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Keywords

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

Disciplines

Chemical Engineering

Comments

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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 dolime 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,



and the water–gas shift reaction:



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.¹ 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 hydrotalcite. 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 hydrotalcite 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

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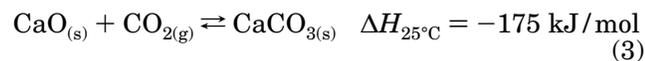
which can be achieved with different methods of overcoming the reaction equilibrium barrier.⁷ These methods included (a) removing H₂ with permselective membranes, (b) removing CO₂ by reaction with CaO, and (c) a combination of both methods. Solid particles of a reforming catalyst were also assumed to be present. The results showed that methods (a) and (b) would improve CH₄ conversion equally well, while (b) would increase H₂ 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.^{8–11} 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 CO₂. 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 CO₂ 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 CO₂ and that the system would be in equilibrium with respect to reactions 1 and 2 as well as reaction 3 shown below.



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.^{12,13} 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 consid-

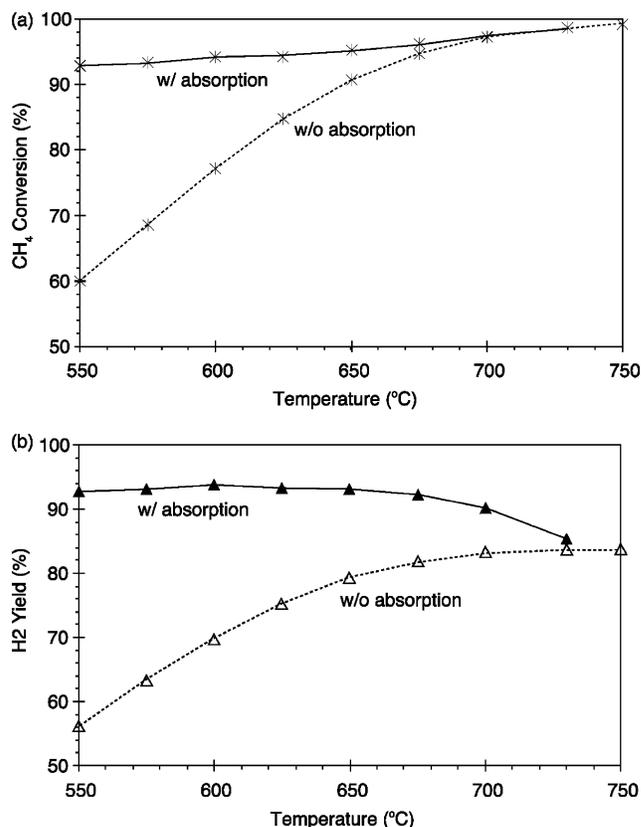


Figure 1. Methane conversion and H₂ yield obtainable by steam reforming CH₄ under equilibrium conditions both with and without CO₂ absorption. Total pressure = 1.0 atm, feed = 3 mol of H₂O/mol of CH₄.

ered, while above the range the absorption of CO₂ is too small to consider.

Figure 1 shows how the equilibrium conversion of methane and hydrogen yield vary with temperature when CO₂ is absorbed and also when CO₂ is not absorbed. When the CO₂ 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 H₂ to drop. Hydrogen yield was taken to be the ratio of the quantity of H₂ 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 CO₂ sorbent is present to that which would result without the sorbent present. With the sorbent present the concentration of H₂ is always greater and the concentrations of CO, CO₂, and CH₄ 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.

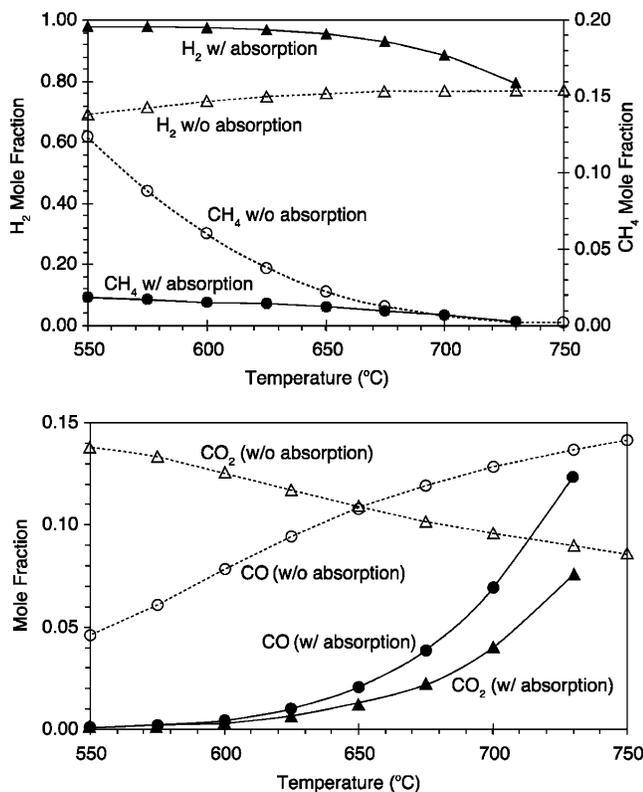


Figure 2. Product composition (dry basis) obtainable by steam reforming CH₄ under equilibrium conditions both with and without CO₂ absorption. Total pressure = 1.0 atm, feed: 3 mol of H₂O/mol of CH₄.

Experimental Methods and Materials

Materials. Limestone with 97 wt % CaCO₃ 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 Almatris 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(NO₃)₂·6H₂O] with a purity of 99.999% was used for preparing the catalyst. The gases used for testing the catalyst/sorbent pellets included technical-grade H₂ and CH₄ (98%), CP-grade propane (99%), and ultra-high-purity N₂ (5 ppm O₂).

Preparation Methods. The core-in-shell pellets were prepared with a small revolving drum pelletizer as described previously.⁸ 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 CO₂ 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 H₂ 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:

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

where ΔW 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 Micromeritics 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 adsorbed at 77 K.

The microstructural characteristics of the core-in-shell pellets were determined with a JEOL 6100 scanning

electron microscope with a tungsten filament. For this determination the pellets were mounted and polished to expose the pellet cross section for viewing the microstructure of the material. In addition, energy dispersive spectrometry was used to determine how individual elements were distributed within the core and shell of a pellet.

The overall diameter and shell thickness of the core-in-shell pellets were measured with a handheld caliper. Because of the variation in these dimensions for any individual pellet, several measurements were made to determine the average values. The mass fraction of the core was determined by breaking several core-in-shell pellets which had been weighed previously and then weighing the separated core material.

Performance Testing Methods. A Perkin-Elmer, TGA 7, thermogravimetric analyzer was employed for the preliminary performance evaluation of the combined catalyst/sorbent pellets. The TGA was used to measure the change in weight of a single pellet as it absorbed CO_2 produced by reforming CH_4 or C_3H_8 or as it released CO_2 when the sorbent was regenerated. The weight of the pellet was recorded and displayed by a digital computer which also displayed and controlled the temperature of the system. The reacting pellet was suspended within a tubular reactor from a sensitive electrobalance which was protected by continuously flushing the system with N_2 . During a typical test the pellet was surrounded by a flowing stream of CH_4 or C_3H_8 , N_2 , and H_2O (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 $750\text{ }^\circ\text{C}$ to ensure that no CaCO_3 or $\text{Ca}(\text{OH})_2$ 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.

A fixed-bed reactor system was used for a more comprehensive evaluation of the catalyst/sorbent pellets (see Figure 3). The body of the reactor consisted of a quartz tube having an overall length of 42 cm and an inside diameter of 12.7 mm. The reactor was mounted vertically within a 30 cm long tubular electric furnace so that the bed of catalyst/sorbent pellets was centered within the furnace. A bed support in the form of a porous, sintered quartz plate was located in the lower end of the reactor. The plate supported a mixture consisting of 6 g of catalyst/sorbent pellets having an average diameter of 4.5 mm and 4 g of SiC pellets having a diameter of 1–2 mm which together provided a bed depth of 12–13 cm. The purpose of the SiC pellets was to reduce the void space and reduce gas flow bypassing as well as improve the heat transfer properties of the bed. The reactor was supplied with several different gases which were controlled individually and metered separately with calibrated rotameters. Water was also supplied at a controlled rate by a peristaltic

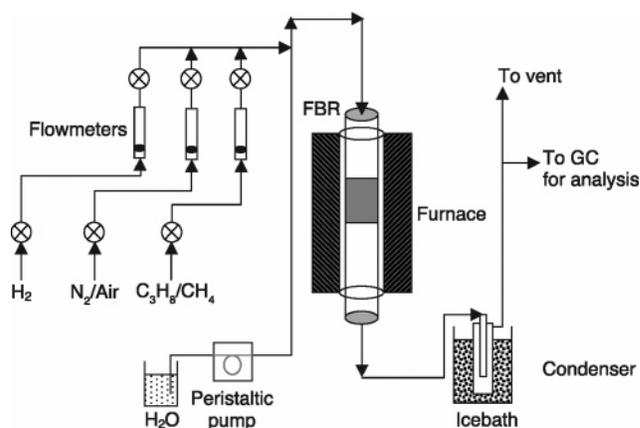


Figure 3. Fixed-bed reactor system used for steam reforming hydrocarbons.

pump. As the water was conducted to the reactor through a heated tube, it was vaporized and mixed with other gases. Product gases exiting the reactor were cooled to condense unreacted steam and then vented to a hood. During a test, samples of the product gas were taken frequently and analyzed with a gas chromatograph.

For a typical test of the catalyst/sorbent pellets, the bed of pellets was preheated in a stream of air or N_2 to $750\text{ }^\circ\text{C}$ for about 1.0 h to make sure that the sorbent was in the form of CaO . The pellets were then treated at $550\text{ }^\circ\text{C}$ with pure H_2 or an equimolar mixture of H_2 and N_2 for 4 h or more to reduce NiO to elemental Ni . The temperature of the system was subsequently adjusted 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 CH_4 and H_2O corresponded to a flow rate of 2.41 mmol/(min) based on a 3:1 mole ratio of $\text{H}_2\text{O}:\text{CH}_4$.

While the run was progressing, samples of the product gas were collected frequently and analyzed with a gas chromatograph to determine concentrations of H_2 , CO , CO_2 , CH_4 , and C_3H_8 . The run was continued well beyond the point where CO_2 was no longer absorbed so that the results with and without CO_2 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 ($-297/+44\ \mu\text{m}$).⁸ When core-in-shell pellets having shells made of this material were calcined at $1100\text{ }^\circ\text{C}$ 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 microporosity 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

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

shell mix	mix composition, wt %				calcin. temp., °C	surface area, m ² /g	breaking force, N
	CP-7	T-64	A-16SG	lime ^a			
C1	0	48	32	20	900	5.0	45
C1	0	48	32	20	1100	2.4	409
C2	48	0	32	20	900	64.0	8
C2	48	0	32	20	1100	36.2	36

^a Limestone, -297/+44 μm.

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 dolime 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 dolime cores had been shown previously to be more stable and have greater resistance to sintering than limestone cores.^{8,11} 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 dolime 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 2. Properties of Batch T3 Core-in-Shell Pellets Evaluated as a Combined Catalyst and Sorbent

initial core material	dolime
initial shell composition	80 wt % α -alumina (48 wt % T-64, 32 wt % A16-SG) 20 wt % limestone ($-210/+44 \mu\text{m}$)
overall pellet diameter	$4.5 \pm 0.2 \text{ mm}$
shell thickness	$0.4 \pm 0.1 \text{ mm}$
pellet calcination temperature	$1100 \text{ }^\circ\text{C}$
aqueous Ni loading solution	5.0 M $\text{Ni}(\text{NO}_3)_2$ 8.5 M urea
reducible nickel content ^a	$\sim 6 \text{ wt } \%$
mass fraction of core	~ 0.4
practical CO_2 absorption capacity	$\sim 2.0 \text{ mmol/g}$ of pellet
pellet crush strength	$7.0 \pm 2.9 \text{ N/mm}$

^a Achieved by impregnating the pellets twice.

Table 3. Properties of Batch T6 Core-in-Shell Pellets Evaluated as a Combined Catalyst and Sorbent

initial core material	50 wt % dolime 50 wt % limestone
initial shell composition	66 wt % α -alumina (28 wt % T-64, 38 wt % A16-SG) 29 wt % γ -alumina (CP-7) 5 wt % limestone ($-210/+44 \mu\text{m}$)
overall pellet diameter	$4.5 \pm 0.2 \text{ mm}$
shell thickness	$0.5 \pm 0.2 \text{ mm}$
pellet calcination temperature	$800 \text{ }^\circ\text{C}$
Ni loading solution (organic)	1.85 M in THF
reducible nickel content ^a	$\sim 6 \text{ wt } \%$
mass fraction of core	~ 0.4
practical CO_2 absorption capacity	$\sim 2.5 \text{ mmol/g}$ of pellet
pellet crush strength	$4.5 \pm 1.2 \text{ N/mm}$

^a Achieved by impregnating the pellets twice.

a 3:1 mole ratio of $\text{H}_2\text{O}:\text{C}$. 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 $650 \text{ }^\circ\text{C}$, the pellet gained weight rapidly, showing that CO_2 was being produced and absorbed. In other words, propane was being reformed. After about 20 min the rate of weight gain slowed considerably, indicating that the sorbent was becoming saturated. Although a temperature of $650 \text{ }^\circ\text{C}$ was maintained for another 63 min, the gain in weight of the pellet was modest. At this point the temperature was increased to $760 \text{ }^\circ\text{C}$ which caused CO_2 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 $650 \text{ }^\circ\text{C}$, a second cycle of CO_2 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 CO_2 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 % CH_4 , 2 mol % H_2 , and 83 mol % N_2 . Again the mole ratio of steam to carbon was 3:1. When the freshly regenerated pellet was treated with this mixture at $650 \text{ }^\circ\text{C}$, 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 $750 \text{ }^\circ\text{C}$. 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 $750\text{--}770 \text{ }^\circ\text{C}$. 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

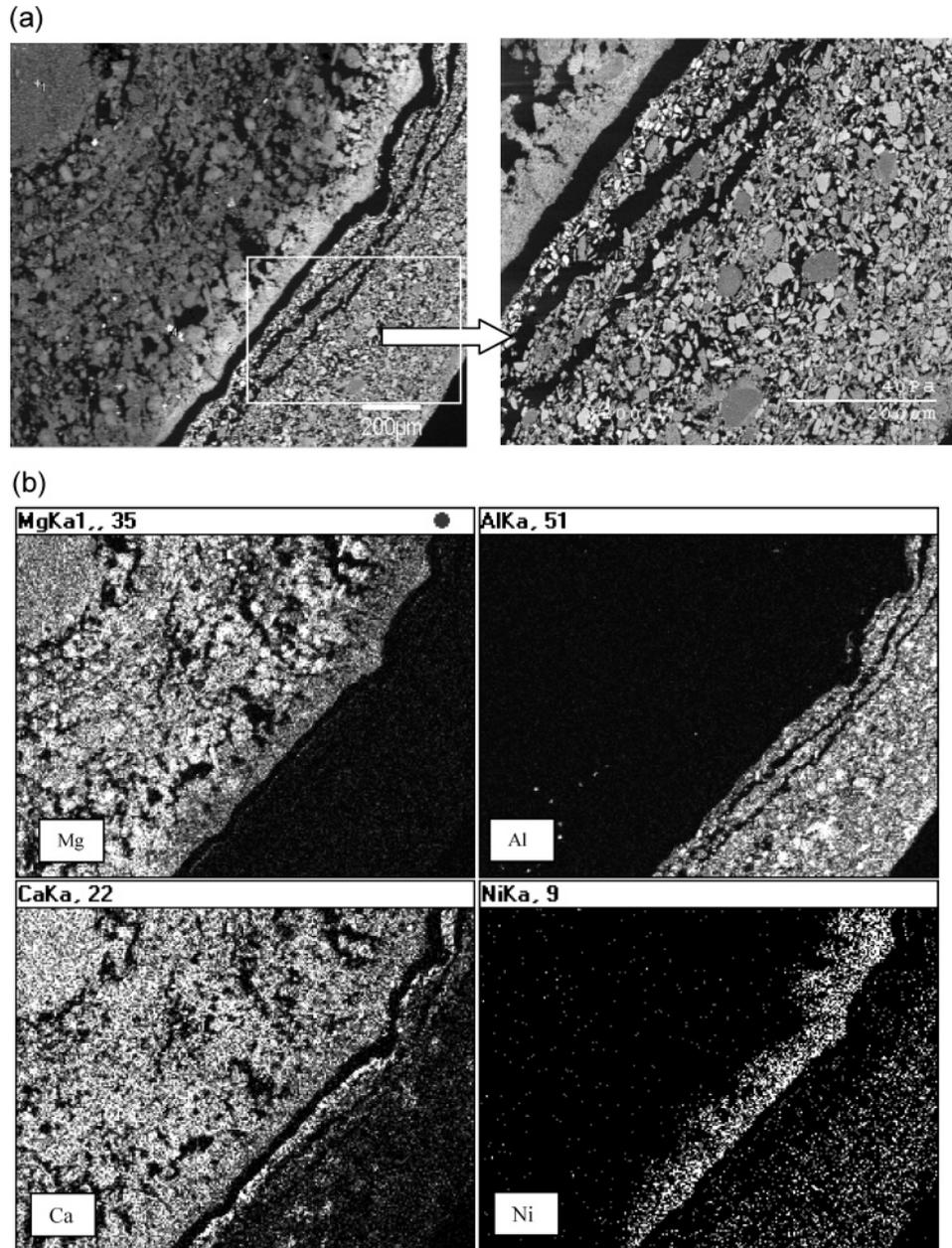


Figure 4. Electron micrographs of a small portion of a core-in-shell pellet: (a) SEM views at 80× and 200× magnifications; (b) maps showing the distribution of different elements in core and shell.

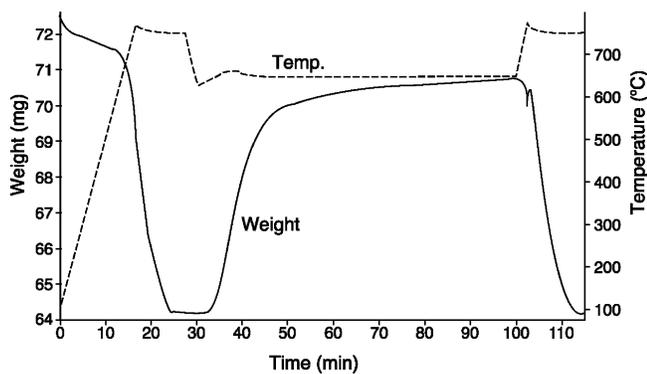


Figure 5. TGA results of a CO₂ absorption and regeneration test conducted with a core-in-shell pellet from batch T3.

rate of steam and hydrocarbon was 2.41 mmol/min when CH₄ was fed or 2.01 mmol/min when propane was fed.

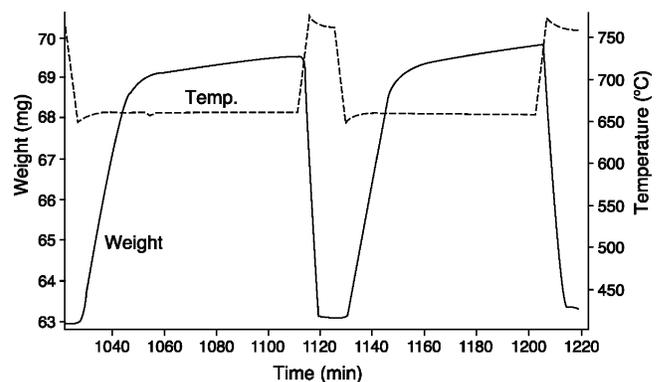


Figure 6. TGA results of a 2 cycle test of C₃H₈ reforming and sorbent regeneration using a core-in-shell pellet from batch T6. Total pressure = 1.0 atm, feed: 3 mol of H₂O/mol of C.

The results of a typical performance test of the steam reforming of propane are presented in Figure 8, which

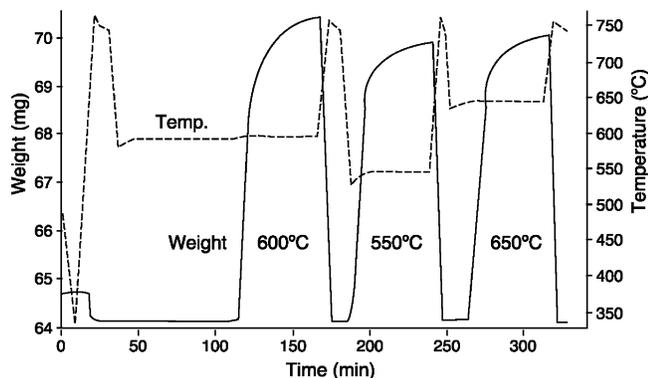


Figure 7. TGA results of a 3 cycle test of CH₄ reforming and sorbent regeneration using a catalyst-activated core-in-shell pellet from batch T6. Total pressure = 1.0 atm, feed: 3 mol of H₂O/mol of C.

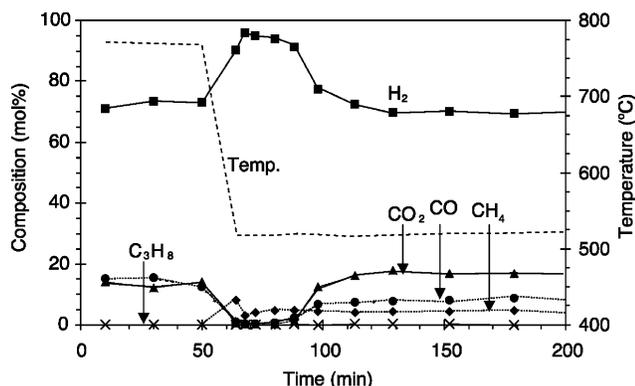


Figure 8. Product gas composition on a dry basis produced by steam reforming C₃H₈ in the fixed-bed reactor packed with core-in-shell pellets from batch T6. Total pressure = 1.0 atm, feed: 3 mol of H₂O/mol of C.

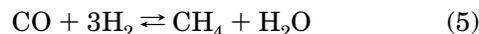
shows the composition of the gas produced by the fixed-bed reactor over time. At the start of the test the reactor temperature was 770 °C, and all of the propane reacted due to the high temperature even though no CO₂ was absorbed. This resulted in a product gas mixture with 70–72% H₂, 13–15% CO₂, and 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 a 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 propane reacted and some of the propane was converted into CH₄. Therefore, the product contained about 1% C₃H₈ and 4% CH₄. After about 90 min from the start of the operation the H₂ concentration dropped rather rapidly and the CO₂ concentration increased because the pellet cores became saturated and no longer absorbed CO₂. The CO concentration also increased markedly and the concentrations of C₃H₈ and CH₄ increased slightly. After conditions had stabilized, the product mixture consisted of 68–70% H₂, 17–18% CO₂, 8–10% CO, 4–5% CH₄, and 1–2% C₃H₈ on a dry basis.

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 absorp-

Table 4. Product Composition Resulting from Propane Reforming with 3:1 Mole Ratio of Steam to Carbon and 1.00 Atm Total Pressure

operating mode	temp., °C	gas composition (dry basis), mol %				
		H ₂	CO	CO ₂	CH ₄	C ₃ H ₈
CO ₂ absorption	650	80	5.1	9.0	3.2	trace
no absorption	650	72	7.4	14.7	4.3	trace
CO ₂ absorption	580	93	1.8	3.2	2.0	trace
no absorption	580	70	9.5	16.0	4.5	trace
CO ₂ absorption	560	96	1.0	1.1	1.5	0.1
no absorption	560	69	10.6	17.5	2.3	0.4
CO ₂ absorption	520	94	0.7	0.4	4.0	1.0
no absorption	520	68	8.0	17.0	4.6	2.4

tion 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

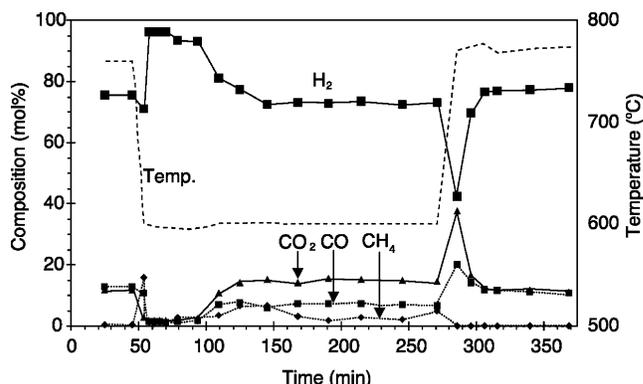


Figure 9. Product gas composition on a dry basis produced by steam reforming CH₄ in the fixed-bed reactor packed with core-in-shell pellets from batch T6. Total pressure = 1.0 atm, feed: 3 mol of H₂O/mol of C.

Table 5. Product Composition Resulting from Methane Reforming with 3:1 Mole Ratio of Steam to Carbon and 1.0 atm Total Pressure

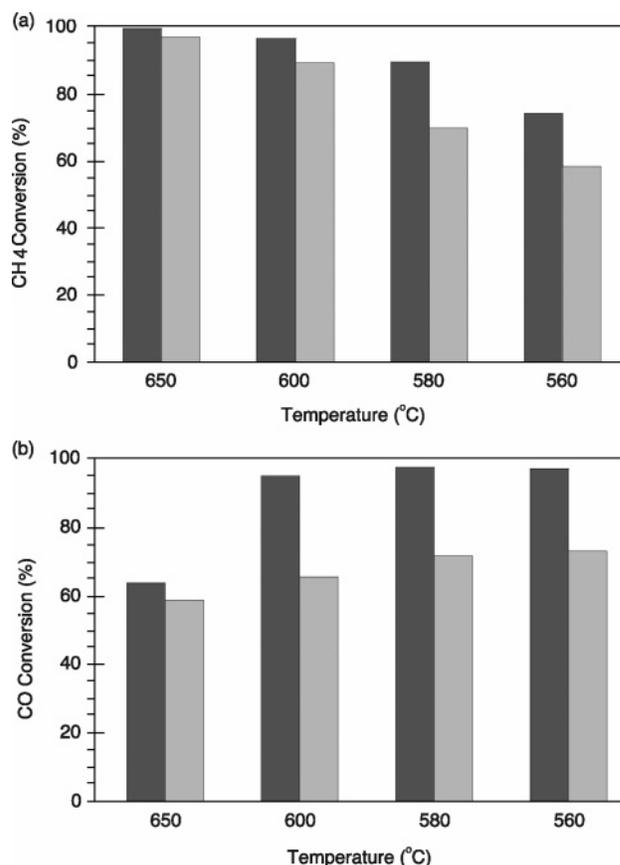
operating mode	temp., °C	gas composition (dry basis), mol %			
		H ₂	CO	CO ₂	CH ₄
CO ₂ absorption	650	84.3	8.5	7.0	0.2
no absorption	650	76.0	8.8	12.5	0.7
CO ₂ absorption	600	96.3	1.3	1.7	0.9
no absorption	600	75.5	7.2	15.1	2.3
CO ₂ absorption	580	95.3	0.7	1.2	2.8
no absorption	580	71.5	5.5	14.1	8.4
CO ₂ absorption	560	90.5	0.7	0.8	8.0
no absorption	560	68.0	5.0	14.0	13.0

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 CO₂, the H₂ concentration dropped, and the CO₂ 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 CO₂ to be desorbed and increased the CO₂ concentration in the reactor effluent for a short time. At the same time the CO concentration also spiked and the H₂ concentration dipped. This result could have been due in part to the effect of an increase in both temperature and CO₂ concentration on the water–gas shift reaction equilibrium.

Additional steam reforming experiments were conducted with methane using different temperatures for the CO₂ 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 CO₂ 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 H₂ was always greater and the concentrations of CO₂ and CO were always lower while CO₂ was being absorbed. One of the differences in the results was the higher temperature (600 °C) required for reforming CH₄ in order to maximize the H₂ concentration. Also it is apparent that while most of the C₃H₈ was converted at 560 °C, considerable CH₄ 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 CH₄ by reaction 1 and the conversion of 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 CO₂ was absorbed and Mode II the period when it was not absorbed (i.e., the post-absorption period). In either mode CH₄ conversion increased as reaction temperature increased, whereas CO conversion decreased. These trends largely reflect the effect of temperature on the thermodynamic equi-

**Figure 10.** Effects of temperature and operating mode on (a) CH₄ conversion and (b) CO conversion. Black bars represent Mode I; gray bars represent Mode II.

librium of each reaction. Since reaction 1 is endothermic, the equilibrium conversion of CH₄ increases with temperature, and since reaction 2 is exothermic, the equilibrium conversion of CO decreases. Of course, the system was probably not completely in equilibrium because gas diffusion and reaction kinetics could also have played a role, especially outside of the 580–600 °C temperature range.

Because of CO₂ absorption in Mode I but not in Mode II, the conversion of CH₄ or CO was always greater for Mode I than for Mode II at any temperature. Furthermore, the difference in conversion between modes also varied with temperature. These differences in conversion can be seen in Figure 10. It is also apparent that CO₂ absorption had a larger effect on CO conversion than on CH₄ conversion because it directly affected reaction 2 and only indirectly affected reaction 1 through reaction 2.

The difference in conversion for the two modes divided by the Mode II conversion can be regarded as the conversion enhancement resulting from CO₂ absorption. This quantity expressed as a percentage is indicated in Figure 11 for the results obtained at different temperatures. The results emphasize the extent to which the conversion of each reaction was enhanced by CO₂ absorption and also the difference in the degree of enhancement of the two reactions which was particularly striking at 600 °C. At 580 °C both reaction conversions were greatly enhanced by CO₂ absorption, whereas at 650 °C neither reaction conversion was enhanced very much. These results reflect the thermodynamic driving force for CO₂ absorption which declines with increasing temperature.

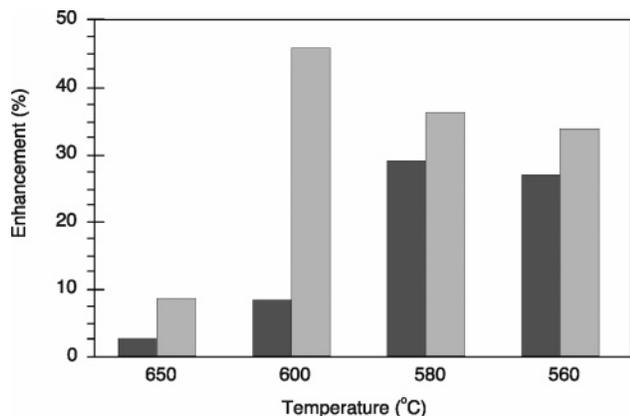


Figure 11. The extent to which CH₄ conversion (black bars) and CO conversion (gray bars) were enhanced by CO₂ absorption during CH₄ reforming at different temperatures.

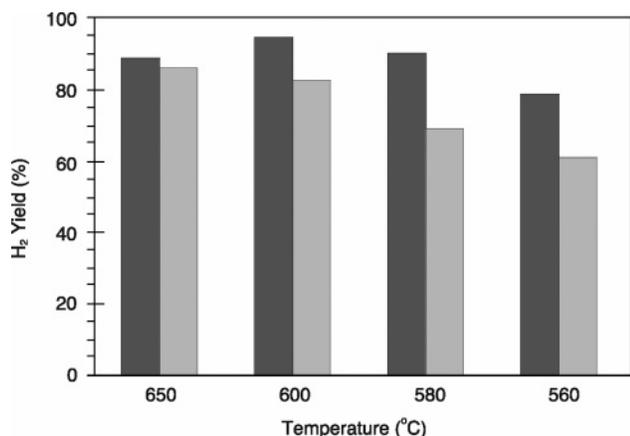


Figure 12. Effects of temperature and operating mode on yield of H₂ produced by CH₄ reforming. Black bars: Mode I; gray bars: Mode II.

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 the material can be derived from an advanced calcium-based sorbent composed of core-in-shell pellets such that each pellet consists of a CaO core and an alumina-based shell. When a nickel catalyst was incorporated in the shell, a combined catalyst and sorbent was prepared to facilitate the reaction of hydrocarbons with steam. It was shown

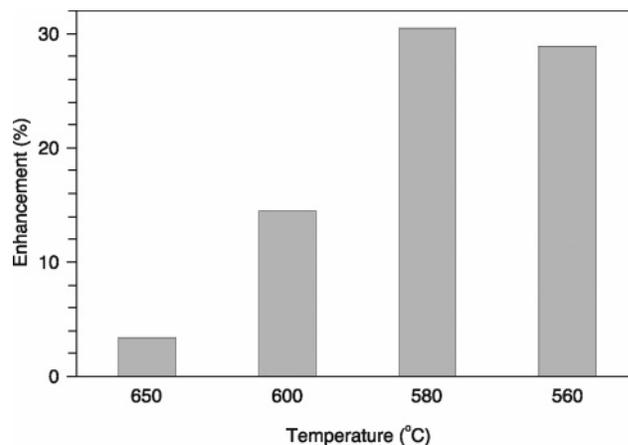


Figure 13. The extent to which H₂ yield was enhanced by CO₂ absorption during CH₄ reforming at different temperatures.

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

- (1) Czuppon, T. A.; Knez, S. A.; Newsome, D. S. Hydrogen. In *Encyclopedia of Chemical Technology*; Kroschwitz, J. I., Howe-Grant, M., Eds.; John Wiley & Sons: New York, 1995; Vol. 13, pp 852–859.
- (2) Balasubramanian, B.; Ortiz, A. L.; Kaytakoglu, S.; Harrison, D. P. Hydrogen from methane in a single-step process. *Chem. Eng. Sci.* **1999**, *54*, 3543–3552.
- (3) Harrison, D. P.; Peng, Z. Low-Carbon Monoxide Hydrogen by Sorption-Enhanced Reaction. *Int. J. Chem. React. Eng.* **2003**, *1*, Article A37, 1–9.
- (4) Hufton, J. R.; Mayorga, S.; Sircar, S. Sorption-Enhanced Reaction Process for Hydrogen Production. *AIChE J.* **1999**, *45*, 248–256.

(5) Ding, Y.; Alpay, E. Adsorption-enhanced steam-methane reforming. *Chem. Eng. Sci.* **2000**, *55*, 3929–3940.

(6) Prasad, P.; Elnashaie, S. S. E. H. Coupled Steam and Oxidative Reforming for Hydrogen Production in a Novel Membrane Circulating Fluidized-Bed Reformer. *Ind. Eng. Chem. Res.* **2003**, *42*, 4715–4722.

(7) Prasad, P.; Elnashaie, S. S. E. H. Novel Circulating Fluidized-Bed Membrane Reformer Using Carbon Dioxide Sequestration. *Ind. Eng. Chem. Res.* **2004**, *43*, 494–501.

(8) Akiti, T. T.; Constant, K. P.; Doraiswamy, L. K.; Wheelock, T. D. A Regenerable Calcium-Based Core-in-Shell Sorbent for Desulfurizing Hot Coal Gas. *Ind. Eng. Chem. Res.* **2002**, *41*, 587–597.

(9) Wheelock, T. D.; Akiti, T. T. Core-in-Shell Sorbent for Hot Coal Gas Desulfurization. U.S. Patent 6,689,714 B2, 2004.

(10) Hasler, D. J. L.; Doraiswamy, L. K.; Wheelock, T. D. A Plausible Model for the Sulfidation of a Calcium-Based Core-in-Shell Sorbent. *Ind. Eng. Chem. Res.* **2003**, *42*, 2644–2653.

(11) Wheelock, T. D.; Doraiswamy, L. K.; Constant, K. P. *Engineering a New Material for Hot Gas Cleanup*; Final Technical Report, DOE Award No. DE-FG26-99FT40587; Iowa State University: Ames, IA, 2003.

(12) *Catalyst Handbook*, Second Edition; Twigg, M. V., Ed.; Manson Publishing: London, 1996; pp 537–548.

(13) Kubaschewski, O.; Alcock, C. B. *Metallurgical Thermochemistry*, 5th Edition; Pergamon Press: New York, 1958; p 379.

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