Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supplementary information

Enzymatic conversion of carbon dioxide

Jiafu Shi[1, 2,3, †], *Yanjun Jiang*[4, †], *Zhongyi Jiang*[1, 3,*], *Xueyan Wang*[1,3], *Xiaoli Wang*[1,3], *Shaohua Zhang*[1,3], *Pingping Han* [1,3], *Chen Yang*[1,3]

[1] *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.*

[2] *School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China*

[3] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 300072, China*

[4] *School of Chemical Engineering and Technology, HeBei University of Technology, Tianjin 300130, China*

[†] *JF Shi and YJ Jiang contributed equally.*

Table S1. Pathways for autotrophic CO_2.

Pathway	CO_2-fixing enzymes (active "CO_2" species)	Selected intermediates	Major enzymes	Occurrence
Calvin cycle	Rubisco (CO_2)	3-phosphoglycerate, triose phosphates, sugar phosphates	Rubisco, phosphoglyceraldehyde dehydrogenase, phosphoribulokinase	Plants, algae, cyanobacteria, most aerobic or facultative aerobic *Eubacteria*
Reductive citric acid cycle	2-Oxoglutarate synthase (CO_2), α-ketoglutarate synthase (CO_2); isocitrate dehydrogenase (CO_2), PEP carboxylase (HCO_3^-), pyruvate synthase (CO_2)	Acetyl-CoA, pyruvate, oxaloacetate, succinyl-CoA, α -ketoglutarate, 2-oxogluarate	2-Oxoglutarate synthase , α-ketoglutarate synthase, isocitrate dehydrogenase, pyruvate synthase, pyruvate carboxylase, PEP carboxylase, ATP-citrate lyase	*Chlorobiales*, *Aquificales*, *Epsilonproteobacteria*, some *Deltaproteobacteria*, few *Alphaproteobacteria* (*Magnetococcus*), *Nitrospirae*
Reductive acetyl-CoA pathway	CO dehydrogenase (CO_2), formate dehydrogenase (CO_2),	Acetyl-CoA, methyl-H_4folate, methylated corrinoid protein, formate	Acetyl-CoA synthase, CO dehydrogenase, formate dehydrogenase, corrinoid iron-sulfur protein methyltransferase, enzymes reducing formate to methyl-H_4folate	*Methanogenic* and sulfate reducing *Euryarchaeota*, acetogenic *Firmicutes*, some *Spirochaetes*, many *Deltaproteobacteria*, annamox bacteria of *Planctomycetes*
3-Hydroxypropionate bi-cycle	Acetyl-CoA-carboxylase (HCO_3^-), propionyl-CoA carboxylase (HCO_3^-)	Acetyl-CoA, malony-CoA, propionyl-CoA, methylmalonyl-CoA, succinyl -CoA, malyl-CoA	Acetyl-CoA-carboxylase, propionyl-CoA carboxylase	*Chloroflexaceae*
3-Hydroxypropionate/ 4-hydroxybutyrate Cycle	Acetyl-CoA carboxylase (HCO_3^-), pyruvate synthase (CO_2), propionyl-CoA carboxylase (HCO_3-)	Acetyl-CoA, succinyl-CoA, methylmalonyl-CoA, 3-phosphate glyceraldehyde	Acetyl-CoAcarboxylase, propionyl -CoA carboxylase, 4-hydroxybutyryl-CoA dehydratase, pyruvate synthase	Aerobic *Sulfolobales* (*Crenarchaeota*), possibly marine and soil ammonia oxidizing *Crenarchaeota*
Dicarboxylate/4-hydroxybutyrate cycle	Pyruvate synthase (CO_2), PEP carboxylase (HCO_3^-)	Acetyl-CoA, pyruvate, PEP, oxaloacetate, succinyl-CoA, oxaloacetate	4-Hydroxybutyryl-CoA dehydratase, PEP carboxylase, pyruvate synthase	Anaerobic *Thermoproteales*, *Desulfurococcales*

Figure S1. The Calvin cycle.

Figure S2. The reductive citric acid cycle.

Figure S3. The reductive acetyl-CoA route.

Figure S4. The 3-hydroxypropionate cycle.

S*

Figure S5. The 3-hydro

Figure S6. The dicarboxylate/4-hydroxybutyrate cycle.

Figure S7. Facilitated transport mechanism of the membrane reactor. Reproduced with permission from ref. 31. Copyright 2010 Elsevier.

Figure S8. Schamtic converting prcoess of CO_2 into $CaCO_3$ utilizing CA-encapsulated bioinspired silica as the catalysts. Reproduced with permission from ref. 34. Copyright 2013 Royal Society of Chemistry.

Table S2. Comparison of enzyme catalytic performance (pH 7.0, 20 ^{o}C). Reproduced with permission from ref. 34. Copyright 2013 Royal Society of Chemistry.

Sample	**CO_2 removal efficiency %**	**V_{max} [mM min^{-1}]**	**K_M [mM]**	***Sp.* Activity [U mg^{-1}]**	**Activity %**
Immobilized enzyme	**86**	**$5.4*10^{-3} \pm 1*10^{-4}$**	**0.43 ± 0.02**	**1.1 ± 0.1**	**58 ± 5**
Free enzyme	**90**	**$5.4*10^{-3} \pm 1*10^{-4}$**	**0.37 ± 0.02**	**1.9 ± 0.1**	**100**

A V_{max}=maximum rate; K_M=Michaelis-Menten constant (see ESI for experimental details and Table S2 for details on $CaCO_3$ yields.

Table S3. Microorganisms and responsible enzyme able to catalyse biocatalytic carboxylations. Reproduced with permission from ref. 1. Copyright 2010 Royal Society of Chemistry.

Microorganism	Responsible enzyme	Substrates
Xanthobacter	Epoxide carboxylase	Epoxides
Thauera aromatica	Phenylphosphate carboxylase	Phenol, catechol, o-cresol
Enterobacter cloacae	4-Hydroxybenzoate decarboxylase	Phenol
Chlamydophila pneumoniae	4-Hydroxybenzoate decarboxylase	Phenol
Clostridium hydroxybenzoicum	4-Hydroxy- and 3,4-dihydroxybenozate decarboxylase	Phenol, catechol
Sedimentibacter hydroxybenzoicus	4-Hydroxy- and 3,4-dihydroxybenozate decarboxylase	Phenol, catechol
Agrobacterium tumefaciens	2,6-Dihydroxybenzoate decarboxylases	γ-Resorcinol
Pandoraea sp.	2,6-Dihydroxybenzoate decarboxylases	Phenol, 1,2- and 1,3-dihydroxybenzene
Rhizobium radiobacter, Rhizobium sp.	γ-Resorcylic acid decarboxylase	γ-Resorcinol, catechol
Bacillus megaterium, Serratia sp.	Pyrrole-2-carboxylate decarboxylase	Pyrrole
Brewer's yeast	Pyruvate decarboxylase	Acetaldehyde

Figure S9. Proposed mechanism of carboxylation of pyrrole-2-carboxylate decarboxylase. (R-CO_2^- represents the organic acid required as 'cofactor'.). Reproduced with permission from ref. 1. Copyright 2010 Royal Society of Chemistry.

A possible mechanism of action of pyrrole-2-carboxylate decarboxylase has been proposed, which suggests that the organic acid acting as "cofactor" to deprotonate the NH-moiety, thus causing a nucleophilic attack of C atom at the electrophile CO_2. After tautomerisation, the intermediate regains aromaticity. However, in view of the low acidity of the NH-moiety of pyrrole (pKa 16.5), this mechanism needs further exploitation.

Figure S10. An illustration of the BR/F_0F_1ATP synthase vesicle solar conversion system coupled to the Rubisco CBB cycle and trapped within the foam channels. Sunlight is converted into ATP which is then used by the CBB enzymes to generate sugar from CO_2 and NADH. Reproduced with permission from ref. 48. Copyright 2010 American Chemistry Society.

Other references related to this *tutorial review*

Conversion of CO_2 to formate by formate dehydrogenase or CO_2 reductase

1. M. Yoshimoto, R. Yamasaki, M. Nakao, T. Yamashita, *Enzym. Microb. Technol.,* 2010, **46**, 588-593.
2. F. Kurayama, S. Suzuki, N. M. Bahadur, T. Furusawa, H. Ota, M. Sato, N. Suzuki, *J. Mater. Chem.*, 2012, **22**, 15405-15411.
3. R. Miyatani and Y. Amao, *Biotechnol. Lett.*, 2002, **24**, 1931-1934.

Conversion of CO_2 to CO by CO dehydrogenase

1. M. Can, F. A. Armstrong, S. W. Ragsdale, *Chem. Rev.*, 2014, **114**, 4149-4174.
2. A. Bachmeier, S. Hall, S. W. Ragsdale, F. A. Armstrong, *J. Am. Chem. Soc.*, 2014, **136**, 13518-13521.

Conversion of CO_2 to methanol by multiple dehydrogenases

- I. Ganesh., *Renew. Sustain. Energy Rev.*, 2014*,* 31, 221-257.
- J. F. Shi, L. Zhang and Z. Y. Jiang, *ACS Appl. Mater. Interfaces*, 2011, **3**, 881-889.
- J. F. Shi, X. L. Wang, Z. Y. Jiang, Y. P. Liang, Y. Y. Zhu and C. H. Zhang, *Bioresour. Technol.*, 2012, **118**, 359-366.

Other references related to this *tutorial review*

Conversion of CO_2 to biodegradable chemicals by other decarboxylases

1. C. A. G. M. Weijers, H. Jongejan, M. C. R. Franssen, A. de Groot and J. A. M. de Bont, *Appl. Microbiol. Biotechnol.*, 1995, **42**, 775-781
2. Z. He and J. Wiegel, *Eur. J. Biochem.*, 1995, **229**, 77-82.
3. Z. He and J. Wiegel, *J. Bacteriol.*, 1996, **178**, 3539-4353.
4. T. Matsui, T. Yoshida, T. Hayashi and T. Nagasawa, *Arch. Microbiol.*, 2006, **186**, 21-29.
5. J. Liu, X. Zhang, S. Zhou, P. Tao and J. Liu, *Curr. Microbiol.*, 2007, **54**, 102-107.
6. T. Yoshida, Y. Hayakawa, T. Matsui and T. Nagasawa, *Arch. Microbiol.*, 2004, **181**, 391-397.
7. Y. Ishii, Y. Narimatsu, Y. Iwasaki, N. Arai, K. Kino and K. Kirimura, *Biochem. Biophys. Res. Commun.*, 2004, **324**, 611-620.
8. M. Yoshida, N. Fukuhara and T. Oikawa, *J. Bacteriol.*, 2004, **186**, 6855-6863.
9. M. Wieser, T. Yoshida and T. Nagasawa, *J. Mol. Catal. B: Enzym.*, 2001, **11**, 179-184.
10. M. Wieser, N. Fujii, T. Yoshida and T. Nagasawa, *Eur. J. Biochem.*, 1998, **257**, 495-499.
11. M. Miyazaki, M. Shibue, K. Ogino, H. Nakamura and H. Maeda, *Chem. Commun.*, 2001, 1800-1801.
12. H. Omura, M. Wieser and T. Nagasawa, *Eur. J. Biochem.*, 1998, **253,** 480-484.

Table S4-1. Enzymes presented in the *tutorial review* and their classification numbers.

Enzyme	Classification number	Enzyme	Classification number
1,5-bisphosphate ribulose bisphosphate carboxylase (Rubisco)	EC 4.1.1.39	CO dehydrogenase (CODH)	EC 1.2.2.4
phosphoglyceraldehyde dehydrogenase	EC 1.2.1.12	acetyl-CoA synthase	EC 2.3.1.194
phosphoribulokinase	EC 2.7.1.19	acetyl-CoA carboxylase	EC 6.4.1.2
α-ketoglutarate synthase/2-oxoglutarate synthase	EC 1.2.7.3	propionyl-CoA carboxylase	EC 6.4.1.3
isocitrate dehydrogenase	EC 1.1.1.42	malonate semialdehyde reductase	EC 1.1.1.298
ATP citrate lyase	EC 2.3.3.8	3-hydroxypropionyl-CoA synthetase	EC 6.2.1.36
pyruvate synthase	EC 1.2.7.1	3-hydroxypropionyl-CoA dehydratase	EC 4.2.1.116
pyruvate kinase	EC 2.7.1.40	acryloyl-CoA reductase	EC 1.3.1.95
NADH-dependent formate dehydrogenase (FateDH)	EC 1.2.1.2	propionyl-CoA carboxylase	EC 6.4.1.3
methyltransferase	EC 2.1.1.103	4-hydroxybutyryl-CoA dehydratase	EC 4.2.1.120

Table S4-2. Enzymes presented in the *tutorial review* and their classification numbers.

Enzyme	Classification number	Enzyme	Classification number
carbonic anhydrase (CA)	EC 4.2.1.1	pyruvate decarboxylase	EC 4.1.1.1
CO_2 reductase	Unavailable	methanol dehydrogenase (MDH)	EC 1.1.2.7
remodeled nitrogenase	Unavailable	formaldehyde dehydrogenase (FaldDH)	EC 1.2.1.1
formate dehydrogenase (FdhF1/2)	EC 1.2.1.2	alcohol dehydrogenase (ADH)	EC 1.1.1.1
iron-iron hydrogenase (HydA2)	EC 1.12.1.4	glutamate dehydrogenase (GDH)	EC 1.4.1.2
[NiFe] CO dehydrogenases ([NiFe] CODH)	EC 1.2.7.4	phosphate dehydrogenase (PTDH)	EC 1.1.1.17
nitrogenase	EC 1.18.6.1	acetolactate synthase (AlsS)	EC 2.2.1.6
4-hydroxybenzoate decarboxylases	EC 4.1.1.63	acetohydroxy acid isomeroreductase (IlvC)	EC 1.1.1.86
3,4-dihydroxy-benzoate decarboxylase	EC 4.1.1.43	dihydroxy-acid dehydratase (IlvD)	EC 4.2.1.9
γ-resorcylic acid decarboxylases (or 2,6-dihydroxybenzoate decarboxylases)	Unavailable	2-ketoacid decarboxylase (Kdc)	EC 1.2.4.1
pyrrole-2-carboxylate decarboxylase	EC 4.1.1.93	L-Lactic acid by lactate dehydrogenase (LDH)	EC 1.1.1.27