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Abstract
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Keywords
fixed-bed reactors, reaction equilibrium, spherical pellets, catalysts, chemical reactors, hydrogen, phase equilibria, thermal effects

Disciplines
Chemical Engineering

Comments
Development of a Novel Combined Catalyst and Sorbent for Hydrocarbon Reforming

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A combined catalyst and sorbent was prepared and utilized for steam reforming methane and propane in laboratory-scale systems. The material was prepared in the form of small spherical pellets having a layered structure such that each pellet consisted of a highly reactive lime or dolomite core enclosed within a porous but strong protective shell made of alumina in which a nickel catalyst was loaded. The material served two functions by catalyzing the reaction of hydrocarbons with steam to produce hydrogen while simultaneously absorbing carbon dioxide formed by the reaction. The in situ removal of CO2 shifted the reaction equilibrium toward increased H2 concentration and production. The concept was proved by using both a thermogravimetric analyzer and a fixed-bed reactor loaded with the material to reform hydrocarbons. Tests conducted with the fixed-bed reactor at atmospheric pressure and with temperatures in the range of 520–650 °C produced a product containing a large concentration of H2 (e.g., 94–96 mol %) and small concentration of CO and CO2. Therefore, the results achieved in a single step were as good as or better than those achieved in a conventional multistep reaction and separation process.

Introduction

Hydrogen is an important commodity that is widely used for the production of ammonia and methanol and in a variety of other applications. In the future hydrogen may be utilized in fuel cells for the highly efficient generation of electric power. Although there are several ways of producing hydrogen, one of the most widely used methods is by steam reforming hydrocarbons. While hydrogen can also be generated by gasifying coal or biomass, the hydrogen content of the raw gas is low because of the presence of other gases such as CO, CO2, CH4, and N2. The hydrogen content of such mixtures can be increased by applying a combination of the steam reforming reaction,

CH4 + H2O ⇌ 3H2 + CO \quad \Delta H_{\text{25°C}} = 210 \text{ kJ/mol (1)}

and the water–gas shift reaction:

CO + H2O ⇌ H2 + CO2 \quad \Delta H_{\text{25°C}} = -42 \text{ kJ/mol (2)}

Of course, these are also the reactions which are widely used for producing hydrogen from natural gas. Since both reactions tend to be limited by thermodynamic equilibrium as well as reaction kinetics, they require catalysts and appropriate reaction temperatures. Because reaction 1 is endothermic, the equilibrium conversion of methane by this reaction is favored by higher temperatures. On the other hand, since reaction 2 is exothermic, the equilibrium conversion of carbon monoxide is favored by lower temperatures. In a conventional methane reforming process reaction 1 is carried out with a nickel catalyst at 800–870 °C, whereas reaction 2 is carried out in two stages operating at lower temperatures. A reaction temperature of 350–450 °C and an iron oxide/chromium oxide catalyst are employed in the first stage while a temperature of 200–215 °C and a copper–zinc oxide catalyst are used in the second stage. The product mixture is subsequently separated by scrubbing it with a solvent for CO2.

It had been shown in several previous studies that it is possible to replace this continuous but complex multistep process by a much simpler single-step process which employs a mixed bed of catalyst and sorbent particles that operates in an intermediate temperature range.2–5 Laboratory-scale demonstrations of such a process were conducted with beds composed of crushed commercial nickel-based reforming catalysts and sorbent particles selected for removing CO2 from the reaction mixture. Different sorbents were used including calcium oxide and a potassium carbonate promoted hydroxylcrite. Excellent results were achieved while reforming methane in beds composed of the nickel catalyst and a lime sorbent with temperatures ranging from 450 to 725 °C and under a total pressure of 15 atm.2,3 Good results were also realized with the hydroxylcrite sorbent at 450 °C and 4.7 atm.4,5 These studies demonstrated that with removal of CO2 from the system, reaction 2 is limited less by thermodynamic equilibrium so it can be conducted at higher temperatures with a less active catalyst. Of course, the sorbent must be regenerated periodically, and if the process is conducted under pressure, regeneration can be accomplished by pressure swing absorption.4 Depending on the method of regeneration, relatively pure CO2 can be produced as a by-product.

Another promising concept which has been suggested for overcoming the reaction equilibrium limitation is to conduct steam reforming in a reaction system fitted with semipermeable membranes that selectively remove hydrogen from the system so that the concentration of hydrogen is maintained below the equilibrium value.6,7 A recent modeling investigation of methane reforming in a fast circulating fluidized-bed reactor compared the improvement in methane conversion and hydrogen yield...
which can be achieved with different methods of overcoming the reaction equilibrium barrier. These methods included (a) removing H\(_2\) with permselective membranes, (b) removing CO\(_2\) by reaction with CaO, and (c) a combination of both methods. Solid particles of a reforming catalyst were also assumed to be present. The results showed that methods (a) and (b) would improve CH\(_4\) conversion equally well, while (b) would increase H\(_2\) yield much more than (a) would. The increases produced by method (c) would be equal to the sum of the increases produced by (a) and (b).

While the previous laboratory studies produced highly encouraging results, they were conducted with fixed-bed reactors packed with mixtures of very small catalyst and sorbent particles. Such a reaction system could prove difficult to scale up to larger sizes in practice. To overcome this potential problem, a new material is being developed which combines the catalyst and sorbent materials into a single pellet. This development is an outgrowth of a previous study which led to the creation of an advanced calcium-based sorbent for desulfurizing hot coal gas. This material was in the form of small spherical pellets such that each pellet consisted of a CaO core surrounded by a protective shell made largely of porous alumina. Since alumina is widely used as a catalyst support, especially for nickel reforming catalysts, the new “core-in-shell” pellets appeared ideally suited as a means for combining a reforming catalyst with a sorbent for CO\(_2\). Furthermore, by varying the size of the pellets, it may become possible to adapt the material for use in either fixed-bed, moving-bed, or fluidized-bed reactors. However, the overall objective of this initial study was to show that core-in-shell pellets could be impregnated with a nickel catalyst and then used successfully to convert methane or propane into hydrogen largely free of CO\(_2\) in a single step.

To achieve this objective, numerous batches of core-in-shell pellets were prepared and impregnated with a nickel catalyst. In searching for a useful material to demonstrate the basic concept, various pellet formulations and preparation conditions were investigated, and the resulting pellets were tested by reforming methane or propane in laboratory reaction systems.

**Thermodynamic Analysis**

The thermodynamic principles which underlie the single-step process for producing hydrogen were revealed by an analysis of the chemical reaction equilibrium. For this analysis it was assumed that calcium oxide would be the sorbent for CO\(_2\) and that the system would be in equilibrium with respect to reactions 1 and 2 as well as reaction 3 shown below.

\[
\text{CaO(s)} + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \quad \Delta H_{25°C} = -175 \text{ kJ/mol} \tag{3}
\]

A solution of the appropriate equilibrium expressions and material balances provided the results presented in Figures 1 and 2. These results are for a reaction system supplied initially with steam and methane in a 3:1 mole ratio and kept under a total pressure of 1.0 atm. Values of the necessary reaction equilibrium constants were taken from the technical literature. The analysis was restricted to the 550–750 °C temperature range. Below this range the possible reaction of steam with calcium oxide would have had to be considered, while above the range the absorption of CO\(_2\) is too small to consider.

Figure 1 shows how the equilibrium conversion of methane and hydrogen yield vary with temperature when CO\(_2\) is absorbed and also when CO\(_2\) is not absorbed. When the CO\(_2\) sorbent is present, the equilibrium conversion of methane remains very high over the entire temperature range, whereas without the sorbent the conversion decreases considerably at lower temperatures. The hydrogen yield reflects a somewhat similar trend, although the yield resulting from having the sorbent present falls off at higher temperatures because of the exothermic nature of reaction 2 which causes the conversion of CO to H\(_2\) to drop. Hydrogen yield was taken to be the ratio of the quantity of H\(_2\) produced to the theoretical quantity produced by reactions 1 and 2 carried to completion.

Figure 2 compares the equilibrium gas composition which would result from reacting methane and steam when the CO\(_2\) sorbent is present to that which would result without the sorbent present. With the sorbent present the concentration of H\(_2\) is always greater and the concentrations of CO, CO\(_2\), and CH\(_4\) are almost always smaller than the corresponding concentrations which result without the sorbent present. These differences are greater at lower temperatures than at higher temperatures. For CO the greatest difference in concentration for the two cases appears at 650 °C.

An additional advantage of conducting methane reforming in the presence of CaO is that the heat generated by reaction 3 plus the heat generated by reaction 2 is essentially equal to that absorbed by reaction 1. Consequently, the reaction system can be operated adiabatically.
Experimental Methods and Materials

Materials. Limestone with 97 wt % CaCO$_3$ was obtained from the Ames, Iowa, quarry of Martin Marietta Aggregates, and it was used in both the core and shell of the prepared pellets. This material was first ground and screened to provide −210/+63 μm size particles for pelletizing. Another core material was type S dolime supplied by Graymont Dolime (OH) Inc. which had prepared the material by calcining Ohio dolomite and then hydrating the product. The dolime particles were in the −210/+44 μm size range. Several grades of alumina powders were supplied by Alcoa (now Almatis AC, Inc.) for making the pellet shells. These included two grades of α-alumina: (1) T-64 tabular with a median particle diameter of 8.65 μm and (2) A-16SG powder with a median particle diameter of 0.88 μm. It also included CP-7 activated γ-alumina hydrate powder with an average particle size of 7 μm and with 90 wt % finer than 20 μm. Reagent-grade nickel nitrate [Ni(NO$_3$)$_2$·6H$_2$O] with a purity of 99.999% was used for preparing the catalyst. The gases used for testing the catalyst/sorbent pellets included technical-grade H$_2$ and CH$_4$ (98%), CP-grade propane (99%), and ultra-high-purity N$_2$ (5 ppm O$_2$).

Preparation Methods. The core-in-shell pellets were prepared with a small revolving drum pelletizer as described previously. The drum had a maximum diameter of 25 cm, and it could be operated at different speeds. The general procedure for preparing pellets involved preparing the cores with the sorbent material, limestone or dolime, followed by coating the cores with a mixture of alumina and limestone. The cores were prepared in stages by adding small amounts of powder to the revolving drum and spraying the material with water frequently which caused the material to ball up, forming small spherical pellets and then larger pellets. When the desired size had been achieved, the pellets were allowed to tumble for some additional time to improve their sphericity and uniformity. During this time the pellets were sprayed frequently to prevent drying and breakage. Finished cores were separated into various sizes by screening, and cores of the desired size were reloaded into the pelletizer for coating. The cores were hardened further by allowing them to tumble in the pelletizer for some time while they were sprayed intermittently with a dilute lignin solution. When the cores appeared saturated, the coating material was added gradually while the pellets were sprayed intermittently with the lignin solution. After the desired coating thickness had been achieved, the coated pellets were subjected to a hardening process which involved tumbling for an extended period starting at 25 rpm and gradually increasing the drum speed to 90 rpm. During this period and throughout the process, control of moisture content was critical and could only be managed by an experienced operator. The coated pellets were subsequently screened, and those of the proper size were calcined between 800 and 1100 °C for 2.0 h to strengthen the coating by partially sintering the material.

Before the catalyst was introduced, the calcined pellets were first treated with CO$_2$ at 650 °C to convert the cores to the carbonate form. The pellets were then immersed in a solution of nickel nitrate which was either an aqueous solution of the salt and urea or an organic solution of the salt in tetrahydrofuran (THF). The nickel-impregnated pellets were dried in an oven and then calcined at 500 °C for 2 h or more to decompose the nickel salt. The resulting nickel oxide was reduced with H$_2$ at 550 °C for 4 h to elemental nickel. In some cases after the pellets had been impregnated with nickel nitrate and dried, the pellets were impregnated a second time to increase the nickel content. By measuring the change in weight of the pellets caused by hydrogen reduction, it was possible to calculate the reducible nickel content by application of the following expression:

$$\text{Ni(%) } = \frac{\Delta W}{W_t} \times \frac{58.7}{16} \times 100 \quad (4)$$

where $\Delta W$ and $W_t$ are the change in weight of the pellets during reduction and the total weight of pellets after reduction, respectively.

Physical Characterization Methods. The force required to fracture a single pellet was measured with an Accuforce EZ 250 testing machine. The test was conducted by placing the pellet on the fixed base plate of the machine and then lowering a movable flat plate, which was located directly above and parallel to the base plate, at a constant rate of 10 mm/min. The force that caused the material to fracture was taken to be the breaking force. The test was repeated with several different pellets from each batch so that the average breaking force and its standard deviation could both be determined.

A surface area analysis of the pellets was conducted with a Micromeretics 2000 surface area analyzer. This instrument employed the BET method of determining the surface area of a porous material by measuring the quantity of nitrogen absorbed at 77 K.

The microstructural characteristics of the core-in-shell pellets were determined with a JEOL 6100 scanning electron microscope.
was also supplied at a controlled rate by a peristaltic
metered separately with calibrated rotameters. Water
different gases which were controlled individually and
bypassing as well as improve the heat transfer proper-
was to reduce the void space and reduce gas flow
pellet, and the run was continued until the weight either
monitored by observing the change in weight of the
individual pellet, several measurements were made to
individual elements were distributed within the core
microstructure of the material. In addition, energy
dispersive spectrometry was used to determine how
furnace. A bed support in the form of a
vertically within a 30 cm long tubular electric furnace
inside diameter of 12.7 mm. The reactor was mounted
quartz tube having an overall length of 42 cm and an
was placed in the thermogravimetric analyzer and
reduced to its elemental form and activated, the pellet
had been calcined previously and had the nickel catalyst
pellet was surrounded by a flowing stream of CH4 or
C3H8, N2, and H2O (steam). The gas flow rates were
controlled manually and measured with calibrated
rotameters. Steam was generated by supplying water
with a syringe pump to a small, porous tube within the
heated reactor where the liquid vaporized.

For a typical test of a catalyst/sorbent pellet, which
had been calcined previously and had the nickel catalyst
reduced to its elemental form and activated, the pellet
was placed in the thermogravimetric analyzer and
heated to 750 °C to ensure that no CaCO3 or Ca(OH)2
was present in the core. The temperature of the system
was then set for the desired reaction temperature, and
the steam and hydrocarbon reactants were introduced
at a controlled rate. The progress of the reaction was
monitored by observing the change in weight of the
pellet, and the run was continued until the weight either
approached a constant value or changed too slowly to
be of practical interest.

For a typical test of the catalyst/sorbent pellets, the
bed of pellets was preheated in a stream of air or N2 to
750 °C for about 1.0 h to make sure that the sorbent
was in the form of CaO. The pellets were then treated
at 550 °C with pure H2 or an equimolar mixture of H2 and
N2 for 4 h or more to reduce NiO to elemental Ni.
The temperature of the system was subsequently ad-
justed to a value appropriate for steam reforming a
particular hydrocarbon, and the flow of hydrocarbon and
steam was initiated. For methane reforming, the
combined flow of CH4 and H2O corresponded to a flow rate
of 2.41 mmol/(min) based on a 3:1 mole ratio of H2O:
CH4.

While the run was progressing, samples of the product
gas were collected frequently and analyzed with a gas
chromatograph to determine concentrations of H2, CO,
CO2, CH4, and C3H8. The run was continued well beyond
the point where CO2 was no longer absorbed so that the
results with and without CO2 absorption could be
compared.

**Experimental Results and Discussion**

Previous work, which led to the development of a
unique pelletized sorbent, had shown that a suitable
shell material can be made by combining 48 wt % T-64
tabular alumina, 32 wt % A-16SG alumina powder, and
20 wt % limestone (-297/+44 μm). When core-in-shell
pellets having shells made of this material were calcined
at 1100 °C for 2 h, the resulting pellets were strong and
yet the shells were quite porous. On the other hand, the
α-alumina which had been used is known to have little
microporosity and is not regarded as a prime catalyst
support. Therefore, consideration was given to the
substitution of γ-alumina with considerable microporos-
ity for a portion of the α-alumina. For an initial
evaluation of the shell material, small cylindrical tablets
of the material were prepared by mixing the powdered
ingredients with sufficient water containing 5 wt %
lignin to form a thick slurry which was poured into a
plastic mold. This operation produced a large number
of cylindrical tablets having a diameter of 6 mm and
length of 6 mm. The tablets were subsequently dried
and then calcined for 2 h at either 900 or 1100 °C. One batch of tablets was prepared with the α-alumina formulation described above while another batch was prepared by replacing the T-64 α-alumina with CP-7 γ-alumina. Samples of tablets from the two batches were subsequently subjected to compression testing and surface area analysis. The results presented in Table 1 show that tablets made of the C1 mix with T-64 α-alumina were much stronger but had a smaller surface area than tablets made of the C2 mix with CP-7 γ-alumina. Tablets made of either formulation experienced a large increase in strength and a decrease in surface area when the calcination temperature was raised from 900 to 1100 °C. Similar trends were observed when small spherical pellets of shell material were prepared by pan pelletization and then tested, although the absolute values of surface area and crushing strength were not the same as those for the cast tablets.

To develop core-in-shell pellets capable of reforming hydrocarbons in a single step, numerous batches of pellets were prepared with different shell formulations and sometimes different core formulations. The goal was a material which not only had the necessary catalytic and sorbent properties but also had the necessary physical strength. Two of the more promising batches were selected for the present discussion. These two batches represented differences in core composition, shell composition, nickel impregnation conditions, and calcination conditions (see Tables 2 and 3).

Batch T3 (Table 2) was made with dolomite cores and shells made entirely of α-alumina and limestone (∼210/44 µm). Except for the difference in limestone particle size, the shell formulation was the same as that of the C1 mix. The dolomite cores had been shown previously to be more stable and have greater resistance to sintering than limestone cores. After the pellets had been calcined at 1100 °C for 2 h, the pellets exhibited an average crushing strength of 7.0 ± 2.9 N/mm based on pellet diameter. The calcined pellets were impregnated twice with an aqueous solution of Ni(NO₃)₂ and urea which resulted in a reducible nickel content of 6–7 wt %.

Batch T6 (Table 3) of catalyst/sorbent pellets differed from the preceding batch in both core and shell composition and other preparation conditions. One-half of the dolomite in the core was replaced by limestone to increase the effective sorbent concentration. In addition, γ-alumina was added to the shell mixture to increase the surface area on which nickel was deposited. The pellets were calcined at 800 °C for 2 h instead of 1100 °C to minimize the loss of surface area which γ-alumina undergoes at high temperature. Unfortunately, the change in shell composition and lower calcination temperature also reduced the pellet crushing strength to 4.5 ± 1.2 N/mm, which is considered too low. On the other hand, the “practical” absorption capacity of the pellets was increased to 2.5 mmol of CO₂/g because of the addition of limestone to the cores. The “practical” capacity represents the loading which can be achieved rapidly in contrast to the ultimate capacity which requires a very long time to reach. The calcined pellets were impregnated twice with a solution of nickel nitrate in tetrahydrofuran (THF) which provided a reducible nickel content of 6 wt %.

When a representative fresh pellet from batch T3 was cross-sectioned and examined with a scanning electron microscope (SEM), the electron micrographs shown in Figure 4 were obtained. The upper two views show the morphology of the pellet at different levels of magnification, whereas the lower views show the distribution of four different elements within the same region which was a small portion of the pellet cross section next to the outer edge of the pellet. The largest crack, which is most apparent in the upper two views, marked the boundary between the core and shell. Everything to the right of the crack was shell material and everything to the left was core material. The outer boundary of the shell appears in the extreme lower right-hand corner of each view. It is quite apparent that both the core and the shell were porous and that the microstructure of the core was coarser than that of the shell. Also, magnesium was largely confined to the core and aluminum to the shell, whereas calcium was present in both the core and shell but in different concentrations. While much of the nickel was distributed throughout the shell, some nickel showed up in the core, mainly within a narrow band next to the outer edge of the core.

**Catalyst/Sorbent Testing by Thermogravimetric Analysis.** Another pellet from batch T3 of nickel-impregnated pellets was subjected to a CO₂ absorption test by employing a thermogravimetric analysis (TGA) system. The results of this test are shown in Figure 5. Since the pellet had been stored in the carbonated form, it lost weight when it was heated in a stream of nitrogen. After the weight of the pellet had stabilized at 750 °C, the temperature of the system was reduced to 650 °C, and a stream with 5 mol % CO₂ in N₂ was introduced under a total pressure of 1.0 atm. As CO₂ was absorbed, the pellet weight increased rapidly at first and then more gradually. During the first 15 min of absorption, the pellet weight increased 9% while after 60 min the weight had increased only 10%. These levels corresponded to absorption capacities of 2.0 and 2.3 mmol of CO₂/g, respectively. The lower level was considered to be a “practical level” since beyond this level the absorption rate became very slow. When the pellet was subsequently calcined in pure N₂ at 650 °C, the loss in weight was too slow for practical regeneration. However, when treated at 750 °C in pure nitrogen, the pellet was completely regenerated within 10 min. Similar absorption tests were conducted with other pellets which had been impregnated with nickel only once or not at all. Since these tests gave similar results, it appeared that the nickel loading did not affect the CO₂ absorption capacity of the core.

To test the performance of the catalyst and sorbent under steam reforming conditions, another pellet from batch T3 was utilized for this purpose in a run made with the TGA system. The results of this test are presented in Figure 6. Throughout this test a mixture of propane (6 mol %) and nitrogen (94 mol %) was fed continuously together with sufficient steam to provide

---

**Table 1. Properties of Cast Tablets of Shell Material after Calcining for 2 h at Different Temperatures**

<table>
<thead>
<tr>
<th>mix composition, wt %</th>
<th>calcin. temp., °C</th>
<th>surface area, m²/g</th>
<th>breaking force, N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 0 48 32 20</td>
<td>900</td>
<td>5.0</td>
<td>45</td>
</tr>
<tr>
<td>C1 0 48 32 20</td>
<td>1100</td>
<td>2.4</td>
<td>409</td>
</tr>
<tr>
<td>C2 48 0 32 20</td>
<td>900</td>
<td>64.0</td>
<td>8</td>
</tr>
<tr>
<td>C2 48 0 32 20</td>
<td>1100</td>
<td>36.2</td>
<td>36</td>
</tr>
</tbody>
</table>

* Limestone, ∼297+/+44 µm.
a 3:1 mole ratio of H₂O:C. The total flow rate of gas and steam was equivalent to 13.7 mmol/min. When this mixture was brought into contact with a freshly regenerated pellet at 650 °C, the pellet gained weight rapidly, showing that CO₂ was being produced and absorbed. In other words, propane was being reformed. After about 20 min the weight gain slowed considerably, indicating that the sorbent was becoming saturated. Although a temperature of 650 °C was maintained for another 63 min, the gain in weight of the pellet was modest. At this point the temperature was increased to 760 °C which caused CO₂ to be desorbed, and the pellet weight dropped to its initial value, indicating that the sorbent had been regenerated. Then when the temperature was reduced to 650 °C, a second cycle of CO₂ production and absorption was conducted.

To show that the nickel catalyst was essential for the preceding results to have been achieved, an identical experiment was conducted with a core-in-shell pellet from the same batch as the preceding one except that the pellet had not been loaded with nickel. With use of the same propane reforming conditions as before, no gain in pellet weight was observed which showed that no CO₂ was formed and absorbed by the pellet.

The catalyst/sorbent pellet which had reformed propane successfully was tested for reforming methane under similar conditions. The feed gas exclusive of steam contained 15 mol % CH₄, 2 mol % H₂, and 83 mol % N₂. Again the mole ratio of steam to carbon was 3:1. When the freshly regenerated pellet was treated with this mixture at 650 °C, no gain in weight was observed, which indicated that the catalyst was not sufficiently active to reform methane. This result was not entirely unexpected since methane is known to be more difficult to reform than propane because it is more difficult to break the C–H bond in methane than to break the C–C bonds in propane.

When a fresh pellet from batch T6 was tested for catalytic activity by trying to reform methane in the TGA system as described above, the results were again negative. It was found subsequently that the nickel catalyst had to be activated by using it to reform propane over several hours before it became a satisfactory catalyst for methane. Eventually good results were obtained with the TGA system by using a pellet which had been employed with other pellets from batch T6 in a fixed-bed reactor to reform propane and then methane for a number of hours. Some of these results are presented in Figure 7 for a three-cycle test of methane reforming and sorbent regeneration conducted with the activated catalyst pellet. Steam and methane were supplied continuously in a 3:1 mole ratio at a total flow rate of 2.41 mmol/min. However, each reforming cycle was conducted at a different temperature, to possibly gain insight into the rate-controlling mechanism, but the differences in the rate of absorption from cycle to cycle were too small to achieve this purpose. The sorbent was always regenerated by increasing the temperature to 750 °C. Regeneration was more rapid than before (see Figure 6) and complete within 10 min, which suggests that the shell was more porous due to the difference in either composition or calcination temperatures or both.

**Fixed-Bed Reactor Tests.** A number of tests were conducted with the fixed-bed reactor to demonstrate steam reforming of methane and propane with the combined catalyst/sorbent pellets at different temperatures. The results reported below were achieved by utilizing pellets from batch T6 having the properties listed in Table 3. However, the catalyst in these pellets had first been activated by utilizing the pellets for reforming propane and methane over several hours at 750–770 °C. For the following tests the tubular reactor was packed with 6 g of activated catalyst pellets and 4 g of SiC pellets which provided a bed depth of 12–13 cm. The reactor was supplied with steam and either methane or propane in a 3:1 mole ratio of steam to carbon. The total mass flow...
The rate of steam and hydrocarbon was 2.41 mmol/min when CH₄ was fed or 2.01 mmol/min when propane was fed.

Figure 4. Electron micrographs of a small portion of a core-in-shell pellet: (a) SEM views at 80× and 200× magnifications; (b) maps showing the distribution of different elements in core and shell.

Figure 5. TGA results of a CO₂ absorption and regeneration test conducted with a core-in-shell pellet from batch T3.

Figure 6. TGA results of a 2 cycle test of C₃H₈ reforming and sorbent regeneration using a core-in-shell pellet from batch T6. Total pressure = 1.0 atm, feed: 3 mol of H₂O/mol of C.

The results of a typical performance test of the steam reforming of propane are presented in Figure 8, which
shows the composition of the gas produced by the fixed-bed reactor over time. At the start of the test the reactor temperature was 770 °C, and all of the propane reacted due to the high temperature even though no CO2 was absorbed. This resulted in a product gas mixture with 70–72% H2, 13–15% CO2, and 13–15% CO, all on a dry basis. About 50 min into the run the steam and gas flow was interrupted and the temperature was reduced over the next 15 min from 770 to 520 °C. As the temperature approached 520 °C, the flow of steam and propane was resumed, and the concentration of H2 in the gaseous product quickly climbed to 94% while the concentration of CO2 dropped to 0.4% because for a time most of the CO2 was absorbed by the pellet cores. The CO concentration also dropped to a low level (0.7%), but at 520 °C not all of the CO2 was absorbed and CH4 could be produced by the methanation reaction.

Similar experiments were conducted with propane and steam at different reaction/absorption temperatures using the same bed of catalyst/sorbent pellets. The composition of the product gas during the CO2 absorption phase of each test run is indicated in Table 4 together with the composition following the absorption phase. It can be seen that at any temperature the H2 concentration was always greater and the concentrations of CO2, CO, and CH4 were always lower during the CO2 absorption phase even though not all of the CO2 was absorbed. For the absorption phase the maximum H2 concentration (96%) and minimum CH4 concentration (1.5%) were observed at 560 °C. At higher temperatures less CO2 was absorbed and less CO was converted by the water-gas shift reaction, whereas at lower temperatures more C3H8 was converted to CH4. Consequently, for the absorption phase the minimum H2 concentration (80%) and maximum CO2 and CO concentrations (9.0% and 5.1%, respectively) were observed at 650 °C. On the other hand, at 520 °C the CH4 concentration (4.0%) was high because either more CH4 was produced by the methanation reaction or less CH4 was reformed. Since reaction 5 is exothermic, it is favored by lower temperature.

The same bed of catalyst/sorbent pellets which had been used for reforming propane was also used for reforming methane. The results of a typical test run with methane are reproduced in Figure 9. These results appear to be generally similar to those achieved with propane (Figure 8). At the initial operating temperature of 760–770 °C, the gas composition achieved by reforming methane was very similar to that achieved by reforming propane. However, when the reactor temperature was lowered to 600 °C to demonstrate methane reforming during CO2 absorption, the results were similar to those obtained while reforming propane at a

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (5)
\]
Table 5. Product Composition Resulting from Methane Reforming with 3:1 Mole Ratio of Steam to Carbon and 1.0 atm Total Pressure

<table>
<thead>
<tr>
<th>Operating Mode</th>
<th>Temp., °C</th>
<th>( \text{H}_2 )</th>
<th>CO</th>
<th>( \text{CO}_2 )</th>
<th>( \text{CH}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2 absorption</td>
<td>650</td>
<td>84.3</td>
<td>8.5</td>
<td>7.0</td>
<td>0.2</td>
</tr>
<tr>
<td>no absorption</td>
<td>650</td>
<td>76.0</td>
<td>8.8</td>
<td>12.5</td>
<td>0.7</td>
</tr>
<tr>
<td>CO2 absorption</td>
<td>600</td>
<td>96.3</td>
<td>1.3</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>no absorption</td>
<td>600</td>
<td>75.5</td>
<td>7.2</td>
<td>15.1</td>
<td>2.3</td>
</tr>
<tr>
<td>CO2 absorption</td>
<td>580</td>
<td>95.3</td>
<td>0.7</td>
<td>1.2</td>
<td>2.8</td>
</tr>
<tr>
<td>no absorption</td>
<td>580</td>
<td>71.5</td>
<td>5.5</td>
<td>14.1</td>
<td>8.4</td>
</tr>
<tr>
<td>CO2 absorption</td>
<td>560</td>
<td>90.5</td>
<td>0.7</td>
<td>0.8</td>
<td>8.0</td>
</tr>
<tr>
<td>no absorption</td>
<td>560</td>
<td>68.0</td>
<td>5.0</td>
<td>14.0</td>
<td>13.0</td>
</tr>
</tbody>
</table>

lower temperature (e.g., 560 °C), which again showed that it is easier to reform propane than methane. After approximately 100 min of operation with methane, the sorbent became saturated with \( \text{CO}_2 \), the \( \text{H}_2 \) concentration dropped, and the \( \text{CO}_2 \) and CO concentrations climbed just as they had while reforming propane. After 270 min of operation the reactor temperature was raised to 775 °C, which caused \( \text{CO}_2 \) to be desorbed and increased the \( \text{CO}_2 \) concentration in the reactor effluent for a short time. At the same time the CO concentration also spiked and the \( \text{H}_2 \) concentration dipped. This result could have been due in part to the effect of an increase in both temperature and \( \text{CO}_2 \) concentration on the water–gas shift reaction equilibrium.

Additional steam reforming experiments were conducted with methane using different temperatures for the \( \text{CO}_2 \) absorption phase of each run. The same bed of activated catalyst/sorbent pellets was used as before. The composition of the product gas during and following the \( \text{CO}_2 \) absorption phase is shown in Table 5. Although the results were generally similar to those achieved with propane, there were some significant differences. The results were similar in that with either hydrocarbon the concentration of \( \text{H}_2 \) was always greater and the concentrations of \( \text{CO}_2 \) and CO were always lower while \( \text{CO}_2 \) was being absorbed. One of the differences in the results was the higher temperature (600 °C) required for reforming \( \text{CH}_4 \) in order to maximize the \( \text{H}_2 \) concentration. Also it is apparent that while most of the \( \text{C}_3\text{H}_8 \) was converted at 560 °C, considerable \( \text{CH}_4 \) remained unconverted at this temperature.

A comparison of the product gas composition reported in Table 5 for methane reforming with the equilibrium gas composition indicated by Figure 2 shows reasonably good agreement between the two sets of values at 580–600 °C which suggests equilibrium control of the process. However, at either higher or lower temperature the agreement was poorer. At high temperature the process may have been controlled by the rate of diffusion of the reactants, whereas at lower temperature the process may have been controlled by reaction kinetics.

**Further Analysis of Results.** The gas composition data reported in Table 5 were used as a basis for determining the conversion of \( \text{CH}_4 \) by reaction 1 and the conversion of \( \text{CO} \) by reaction 2 for each reaction temperature and mode of operation, and the results are shown in Figure 10. In each case Mode I represents the period of operation when \( \text{CO}_2 \) was absorbed and Mode II the period when it was not absorbed (i.e., the post-absorption period). In either mode \( \text{CH}_4 \) conversion increased as reaction temperature increased, whereas \( \text{CO} \) conversion decreased. These trends largely reflect the effect of temperature on the thermodynamic equi-
The overall yield of H₂ produced by reactions 1 and 2 was also determined for the different temperatures and operating modes listed in Table 5. The yield was taken to be the ratio of the actual quantity of H₂ produced to the theoretical quantity produced by reactions 1 and 2 carried to completion. The resulting H₂ yield is indicated in Figure 12 for the different temperatures and operating modes. The maximum H₂ yield (95%) was achieved by operating with Mode I at 600 °C. Switching to Mode II at this temperature reduced the H₂ yield to 82%. In other words, switching from Mode II to Mode I would have enhanced the H₂ yield by 16% at 600 °C. The H₂ yield enhancement achieved at other temperatures is indicated in Figure 13. The maximum enhancement (38%) was observed at 580 °C, although the enhancement at 560 °C (36%) was nearly as great.

Conclusions

This work has led to the initial development of a very promising material which has the potential to greatly simplify hydrocarbon reforming for the production of H₂ and to improve the overall efficiency and economics of the process. It was shown that this material not only catalyzes the reactions of methane and propane with steam but also absorbs CO₂ simultaneously, and thereby separates the principal reaction products, H₂ and CO₂. Furthermore, the absorption of CO₂ permits the water–gas shift reaction to proceed much further toward completion at temperatures where otherwise it would be limited severely by thermodynamic equilibrium. Therefore, an additional water–gas shift reaction step would not be required to achieve low concentrations of CO. In a test of methane reforming at 600 °C and 1 atm it was possible to produce a gaseous product containing 96% H₂ (dry basis) while also achieving a H₂ yield of 95%. Methane reforming under these conditions without CO₂ absorption provided a H₂ concentration of 75% and yield of 82%.

Although the combined catalyst/sorbent has been regenerated and reused multiple times without seriously degrading its catalytic properties or absorption capacity, the development of the material is far from complete. Work is continuing to improve the life cycle performance of the catalyst and sorbent as well as the physical strength, attrition resistance, and sulfur tolerance of the material. In addition, the material will be tested at higher pressures and over a wider range of operating conditions to broaden its possible field of application.

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Literature Cited


