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A Combined Catalyst and Sorbent for Enhancing Hydrogen Production from Coal or Biomass[†]

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Future large-scale production of H_2 for use as a clean fuel will likely depend upon gasifying coal or biomass followed by steam reforming the resulting gas mixture and separating the CO_2 byproduct. The process of steam reforming and CO_2 separation can be greatly simplified by utilizing a new material that combines a reforming catalyst with a sorbent for CO_2. Such a material was prepared in the form of small pellets with cores made of calcium and magnesium oxides and shells made largely of alumina impregnated with a nickel catalyst. Subsequent laboratory performance tests of the material showed that CO, CH_4, and toluene, which are representative products of gasification, were largely converted to H_2 by reacting the material with steam in the presence of the catalyst/sorbent, so that CO_2 was absorbed as it was produced. The sorbent was easily regenerated by raising its temperature, which made it possible to reuse the catalyst/sorbent repeatedly.

1. Introduction

The production of hydrogen from coal or biomass involves gasification followed by several steps to clean, convert, and separate a multicomponent gas mixture. Although the composition of the gas produced by gasification will vary depending upon the feedstock, method employed, and operating conditions, the principal components of the gas will include H_2, CO, CO_2, CH_4, and H_2O.[1,2] The gas will also contain some H_2S, tar, and dust, which are removed in an initial cleaning step. This step is followed by steam reforming of methane over a nickel catalyst at 800−870 °C in accordance with the following reaction:

$$CH_4 + H_2O \leftrightarrows 3H_2 + CO \qquad \Delta H_{25\,°C} = 210 \text{ kJ/mol} \quad (1)$$

Next, the CO in the mixture is reacted with steam by means of the water gas shift reaction:

$$CO + H_2O \leftrightarrows H_2 + CO_2 \qquad \Delta H_{25\,°C} = -42 \text{ kJ/mol} \quad (2)$$

Because this exothermic reaction is severely limited by thermodynamic equilibrium, it is conducted at the lowest possible temperature consistent with reaction kinetics. Therefore, it has been common practice to conduct reaction 2 in two stages using an iron oxide/chromium oxide catalyst in the first stage, operating at 350−450 °C, and a copper−zinc oxide catalyst in the second stage, operating at 200−215 °C. These steps are followed by solvent scrubbing to remove CO_2, leaving nearly pure H_2.

It has been proposed to replace this complex multistep process with a much simpler process, which would conduct reactions 1 and 2 in a single step using a mixed bed of catalyst and sorbent particles, with the sorbent being capable of removing CO_2 from the reaction mixture and driving reaction 2 toward completion. Excellent experimental results have been achieved by employing either calcium oxide or a potassium-carbonate-promoted hydrotalcite as an absorbent together with a crushed commercial nickel-based reforming catalyst.[3−6] When calcium oxide has been employed, the following reaction takes place:

$$CaO + CO_2 \leftrightarrows CaCO_3 \qquad \Delta H_{25\,°C} = -175 \text{ kJ/mol} \quad (3)$$

It is apparent that the heat generated by reactions 2 and 3 essentially balances the heat absorbed by reaction 1; therefore, in theory, an adiabatic reactor can be employed. Also, when we minimize the equilibrium limitation, reaction 2 can be conducted at a higher temperature with a less active catalyst, and excellent results have been achieved by using a nickel catalyst for both reactions 1 and 2. Furthermore, reaction 2 has been shown to proceed rapidly at 550 °C, with only an oxide of calcium, magnesium, or aluminum being present, which suggests that any of these materials may also catalyze the reaction.[7,8]

The preceding experimental results provided the inspiration for the development of a novel combined catalyst and sorbent,

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which makes it possible to conduct all three of the preceding reactions within the same pellet of material consisting of a sorbent core encased in a strong, porous shell that serves as a catalyst support. This approach not only reduces the number of physically separate materials required but also provides a practical means for supporting a sorbent material that is structurally weak and friable and not easily handled without serious decrepitation. Furthermore, in situations where only reactions 2 and 3 are required, the calcium-based sorbent may well serve as the only catalyst needed. Alternatively, because the shell is likely to be made of aluminum oxide, it may also prove to be an adequate catalyst.

Core-in-shell sorbent pellets without a catalyst were developed initially to desulfurize hot coal gas.[9−12] Each spherical pellet consisted of a CaO core surrounded by a protective shell made largely of alumina. Because alumina is widely used as a catalyst support, the core-in-shell pellets seemed well-suited for use as both a catalyst support and sorbent for CO_2. Therefore, it seemed likely that a serviceable material could be developed by impregnating the previously developed core-in-shell pellets with nickel nitrate, followed by calcination to decompose the salt, and then reduction with H_2 to form a dispersion of elemental nickel within the shell material. While this generally proved to be the case, the activity of the resulting catalyst was somewhat limited for reforming hydrocarbons, so that the catalyst was capable of reforming propane but not methane at 650 °C. The low activity was apparently the result of making the pellet shells out of α-alumina with a low surface area, which resulted in a poorly dispersed catalyst. It was subsequently found that a more active catalyst could be made by substituting a higher surface-area-activated alumina for a portion of the α-alumina.[13,14] With the improved catalyst, methane as well as propane was reformed. Recent results achieved with the improved catalyst are reported below.

2. Experimental Section

The improved catalyst/sorbent pellets were prepared by first pelletizing the cores using a mixture composed of equal parts by weight of type S dolime and pulverized limestone. The dolime was supplied by Graymont Dolime, Inc. (OH), which had prepared the material from Ohio dolomite by a process of calcination, hydration, and screening. The dolime particles fell within the −210/+44 μm size range. The limestone was supplied by Martin Marietta Aggregates from a quarry near Ames, IA. It contained 97 wt % $CaCO_3$ and consisted of particles in the −210/+63 μm size range. The pellet cores were subsequently coated with a shell-forming mixture having the following composition: 29 wt % noncrystalline alumina (CP-7), 28 wt % α-alumina (T-64), 38 wt % α-alumina (A16-SG), and 5 wt % limestone, −210/+44 μm. The various grades of alumina were supplied by Alcoa (now Almatis AC, Inc.).

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The CP-7 grade was an activated noncrystalline alumina hydrate powder with an average particle size of 7 μm and surface area of 250 m^2/g. The T-64 grade was a tabular α-alumina with a median particle diameter of 8.65 μm and a surface area of less than 1 m^2/g. The A-16SG grade was a calcined α-alumina with a median particle diameter of 0.48 μm and surface area of 8.2 m^2/g.

The coated pellets were calcined at 800 °C for 2.0 h to partially sinter the shell material. Pellets having an overall diameter of 4.5 ± 0.2 mm were selected for impregnation with a nickel catalyst. The pellets were first immersed in a 1.85 M solution of nickel nitrate in tetrahydrofuran for 1.0 h, drained, and dried at room temperature overnight. The pellets were dried further at 110 °C and then calcined at 500 °C to decompose the nickel salt into nickel oxide. The preceding steps were repeated to increase the nickel content of the pellets. The two-step impregnation method produced pellets having a reducible nickel content of 6 wt %, determined by measuring the change in weight of the pellets as the nickel oxide was reduced to elemental nickel by treating the pellets with H_2 at 550 °C.

The performance of the catalyst/sorbent pellets was tested with a fixed bed tubular reactor made of quartz tubing and packed with a mixture of the pellets and inert silicon carbide pellets. The latter were added to reduce void space and to improve the heat- and mass-transfer characteristics of the bed. The reactor had an overall length of 42 cm and an inside diameter of 12.7 mm, and it was placed vertically within a 30 cm long tubular electric furnace, so that the bed of pellets was centered within the furnace. The bed was supported by a porous, sintered quartz plate, and a thermocouple was located directly below and close to the plate to measure the system temperature. The bed had a depth of 12−13 cm and consisted of 6 g of catalyst/sorbent pellets and 4 g of SiC pellets. The former had an average diameter of 4.5 mm, whereas the latter had a diameter of 1−2 mm. During a performance test, the reactor was supplied with a mixture of steam and one or more hydrocarbon gases. Steam was generated in a heated tube that was supplied water at a rate controlled by a metering pump. The other gases were metered individually with calibrated rotameters. Gases exiting the reactor were cooled to condense unreacted steam and then vented. Samples of the gas were collected and subsequently analyzed with a gas chromatograph.

To conduct a performance test of catalyst/sorbent pellets, the pellet bed was first heated in a stream of air or nitrogen to 750 °C to ensure that the sorbent was regenerated. The pellets were then treated with H_2 or a mixture of H_2 and N_2 in equal concentrations at 550 °C for 4 h or more to reduce NiO to elemental Ni. The temperature of the system was then set for the reforming test, and the flow of steam and hydrocarbon were initiated and maintained at a constant rate, except possibly for a short interval at the beginning of an absorption cycle if the temperature had to be reduced to a level where absorption would take place. As the test progressed, samples of the product gas were collected and analyzed. The test was continued until CO_2 was no longer absorbed and the system was at steady state. Then, the test was either discontinued or another cycle of regeneration and reforming was carried out. The entire test was conducted at 1.0 atm.

3. Results and Discussion

The improved catalyst/sorbent was evaluated by conducting a series of hydrocarbon-reforming tests with the material. These tests included steam reforming of methane (CH_4) and toluene (C_7H_8) individually and steam reforming of a mixture of CO, CH_4, and C_7H_8. Toluene was included in the series because it is representative of the more volatile components of coal tar. When we show that toluene can be reformed together with the principal components of coal gas, the foundation will be laid for converting at least part of the tar into hydrogen.

The same bed of catalyst/sorbent pellets was used for all of the tests reported below. The catalyst had first been activated by employing the material to reform methane and propane for
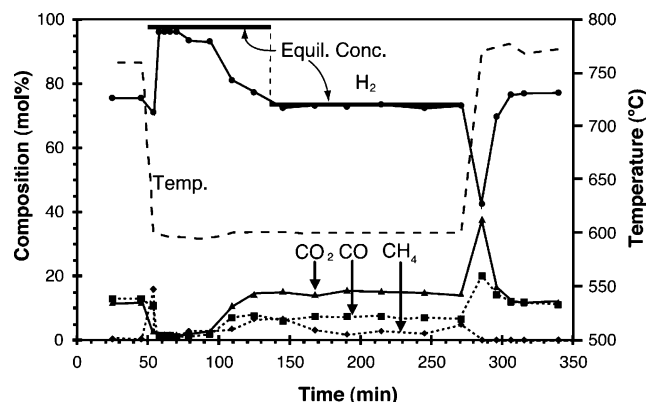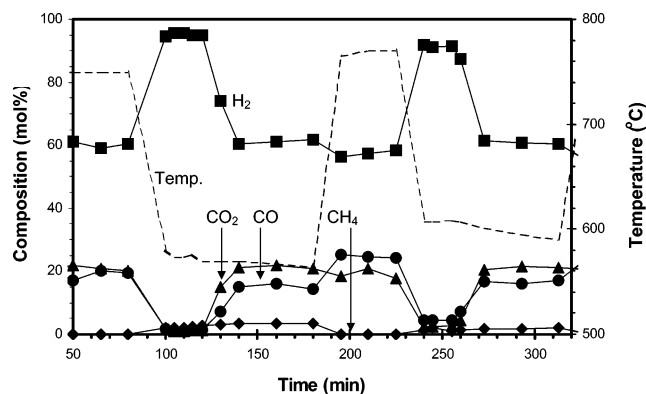
Figure 1. Product gas composition (dry basis) produced by reacting H_2O and CH_4 in a 3:1 mol ratio at 1.0 atm.

Figure 2. Product gas composition (H_2O and C_7H_8 free) produced by reacting steam and toluene using 3 mol of H_2O/mol of C at 1.0 atm.

several hours. Before undergoing this period of activation, the catalytic activity of the material was generally low.

The results of a typical test of methane reforming with the activated material are presented in Figure 1, which shows how the composition of the product gas changed over time, while the system temperature was varied to control the absorption of CO_2. Among the three temperature levels employed, absorption could take place only at the 600 °C level, where the $CaCO_3$ product of absorption was stable. At both the initial 760 °C level and final 775 °C level, this product could not exist. Except for a short period at the beginning of the absorption cycle when the temperature was reduced, the reactor was supplied with steam and methane in a 3:1 mol ratio and at the feed rates shown for test 1 in Table 1.

Initially, all of the methane reacted because of the high reactor temperature (760 °C), even though no CO_2 was absorbed. This produced a product gas mixture with 75% H_2, 13% CO, and 12% CO_2, all on a dry basis. About 45 min into the run, the methane and steam flow was interrupted, while the temperature was reduced. As the temperature approached the 600 °C level, the flow of steam and methane was resumed and the CO_2 absorption phase was initiated. The H_2 concentration quickly rose to 96%, and the CO_2 concentration dropped to 1.7%. Other concentrations are indicated in Table 1 for this phase. The observed H_2 concentration was only slightly less than the predicted equilibrium concentration of 97.7%, which is indicated by the horizontal bar in Figure 1. For the next 35 min, the product gas composition changed only slightly, but as the sorbent became saturated, the H_2 concentration fell and the CO_2 concentration rose. After the sorbent became saturated and conditions stabilized, the product gas composition was that shown in Table 1 for the no CO_2 absorption phase. Again, the H_2 concentration was nearly equal to its equilibrium value.

Although the sorbent could have been regenerated soon after it had become saturated, regeneration was postponed to obtain an accurate indication of the product composition under stable, saturated operating conditions. Eventually, the temperature was raised to 775 °C to regenerate the sorbent. As the temperature

was raised, there was a sharp increase in the CO_2 concentration as CO_2 was desorbed and a corresponding decrease in the H_2 concentration. Soon, the product composition returned to what it had been at the start of the run, indicating that the sorbent was regenerated. Experience showed that this cycle of absorption and regeneration could have been repeated numerous times with similar results because the catalyst/sorbent had been utilized for more than 100 h of testing and was well-stabilized.

When a similar test was conducted with steam and toluene using a 3:1 mol ratio of steam to carbon and the feed rates listed for test 2 in Table 1, the results shown in Figure 2 were obtained. In this case, two cycles of CO_2 absorption and sorbent regeneration were conducted. The first cycle of absorption was conducted at 570 °C, while the second cycle was conducted at 600 °C. Results for the second cycle are given in Table 1. The gas composition indicated in Figure 2 and Table 1 for this test is on a moisture- and toluene-free basis because the unreacted materials were condensed but not recovered. While most of the toluene was converted into H_2, a small portion was converted into methane. However, as in the previous case, the concentration of H_2 was much higher and the concentrations of CO and CO_2 were much lower during the CO_2 absorption phase of each cycle than during the no absorption phase. On the other hand, at 600 °C, the H_2 concentration was not as high and the CO and CO_2 concentrations were not as low for the toluene test as for the methane test. While an accurate determination of the toluene conversion was not achieved, the results suggest that a large fraction of the toluene was converted, especially during the absorption phase of each cycle.

For a third test, CO, CH_4, and C_7H_8 were supplied to the reactor at the feed rates indicated in Table 1 for test 3, which provided a 3:1 mol ratio of steam to carbon. In this test, two of the principal components of raw coal gas (CO and CH_4) and an important component of coal tar (toluene) were included in the feed. The results of the two-cycle test are shown in Figure 3. The first absorption cycle was conducted at 575 °C, and the second absorption cycle was conducted at 600 °C. The results were rather similar to those achieved in the previous test with

Table 1. Product Gas Composition (Dry Basis) Resulting from Reforming Different Hydrocarbons by Using a 3:1 mol Ratio of Steam to Carbon, a Total Pressure of 1.00 atm, and 600 °C

test number	operating phase	feed rate (mmol/h)				product gas composition (mol %)			
		H_2O	CH_4	C_7H_8	CO	H_2	CO	CO_2	CH_4
1	CO_2 absorption	109.2	36.4			96.3	1.3	1.7	0.9
	no absorption	109.2	36.4			75.5	7.2	15.1	2.3
2	CO_2 absorption	102.9		4.9		90.5	5.1	3.0	1.4
	no absorption	102.9		4.9		60.8	16.5	20.9	1.8
3	CO_2 absorption	160.7	18.2	2.45	18.2	90.5	4.0	2.9	2.4
	no absorption	160.7	18.2	2.45	18.2	60.2	15.6	18.5	5.7
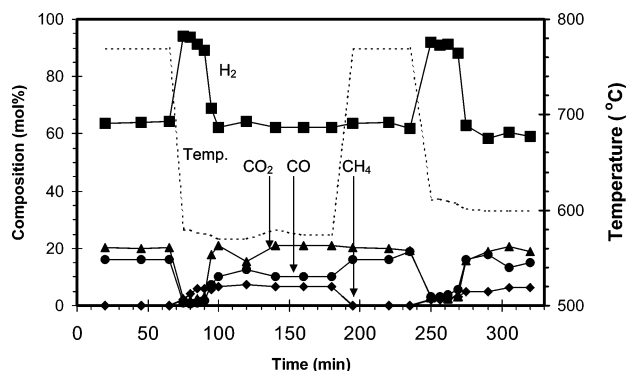
Figure 3. Product gas composition (H_2O and C_7H_8 free) produced by reacting steam with CO, CH_4, and C_7H_8 using 3 mol of H_2O/mol of C at 1.0 atm.
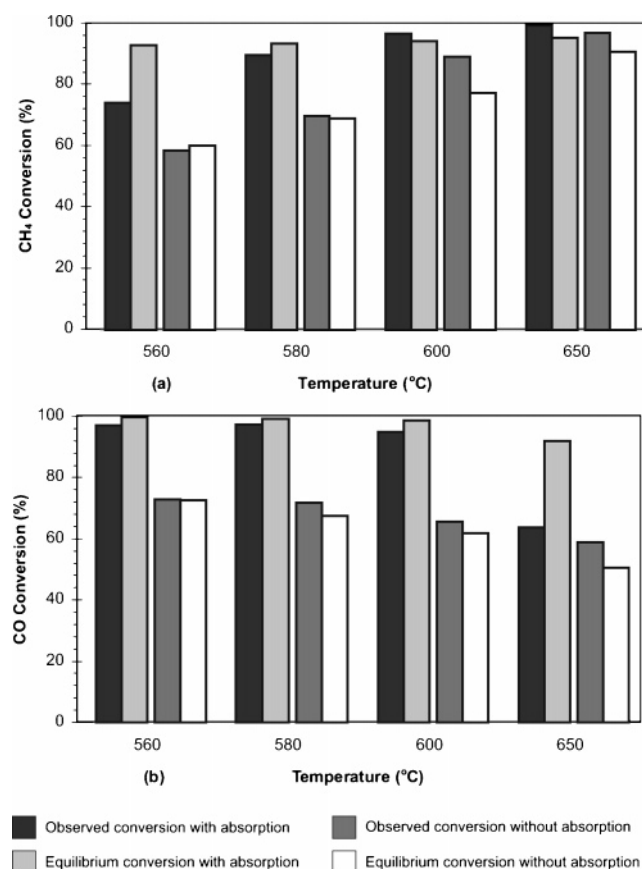
Figure 4. Effects of the temperature and CO_2 absorption on both observed and equilibrium values of (a) CH_4 conversion and (b) CO conversion.

toluene. This similarity is also indicated by the gas composition data reported in Table 1 for the second cycle. Although the conversion of the individual reactants could not be determined from the available data, the results suggest that a large portion of each reactant was converted.

On the other hand, the results of the earlier test with methane and steam were sufficiently complete to determine the conversion of both CH_4 and CO, which took place at 600 °C. These values are indicated in parts a and b of Figure 4, respectively, together with other conversion values that had been determined for similar tests conducted at both higher and lower temperatures. For a comparison, the predicted equilibrium conversions of CH_4 and CO are also presented. It is apparent that the observed CH_4 conversion was quite high in the 600−650 °C temperature range, and within this range, the conversion was

affected only slightly by CO_2 absorption, while at lower temperatures, CO_2 absorption had a more pronounced affect. It is also apparent that the observed CO conversion was very high in the 560−600 °C range and that within this range the absorption of CO_2 had a large effect.

While the predicted equilibrium conversions exhibited similar trends, there were significant differences between the observed and equilibrium values. As the temperature was reduced from 600 to 560 °C and CO_2 was being absorbed, the observed CH_4 conversion declined much more than the equilibrium CH_4 conversion. On the other hand, within this temperature range and while CO_2 was absorbed, the CO conversion remained very high. These results suggest that, as the temperature was reduced, the kinetics of reaction 1 became rate-controlling as opposed to the kinetics of reaction 2 or the resistance to gas diffusion.

At both 600 and 650 °C, the observed CH_4 conversion appeared to exceed the predicted equilibrium value for both the CO_2 absorption and no CO_2 absorption phases. Also, for the CO_2 absorption phase, the observed CO conversion at 650 °C fell far below the equilibrium conversion, whereas at lower temperatures, the observed CO conversion was only slightly less than the equilibrium conversion. These results suggest that the observed temperature may have been less than the actual bed temperature because a higher bed temperature would increase the equilibrium conversion of CH_4 and decrease the equilibrium conversion of CO. An error in temperature measurement may have resulted from assuming that a thermocouple located immediately below the bed of catalyst/sorbent pellets and directly in the flow of gases exiting the bed would be indicative of the actual bed temperature. This expedient was used because of the lack of space within the small reactor for a temperature probe.

While the preceding results achieved with the improved catalyst/sorbent material are highly encouraging, there is room for still further improvement in both the material and method of testing. Even though the material has been regenerated and reused numerous times without serious degradation, work is continuing to improve the life-cycle performance of the material as well as its physical strength, attrition resistance, and sulfur tolerance. Also, the material will be tested at higher pressures in an improved reaction system, which will provide far more accurate measurements of temperature, gas flow rates, and other operating conditions. When we operate at higher pressures, the absorption of CO_2 can be carried further to completion, which will not only enhance the conversion of CO but also reduce the concentrations of CO and CO_2 in the product to very low levels, while further increasing the H_2 concentration. A very low concentration of CO is essential when the H_2 is to be utilized in some types of fuel cells.

Although the present material has only been tested in fixed bed reactors, it may also lend itself to moving bed and even fluidized bed reactors, with further improvement in attrition resistance and compressive strength. With either moving bed or fluidized bed reactors, the cyclic process of absorption and regeneration can become a continuous process. Adapting the material to a specific type of reactor will require further consideration of its physical properties, including pellet diameter. While most of the testing has been conducted with 4−5 mm diameter pellets, larger pellets can be made that may be better suited for either fixed bed or moving bed reactors. On the other hand, smaller diameter pellets would normally be used in fluidized bed reactors, although other pellets as large as 5 mm in diameter have been treated successfully in spouted fluidized beds. Fortunately, practical methods are available for producing

spherical pellets of various sizes and applying uniform coatings to such pellets. Therefore, it should be possible to produce smaller core-in-shell pellets for use in conventional fluidized beds.

Preliminary tests have shown that reactions 2 and 3 can be carried out at higher temperature (e.g., 600 °C) by employing the bare core-in-shell pellets, which have not been impregnated with the nickel catalyst. Hence, either the Al_2O_3 in the shell or the CaO and MgO in the core must have been sufficiently catalytic to produce such results, which agree with those of Han and Harrison.[7,8] Further consideration will be given to the development of core-in-shell pellets that would only be used

for the water gas shift reaction and, therefore, do not require a separate catalyst.

While the preceding discussion has focused on the use of the combined catalyst/sorbent for treating the products of coal gasification, it offers the same potential for treating the products of biomass gasification and treating natural gas directly.

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