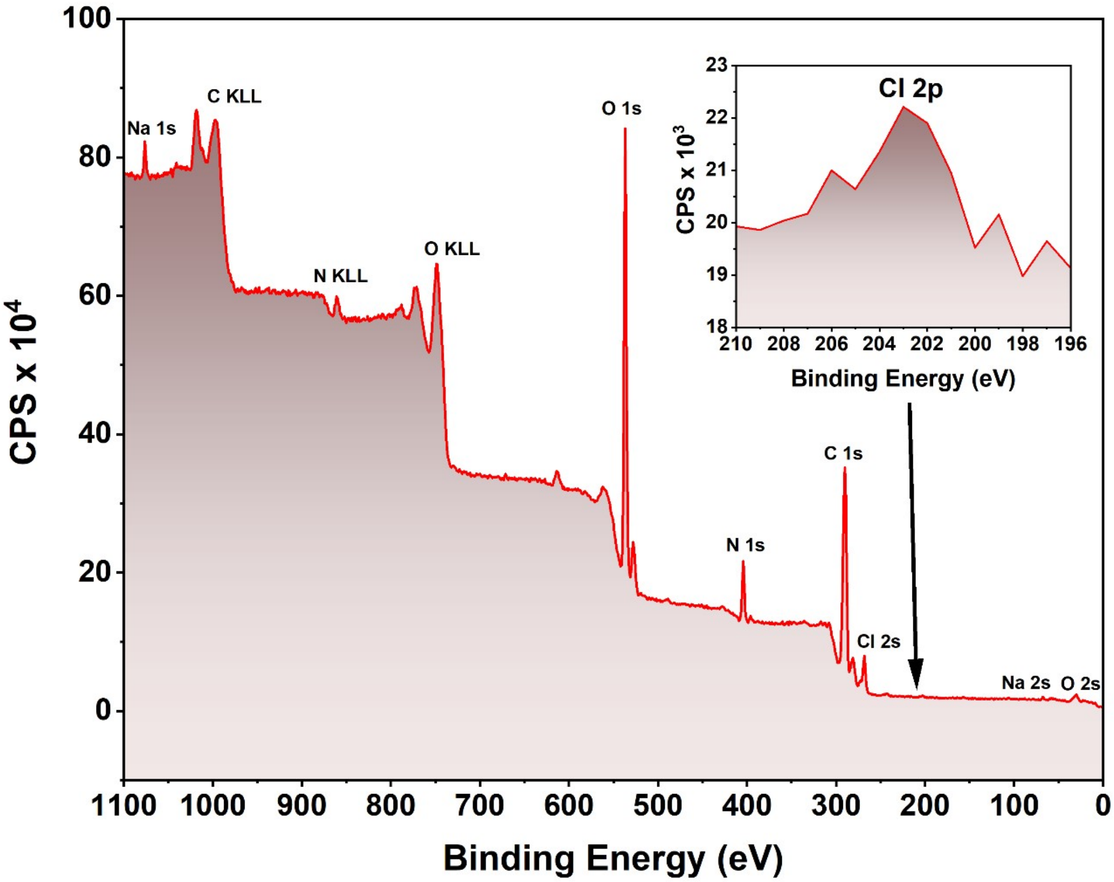

Figure S8. XPS wide scan survey of pristine Arg-NaAlg. The inset is an enlargement of the Cl 2p peak observed.

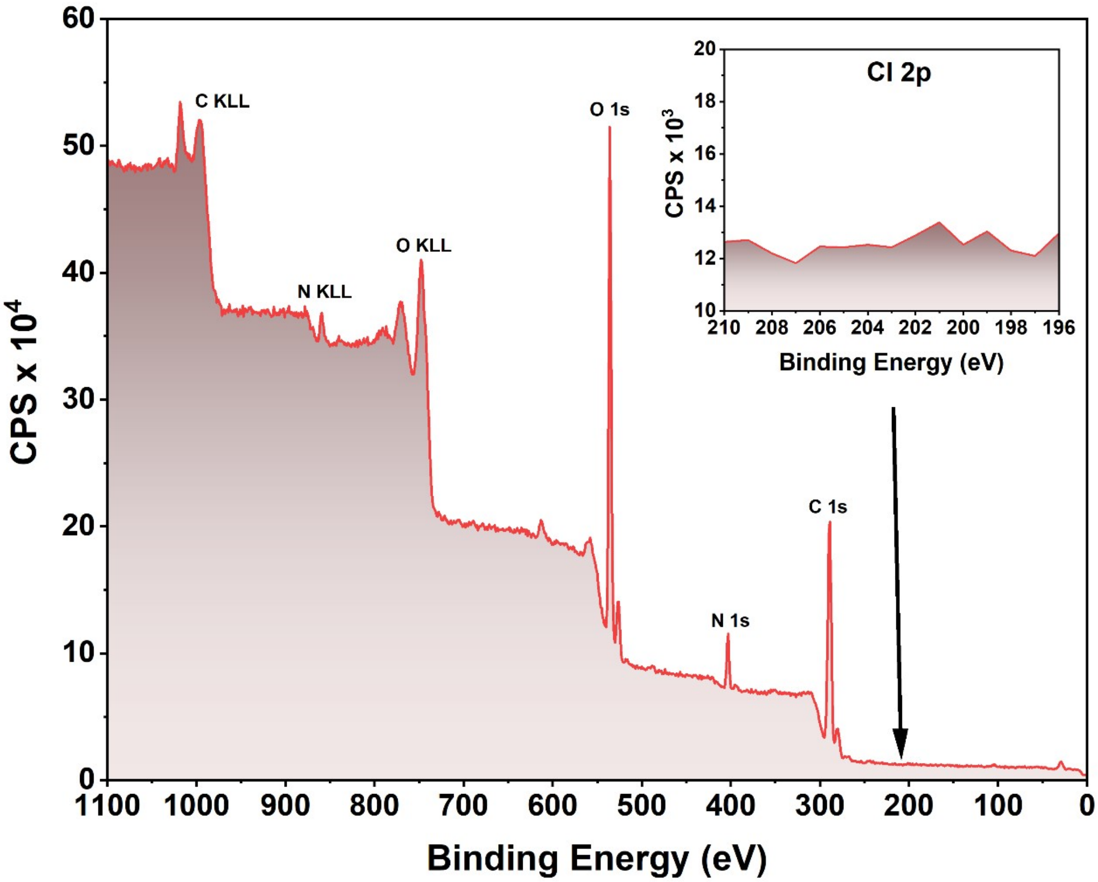

Figure S9. XPS wide scan survey of spent Arg-NaAlg_1a-u after 4 reaction cycles. The inset is an enlargement of the Cl 2p peak observed.

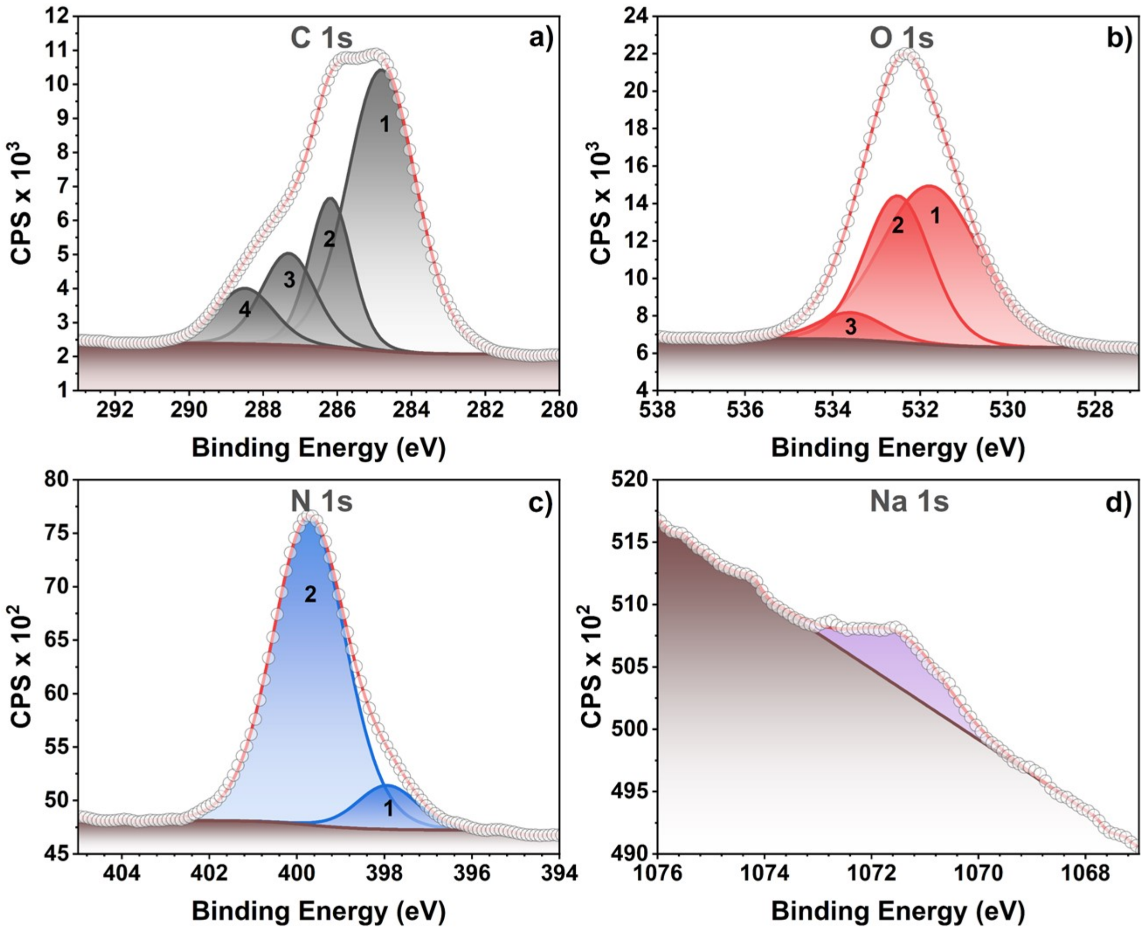

Figure S10. High resolution XPS spectra of Arg-NaAlg_1a-u in the a) C 1s, b) O 1s, c) N 1s and d) Na 1s spectral regions.

Table S6. GPC results of NaAlg, pristine Arg-NaAlg and spent Arg-NaAlg after recyclability tests.

Molecular weights	NaAlg	Arg-NaAlg	Arg-NaAlg_2a-d	Arg-NaAlg_1a-u	Arg-NaAlg_1b-u	Arg-NaAlg_1b-d
M_n *(g/mol)*	2,934	6,192	6,432	3,040	2,860	3,820
M_w *(g/mol)*	221,800	53,020	52,210	34,450	23,500	24,150
Đ	76	9	8	11	8	6

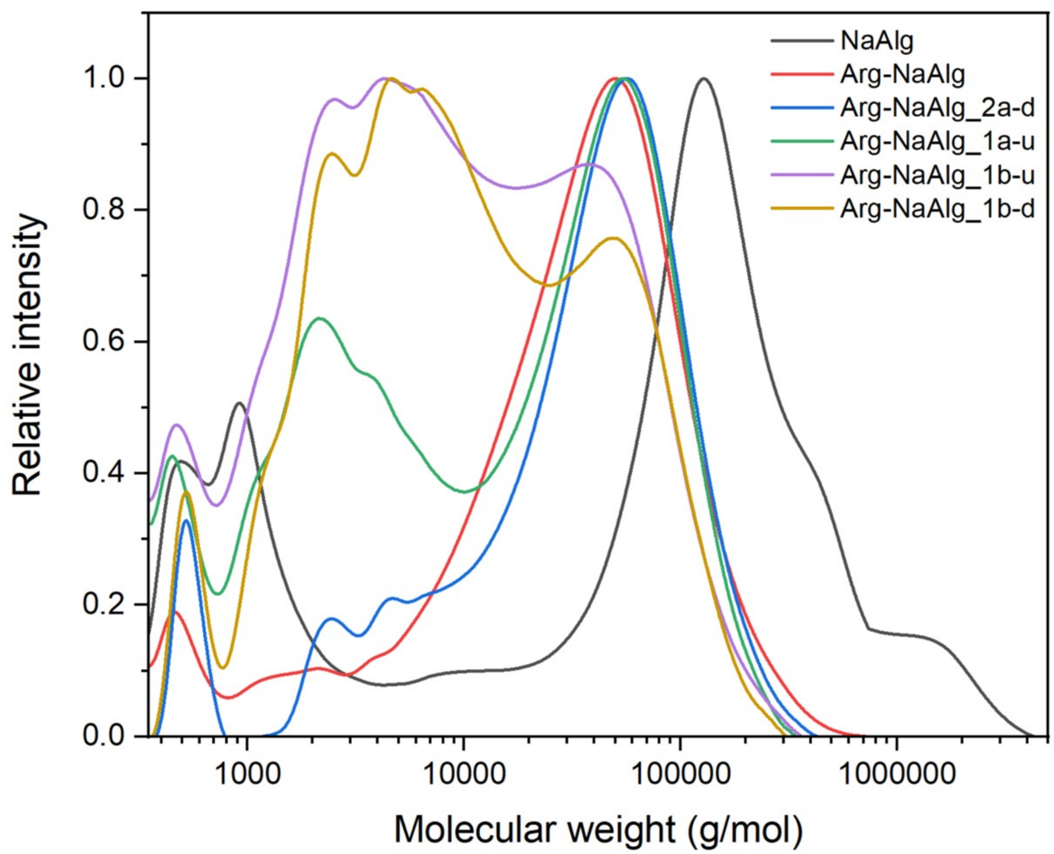

Figure S11. Normalized GPC chromatograms of the NaAlg, pristine Arg-NaAlg and spent Arg-NaAlg catalysts.

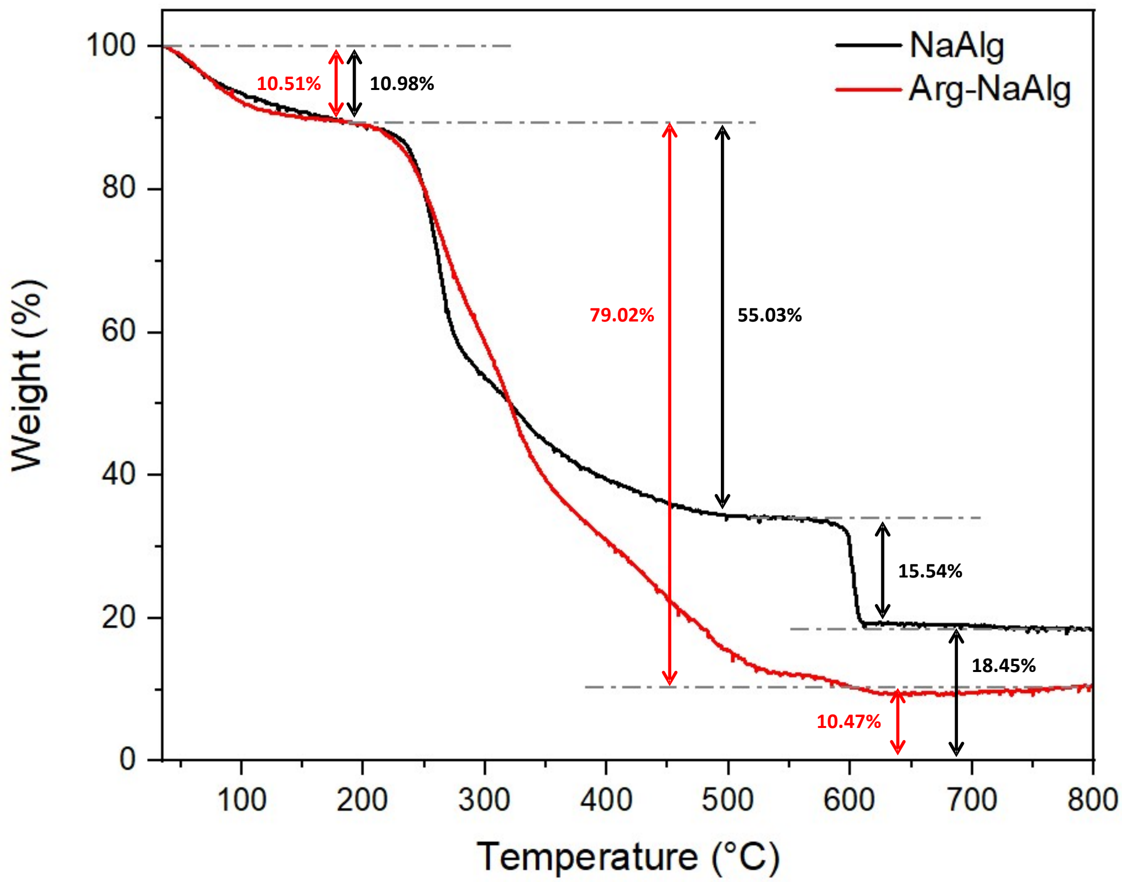

Figure S12. TGA analysis profiles of NaAlg (black) and Arg-NaAlg (red).

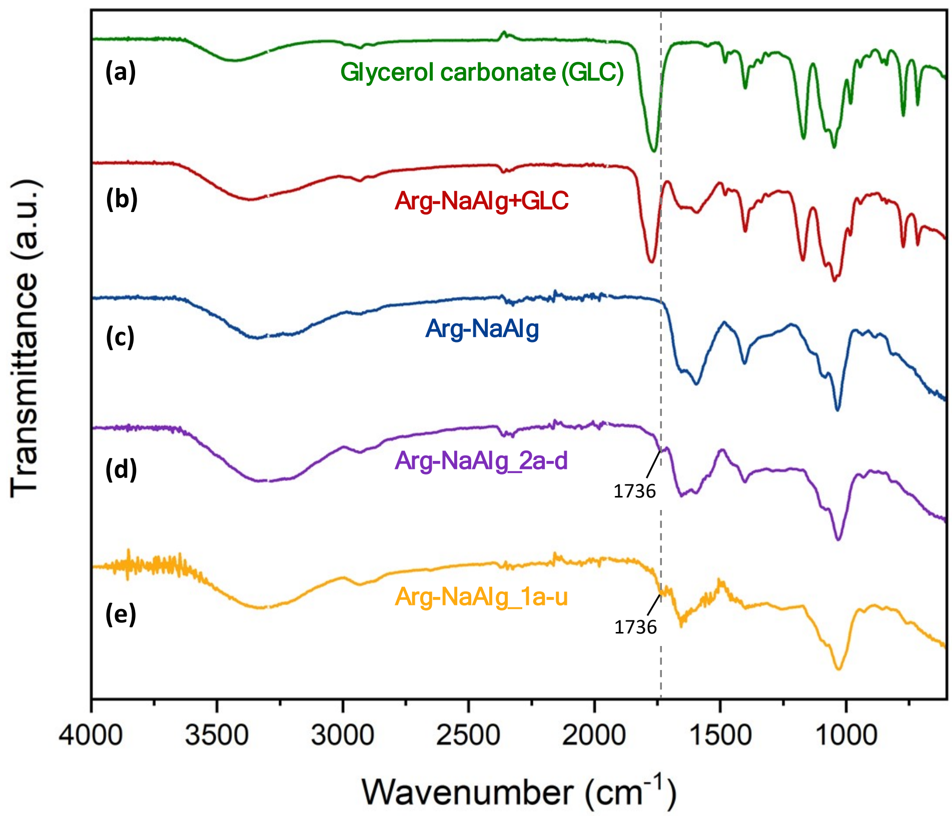

Figure S13. Investigation of the 1736 cm^{-1} peak in the FTIR spectra of the spent catalysts Arg-NaAlg_2a–d (d) and Arg-NaAlg_1a–u (e), compared with the spectra of pristine Arg-NaAlg, glycerol carbonate (GLC), and a mixture of Arg-NaAlg and GLC.

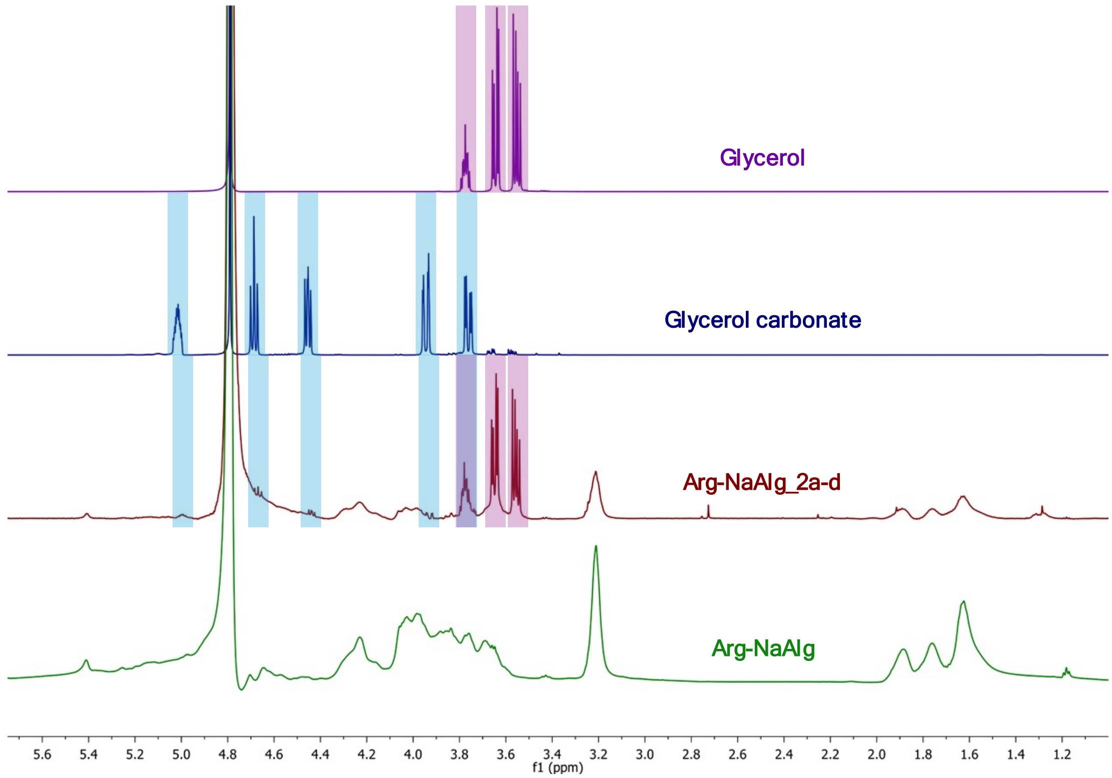

Figure S14. H^1-NMR spectrum (in D_2O) of the spent Arg-NaAlg_2a-d catalyst after 4 cycles compared with pristine Arg-NaAlg and glycerol carbonate and glycerol.

The H^1-NMR spectrum of the spent Arg-NaAlg_2a-d (red) showed that some glycerol carbonate (highlighted in blue) and glycerol (highlighted in purple) residue remained adsorbed on the catalyst surface after the reaction, even after catalyst washing. While all substrates possess at least one hydroxyl group, glycerol contains three, which may account for its stronger interaction with the catalyst. This enhanced interaction is likely mediated by hydrogen bonding with Arg-NaAlg, which presents multiple hydroxyl groups from sodium alginate and amine functionalities from arginine.

S5 Recyclability of Arg-NaAlg

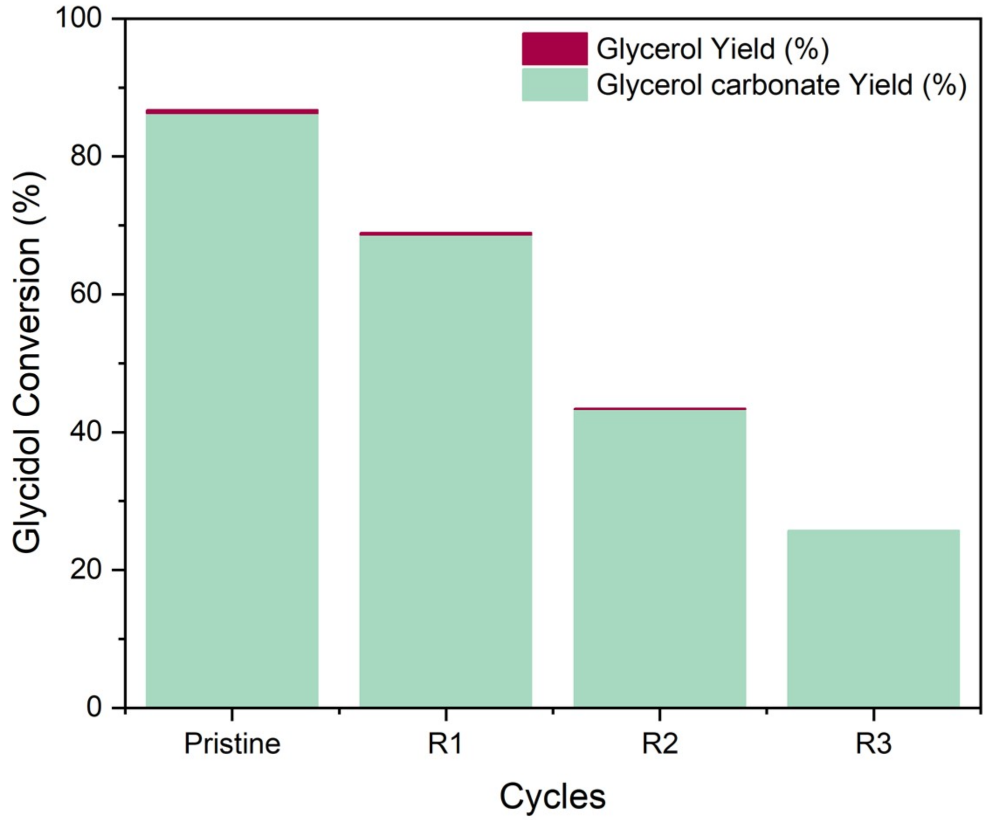

Figure S15. Recyclability tests of Arg-NaAlg_1a-u. Starting reaction conditions: 100 mmol glycidol (undried), 1.5 wt% catalyst, 80 °C, 3 h, 50 bar CO_2.

*For cycles R1-R3, the amount of glycidol and internal standard used was adjusted according to the amount of catalyst recovered after each cycle to keep the relative ratios of catalyst, glycidol, and internal standard constant. The CO_2 pressure was kept the same in all tests.

The %mass of the remaining catalyst after R3 was 15.6%.

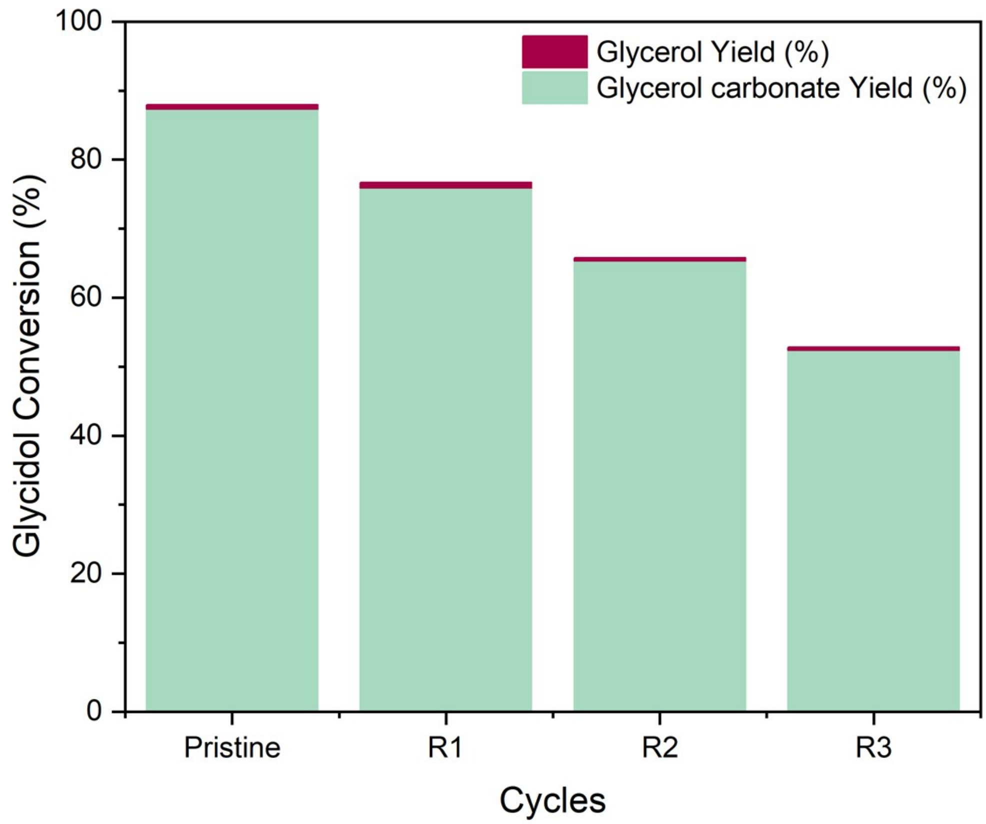

Figure S16. Recyclability tests of Arg-NaAlg_1b-u. Starting reaction conditions: 100 mmol glycidol (undried), 1.5 wt% catalyst, 80 °C, 3 h, 50 bar CO_2.

*For cycles R1-R3, the amount of glycidol and internal standard used was adjusted according to the amount of catalyst recovered after each cycle to keep the relative ratios of catalyst, glycidol, and internal standard constant. The CO_2 pressure was adjusted to keep the glycidol-to-CO_2 ratio constant in all tests.

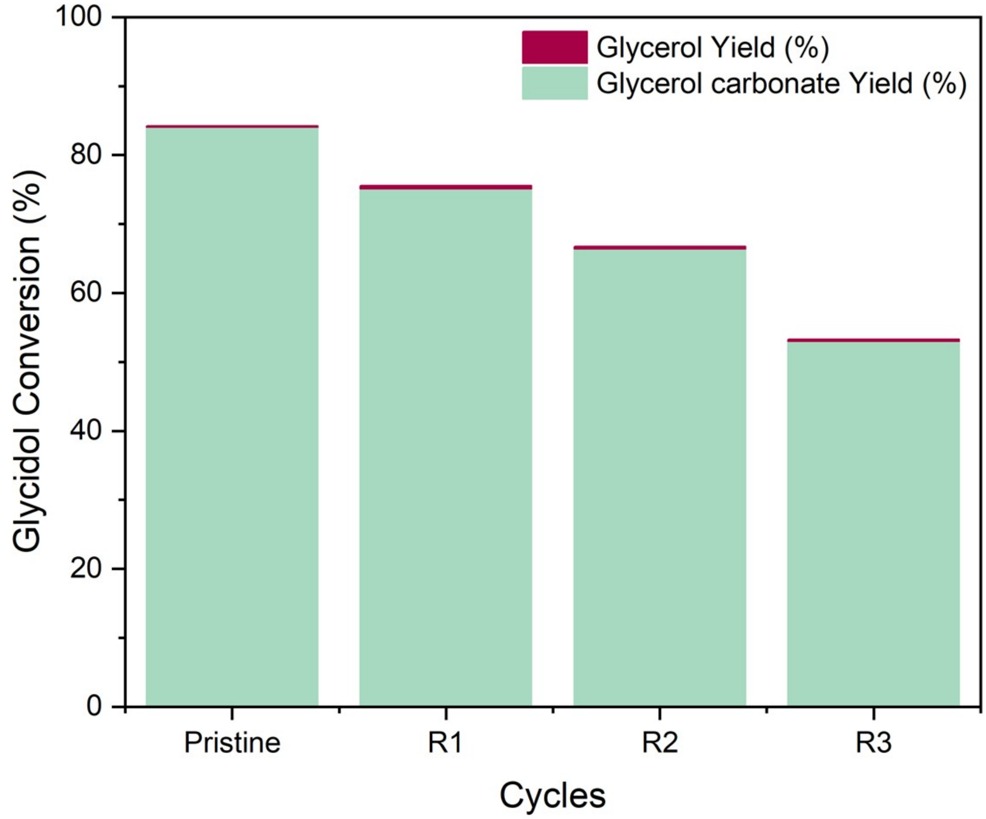

Figure S17. Recyclability tests of Arg-NaAlg_1b-d. Starting reaction conditions: 100 mmol glycidol (dried), 1.5 wt% catalyst, 80 °C, 3 h, 50 bar CO_2.

*For cycles R1-R3, the amount of glycidol and internal standard used was adjusted according to the amount of catalyst recovered after each cycle to keep the relative ratios of catalyst, glycidol, and internal standard constant. The CO_2 pressure was adjusted to keep the glycidol-to-CO_2 ratio constant in all tests.

The %mass of the remaining catalyst after R3 was 24.5%.

S6 Isolation of the glycerol carbonate product

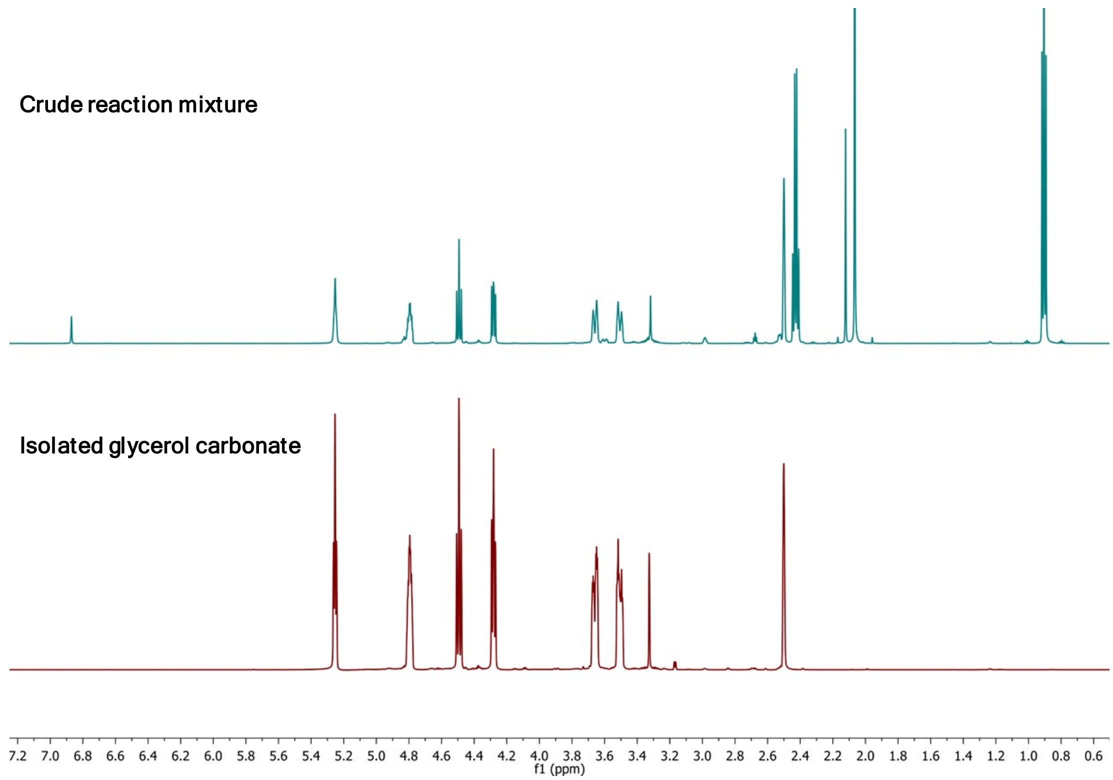

Figure S18. NMR spectra of the crude reaction mixture (top) compared to the isolated carbonate product (bottom). The spectra are displayed with adjusted vertical scaling for clarity. The crude was obtained from the reaction catalyzed by 3 wt% Arg-NaAlg at 80 °C under 10 bar CO_2 for 3 h. The catalytic test gave 91% glycidol conversion, 97% glycerol carbonate (GLC) selectivity, and 88% GLC yield. The isolated GLC yield was 77% (1.7477 g).

Purification was carried out by column chromatography on silica gel using dichloromethane (DCM)/methanol as the eluent. The eluent composition was gradually adjusted from 100:0 to 98:2 and then to 95:5 (DCM/methanol).

Table S7: Comparison of the catalytic performance of different halide-free heterogeneous catalysts for the reaction of glycidol and CO_2 to produce glycerol carbonate.

Entry	Catalyst	Loading (wt%)[b]	T (° C)	p_{CO_2} (bar)	Time (h)	Yield (%)	Selectivity (%)	TON	TOF (h^{-1})	Ref.
1	Arg-NaAlg	1.5	80	10	3	78	97	122	41	This work
2	Arg-NaAlg	3	80	10	3	93	98	73	24	This work
3[a]	TBD@Merrifield	0.3 mol%	70	5	18	82	92	273	15	5
4	P-DVB-AEImIm	4.5	100	10	1	86	98	135	135	6
5	MFM-KUST	1.65	110	10	8	98	98	82	10	7
6	PMP-TDNs-MI	1.65	110	10	8	>98	>98	186	23	8

[a] Methyl ethyl ketone (MEK) was used as the solvent. Unless otherwise specified, all reactions were performed under solvent-free conditions. [b] Relative to glycidol. The turnover number (TON) is defined as moles of glycerol carbonate/moles of active sites. The turnover frequency (TOF) is defined as TON/reaction time.

References

1 H. Grasdalen, B. Larsen and O. Smidsrød, *Carbohydrate Research*, 1979, **68**, 23–31.

2 H. M. Jensen, F. H. Larsen and S. B. Engelsen, in *Natural Products From Marine Algae: Methods and Protocols*, eds. D. B. Stengel and S. Connan, Springer, New York, NY, 2015, pp. 347–363.

3 F. Labre, S. Mathieu, P. Chaud, P.-Y. Morvan, R. Vallée, W. Helbert and S. Fort, *Carbohydr. Polym.*, 2018, **184**, 427–434.

4 J. Poolwong, V. Aomchad, S. Del Gobbo, A. W. Kleij and V. D'Elia, *ChemSusChem*, 2022, **15**, e202200765.

5 N. Zanda, A. Sobolewska, E. Alza, A. W. Kleij and M. A. Pericàs, *ACS Sustainable Chem. Eng.*, 2021, **9**, 4391–4397.

6 Y. He, X. Li, W. Cai, H. Lu, J. Ding, H. Li, H. Wan and G. Guan, *ACS Sustainable Chem. Eng.*, 2021, **9**, 7074–7085.

7 Z. Yue, T. Hu, H. Su, W. Zhao, Y. Li, H. Zhao, Y. Liu, Y. Liu, H. Zhang, L. Jiang, X. Tang, S. Shan and Y. Zhi, *Fuel*, 2022, **326**, 125007.

8 Z. Yue, T. Hu, W. Zhao, H. Su, W. Li, Z. Chen, Y. Chen, S. Li, L. Wang, Y. Liu, H. Zhang, S. Shan and Y. Zhi, *Appl. Catal. A: Gen.*, 2022, **643**, 118748.