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A CALCIUM OXIDE SORBENT PROCESS
FOR BULK SEPARATION OF CARBON DIOXIDE

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E Executive Summary

This research project is investigating the technical feasibility of a high-temperature, high pressure (HTHP) process for the bulk separation of CO_2 from coal-derived gas. The original contract for two years was awarded in September 1989 as a result of solicitation number DE-RA21-89MC26040 entitled "Novel Concepts for Bulk Separation of Gases in Coal Gasification Systems." Two no-cost extensions without a change in the statement of work extended the performance period by six months to March 1992. At that time a two-year contract extension with an enlarged scope of work and additional funding was approved so that the research is now scheduled to end in March 1994.

Phase I research, in which an electrobalance reactor was used to establish the technical feasibility of the regenerable sorbent process, was completed in March 1992 and results have been fully described in earlier quarterly reports. In Phase I, the calcination and carbonation characteristics of three calcium sorbents were studied as a function of calcination and carbonation temperature and pressure, mol fraction CO_2 in the carbonation gas, and carbonation background gas composition. Desirable reaction conditions required for high reactivity and good sorbent durability were determined. Multicycle tests consisting of as many as ten complete calcination and carbonation cycles were completed. Indirect evidence which suggested that the water-gas shift reaction occurred simultaneously with CO_2 removal was found. Occurrence of the simultaneous reactions created the possibility of a direct one-step process for the manufacture of hydrogen from coal-gas while at the same time separating a concentrated stream of CO_2 . The concentrated CO_2 stream could be quite significant if, in the future, environmental regulations restrict atmospheric CO_2 emissions.

Phase II research involves a scale-up from microgram to gram quantities of sorbent and a switch from the electrobalance reactor to a fixed-bed reactor with capability for feed and product gas analysis. By the end of the previous quarter, the fixed-bed reactor had been constructed and commissioned, analytical procedures had been developed, and initial reactor tests involving sorbent calcination followed by carbonation using simple feed gases consisting only of CO_2 in N_2 had been completed.

A number of reaction tests involving more complex feed gas mixtures were completed during the present quarter. Positive proof of the simultaneous occurrence of the water gas shift and carbonation reactions has been obtained, and greater than 99% removal of total carbon oxides (CO and CO_2) has been achieved during the prebreakthrough period of the fixed-bed reactor response. The effect of carbonation temperature, gas space velocity, and feed gas composition has been studied. All experimental results have been qualitatively as expected with total carbon oxide removal being favored by low temperature and low space velocity.

Reaction Tests

By the end of the previous quarter, a number of one-cycle calcination-carbonation tests in which the carbonation gas contained CO_2 in N_2 had been completed. CO_2 breakthrough curves were obtained which proved the ability of the calcined dolomite sorbent to remove large fractions of the CO_2 at reaction conditions of interest. However, gas leaks in the reactor feed and product lines were encountered near the end of the quarter when initial tests involving more complex feed gas mixtures were attempted.

The gas leaks were corrected and a total of 13 tests were completed during the quarter. Reaction conditions for these tests are summarized in Table I. The sorbent precursor in all tests was dolomite having a particle size range of 149-210 μm . The initial mass ranged from 12.3 to 22.0 grams. A new precursor charge was used in all tests except 12 through 15. In that sequence, the sorbent first used in test 11 was reused and subjected to a total of five calcination and carbonation cycles.

The calcination conditions were the same in all tests except for the fact that dolomite ($\text{CaCO}_3 \bullet \text{MgCO}_3$) was the sorbent precursor in all first cycle tests while half-calcined dolomite ($\text{CaCO}_3 \bullet \text{MgO}$) was the precursor in tests 12 through 15. The sorbent precursor at 3.3 atm was heated at a nominal rate of $5^\circ\text{C}/\text{min}$ to 750°C and held at that temperature until calcination was complete. N_2 flowing at 700 sccm was used to sweep away the CO_2 produced during carbonate decomposition. Typical calcination curves showing percent CO_2 in the product gas as a function of time were presented in previous quarterly reports.

The shift and/or carbonation reactions were studied at 15 atm over a temperature range of 550 to 750°C and a space velocity range of 445 to $2280 \text{ hr}^{-1}(\text{stp})$. Gas composition ranged from the simple CO_2 in N_2 to a mixture containing CO , CO_2 , H_2 , H_2O , and N_2 , all of the principle components of a sulfur-free coal gas.

F Fixed Gas Composition

Multiple, and sometimes contradictory, methods of calculating feed gas composition are available. All gases are fed from high pressure cylinders through calibrated mass flow controllers. Water is added as a liquid using a high-pressure positive displacement

TABLE 1. SUMMARY OF REACTION TEST CONDITIONS

Run	10	11	12	13	14	15	16	18	19	20	21	22	23
Sorbent	D	D	D	D	D	D	D	D	D	D	D	D	D
Cycle	1	1	2	3	4	5	1	1	1	1	1	1	1
Initial Mass, g	22.0	14.5	14.5	14.5	14.5	14.5	14.1	13.6	13.7	14.7	13.2	14.4	12.3
Particle Size	149-	149-	149-	149-	149-	149-	149-	149-	149-	149-	149-	149-	149-
Range, μm	210	210	210	210	210	210	210	210	210	210	210	210	210
Calcination Cycle													
Temp., °C	750	750	750	750	750	750	750	750	750	750	750	750	750
Pressure, atm.	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Gas Comp., % N ₂	100	100	100	100	100	100	100	100	100	100	100	100	100
Flow Rate, SCCM	700	700	700	700	700	700	700	700	700	700	700	700	700
Carbonation Cycle													
Temp., °C	550	550	550	550	550	550	550	550	550	650	750	550	550
Pressure, atm	15	15	15	15	15	15	15	15	15	15	15	15	15
Feed Gas Comp., %CO	0	0	0	0	0	11.9	5.6	6.4	5.8	5.6	5.6	15.3	3.9
CO ₂	14.7	17.8	17.1	16.9	17.1	0	0	5.6	0	0	0	5.0	3.9
H ₂	0	0	0	0	0	0	0	4.7	0	0	0	12.2	15.4
H ₂ O	20.1	0	0	0	19.1	19.6	19.9	20.1	20.0	20.0	20.0	28.7	22.9
H ₂	65.2	82.2	82.9	83.1	63.4	68.5	74.5	63.2	74.2	74.4	74.4	38.8	53.9
Flow Rate, SCCM	100	100	100	100	100	100	400	250	250	250	250	244	218
Space Velocity (stp), hr ⁻¹	455	570	570	570	570	570	2280	1425	1425	1425	1425	1392	1243

s) syringe pump. Knowing the flow rates of the individual components, the feed gas
co composition can be directly calculated. Alternately, the composition of the feed gas can
bi be determined by assuming that correct flow rates are obtained from the N_2 flow meter
ai and the H_2O syringe pump, and using the chromatographic analysis of the feed to
d determine the CO , CO_2 and H_2 concentrations. Table II compares the feed gas
ci composition for run 18, in which all five feed components are present, using the two
c calculation methods.

All feed gas compositions listed in Table I are based upon the second method.
T That is, the chromatographic analysis for CO , CO_2 , and H_2 coupled with measured flow
ri rates for N_2 and H_2O . Since the CO , CO_2 , and H_2 concentrations in the reactor product
n must be measured by chromatography, the selected approach means that the calculation
b basis for the feed and product streams is consistent.

F Reactor Response Curves

The form of the fixed-bed reactor response curve depends primarily on the
c composition of the feed gas. Three feed gas categories are represented in Table 1. In
ti tests 10, 11, 12, 13, and 14, CO_2 is the only reactive gas present in the feed and
c carbonation of CaO is the only possible reaction. The feed gas in tests 15, 16, 19, 20,
e and 21 contains only CO and H_2O in N_2 . With no CO_2 in the feed gas, carbonation of
C CaO can occur only as a result of the production of CO_2 via the shift reaction. Finally,
i in tests 18, 22, and 23, the reactor feed contained all of the primary components of a sulfur-
f free coal gas, and both the shift and carbonation reactions may occur simultaneously.

**Table II. Feed Gas Composition for Test 18
Using Two Calculation Methods**

Component	Using All Flow Meters and Syringe Pump		Using N ₂ Flow Meter, Syringe Pump and Chromatograph	
	Mol Fraction	SCCM	Mol Fraction	SCCM
CO	0.06	15.0	0.064	16.0
CO ₂	0.06	15.0	0.056	13.8
H ₂	0.06	12.5	0.047	11.7
H ₂ O	0.20	50.0	0.200	50.0
N ₂	0.63	157.5	0.633	157.0

Figure 1 shows the reactor response curve for test 13 in which the reactor feed consisted of 16.9% CO₂ in N₂. Both the calcination and carbonation phases are shown and zero time corresponds to the beginning of calcination. Since test 13 represented the third cycle of the sorbent first used in test 11, the starting material was half-calcined dolomite (CaCO₃•MgO), and the absence of the initial sharp CO₂ calcination peak is due to the absence of MgCO₃. Decomposition of CaCO₃, which occurred in the 120 to 220 minute time span, began before the final temperature of 750°C was achieved. After calcination was complete at about 220 minutes, the reactor temperature was reduced to 550°C in preparation for the carbonation phase. The high CO₂ concentration in the three samples at about 320 minutes represents a temporary sampling valve switch to permit the feed gas composition to be analyzed.

Carbonation was initiated at 370 minutes when the valves controlling the feed gas flow path were switched from reactor bypass to the reactor inlet. No CO₂ was found in the reactor product for the first 55 minutes of carbonation. CO₂ breakthrough began at $t = 420$ minutes and the CO₂ concentration in the product gas quickly increased as shown in Figure 1. Since the slope of the breakthrough curve is related to the global reaction rate, it is obvious that carbonation is characterized by an initial rapid reaction period followed by an abrupt transition to a slow reaction. This characteristic is consistent with the Phase I electrobalance reactor results.

New small condensers in the reactor product and feed bypass lines were used for the first time in test 13. Previously we had been using condensers having a volume of approximately 500 cm³ which had been constructed for the electrobalance studies. Because CO₂ present in this large dead volume between the reactor outlet and the gas

Figure 1. Fixed-Bed Reactor Response. Test 13

sampling point was "counted" as being removed by the sorbent, significant material balance error resulted. The new condensers had a volume of approximately 50 cm³ which did not eliminate the dead volume, but reduced the magnitude of the problem to one which could be handled by introducing a dead volume correction factor.

Figure 2 shows the reactor response from test 15 in which the reactor feed contained only CO, H₂O, and N₂. For the first time, all components required for the water gas shift reaction were present in the reactor feed. Since no CO₂ or H₂ was fed, the shift reaction must occur before either H₂ or CO₂ can appear in the reactor product. Test 15 is also significant in that the dolomite sorbent precursor originally used in test 11 was subjected to the fifth calcination/carbonation cycle.

CO, H₂O, and N₂ were introduced into the reactor at t = 368 minutes. H₂ began to appear in the reactor product about 30 minutes later, and the H₂ concentration increased to a constant level of about 14.5% (dry basis) in the time period 470 to 530 minutes. Small concentrations of CO were found in the product in the time period 390 to 430 minutes, and an even smaller amount of CO₂ was detected in one product sample at 410 minutes. The concentrations of CO and CO₂ quickly decreased and were below the detection limits of the TCD from 430 to 530 minutes. Breakthrough of CO and CO₂ began at 530 minutes and the H₂ concentration began to decrease at the same time. After approximately 620 minutes, a new steady-state was reached in which the reactor product contained about 9.4% H₂ and CO₂ and 4.1% CO (all dry basis). These concentrations were maintained until the run was terminated after 790 minutes.

The time required for the H₂ concentration to increase to the 14.5% level is attributed to the time required for the reactor feed gas to displace the inert gas in the

Figure 2. Fixed-Bed Reactor Response. Test 15

system volume between the feed gas valve and the product sampling valve. The source of the small amounts of CO and CO₂ during this period is unknown. When only H₂ and N₂ were detected by the TCD, both the shift and carbonation reactions proceeded essentially to completion. During this period the more sensitive FID indicated approximately 200 ppm of CO and 400 ppm of CO₂ in the product gas. The H₂ concentration in the product gas corresponding to complete shift and carbonation reactions would be 14.8%, quite close to the 14.5% experimental value. Breakthrough of CO and CO₂ corresponded to the leading edge of the carbonation reaction front just reaching the end of the sorbent bed, while the second steady-state beginning at about 620 minutes corresponded to essentially complete conversion of CaO to CaCO₃. Only the gas phase shift reaction was possible after this time. The fact that the final CO₂ and H₂ concentrations were equal is consistent with the water gas shift stoichiometry with no CO₂ or H₂ in the feed.

Test 15 was significant for a number of reasons. First, this run provided definite proof that the shift and carbonation reactions would occur simultaneously at reaction conditions of interest. Also, during the prebreakthrough phase on the test, approximately 99.5% of the total carbon oxides (CO + CO₂) were removed from the gas phase. Finally, this test represented the fifth cycle of the dolomite sorbent, showing that sorbent durability achieved in the electrobalance reactor tests may also be achieved in the fixed-bed reactor.

The addition of CO₂ and H₂ to the reactor feed gas produces a reactor response which is similar to that of Figure 2 during the early stages but quite different during the latter stages of the reaction. To illustrate, Figure 3 shows the reactor response for test

Figure 3. Fixed-Bed Reactor Response. Test 23

23 in which all five major components of coal gas were present in the reactor feed. The sorbent precursor was again dolomite which was used for the first time in this test. Only the shift and carbonation phase of the overall test is shown.

Feed gas having the composition shown in Table I was introduced after 306 minutes. The H_2 concentration in the product increased to about 26.5% (dry basis) during the 350 to 400 minute time span; CO and CO_2 concentrations, which were again below the TCD detection limit during this period, were about 300 ppm and 200 ppm, respectively, according to the FID. Total removal of carbon oxides from the gas phase was again about 99.5%, and the measured H_2 concentration of 26.5% was quite close to the 26.4% calculated on the basis of complete conversion of CO and complete removal of CO_2 .

Initial breakthrough of CO and CO_2 at $t = 400$ minutes again corresponded with the decrease in the H_2 concentration in the reactor product. The second steady-state corresponding to depletion of the active sorbent occurred at about $t = 445$ minutes with the reactor product consisting of 3.1% CO, 6.4% CO_2 , and 21.4% H_2 . The high concentration of H_2 in the feed gas retarded the shift reaction and limited the conversion of CO during this period.

Reactor Temperature Response

Both the shift and carbonation reactions are exothermic and the progress of the reaction front through the sorbent bed can be followed by monitoring the movement of the temperature front. Figure 4 shows the response of the four thermocouples, axially-spaced within the sorbent bed, as a function of time during test 22. Thermocouple T2 is

Figure 4. Fixed-Bed Reactor Temperature Response. Test 22

near the entrance to the bed with thermocouple T5 near the exit. This test was chosen for illustration because the combined carbon oxide concentration (20.3%) of the feed gas was highest in this test. Feed gases were introduced at $t = 315$ minutes and the temperature maximum at T2 was observed approximately 15 minutes later. The maximum temperature increase at T2 was approximately 20°C . Higher maximum temperature increases of about 35°C above the set point were observed at 335, 345, and 355 minutes, respectively, at T3, T4, and T5. The T5 temperature maximum at 355 minutes occurred just before CO and CO_2 breakthrough began.

Similar temperature responses were measured in the other tests with the temperature increases less than 35°C because of the lower $(\text{CO} + \text{CO}_2)$ feed concentrations in the other tests.

Dimensionless Response Curves

In addition to the dimensional reactor response curves shown in Figures 1 through 3, response curves based upon dimensionless quantities $FCOX$, X^* , and t^* have been developed. These terms are defined by the following equations.

$$t^* = \frac{F^o (y_{\text{CO}_2}^o + y_{\text{CO}}^o) (t - t_D)}{N_{\text{CaO}}^o} \quad (1)$$

$$FCOX = \frac{(y_{\text{CO}_2} + y_{\text{CO}})F}{(y_{\text{CO}_2}^o + y_{\text{CO}}^o)F^o} \quad (2)$$

$$X^* = \frac{1}{N_{\text{CaO}}^o} \sum_i [F^o (y_{\text{CO}_2}^o + y_{\text{CO}}^o) - F (y_{\text{CO}_2} + y_{\text{CO}})] \Delta t_i \quad (3)$$

Where...

$F^o =$ molar rate of total reactor feed (wet basis)

$F =$ molar rate of total reactor product (wet basis)

$y_{CO_2}^o, y_{CO}^o =$ mol fractions of CO_2 and CO in feed gas (wet basis)

$y_{CO_2}, y_{CO} =$ mol fractions of CO_2 and CO in reactor product (wet basis)
as a function of time

$N_{CaO}^o =$ initial mols of CaO in the reactor

$t =$ time from initiation of the carbonation cycle

$t_D =$ dead volume correction time

$\Delta t_i =$ time increment between chromatograph samples

$t^* =$ dimensionless carbonation cycle time

$FCOX =$ dimensionless breakthrough concentration of total carbon oxides.

$X^* =$ axial average fraction of CaO converted to $CaCO_3$

The performance of an idealized fixed-bed reactor is shown in Figure 5a. If both the shift and carbonation reactions are irreversible and the global rates are infinitely fast, no carbon oxides will appear in the reactor product until all CaO has been converted to $CaCO_3$. $FCOX$ will be a step function when plotted versus t^* . $FCOX = 0$ for $t^* < 1.0$ and $FCOX = 1.0$ for $t^* > 1.0$. X^* will increase linearly with t^* and reach the value $X^* = 1.0$ when $t^* = 1.0$. In an actual reactor, the dimensionless response curves will appear as in Figure 5b. For small t^* , the value of $FCOX$ should approach the equilibrium value. As t^* increases, $FCOX$ will increase because of the finite reaction rates, and the traditional S-shaped breakthrough curve will result. For large t^* , $FCOX$ will approach

(a) Idealized Response

(b) General Response

Figure 5. Dimensionless Fixed-Bed Reactor Response

1.0 as the global rates approach zero. Early in the reaction when essentially all carbon oxides are removed, x^* will be proportional to t^* . As $FCOX$ increases to slope of the x^* versus t^* curve will decrease and x^* will asymptotically approach its final value. Complete conversion of all CaO to CaCO₃ would correspond to an asymptotic value of $x^* = 1.0$. However, based upon Phase I results where complete conversion of CaO was seldom achieved, we would expect the asymptotic value of x^* to be in the range of 0.80 to 0.95, depending on sorbent properties and reaction conditions.

The current problem in utilizing the dimensionless response curves is the unknown value of t_D , the dead volume correction time. Since all shift/carbonation tests have been conducted at 15 atm, t_D should be a strong function space velocity (volumetric feed rate) and a weak function of temperature. Tracer-response tests in the absence of chemical reaction are planned for the near future to help define the proper values of t_D . For illustration purposes, Figure 6 shows the dimensionless response curve for test 23 based upon an estimated value of $t_D = 27$ minutes. Initial breakthrough of carbon oxides occurred at $t^* \sim 0.7$ when $x^* \sim 0.7$. At $t^* = 1.0$, $FCOX \sim 0.65$ and $x^* = 0.92$. When the run was terminated at $t^* = 1.4$, the final values were $FCOX = 0.96$ and $x^* = 0.94$. While these results should be considered as approximate, all of the numbers are reasonable. They confirm our ability to approach 100% fractional removal of carbon oxides during the prebreakthrough period, to obtain high fractional conversion of CaO, and to achieve satisfactory material balance closure for the duration of the test.

Figure 6. Dimensionless Fixed-Bed Reactor Response. Test 23

The Effect of Space Velocity

An increase in the space velocity reduces the gas residence time in the reactor, thereby reducing the time available for both the shift and carbonation reactions to occur. When other reaction variables are held constant, increased space velocity will cause the prebreakthrough concentrations of CO and CO₂ to increase, shorten the duration of the prebreakthrough period, decrease the slope of the breakthrough curve, and, finally, decrease the extent of the shift reaction in the postbreakthrough period.

The latter three results are illustrated in Figure 7 where the CO and CO₂ concentrations are shown as a function of time for tests 16 and 19, having space velocities of 2280 hr⁻¹ and 1425 hr⁻¹, respectively. Other reaction conditions were effectively equal in each test. Both tests resulted in prebreakthrough CO and CO₂ concentrations below the TCD detection limit. However, the more sensitive FID indicated about 100 ppm CO and 220 ppm CO₂ during the prebreakthrough period of test 19 compared to 580 ppm CO and 880 ppm CO₂ in the comparable period of test 16.

The shorter breakthrough time from test 16 is due primarily to the increased CO feed rate at the high space velocity. The reduced residence time also contributes to the earlier breakthrough and is primarily responsible for the lower slope of the breakthrough curve. The reduced residence time is also responsible for the fact that lower CO conversion (higher CO concentration) is observed in the postbreakthrough period of test 16.

Figure 7. Effect of Space Velocity on CO and CO₂ Breakthrough Curves. Tests 16 and 19.

The Effect of Temperature

Since both the shift and carbonation reactions are exothermic, the equilibrium conversion is a decreasing function of temperature. However, the global reaction rate increases with increasing temperature, thereby increasing the chances that equilibrium conditions will be closely approached.

Figure 8 compares the CO and CO₂ breakthrough curves from test 19 at 550°C and test 20 at 650°C. The adverse effect of higher temperature during the prebreakthrough period of test 20 is obvious since the CO₂ concentration during this time is about 0.4%, high enough to be detected by the TCD. This compares to a prebreakthrough CO₂ concentration of about 220 ppm at 550°C, well below the TCD detection limit. The CO concentration during the prebreakthrough is still below the TCD detection limit in both tests, but increased from about 110 ppm in test 19 at 550°C to about 700 ppm in test 20 at 650°C. Overall, the fractional removal of total carbon oxides in the prebreakthrough period decreased from about 99.5% at 550°C to about 95% at 650°. During the postbreakthrough period the experimental conversion of CO at 650°C was higher than at 550°C, even though the equilibrium conversion was lower. At 550°C, the reactor product was relatively far away from shift equilibrium while at 650°C the product composition was close to the equilibrium composition.

In test 21 at 750°C, the prebreakthrough concentrations of both CO and CO₂ were well above the TCD detection limit. The CO₂ concentration increased to about 3% and the CO concentration was about 0.6%. Figure 9 shows the prebreakthrough concentrations of CO and CO₂, as well as the fractional removal of total carbon oxides

Figure 8. The Effect of Temperature on the CO and CO₂ Breakthrough Curves. Tests 19 and 20.

Figure 9. The Effect of Temperature on the Prebreakthrough Concentrations of CO and CO₂ and on the Percent Removal of Total Carbon Oxides

In the prebreakthrough period, as a function of temperature. It is significant to note that the removal of total carbon oxides decreased to about 45% at 750°C.

Approach To Equilibrium

When the global rates of reaction are sufficiently rapid, the composition of the reactor product during the prebreakthrough period should approach the equilibrium composition for the combined shift and carbonation reactions. After breakthrough when essentially all of the CaO has been converted to CaCO₃, the reactor product composition should approach that associated with the shift reaction alone. Comparisons of experimental and equilibrium compositions for each of the tests from Table I are found in Table III for the prebreakthrough period and in Table IV for the postbreakthrough period.

All of the prebreakthrough CO and CO₂ concentrations from Table III are equal to or greater than the equilibrium concentrations. At 550°C the CO experimental concentration ranged from 100 to 700 ppm, depending on feed gas composition. In the single runs at 650 and 750°C the experimental CO concentration were 700 and 8100 ppm, respectively. Experimental H₂ concentrations, which ranged from 6.3 to 41.7%, were, with one exception (run 16), within about 3% of the equilibrium values.

Experimental postbreakthrough compositions in Table IV were, as a general rule, further from equilibrium. For example, the experimental CO composition in test 22 was 12.1% compared to the equilibrium value of 6.7%. Because the shift reaction did not approach equilibrium, both CO₂ and H₂ experimental concentrations were below the equilibrium levels. At 650°C (test 20) the experimental and equilibrium compositions

Table III. Comparison of Experimental and Equilibrium Compositions
During the Prebreakthrough Period (all CO and CO₂
concentrations below 0.1% were determined by FID)

Run	(Mol Percent of Component (Dry-Basis))					
	CO		CO ₂		H ₂	
	Equi.	Exp.	Equi.	Exp.	Equi.	Exp.
10	--	--	0.011	0.014	--	--
11	--	--	0.008	0.061	--	--
12	--	--	0.008	0.065	--	--
13	--	--	0.008	0.028	--	--
14	--	--	0.011	0.047	--	--
15	0.004	0.026	0.009	0.043	15.0	14.5
16	0.0002	0.061	0.010	0.088	7.0	7.6
18	0.001	0.002	0.010	0.028	15.0	15.1
19	0.03	0.001	0.010	0.022	7.2	7.3
20	0.41	0.07	0.150	0.42	6.9	7.0
21	0.006	0.81	1.41	1.6	6.4	6.3
22	0.003	0.07	0.010	0.013	41.5	41.7
23		0.03	0.011	0.023	26.3	26.6

Table IV. Comparison of Experimental and Equilibrium Compositions
During the Postbreakthrough Period

Run	(Mol Percent of Component (Dry-Basis))					
	CO		CO ₂		H ₂	
	Equi.	Exp.	Equi.	Exp.	Equi.	Exp.
10	--	--	18.4	20.5	--	--
11	--	--	17.8	17.4	--	--
12	--	--	17.1	16.8	--	--
13	--	--	16.9	16.1	--	--
14	--	--	22.0	21.3	--	--
15	3.0	4.2	10.4	9.4	10.4	9.3
16	0.63	2.6	5.9	4.1	5.9	4.3
18	2.20	4.4	12.0	10.0	11.0	9.3
19	0.66	2.0	6.1	4.8	6.1	4.8
20	0.93	1.0	5.7	5.6	5.7	5.6
21	1.2	--	4.5	--	5.3	--
22	6.7	12.1	18.4	13.4	27.2	24.2
23	2.0	3.1	7.7	6.4	22.3	21.4

were reasonably close for all components. Test 21 at 750°C was terminated before the postbreakthrough period was reached.

The fact the shift equilibrium was closely approached at the low prebreakthrough concentrations in 550°C runs, but not at the higher postbreakthrough concentrations suggests a possible catalytic effect of CaO, but not CaCO₃, on the shift reaction. Close approach to postbreakthrough equilibrium at 650°C would then be attributed to the increased rate of the thermal shift reaction at the higher temperature. While the possible catalytic effects are largely speculative at this time, additional data to be acquired should confirm or disprove the speculation.

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