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APPENDIX

A. Specification of Alumina Support (Al₂O₃) Type NKH-3 from Sumitomo

Aluminium Smelting Co., LTD.

Table A1 Specification of Alumina Support (NKH-3).

Chemical composition (weight percent)

Al ₂ O ₃	60-70	%
SiO ₂	30-35	%
Fe ₂ O ₃	0.3-0.5	%
TiO ₂	0.5-0.7	%
CaO	0.1-0.2	%
MgO	0.2-0.4	%
Na ₂ O	0.3-0.4	%
K ₂ O	0.2-0.3	%
ZrO ₂ + HfO ₂	0.03-0.04	%

Physical Properties

Bulk density (g/ml)	1.3-1.5
Apparent specific gravity	3.1-3.3
Packing density (lb/ft ³)	20-25
Pore volume (ml/g)	1.0-1.3
Surface area (m ² /g)	340-350

B. Calculation of Designed Metal Loading for Catalyst Preparation.

The sample of calculation shown below is for (0.3 wt%)Pt / Al₂O₃. The hydrochloric acid is also added to the impregnating by 5 wt% of the support. The alumina support weight used for all preparation is 2 grams.

If the weight of alumina support used is x gram. So, each 100 grams of the catalyst would compose of

Platinum	0.3	gram.
Hydrochloric acid	(0.5)*(x)	gram.
Alumina support	x	gram.
Then,	$0.30 + (0.05) * x + x$	= 100 gram.
	x	= 94.10 gram.

The platinum compound used for supplying the platinum metal component is chloroplatinic acid (H₂ PtCl₆* 6H₂O), its molecular weight is 517.92, and the platinum content in the compound is 37.67 %.

Concentration of hydrochloric acid solution is 37 % volume by volume, its density is 1.19 kilogram per liter.

The calculation procedure of the amount of each ingredients for the required composition of the (0.3 wt%)Pt / Al₂O₃ catalyst shows belows

For 2 grams of alumina support used:

$$\begin{aligned} 1. \text{ Platinum required} &= (0.03/94.10)(2) && \text{gram.} \\ &= 6.376 \times 10^{-3} && \text{gram.} \end{aligned}$$

Chloroplatnic acid require

$$\begin{aligned} &= (100/37.67)(6.376 \times 10^{-3}) * 25 \text{ ml.} \\ &= 0.419 && \text{ml.} \end{aligned}$$

2. Hydrochloric acid solution required

$$\begin{aligned} &= 2 * 0.5 && \text{gram.} \\ &= 0.1 && \text{gram.} \end{aligned}$$

The amount of HCl by volume

$$\begin{aligned} &= 0.11 / (1.19 * 0.37) && \text{ml.} \\ &= 0.23 && \text{ml.} \end{aligned}$$

As the pore volume of the alumina support is 1 ml/g., the total volume of impregnation solution that must be used is 2 ml. By the requirement of the incipient impregnate method, the de-ionized water is added to the above solution until the volume equals to the alumina pore volume. This solution is used as the impregnation solution.

C. Calculation of Flow H₂ and C₃H₈ when varied H/HC Mole Ratio.

At ratio of H₂ / HC = 1

From C₃H₈ 20 % balance with N₂

$$\text{C}_3\text{H}_8 / \text{N}_2 = 20 / 80 = 1 / 4$$

$$4\text{C}_3\text{H}_8 = \text{N}_2$$

Feed input is 30 cc/min.

$$\text{Thus, } \text{C}_3\text{H}_8 + \text{N}_2 + \text{H}_2 = 30 \text{ ml/min.}$$

$$\text{C}_3\text{H}_8 + 4\text{C}_3\text{H}_8 + \text{C}_3\text{H}_8 = 30 \text{ ml/min.}$$

$$\text{C}_3\text{H}_8 = 30 / 60 \text{ ml/min.}$$

$$= 5 \text{ ml/min.}$$

$$\text{Thus; flow rate of hydrogen} = 5 \text{ ml/min.}$$

$$\text{flow rate of C}_3\text{H}_8 = 25 \text{ ml/min.}$$

Table C1 Data of flow rate at differ H/HC mole ratio.

H ₂ /HC	Ar (ml/min)	C ₃ H ₈ (ml/min)	H ₂ (ml/min)
0	30	30	0
1	30	25	5
3	30	18.75	11.25

D. Data of Experiment.

Table D-1 Data of figure 5.1.

Pt/Al₂O₃

PURGE Ar 2 hr. before cooldown		NO purge Ar before cooldown	
TEMP.(c)	AREA CO2	TEMP.(c)	AREA CO2
50	0	50	10
112	61	102	52
140	28	97	12
151	0	118	75
171	28	157	57
201	63	183	83
227	93	206	97
254	133	230	142
277	187	255	117
301	293	280	169
327	503	305	283
353	907	330	487
377	1512	358	904
402	2465	380	1424
426	3626	405	2261
454	4589	430	3237
478	4634	457	4328
501	6174	480	4690
526	6308	505	6072
556	738	531	6602
577	68	557	268
602	44	580	197
626	28	605	176
657	0	630	168
678	0	656	169
700	0	680	163
		700	168

Table D-2 Data of figure 5.2.

Pt/Al₂O₃

Heating Rate = 5 C/min.

TEMP.(C)	RXN.TEMP.(C)		
	600	650	550
50	10	0	0
97	52	49	27
102	12	13	0
118	75	27	0
157	57	663	29
183	83	67	21
206	97	92	35
230	142	138	56
255	117	215	81
280	169	307	128
305	283	513	221
330	487	854	397
358	904	1706	721
380	1424	2421	926
405	2261	4250	1272
430	2937	6947	1467
457	3328	9160	1767
480	3890	8041	1718
505	5272	9479	761
531	2802	11941	159
557	268	12201	78
580	197	1893	46
605	176	66	31
630	168	43	20
656	169	27	19
680	163	31	19
700	168	32	28

Table D-3 Data of figure 5.3.

Pt/Al₂O₃

Heating Rate = 5 C/min.

TEMP.(c)	H ₂ /HC (mole ratio)		
	0	1	3
50	0	0	0
111	28	36	26
140	61	89	73
150	0	15	0
171	28	23	0
201	63	46	41
228	93	67	67
253	133	106	107
277	187	135	131
302	293	205	202
326	503	346	359
353	907	664	636
377	1512	1121	1131
401	2465	1965	2061
426	3626	3162	3428
454	4589	4197	4247
477	4634	3904	4223
501	6174	4952	5449
529	6308	3375	4031
556	738	164	192
577	68	46	48
601	44	34	34
626	28	29	27
656	0	26	25
677	0	28	23
700	0	25	24

Table D- 4 Data of figure 5.4.

RXN.TEMP. = 550C

Pt/Al₂O₃

FIXED TEMP. = 400C

T (min)	T (sec)	CO ₂	RATE	AREA	SUM	C ^{0.5}
0	0	3722	1861	459450	1649100	1284.173
5	300	2404	1202	261750	1189650	1090.711
10	600	1086	543	137625	927900	963.2757
15	900	749	374.5	101250	790275	888.9741
20	1200	601	300.5	81300	689025	830.0753
25	1500	483	241.5	65400	607725	779.5672
30	1800	389	194.5	52050	542325	736.4272
35	2100	305	152.5	44400	490275	700.1964
40	2400	287	143.5	40875	445875	667.7387
45	2700	258	129	37575	405000	636.3961
50	3000	243	121.5	34875	367425	606.1559
55	3300	222	111	32400	332550	576.6715
60	3600	210	105	29250	300150	547.8595
65	3900	180	90	25650	270900	520.4805
70	4200	162	81	23700	245250	495.2272
75	4500	154	77	23175	221550	470.691
80	4800	155	77.5	21600	198375	445.3931
85	5100	133	66.5	19500	176775	420.4462
90	5400	127	63.5	18900	157275	396.5791
95	5700	125	62.5	18000	138375	371.9879
100	6000	115	57.5	17475	120375	346.951
105	6300	118	59	16800	102900	320.7803
110	6600	106	53	15600	86100	293.428
115	6900	102	51	15600	70500	265.5184
120	7200	106	53	13500	54900	234.3075
150	9000	74	37	9525	41400	203.4699
180	10800	53	26.5	7275	31875	178.5357
210	12600	44	22	5775	24600	156.8439
240	14400	33	16.5	4650	18825	137.2042
270	16200	29	14.5	4200	14175	119.0588
300	18000	27	13.5	3600	9975	99.87492
330	19800	21	10.5	2775	6375	79.8436
360	21600	16	8	2400	3600	60
390	23400	16	8	1200	1200	34.64102
420	25200	0	0	0	0	0
450	27000	0	0	0	0	

Table D-5 Data of figure D-1.

RXN.TEMP. = 550C

Pt/Al2O3

FIXED TEMP. = 360C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{-0.5}
0	0	1460	730	182325	811200	900.6664
5	300	971	485.5	108975	628875	793.0164
10	600	482	241	65700	519900	721.0409
15	900	394	197	48675	454200	673.9436
20	1200	255	127.5	32925	405525	636.8084
25	1500	184	92	27825	372600	610.4097
30	1800	187	93.5	31125	344775	587.1754
35	2100	228	114	30975	313650	560.0446
40	2400	185	92.5	26100	282675	531.6719
45	2700	163	81.5	23475	256575	506.5323
50	3000	150	75	21675	233100	482.8043
55	3300	139	69.5	19500	211425	459.8097
60	3600	121	60.5	17550	191925	438.0925
65	3900	113	56.5	16650	174375	417.5823
70	4200	109	54.5	15975	157725	397.1461
75	4500	104	52	15600	141750	376.497
80	4800	104	52	14625	126150	355.176
85	5100	91	45.5	14100	111525	333.9536
90	5400	97	48.5	12600	97425	312.1298
120	7200	71	35.5	10500	84825	291.2473
150	9000	69	34.5	9225	74325	272.6261
180	10800	54	27	7050	65100	255.147
210	12600	40	20	6975	58050	240.9357
240	14400	53	26.5	7425	51075	225.9978
270	16200	46	23	5775	43650	208.9258
300	18000	31	15.5	4725	37875	194.615
330	19800	32	16	4875	33150	182.0714
360	21600	33	16.5	4500	28275	168.1517
450	27000	27	13.5	4200	23775	154.1914
480	28800	29	14.5	4050	19575	139.9107
540	32400	25	12.5	3600	15525	124.5994
570	34200	23	11.5	3450	11925	109.2016
600	36000	23	11.5	3150	8475	92.05976
630	37800	19	9.5	3000	5325	72.9726
660	39600	21	10.5	2325	2325	48.21825
720	43200	10	5			

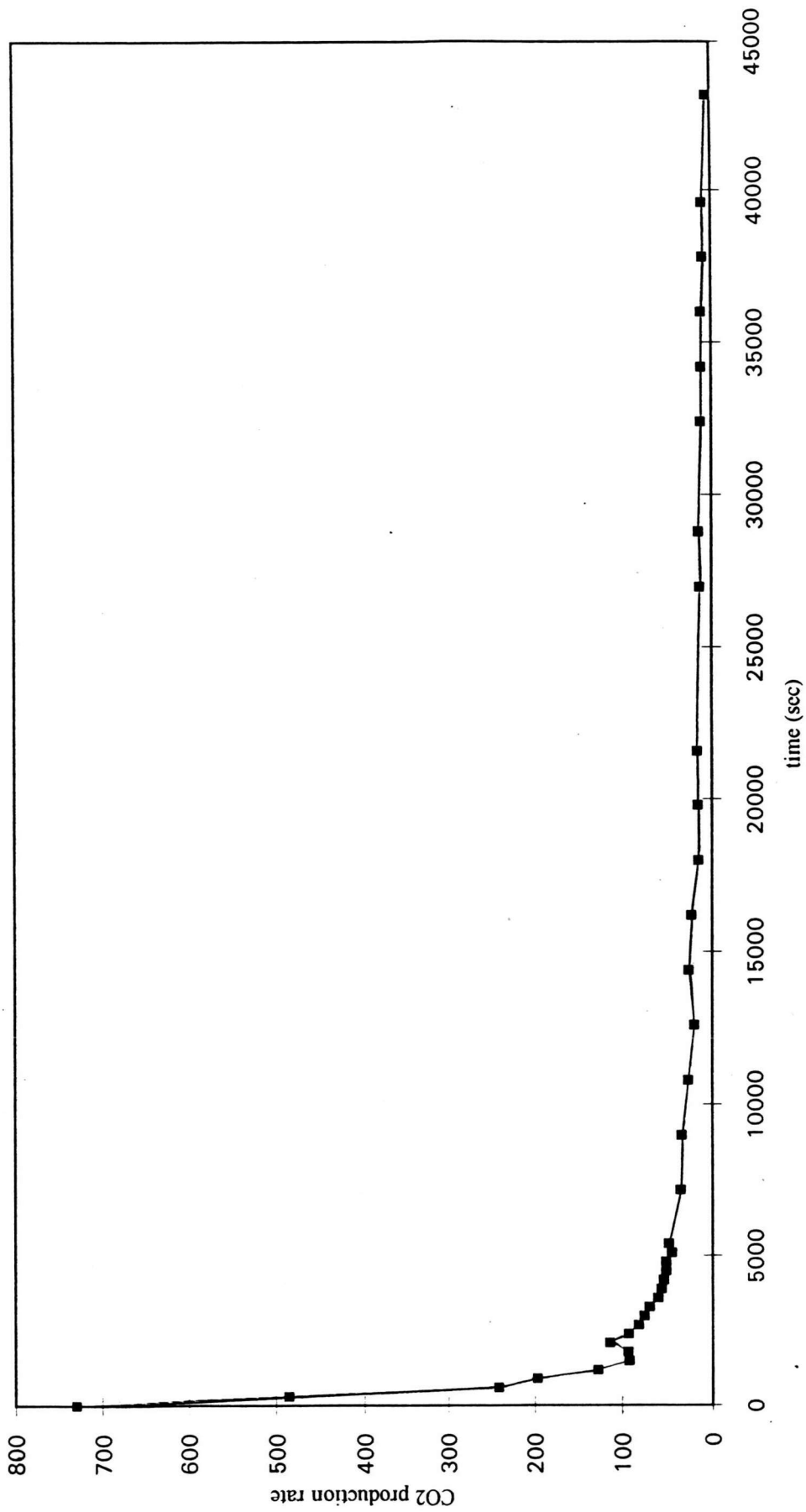


Figure D-1 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (360 °C) for dehydrogenation reaction temperature (550 °C).

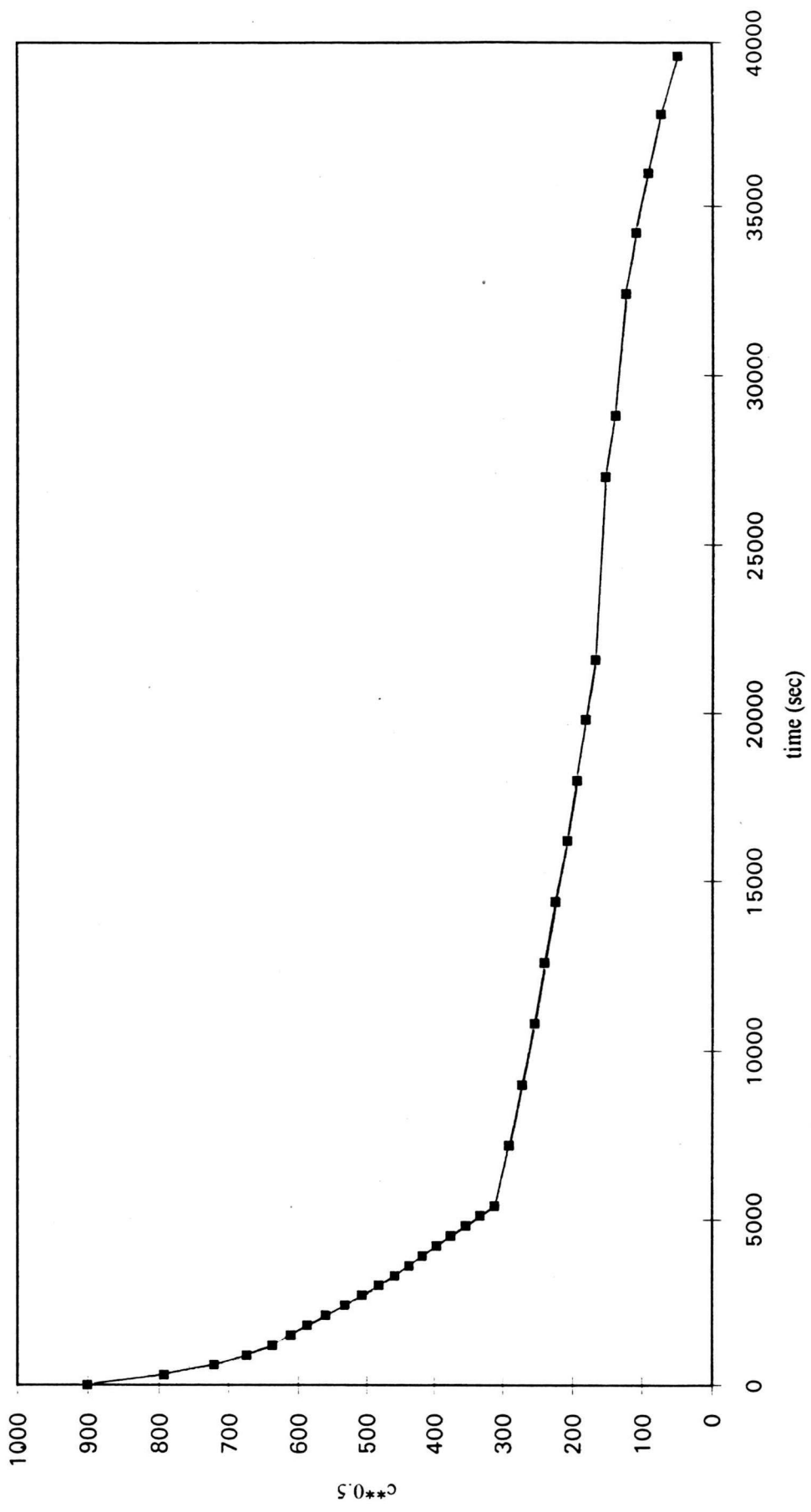


Figure D-2 Plot between $C^{0.5}$ versus time of the results shown in figure D-1.

Table D-6 Data of figure D-3.

RXN.TEMP. = 550C

Pt/Al₂O₃

FIXED TEMP. = 450C

TIME(min)	TIME (sec)	CO ₂	RATE	AREA	SUM	C ^{0.5}
0	0	12100	6050	1438275	2878050	1696.482
5	300	7077	3538.5	669750	1439775	1199.906
10	600	1853	926.5	222900	770025	877.5107
15	900	1119	559.5	143325	547125	739.679
20	1200	792	396	102000	403800	635.4526
25	1500	568	284	74025	301800	549.3633
30	1800	419	209.5	55125	227775	477.2578
35	2100	316	158	39675	172650	415.5117
40	2400	213	106.5	27675	132975	364.6574
45	2700	156	78	20550	105300	324.4996
50	3000	118	59	15600	84750	291.1185
55	3300	90	45	11475	69150	262.9639
60	3600	63	31.5	8100	57675	240.1562
65	3900	45	22.5	6000	49575	222.6544
70	4200	35	17.5	4875	43575	208.7463
75	4500	30	15	4200	38700	196.7232
80	4800	26	13	3525	34500	185.7418
85	5100	21	10.5	3000	30975	175.9972
90	5400	19	9.5	2775	27975	167.2573
95	5700	18	9	3000	25200	158.7451
100	6000	22	11	2700	22200	148.9966
105	6300	14	7	1950	19500	139.6424
110	6600	12	6	1950	17550	132.4764
115	6900	14	7	1875	15600	124.9
120	7200	11	5.5	1950	13725	117.1537
125	7500	15	7.5	2625	11775	108.5127
130	7800	20	10	2175	9150	95.65563
135	8100	9	4.5	1500	6975	83.51647
140	8400	11	5.5	1275	5475	73.99324
145	8700	6	3	1425	4200	64.80741
150	9000	13	6.5	1875	2775	52.67827
155	9300	12	6	900	900	30
160	9600	0	0			

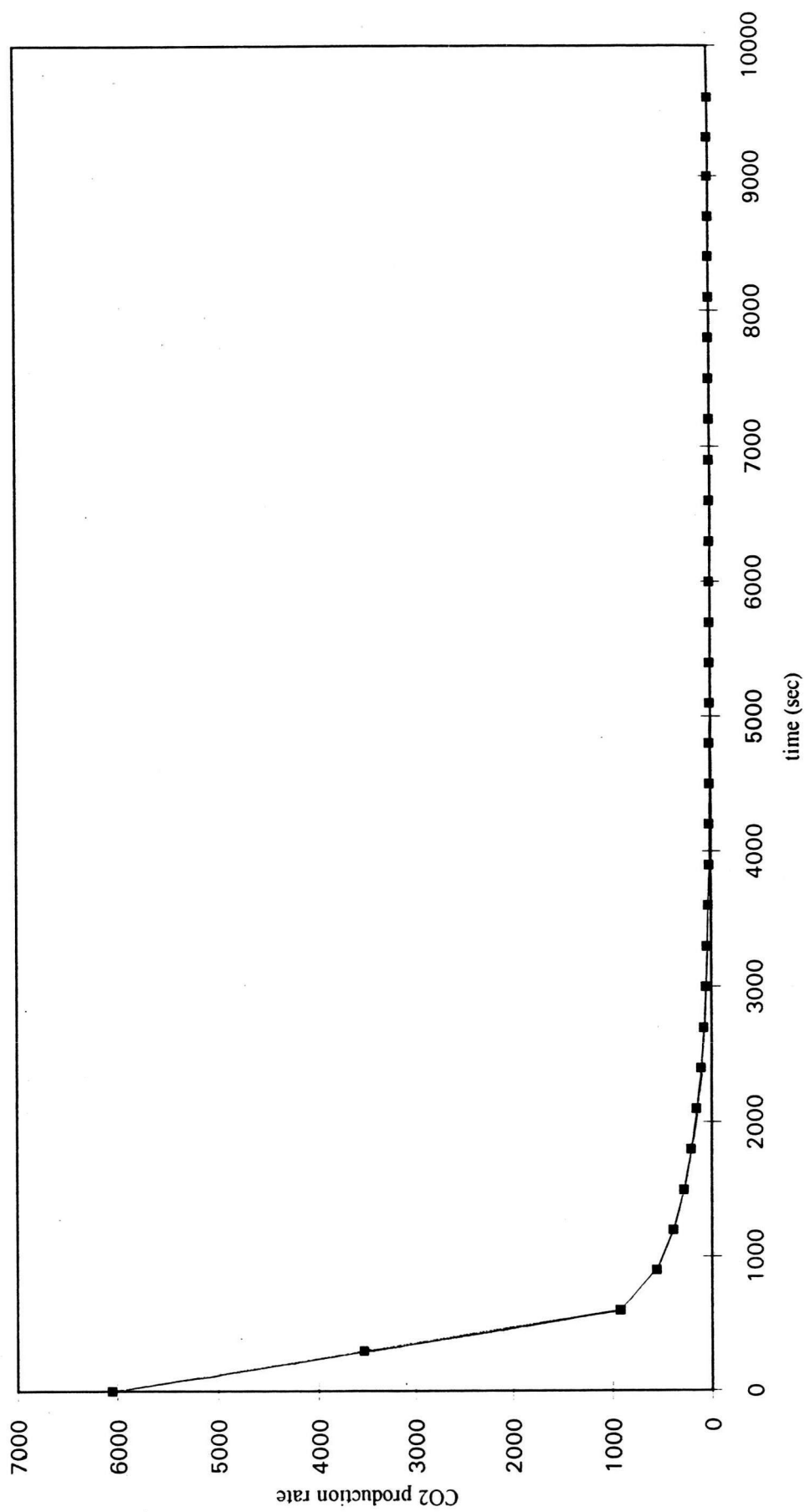


Figure D-3 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (450 °C) for dehydrogenation reaction temperature (550 °C).

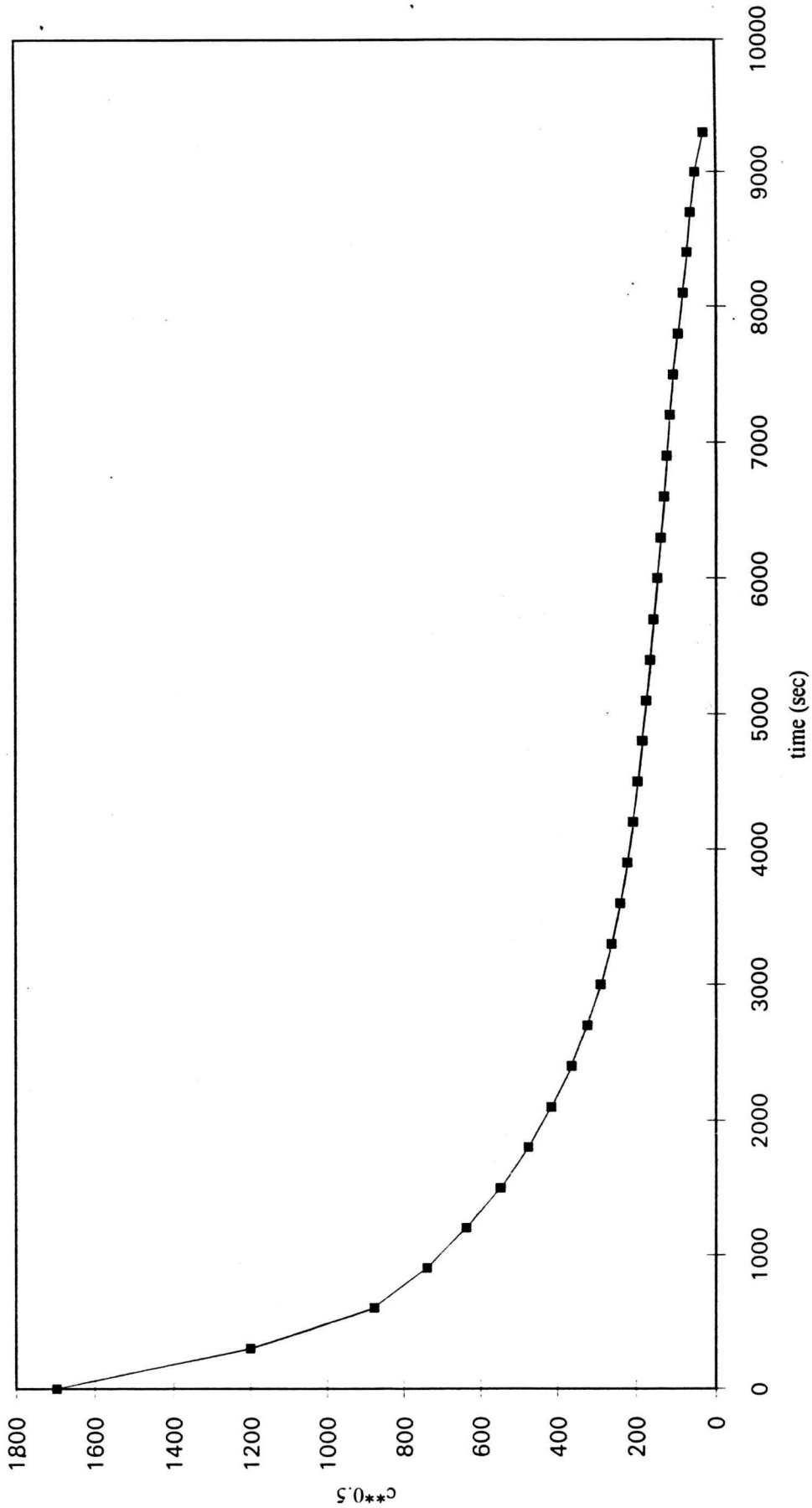


Figure D-4 Plot between $C^{0.5}$ versus time of the results shown in figure D-3.

Table D-7 Data of figure D-5.

RXN.TEMP. = 550C

Pt/Al₂O₃

FIXED TEMP. = 480C

TIME (min)	TIME (sec)	CO ₂	RATE	AREA	SUM	C ^{0.5}
0	0	23900	11950	2736600	4102350	2025.426
5	300	12588	6294	1071450	1365750	1168.653
10	600	1698	849	173550	294300	542.4942
15	900	616	308	61500	120750	347.491
20	1200	204	102	21225	59250	243.4132
25	1500	79	39.5	9300	38025	195
30	1800	45	22.5	5850	28725	169.4845
35	2100	33	16.5	4425	22875	151.2448
40	2400	26	13	3150	18450	135.8308
45	2700	16	8	2475	15300	123.6932
50	3000	17	8.5	2700	12825	113.2475
55	3300	19	9.5	2175	10125	100.6231
60	3600	10	5	1500	7950	89.16277
65	3900	10	5	1800	6450	80.31189
70	4200	14	7	2250	4650	68.19091
75	4500	16	8	1200	2400	48.98979
80	4800	0	0	600	1200	34.64102
85	5100	8	4	600	600	24.4949
90	5400	0	0	0	0	
95	5700	0	0	0	0	

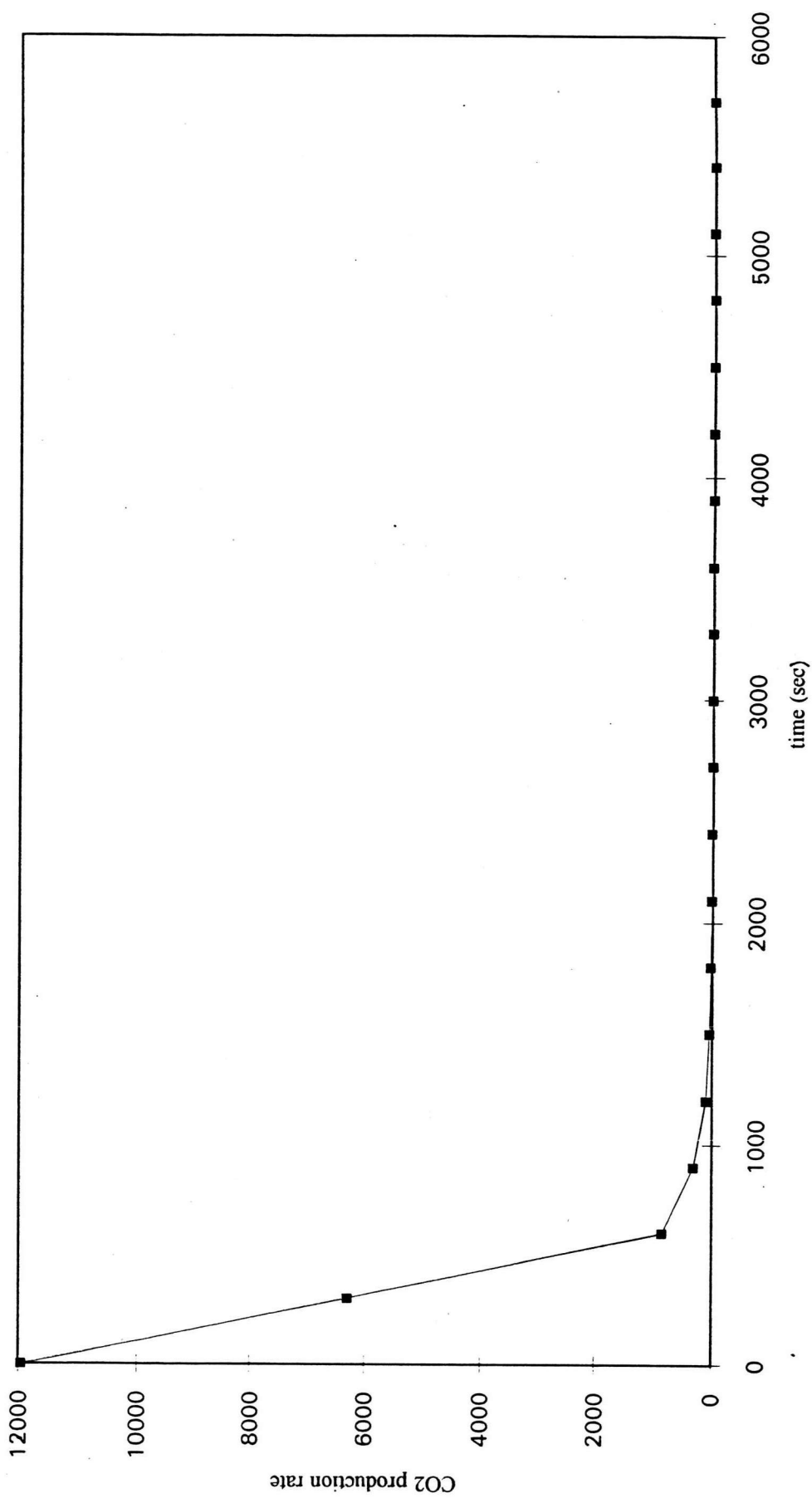


Figure D-5 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (480 °C) for dehydrogenation reaction temperature (550 °C).

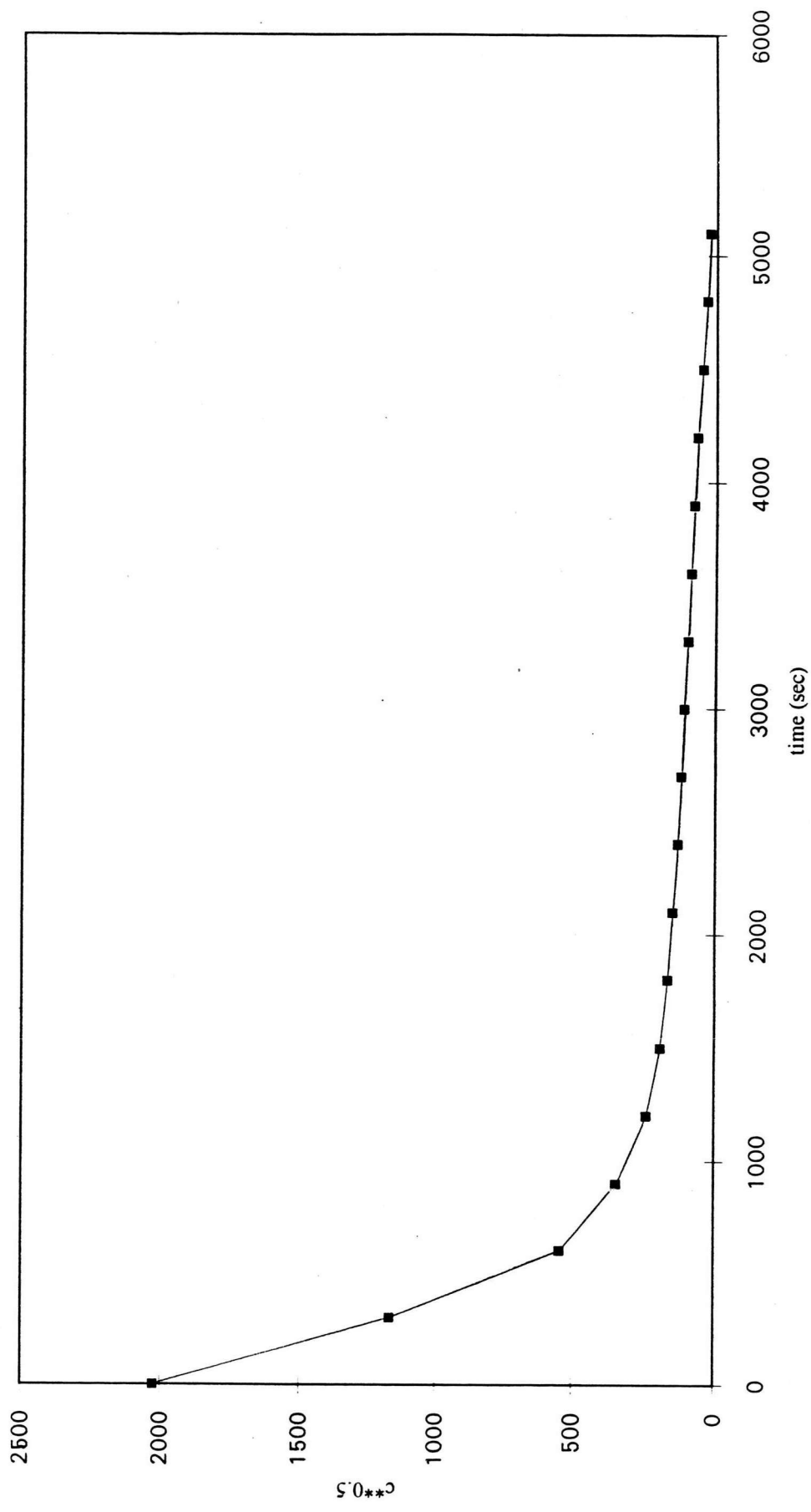


Figure D-6 Plot between $C^{0.5}$ versus time of the results shown in figure D-5.

Table D-8 Data of figure D-7.

RXN.TEMP. = 550C

Pt/Al2O3

FIXED TEMP. = 520C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	27212	13606	3074700	4182450	2045.104
5	300	13784	6892	1060500	1107750	1052.497
10	600	356	178	30900	47250	217.3707
15	900	56	28	6150	16350	127.8671
20	1200	26	13	3375	10200	100.995
25	1500	19	9.5	2550	6825	82.61356
30	1800	15	7.5	1725	4275	65.38348
35	2100	8	4	1575	2550	50.49752
40	2400	13	6.5	975	975	31.22499
45	2700	0				

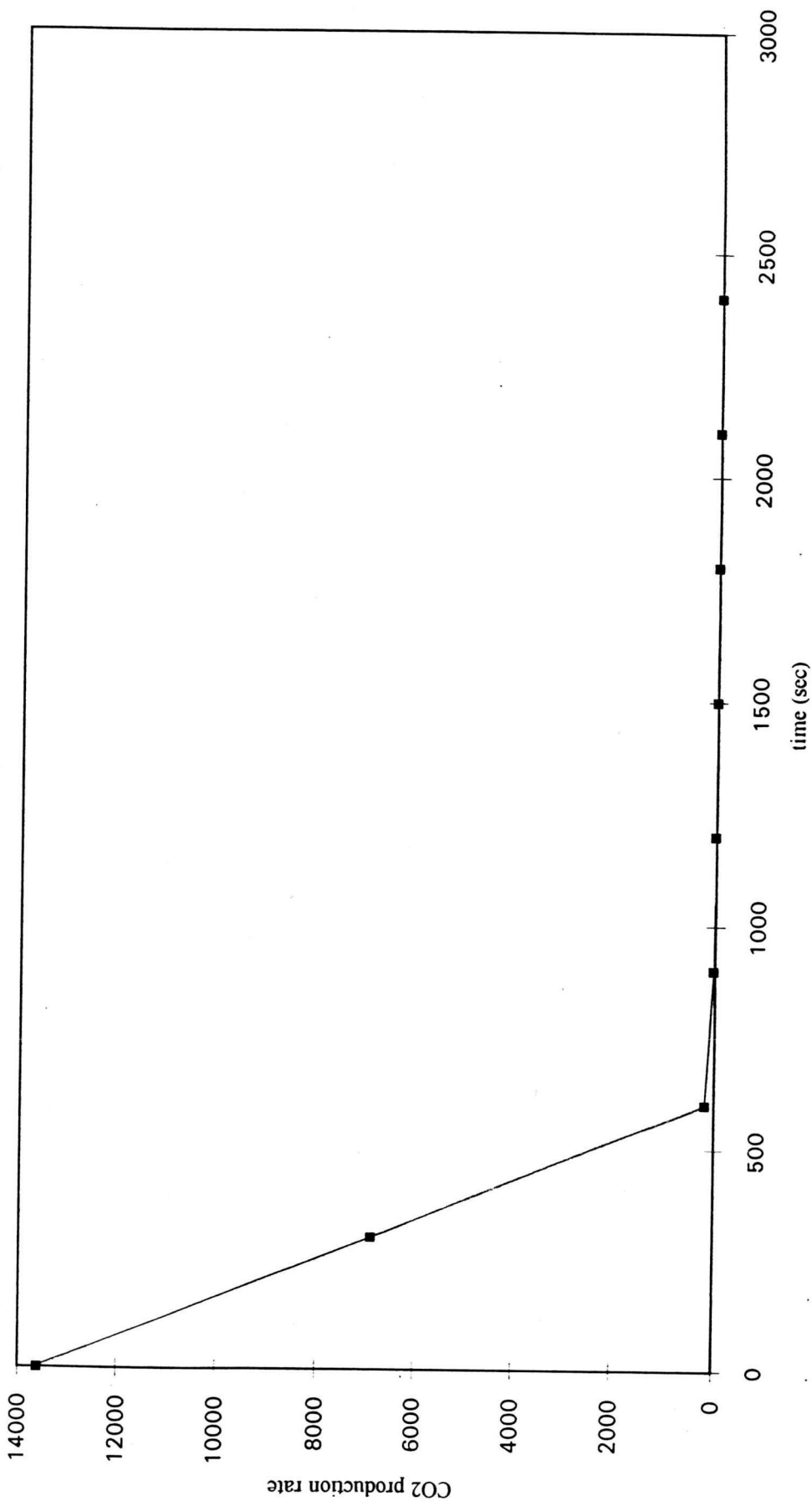


Figure D-7 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (520 °C) for dehydrogenation reaction temperature (550 °C).

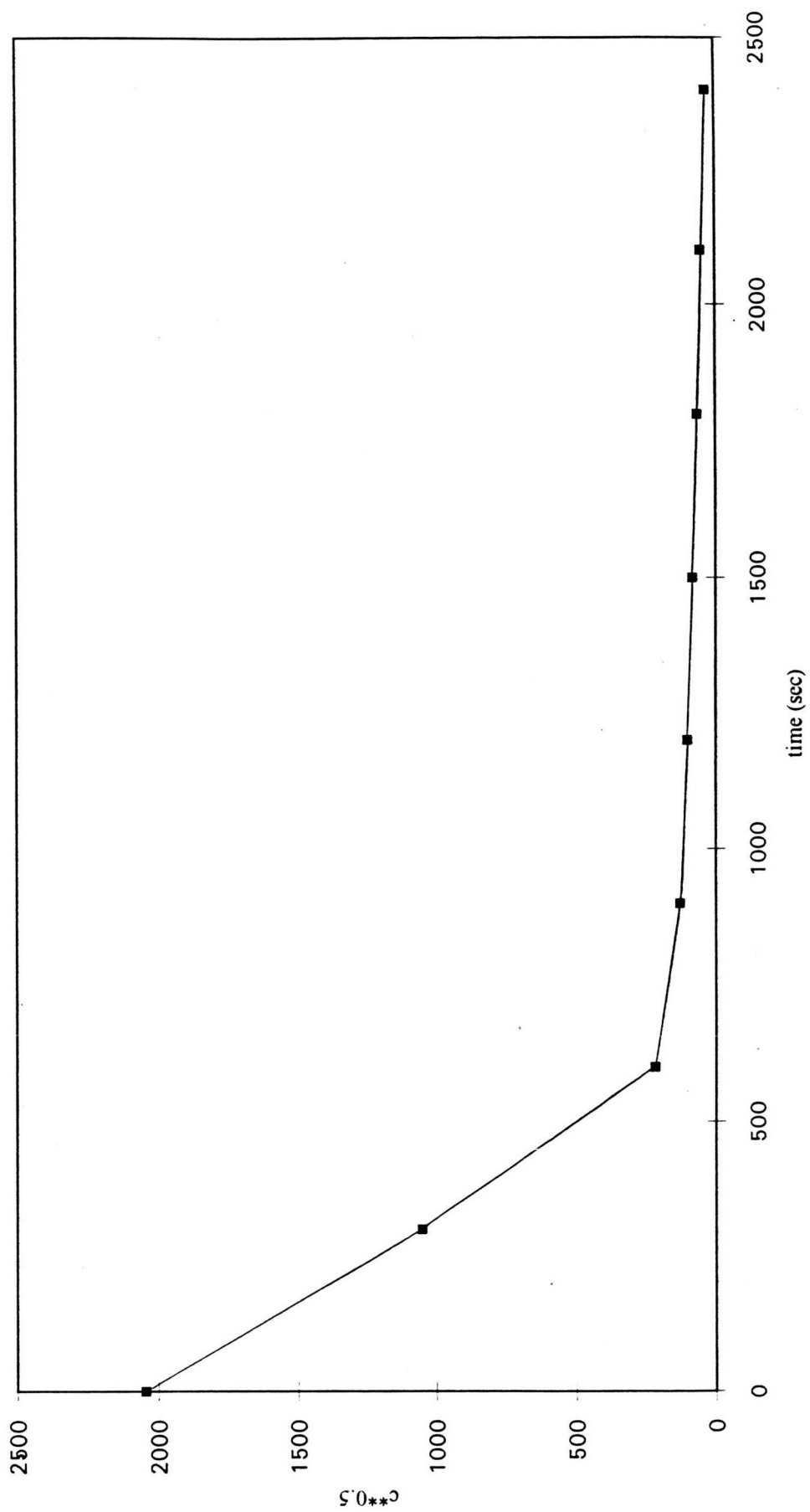


Figure D-8 Plot between $C^{0.5}$ versus time of the results shown in figure D-7.

Table D-9 Data of figure D-9.

RXN.TEMP. = 550C

Pt/Al2O3

FIXED TEMP. = 530C

TIME (min)	TIME(sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	26593	13296.5	3016425	4145625	2036.081
5	300	13626	6813	1071375	1129200	1062.638
10	600	659	329.5	50925	57825	240.4683
20	1200	20	10	2475	6900	83.06624
25	1500	13	6.5	2025	4425	66.52067
30	1800	14	7	1725	2400	48.98979
35	2100	9	4.5	675	675	25.98076
40	2400	0	0			

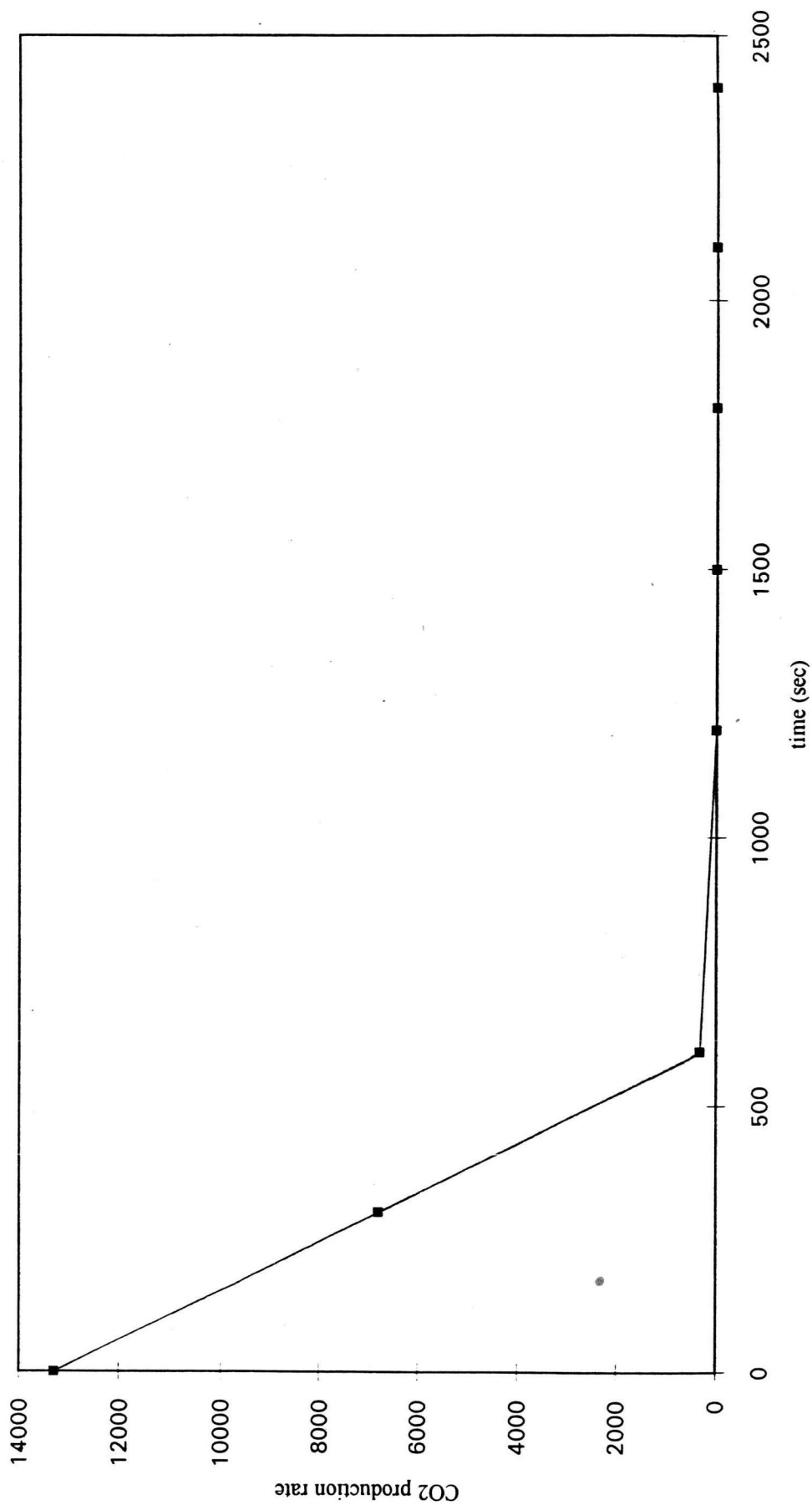


Figure D-9 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (530 °C) for dehydrogenation reaction temperature (550 °C).

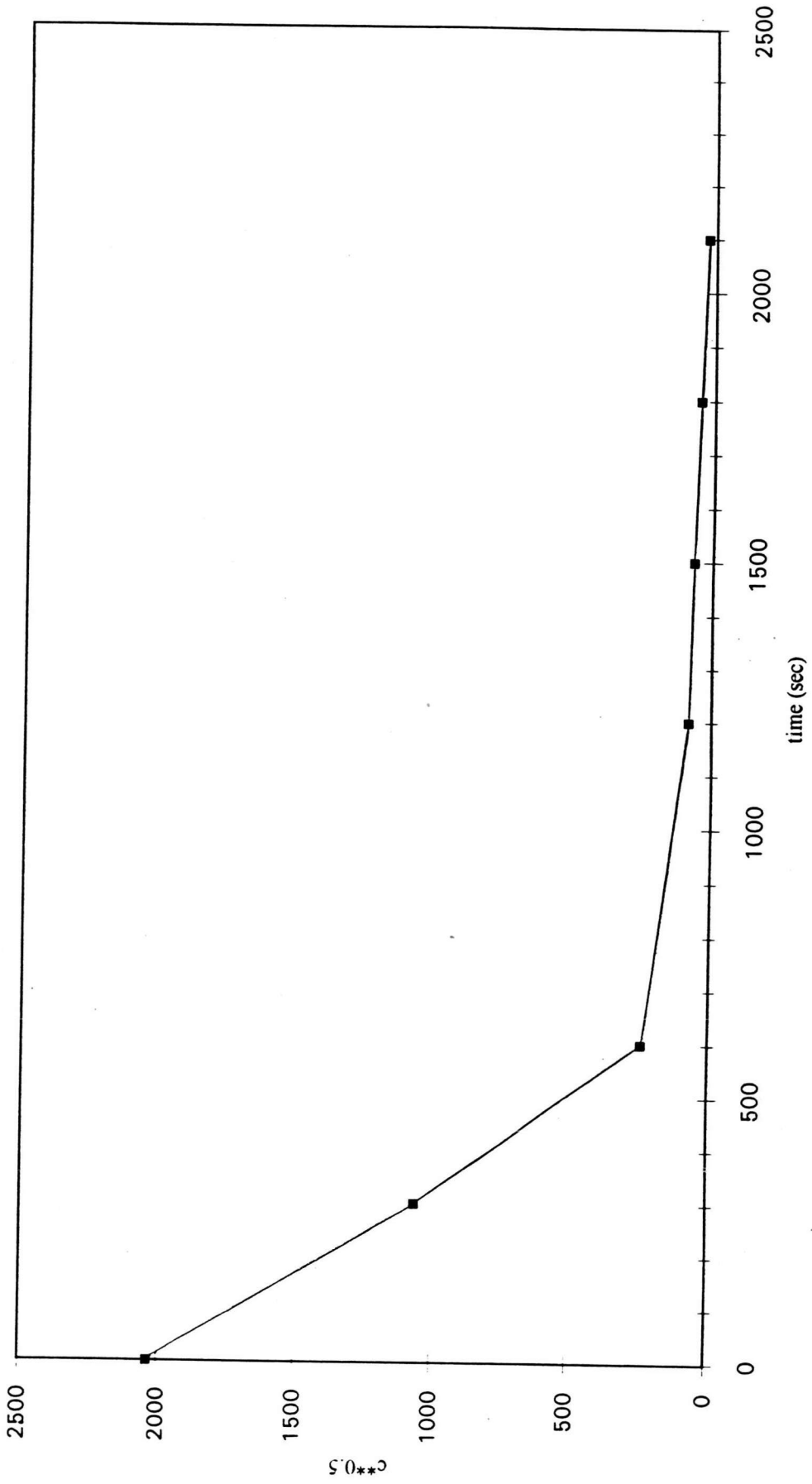


Figure D-10 Plot between $C^{0.5}$ versus time of the results shown in figure D-9.

Table D-10 Data of figure D-11.

RXN.TEMP. = 600 C

Pt/AI2O3

FIX TEMP. = 400 C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	4742	2371	593550	2988525	1728.735
5	300	3172	1586	358050	2394975	1547.571
10	600	1602	801	211050	2036925	1427.209
15	900	1212	606	162450	1825875	1351.249
20	1200	954	477	131100	1663425	1289.738
25	1500	794	397	113100	1532325	1237.871
30	1800	714	357	102525	1419225	1191.312
35	2100	653	326.5	89025	1316700	1147.475
40	2400	534	267	74925	1227675	1108.005
45	2700	465	232.5	67425	1152750	1073.662
50	3000	434	217	63525	1085325	1041.789
55	3300	413	206.5	59400	1021800	1010.841
60	3600	379	189.5	54975	962400	981.0199
65	3900	354	177	51825	907425	952.5886
70	4200	337	168.5	49650	855600	924.9865
75	4500	325	162.5	48225	805950	897.7472
80	4800	318	159	45675	757725	870.474
85	5100	291	145.5	42675	712050	843.8306
90	5400	278	139	40950	669375	818.1534
95	5700	268	134	39150	628425	792.7326
100	6000	254	127	37500	589275	767.6425
105	6300	246	123	36450	551775	742.8156
110	6600	240	120	35550	515325	717.8614
115	6900	234	117	34350	479775	692.6579
120	7200	224	112	33300	445425	667.4017
125	7500	220	110	32400	412125	641.9696
130	7800	212	106	31425	379725	616.2183
135	8100	207	103.5	30675	348300	590.1695
140	8400	202	101	30450	317625	563.5823
145	8700	204	102	30300	287175	535.8871
150	9000	200	100	28800	256875	506.8284
160	9600	184	92	26025	228075	477.572
170	10200	163	81.5	24375	202050	449.4997
180	10800	162	81	22500	177675	421.5151
210	12600	138	69	18975	155175	393.9226
240	14400	115	57.5	16800	136200	369.0528
270	16200	109	54.5	14925	119400	345.5431
300	18000	90	45	12525	104475	323.2259
330	19800	77	38.5	11625	91950	303.2326
360	21600	78	39	10500	80325	283.4167
390	23400	62	31	9000	69825	264.2442
420	25200	58	29	8325	60825	246.6272
450	27000	53	26.5	7725	52500	229.1288
480	28800	50	25	7050	44775	211.601
510	30600	44	22	6450	37725	194.2292
540	32400	42	21	6000	31275	176.8474
570	34200	38	19	5250	25275	158.9811
600	36000	32	16	4725	20025	141.5097
630	37800	31	15.5	4125	15300	123.6932
660	39600	24	12	3225	11175	105.7119
690	41400	19	9.5	2700	7950	89.16277
720	43200	17	8.5	2550	5250	72.45688
750	45000	17	8.5	2700	2700	51.96152
780	46800	19	9.5			

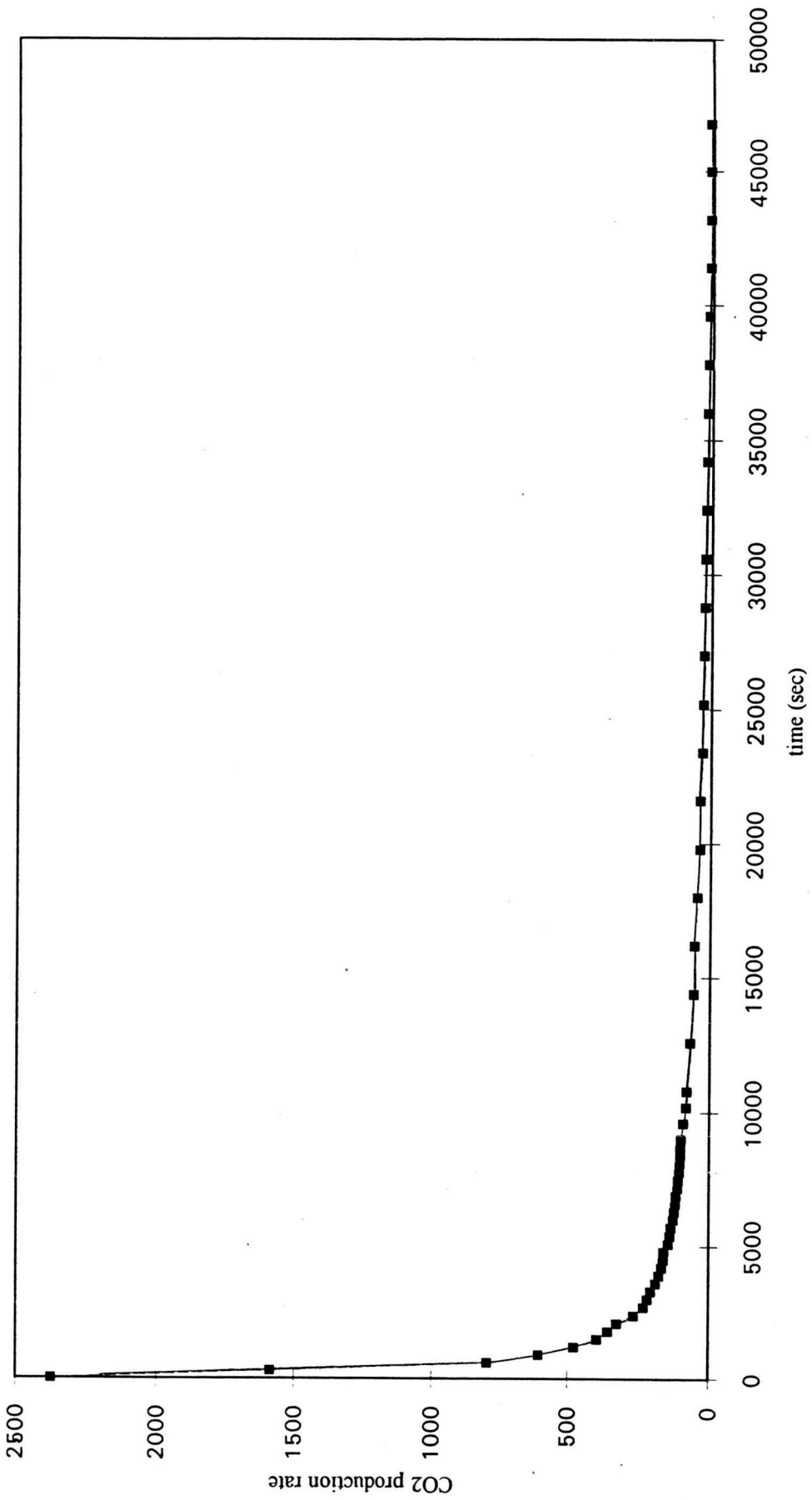


Figure D-11 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (400 °C) for dehydrogenation reaction temperature (600 °C).

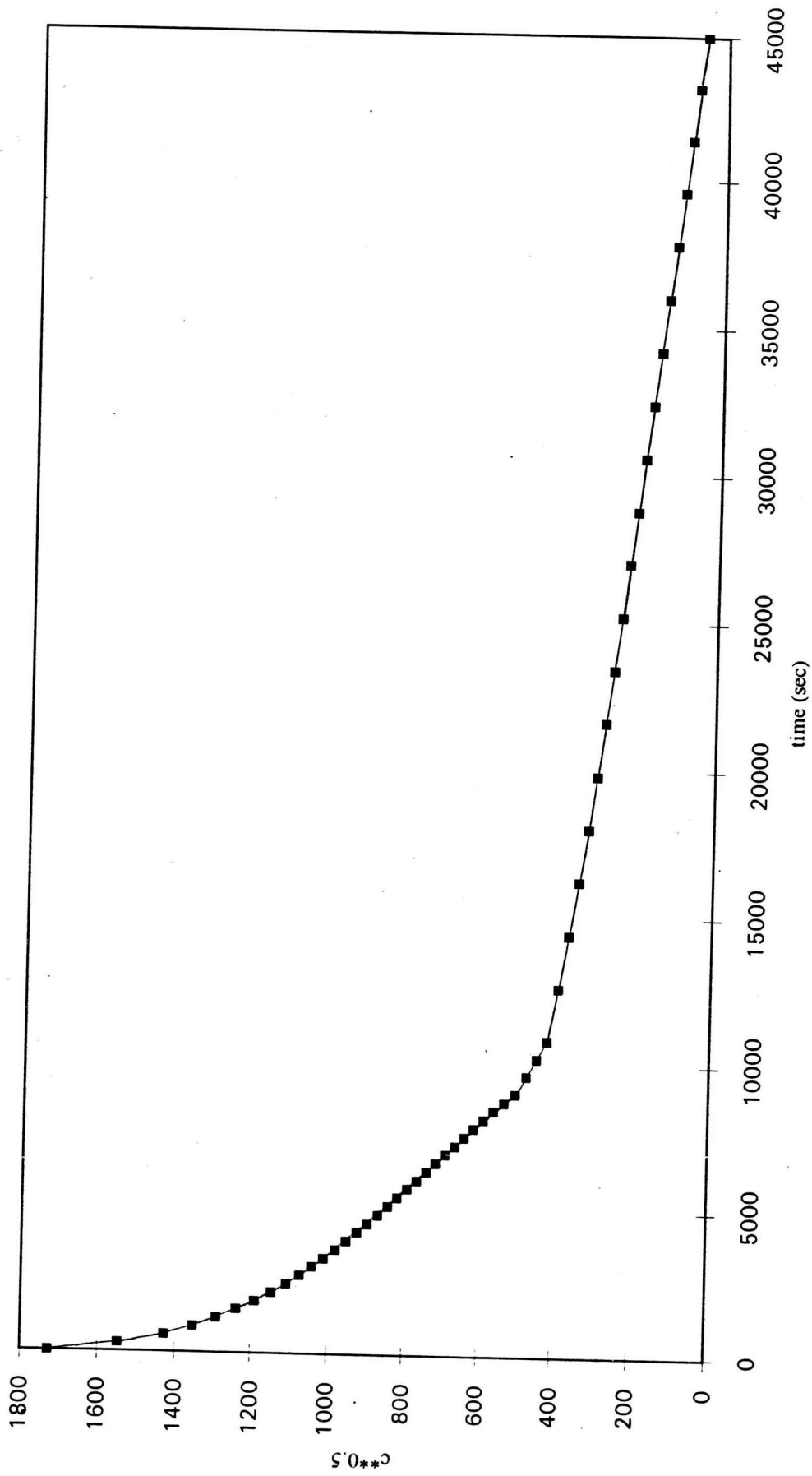


Figure D-12 Plot between $C^{0.5}$ versus time of the results shown in figure-D11.

Table D-11 Data of figure D-13.

RXN.TEMP. = 600C

Pt/AI2O3

FIXED TEMP. = 450C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	18512	9256	2259825	6687300	2585.981
5	300	11619	5809.5	1225875	4427475	2104.157
10	600	4726	2363	585150	3201600	1789.302
15	900	3076	1538	397800	2616450	1617.544
20	1200	2228	1114	295425	2218650	1489.513
25	1500	1711	855.5	241200	1923225	1386.804
30	1800	1505	752.5	214500	1682025	1296.929
35	2100	1355	677.5	185850	1467525	1211.414
40	2400	1123	561.5	159450	1281675	1132.111
45	2700	1003	501.5	144900	1122225	1059.351
50	3000	929	464.5	134400	977325	988.5975
55	3300	863	431.5	123075	842925	918.1095
60	3600	778	389	109050	719850	848.4397
65	3900	676	338	89850	610800	781.5369
70	4200	522	261	73275	520950	721.7687
75	4500	455	227.5	64200	447675	669.0852
80	4800	401	200.5	56400	383475	619.2536
85	5100	351	175.5	49275	327075	571.9047
90	5400	306	153	42750	277800	527.0674
95	5700	264	132	36525	235050	484.8196
100	6000	223	111.5	30900	198525	445.5614
105	6300	189	94.5	26025	167625	409.4203
110	6600	158	79	21975	141600	376.2978
115	6900	135	67.5	18525	119625	345.8685
120	7200	112	56	15300	101100	317.9623
125	7500	92	46	12600	85800	292.9164
130	7800	76	38	10500	73200	270.555
135	8100	64	32	9000	62700	250.3997
140	8400	56	28	7500	53700	231.7326
145	8700	44	22	6225	46200	214.9419
150	9000	39	19.5	5625	39975	199.9375
155	9300	36	18	4725	34350	185.3375
160	9600	27	13.5	3600	29625	172.1191
165	9900	21	10.5	3000	26025	161.3227
170	10200	19	9.5	2625	23025	151.7399
175	10500	16	8	2475	20400	142.8286
180	10800	17	8.5	2775	17925	133.8843
185	11100	20	10	2850	15150	123.0853
190	11400	18	9	2475	12300	110.9054
195	11700	15	7.5	2250	9825	99.12114
200	12000	15	7.5	2025	7575	87.03448
205	12300	12	6	1875	5550	74.49832
210	12600	13	6.5	1575	3675	60.62178
220	13200	8	4	1350	2100	45.82576
230	13800	10	5	750	750	27.38613
240	14400	0	0	0	0	

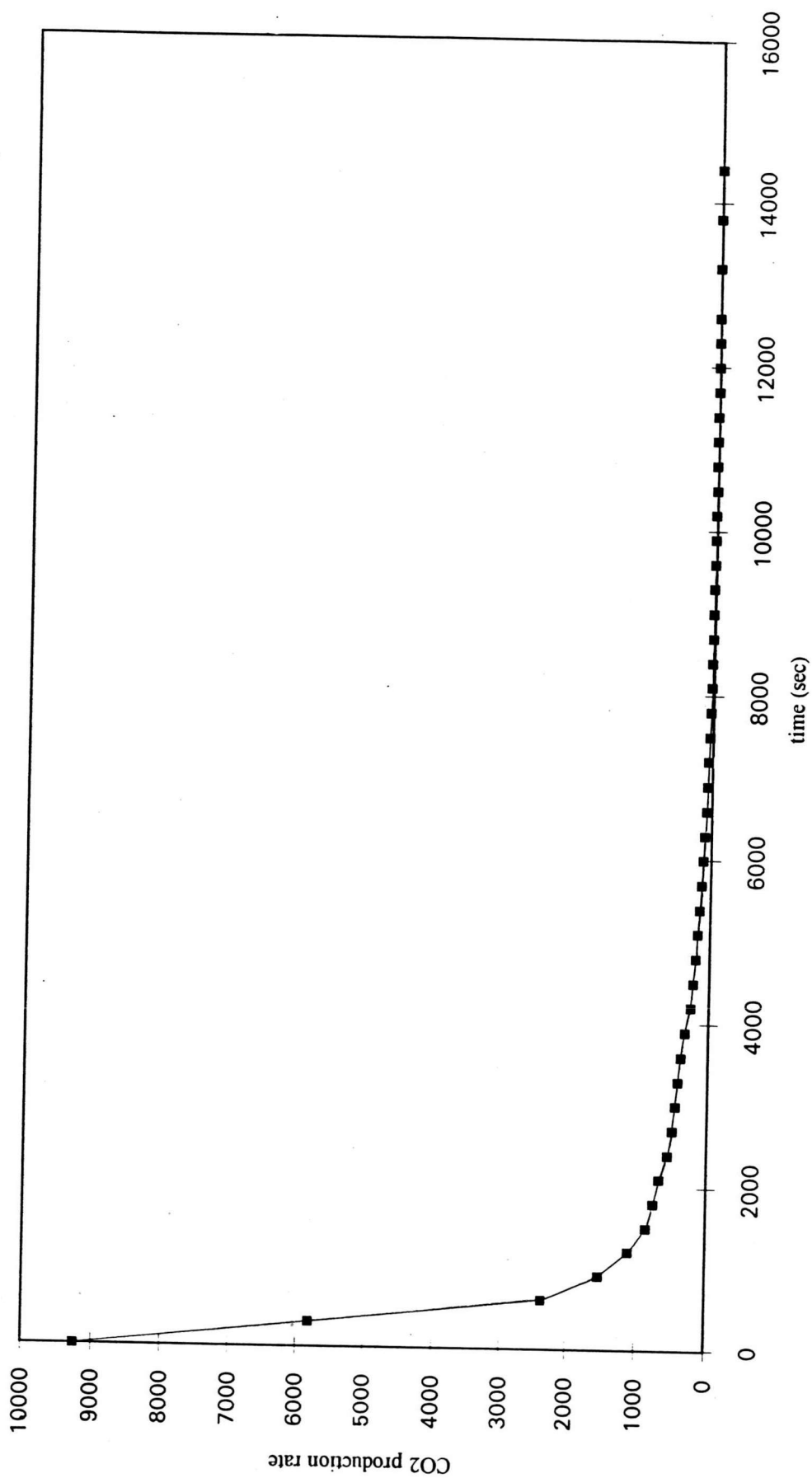


Figure D-13 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (450 °C) for dehydrogenation reaction temperature (600 °C).

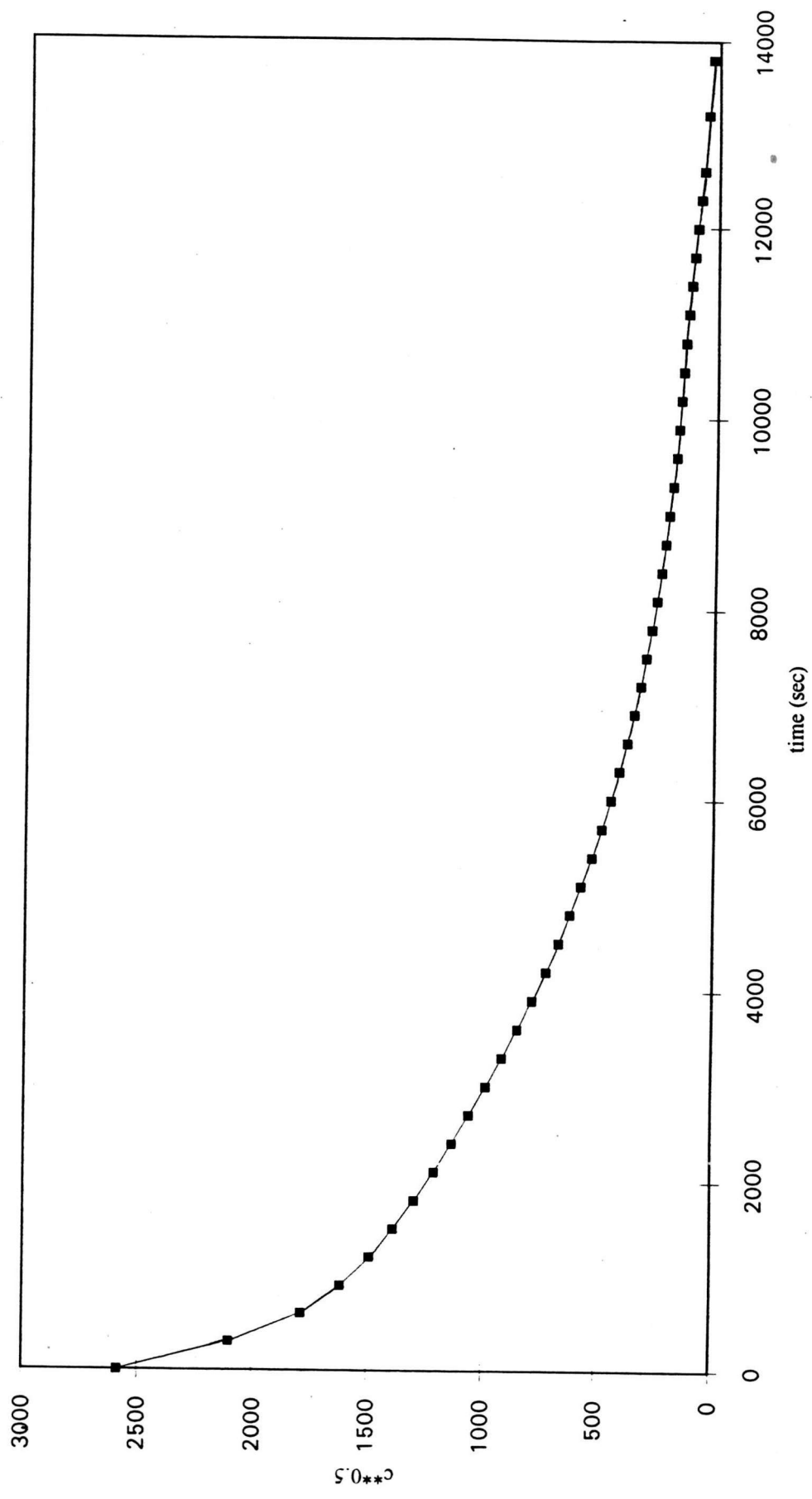


Figure D-14 Plot between $C^{0.5}$ versus time of the results shown in figure D-13.

Table D-12 Data of figure D-15.

RXN.TEMP. = 600C

Pt/AI2O3

FIXED TEMP. = 500C

TIME (min)	TIME (sec)	CO2	Rate	AREA	SUM	C ^{0.5}
0	0	32200	16100	3489225	6682125	2584.981
5	300	14323	7161.5	1552800	3192900	1786.869
10	600	6381	3190.5	794325	1640100	1280.664
15	900	4210	2105	482700	845775	919.6603
20	1200	2226	1113	224475	363075	602.5571
25	1500	767	383.5	73425	138600	372.2902
30	1800	212	106	21525	65175	255.2939
35	2100	75	37.5	8175	43650	208.9258
40	2400	34	17	4200	35475	188.3481
45	2700	22	11	3075	31275	176.8474
50	3000	19	9.5	3000	28200	167.9286
55	3300	21	10.5	2850	25200	158.7451
60	3600	17	8.5	2175	22350	149.4992
65	3900	12	6	1500	20175	142.0387
70	4200	8	4	1350	18675	136.6565
75	4500	10	5	1275	17325	131.6245
80	4800	7	3.5	975	16050	126.6886
85	5100	6	3	1200	15075	122.7803
90	5400	10	5	1500	13875	117.7922
95	5700	10	5	1350	12375	111.243
100	6000	8	4	1200	11025	105
105	6300	8	4	1425	9825	99.12114
110	6600	11	5.5	1350	8400	91.65151
115	6900	7	3.5	1050	7050	83.96428
120	7200	7	3.5	1050	6000	77.45967
125	7500	7	3.5	1050	4950	70.35624
130	7800	7	3.5	1500	3900	62.44998
135	8100	13	6.5	1425	2400	48.98979
140	8400	6	3	975	975	31.22499
145	8700	7	3.5		0	

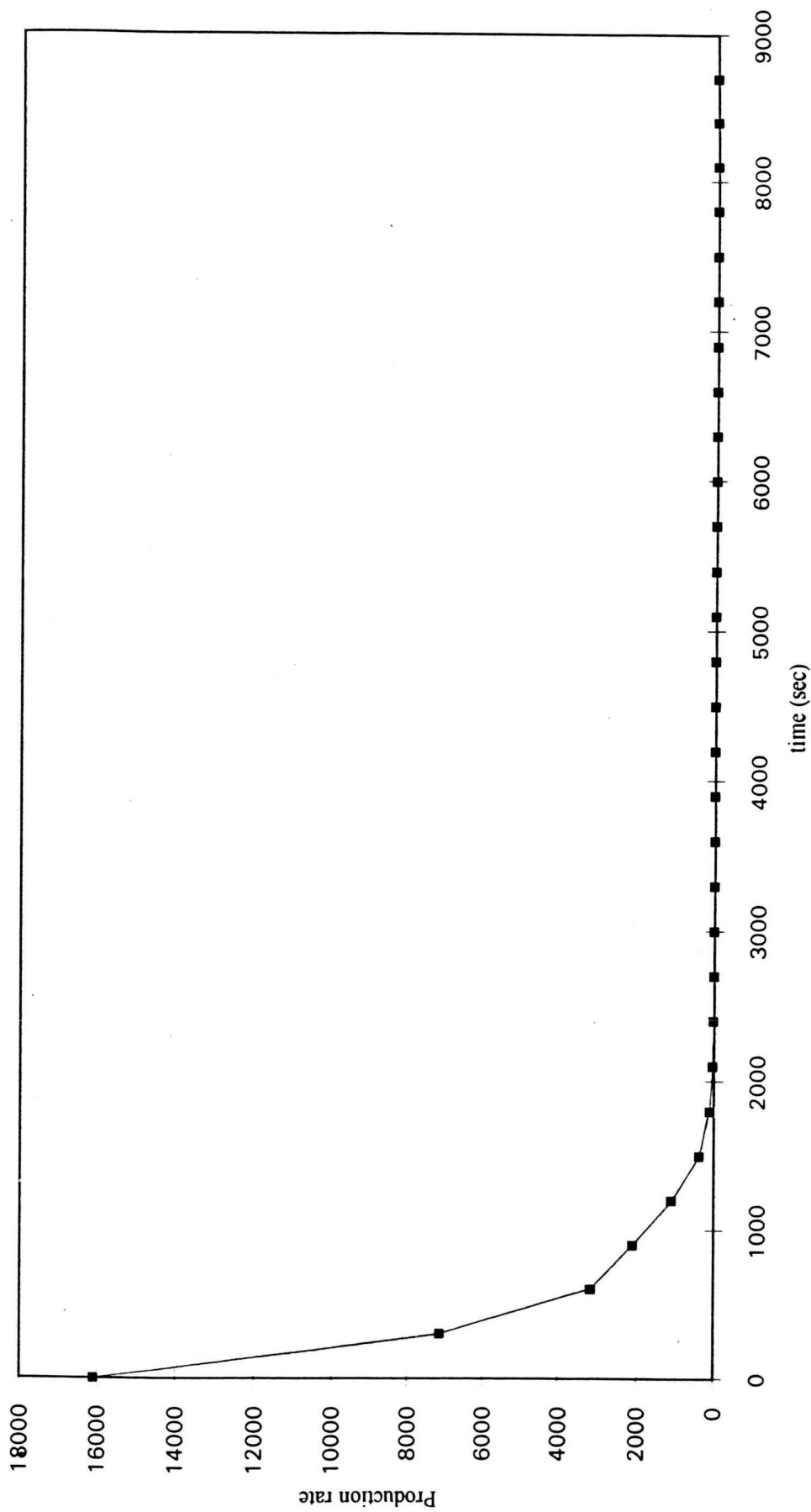


Figure D-15 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (500 °C) for dehydrogenation reaction temperature (600 °C).

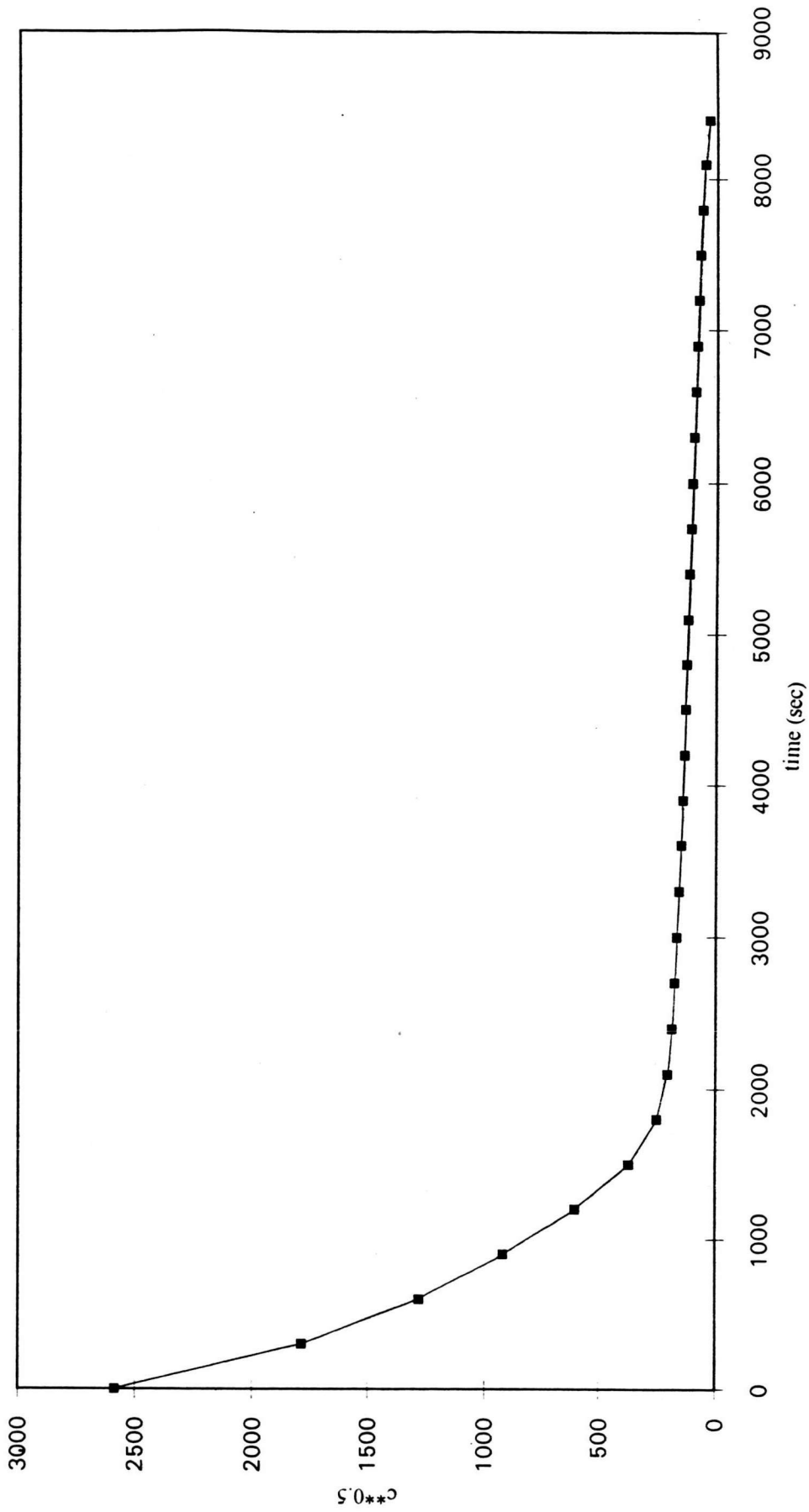


Figure D-16 Plot between $C^{0.5}$ versus time of the results shown in figure D-15.

Table D-13 Data of figure D-17.

RXN.TEMP. = 600C

Pt/Al2O3

FIXED TEMP. = 550C

TIME (min)	TIME(sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	39000	19500	4E+06	8E+06	2804.8
5	300	14296	7148	2E+06	4E+06	1967.2
10	600	14761	7380.5	1E+06	2E+06	1300.2
15	900	3589	1794.5	277050	314175	560.51
20	1200	105	52.5	11175	37125	192.68
25	1500	44	22	5625	25950	161.09
30	1800	31	15.5	4050	20325	142.57
35	2100	23	11.5	3150	16275	127.57
40	2400	19	9.5	2400	13125	114.56
45	2700	13	6.5	2175	10725	103.56
50	3000	16	8	2175	8550	92.466
55	3300	13	6.5	1725	6375	79.844
60	3600	10	5	1875	4650	68.191
65	3900	15	7.5	1950	2775	52.678
70	4200	11	5.5	825	825	28.723
75	4500	0	0			

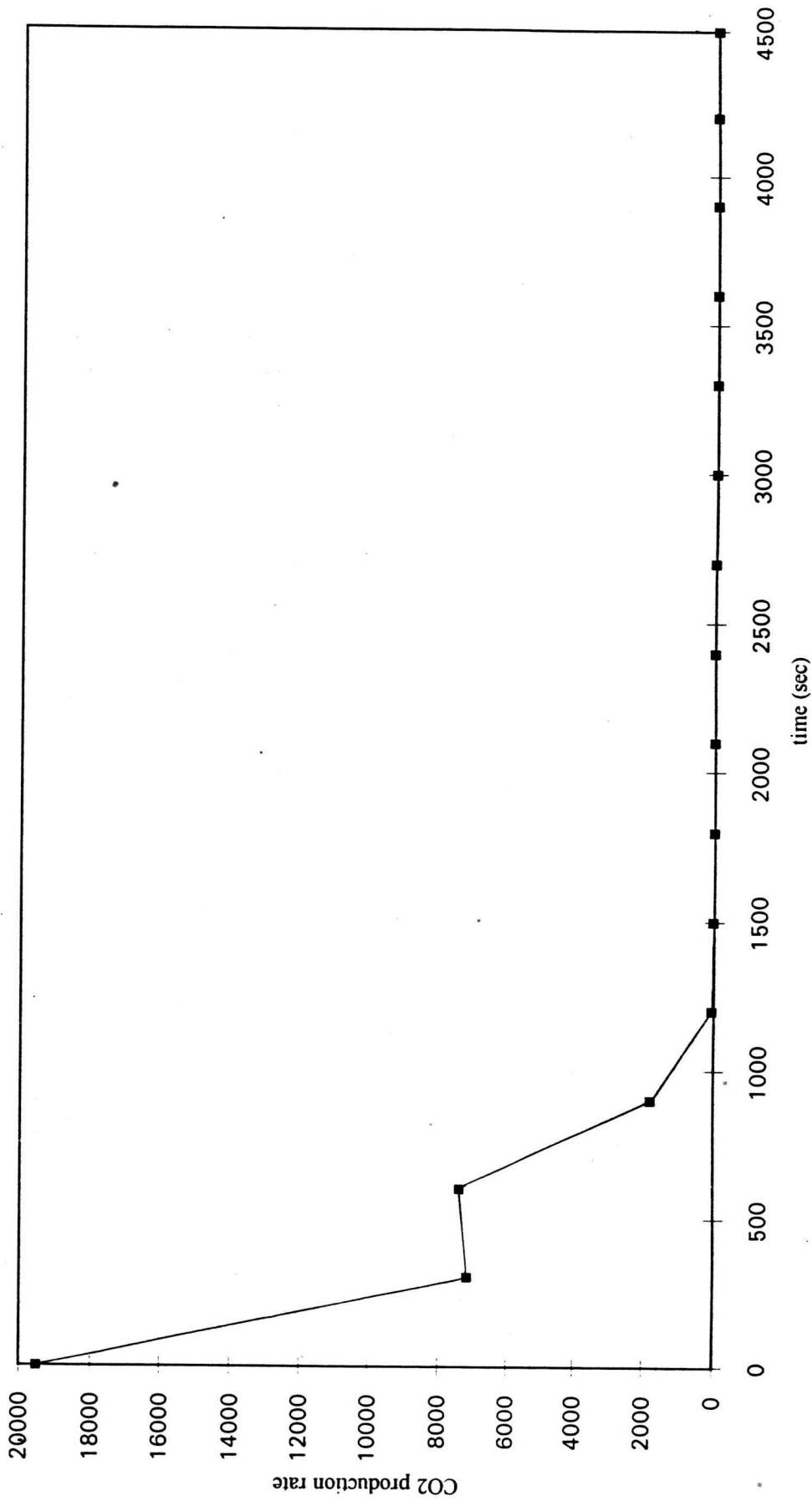


Figure D-17 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (550 °C) for dehydrogenation reaction temperature (600 °C).

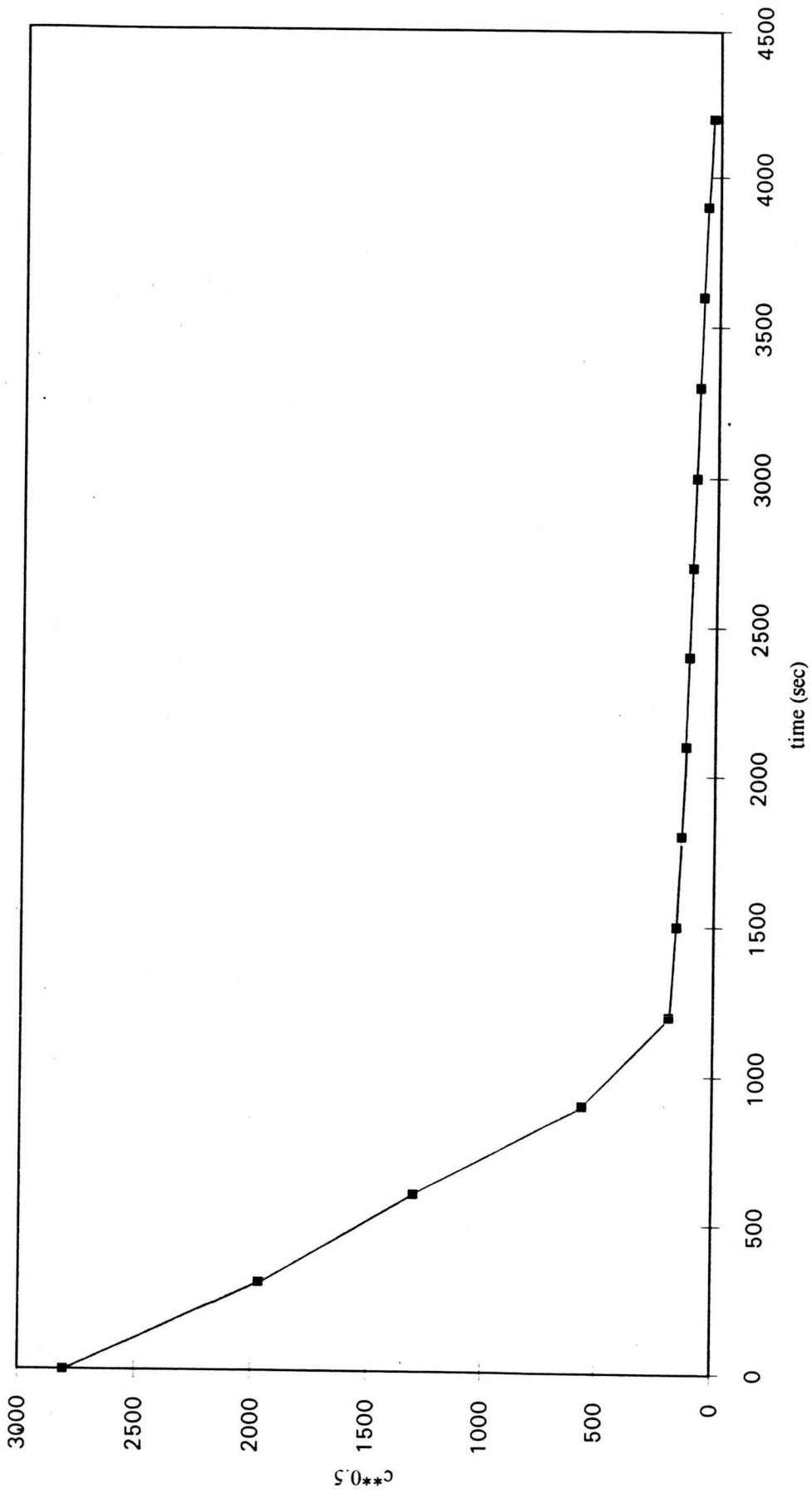


Figure D-18 Plot between $C^{0.5}$ versus time of the results shown in figure D-17.

Table D-14 Data of figure D-19.

RXN.TEMP. = 600C

Pt/AI2O3

FIXED TEMP. = 575C

TIME (min)	TIME(sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	28000	14000	3144075	6381300	2526.124
5	300	13921	6960.5	2113875	3237225	1799.229
10	600	14264	7132	1089225	1123350	1059.882
15	900	259	129.5	21825	34125	184.7295
20	1200	32	16	3900	12300	110.9054
25	1500	20	10	2400	8400	91.65151
30	1800	12	6	1725	6000	77.45967
35	2100	11	5.5	1725	4275	65.38348
40	2400	12	6	1725	2550	50.49752
45	2700	11	5.5	825	825	28.72281
50	3000	0	0			

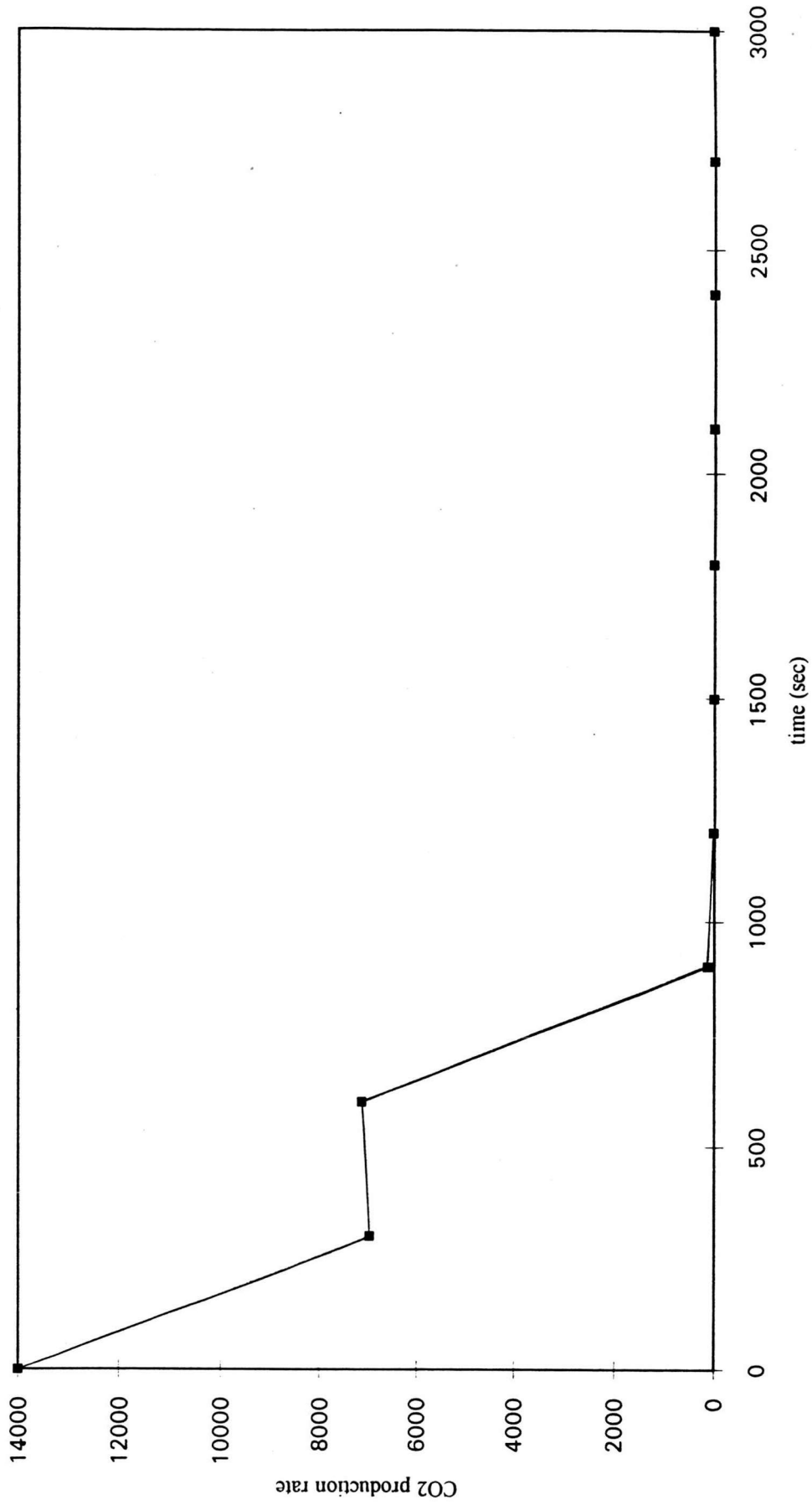


Figure D-19 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (575 °C) for dehydrogenation reaction temperature (600 °C).

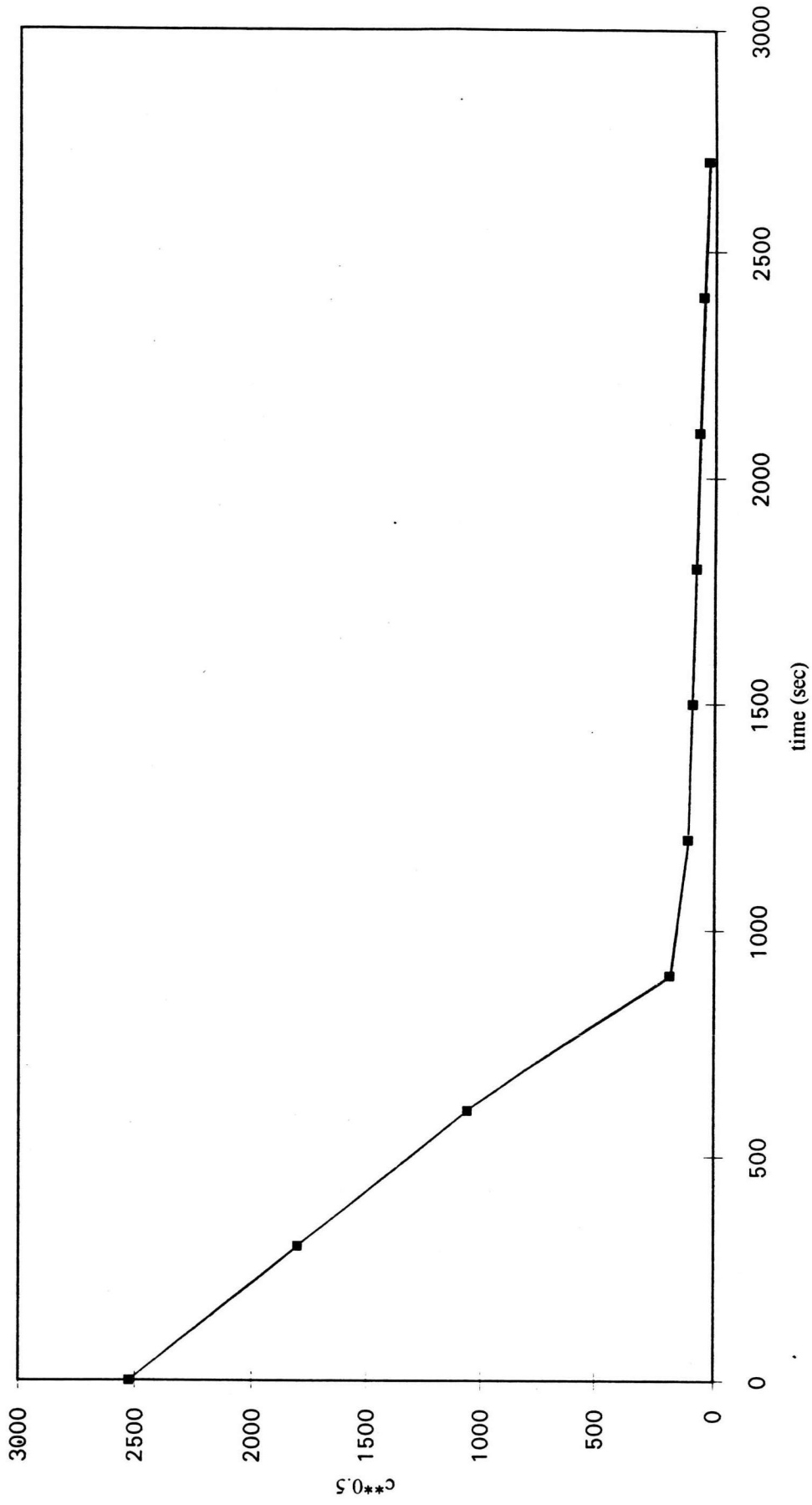


Figure D-20 Plot between $C^{0.5}$ versus time of the results shown in figure D-19.

Table D-15 Data of figure D-21.

RXN.TEMP. = 650C

Pt/AI2O3

FIXED TEMP. = 450C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C*0.5
0	0	11250	5625	1686525	12347625	3513.919
5	300	11237	5618.5	1676250	10661100	3265.134
10	600	11113	5556.5	1415100	8984850	2997.474
15	900	7755	3877.5	975600	7569750	2751.318
20	1200	5253	2626.5	684300	6594150	2567.908
25	1500	3871	1935.5	524475	5909850	2431.018
30	1800	3122	1561	435750	5385375	2320.641
35	2100	2688	1344	377550	4949625	2224.775
40	2400	2346	1173	332025	4572075	2138.241
45	2700	2081	1040.5	301575	4240050	2059.138
50	3000	1940	970	282450	3938475	1984.559
55	3300	1826	913	260700	3656025	1912.073
60	3600	1650	825	244500	3395325	1842.641
65	3900	1610	805	234000	3150825	1775.056
70	4200	1510	755	215175	2916825	1707.871
75	4500	1359	679.5	203175	2701650	1643.67
80	4800	1350	675	198075	2498475	1580.657
85	5100	1291	645.5	188700	2300400	1516.707
90	5400	1225	612.5	180675	2111700	1453.169
95	5700	1184	592	172800	1931025	1389.613
100	6000	1120	560	162900	1758225	1325.981
105	6300	1052	526	154575	1595325	1263.062
110	6600	1009	504.5	147075	1440750	1200.312
115	6900	952	476	137625	1293675	1137.398
120	7200	883	441.5	128550	1156050	1075.198
125	7500	831	415.5	119175	1027500	1013.657
130	7800	758	379	110175	908325	953.0609
135	8100	711	355.5	101775	798150	893.3924
145	8700	646	323	94500	696375	834.4909
150	9000	614	307	88425	601875	775.806
155	9300	565	282.5	82950	513450	716.5543
160	9600	541	270.5	78075	430500	656.125
165	9900	500	250	72750	352425	593.6539
170	10200	470	235	67650	279675	528.8431
175	10500	432	216	63075	212025	460.4617
180	10800	409	204.5	51900	148950	385.9404
210	12600	283	141.5	35100	97050	311.5285
240	14400	185	92.5	22500	61950	248.8976
270	16200	115	57.5	13725	39450	198.6202
300	18000	68	34	8550	25725	160.3901
330	19800	46	23	5025	17175	131.0534
360	21600	21	10.5	2775	12150	110.227
390	23400	16	8	2025	9375	96.82458
420	25200	11	5.5	1425	7350	85.73214
450	27000	8	4	1200	5925	76.97402
480	28800	8	4	1500	4725	68.73864
510	30600	12	6	1575	3225	56.78908
540	32400	9	4.5	1650	1650	40.62019
570	34200	13	6.5	975		

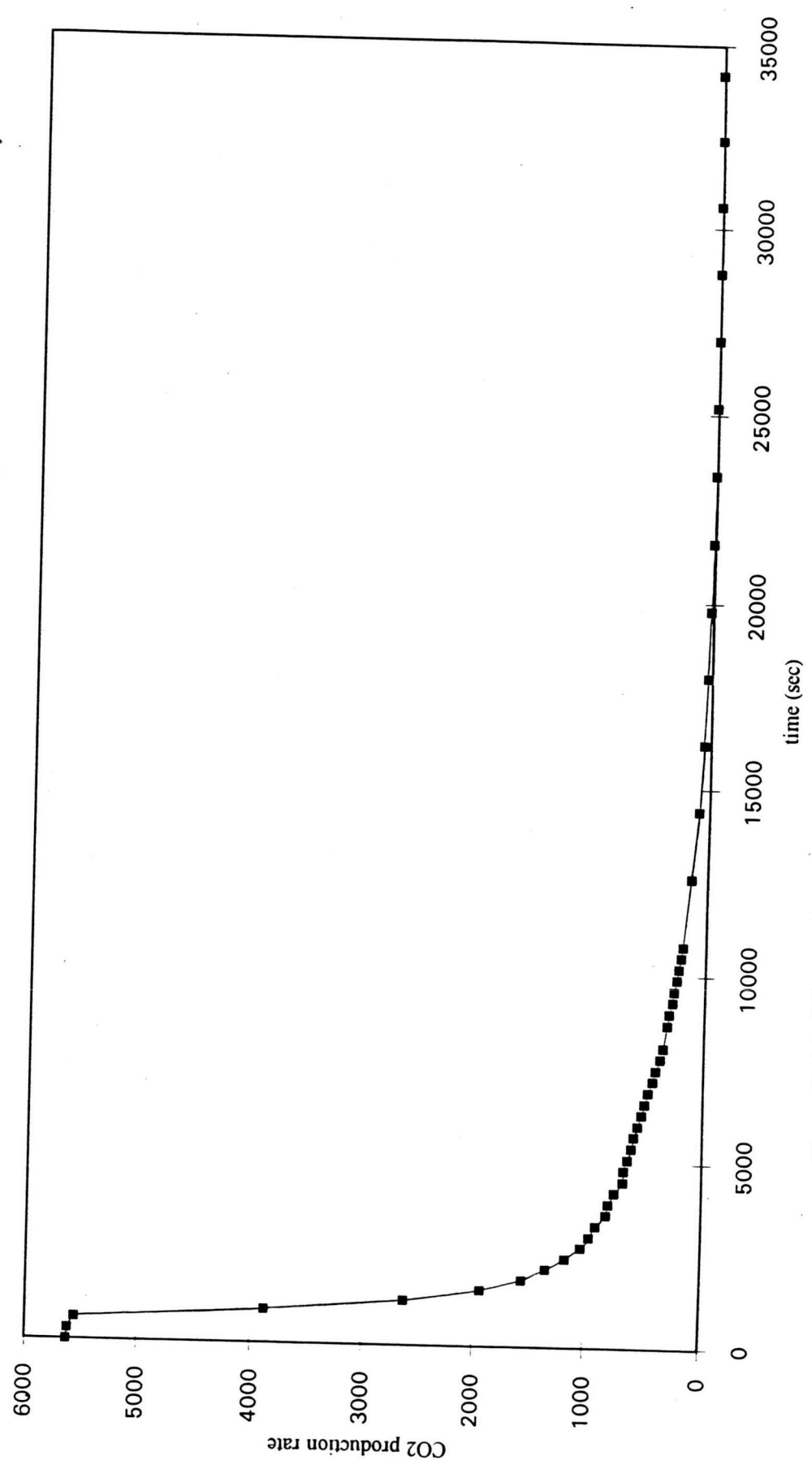


Figure D-21 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (450 °C) for dehydrogenation reaction temperature (650 °C).

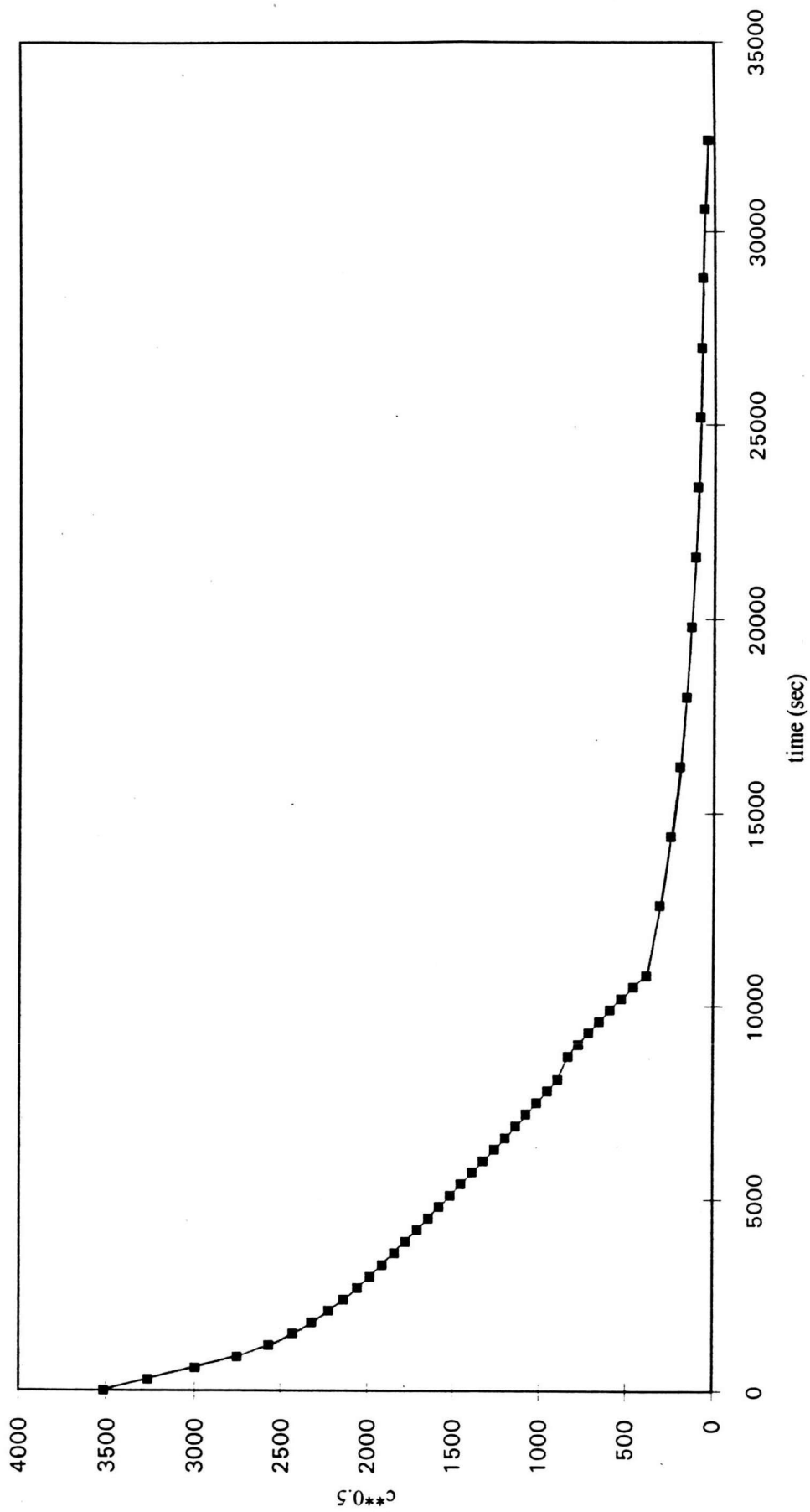


Figure D-22 Plot between $C^{0.5}$ versus time of the results shown in figure D-21.

Table D-16 Data of figure D-23.

RXN.TEMP. = 650C

Pt/AI2O3

FIXED TEMP. = 480C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	13500	6750	2011950	11332950	3366.445
5	300	13326	6663	1993350	9321000	3053.031
10	600	13252	6626	1598025	7327650	2706.963
15	900	8055	4027.5	985800	5729625	2393.664
20	1200	5089	2544.5	687375	4743825	2178.032
25	1500	4076	2038	570300	4056450	2014.063
30	1800	3528	1764	501150	3486150	1867.123
35	2100	3154	1577	449100	2985000	1727.715
40	2400	2834	1417	392250	2535900	1592.451
45	2700	2396	1198	336900	2143650	1464.121
50	3000	2096	1048	294300	1806750	1344.154
55	3300	1828	914	259275	1512450	1229.817
60	3600	1629	814.5	227550	1253175	1119.453
65	3900	1405	702.5	195075	1025625	1012.731
70	4200	1196	598	165450	830550	911.3452
75	4500	1010	505	137475	665100	815.5366
80	4800	823	411.5	112275	527625	726.378
85	5100	674	337	90525	415350	644.4765
90	5400	533	266.5	71700	324825	569.9342
95	5700	423	211.5	56625	253125	503.1153
100	6000	332	166	44025	196500	443.2832
105	6300	255	127.5	34575	152475	390.4805
110	6600	206	103	27525	117900	343.3657
115	6900	161	80.5	20775	90375	300.6244
120	7200	116	58	14925	69600	263.8181
125	7500	83	41.5	10950	54675	233.8269
130	7800	63	31.5	8925	43725	209.1052
135	8100	56	28	7050	34800	186.5476
140	8400	38	19	4875	27750	166.5833
145	8700	27	13.5	3900	22875	151.2448
150	9000	25	12.5	3450	18975	137.7498
155	9300	21	10.5	2775	15525	124.5994
160	9600	16	8	2775	12750	112.9159
165	9900	21	10.5	2700	9975	99.87492
170	10200	15	7.5	2175	7275	85.29361
175	10500	14	7	2100	5100	71.41428
180	10800	14	7	2025	3000	54.77226
185	11100	13	6.5	975	975	31.22499
190	11400	0	0	0		

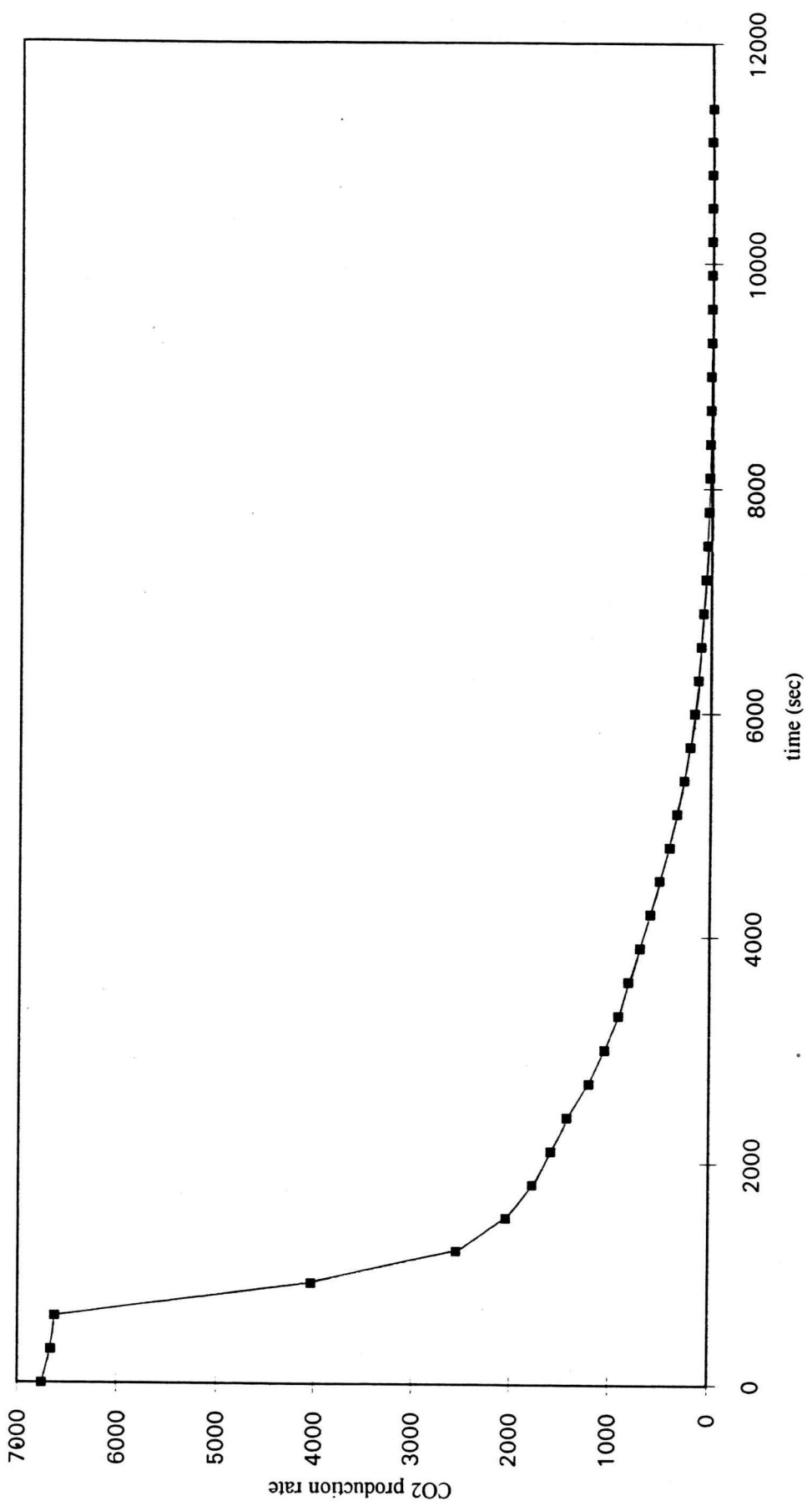


Figure D-23 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (480 °C) for dehydrogenation reaction temperature (650 °C).

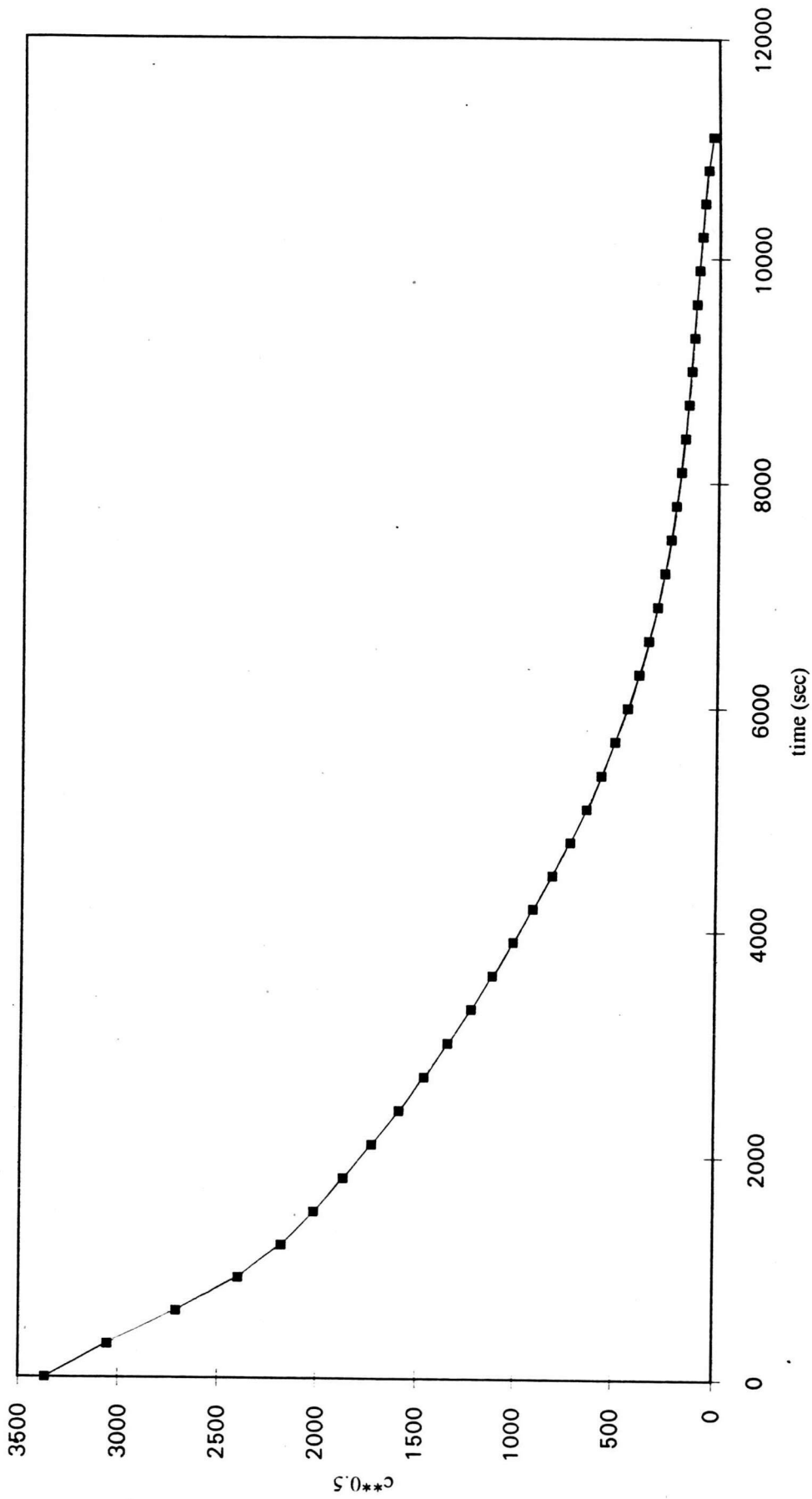


Figure D-24 Plot between $C^{0.5}$ versus time of the results shown in figure D-23.

Table D-17 Data of figure D-25.

RXN.TEMP. = 650C

Pt/AI2O3

FIXED TEMP. = 530C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	12600	6300	1945125	13795050	3714.169
5	300	13335	6667.5	2053950	11849925	3442.372
10	600	14051	7025.5	2121975	9795975	3129.852
15	900	14242	7121	2135850	7674000	2770.199
20	1200	14236	7118	1908000	5538150	2353.327
25	1500	11204	5602	1432650	3630150	1905.295
30	1800	7898	3949	1001175	2197500	1482.397
35	2100	5451	2725.5	635325	1196325	1093.766
40	2400	3020	1510	328200	561000	748.9993
45	2700	1356	678	135150	232800	482.4935
50	3000	446	223	41550	97650	312.49
55	3300	108	54	11025	56100	236.8544
60	3600	39	19.5	4425	45075	212.3087
65	3900	20	10	2850	40650	201.6185
70	4200	18	9	3375	37800	194.4222
75	4500	27	13.5	3675	34425	185.5398
80	4800	22	11	3000	30750	175.3568
85	5100	18	9	2850	27750	166.5833
95	5700	20	10	2775	24900	157.7973
100	6000	17	8.5	2775	22125	148.7447
105	6300	20	10	2625	19350	139.1043
110	6600	15	7.5	2325	16725	129.3252
115	6900	16	8	2100	14400	120
120	7200	12	6	1950	12300	110.9054
125	7500	14	7	1950	10350	101.7349
130	7800	12	6	1725	8400	91.65151
135	8100	11	5.5	1800	6675	81.70067
140	8400	13	6.5	1650	4875	69.8212
145	8700	9	4.5	1425	3225	56.78908
150	9000	10	5	1275	1800	42.42641
155	9300	7	3.5	525	525	22.91288
160	9600	0	0			

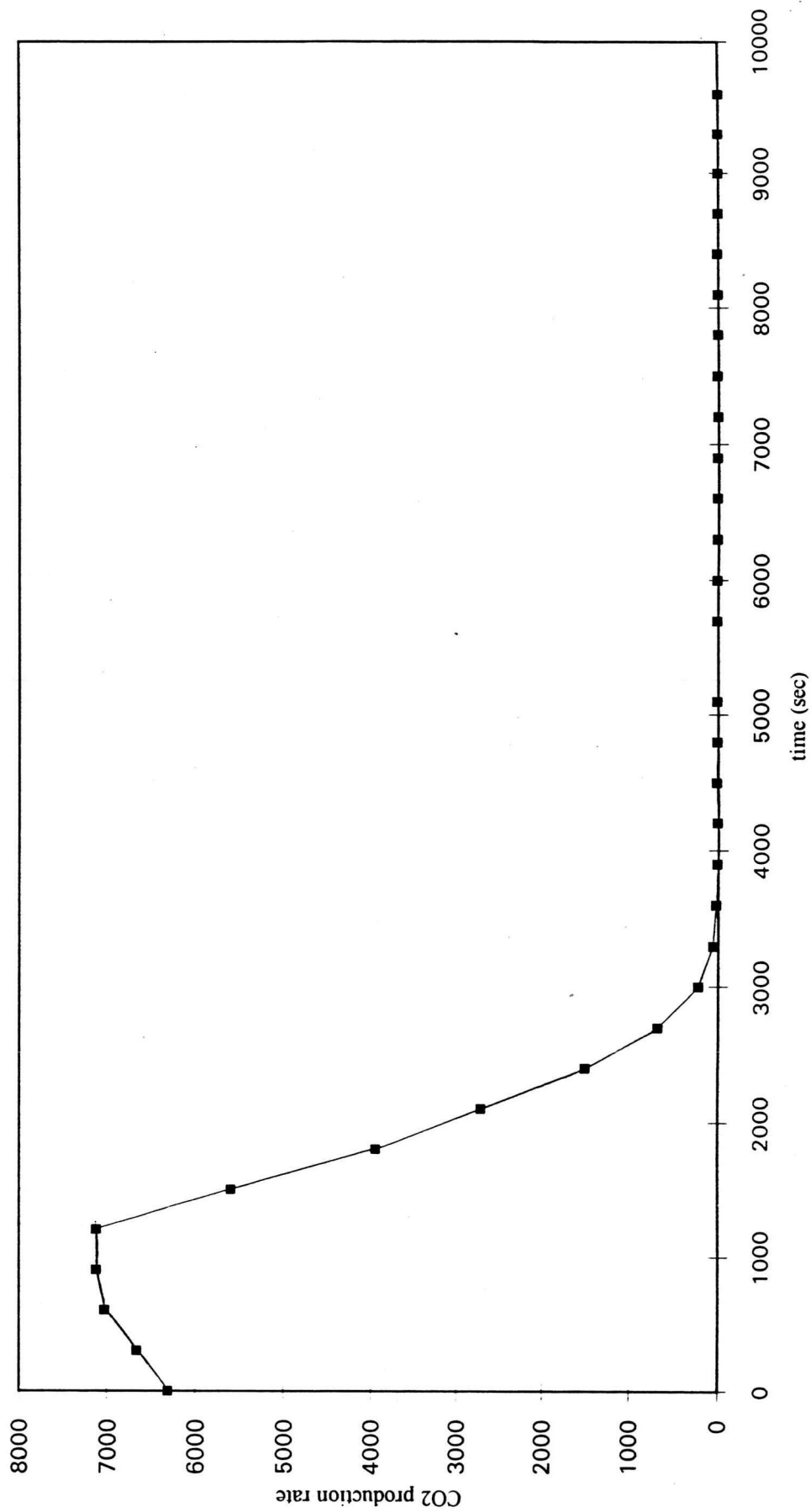


Figure D-25 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (530 °C) for dehydrogenation reaction temperature (650 °C).

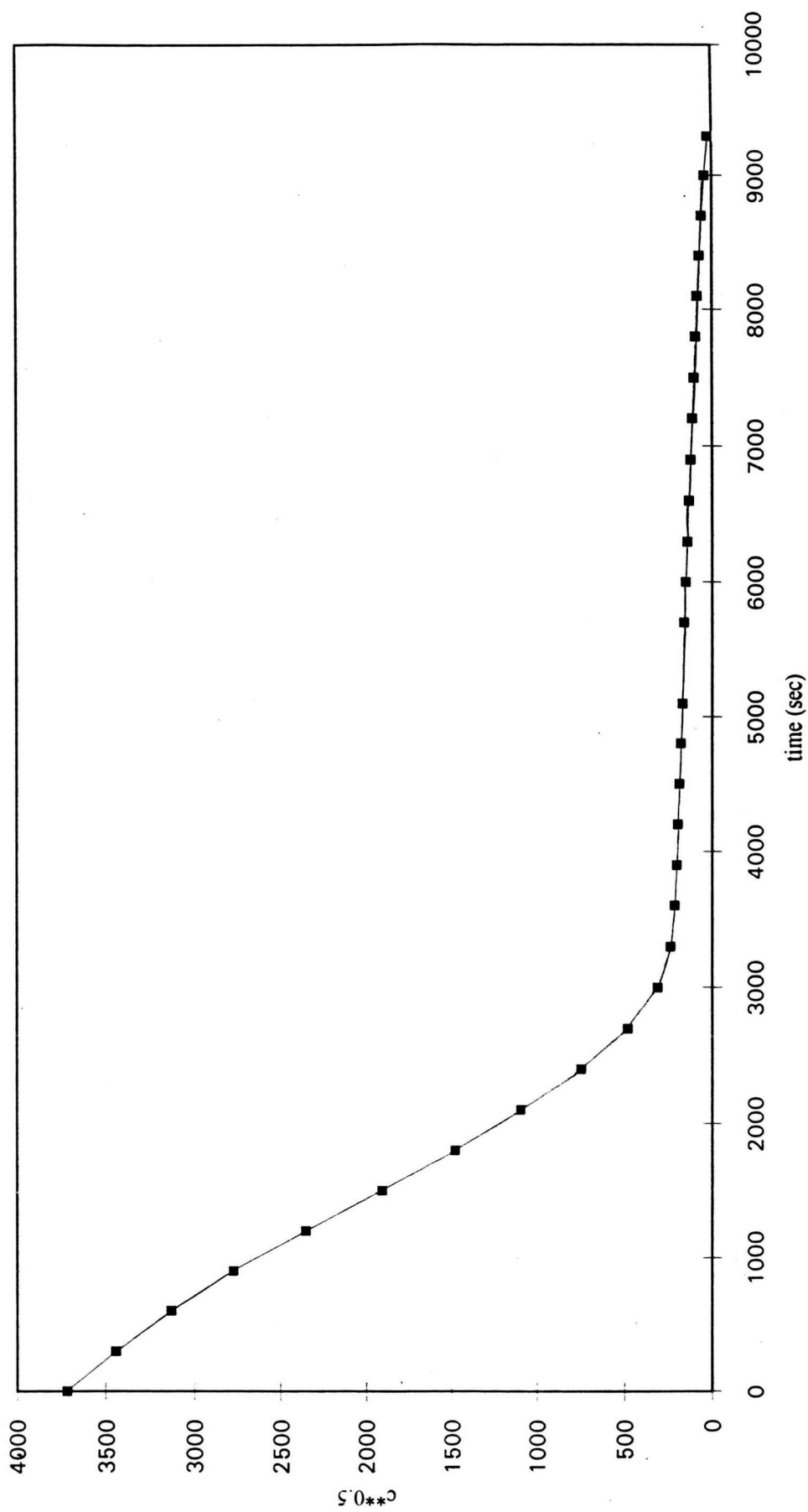


Figure D-26 Plot between $C^{0.5}$ versus time of the results shown in figure D25.

Table D-18 Data of figure D-27.

RXN.TEMP. = 650C

Pt/Al₂O₃

FIXED TEMP. = 560C

TIME (min)	TIME(sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	12100	6050	1904025	13904700	3728.901
5	300	13287	6643.5	2075550	12000675	3464.199
10	600	14387	7193.5	2171025	9925125	3150.417
15	900	14560	7280	2183025	7754100	2784.618
20	1200	14547	7273.5	2177625	5571075	2360.312
25	1500	14488	7244	1875525	3393450	1842.132
30	1800	10519	5259.5	1108275	1517925	1232.041
35	2100	4258	2129	352800	409650	640.0391
40	2400	446	223	36900	56850	238.4324
45	2700	46	23	5100	19950	141.2445
50	3000	22	11	2925	14850	121.8606
55	3300	17	8.5	2025	11925	109.2016
60	3600	10	5	2250	9900	99.49874
65	3900	20	10	2250	7650	87.46428
70	4200	10	5	1425	5400	73.48469
75	4500	9	4.5	1650	3975	63.0476
80	4800	13	6.5	1650	2325	48.21825
85	5100	9	4.5	675	675	25.98076
90	5400	0	0	0	0	

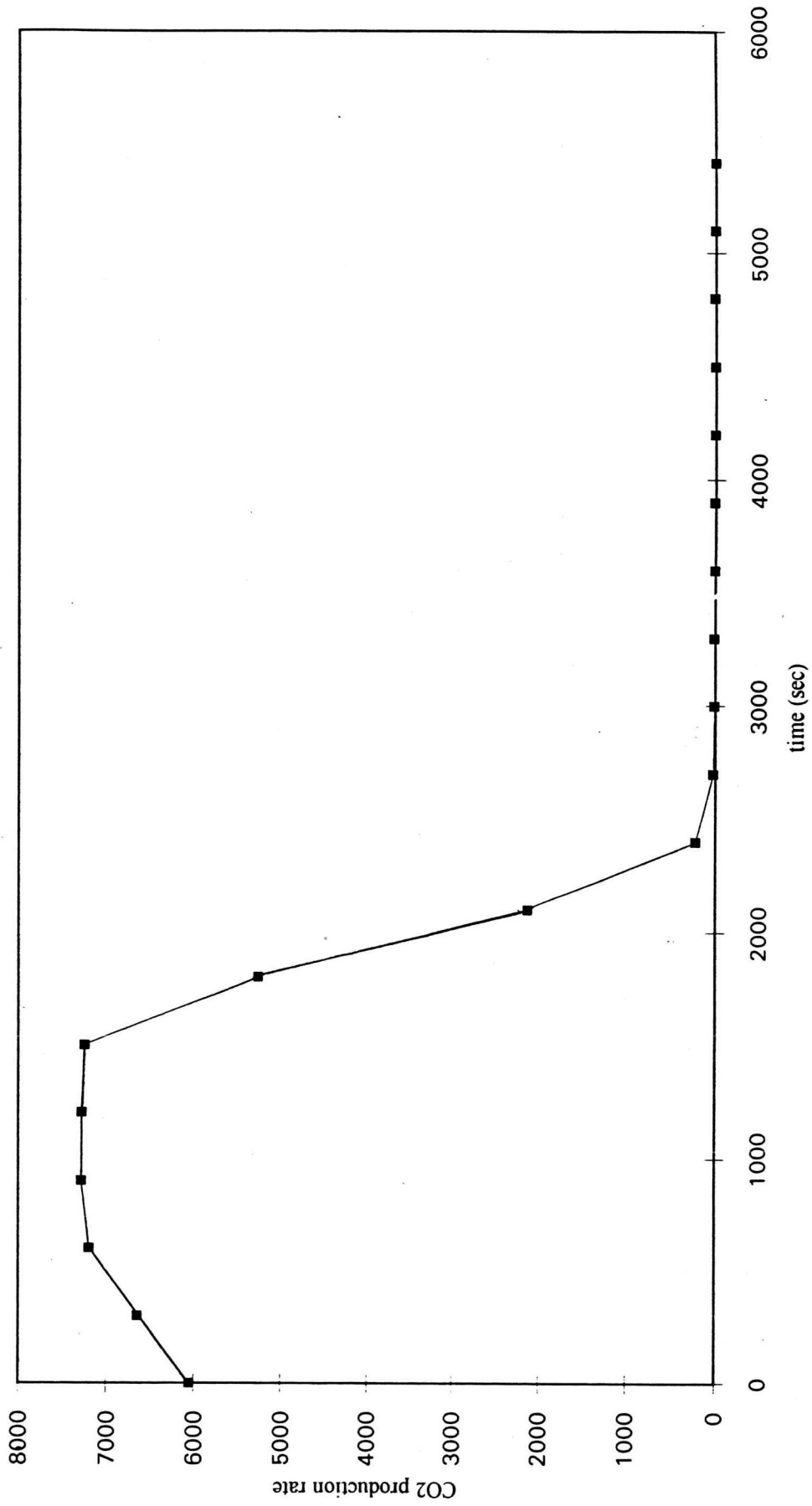


Figure D-27 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (560 °C) for dehydrogenation reaction temperature (650 °C).

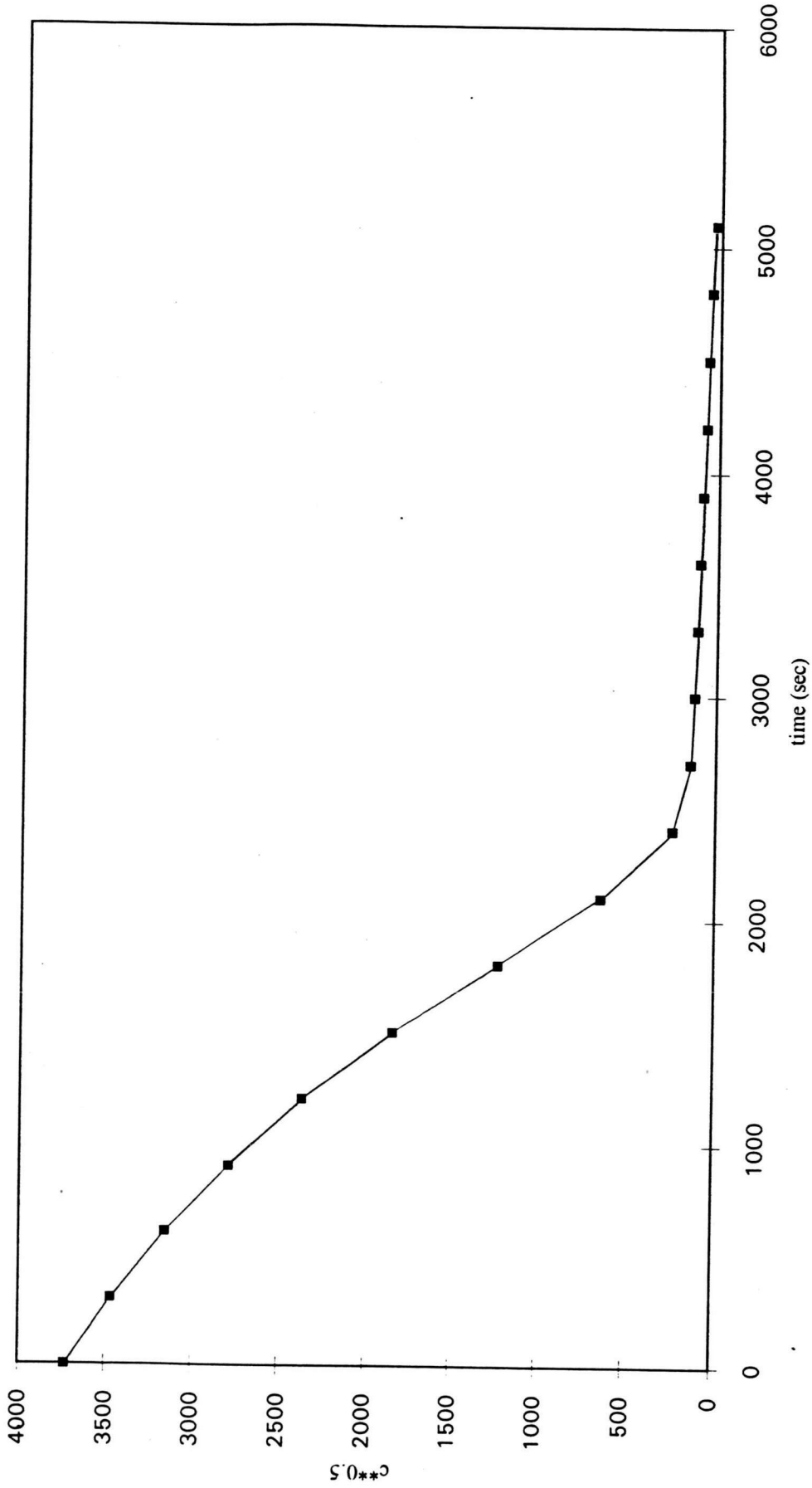


Figure D-28 Plot between $C^{0.5}$ versus time of the results shown in figure D27.

Table D-19 Data of figure D-29.

RXN.TEMP. = 650C

Pt/Al₂O₃

FIXED TEMP. = 580C

TIME (min)	TIME (sec)	CO ₂	RATE	AREA	SUM	C ^{0.5}
0	0	12615	6307.5	1964175	14781525	3844.675
5	300	13574	6787	2096550	12817350	3580.133
10	600	14380	7190	2168925	10720800	3274.263
15	900	14539	7269.5	2178000	8551875	2924.359
20	1200	14501	7250.5	2161350	6373875	2524.653
25	1500	14317	7158.5	2041350	4212525	2052.444
30	1800	12901	6450.5	1527375	2171175	1473.491
35	2100	7464	3732	594900	643800	802.3715
40	2400	468	234	36975	48900	221.1334
45	2700	25	12.5	3450	11925	109.2016
50	3000	21	10.5	2850	8475	92.05976
55	3300	17	8.5	2625	5625	75
60	3600	18	9	2175	3000	54.77226
65	3900	11	5.5	825	825	28.72281
70	4200	0	0	0	0	

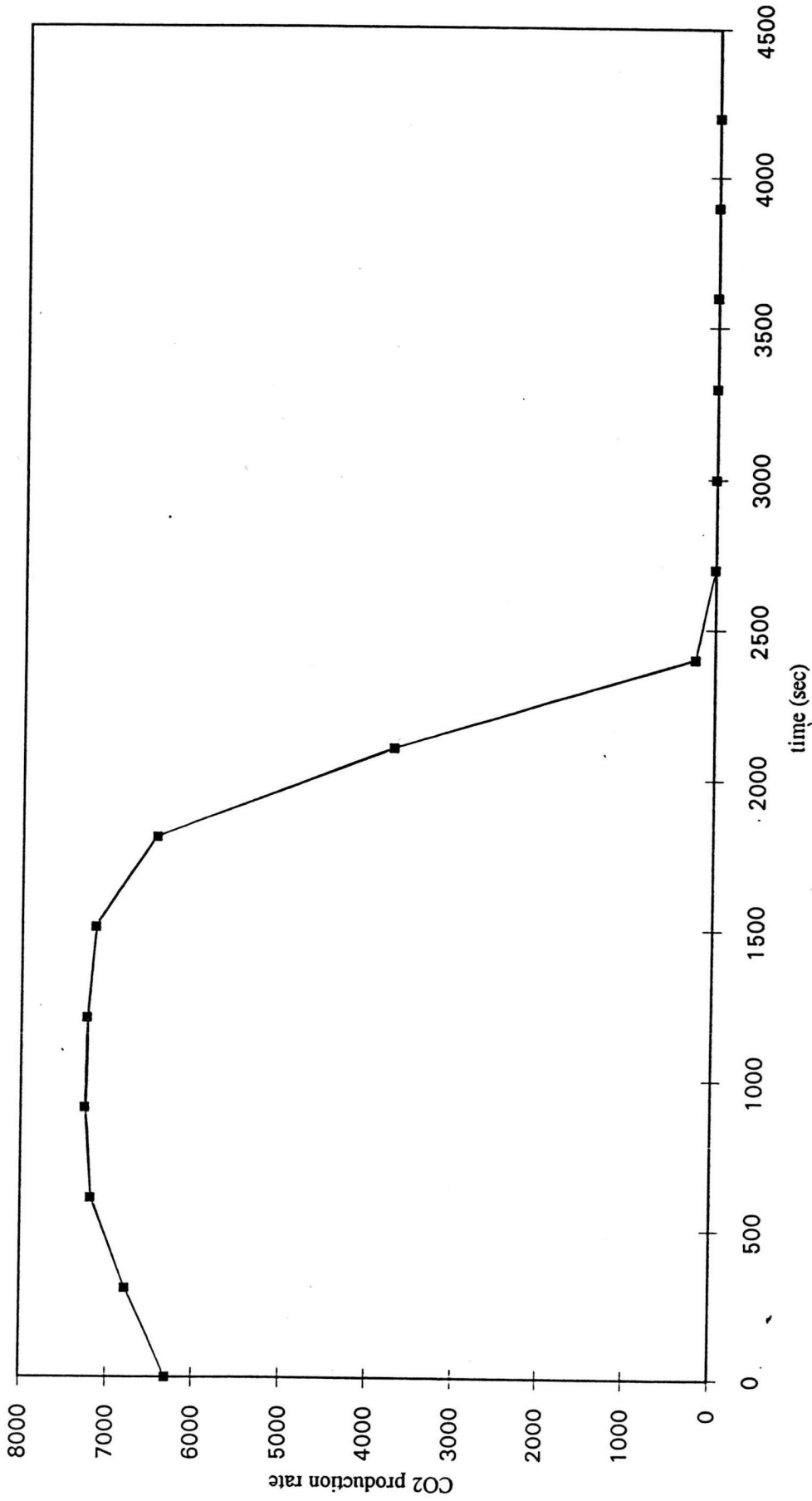


Figure D-29 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (580 °C) for dehydrogenation reaction temperature (650 °C).

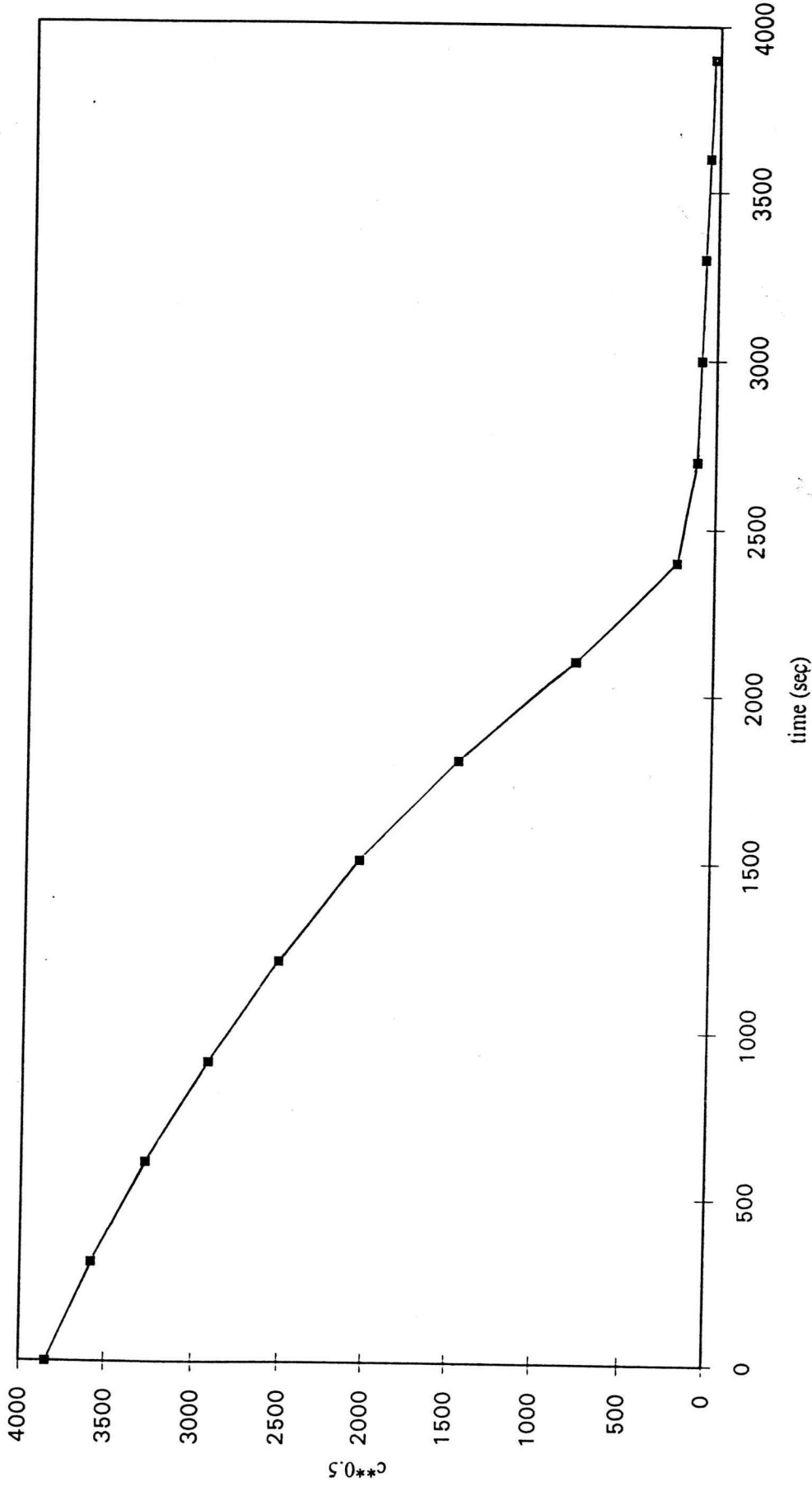


Figure D-30 Plot between $C^{0.5}$ versus time of the results shown in figure D-29.

Table D-20 Data of figure D-31.

RXN.TEMP. = 650C

Pt/AI2O3

FIXED TEMP. = 600C

TIME (min)	TIME (sec)	CO2	RATE	AREA	SUM	C ^{0.5}
0	0	13000	6500	2004075	13522200	3677.254
5	300	13721	6860.5	2107875	11518125	3393.836
10	600	14384	7192	2158875	9410250	3067.613
15	900	14401	7200.5	2163375	7251375	2692.838
20	1200	14444	7222	2152800	5088000	2255.66
25	1500	14260	7130	1952100	2935200	1713.243
30	1800	11768	5884	920625	983100	991.514
35	2100	507	253.5	40575	62475	249.95
40	2400	34	17	4875	21900	147.9865
45	2700	31	15.5	4575	17025	130.4799
50	3000	30	15	3600	12450	111.5796
55	3300	18	9	2325	8850	94.07444
60	3600	13	6.5	2025	6525	80.77747
65	3900	14	7	1800	4500	67.08204
70	4200	10	5	1725	2700	51.96152
75	4500	13	6.5	975	975	31.22499
80	4800	0	0	0	0	0

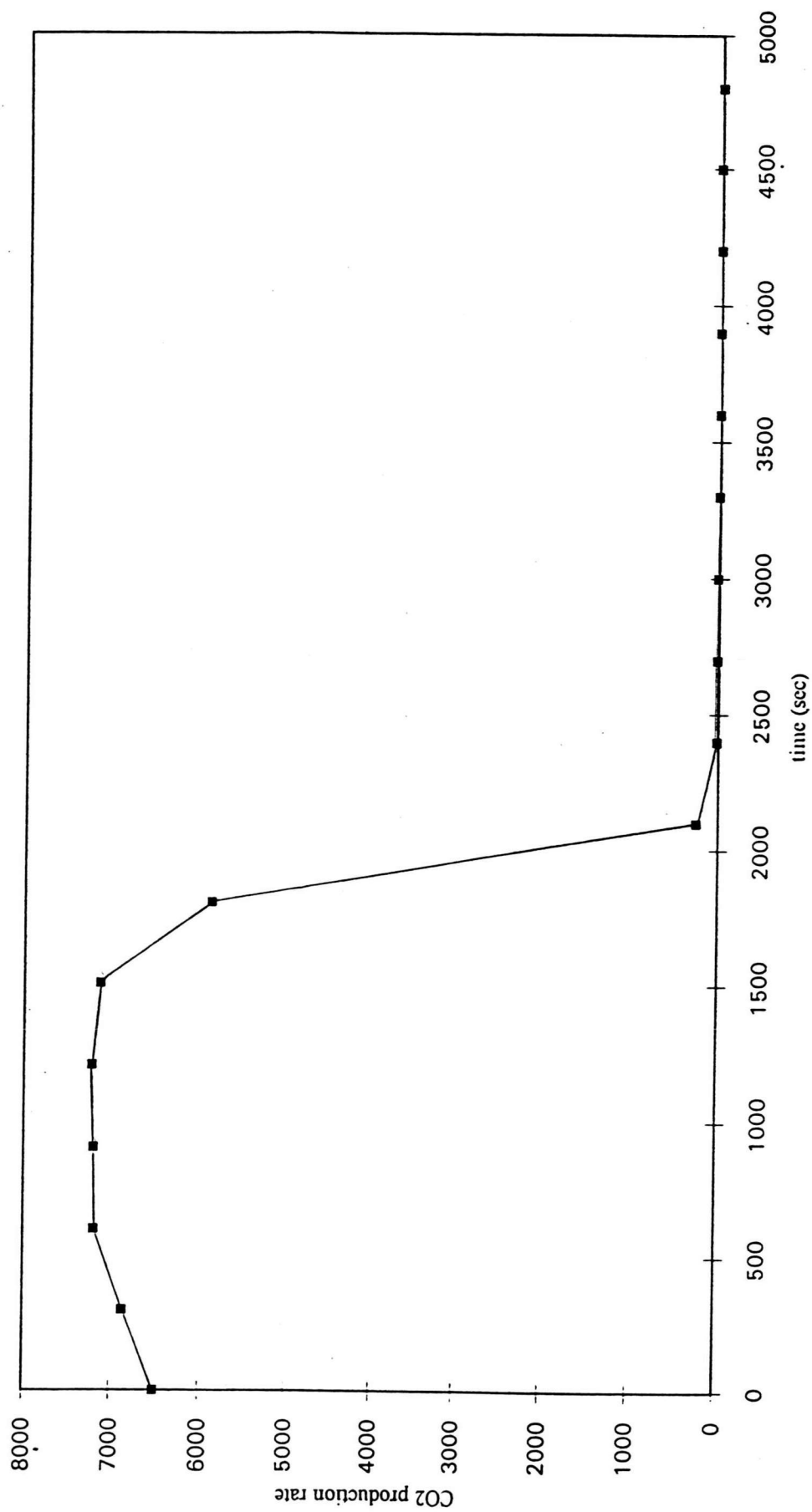


Figure D-31 CO₂ production rate versus time of a coked catalyst burnt at constant temperature (600 °C) for dehydrogenation reaction temperature (650 °C).

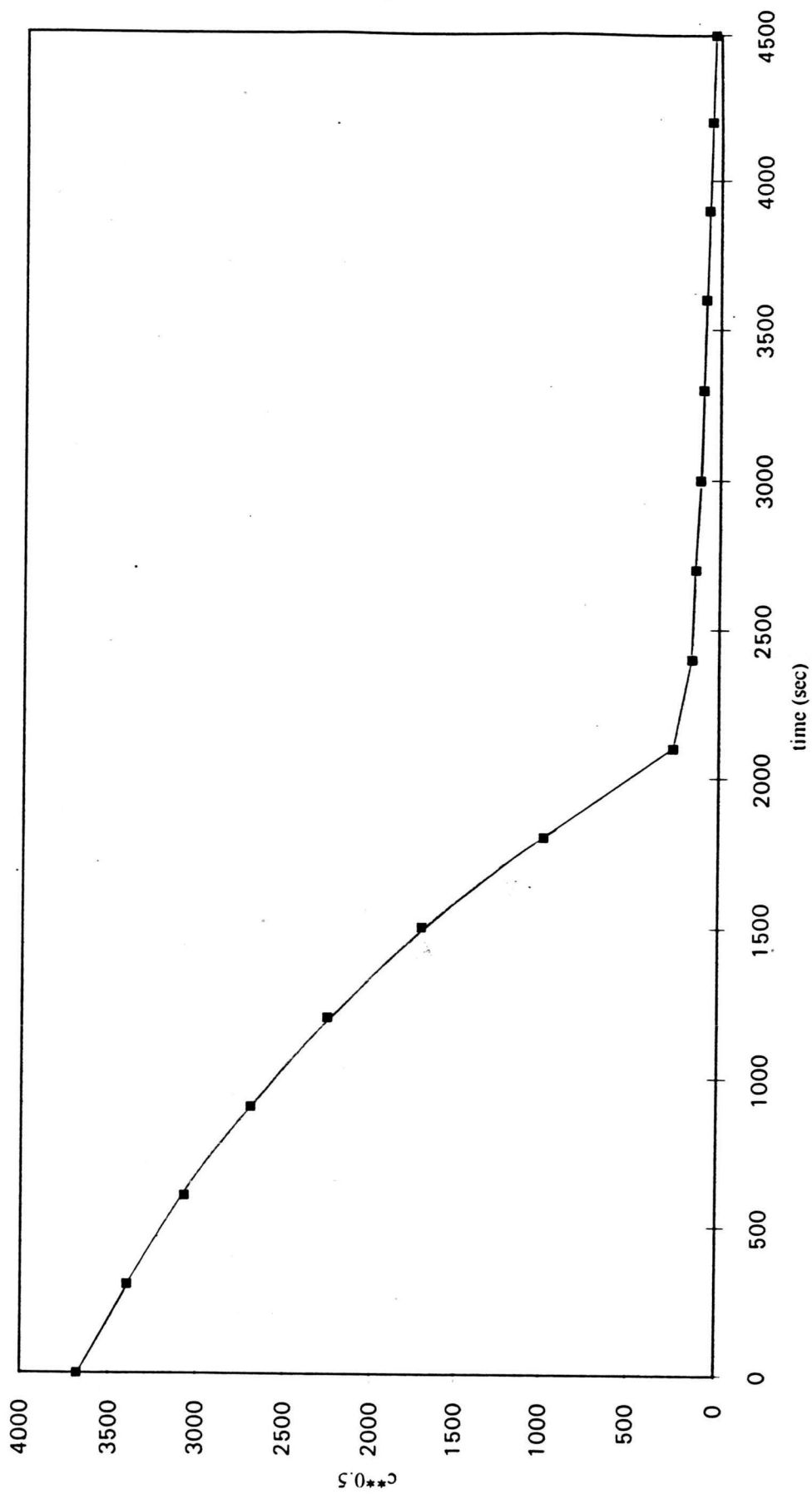


Figure D-32 Plot between $C^{0.5}$ versus time of the results shown in figure D-31.

Table D-21 Data of figure 5.8.

TPO of coke formed at 550 C				
coke 2 = 0.8d6				
coke 3 = 0.3d6				
T(C)	dc2/dt	dc3/dt	dc2 + dc3	dc/sec
55	1.29E-04	0.00E+00	1.29E-04	0.001286
60	2.14E-04	0.00E+00	2.14E-04	0.00214
65	3.51E-04	0.00E+00	3.51E-04	0.003508
70	5.67E-04	0.00E+00	5.67E-04	0.005668
75	9.03E-04	0.00E+00	9.03E-04	0.009033
80	1.42E-03	0.00E+00	1.42E-03	0.014206
85	2.21E-03	0.00E+00	2.21E-03	0.022059
90	3.38E-03	0.00E+00	3.38E-03	0.033841
95	5.13E-03	0.00E+00	5.13E-03	0.051315
100	7.69E-03	0.00E+00	7.69E-03	0.076947
105	1.14E-02	0.00E+00	1.14E-02	0.11415
110	1.68E-02	0.00E+00	1.68E-02	0.167604
115	2.44E-02	0.00E+00	2.44E-02	0.243662
120	3.51E-02	0.00E+00	3.51E-02	0.350874
125	5.01E-02	0.00E+00	5.01E-02	0.500644
130	7.08E-02	0.00E+00	7.08E-02	0.708064
135	9.93E-02	0.00E+00	9.93E-02	0.992935
140	1.38E-01	0.00E+00	1.38E-01	1.38105
145	1.91E-01	0.00E+00	1.91E-01	1.90575
150	2.61E-01	0.00E+00	2.61E-01	2.609828
155	3.55E-01	0.00E+00	3.55E-01	3.547837
160	4.79E-01	0.00E+00	4.79E-01	4.788857
165	6.42E-01	0.00E+00	6.42E-01	6.419808
170	8.55E-01	0.00E+00	8.55E-01	8.549388
175	1.13E+00	0.00E+00	1.13E+00	11.31272
180	1.49E+00	0.00E+00	1.49E+00	14.87683
185	1.94E+00	0.00E+00	1.94E+00	19.447
190	2.53E+00	0.00E+00	2.53E+00	25.27423
195	3.27E+00	0.00E+00	3.27E+00	32.66379
200	4.20E+00	0.00E+00	4.20E+00	41.98511
205	5.37E+00	0.00E+00	5.37E+00	53.68312
210	6.83E+00	0.00E+00	6.83E+00	68.2911
215	8.64E+00	0.00E+00	8.64E+00	86.44534
220	1.09E+01	0.00E+00	1.09E+01	108.9017
225	1.37E+01	0.00E+00	1.37E+01	136.5539
230	1.70E+01	0.00E+00	1.70E+01	170.4549
235	2.12E+01	0.00E+00	2.12E+01	211.8391
240	2.62E+01	0.00E+00	2.62E+01	262.1486
245	3.23E+01	0.00E+00	3.23E+01	323.061
250	3.97E+01	0.00E+00	3.97E+01	396.5203
255	4.85E+01	0.00E+00	4.85E+01	484.7701
260	5.90E+01	0.00E+00	5.90E+01	590.3899
265	7.16E+01	0.00E+00	7.16E+01	716.3338
270	8.66E+01	0.00E+00	8.66E+01	865.9712
275	1.04E+02	0.00E+00	1.04E+02	1043.13

280	1.25E+02	0.00E+00	1.25E+02	1252.14
285	1.50E+02	0.00E+00	1.50E+02	1497.88
290	1.79E+02	0.00E+00	1.79E+02	1785.821
295	2.12E+02	0.00E+00	2.12E+02	2122.069
300	2.51E+02	0.00E+00	2.51E+02	2513.403
305	2.97E+02	0.00E+00	2.97E+02	2967.313
310	3.49E+02	0.00E+00	3.49E+02	3492.017
315	4.10E+02	0.00E+00	4.10E+02	4096.477
320	4.79E+02	0.00E+00	4.79E+02	4790.389
325	5.58E+02	0.00E+00	5.58E+02	5584.153
330	6.49E+02	0.00E+00	6.49E+02	6488.803
335	7.52E+02	0.00E+00	7.52E+02	7515.906
340	8.68E+02	0.00E+00	8.68E+02	8677.396
345	9.99E+02	0.00E+00	9.99E+02	9985.348
350	1.15E+03	0.00E+00	1.15E+03	11451.65
355	1.31E+03	0.00E+00	1.31E+03	13087.6
360	1.49E+03	0.00E+00	1.49E+03	14903.29
365	1.69E+03	0.00E+00	1.69E+03	16906.97
370	1.91E+03	0.00E+00	1.91E+03	19103.99
375	2.15E+03	0.00E+00	2.15E+03	21495.74
380	2.41E+03	0.00E+00	2.41E+03	24078.05
385	2.68E+03	0.00E+00	2.68E+03	26839.4
390	2.98E+03	0.00E+00	2.98E+03	29758.58
395	3.28E+03	0.00E+00	3.28E+03	32801.88
400	3.59E+03	0.00E+00	3.59E+03	35919.54
405	3.90E+03	0.00E+00	3.90E+03	39041.56
410	4.21E+03	0.00E+00	4.21E+03	42072.5
415	4.49E+03	0.00E+00	4.49E+03	44885.21
420	4.73E+03	0.00E+00	4.73E+03	47313.25
425	4.91E+03	0.00E+00	4.91E+03	49141.73
430	5.01E+03	0.00E+00	5.01E+03	50096.21
435	4.98E+03	0.00E+00	4.98E+03	49829.17
440	4.79E+03	0.00E+00	4.79E+03	47903.17
445	4.38E+03	0.00E+00	4.38E+03	43768.84
450	3.67E+03	0.00E+00	3.67E+03	36732.32
455	2.59E+03	0.00E+00	2.59E+03	25887.8
460	9.76E+02	0.00E+00	9.76E+02	9757.037
465	0.00E+00	5.67E+03	5.67E+03	56690.85
470	0.00E+00	5.26E+03	5.26E+03	52625.74
475	0.00E+00	4.78E+03	4.78E+03	47794.04
480	0.00E+00	4.21E+03	4.21E+03	42125.68
485	0.00E+00	3.55E+03	3.55E+03	35543.44
490	0.00E+00	2.80E+03	2.80E+03	27958.69
495	0.00E+00	1.93E+03	1.93E+03	19257.61
500	0.00E+00	9.23E+02	9.23E+02	9225.762
505	0.00E+00	0.00E+00	0.00E+00	0

Table D-22 Data of figure 5.9.

TPO of coke formed at 600 C				
coke 2 = 1.5d6				
coke 3 = 1.5d6				
T (C)	dc2/0.1 m	dc3/0.1 m	dc2 + dc3	dc/min
55	1.98E-04	0.00E+00	1.98E-04	0.001982
60	3.30E-04	0.00E+00	3.30E-04	0.003298
65	5.41E-04	0.00E+00	5.41E-04	0.005407
70	8.74E-04	0.00E+00	8.74E-04	0.008736
75	1.39E-03	0.00E+00	1.39E-03	0.013921
80	2.19E-03	0.00E+00	2.19E-03	0.021892
85	3.40E-03	0.00E+00	3.40E-03	0.033995
90	5.22E-03	0.00E+00	5.22E-03	0.052153
95	7.91E-03	0.00E+00	7.91E-03	0.079082
100	1.19E-02	0.00E+00	1.19E-02	0.118583
105	1.76E-02	0.00E+00	1.76E-02	0.175918
110	2.58E-02	0.00E+00	2.58E-02	0.258296
115	3.76E-02	0.00E+00	3.76E-02	0.375509
120	5.41E-02	0.00E+00	5.41E-02	0.540732
125	7.72E-02	0.00E+00	7.72E-02	0.771545
130	1.09E-01	0.00E+00	1.09E-01	1.0912
135	1.53E-01	0.00E+00	1.53E-01	1.530217
140	2.13E-01	0.00E+00	2.13E-01	2.128343
145	2.94E-01	0.00E+00	2.94E-01	2.936961
150	4.02E-01	0.00E+00	4.02E-01	4.022022
155	5.47E-01	0.00E+00	5.47E-01	5.467597
160	7.38E-01	0.00E+00	7.38E-01	7.380147
165	9.89E-01	0.00E+00	9.89E-01	9.893632
170	1.32E+00	0.00E+00	1.32E+00	13.17557
175	1.74E+00	0.00E+00	1.74E+00	17.43422
180	2.29E+00	0.00E+00	2.29E+00	22.92699
185	3.00E+00	0.00E+00	3.00E+00	29.97029
190	3.90E+00	0.00E+00	3.90E+00	38.95097
195	5.03E+00	0.00E+00	5.03E+00	50.33958
200	6.47E+00	0.00E+00	6.47E+00	64.70559
205	8.27E+00	0.00E+00	8.27E+00	82.73489
210	1.05E+01	0.00E+00	1.05E+01	105.2497
215	1.33E+01	0.00E+00	1.33E+01	133.2311
220	1.68E+01	0.00E+00	1.68E+01	167.8447
225	2.10E+01	0.00E+00	2.10E+01	210.4694
230	2.63E+01	0.00E+00	2.63E+01	262.7293
235	3.27E+01	0.00E+00	3.27E+01	326.5301
240	4.04E+01	0.00E+00	4.04E+01	404.0982
245	4.98E+01	0.00E+00	4.98E+01	498.0255
250	6.11E+01	0.00E+00	6.11E+01	611.3168
255	7.47E+01	0.00E+00	7.47E+01	747.4433
260	9.10E+01	0.00E+00	9.10E+01	910.3999
265	1.10E+02	0.00E+00	1.10E+02	1104.767
270	1.34E+02	0.00E+00	1.34E+02	1335.775
275	1.61E+02	0.00E+00	1.61E+02	1609.381
280	1.93E+02	0.00E+00	1.93E+02	1932.336
285	2.31E+02	0.00E+00	2.31E+02	2312.267
290	2.76E+02	0.00E+00	2.76E+02	2757.755
295	3.28E+02	0.00E+00	3.28E+02	3278.42
300	3.88E+02	0.00E+00	3.88E+02	3884.994
305	4.59E+02	0.00E+00	4.59E+02	4589.406
310	5.40E+02	0.00E+00	5.40E+02	5404.847
315	6.35E+02	0.00E+00	6.35E+02	6345.834

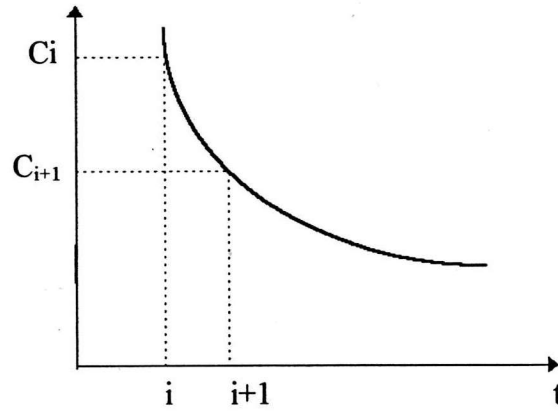
320	7.43E+02	0.00E+00	7.43E+02	7428.253
325	8.67E+02	0.00E+00	8.67E+02	8669.389
330	1.01E+03	0.00E+00	1.01E+03	10087.91
335	1.17E+03	0.00E+00	1.17E+03	11703.85
340	1.35E+03	0.00E+00	1.35E+03	13538.47
345	1.56E+03	0.00E+00	1.56E+03	15614.14
350	1.80E+03	0.00E+00	1.80E+03	17954.08
355	2.06E+03	0.00E+00	2.06E+03	20582.01
360	2.35E+03	0.00E+00	2.35E+03	23521.67
365	2.68E+03	0.00E+00	2.68E+03	26796.17
370	3.04E+03	0.00E+00	3.04E+03	30427.17
375	3.44E+03	0.00E+00	3.44E+03	34433.76
380	3.88E+03	0.00E+00	3.88E+03	38831.08
385	4.36E+03	0.00E+00	4.36E+03	43628.56
390	4.88E+03	0.00E+00	4.88E+03	48827.73
395	5.44E+03	0.00E+00	5.44E+03	54419.5
400	6.04E+03	0.00E+00	6.04E+03	60380.76
405	6.67E+03	0.00E+00	6.67E+03	66670.32
410	7.32E+03	0.00E+00	7.32E+03	73223.85
415	7.99E+03	0.00E+00	7.99E+03	79947.82
420	8.67E+03	0.00E+00	8.67E+03	86712.14
425	9.33E+03	0.00E+00	9.33E+03	93341.33
430	9.96E+03	0.00E+00	9.96E+03	99603.91
435	1.05E+04	0.00E+00	1.05E+04	105199.7
440	1.10E+04	0.00E+00	1.10E+04	109744.7
445	1.13E+04	0.00E+00	1.13E+04	112752.8
450	1.14E+04	0.00E+00	1.14E+04	113614.2
455	1.12E+04	0.00E+00	1.12E+04	111568.7
460	1.06E+04	0.00E+00	1.06E+04	105672.9
465	9.48E+03	0.00E+00	9.48E+03	94756.13
470	7.74E+03	0.00E+00	7.74E+03	77351.09
475	5.15E+03	0.00E+00	5.15E+03	51529.27
480	1.36E+03	0.00E+00	1.36E+03	13599.86
485	0.00E+00	1.72E+04	1.72E+04	171997.8
490	0.00E+00	1.70E+04	1.70E+04	170003.9
495	0.00E+00	1.67E+04	1.67E+04	167112.3
500	0.00E+00	1.63E+04	1.63E+04	163242.5
505	0.00E+00	1.58E+04	1.58E+04	158309.7
510	0.00E+00	1.52E+04	1.52E+04	152224.3
515	0.00E+00	1.45E+04	1.45E+04	144891.4
520	0.00E+00	1.36E+04	1.36E+04	136210.7
525	0.00E+00	1.26E+04	1.26E+04	126076.2
530	0.00E+00	1.14E+04	1.14E+04	114374.5
535	0.00E+00	1.01E+04	1.01E+04	100984.2
540	0.00E+00	8.58E+03	8.58E+03	85772.26
545	0.00E+00	6.86E+03	6.86E+03	68587.47
550	0.00E+00	4.92E+03	4.92E+03	49239.34
555	0.00E+00	2.74E+03	2.74E+03	27404.94
560	0.00E+00	0.00E+00	0.00E+00	0

Table D-23 Data of figure 5,10.

TPO of coke formed at 650 C				
coke 2 = 5.0d6				
coke 3 = 6.0d6				
T (C)	dc2/0.1 m	dc3/0.1 m	dc2 + dc3	dc/dt (m)
55	3.22E-04	0.00E+00	3.22E-04	0.003215
60	5.35E-04	0.00E+00	5.35E-04	0.005351
65	8.77E-04	0.00E+00	8.77E-04	0.008771
70	1.42E-03	0.00E+00	1.42E-03	0.014171
75	2.26E-03	0.00E+00	2.26E-03	0.022582
80	3.55E-03	0.00E+00	3.55E-03	0.035514
85	5.51E-03	0.00E+00	5.51E-03	0.055148
90	8.46E-03	0.00E+00	8.46E-03	0.084603
95	1.28E-02	0.00E+00	1.28E-02	0.128288
100	1.92E-02	0.00E+00	1.92E-02	0.192368
105	2.85E-02	0.00E+00	2.85E-02	0.285376
110	4.19E-02	0.00E+00	4.19E-02	0.419011
115	6.09E-02	0.00E+00	6.09E-02	0.609155
120	8.77E-02	0.00E+00	8.77E-02	0.877184
125	1.25E-01	0.00E+00	1.25E-01	1.251611
130	1.77E-01	0.00E+00	1.77E-01	1.77016
135	2.48E-01	0.00E+00	2.48E-01	2.48234
140	3.45E-01	0.00E+00	3.45E-01	3.452631
145	4.76E-01	0.00E+00	4.76E-01	4.764385
150	6.52E-01	0.00E+00	6.52E-01	6.52459
155	8.87E-01	0.00E+00	8.87E-01	8.869628
160	1.20E+00	0.00E+00	1.20E+00	11.97221
165	1.60E+00	0.00E+00	1.60E+00	16.04964
170	2.14E+00	0.00E+00	2.14E+00	21.37369
175	2.83E+00	0.00E+00	2.83E+00	28.28221
180	3.72E+00	0.00E+00	3.72E+00	37.19278
185	4.86E+00	0.00E+00	4.86E+00	48.61873
190	6.32E+00	0.00E+00	6.32E+00	63.18769
195	8.17E+00	0.00E+00	8.17E+00	81.66307
200	1.05E+01	0.00E+00	1.05E+01	104.9688
205	1.34E+01	0.00E+00	1.34E+01	134.2179
210	1.71E+01	0.00E+00	1.71E+01	170.7445
215	2.16E+01	0.00E+00	2.16E+01	216.1407
220	2.72E+01	0.00E+00	2.72E+01	272.2984
225	3.41E+01	0.00E+00	3.41E+01	341.4559
230	4.26E+01	0.00E+00	4.26E+01	426.25
235	5.30E+01	0.00E+00	5.30E+01	529.7754
240	6.56E+01	0.00E+00	6.56E+01	655.649
245	8.08E+01	0.00E+00	8.08E+01	808.0821
250	9.92E+01	0.00E+00	9.92E+01	991.9603
255	1.21E+02	0.00E+00	1.21E+02	1212.93
260	1.48E+02	0.00E+00	1.48E+02	1477.494
265	1.79E+02	0.00E+00	1.79E+02	1793.113
270	2.17E+02	0.00E+00	2.17E+02	2168.321
275	2.61E+02	0.00E+00	2.61E+02	2612.843
280	3.14E+02	0.00E+00	3.14E+02	3137.72
285	3.76E+02	0.00E+00	3.76E+02	3755.451
290	4.48E+02	0.00E+00	4.48E+02	4480.132
295	5.33E+02	0.00E+00	5.33E+02	5327.604
300	6.32E+02	0.00E+00	6.32E+02	6315.608
305	7.46E+02	0.00E+00	7.46E+02	7463.938
310	8.79E+02	0.00E+00	8.79E+02	8794.598
315	1.03E+03	0.00E+00	1.03E+03	10331.95
320	1.21E+03	0.00E+00	1.21E+03	12102.84
325	1.41E+03	0.00E+00	1.41E+03	14136.77
330	1.65E+03	0.00E+00	1.65E+03	16465.94

335	1.91E+03	0.00E+00	1.91E+03	19125.35
340	2.22E+03	0.00E+00	2.22E+03	22152.82
345	2.56E+03	0.00E+00	2.56E+03	25588.97
350	2.95E+03	0.00E+00	2.95E+03	29477.08
355	3.39E+03	0.00E+00	3.39E+03	33862.89
360	3.88E+03	0.00E+00	3.88E+03	38794.29
365	4.43E+03	0.00E+00	4.43E+03	44320.79
370	5.05E+03	0.00E+00	5.05E+03	50492.86
375	5.74E+03	0.00E+00	5.74E+03	57360.99
380	6.50E+03	0.00E+00	6.50E+03	64974.49
385	7.34E+03	0.00E+00	7.34E+03	73379.89
390	8.26E+03	0.00E+00	8.26E+03	82618.94
395	9.27E+03	0.00E+00	9.27E+03	92726.1
400	1.04E+04	0.00E+00	1.04E+04	103725.3
405	1.16E+04	0.00E+00	1.16E+04	115626.3
410	1.28E+04	0.00E+00	1.28E+04	128419.4
415	1.42E+04	0.00E+00	1.42E+04	142070.1
420	1.57E+04	0.00E+00	1.57E+04	156511.8
425	1.72E+04	0.00E+00	1.72E+04	171637.2
430	1.87E+04	0.00E+00	1.87E+04	187288.2
435	2.03E+04	0.00E+00	2.03E+04	203243.4
440	2.19E+04	0.00E+00	2.19E+04	219203.6
445	2.35E+04	0.00E+00	2.35E+04	234774.3
450	2.49E+04	0.00E+00	2.49E+04	249445.4
455	2.63E+04	0.00E+00	2.63E+04	262566.2
460	2.73E+04	0.00E+00	2.73E+04	273317.3
465	2.81E+04	0.00E+00	2.81E+04	280676
470	2.83E+04	0.00E+00	2.83E+04	283376.5
475	2.80E+04	0.00E+00	2.80E+04	279860.9
480	2.68E+04	0.00E+00	2.68E+04	268220.8
485	2.46E+04	0.00E+00	2.46E+04	246120.9
490	2.11E+04	0.00E+00	2.11E+04	210690.2
495	1.58E+04	0.00E+00	1.58E+04	158312.2
500	8.38E+03	0.00E+00	8.38E+03	83845.63
505	0.00E+00	3.68E+04	3.68E+04	368229.2
510	0.00E+00	3.70E+04	3.70E+04	370179.6
515	0.00E+00	3.71E+04	3.71E+04	371088.4
520	0.00E+00	3.71E+04	3.71E+04	370859.6
525	0.00E+00	3.69E+04	3.69E+04	369392
530	0.00E+00	3.67E+04	3.67E+04	366579.5
535	0.00E+00	3.62E+04	3.62E+04	362310.6
540	0.00E+00	3.56E+04	3.56E+04	356468.2
545	0.00E+00	3.49E+04	3.49E+04	348929.8
550	0.00E+00	3.40E+04	3.40E+04	339566.8
555	0.00E+00	3.28E+04	3.28E+04	328244.5
560	0.00E+00	3.15E+04	3.15E+04	314821.6
565	0.00E+00	2.99E+04	2.99E+04	299150.1
570	0.00E+00	2.81E+04	2.81E+04	281074.5
575	0.00E+00	2.60E+04	2.60E+04	260431.4
580	0.00E+00	2.37E+04	2.37E+04	237047.7
585	0.00E+00	2.11E+04	2.11E+04	210739.1
590	0.00E+00	1.81E+04	1.81E+04	181305.8
595	0.00E+00	1.49E+04	1.49E+04	148524
600	0.00E+00	1.12E+04	1.12E+04	112121.7
605	0.00E+00	7.17E+03	7.17E+03	71694.12
610	0.00E+00	2.61E+03	2.61E+03	26074.95
615	0.00E+00	0.00E+00	0.00E+00	0

E. Calculation Simulation by using explicit Euler's method.



$$\frac{C_{i+1} - C_i}{\Delta t} = k_0 P_{O_2}^m e^{(-E_a/RT)} C_i^{0.5}$$

$$T = 323 + t/12$$

$$= 323 + i \Delta t / 12$$

$$\frac{C_{i+1} - C_i}{\Delta t} = (k_0 P_{O_2}^m) e^{(-E_a/R) * 1/(323+i\Delta t/12)} * C_i^{0.5}$$

$$C_{i+1} = (k_0 P_{O_2}^m) e^{(-E_a/R) * 1/(323+i\Delta t/12)} * C_i^{0.5} \Delta t + C_i$$

F. Published Paper.

This appendix present one published paper which have emerged during this study.

The paper "**Combustion of coke on dehydrogenation catalysts**", was presented in Chemical Engineering Seminar of Thailand (4th) by Chemical Engineering Department, Khon Kaen University, at Kaen Inn Hotel, 20-21 October 1994.

COMBUSTION OF COKE ON DEHYDROGENATION

CATALYSTS

Atchara Saengpoo, Piyasarn Prasertam, Tharathon Mongkhonsi*

Department of Chemical Engineering, Faculty of Engineering,

Chulalongkorn University, Bangkok 10330 Thailand.

* To whom all correspondence should be addressed

Abstract

Experimental evidences suggest that coke can deposit on dehydrogenation catalysts in three forms regardless of catalyst compositions : 1) on metal sites but does not completely cover the sites, 2) on metal sites and completely cover the sites and 3) on support. Three laboratory catalysts for the dehydrogenation reaction of propane to propylene are used in this study. Temperature programmed oxidation (TPO) and constant temperature oxidation reveal that coke type (1) is the easiest that can be removed while coke type (3) is the hardest. Kinetic parameters emerge from this research work can be used in developing mathematical models for catalyst regenerator design and control.

การเผาไหม้ของไค้กบนตัวเร่งปฏิกิริยาดีไฮโดรจีเนชัน

อัจฉรา แสงภู, ปิยะสาร ประเสริฐธรรม, ธราธร มงคลศรี*

ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพฯ 10330

บทคัดย่อ

ผลการทดลองได้แสดงให้เห็นว่า ไค้กสามารถสะสมบนตัวเร่งปฏิกิริยาดีไฮโดรจีเนชันได้ถึง 3 รูปแบบด้วยกัน โดยไม่ขึ้นอยู่กับองค์ประกอบของตัวเร่งปฏิกิริยา คือ 1) สะสมบนโลหะแต่ไม่ได้ปกคลุมผิวโลหะทั้งหมด 2) สะสมบนโลหะและปกคลุมผิวโลหะทั้งหมด และ 3) สะสมบนตัวรองรับ การศึกษากระทำบนตัวเร่งปฏิกิริยาดีไฮโดรจีเนชันของโพรเพนไปเป็นโพรพิลีน ที่ใช้งานในเชิงพาณิชย์และอีก 3 ชนิดที่เตรียมขึ้นในห้องปฏิบัติการ การเผาไค้กโดยควบคุมอัตราการเปลี่ยนแปลงอุณหภูมิ และการเผาไหม้ที่อุณหภูมิคงที่ แสดงให้เห็นว่าไค้กชนิดที่ (1) ถูกกำจัดได้ง่ายที่สุด ในขณะที่ไค้กชนิด (3) ถูกกำจัดได้ยากที่สุดค่า ตัวแปรต่างๆที่จะได้จากการวิจัยนี้สามารถนำไปใช้ในการสร้างแบบจำลองทางคณิตศาสตร์สำหรับการออกแบบหรือควบคุมอุปกรณ์พื้นสภาพตัวเร่งปฏิกิริยา

Introduction

Heterogeneous catalysts are widely used in petrochemical industry. An inevitable phenomenon when a catalyst is used with a hydrocarbon feed stock is the deactivation by the deposition of some carbonaceous compounds, commonly called "coke". Rate of coke deposition on the catalyst surface depends upon several factors *eg* feed stock composition, operating temperature and also catalyst composition. If the deactivation rate is slow, a continuous catalyst regeneration process may not be necessary. Many reactions, however, occur at high temperatures which encourage the formation of coke. This result in rapid deactivation of the catalyst, therefore, a continuous regeneration process is necessitated.

Coke removal can be accomplished by burning the coked catalyst, using a gas mixture containing oxygen, at a suitable temperature over a period of time. It is well known that rapid removal of coke can be achieved by using a high temperature. This condition, however, may deactivate the catalyst by any other mechanisms such as sintering of metal sites or changes of catalyst structure, which are likely to be irreversible processes. On the contrary, the regeneration time required by an operation at a too low temperature may be too long to be economical and may not be able to completely remove all the coke deposit. Therefore, a compromise has to be reached to select a suitable regeneration conditions which is not too mild or too strong. In order to achieve this aim, kinetic parameters those describe the rate of coke combustion should be obtained.

Because reaction mechanism on a heterogeneous catalyst has a tendency to depend upon catalyst composition, whether that reaction is a selective or a nonselective. For this reason, using catalysts with different composition may not effect only the amount of coke that can deposit on the catalyst, but also the composition of coke itself. Hence, it should be very useful if the coke characteristics are known.

Dehydrogenation of propane to propylene is a commercial process that has utilised catalyst. Thermodynamic of this reaction indicates that this reaction requires a high temperature to achieve a high propane conversion. This operating condition, however, also favours the deposition of coke. Consequently, it is unavoidable that the catalyst has to experience the deactivation by the deposition of some carbonaceous compounds.

Initially it was proposed that only two forms of coke could deposit on the catalyst surface *ie.* coke on metal sites and coke on support (1). Temperature programmed oxidation showed that the coke on metal sites could be oxidised at a temperature of 400°C while a higher temperature (*eg* about 500) was necessary to burn the coke on support (1,2). Subsequent experiments (3,4) demonstrated that it also has possibility that up to 3 forms of coke could exist on the catalyst surface. The coke type 1 is suggested to be the coke precursor which deposit on a metal site but does not completely cover the site. The coke type 2 is suggested to be the coke that deposit on a metal site and completely cover that site while the coke type 3 is believed

to be the coke that deposits on the support. However, temperature programmed oxidations show a disagreement on the temperature that the coke type 1 can be burnt off. Amornchantanakorn (3) has demonstrated that this type of coke could be removed by the oxidation at a temperature of only around 100°C while Liu (4) reported that this oxidising temperature was around 350°C. The low oxidation temperature observed (3) was criticised (4) that it was likely to be the reactant, that might still remain on the catalyst surface, rather than the coke precursor that was oxidised.

With all of the expressed reasons, it is believed that a research work is necessary to clarify the situation and to obtain some useful information, especially the kinetic parameters which can be used in mathematical modelling. The dehydrogenation reaction of propane to propylene in a micro reactor is chosen for the preparation of coked catalysts in this research.

Experimental systems

Three types of catalyst are used in this study (Pt/Al₂O₃, Pt-Sn/Al₂O₃ and Pt-Sn-Li/Al₂O₃). The preparation methods of these catalysts are reported elsewhere (3).

The reaction system consists of a micro reactor installed in a tube furnace. The diagram of the system is exhibited schematically in figure 1. The furnace temperature is controlled by a temperature controller. The micro reactor is constructed from a

quartz tube. Further details of the reactor system are already described elsewhere (3). A gas mixture (20% C₃H₈ + 80% N₂) is used as a reactant gas. Coked catalysts were prepared by passing the gas mixture through the catalyst bed which was maintained at a temperature of 600°C for 40 minutes. During the experiment, the reaction temperature is monitored using a thermocouple and a digital temperature indicator. The effluent gas is analysed by a gas chromatography equipped with a flame ionisation detector. Blank runs show that at this operating temperature, the thermal cracking of the reactant gas and/or the reaction between propane and the equipment are insignificant.

After the reaction, the reaction was terminated by purging the reactor with argon gas, in order to preserve the compounds deposited on the catalyst surface. In one experiment, the catalyst was allowed to immediately cool down by the inert gas while in the other experiments the reactor temperature during the purging process was still maintained at 600°C for at least 2 hours, to remove all the reactant that might still remain on the catalyst surface, before the catalyst was cooled down. The purpose of these experimental procedures was to confirm whether the adsorbed reactant contributed to the peak observed at low temperatures during the temperature programmed oxidation or not.

Temperature programmed oxidation of the catalyst was carried out in a quartz tube located in a tube furnace. The furnace temperature was controlled by a microprocessor base temperature controller. Further detail of temperature programmed oxidation system are already described elsewhere(3). A gas mixture consisted of 1% oxygen in helium was used as an oxidising gas. The temperature programmed oxidation process began by heating up the catalyst at a rate of 5°C/min. The oxidation process was performed until the furnace temperature reached 700°C. During the oxidation, the amount of CO₂ in the effluent gas was first analysed when the catalyst temperature reached 50°C, then at an interval of 5 minutes, using a gas chromatography equipped with a gas sampling valve and a thermal conductivity detector.

Results and discussions

Typical temperature programmed oxidation results are illustrated in figure 2. The results clearly exhibited three peaks at temperatures around 110, 450 and 500°C respectively. Comparison between temperature programmed oxidation results obtained from using the catalyst immediately cooled down after the reaction and the catalyst purged for at least 2 hours before being cooled down does not show any significant discrepancy, especially the first peak which locates at 110°C. This result strengthens the hypothesis that the first peak is caused by the burning of the coke precursor rather than the adsorbed reactant. The discrepancy between the location of the peak of the coke type 1 as observed in this research, as well as in the previous

work (3), and that observed by Liu(4) is possibly caused by the difference in the composition of the catalyst and/or the preparation method.

Temperature programmed oxidation results and experimental results obtained from the oxidation at a constant temperature suggest that the coke type 1 should have its chemical composition (C:H ratio) different from the coke type 2 and 3. However, it is arguable whether the coke type 2 and type 3 should have the same chemical composition or not. Liu(4) hypothesised that the coke type 2 and type 3 had the same chemical composition but both were burnt off with different mechanism, because of their locations. On the contrary, one can also express that both types of coke have different chemical composition, therefore, can be burnt off at different temperatures. It is also widely known that during the combustion of coke, the C-H bond can be easily broken (5) when compared with the C-C bond. This phenomenon was confirmed by the appearance of a large amount of water, which was observed in this study, during the oxidation at relatively low temperatures. For this reason, one can not eliminate the coke which can be removed at low temperatures while maintaining the chemical composition (C:H ratio) of the coke still remain on the catalyst surface. However, the experimental results reported by some previous workers (3,6) and obtained in this research imply that the coke type 2 and type 3 should have different chemical composition.

Preliminary kinetic study indicates that the combustion rate of each type of coke can be approximated by the following equation

$$-\frac{dc_i}{dt} = (k_i P_{O_2}^m) c_i^n$$

where c_i is the amount of coke (i), k_i is the rate constant for coke (i), P_{O_2} is the partial pressure of oxygen and m, n are order of reaction with respect to oxygen partial pressure and coke content respectively. The amount of coke remained on the catalyst surface at any time t can be calculated from the amount of CO_2 . Experimental and computational results indicate that the combustion rate is first order with respect to the coke content (*ie.* $n = 1$), regardless of the types of coke. Further experimental and computational results emerge from this study should be available in the near future.

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VITA

Miss Atchara Saengpoo was born in Rayong on July 4, 1971. She recieved her Bachelor of Science Degree in Chemical Technology in major of Chemical Engineering, from the Faculty of Science, Chulalongkorn University in 1993.