Electronic Supplementary Material

Non-isothermal kinetics and characteristics of calcium carbide nitridation reaction with calcium-based additives

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The purity of CaC_2 in calcium carbide (CC) sample is calculated backwards from the amount of acetylene (C_2H_2) produced by its reaction with water. Using the drainage method, the volume of the brine bottle was measured to be 604 mL. The 0.1g of CC was placed in the brine bottle at atmospheric pressure, quickly sealed with a rubber stopper, and then injected with 5mL of H_2O by syringe to make it fully react and produce C_2H_2. The C_2H_2 concentration and the purity of CC are calculated as follows:

$$C_2H_2(vol.\%) = \frac{V_{C_2H_2}}{604 + V_{C_2H_2}} \times 100\% \tag{S1}$$

$$CaC_2(\%) = \frac{V_{C_2H_2}/(24.5 \times 1000) \times 64.1}{0.1} \times 100\% \tag{S2}$$

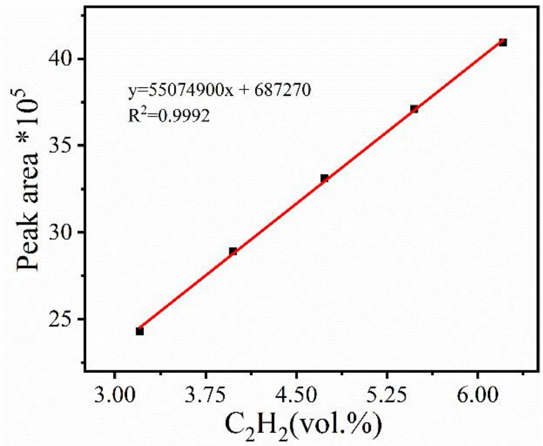

Fig. S1 The linear fitness curve of peak areas of C_2H_2 versus the concentration of C_2H_2.

The analysis and quantification of C_2H_2 was carried out on a gas chromatograph

(GC) using the external standard method. The C_2H_2 mixtures of different volume fractions were made using syringes, and their experimental data were fitted to obtain the GC standard curve of C_2H_2 as shown in Fig. S1. The concentration of C_2H_2 in the gas product was calibrated using the standard curve Eq. S3. and then the purity of CaC_2 was found to be 80.75% according to Eq. S2. (which satisfied the process requirements for calcium carbide).

$$y = 55074900x + 687270 \quad R^2 = 0.9992 \tag{S3}$$

where “y” is the peak area of acetylene in the GC chromatogram, “x” is the volume fraction of acetylene standard gas.

Table S1 Chemical compositions of raw Calcium carbide powder determined by XRF expressed in terms of weight percent of oxides. (%, w/w)

Composition	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	TeO_2	MgO	Others*
Mass fraction/%	92.93	3.55	1.97	0.55	0.41	0.14	0.12	0.33

Others*: SrO, TiO_2, P_2O_5, Au, Na_2O, Pt, MoO_3, Re, Cr_2O_3, CuO, Hg, K_2O.

Table S2 Details of model-free methods for non-isothermal nitridation reaction of CC.

a	FWO		KAS		Starink		FR	
	E_a/(kJ/mol)	R^2	E_a/(kJ/mol)	R^2	E_a/(kJ/mol)	R^2	E_a/(kJ/mol)	R^2
0.1	176.73	0.9882	162.01	0.9841	163.05	0.9845	338.86	0.8861
0.15	263.81	0.9276	252.98	0.9151	253.96	0.9151	675.28	0.8856
0.2	488.13	0.9374	487.50	0.9311	489.19	0.9317	1218.44	0.9866
0.25	615.63	0.9486	622.24	0.9445	622.93	0.9449	766.82	0.8989
0.3	586.59	0.9039	592.73	0.8983	592.37	0.8969	542.22	0.7791
0.35	586.59	0.9039	592.51	0.8976	592.30	0.8968	460.32	0.7803
0.4	618.13	0.9350	623.97	0.9293	625.36	0.9304	441.04	0.8179
0.45	568.57	0.9213	573.07	0.9150	573.26	0.9152	377.13	0.8054
0.5	572.15	0.9223	575.74	0.9159	576.97	0.9164	365.54	0.8250
0.55	525.28	0.9077	527.73	0.9004	527.71	0.9001	327.28	0.8163
0.6	510.87	0.9378	512.80	0.9317	512.53	0.9323	318.22	0.8653
0.65	492.40	0.9178	493.34	0.9107	493.09	0.9104	312.02	0.8685
0.7	510.87	0.9378	511.35	0.9315	512.42	0.9323	331.50	0.8918
0.75	479.28	0.9449	479.04	0.9393	479.18	0.9397	326.64	0.9256
0.8	462.39	0.9484	461.63	0.9427	461.39	0.9432	335.12	0.9206
Mean	497.16	0.9322	497.91	0.9258	498.38	0.9260	475.76	0.8635

Table S3 Details of model-fitting method for CC nitridation reaction.

Model	R^2	E_a/(kJ/mol)	A/s^{-1}
D1	0.9524	814.23	3.87E+25
D2	0.9100	268.91	5.55E+06
D3	0.9820	1111.52	2.18E+35
D4	0.9732	990.84	1.01E+31
F0	0.9494	394.57	1.33E+11
F1	0.9867	646.62	1.95E+20
F2	0.9580	1080.63	7.52E+35
F3	0.9174	1637.09	1.10E+56
R2	0.9752	499.37	4.49E+14
R3	0.9812	543.21	1.17E+16
A2	0.9857	310.76	2.63E+08
A3	0.9845	198.81	2.38E+04
A4	0.9832	142.83	2.03E+02

Table S4 Details of model-free methods for non-isothermal nitridation reaction of different calcium carbide samples.

Methods	FWO		KAS		Starink		FR	
	E_a/(kJ/mol)	R^2	E_a/(kJ/mol)	R^2	E_a/(kJ/mol)	R^2	E_a/(kJ/mol)	R^2
a				CCCl				
0.1	196.40	0.9215	187.91	0.9065	188.18	0.9068	162.41	0.8726
0.15	185.91	0.9428	175.99	0.9301	176.58	0.9306	184.09	0.9429
0.2	199.51	0.9361	189.62	0.9224	190.38	0.9232	219.28	0.9307
0.25	208.35	0.9327	198.61	0.9191	199.27	0.9196	220.09	0.9364
0.3	214.80	0.9384	205.04	0.9258	205.74	0.9266	216.24	0.9384
0.35	219.91	0.9308	209.65	0.9171	210.81	0.9178	215.40	0.9113
0.4	213.09	0.9249	202.91	0.9108	203.38	0.9102	205.18	0.9013
0.45	214.80	0.9384	204.61	0.9253	204.94	0.9260	205.86	0.9262
0.5	214.80	0.9384	204.21	0.9248	204.70	0.9258	203.57	0.9378
0.55	214.80	0.9384	204.07	0.9251	204.48	0.9257	203.63	0.9398
0.6	221.69	0.9451	210.52	0.9329	211.51	0.9339	212.42	0.9417
0.65	218.22	0.9414	207.01	0.9285	207.65	0.9291	210.31	0.9363
0.7	221.58	0.9442	210.11	0.9317	210.99	0.9326	213.99	0.9274
0.75	218.68	0.9435	207.06	0.9305	207.74	0.9314	208.43	0.9057
0.8	222.61	0.9309	210.54	0.9162	211.67	0.9166	200.34	0.8406
Mean	212.34	0.9365	201.86	0.9231	202.53	0.9237	205.42	0.9193
a				CCF				
0.1	362.70	0.7914	361.10	0.7725	361.14	0.7733	351.11	0.8610

0.15	351.55	0.9004	348.75	0.8891	348.92	0.8900	279.63	0.9496
0.2	324.67	0.9456	319.60	0.9383	320.34	0.9390	230.47	0.9915
0.25	294.71	0.9702	287.87	0.9659	288.59	0.9660	221.60	0.9998
0.3	279.97	0.9833	272.27	0.9807	272.85	0.9807	233.51	0.9990
0.35	270.87	0.9868	262.67	0.9850	263.09	0.9848	253.41	0.9978
0.4	280.29	0.9910	271.59	0.9897	272.79	0.9896	281.01	0.9949
0.45	280.29	0.9910	271.66	0.9897	272.62	0.9896	292.47	0.9924
0.5	280.29	0.9910	271.73	0.9898	272.47	0.9896	295.82	0.9897
0.55	280.29	0.9910	272.08	0.9897	272.32	0.9896	298.09	0.9899
0.6	290.65	0.9881	282.12	0.9866	283.05	0.9863	308.71	0.9830
0.65	292.51	0.9944	284.21	0.9934	284.85	0.9936	308.79	0.9832
0.7	301.40	0.9922	293.11	0.9909	294.07	0.9911	315.13	0.9817
0.75	296.72	0.9917	288.67	0.9903	289.00	0.9904	303.93	0.9636
0.8	304.53	0.9853	296.14	0.9832	297.06	0.9831	301.53	0.9380
Mean	299.43	0.9662	292.24	0.9623	292.88	0.9624	285.01	0.9743
a				CCM				
0.1	211.26	0.9744	202.94	0.9700	203.63	0.9700	223.01	0.9965
0.15	213.60	0.9973	205.12	0.9968	205.48	0.9968	210.22	0.9918
0.2	213.85	0.9984	204.75	0.9982	205.27	0.9981	204.12	0.9988
0.25	212.78	0.9994	203.12	0.9993	203.75	0.9993	201.67	1.0000
0.3	212.78	0.9994	202.78	0.9994	203.43	0.9994	206.89	0.9988
0.35	217.87	0.9999	207.55	0.9999	208.45	0.9999	214.96	0.9997
0.4	216.47	0.9996	206.09	0.9995	206.69	0.9994	212.83	0.9990
0.45	216.47	0.9996	205.95	0.9995	206.45	0.9995	210.88	0.9974
0.5	216.47	0.9996	205.76	0.9995	206.23	0.9995	206.23	0.9959
0.55	221.39	0.9984	210.18	0.9982	211.19	0.9982	207.58	0.9903
0.6	221.39	0.9984	209.92	0.9981	210.99	0.9982	208.91	0.9869
0.65	215.97	0.9972	204.54	0.9966	205.10	0.9967	209.11	0.9696
0.7	218.33	0.9908	206.78	0.9891	207.42	0.9889	216.86	0.9353
0.75	219.26	0.9888	207.57	0.9863	208.22	0.9865	216.66	0.9144
0.8	217.42	0.9805	205.65	0.9762	206.11	0.9765	214.33	0.8735
Mean	216.36	0.9948	205.91	0.9938	206.56	0.9938	210.95	0.9765

Table S5 Details of model-fitting method for different calcium carbide samples nitridation reaction.

Model	CCCl			CCF			CCM		
	R^2	E_a/ (kJ/mol)	A/s^{-1}	R^2	E_a/ (kJ/mol)	A/s^{-1}	R^2	E_a/ (kJ/mol)	A/s^{-1}
D1	0.9815	197.54	7.75E+04	0.9914	327.67	3.93E+09	0.9765	228.76	1.05E+06
D2	0.9297	72.47	8.14E-01	0.9717	137.55	3.09E+02	0.9309	89.78	4.26E+00
D3	0.9969	232.05	5.27E+05	0.9946	356.26	1.05E+10	0.9919	253.91	2.31E+06
D4	0.9940	217.93	9.89E+04	0.9948	345.24	3.09E+09	0.9877	244.45	7.54E+05
F0	0.9755	88.97	3.45E+00	0.9897	153.73	1.01E+03	0.9703	104.57	1.39E+01
F1	0.9888	118.55	1.35E+02	0.9893	177.15	1.47E+04	0.9936	124.80	1.67E+02
F2	0.8561	172.60	8.78E+04	0.9325	212.96	8.31E+05	0.9718	153.39	5.27E+03
F3	0.7279	240.32	5.06E+08	0.8412	257.38	2.37E+08	0.9159	188.57	6.97E+05
R2	0.9939	101.08	7.86E+00	0.9941	163.99	1.64E+03	0.9861	113.68	2.14E+01
R3	0.9962	106.23	9.91E+00	0.9939	168.02	1.73E+03	0.9897	117.15	2.18E+01
A2	0.9858	49.48	1.03E-01	0.9869	78.47	1.36E+00	0.9902	52.59	1.19E-01
A3	0.9804	26.45	6.76E-03	0.9834	45.57	4.68E-02	0.9835	28.52	7.68E-03
A4	0.9692	14.94	1.34E-03	0.9780	29.13	7.29E-03	0.9691	16.48	1.53E-03