Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Solvent- and Catalyst-free Reduction of CO_2 with Ammonia Borane

Loris Lombardo,[a] Taichi Nishiguchi,[b] Youngdon Ko,[c,d] Liping Zhong,[c,d] Nao Horike,[e] Andreas Züttel,[c,d] Satoshi Horike*[a,e,f]*

[a] Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
[b] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[c] Institute of Chemical Sciences and Engineering, Basic Science Faculty, École polytechnique fédérale de Lausanne (EPFL) Valais/Wallis, Energypolis, Rue de l'Industrie 17, CH-1951 Sion, Switzerland
[d] Empa Materials Science & Technology, CH-8600 Dübendorf, Switzerland
[e] Institute for Integrated Cell-Material Sciences, Institute for Advanced Study, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan
[f] Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Table of Contents

Experimental part

Ammonia Borane (AB, < 85%, TCI) and pyrrolidine (> 98.0% (GC), TCI) were used without additional treatment.

CO_2 reduction experiment

In a typical experiment, AB (50 mg) was weighted in an Ar-filled glove box and quickly transferred into a stainless-steel autoclave. The autoclave was put under vacuum and then loaded with CO_2 at the desired pressure. The reactor was placed into an oil bath at a fixed temperature and the amount of CO_2 reduced was determined gravimetrically at the end of the reaction. For the microbalance measurement, AB (50 mg) was placed into a magnetic suspension balance (MSB; Rubotherm, Germany). The chamber was evacuated for 30 min before starting measurements. Then, CO_2 was flown into the chamber to reach the target pressure before heating. The experiments were done at different temperatures and pressures under constant CO_2 flow (20 mL min^{-1}).

Characterization

AB was characterised before and after CO_2 exposure with Fourier-transform infrared spectroscopy (FT-IR; Bruker Optics ALPHA, ATR accessory, Germany) and nuclear magnetic resonance spectroscopy (^{1}H, ^{13}C, and ^{11}B NMR; Bruker 500 MHz AVIII, Germany) with DMSO-d_6 as solvent. Solid-state nuclear magnetic resonance spectra (CP-MAS ^{13}C-, ^{11}B-NMR) were collected on a JEOL JNM-ECA 600 MHz. The evolution of the crystal structure was measured by PXRD (Rigaku Miniflex, CuKα radiation, Japan) using a closed sample holder to avoid contact with air. The scanning electron microscopy (SEM) images were collected using a Hitachi S-3000N system after osmium coating. The high-resolution X-ray photoelectron spectra (XPS) were collected on a Kratos Axis Supra XPS equipment. Monochromated Kα of aluminum X-ray source (1486.6 eV) was used with a pass energy of 20 eV for the analyser setting in order to get highly resolved spectra. The sample was loaded into XPS at atmospheric conditions while the spectra were measured under ultra-vacuum conditions. The deconvolution of spectra was completed with CasaXPS software, while the attribution of different species was based on literatures.

N-formylation reaction

AB was tested for the *N*-formylation of pyrrolidine. AB and pyrrolidine (2-1 mol ratio) were loaded into the stainless-steel autoclave and pressurized to 0.5 MPa. The reaction was heated at 80 °C for 24 hours. Yield was determined with ^{1}H NMR by using benzyl benzoate as internal standard.

Calcination

The calcination of the product between AB and CO_2 was conducted in a tubular furnace under Ar flow (200 mL min^{-1}). The powder was placed into a ceramic crucible and heated from room temperature to 750 °C at 5 °C · min^{-1} and then let it cool down.

DFT calculation

We used GAMESS package to conduct structural optimization, frequency analyses, and intrinsic reaction coordination calculations.[1–3] We employed TPSS functional with BJ-damped D3 dispersion correction and valence triple zeta basis with a set of single polarization (TPSS-D3/TZVP level), following a precedent report.[4,5]

Results

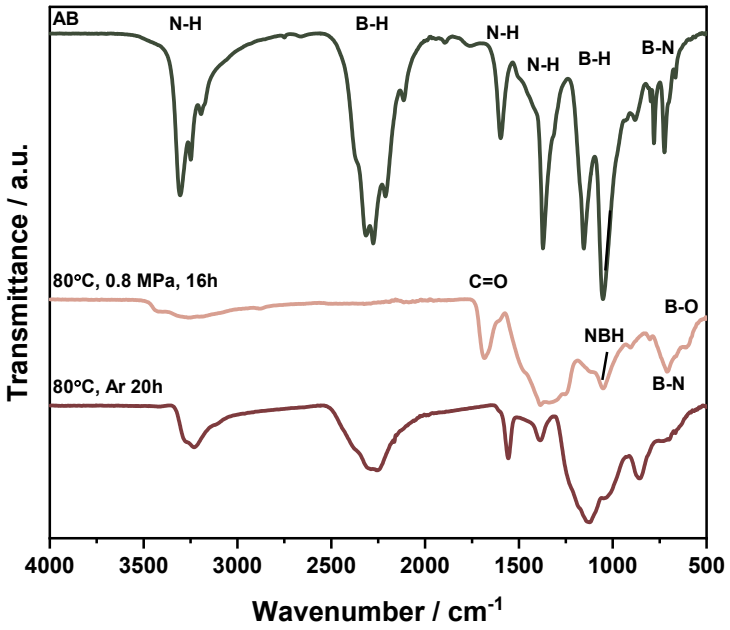

Figure S1: FT-IR spectra of AB, AB after reaction with CO_2 at 0.8 MPa and 80 °C for 16h, and AB heated at 80 °C for 16h under Ar.

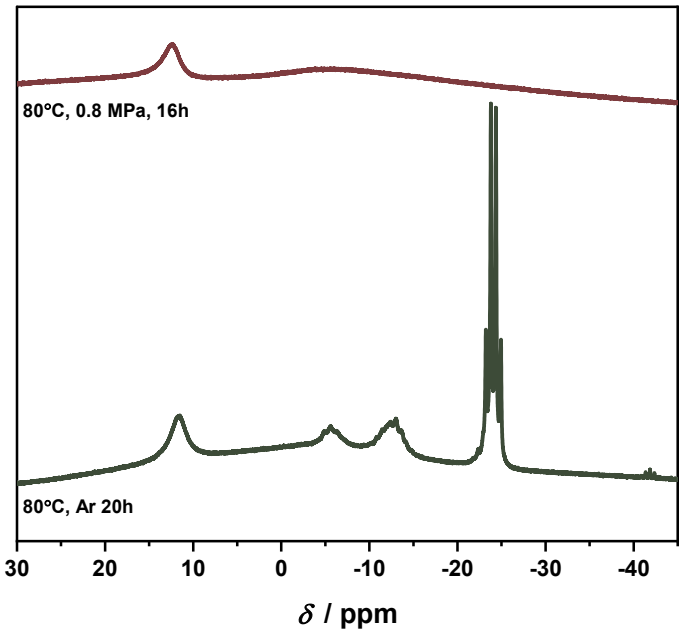

Figure S2: ^{11}B NMR of AB heated at 80 °C under Ar and 0.8 MPa CO_2.

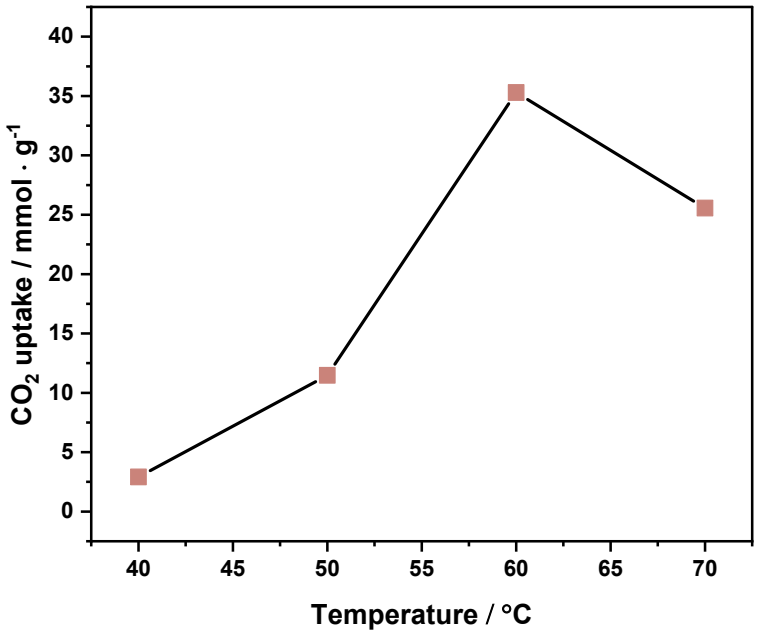

Figure S3: The amount of CO_2 reduced by AB at 0.8 MPa and different temperatures.

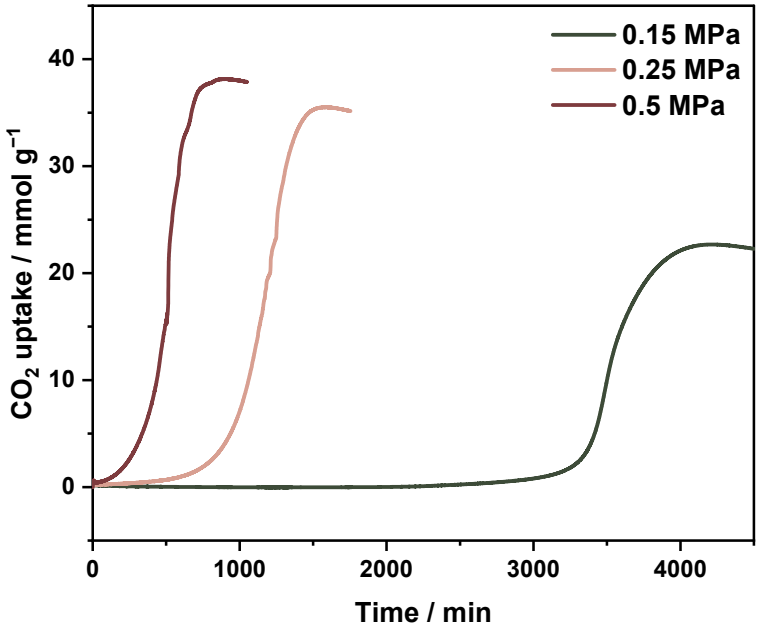

Figure S4: MSB CO_2 absorption curves of ammonia borane at 60 °C and different pressures.

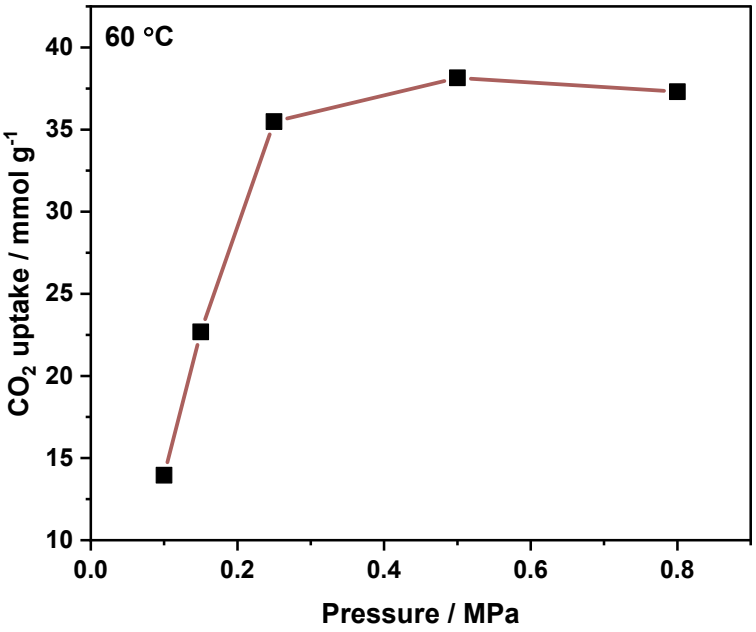

Figure S5: CO_2 uptake amount of ammonia borane at 60 °C and different pressures.

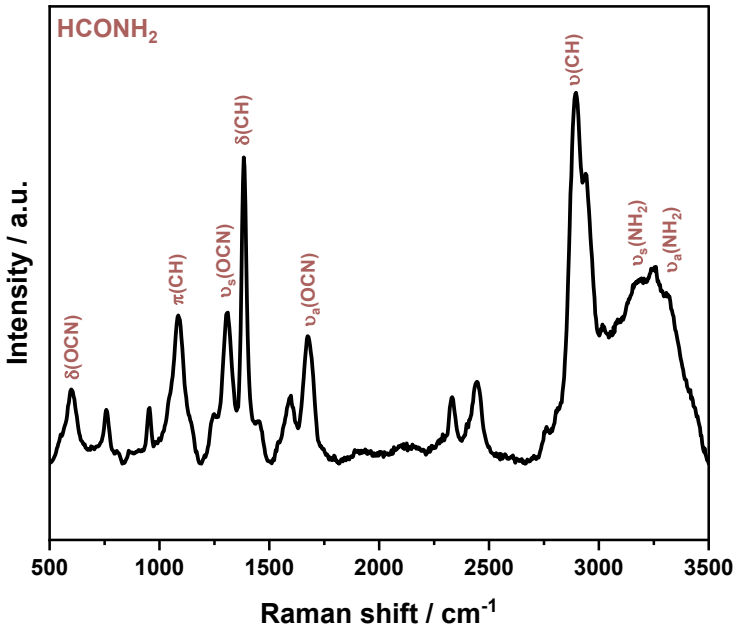

Figure S6: Raman spectrum of AB after reaction with 0.5 MPa of CO_2 at 60 °C for 24h.

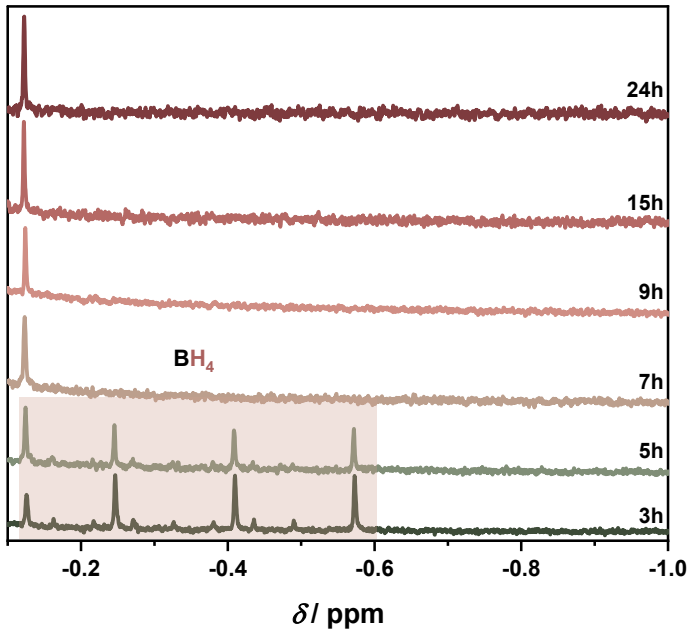

Figure S7: Evolution of AB ^{1}H NMR in function of time showing the formation of borohydride at the early stage (0.5 MPa, 60 °C).

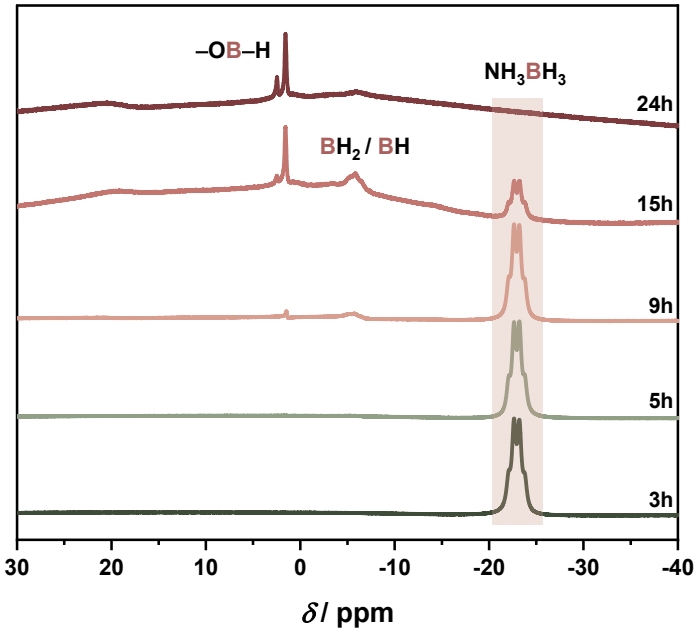

Figure S8: Evolution of AB ^{1}H NMR in function of time under CO_2 pressure (0.5 MPa, 60 °C).

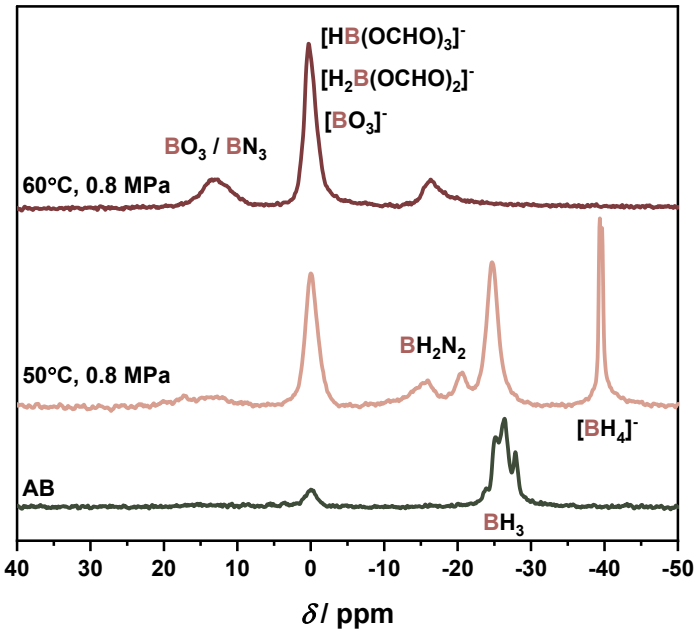

Figure S9: Solid-state ^{11}B MAS NMR of AB and AB exposed to 0.8 MPa of CO_2 for 16h at 50 °C and 60 °C.

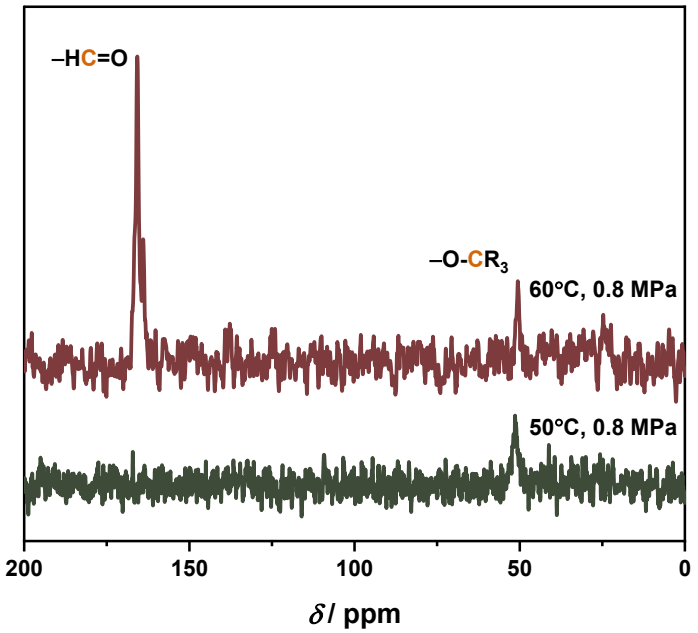

Figure S10: Solid-state ^{13}C MAS NMR of AB exposed to 0.8 MPa of CO_2 for 16h at 50 °C and 60 °C.

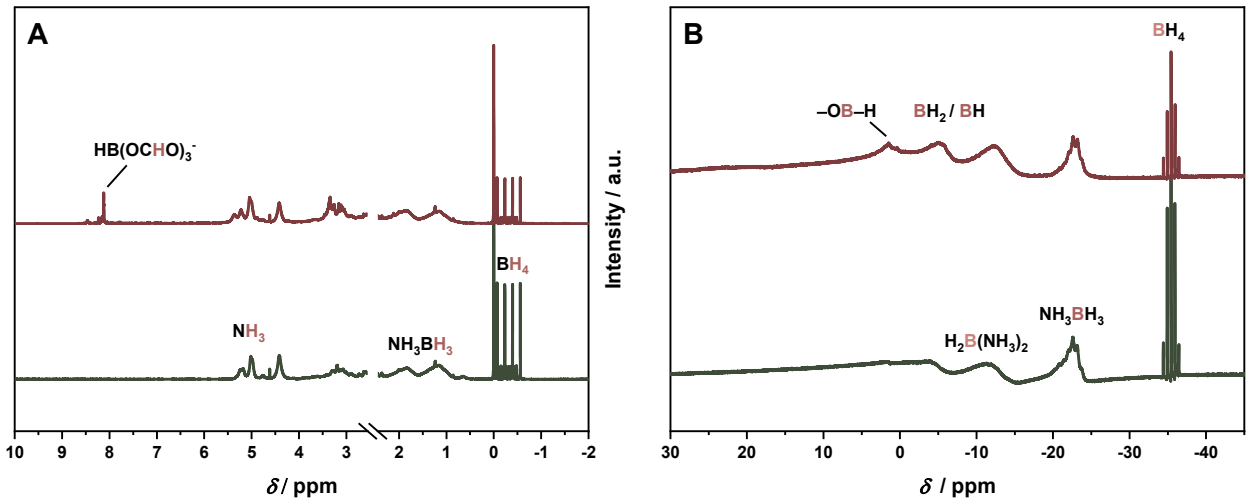

Figure S11: **A** ^{1}H and **B** ^{11}B MAS NMR of AB heat treated at 75 °C for 16 hours (green) and then exposed to 0.5 MPa of CO_2 at 60 °C for 3 hours (red).

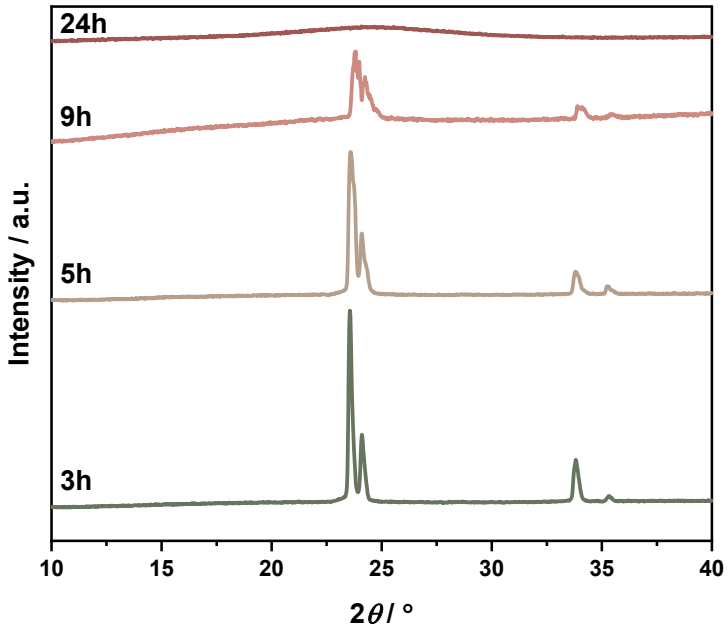

Figure S12: PXRD patterns of AB in function of time under CO_2 pressure (0.5 MPa, 60 °C).

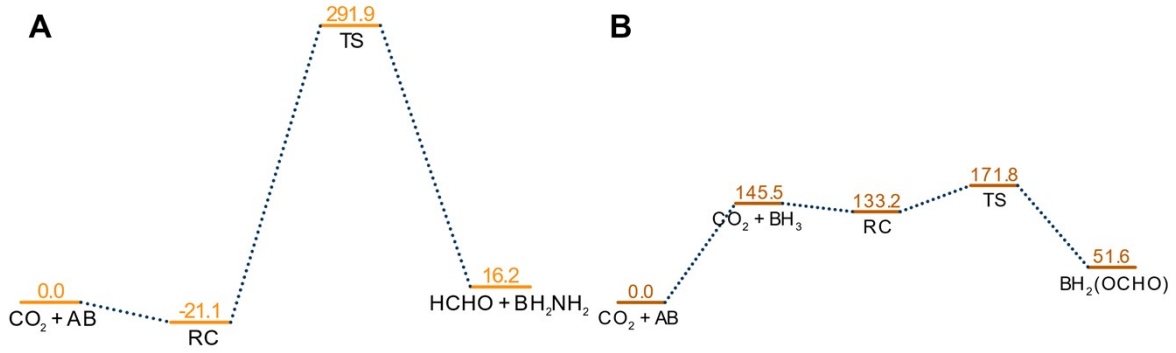

Figure S13: Total energy in kJ mol^{-1} against reaction coordinates of **A** direct reaction between CO_2 and AB, and **B** reaction between AB and BH_3 produced from AB. TS and RC indicate transition states and reaction complexes respectively.

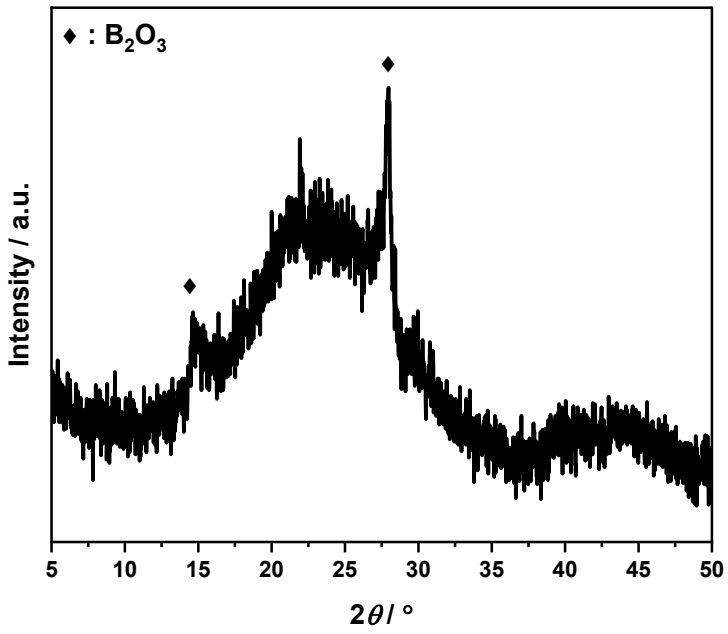

Figure S14: PXRD pattern of AB-CO_2 after calcination at 750 °C under Ar.

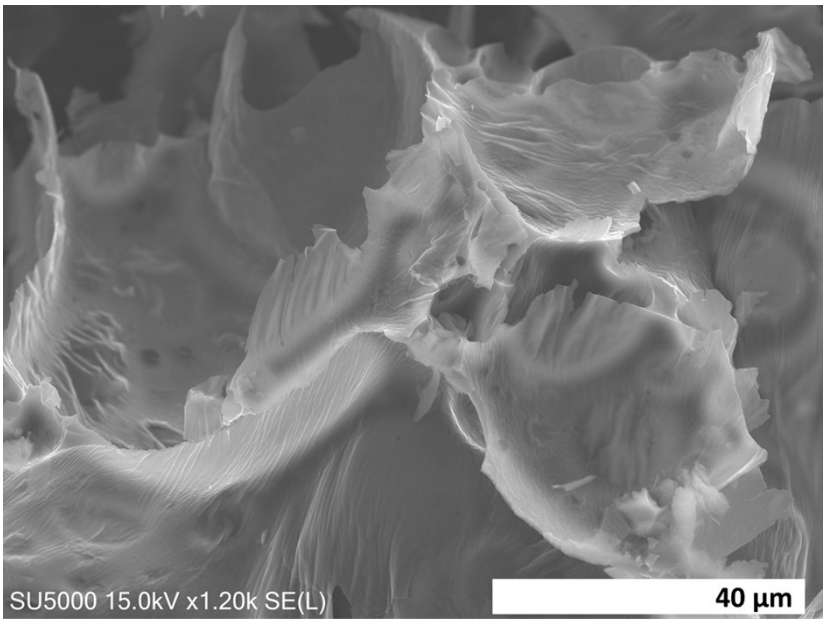

Figure S15: SEM image of AB-CO_2 after calcination at 750 °C under Ar.

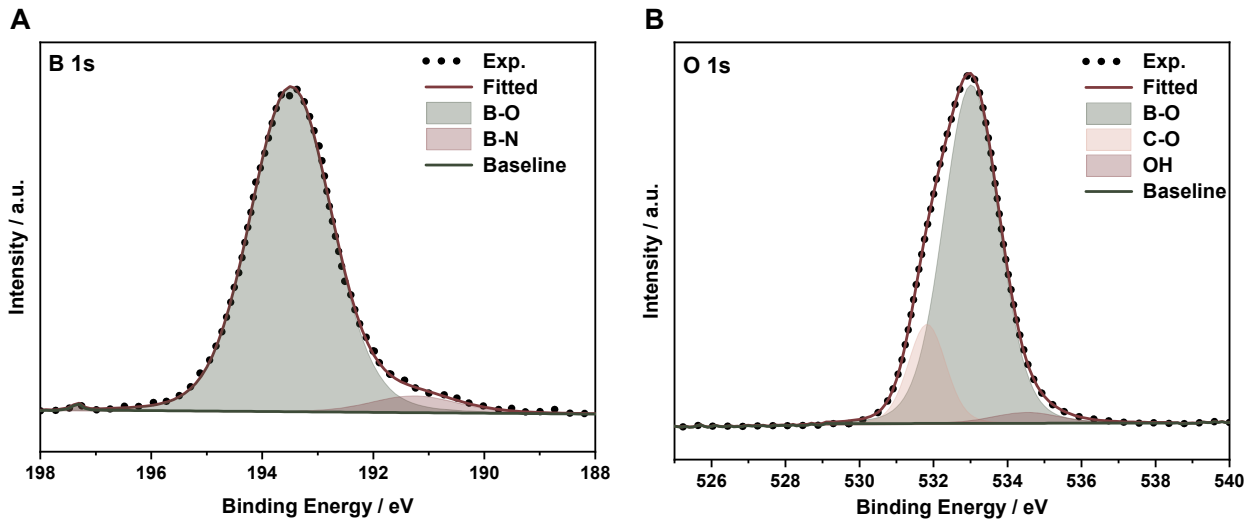

Figure S16: High-resolution XPS spectra of **A** the boron region (B 1s), and **B** oxygen region (O 1s) of AB-CO_2 calcinated at 750 °C under Ar.

Table S1: Total energy and coordinates of atoms of structures optimized fully and optimized for transition states. Total energy is in atomic unit Hartree and the coordinates are in angstrom.

CO_2

Total energy = −188.6840592587

C	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	−0.0000000000	−1.1701143267
O	0.0000000000	0.0000000000	1.1701143267

AB

Total energy = −83.2659255686

B	0.0000000000	−0.0000000000	−0.8614328472
N	0.0000000000	−0.0000000000	0.8112776190
H	−0.3339751308	−0.8911485831	1.1822019080
H	0.9387448769	0.1563433440	1.1822019080
H	−0.6047697461	0.7348052390	1.1822019080
H	0.7453069361	−0.9064709520	−1.1654834985
H	0.4123734042	1.0986902162	−1.1654834985
H	−1.1576803402	−0.1922192643	−1.1654834985

BH_3

Total energy = −26.6258097188

B	0.0000000000	0.0000000000	0.0000000000
H	−1.0342758332	−0.5971394307	−0.0000000000
H	1.0342758332	−0.5971394307	−0.0000000000
H	0.0000000000	1.1942788615	−0.0000000000

NH_3

Total energy = −56.5846978298

N	0.0000000000	−0.0000000000	0.4111912289
H	−0.8186458867	−0.4726454231	0.0296029237
H	0.8186458867	−0.4726454231	0.0296029237
H	−0.0000000000	0.9452908462	0.0296029237

RC in direct reaction between CO_2 and AB

Total energy = −271.9580230250

H	−1.5722513453	−0.8779478906	0.0439802436
H	0.6811677455	−1.3791615665	−1.0698934096
C	0.6769862445	1.1304810285	0.3190771000
O	−0.4960858610	1.0707553848	0.3182013055
O	1.8372017936	1.2388135765	0.3270851748
H	−1.7666540990	−2.4007013420	0.6571445425
H	−1.7770376566	−2.1641530152	−0.9739466289
H	0.4880298649	−3.2516383648	−0.3149853513
H	0.6945320613	−1.6731045997	0.9414465130
N	−1.3413689552	−1.8642067716	−0.1004958682
B	0.3087739733	−2.0670561450	−0.1407557264

TS in direct reaction between CO_2 and AB

Total energy = −271.8388126223

H	−0.7255673233	−0.0393396181	0.0000251995
H	1.1405171671	−0.8792375410	−0.0003141749
C	−0.0405182735	1.0297339557	−0.0001065166
O	−0.6919382408	2.0615857327	0.0000411550
O	1.1429710813	0.6361142112	−0.0003467195

H −1.4849288193 −1.5171726815 0.8379012498

H −1.4852134560 −1.5173733178 −0.8373470304

H 0.7955075314 −2.4896710565 −1.0681492281

H 0.7959399117 −2.4893302687 1.0681274670

N −0.9062834505 −1.4644906438 0.0001724582

B 0.4571589817 −2.0539767024 −0.0000038650

HCHO + BH_2NH_2

Total energy = −271.9438313013

H −0.8164959959 0.4743048232 −0.0437601999

H 1.2541853527 −0.0082251183 −0.0666666793

C −0.1203868900 1.3331204459 −0.0146362473

O −0.4627494108 2.4854154161 0.0136452021

O 1.1916129830 0.9641653149 −0.0099017299

H −1.6348995074 −2.3816618267 0.8267692497

H −1.5979743652 −2.2101308222 −0.8550185913

H 0.9334472243 −2.3046782644 −1.0119690619

H 0.8865378649 −2.5376102014 1.0729296708

N −1.0580950381 −2.3032281551 −0.0026549411

B 0.3347092994 −2.4069307980 0.0207444498

RC in reaction between CO_2 and BH_3

Total energy = −215.3145640493

H 0.3582818892 −0.0689732230 −1.0468177551

H 0.3818712888 −0.0802700782 1.0218021756

C −1.8996523959 2.3764347375 0.0262074015

O −0.7881020534 1.9965877904 0.0120112907

O −2.9968263998 2.7671021682 0.0403091764

H −1.3623592485 −0.5185495311 0.0048504101

B −0.2196366503 −0.1600144714 −0.0062460851

TS in reaction between CO_2 and BH_3

Total energy = −215.2998673978

H −0.2799325437 0.0218745550 −1.0613311109

H −0.2556727255 0.0109406421 1.0518148532

C −1.8051418374 1.9804349835 0.0230491271

O −0.5666527146 2.0796203529 0.0093815703

O −2.8719091920 2.4799150118 0.0378382757

H −1.9277809719 0.4624133893 0.0165947625

B −0.6242236349 0.4312267755 0.0014801722

BH_2(OCHO)

Total energy = −215.3456213708

H 1.0582126315 0.6572972305 −0.5490575023

H −0.4392177697 −0.1923974636 0.6700928537

C −2.1306840327 1.7993205114 0.1308412290

O −0.8411373639 1.7231216011 −0.3946900700

O −2.8642838762 2.7050188712 −0.1295881130

H −2.3669103419 0.9447520123 0.7904825533

B −0.0285602725 0.6592261835 −0.0659607492

TS1 in reaction between AB and CO_2 via DADB

Total energy = −166.5122902287

H 0.9503442506 1.1969588431 0.0029961564

H −0.3725565555 −0.0601806304 1.0403114778

H −0.3712580210 −0.0579992910 −1.0398627209

H −0.9781250519 1.6329303991 0.0015882132

H 2.9499755981 −1.2881791344 −0.0025780695

H 1.5089196395 −1.1591092973 0.8228392665

H 1.5008398767 −1.1597575872 −0.8142308407

H 2.6706043293 1.1165174306 1.0248720724

H 2.6647497191 1.1143246921 −1.0291591535

N 2.0312367150 −0.8429867297 0.0016257339

B 2.1284135657 0.7875056081 −0.0002775458

B −0.4871107423 0.5409425939 0.0008007225

N −2.8867000900 −0.2253625405 −0.0017237763

H −3.1525715895 −1.2089610125 −0.0048668975

H −3.3001869417 0.2127120523 −0.8230467779

H −3.3014454722 0.2078076436 0.8215687394

NH_3 + BH_3–AB

Total energy = −166.5339133144

H 2.8590779564 0.3223166311 0.4883827812

H 3.0675631268 −1.6765858665 0.3846298070

H 2.9929303304 −0.6223587898 −1.3734106549

H 4.5391520776 −0.3321353212 −0.0775327203

H −0.3357924189 −0.1300274879 0.0163230350

H 0.8942354180 −0.8304362248 −0.9215526992

H 0.7414381163 −1.2739797914 0.6480446068

H 1.4236628334 1.0163002496 1.5618981283

H 1.5603343434 1.5890550706 −0.3988444602

N 0.6515776862 −0.4816716332 0.0094144510

H −1.4656334347 1.8656352333 0.3410456519

H −2.4377115843 1.0763459384 −0.7163541527

H −2.5404140177 0.7558158045 0.8871267770

N −1.8844629160 0.9577528779 0.1324565915

B 1.6404198361 0.7107041546 0.4157328929

B 3.4021367281 −0.6913662428 −0.2369880249

TS2 in reaction between AB and CO_2 via DADB

Total energy = −166.4912816769

H 2.6512264647 0.4773640950 0.3372361950

H 2.9764789713 −1.4842926174 0.4990430143

H 3.1681900598 −0.5738912537 −1.3009038340

H 4.5324844583 −0.2465163894 0.1833173029

H −0.0677937858 −1.3289026323 0.4490938494

H 0.4719344954 −0.9981980961 −1.0896371070

H 1.6151432148 −1.2348817183 0.1213105706

H 0.8698263470 0.9400846676 1.4251655981

H 0.9921853658 1.4510042862 −0.6301517870

N 0.6364258693 −0.8314818977 −0.0963952763

H −1.2075067313 2.1467388966 0.4539863453

H −1.7345941328 1.0713228612 −0.6659614874

H −1.8678088760 0.7281324001 0.9441365495

N −1.2638463492 1.1514665185 0.2370312124

B 0.7813638720 0.6985327430 0.2635873605

B 3.3749359165 −0.4538007935 −0.1004945063

DADB

Total energy = −166.5075831829

H 3.3675830633 0.3867835755 −0.6892000561

H 3.0870742290 −0.9578342086 0.7893566650

H 3.1186158453 −1.5714463659 −1.1363483422

H 4.8054254320 −0.9589428690 −0.1850938461

H 0.3037335624 −1.3838055738 0.2662707367

H 0.9759524347 −0.5174963870 −0.9785374231

H 1.8578451914 −0.6816834740 0.3851595249

H 0.0872804381 0.6918176780 1.8298869278

H 0.8885020002 1.7408837909 0.2733994597

N 0.8031621750 −0.5235401012 0.0311512324

H	−1.6235263979	1.9482466772	0.4188352521
H	−1.3023397619	1.1506717055	−0.9834477171
H	−1.9622341775	0.3420654719	0.3010127669
N	−1.2844852379	1.0618203098	0.0362814696
B	0.2416588096	0.8026311858	0.6422868740
B	3.6186131591	−0.7660955068	−0.3462434940

TS3 in reaction between AB and CO_2 via DADB

Total energy = −215.9729212020

C	−1.6812746472	2.5618190371	−0.0013755770
O	−0.8835159642	3.0242447953	−0.7471355511
O	−2.5501075142	2.5247961070	0.8049388902
H	−1.5152456095	0.7399972918	−0.4097233150
H	−0.0966944701	0.3058317677	0.9780593489
H	−1.5613275489	−1.0242136552	0.5163864796
H	−0.0940876355	−0.5872963211	−0.8468143877
B	−0.7885009505	−0.1721495527	0.0800498621

BH_3–H–CO_2

Total energy = −215.9745561185

C	−1.6534200072	2.2317535676	−0.0525427732
O	−0.7095932813	2.9653382368	−0.2477963318
O	−2.8572701922	2.1660978584	0.0643227792
H	−1.1363058392	0.9045475345	0.1111851274
H	0.4469936186	−0.1923232460	0.6337647894
H	−1.4674596789	−0.9151354256	0.8607811240
H	−0.6696730591	−0.6839710278	−1.0160205786
B	−0.6620420454	−0.3385628449	0.1524576235

TS4 in reaction between AB and CO_2 via DADB

Total energy = −215.9437853876

C	−1.8838398672	2.0365609986	0.0035134283
O	−0.7315575854	2.4320709640	−0.3173708307
O	−2.9405454953	2.6593470136	0.2299636268
H	−1.9764856720	0.8846829330	0.1099825044
H	0.7579868416	0.3344922248	0.3698343832
H	−0.9186588727	−0.7778132143	0.8154775198
H	−0.4622929085	−0.3602238535	−1.1537166417
B	−0.2744566905	−0.1513538662	0.0122222099

BH_3(OCHO)

Total energy = −216.0078636008

C	−2.1091961504	1.8946376559	0.1436873766
O	−0.9024563893	1.7664379781	−0.3349832307
O	−2.7954966325	2.9185609634	0.0931422645
H	−2.4945490945	0.9662465129	0.6254835929
H	0.9005613822	0.6432305473	0.4230847830
H	−0.8352254956	−0.4041284270	0.3722593778
H	0.1334330205	0.0407763396	−1.3528998539
B	−0.1245323825	0.4166973256	−0.2131478894

References

1 J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.

2 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

3 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

4 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

5 Z.-W. Qu, H. Zhu, R. Streubel and S. Grimme, *Phys. Chem. Chem. Phys.*, 2022, **24**, 14159–14164.