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A CALCIUM OXIDE SORBENT PROCESS
FOR BULK SEPARATION OF CARBON DIOXIDE

Contract No. DE-AC21-89MC26366

Quarterly Progress Report 19
January 1994 - March 1994

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April 1994

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EXECUTIVE SUMMARY

This research project is investigating the technical feasibility of a high-temperature, high-pressure (HTHP) process for the bulk separation of CO₂ 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 was re-scheduled to end in March 1994. A third no-cost extension for seven months was approved during the present quarter so that the project completion date is now October 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 CO₂ 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 CO₂ 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 CO₂.

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The concentrated CO₂ stream could be quite significant if, in the future, environmental regulations restrict atmospheric CO₂ 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. Parameters being studied in Phase II are essentially the same as in Phase I. The reactor response is being studied as a function of calcination and carbonation temperature and pressure, composition of the calcination and carbonation feed gas, and space velocity during the carbonation cycle. Multicycle tests are also being conducted to extend the information on sorbent durability.

Previous quarterly reports have described the design, construction, and commissioning of the fixed-bed reactor, development of analytical procedures, and results of a number of tests using dolomite sorbent precursor. During the current quarter, additional tests were carried out to study the effects of calcination gas composition, temperature, and space velocity using the standard dolomite sorbents. Alternate sorbents were tested to provide direct comparison of dolomite and limestone performance. Tests were performed using an empty reactor and reactor packed with commercial shift catalyst to learn more of the characteristics of the shift reaction in the absence of carbonation. Toward the end of the quarter, emphasis changed to sorbent durability and a number of multicycle tests were completed.

REACTION TESTS

Fifteen tests comprising 29 complete calcination/carbonation cycles were completed during the quarter; reaction conditions are summarized in Table 1. These tests

Table 1. Summary of Reaction Test Conditions (January - March 1994)

Test	50	51	53	54	55	56	57	58	60	61	62	63
Sorbent [*]	E	D	D	D	D	D	L	SC	D	MC	D	MC
Cycles	1	2	1	1	1	5	1	1	5	1	5	5
Initial Mass, g	-	13.2	13.2	13.2	13.2	13.2	11.7	9.5	13.2	12.1	13.2	12.1
Particle Size Range, μm	-	149-210	149-210	149-210	149-210	149-210	149-210	149-210	149-210	149-210	149-210	149-210
Calcination Phase												
Temp., °C	-	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
Gas Comp., %N ₂	-	100	100	100	100	100	100	-	100	100	100	100
%H ₂ O	-	0	0	0	0	0	0	-	0	0	0	0
Flow Rate, sccm	-	700	700	700	700	700	700	-	700	700	700	700
Carbonation Phase												
Temp., °C	550	550	550	550	550	650	550	550	600	550	550	550
Pressure, atm	15	15	15	15	15	15	15	15	15	15	15	15
Feed Gas Comp.												
%CO	5.6	5.6	7.0	6.6	7.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
%CO ₂	0	0	3.3	3.1	3.6	0	0	0	0	0	0	0
%H ₂	0	0	5.0	4.6	5.4	0	0	0	0	0	0	0
%H ₂ O	20.0	20.0	21.2	26.4	15.2	20.0	20.0	20.0	20.0	20.0	20.0	20.0
%N ₂	74.4	74.4	63.5	59.3	68.2	74.4	74.4	74.4	74.4	74.4	74.4	74.4
Flow Rate, sccm	250	250	250	250	250	250	250	250	250	250	525	250
Space Velocity (stp), hr ⁻¹	1425	1425	1425	1425	1425	1425	1425	1425	1425	1425	3000	1425

*Sorbent E - empty reactor, no sorbent

D - dolomite

L - limestone

SC - commercial shift catalyst

MC - marble chips

provided additional information on the effects of carbonation temperature, gas composition and flow rate, and on the nature of the shift reaction at reaction conditions where carbonation was not occurring. Multicycle durability of the sorbent was studied at a variety of reaction conditions. The following discussion is organized according to these topics.

The Nature of the Shift Reaction

Experimental results leave no doubt that the shift reaction occurs over the range of reaction conditions studied. During the prebreakthrough period both the shift and carbonation reactions are sufficiently fast that greater than 99% removal of total carbon oxides has been routinely achieved over a range of reaction conditions. During the postbreakthrough period, when the carbonation reaction has effectively ended, the shift reaction still occurs to some extent. Without the ability to remove CO_2 from the gas phase, the extent of the shift reaction is, of course, limited by equilibrium. Although its occurrence is definite, the driving force for the shift reaction is not clear. One possibility is that the reaction is strictly a homogenous gas phase reaction. In commercial operation, a heterogeneous catalyst is required to increase the rate of the shift reaction to values of interest. But commercial shift reactors operate at least 150°C below the temperature of primary interest in this project. The shift reaction may also occur as the result of a heterogeneous catalyst in this study. If so, the question immediately arises as to what is the nature of the catalyst. With the standard dolomite sorbent, at least three chemical species which might serve to catalyze the reaction are present -- CaO , CaCO_3 , and MgO . MgO has been reported in the literature to be a shift catalyst, but we have found no claims that either CaO or CaCO_3 serve as shift catalysts. Another possibility which

should not be overlooked is the possible catalytic effect of the stainless steel reactor walls and/or the porous stainless steel disks used to separate the sorbent sections.

In an attempt to shed additional light on this question, a number of tests were carried out in which other materials were substituted for the standard dolomite sorbent. In one test (test 50) no packing was used so that shift reaction in this case would necessarily be the result of the homogeneous reaction and/or the catalytic effect of stainless steel. In another test (test 49 completed in the previous quarter) Al_2O_3 was substituted for dolomite packing. To the best of our knowledge, the literature contains no references to Al_2O_3 serving as a shift catalyst. Commercial iron-cobalt shift catalyst obtained from United Catalysts, Inc. was used in test 58. It should be emphasized that the reaction temperature for test 58 was some 200°C above the normal operating temperature of the catalyst. Finally, the limestone and marble chips used in tests 57 and 61, respectively, provide information when CaO and CaCO_3 were present, but without the MgO component of dolomite.

When the reactor was packed with active CO_2 sorbent, the extent of the shift reaction was calculated using measured CO concentrations in the postbreakthrough period. With no sorbent present to remove CO_2 , only the shift reaction occurred and the reactor response, as shown in Figure 1 for the empty reactor test 50, was independent of time after the initial unsteady state period.

Unfortunately, the tests did little to clarify the picture. As shown in Figure 2 the shift reaction occurred to at least some extent in all tests. The fractional CO conversion ranged from 0.26 in the empty reactor to 0.87 in the reactor packed with Al_2O_3 . The latter result was particularly unexpected since no reference to catalysis by Al_2O_3 is known. The similar performance of dolomite and limestone (tests 51-1 and 57) is also surprising since

Figure 1. Component Breakthrough Curves in the Empty Reactor Test

Figure 2. Fractional Extent of the Shift Reaction Using Various Reactor Packings

the MgO component of the dolomite is reported to have shift catalytic activity. However, the composition of the limestone is not known and it is possible that impurities acted as shift catalysts. Overall, it does appear that heterogeneous catalysis is responsible, at least in part, for the shift reaction, but it is not possible to attribute the catalytic effect to a single component.

Results of the multicycle tests using dolomite further complicate the postbreakthrough analysis. As shown in Figure 3, the postbreakthrough concentrations of CO₂ and H₂ decrease while the CO concentration increases with cycle number. This suggests that the extent of the shift reaction decreases with cycle number, a result which is consistent with a heterogeneous catalytic mechanism with gradual catalyst deactivation. However, the results provide no further information to pinpoint either the material responsible for catalysis or the cause of the deactivation.

The results from Figure 3 also suggest the presence of a secondary reaction in which CO₂ is consumed and additional CO is formed. A possible stoichiometry is

If only the shift reaction occurs, the CO₂ and H₂ concentrations in the product should be equal. Instead, the H₂ concentration is somewhat larger. This result is not limited to test 62 (Figure 3) but has been observed in a number of other tests as well. Other evidence for the above reaction also exists. At times during the calcination cycle, small quantities of CO have been detected even though CO₂ should be the only calcination product. The source of carbon could be either from the stainless steel or from small amounts of carbon deposited from the gas phase during some stage of the reaction. Deposited carbon could also be cause of the catalyst poison.

Figure 3. Postbreakthrough CO, CO₂, and H₂ Concentration as a Function of Cycle Number in Test 62

Although these results during the postbreakthrough period are of interest, they are less important to the overall project than are the results during the prebreakthrough period. These results are discussed in the following sections.

ALTERNATE SORBENTS

Limestone sorbent precursor, which is primarily CaCO_3 , has a larger CO_2 capacity than does dolomite because of the presence of inert MgCO_3 in the latter. Two single-cycle tests (57 and 61) were completed during the quarter using two different limestone sources. The exact composition of neither limestone is available. Calcination results suggest that the limestone used in test 57 contained significant concentrations of impurities while test 61 calcination results suggest that the CaCO_3 content of the marble chips was close to 100%. These conclusions were based on the measured amount of CO_2 liberated during calcination.

Standard shift/carbonation reaction conditions were used in each test and results are compared with dolomite results at the same conditions in Figure 4, where the fractional removal of total carbon oxides (based on TCD analysis) is plotted as a function of time. Effectively complete carbon oxide removal was achieved during the early stages of the reaction in all three tests. Initial breakthrough with limestone (test 57) began after about 50 minutes compared to 100 minutes with dolomite and 130 minutes with marble chips. The slope of the limestone breakthrough curve was also much lower, and reaction was not complete until 225 minutes of total elapsed time. The slopes of the breakthrough curves using dolomite and marble chips were similar, with only about 40 minutes from initial breakthrough to complete reaction. The longer time to initial breakthrough using marble chips is simply a reflection of the increased capacity of the high calcium marble

Figure 4. Comparison of CO₂ Breakthrough Curves Using Limestone, Marble Chips, and Dolomite Sorbents

chips compared to dolomite. When the marble chips and dolomite results are compared on a dimensionless time basis (which eliminates the capacity differences) as in Figure 5, we see that the calcium in dolomite is more accessible to the CO_2 . Initial breakthrough did not occur until approximately 80% of the calcium in dolomite had reacted, while initial breakthrough with marble chips occurred at about 68% calcium conversion.

Because of the high CO_2 capacity and relatively favorable first-cycle reactivity, a five-cycle test (test 63) was conducted at standard reaction conditions using marble chips as the sorbent precursor. Figure 6 compares the CO and CO_2 breakthrough curves from cycles 1 and 5 (using both the FID and TCD analyzers). A prebreakthrough steady-state was reached in cycle 1 with CO concentration in the range of 30 to 40 ppm and CO_2 concentration of about 200 ppm. These concentrations, which correspond to 99.7% carbon oxide removal, compare favorably with the prebreakthrough concentrations obtained using dolomite sorbent precursor at the same reaction conditions. By the fifth cycle, however, no steady-state postbreakthrough period was observed. Instead, both the CO and CO_2 concentrations increased continuously after the reaction was initiated.

Poor multicycle durability of pure CaCO_3 sorbent precursors was observed in Phase I of this study, and the results shown in Figure 6 simply confirm that observation. Further evidence of the more rapid deterioration of the high CaCO_3 sorbent compared to dolomite is shown in Figure 7 where the dimensionless time, t^* , at which the CO and CO_2 concentrations in the reactor product reached 100 and 500 ppm, respectively, is plotted versus cycle number. Data from earlier multicycle test 27 using dolomite is included for comparison. The negative slopes of each of the four lines indicate poorer performance of both sorbents in each succeeding cycle. Although first-cycle times are comparable,

Figure 5. Comparison of CO_x Breakthrough Curves Using Marble Chips and Dolomite Sorbents^x on the Basis of Dimensionless Time

Figure 6. CO and CO₂ Breakthrough Curves from the First and Fifth Cycles of Test 63 Using Marble Chips Sorbent

Figure 7. Comparison of the Multicycle Deterioration of Dolomite (Test 27) and Marble Chips (Test 63)

the performance of the marble chips decreases more rapidly and the superior durability of the dolomite is clearly evident.

RESULTS USING DOLOMITE

Three single-cycle tests (tests 53, 54, and 55) in which the reactor feed contained all major constituents of a coal gas but with varying ratios of H₂O to CO were completed during the quarter. The base composition for each test was:

CO	-	8.0%
CO ₂	-	3.8%
H ₂	-	5.6%
H ₂ O	-	10.6%
N ₂	-	72.0%

Except for the large N₂ concentration, the ratios of CO, CO₂, H₂ and H₂O are representative of a Texaco gas. Sufficient additional H₂O was then added to provide molar ratios of H₂O to CO equal to 2, 3, and 4, with the final overall feed gas compositions shown in Table I.

The breakthrough curve for test 53 (3 mol H₂O per mol CO) as determined by the thermal conductivity detector is shown in Figure 8. The total CO_x molar feed rate was approximately 85% greater than the CO_x feed rate associated with the standard gas composition. In spite of the larger feed rate, a prebreakthrough steady-state with CO and CO₂ concentrations below the TCD detection limit was established. The H₂ concentration during this period was effectively constant at 15.2%, which is reasonably close to the value of 15.9%, which was calculated by material balance assuming complete conversion

Figure 8. CO, CO₂, and H₂ Breakthrough Curves from Test 53

of CO and complete removal of CO₂. Similar prebreakthrough steady states were achieved in tests 54 and 55.

The prebreakthrough CO and CO₂ concentrations as determined by the flame ionization detector for these three runs are plotted versus the H₂O to CO ratio in Figure 9. Equilibrium concentrations are shown for reference purposes. CO concentration decreased significantly as the H₂O to CO ratio increased from 2 to 3; a further small concentration decrease occurred when the ratio was increased to 4. The CO₂ concentration was relatively constant at each of the feed gas compositions. The prebreakthrough concentrations from Figure 9 are appreciably higher than obtained in previous tests at the same H₂O to CO ratios but with lower concentrations of total CO_x in the feed gas. However, the fractional removal of total carbon oxides was effectively constant, varying only from 0.996 to 0.997 in the six tests.

It appears, therefore, that the addition of CO₂ and H₂ to produce a feed gas containing all principle components of coal gas does not adversely affect the fractional removal of carbon oxides during the first shift/carbonation cycle. Fractional removals exceeding 0.995 were achieved over a reasonably wide range of gas compositions at the operating conditions of 550°C, 15atm, and a space velocity of 1425hr⁻¹. A multicycle test using the more complex synthetic coal gas feed composition is planned for the next quarter.

The remaining tests using dolomite completed during the quarter investigated the effect of shift/carbonation temperature and space velocity over five complete cycles. Tests 56 and 60, coupled with earlier test 27, provide a series of five-cycle tests in which the shift/carbonation temperature was varied while standard conditions were used for all other reaction parameters. A prebreakthrough steady-state was achieved in all cases and

Figure 9. Prebreakthrough CO and CO₂ Concentrations as a Function of the H₂O to CO Ratio of the Feed Gas

prebreakthrough CO and CO₂ concentrations as a function of cycle number are shown in Figures 10 and 11, respectively. At both 550°C and 600°C, the prebreakthrough concentrations were reasonably constant as the number of cycles increased. The variation in the concentrations of both components at 650°C is attributed, at least in part, to analytical uncertainty. These concentrations, on the order of 1000 to 6000ppm (0.1 to 0.6%) are difficult to analyze with precision. The lower concentration limit for the TCD is about 5000ppm while the upper concentration limit for methanation and FID analysis is about 1000ppm. Although the quantitative values at 650°C are somewhat uncertain, the results suggest improved performance as the number of cycles increases. The increase in prebreakthrough concentrations with increasing temperature reflects the expected effect of temperature on the equilibrium of the combined reactions.

Figure 12 shows the fractional removal of total carbon oxides, FCOX, during the prebreakthrough period as a function of temperature period as a function of temperature and cycle number. At 550°C, FCOX was equal to 0.996 in each of the five cycles. At 600°C, FCOX varied between 0.979 and 0.986, while at 650°C, FCOX increased from 0.904 in cycle 1 to 0.941 in cycle 5. The apparent increase at 650°C is due primarily to the decreasing CO₂ concentrations shown in Figure 11.

While the relatively constant prebreakthrough concentration results are quite positive, some deterioration in sorbent performance with cycle number was observed. In general, the duration of the prebreakthrough period decreased with increasing cycle number. This is shown in Figures 13 and 14. In Figure 13, fractional carbon oxide removal (based upon TCD analysis) is plotted versus dimensionless time for cycles 1 and 5 of test 56 (650°C). In cycle 1, active breakthrough occurred over the range of t^* values between 0.9 and 1.2, while in cycle 5 breakthrough began at $t^* \sim 0.7$. Another measure

Figure 10. Prebreakthrough CO Concentration as a Function of Temperature and Cycle Number

Figure 11. Prebreakthrough CO₂ Concentration as a Function of Temperature and Cycle Number

Figure 12. Fractional Removal of Total Carbon Oxides as a Function of Temperature and Cycle Number

Figure 13. Fractional Removal of Total Carbon Oxides During the First and Fifth Cycles of Test 56

Figure 14. CO and CO₂ Breakthrough Curves From the First and Fifth Cycles of Test 60

of sorbent deterioration is that the final conversion of CaO to CaCO₃ decreased from 0.89 in cycle 1 to 0.78 in cycle 5.

In Figure 14, CO and CO₂ breakthrough curves, using combined FID and TCD results, from the first and fifth cycles of test 60 (600°C) are plotted versus dimensionless time. Prebreakthrough CO concentrations were approximately constant at 400ppm in both cycles, but the CO concentration reached 1000ppm at $t^* = 0.96$ in cycle 1 and at $t^* = 0.76$ in cycle 5. The prebreakthrough CO₂ concentration was actually lower in cycle 5, 570ppm versus 890ppm, but the duration of the CO₂ prebreakthrough period was shorter in the fifth cycle.

The deterioration in performance with increasing cycle number was most severe at 650°C. This is illustrated in Figure 15 where the dimensionless time at which the fractional carbon oxide removal decreased to 70% is plotted versus cycle number. At 650°C this occurred at $t^* = 0.99$ in the first cycle, but at $t^* = 0.78$ in the fifth cycle. At 600°C, the decrease was from 0.99 in cycle 1 to 0.87 in cycle 5. All values of t^* at 550°C were somewhat lower but deterioration was moderate, from $t^* = 0.83$ in cycle 1 to $t^* = 0.75$ in cycle 5. These lower values of t^* at 550°C are the result of the achievable fractional conversion of CaO being lower at the low temperature. For example, the final fractional conversions of CaO for the first cycles of the three tests were 0.84, 0.99, and 0.89 at 550, 600, and 650°C, respectively. By the fifth cycle, the final fractional conversions were 0.80, 0.89, and 0.78.

In test 62, dolomite was tested over five cycles at the larger space velocity of 3000hr⁻¹ (STP), more than double the standard value of 1425 hr⁻¹ (STP). Standard values were used for the other reaction parameters. Previous single-cycle tests at the larger space velocity showed only a small increase in prebreakthrough CO and CO₂

Figure 15. Sorbent Deterioration in Multicycle Tests as a Function of Temperature

concentrations; the objective of the multicycle test, therefore, was to determine the effect of the larger space velocity on sorbent durability.

CO breakthrough curves based upon the combined FID and TCD analyzers for the five cycles are shown in Figure 16. Because of the large space velocity there is little evidence of a prebreakthrough steady state; instead, CO concentrations increased continually with time. The important result from Figure 16 is that breakthrough performance in cycles 2 through 5 was quite similar; little or no deterioration in sorbent performance occurred after the first cycle. CO concentrations during the early stages of the reaction were in the range of 10 to 40ppm, and are only marginally larger than the prebreakthrough CO concentrations found in each cycle of the comparable test at 1425 hr^{-1} (STP) space velocity.

The fact that little or no deterioration in sorbent performance occurred after the first cycle is emphasized in Figure 17 where the dimensionless times required for the CO and CO₂ concentrations in the product gas to reach 100ppm and 500ppm, respectively, are plotted versus cycle number. Comparable results from test 27 at 1425 hr^{-1} (STP) space velocity are included for comparison purposes. Except for the fact that the decrease between cycles 1 and 2 was more significant at 3000 hr^{-1} (STP), the overall results for the two tests are quite similar. Small improvements in performance actually occurred in test 62 between cycles 3 and 4, and between cycles 4 and 5. Thus, we conclude that increased space velocity does not have a negative effect on sorbent durability.

STRUCTURAL PROPERTY MEASUREMENTS

At the conclusion of two tests (51-2 and 56-5), sorbent was removed from each of the four axial sections of the reactor and pore volume and pore size distribution were

Figure 16. CO Breakthrough Curves for the Five Cycles of Test 62

Figure 17. Dimensionless Times Required for the CO and CO₂ Concentrations to Reach 100 and 500 ppm as a Function of Space Velocity and Cycle Number

measured using the mercury porosimeter. Calcination in test 51 was conducted in a nitrogen atmosphere, which according to previous measurements, produced significantly smaller pores than when calcination was carried out in a $\text{H}_2\text{O}/\text{N}_2$ mixture. The shift/calcination phase of cycle 2 was purposely terminated at $t^* = x^* \sim 0.4$ to provide an axial distribution in the extent of carbonation. Roughly speaking, carbonation in the first (top) section should approach completeness with decreasing extents of carbonation in sections 2 and 3 and essentially no carbonation in section 4 (bottom).

Pore size distribution curves as well as the pore volume for each section are shown in Figure 18 (a through d). Equivalent data from an earlier test in which the calcination atmosphere was 60% $\text{H}_2\text{O}/\text{N}_2$ are included for comparison. All samples show a clear difference in the pore size distributions, with the $\text{H}_2\text{O}/\text{N}_2$ calcination atmosphere producing pores which are approximately twice as large as the pores produced in N_2 . Total pore volumes were reasonably similar in each atmosphere, and the pore volume decreased from top to bottom in accordance with the expected variation in extent of carbonation. The range of pore diameters in each of the four sections from test 51 was from approximately 0.05 to 0.3 microns with the peak in the distribution curve dropping from about 0.18 microns at minimum carbonation (bottom section) to 0.1 microns at maximum carbonation (top section).

Similar porosimetry tests were carried out following the fifth complete cycle of test 56 which utilized the higher 650°C shift/carbonation temperature. The overall fractional carbonation at the end of the fifth cycle was 0.77 and the degree of carbonation should be relatively independent of axial position. Porosimetry test results are presented in Figure 19 (a through d). Pore volumes in all sections are considerably lower than those presented in Figure 18. The lower pore volumes are consistent with both the higher

Figure 18. Pore Volume and Pore Size Distribution Curves for Partially Carbonated Sorbent Showing the Effect of Calcination Atmosphere and Axial Position in the Reactor

Figure 19. Pore Volume and Pore Size Distribution Curves From Axial Sections Following the Fifth Cycle of Test 56.

reaction temperature and the fact that the reaction was carried out until carbonation was essentially complete. In all four sections, the pore volume was in the range of 0.02 to 0.03 cm³/g; no distribution curve was visible in the two top sections, and only small peaks in the 0.2 to 0.3 μm diameter range were present in the bottom sections.

The low pore volume after five complete cycles is consistent with the reaction results (see Figure 15) which show large deterioration in performance after five cycles at the 650°C temperature. Sintering is the likely reason for the low pore volumes.

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