DEVELOPMENT OF A CATALYST/SORBENT FOR METHANE REFORMING

FINAL TECHNICAL REPORT

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B. H. Shanks and T. D. Wheelock
Principal Investigators

Justinus A. Satrio
Research Associate

Timothy Diehl and Brigitte Vollmer
Undergraduate Assistants

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Chemical Engineering Department and
Center for Sustainable Environmental Technologies
2114 Sweeney Hall
Iowa State University
Ames, IA 50011-2230

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ABSTRACT

This work has led to the initial development of a very promising material that has the potential to greatly simplify hydrocarbon reforming for the production of hydrogen and to improve the overall efficiency and economics of the process. This material, which was derived from an advanced calcium-based sorbent, was composed of core-in-shell pellets such that each pellet consisted of a CaO core and an alumina-based shell. By incorporating a nickel catalyst in the shell, a combined catalyst and sorbent was prepared to facilitate the reaction of hydrocarbons with steam. It was shown that this material not only catalyzes the reactions of methane and propane with steam, it 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 towards 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 laboratory test of methane reforming at 600°C and 1 atm it was possible to produce a gaseous product containing 96 mole% 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 mole% and yield of 82%. Similar results were achieved in a test of propane reforming at 560°C and 1 atm which produced a product containing 96 mole% H₂ while CO₂ was being absorbed but which contained only 69 mole% H₂ while CO₂ was not being absorbed. These results were achieved with an

improved catalyst support that was developed by replacing a portion of the α -alumina in the original shell material with γ -alumina having a much greater surface area. This replacement had the unfortunate consequence of reducing the overall compressive strength of the core-in-shell pellets. Therefore, a preliminary study of the factors that control the surface area and compressive strength of the shell material was conducted. The important factors were identified as the relative concentrations and particle size distributions of the α -alumina, γ -alumina, and limestone particles plus the calcination temperature and time used for sintering the shell material. An optimization of these factors in the future could lead to the development of a material that has both the necessary mechanical strength and catalytic activity.

TABLE OF CONTENTS

DISCLAIMER	ii
ABSTRACT	iii
LISTS OF GRAPHICAL MATERIALS	vi
INTRODUCTION	1
EXECUTIVE SUMMARY	5
THERMODYNAMIC ANALYSIS	7
EXPERIMENTAL	10
Materials	10
Preparation Methods	11
Characterization Methods	13
Performance Testing Methods	15
RESULTS AND DISCUSSION	18
Catalyst/Sorbent Testing by Thermogravimetric Analysis	22
Fixed Bed Reactor Tests of Different Catalyst Formulations	28
Tests of Simultaneous Reaction and Absorption	35
Physical Properties Study	44
CONCLUSIONS	57
REFERENCES	59

LISTS OF GRAPHICAL MATERIALS

	Page
Figure 1 Methane conversion and H ₂ yield obtainable by steam reforming CH ₄ under equilibrium conditions both with and without CO ₂ absorption. Total pressure = 1.0 atm, Feed = 3 moles H ₂ O/mole CH ₄ .	8
Figure 2 Product composition (dry basis) obtainable by steam reforming CH ₄ under equilibrium conditions both with and without CO ₂ absorption. Total pressure = 1.0 atm, Feed: 3 moles H ₂ O/mole CH ₄ .	9
Figure 3 Fixed bed reactor system used for steam reforming hydrocarbons.	17
Figure 4. Electron micrographs of a small portion of a core-in-shell pellet from batch T3: (a) SEM views at 80X and 200X magnifications, (b) maps showing the distribution of different elements in core and shell.	21
Figure 5. TGA results of a CO ₂ absorption and regeneration test conducted with a core-in-shell pellet from batch T3.	23
Figure 6. TGA results of a 2 cycle test of C ₃ H ₈ reforming and sorbent regeneration using a core-in-shell pellet from batch T3. Total pressure = 1.0 atm, Feed: 3 moles H ₂ O/mole C.	27
Figure 7. TGA results of a 3 cycle test of CH ₄ reforming and sorbent regeneration using a catalyst-activated core-in-shell pellet from batch T6. Total pressure = 1.0 atm, Feed: 3 moles H ₂ O/mole C.	28
Figure 8 Product gas composition on a dry basis produced by steam reforming C ₃ H ₈ in the fixed bed reactor packed with core-in-shell pellets from batch T6. Total pressure = 1.0 atm, Feed: 3 moles H ₂ O/mole C.	37
Figure 9 Product gas composition on a dry basis produced by steam reforming CH ₄ in the fixed bed reactor packed with core-in-shell pellets from batch T6. Total pressure = 1.0 atm, Feed: 3 moles H ₂ O/mole C.	40
Figure 10. Effects of temperature and operating mode on (a) CH ₄ conversion, (b) CO conversion. Black bars represent Mode I, grey bars represent Mode II.	42
Figure 11. The extent to which CH ₄ conversion (black bars) and CO conversion (grey bars) were enhanced by CO ₂ absorption during CH ₄ reforming at different temperatures.	43

Figure 12. Effects of temperature and operating mode on yield of H ₂ produced by CH ₄ reforming. Black bars: Mode I; Grey bars: Mode II.	45
Figure 13. The extent to which H ₂ yield was enhanced by CO ₂ absorption during CH ₄ reforming at different temperatures.	45
Figure 14. Effect of CP-7 concentration on surface area of cast tablets after calcining at 1100°C.	48
Figure 15. Effect of CP-7 concentration on micropore volume of cast tablets after calcining at 1100°C.	48
Figure 16. Effect of CP-7 concentration on compressive strength of cast tablets after calcining at 1100°C.	49
Figure 17. Effect of limestone concentration on compressive strength of cast tablets after calcining at 1100°C.	50
Figure 18. Effect of A-16SG concentration on compressive strength of cast tablets after calcining at 1100°C.	52
Figure 19. Effect of calcination temperature on compressive strength of tablets made with different mixtures.	54
Figure 20. Effect of calcination temperature on surface area of tablets and pellets made with different mixtures.	54

INTRODUCTION

The goal of this innovative project was to carry out the initial development of a unique material for promoting steam-methane reforming that would enhance the production of hydrogen from coal. The material would combine a catalyst for both the reforming and water gas shift reactions with a sorbent for carbon dioxide, the principal byproduct of these reactions. By conducting both of these reactions in the presence of the sorbent it would be possible to replace a complex, multistep reaction and product separation method with a much simpler, single-step reaction and separation process. This simplification could result in a much more efficient and less costly method of producing hydrogen from coal.

To combine the necessary catalyst and sorbent into a single material, advantage was taken of another unique material that had been developed recently.¹⁻⁴ This material consists of small pellets such that each pellet has a CaO core encased in a shell composed largely of aluminum oxide. In this way a highly reactive but physically challenged core is protected by a strong but highly porous shell. Although the material was developed initially for desulfurizing hot coal gas, it can also be used as a sorbent for CO₂. Furthermore, since aluminum oxide is widely used as a support for the nickel catalyst that is used for steam reforming hydrocarbons, the combination of a CaO core and a shell that can support a catalyst seemed ideally suited for the intended application. Therefore, the main thrust of this project was to show that a suitable catalyst can be introduced into the shell of the core-in-shell pellets and that the resulting material can be used successfully for combining steam reforming, water gas shifting and product separation into a single step. In other words, the desired material would make it possible to conduct all three of the following reactions within the same material:

Since reactions 1 and 2 are limited by thermodynamic equilibrium, the absorption of CO_2 by CaO in reaction 3 drives reaction 2 towards completion which in turn enhances the driving force for reaction 1. 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 $800\text{--}870^\circ\text{C}$, whereas reaction 2 is carried out in two stages operating at lower temperatures.⁵ A reaction temperature of $350\text{--}450^\circ\text{C}$ and an iron oxide/chromium oxide catalyst are employed in the first stage while a temperature of $200\text{--}215^\circ\text{C}$ 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 CO_2 .

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 that employs a mixed bed of catalyst and sorbent particles operating in an intermediate temperature range.⁶⁻⁹ 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 CO_2 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 .^{6,7} Good results were also realized with

the hydrotalcite sorbent at 450°C and 4.7 atm.^{8,9} These studies demonstrated that by removing CO₂ from the system, reaction 2 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.⁸ Depending on the method of regeneration, relatively pure CO₂ can be produced as a byproduct.

While the previous 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 would be difficult to scale up to larger sizes in practice and could be subject to various operating difficulties. The proposed material that combines a catalyst and sorbent into a single pellet would potentially overcome these problems

To achieve the goals of the present investigation, steps were taken to adapt the core-in-shell pellets, which had been developed previously to serve only as a sorbent, to also serve as a catalyst support. Since the pellet shells had been made largely of α -alumina particles having a small surface area, the material did not appear to be as well suited for supporting a catalyst as one made of γ -alumina particles with a much larger surface area. Therefore, consideration was given to the substitution of γ -alumina for the α -alumina, but the resulting shells were weaker. Consequently, it became necessary to consider the trade off between catalyst activity and mechanical strength. This in turn led to consideration of other factors that affect shell strength and/or catalytic activity. The factors include, the concentrations of minor constituents, the particle size distribution of the shell forming materials, and the calcination temperature used for sintering the material. Of course, the way in which the catalyst is introduced into the shell and the resulting concentration are also important. While the available resources and limited time

did not make it possible to conduct a thorough study of all these factors, it was possible to identify and determine the effects of some of the more important ones.

Considerable effort was also devoted to evaluating the performance of the combined catalyst and sorbent when applied to reforming methane and sometimes propane. The performance of single, core-in-shell pellets was evaluated by employing a thermogravimetric analyzer. The performance of fixed beds of catalyst/sorbent pellets was evaluated by using a vertical tubular reactor. This effort produced highly encouraging results and demonstrated the fundamental feasibility of the concept.

EXECUTIVE SUMMARY

This innovative research project was carried out to conduct the initial development of a unique material that has the potential for advancing the technology of producing hydrogen from coal. Traditionally this technology has required treating the product of coal gasification by a complex, multistep process consisting of steam reforming, water gas shifting, and product separation conducted at different temperatures, and with different catalysts. With the successful development of the proposed material these steps can be combined into a single reaction and product separation step. The material would combine a catalyst for both the reforming and water gas shift reactions with a sorbent for carbon dioxide, the principal by-product of these reactions. In principle, the material could be made in the form of small pellets such that each pellet would have an absorbent core for capturing CO_2 surrounded by a porous shell which serves as a catalyst support. The foundation for such a material was laid in a previous project supported by DOE which led to the successful development of a high temperature calcium-based sorbent for desulfurizing hot coal gas. This material consists of small spherical pellets in which each pellet has a CaO core encased in a shell composed largely of aluminum oxide. The basic premise underlying the present project was that by introducing a reforming catalyst such as nickel into the shell, the material could be adapted for producing hydrogen from coal gas. This indeed proved to be true.

It was shown that a nickel catalyst could be introduced into the previously developed core-in-shell pellets by first soaking the pellets in either an aqueous or organic solution of nickel nitrate followed by calcination at 600°C to decompose the salt into NiO which was then reduced with hydrogen to elemental nickel. Subsequent examination of the cross section of a treated pellet showed the nickel to be largely dispersed within the shell. The material was tested by employing thermogravimetric analysis (TGA) and also by employing a small fixed bed tubular reactor. Tests were conducted by reacting methane or propane with steam in the presence of the catalyst/sorbent pellets. A 3:1 mole ratio of steam to carbon was employed and testing was conducted over a temperature range of 550 to 780°C . While the initial catalytic activity of the pellets proved to be low, it improved noticeably after several hours. In other words, the catalyst seemed to require a period of activation.

The shells of the previously developed core-in-shell pellets proved to have a relatively small surface area for supporting the nickel catalyst, which resulted in a material with modest catalytic activity. The low surface area was a result of making the shells out of α -alumina particles that had a small surface area. It was found subsequently that shells made out of γ -alumina particles with a large surface area were a better catalyst support. On the other hand, shells made of γ -alumina had less compressive strength than those made of α -alumina. However, it was also determined that shells with adequate surface area and good catalytic properties could be made by replacing only a portion of the α -alumina with γ -alumina, which also resulted in pellets having an intermediate compressive strength.

In a test of methane reforming at 600°C and 1 atm with pellets having shells composed of both γ -alumina and α -alumina and under conditions where most of the CO_2 was absorbed, a gaseous product with 96 mole% H_2 (dry basis) was produced while also achieving a H_2 yield of 95%. Methane reforming under these conditions without CO_2 absorption provided a H_2

concentration of 75 mole% and yield of 82%. At the same time, CO₂ absorption caused the CO₂ concentration to drop from 15.1 mole% to 1.7 mole% and the CO concentration to fall from 7.2 mole% to 1.3 mole%. If this test had been conducted at elevated pressure, the concentrations of CO and CO₂ would have been reduced even further. Similar results were also achieved in a test of propane reforming at 560°C and 1 atm. In this case operation with CO₂ absorption produced a product with 96 mole% H₂ (dry basis), whereas operation without CO₂ absorption gave a product with 69 mole%.

The combined catalyst/sorbent that provided the preceding results was regenerated and reused multiple times without serious degradation of its catalytic properties or absorption capacity. Sorbent regeneration was accomplished by increasing the temperature of the pellets to 750°C and passing nitrogen over the pellets.

Although these results are very promising, the development of the material is far from complete. Additional work should be directed towards improving the life cycle performance of the catalyst and sorbent as well as improving the physical strength, attrition resistance, and sulfur tolerance of the material. Also the material should be tested at higher pressures and over a wider range of operating conditions to demonstrate a broader range of possible applications.

THERMODYNAMIC ANALYSIS

Basic thermodynamic principles of chemical reaction equilibria were utilized to analyze the single step process for producing hydrogen from methane and steam. For this analysis it was assumed that CaO would be the sorbent for CO₂ and that the system would be in equilibrium with respect to reactions 1, 2 and 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.^{10,11} The analysis was restricted to the 550 to 750°C temperature range. Below this range the possible reaction of steam with calcium oxide would need to be considered, 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. By having the CO₂ sorbent present, the equilibrium conversion of methane and the yields of hydrogen are both significantly higher than the corresponding parameters without the sorbent present over the relevant range of temperature. The difference in conversion or yield caused by CO₂ absorption is especially great at lower temperatures.

Figure 2 compares the equilibrium gas composition that 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 always smaller than the corresponding concentrations that result without the sorbent present. These differences are greater at lower temperatures

(a)

(b)

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 moles H₂O/mole CH₄.

Figure 2 Product composition (dry basis) obtainable by steam reforming CH_4 under equilibrium conditions both with and without CO_2 absorption. Total pressure = 1.0 atm, Feed: 3 moles H_2O /mole CH_4 .

than at higher temperatures. For CO the greatest difference in concentration for the two cases appears at 650°C.

These results show the potential gains which can be realized by having a CO₂ sorbent present while conducting methane reforming. They also represent an upper limit of results that can be achieved if all reaction kinetic and mass transfer limitations were overcome.

EXPERIMENTAL

Materials

Limestone with 97 wt.% CaCO₃ was obtained from the Ames, Iowa, quarry of Martin Marietta Aggregates. This material was first ground and screened to provide -210/+44 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(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 ultrahigh purity N₂ (5 ppm O₂).

Preparation Methods

Pelletization. The core-in-shell pellets were prepared with a small revolving drum pelletizer as described previously.³ 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 large 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 hr to strengthen the coating by partially sintering the material.

Casting (Molding). For investigating the properties of various shell formulations, an alternate procedure was used for preparing the material. This method produced small tablets by

first preparing a thick aqueous slurry of an appropriate particle mixture and then pouring the slurry into a mold to form cylindrical tablets having a diameter of 6 mm and length of 6 mm. The mold was made from a 6 mm thick sheet of polycarbonate plastic that had been drilled to create a large number of 6 mm diameter holes. The mold was treated with a mold release agent (PAM manufactured by International Food Corp.) , and then placed on a plaster slab, which absorbed some of the water during the casting operation. The material used for casting was prepared by first mixing the dry powdered materials and then adding enough water to form a thick slurry. The slurry was poured into the mold to produce a number of small cylindrical tablets. The tablets were allowed to air dry for at least 24 hr before removing from the mold. The molded tablets were then calcined at either 900 or 1100°C for 2.0 hr.

Catalyst Preparation. The calcined pellets or tablets were impregnated with a nickel catalyst by immersion in either an organic or aqueous solution of nickel nitrate. However, in the case of core-in-shell pellets, the calcined pellets were first treated with CO₂ (25 mole % in N₂) at 650°C to convert the cores to the carbonate form in order to prevent the reaction of CaO with the solvent. In some cases the pellets or tablets were immersed in an aqueous solution of nickel nitrate that also contained urea. In other cases the pellets or tablets were immersed in an organic solution of the salt in tetrahydrofuran (THF). Two methods were employed for bringing the solids into contact with the salt solution. One method involved preheating the solids at 100°C and then rapidly immersing the heated solids in the salt solution, which was at room temperature; the entire operation being conducted under atmospheric pressure. A second method utilized a vacuum desiccator in which the solids were placed and subjected to a partial vacuum. While the solids were under the reduced pressure, the salt solution was admitted to cover the solids whereupon air was admitted to return the pressure to atmospheric. Both methods tended to

reduce the amount of gas present in the pores of the solids when the solids were brought into contact with the salt solution making it easier for the solution to penetrate the pores. With either method the solids remained immersed in the liquid for 1.0 hr whereupon the solids were removed and placed on a paper towel to remove excess solution from the surface. The solids were subsequently air dried over night or longer at room temperature and further dried in an oven at 110°C for several more hours.

The nickel-impregnated pellets or tablets were calcined in a tubular furnace in air at 550-600°C for 4 hr to decompose the nickel nitrate. The resulting nickel oxide was reduced with hydrogen to elemental nickel, the active form of the nickel catalyst. The reduction was conducted at 550-600°C for 2 hr or more. In some cases after the solids had been impregnated with nickel, dried, and calcined, the solids were impregnated a second time to increase the nickel content. When core-in-shell pellets were to be stored for an extended time before being tested or utilized, the material was treated with 25 mole % CO₂ in N₂ at 650°C to recarbonate the cores and render the material more stable in the presence of moisture. Otherwise, the CaO in the cores would absorb moisture from the air and produce Ca(OH)₂ which caused the cores to expand and break the surrounding shells.

Characterization Methods

Nickel Content. The NiO content of the cast tablets, which had been impregnated with nickel nitrate and dried at 100°C, was determined by measuring the change in weight of the tablets when they were heated in air at 600°C to convert the Ni(NO₃)₂ present to NiO. The reducible nickel content of the oxidized core-in-shell pellets was determined by measuring the change in weight of the pellets when they were treated with hydrogen at 600°C for 4 hr to

convert NiO in the shell into elemental nickel. The reducible nickel content was calculated by means of the following equation:

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

where ΔW and W_t are the change in weight of the pellets during reduction and the total weight of pellets after reduction, respectively

Compression Testing. The force required to fracture a single pellet or tablet was measured with an Accuforce EZ 250 testing machine. The test was conducted by placing the pellet or tablet on the fixed base plate of the machine and then lowering a movable 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. For measuring the force required to break a cylindrical tablet, the tablet was placed with one of its flat sides against the base plate. 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.

Surface Area. A surface area analysis of the pellets and tablets 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 absorbed at 77 K. The method also provided a measurement of the specific volume and size distribution of open pores with a diameter smaller than 780 Å.

Pellet Structure. 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.

Pellet Dimensions. The overall diameter and shell thickness of the core-in-shell pellets were measured with a hand held caliper. Because of the variation in these dimensions for any individual pellet, several measurements were made to determine the average values. The fractional shell volume of an individual pellet was calculated by using the following equation:

$$V_{\text{shell}} = 1 - (d_c/d_p)^3$$

where d_c is the average core diameter and d_p is the average overall pellet diameter.

Performance Testing Methods

Thermogravimetric Analysis. A Perkin-Elmer, TGA 7, thermogravimetric analyzer (TGA) was employed for determining the absorption and regeneration characteristics of the sorbent material alone and for determining the performance characteristics of the combined catalyst and sorbent while reforming hydrocarbons. For either determination, a single pellet of material was suspended within a heated tubular reactor from a sensitive electrobalance that was protected by continuously flushing the system with N_2 . The change in weight of the pellet as it absorbed or released CO_2 was recorded and displayed by a digital computer, which also displayed and controlled the temperature of the system. During an absorption test, the reactor was supplied with a flowing stream consisting of CO_2 and N_2 , while during a hydrocarbon reforming test the reactor was supplied with a stream consisting of steam and N_2 and either methane or propane. The gas flow rates were controlled manually with needle valves and were 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 absorption test a pellet was preheated in the TGA to $750^\circ C$ while surrounded by a stream of N_2 to insure that the sorbent was converted to CaO . Then while the temperature was reduced to $650^\circ C$ and subsequently maintained at this level, a mixture of CO_2

and N_2 in known concentrations was used to treat the pellet, and the gain in weight of the sorbent was recorded. At the end of the absorption period, the sorbent was regenerated by raising the temperature to 750°C and treating the pellet with a stream of pure N_2 . The loss in weight of the pellet was recorded as CO_2 was desorbed.

For a typical performance 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 insure that no CaCO_3 or $\text{Ca}(\text{OH})_2$ were 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. Since steam reforming of either methane or propane produced CO_2 as a byproduct, the progress of the reaction could be observed by monitoring the change in weight of the pellet as the generated CO_2 was absorbed by the sorbent core. The run was continued until the weight either approached a constant value or changed too slowly to be of practical interest because the sorbent was effectively loaded. The sorbent was then regenerated as described above.

Fixed Bed Reactor. A vertical tubular reactor packed with catalyst/sorbent pellets was used for a more comprehensive evaluation of the performance of the material (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 such that the bed of catalyst/sorbent pellets was centered within the furnace. A gas distributor in the form of a porous, sintered quartz plate was located in the lower end of the reactor. The distributor 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

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

void space and reduce gas flow bypassing as well as improve the heat transfer properties of the bed. The SiC seemed to have little catalytic effect. The reactor was supplied with several different gases that were controlled individually and metered separately with calibrated rotameters. Water was also supplied at a controlled rate by a peristaltic 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 $750^\circ C$ for about 10 hr 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 hr 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 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.

RESULTS AND DISCUSSION

Numerous batches of core-in-shell pellets were prepared and tested while searching for a combination of materials and preparation conditions that would yield a product capable of reforming methane or propane and separating H₂ from CO₂ in a single step. Pellets were sought that not only had the necessary catalytic and sorbent properties but also the necessary physical strength. Seven of the more promising batches of core-in-shell pellets were selected for testing by means of thermogravimetric analysis or by employing a fixed bed reactor (see Table 1). In addition, three batches of pellets which consisted of only the shell material impregnated with a nickel catalyst were included for testing in the fixed bed reactor; these are identified as batches T8, T9, and T10 in Table 1. The various batches differed in shell composition, core composition, calcination temperature, and in how the nickel catalyst was introduced. Batches T1, T6 and T10 included some γ -alumina (CP-7) in the shell mixture whereas only α -alumina was present in the shell mixtures applied in the other batches. Limestone particles between 44 and 210 μm (based on sieving) were used in the preparation. Several of the batches were

Table 1. Properties of catalyst/sorbent pellets prepared with different formulations

Batch No.	^b Shell composition, wt. %			^c Core, wt. %		Calcin. temp., °C	^d Ni Catalyst		Pellet size, mm		Brk. force ^f N/mm		
	CP-7	T-64	A16-SG	Lime	Dolime		Soln	Times	Ni, wt. %	O.D.		S.T. ^e	
T1	24	24	32	20	0	100	1100	THF	1	6.0	4.1±0.2	0.4±0.1	2.7±0.2
T2	0	48	32	20	100	0	800	THF	1	5.3	4.4±0.2	0.5±0.1	2.9±0.9
T3	0	48	32	20	100	0	1100	H ₂ O	2	6.0	4.5±0.2	0.5±0.2	6.7±1.9
T4 ^g	0	48	32	20	100	0	1100	H ₂ O	2	7.4	4.5±0.2	0.4±0.1	7.0±2.9
T5	0	48	32	20	100	0	1100	---	0	0	4.5±0.2	0.4±0.1	5.0±2.4
T6	28.5	28.5	38	5	50	50	800	THF	2	6.0	4.5±0.2	0.5±0.2	4.5±1.2
T7	0	57	38	5	100	0	1100	H ₂ O	2	2.9	4.3±0.2	0.5±0.1	15.0±3.5
T8	0	48	32	20	---	---	1100	THF	1	4.4	3.8±0.2	---	---
T9	0	48	32	20	---	---	1100	THF	2	5.9	3.7±0.2	---	---
T10	28.5	28.5	38	5	---	---	800	THF	2	6.3	3.5±0.1	---	---

^aAlso corresponds to "Catalyst No." in subsequent tables^bShell formulation^cCore formulation^dImpregnation solution and number of times it was applied^eShell thickness^fBreaking force/pellet diameter^gVacuum impregnation employed for this batch

calcined at 800°C whereas others were calcined at 1100°C before introducing the nickel catalyst. In a majority of cases the catalyst was introduced by soaking the pellets in a THF solution of nickel nitrate, while in a few cases it was introduced by soaking the pellets in an aqueous solution containing both nickel nitrate and urea. Batch T4 was the only one that received the vacuum treatment before soaking in the nickel nitrate solution, and it did end up with the highest nickel content (7.4 wt %). Batch T5 was prepared without nickel for comparison with all the others. Several of the batches were prepared by soaking the pellets only “1 time” in the catalyst solution whereas others were prepared by soaking them “2 times” to achieve a greater nickel content.

In order to determine the distribution of the nickel catalyst within a pore-in-shell pellet, a representative pellet from batch T3 was cross-sectioned and examined with a scanning electron microscope (SEM) producing the electron micrographs shown in Figure 4. 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 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.

(a)

(b)

Figure 4 Electron micrographs of a small portion of a core-in-shell pellet from batch T3: (a) SEM views at 80X and 200X magnifications, (b) maps showing the distribution of different elements in core and shell.

Several pellets from each batch were selected for measurement of their physical properties which included the outside diameter (O.D.), shell thickness (S.T.), and the force required to break the pellets. These measurements were made after the previously calcined pellets had been impregnated with nickel nitrate, calcined at 550-600°C to decompose the nickel nitrate, and recarbonated. Batch T5 represents an exception since it was not impregnated with the catalyst. The properties of this material were measured following its initial calcination at 1100°C and recarbonation. The results of these measurements, which are included in Table 1, indicate that the dimensions of the core-in-shell pellets did not differ greatly from one batch to another. On the other hand, the overall diameter of the pellets made entirely of shell material was somewhat smaller than that of the core-in-shell pellets. The results further indicate that the stronger pellets were made entirely of α -alumina and were calcined at 1100°C before the catalyst impregnation step. The force required to fracture the pellets in batch T7 was especially great. The principal difference between these pellets and those in batch T3 and T4 was the presence of only 5 wt.% limestone in the shell formulation in contrast to 20 wt % in the other formulations.

Catalyst/Sorbent Testing by Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was employed for a preliminary evaluation of the catalyst/sorbent pellets. The absorption characteristics of the pellets were evaluated by conducting CO₂ absorption tests under controlled conditions. Typical results of such a test are shown in Figure 5. These results were obtained with another pellet from batch T3. The pellet was heated first in a stream of nitrogen, which caused it to lose weight since it had been stored previously in the carbonated form. 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

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

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 mmols 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 that 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 evaluate the performance of the catalyst/sorbent pellets under hydrocarbon reforming conditions, several representative pellets from the first six batches of pellets listed in Table 1 were subjected to a series of tests conducted in the TGA system. In each of these tests a single pellet was first heated in a stream of air or nitrogen to 750°C to insure that the sorbent material in the core was in the form of CaO. The catalyst was then reduced by passing a stream containing approximately 6 mole% H₂ in nitrogen over the pellet at 600°C for at least 4 hr. to insure that the catalyst was in the form of elemental nickel. To conduct a test of hydrocarbon reforming, a mixture of either methane or propane and steam diluted with nitrogen was passed over the catalyst/sorbent pellet at a specified temperature and any change in the weight of the pellet was noted and recorded since a gain in weight of the pellet meant CO₂ was being generated by the reforming reaction and was absorbed by the core. For such a test the mole ratio of steam to hydrocarbon was equivalent to a 3:1 mole ratio of H₂O:C, and for methane reforming the total gas flow rate was maintained at 2.38 mmol/min. For propane reforming the total gas flow rate was kept at 2.23 mmol/min. Most of the tests were conducted at 650°C where the partial pressure of CO₂ in equilibrium with CaO would have been 0.0097 atm corresponding to a CO₂ concentration of 0.97 mole% in a system at 1.0 atm.

When a fresh pellet from any one of the first six batches listed in Table 1 was treated at 650°C for several hours with a mixture composed of nitrogen and either CH₄ and H₂O or CH₄, H₂ and H₂O, no change in weight of the pellet was observed. This outcome meant that either no CO₂ was generated or the quantity was insufficient to create the necessary partial pressure for absorption to take place (see Table 2). On the other hand, a gain in weight was observed when pellets from batches T3 and T4 were treated with a mixture of C₃H₈ and H₂O at 650°C. The result meant that the reaction between propane and steam was sufficiently rapid to generate the

Table 2. TGA results of preliminary steam reforming tests of different catalyst formulations

Batch No.	Pellet No.	Pellet wt., mg	Feed gas composition, mole%				Flow, mmol/min.	Temp., °C	Results
			CH ₄	C ₃ H ₈	H ₂	H ₂ O	N ₂		
T1	1	56.3	11.0	---	---	33.0	56.0	2.38 650/680	$\Delta W = 0$ over 20 hr
T2	1	64.0	11.0	---	---	33.0	56.0	2.38 650	$\Delta W = 0$ over 8 hr
			10.6	---	2.1	31.8	55.5	2.42 650	$\Delta W = 0$ over 8 hr
T3	1	64.0	10.6	---	2.1	31.8	55.5	2.42 800/750/700/650	$\Delta W = 0$ over 15 hr
T3	2	65.0	---	3.9	---	35.1	61.0	2.23 650	$\Delta W > 0^b$
			10.6	---	2.1	31.8	55.5	2.42 650	$\Delta W = 0$
T4	1	62.5	---	3.9	---	35.1	61.0	2.23 650	$\Delta W > 0^c$
			11.0	---	---	33.0	56.0	2.38 650	$\Delta W = 0$
T5	1	57.0	---	3.9	---	35.1	61.0	2.23 650	$\Delta W = 0$
T6	1	59.5	10.6	---	2.1	31.8	55.5	2.42 750/700/650	$\Delta W = 0$ over 8 hr
T6 ^a	2	65.0	11.0	---	---	33.0	56.0	2.38 600/550/650	$\Delta W > 0^d$

^aReused pellet from fixed bed reactor tests^bTested over 3 cycles^cTested over 2 cycles^dTested over 3 cycles

necessary CO_2 partial pressure for absorption to take place. However, a similar result did not occur when batch T5 was treated with C_3H_8 and H_2O at 650°C because no nickel was present in this material. Therefore, in at least two fresh batches of pellets the nickel catalyst was sufficiently active to catalyze the reaction of C_3H_8 and H_2O at an observable rate but not the reaction of CH_4 and H_2O . 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. Since pellets from the first two batches were not tested with C_3H_8 and H_2O , it was not determined if they would have produced similar results. Although a fresh pellet from batch T6 was not sufficiently active to demonstrate steam reforming of methane at 650°C with the TGA system, it was discovered later that the catalytic activity of the material improved through use in fixed bed reactor tests. Therefore, it became possible to demonstrate steam reforming of methane in the TGA system by employing a pellet from batch T6 after it had been used in fixed bed reactor tests.

The results of a successful propane reforming test with a pellet from batch T3 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 a 3:1 mole ratio of $\text{H}_2\text{O}:\text{C}$. The total flow rate of gas and steam was equivalent to 2.23 mmol/min. When this mixture was brought into contact with a freshly regenerated pellet at 650°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°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 CO_2 to be desorbed, and the pellet weight dropped to its initial value.

Figure 6. TGA results of a 2 cycle test of C_3H_8 reforming and sorbent regeneration using a core-in-shell pellet from batch T3. Total pressure = 1.0 atm, Feed: 3 moles H_2O /mole C .

indicating that the sorbent had been regenerated. The temperature was then reduced to 650°C and a second cycle of CO_2 production and absorption was conducted.

To demonstrate the catalytic activity of a pellet from batch T6 after it had been used in fixed bed reactor tests, a three cycle test was conducted with the activated catalyst pellet (see Figure 7). The following gas mixture was supplied for reforming: 11 mole% CH_4 , 33 mole% H_2O and 56 mole% N_2 . The total flow rate of gas and steam was equivalent to 2.38 mmol/min. While each reforming cycle was conducted at a different temperature, 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 suggested that the shell was more porous than in the previous case either due to the difference in composition or calcination temperatures.

Figure 7. TGA results of a 3 cycle test of CH_4 reforming and sorbent regeneration using a catalyst-activated core-in-shell pellet from batch T6. Total pressure = 1.0 atm, Feed: 3 moles H_2O /mole C.

Fixed Bed Reactor Tests of Different Catalyst Formulations

The different catalyst/sorbent formulations shown in Table 1 were also evaluated by conducting a series of hydrocarbon reforming tests with a fixed bed reactor. For these tests the vertical tubular reactor was packed with 6 g of catalyst/sorbent pellets (or 5 g catalyst pellets without sorbent cores) and 4 g of SiC pellets, which provided a bed depth of 12-13 cm. For many tests 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 rate of steam and hydrocarbon was 2.41 mmol/min when CH_4 was fed or 2.01 mmol/min when propane was fed. For some tests the reactor was supplied with a 9:1 mole ratio of CH_4 to C_3H_8 or a 9:1 mole ratio of CH_4 to H_2 while maintaining the 3:1 ratio of steam to carbon. For these tests the total mass flow rate of steam and other gases

was 2.31 mmol/min when CH_4 and C_3H_8 were fed together or 2.47 mmol/min when CH_4 and H_2 were fed together. To evaluate catalyst performance the tests were conducted under conditions where the reforming reaction would not be affected by CO_2 absorption. Such conditions were present at higher temperature, e.g., at 760 -780°C, where CO_2 would not be absorbed or at a lower temperature, e.g., at 650°C, after the sorbent had been saturated with CO_2 . It should be noted that typically steam reforming of methane is conducted in practice at 800°C or higher.

One group of tests was conducted to evaluate the performance of the different catalyst formulations for reforming propane at high temperature, i.e., 760-770°C. Performance was based on the composition of the product gas mixture that was produced by the fixed bed reactor. A high concentration of H_2 and a low concentration of C_3H_8 and CH_4 were indicative of good catalyst performance. For the present discussion the various batches of pellets listed in Table 1 will be identified as "catalyst No." rather than "batch No." The results presented in Table 3 show that all of the catalysts tested seemed effective in promoting propane reforming to some degree at 760-770°C. It is apparent that performance varied among the different catalyst formulations and the length of time each catalyst was in service. A comparison of the results obtained with catalyst T8 and T9 shows that the catalyst activity of each material increased with length of time in service. On the other hand, there appeared to be no variation over time in the activity of catalyst T10. For these three materials, the catalytic activity increased from T8 to T9 to T10. Interestingly, the concentration of nickel in these materials also increased in the same order (see Table 1). Among the other catalysts, the one having the greatest activity was T6 which produced results similar to those produced by T10. Since these materials had the same shell formulation, it is not surprising that they displayed the same catalytic activity. The only

Table 3. Results of C_3H_8 reforming tests conducted with 3:1 mole ratio of $H_2O:C$ in feed

^a Catalyst No.	Day	Time, Min.	Temp., °C	^b Product composition, mole%					Total
				CH ₄	CO	CO ₂	C ₃ H ₈	H ₂	
T2	1	120	770	3.1	11.5	14.6	tr.	70.8	100
	2	240	760	0.3	9.3	15.8	tr.	74.6	100
T3	7	20	770	5.0	15.0	20.0	0.0	60.0	100
	8	30	770	1.6	14.8	16.5	0.1	67.0	100
T6	14	10	770	0.0	17.5	12.1	0.0	70.4	100
	14	320	770	0.0	12.9	14.2	0.0	72.9	100
	15	10	770	0.0	15.1	14.0	0.0	70.9	100
	15	320	770	0.0	17.3	11.2	0.0	71.5	100
T8	1	10	770	9.7	7.6	16.0	4.0	62.7	100
	1	30	770	7.6	9.3	15.4	0.1	67.5	100
	1	120	770	3.8	10.1	15.3	0.0	70.8	100
	1	390	770	2.9	10.4	16.2	0.0	70.4	100
T9	1	10	760	4.8	10.7	15.8	0.0	68.7	100
	1	35	760	2.0	11.9	14.9	0.0	71.3	100
	1	120	760	1.0	13.9	13.6	0.0	71.5	100
T10	1	10	770	0.0	13.5	14.4	0.0	72.2	100
	1	30	770	0.0	13.6	14.5	0.0	72.9	101
	1	120	770	0.0	12.5	15.5	0.0	72.1	100

^aCorresponds to "Batch No." in Table 1.^bComposition reported on H_2O -free basis.

known difference in the materials was that T6 was in the form of core-in-shell pellets, whereas T10 was in the form of pellets made entirely of shell material. The superior catalytic activity of these two materials could have been due in part to the presence of γ -alumina (CP-7), since none of the other materials had this component. Consequently, T6 and T10 had a larger specific surface area than any of the other materials for supporting the nickel catalyst, which could have facilitated the dispersion of nickel.

Also of considerable importance is the fact that after 15 days and many hours of testing, the activity of T6 was high and very similar to that of T10 initially, which suggests that the activity of T6 had not declined appreciably with use. Unfortunately, T6 was not tested with propane alone until after 13 days of testing had been completed with methane and mixtures of methane and propane or methane and hydrogen. Therefore, it can only be assumed that T6 would have performed as well as T10 on the first day of testing.

Due to the apparent superiority of T6 and T10, they were selected for testing as methane reforming catalysts over a range of temperature, and the results are presented in Table 4. It is apparent that with either catalyst, methane reforming was essentially complete, providing the temperature was 750-760°C or higher. Also at the highest temperature, the results were similar to those achieved by reforming propane (Table 3) except that the hydrogen concentration was slightly greater. Therefore, at high temperature the two catalysts appeared equally effective for reforming methane and propane. Of course, as the temperature was reduced the concentration of methane increased in the product gas stream indicating a decline in methane conversion. Also as the temperature dropped, the concentration of carbon monoxide declined while the concentration of carbon dioxide remained relatively constant or increased slightly. Furthermore, the concentration of hydrogen did not decline appreciably until the temperature fell below 650°C.

Table 4. Results of CH₄ reforming tests conducted with 3:1 mole ratio of H₂O:CH₄ in feed

^a Catalyst No.	Day	Time, Min.	Temp., °C	^b Product composition, mole%					Total
				CH ₄	CO	CO ₂	C ₃ H ₈	H ₂	
T6	11	340	780	0.0	11.0	11.8	0.0	77.2	100
	12	10	780	0.4	13.6	9.6	0.0	76.4	100
	13	10	780	0.0	8.7	15.5	0.0	75.8	100
	12	400	770	0.0	13.1	11.2	0.0	75.7	100
	13	400	770	0.0	9.2	15.1	0.0	75.7	100
	11	25	760	0.3	12.8	11.7	0.0	75.2	100
	9	120	650	2.7	7.7	13.0	0.0	76.6	100
	10	120	600	10.2	4.5	14.6	0.0	70.7	100
	11	150	600	6.5	5.8	15.3	0.0	72.4	100
	13	280	580	9.3	5.0	15.1	0.0	70.6	100
	12	320	560	12.8	6.8	13.5	0.0	66.9	100
T10	2	30	750	tr.	13.4	10.6	0.0	76.0	100
		180	650	3.2	9.5	12.8	0.0	74.6	100
		330	590	4.9	7.8	13.4	0.0	74.0	100
		420	550	7.8	4.9	15.8	0.0	71.5	100

^aCorresponds to "Batch No." in Table 1^bComposition reported on H₂O-free basis

These results indicate that while the conversion of methane decreased, the conversion of carbon monoxide increased because of the water gas shift reaction, which is thermodynamically favored by lower temperature.

In another group of methane reforming tests, hydrogen was added to the feed to insure reduction of the nickel catalyst, and the results are shown in Table 5 for three different catalysts. For each catalyst the results are arranged in descending order of temperature. On the first day of testing at 780°C neither catalyst T3 nor T6 displayed a high level of catalytic activity since a relatively large concentration of methane (18 or 26 mole%) remained in the product gas while the concentration of hydrogen (60 mole%) was lower than that observed on subsequent days. After several days of testing and repeating the test at 780°C, the concentration of methane dropped to 2.0 mole% and the concentration of hydrogen climbed to 68 mole% in the case of catalyst T3. In the case of catalyst T6, the results were even better with the concentration of methane dropping to 0 mole% and the concentration of hydrogen climbing to 78 mole%. Again the results showed an increase in catalytic activity over the first day or two of testing. Reducing the temperature also had less effect on the results achieved with catalyst T6 than those achieved with catalyst T3 as indicated by the comparative changes in methane and hydrogen concentrations.

A comparison of the results achieved with catalyst T6 while reacting a mixture of methane and hydrogen (Table 5) with those obtained while reacting only methane (Table 4) shows that generally the principal difference was a somewhat higher level of hydrogen concentration in the product gas when hydrogen was added to the feed. Therefore, the addition of hydrogen to the feed seemed to have little or no effect on the actual chemical reaction.

Table 5. Results of CH₄ reforming tests conducted with 9:1 mole ratio of CH₄:H₂ and 3:1 mole ratio of H₂O:CH₄ in feed

^a Catalyst No.	Day	Time, Min.	Temp., °C	^b Product composition, mole%					Total
				CH ₄	CO	CO ₂	C ₃ H ₈	H ₂	
T3	1	120	780	18.0	9.0	13.0	0	60.0	100
	4	240	780	2.0	15.0	15.0	0	68.0	100
	5	20	780	2.0	15.0	15.0	0	68.0	100
	1	350	675	31.1	2.6	12.0	0	54.2	100
	4	15	670	13.0	9.0	12.0	0	66.0	100
	4	150	670	12.8	8.5	14.9	0	63.8	100
	5	150	665	18.0	6.0	13.0	0	63.0	100
	5	80	660	19.0	4.0	6.0	0	71.0	100
	1	120	780	26.0	3.0	11.0	0	60.0	100
	5	20	780	0.0	12.4	9.8	0	77.7	100
T6	6	420	780	0.0	10.4	11.7	0	77.9	100
	7	275	780	0.0	14.0	13.6	0	72.4	100
	8	320	780	0.0	9.2	13.0	0	77.8	100
	5	280	660	0.1	8.2	13.4	0	78.3	100
	6	120	620	0.5	9.5	10.9	0	79.1	100
	8	210	590	6.8	5.7	14.2	0	73.3	100
	7	200	560	10.2	7.3	15.2	0	67.3	100
	3	240	700	28.0	4.0	9.0	0	58.0	99
	4	60	680	44.0	2.0	8.0	0	46.0	100
	3	90	675	60.6	1.1	5.3	0	33.0	100
T7	3	240	700	28.0	4.0	9.0	0	58.0	99
	4	60	680	44.0	2.0	8.0	0	46.0	100
	3	90	675	60.6	1.1	5.3	0	33.0	100

^aCorresponds to "Batch No." in Table 1^bComposition reported on H₂O-free basis

The results obtained with catalyst T7 and presented in Table 5 indicate that this material was not a particularly effective catalyst for methane reforming, which may have been due to the fact that it had the lowest nickel content of any of the catalysts tested (see Table 1). Furthermore, the material had the greatest compressive strength among any of the batches which could have been due to high shell density and, therefore, low porosity.

Other hydrocarbon reforming tests of several different catalysts were conducted with a mixture of methane and propane in a 9:1 mole ratio, and the results are given in Table 6. All of the catalysts in this group proved capable of reforming most of the propane in the mixture at 650°C and all of the propane at 675°C or above. However, catalyst T6 again proved to be the best for reforming methane in the mixture at all three temperature levels since its use always produced the lowest methane concentration and the highest hydrogen concentration in the product gas mixture.

Tests of Simultaneous Reaction and Absorption

The preceding work showed clearly that catalyst T6 was the most active catalyst for steam reforming hydrocarbons. This was the catalyst present in the core-in-shell pellets also identified as batch T6 in Table 1. These pellets, which had a core derived from a mixture of dolime and limestone enclosed by a shell with a superior catalyst, were used for demonstrating hydrocarbon reforming in the presence of a CO₂ absorbent. For this demonstration the previously described fixed bed reactor was packed with a mixture composed of 6 g of core-in-shell pellets and 4 g of SiC pellets. The catalyst had been activated through previous usage. 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 rate of steam and hydrocarbon was 2.41 mmol/min when CH₄ was fed or 2.01 mmol/min when propane was fed.

Table 6. Results of hydrocarbon reforming tests conducted with 9:1 mole ratio of CH_4 : C_3H_8 and 3:1 mole ratio of H_2O :C in feed

^a Catalyst No.	Day	Time, Min.	Temp., °C	^b Product composition, mole%					Total
				CH_4	CO	CO_2	C_3H_8	H_2	
T2	4	240	780	3.1	8.3	14.6	tr.	74.0	100
T3	2	120	780	5.9	16.8	12.9	0.0	64.4	100
T6	2	120	780	0.0	14.0	11.0	0.0	75.0	100
T6	3	360	780	0.0	14.0	11.0	0.0	76.0	100
T7	2	350	780	3.1	19.8	6.3	0.0	70.8	100
T2	3	90	675	18.8	8.9	13.9	0.0	58.4	100
T3	2	240	675	17.0	11.0	12.0	0.0	60.0	100
T6	2	240	675	4.0	11.0	11.0	0.0	74.0	100
T7	3	90	675	27.5	2.6	11.2	0.0	58.6	100
T2	3	90	650	14.2	7.1	14.2	0.4	64.0	100
T2	4	120	650	13.8	7.4	15.9	0.3	62.6	100
T3	3	90	650	14.2	7.1	14.2	0.4	64.0	100
T3	3	125	650	18.0	10.0	12.0	tr.	61.0	101
T6	3	110	650	8.4	7.4	13.7	0.0	70.5	100

^aCorresponds to "Batch No." in Table 1^bComposition reported on H_2O -free basis

Figure 8. Product gas composition on a dry basis produced by steam reforming C_3H_8 in the fixed bed reactor packed with core-in-shell pellets from batch T6. Total pressure = 1.0 atm, Feed: 3 moles H_2O /mole 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 all of the propane was reacted at a reactor temperature of 770°C even though no CO_2 was absorbed. This resulted in a product gas mixture with 70-72% H_2 , 13-15% CO_2 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 H_2 in the gaseous product quickly climbed to 94% while the concentration of CO_2 dropped to 0.4% indicating that most of the CO_2 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

Table 7. Product composition resulting from propane 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	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

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 absorption phase of each test run is indicated in Table 7 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, the minimum H₂ concentration (80%) and maximum CO₂ and CO concentrations (9.0% and 5.1%, respectively) were observed at 650°C for the absorption phase. On the other hand, the CH₄ concentration (4.0%) at 520°C was high because either more CH₄ was produced by the methanation reaction,

or less CH₄ was reformed. Since reaction 4 is exothermic, it is favored by lower temperature.

The same bed of catalyst/sorbent pellets that 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. When the reactor temperature was lowered to 600°C to demonstrate methane reforming while CO₂ was being absorbed, the results were also similar to those obtained while reforming propane at a 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, and 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 causing CO₂ to be desorbed and increasing the CO₂ concentration in the reactor effluent for a short time. At the same time the CO concentration also spiked and the H₂ concentration

Figure 9. Product gas composition on a dry basis produced by steam reforming CH_4 in the fixed bed reactor packed with core-in-shell pellets from batch I6. Total pressure = 1.0 atm, Feed: 3 moles H_2O /mole C.

dipped. This result could have been due in part to the effect of an increase in both temperature and CO_2 concentration on the water gas shift reaction equilibrium.

Additional steam reforming experiments were conducted with methane using different temperatures for the 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 CO_2 absorption phase is shown in Table 8. 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 H_2 was always greater and the concentrations of CO_2 and CO were always lower while CO_2 was being absorbed. One of the differences in the results was the higher temperature (600°C) required for reforming CH_4 in order

Table 8. 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

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.

The gas composition data reported in Table 8 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 equilibrium 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.

(a)

(b)

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

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

The CO₂ absorption in Mode I produced conversions of CH₄ and CO that were 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 equilibrium driving force for CO₂ absorption which declines with increasing temperature.

The overall yield of H₂ produced by reactions 1 and 2 was also determined for the different temperatures and operating modes listed in Table 8. 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 given 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 given in Figure 13. The maximum enhancement (38%) was observed at 580°C, although the enhancement at 560°C (36%) was nearly as great.

Physical Properties Study

The preceding results showed that incorporation of γ -alumina in the form of CP-7 in the catalyst supporting shell material produced a more active catalyst presumably because of the greater surface area of the γ -alumina. However, the substitution of γ -alumina for α -alumina also appeared to reduce the compressive strength of the shell material. Therefore, the interdependence of surface area and compressive strength on the composition and calcination temperature of the shell material was investigated to see whether the compressive strength could be improved without greatly sacrificing surface area.

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

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

Table 9. Properties of cast and calcined tablets of shell material after calcining at 1100°C for 2 hr.

Shell Mix	^a Mix composition, wt.%				Catalyst		Surf. area, m ² /g	^b Pore vol, cm ³ /g	Break. force, N
	CP-7	T-64	A-16SG	Lime	Impreg. times	NiO, wt. %			
C1	0	48	32	20	0	0	2.4	0.004	409
					1	5.4	---	---	---
					2	11.4	---	---	---
C2	48	0	32	20	0	0	36.2	0.093	48
					1	7.8	---	---	---
					2	14.0	---	---	---
C3	24	24	32	20	0	0	5.3	0.015	98
					1	6.9	---	---	---
					2	12.0	---	---	---
C4	36	12	32	20	0	0	23.9	0.067	32
					1	10.3	---	---	---
					2	17.6	---	---	---
C5	30	18	32	20	0	0	15.1	---	43
					1	7.5	---	---	---
					2	13.2	---	---	---
C6	18	30	32	20	0	0	7.4	---	95
					1	7.3	---	---	---
					2	11.1	---	---	---

^aComposition of formulation.^bSpecific volume of micropores.

For a preliminary assessment of the effect of composition on the surface area and compressive strength of the shell material, a series of tablets were cast with the different formulations indicated by Table 9. Among these formulations the relative amounts of CP-7 (γ -alumina) and T-64 (α -alumina) were varied while the concentrations of A-16SG (α -alumina)

and limestone ($-297/+44\ \mu\text{m}$) were kept constant. The solids were suspended in water containing 5 wt.% lignin for casting. As before the cast cylindrical tablets were 6 mm in diameter and 6 mm long. A number of tablets were prepared with each of the compositions listed in the table and then calcined at 1100°C for 2 hr. Some of the calcined tablets were subjected to measurement of surface area by the BET method, which also provided a measure of the specific volume of the micropores, i.e., pores with a diameter smaller than $780\text{\AA}$. Other tablets were crushed to determine the minimum force required to fracture a tablet. The results of these tests are listed in Table 9 and are also plotted in Figures 14 to 16. From the results of these tests it can be seen that the surface area and micropore volume varied directly with CP-7 concentration because CP-7 was the predominant source of micropores and their associated surface area. On the other hand, the force required to fracture any given tablet decreased with increasing CP-7 concentration up to a certain level, i.e., 36-40 wt.%. Beyond this level the force required to fracture a tablet actually seemed to increase with an increase in CP-7 concentration.

Some of the cast tablets, which had been calcined, were also impregnated with the nickel catalyst by immersing the tablets in a THF solution containing the equivalent of 3 g $\text{Ni}(\text{NO}_3)_2$ in 5 ml THF. The preheated tablets were quickly immersed in the solution and allowed to soak for 1 hr. The tablets were subsequently air dried overnight at room temperature and then dried further in an oven at 110°C . The tablets were then calcined at 600°C for 4 hr to convert the nickel salt to NiO. The change in weight of the tablets during calcination provided a measure of the NiO content which is reported in Table 9. The process of impregnation and calcination was also repeated to increase the NiO content. The results of the second impregnation are also shown in this table. The NiO content after the second impregnation was from 1.5 to 2.1 times greater than after the first impregnation. Although the NiO content of the tablets tended to increase in

Figure 14. Effect of CP-7 concentration on surface area of cast tablets after calcining at 1100°C.

Figure 15. Effect of CP-7 concentration on micropore volume of cast tablets after calcining at 1100°C.

Figure 16. Effect of CP-7 concentration on compressive strength of cast tablets after calcining at 1100°C.

proportion to the CP-7 content, the NiO content of the C4 mix was unusually large and, therefore, it seemed anomalous.

The preceding results showed only the effect of substituting CP-7 for I-64 alumina on the crush strength of the tablets. Previous work had shown that the crush strength of similar tablets made with only I-64 and A-16SG alumina and limestone was strongly dependent on the relative proportions of all three materials.^{1,3} The strongest pellets were produced by starting with 48 wt % I-64, 32 wt.% A-16SG, and 20 wt.% limestone, i.e., the C1 mix. The particle size of the limestone had ranged from 44 to 297 μm . To expand on this knowledge base, further consideration was given to the effects of limestone concentration and particle size in the mix and also the concentration of A-16SG alumina in the mix.

Figure 17. Effect of limestone concentration on compressive strength of cast tablets after calcining at 1100°C

To investigate the effect of limestone concentration further, another series of tablets was cast with different limestone concentrations while maintaining the 3:2 ratio of T-64 to A-16SG alumina as in the C1 mix. The limestone particles ranged in size from 44 to 210 μm , and CP-7 alumina was not included in the particle mixture. An aqueous solution containing 5 wt.% lignin was used for preparing the casting slurry. The cast tablets were dried and then calcined at 1100°C for 2 hr. When the tablets were crushed subsequently, the results presented in Figure 17 were obtained. These results were similar to those observed before except that the maximum crush strength was achieved with 10 wt % limestone, whereas previously it had been achieved with 20 wt %. This difference seemed due to the use of limestone having a somewhat smaller particle size distribution since the limestone used previously ranged from 44 to 297 μm in size.

Table 10. Effect of limestone particle size on the compressive strength of cast and calcined (1100°C) tablets formulated with 5 wt % limestone, 57 wt % I-64, and 38 wt % A-16SG alumina.

Limestone particle size		Breaking force, N
Micrometers	Screen size	
37 - 44	-325/+400	811 ± 173
44 - 63	-230/+325	707 ± 40
63 - 210	-70/+230	590 ± 105
44 - 210	-70/+325	368 ± 67

To study the effect of limestone particle size further, another series of tablets was cast using different sizes of limestone particles. For this study as well as other studies involving particles of different sizes, the particles included in any given size range were determined by dry screening the material. Although the accuracy of this method decreases for very small particles, it does provide at least an indication of the effect of particle size. For the present series only 5 wt % limestone was included in the mixture, which also contained T-64 and A-16SG alumina in the same 3:2 ratio. Again 5 wt % lignin was included in the water used for casting. As before the tablets were calcined at 1100°C for 2 hr and crushed. The results are compared in Table 10 with those obtained before with 44 to 210 μm size limestone. It is apparent that the highest compressive strength was achieved with the smallest limestone particles suggesting that even finer size limestone should be investigated in the future to achieve the strongest possible pellets.

Another factor that has a major effect on the compressive strength of the cast and calcined tablets is the concentration of A-16SG alumina in the shell formulation. This can be seen from the results of preparing and testing tablets representing 19 different compositional

Figure 18. Effect of A-16SG concentration on compressive strength of cast tablets after calcining at 1100°C.

formulations. Among these formulations the concentrations of the various components ranged as follows: 0 - 90 wt % A-16SG alumina, 0 - 48 wt % T-64 alumina, 0 - 60 wt % CP-7 alumina, and 10 - 48 wt.% limestone. The limestone chosen for these formulations included particles between 44 and 297 μm . As before a 5 wt % lignin solution was used for casting, and the resulting tablets were calcined at 1100°C for 2 hr before testing. The results of compression testing are given by Figure 18 which shows that the force required to fracture the tablets was proportional to the concentration of A-16SG in the formulation. Although the data are somewhat

scattered due to the variation in the concentrations of the other components, it is apparent that the concentration of A-16SG alumina has a major effect on tablet strength. The strongest tablets were composed of 90 wt.% A-16SG alumina and 10 wt.% limestone, and they failed when a force of 378 ± 134 N was applied. Replacing part of the A-16SG alumina with any of the other materials reduced the compressive strength of the tablets. For example, when part of the A-16SG alumina was replaced by CP-7 alumina resulting in a mixture composed of 70 wt.% A-16SG alumina, 20 wt.% CP-7 alumina, and 10 wt.% limestone, the force required to fracture the tablets decreased to 102 ± 18 N (the third highest point in Figure 18). However, replacing the same amount of A-16SG alumina with a mixture of T-64 and CP-7 alumina was less deleterious. A mixture composed of 70 wt.% A-16SG alumina and 10 wt.% each of T-64 alumina, CP-7 alumina, and limestone required a force of 191 ± 30 N to fracture the tablets. Therefore, this composition provided the second strongest material.

Another factor that has an important effect on both the compressive strength and surface area of the pellets or tablets is the calcination temperature. This effect was studied by first casting a batch of 6 mm diameter by 6 mm long tablets using a mixture composed of 48 wt.% T-64 alumina, 32 wt.% A-16SG alumina, and 20 wt.% limestone having a particle size of 44 to 297 μm . This mixture will be referred to as the T-64 mix in the following discussion. A 5 wt.% lignin solution was used for the casting operation. After the tablets had been dried, different portions were calcined at different temperatures for 2 hr and then subjected to a compression test and BET surface area measurement. The results are presented in Figures 19 and 20, and they show that increasing the calcination temperature from 600°C to 1100°C increased the crush strength 30 fold in the case of the T-64 mix. They also indicate that increasing the calcination temperature from 900° to 1100°C increased the crush strength 10 fold. The effect of calcination

Figure 19. Effect of calcination temperature on compressive strength of tablets made with different mixtures.

Figure 20. Effect of calcination temperature on surface area of tablets and pellets made with different mixtures.

temperature on surface area was less pronounced as Figure 20 shows. The surface area generally decreased with increasing calcination temperature which was to be expected, since surface area is known to be function of the degree of sintering which depends on calcination temperature.

The effect of calcination temperature on tablets formulated with CP-7 alumina in place of T-64 alumina was determined next. Except for this substitution, the composition and preparation of the tablets was the same as before. However, two different batches of tablets were prepared, one using a 5 wt.% lignin solution and another using a 10 wt.% solution. Different portions of these batches were calcined at 900, 1000, and 1100°C, respectively, for 2 hr. The results of compression testing displayed in Figure 19 indicate that while the calcined tablets made of the CP-7 mix and with 10 wt.% lignin solution were slightly stronger than those made with the 5 wt.% lignin solution, they were much weaker than those made with the T-64 mix at any given calcination temperature. On the other hand, the tablets made with the CP-7 mix had a much larger surface area than those made with the T-64 mix for any given calcination temperature (see Figure 20). Also the surface area of the tablets made with CP-7 mix declined slightly with an increase in calcination temperature from 600 to 900°C in contrast to the behavior noted for the tablets made with T-64 mix. However, an increase in calcination temperature from 900 to 1100°C reduced the surface area of the tablets made with the CP-7 mix by 44% which was similar to the 52% reduction experienced by the other tablets.

The effect of nickel impregnation on the surface area of the tablets made with the CP-7 mix was also determined. For this purpose the previously calcined tablets were soaked in a tetrahydrofuran (THF) solution of nickel nitrate and then heated to 550-600°C to decompose the salt into NiO. The results are shown in Figure 20 for different initial calcination temperatures, i.e., the temperatures used in treating the tablets before impregnation. It is quite apparent that

nickel impregnation reduced the surface area over the entire range of calcination temperature. Moreover, the relative change in surface area with calcination temperature was similar to that observed with the Ni-free tablets.

While the preceding results were determined with cast tablets of shell material, it was assumed that the results would also be indicative of how the properties of pellets made by drum pelletization would be affected by material composition and calcination temperature. Although the available resources did not permit complete verification of this assumption, some results were obtained that tended to support the assumption. For example, the surface area of pellets made by drum pelletization were affected by calcination temperature in about the same way as pellets made by casting (see Figure 20). In other words, the surface area declined with increasing temperature, and the rate of decline was greater at higher temperature.

However, Figure 20 also shows that pellets made by drum pelletization of the T-64 mix had a surface area that was 30 to 60% less than that of cast tablets of the same material. A similar difference in surface area between cast tablets and pellets made by drum pelletization was observed with products made of the CP-7 mix and calcined at 1100°C. The resulting surface area of the pellets (18 m²/g) was only half of that shown for Ni-free tablets in Figure 20. The difference in surface area for the pellets and tablets can be attributed to the difference in density of the two materials. Drum pelletization produced a more compact and denser structure than that produced by casting. This observation was also supported by the difference in the specific micropore volume of the two types of materials. For example, cast tablets made with the CP-7 mix and calcined at 1100°C had a micropore volume of 0.094 cm³/g whereas pellets made only of the same shell material and calcined at the same temperature had a micropore volume of 0.076 cm³/g.

The preceding results indicate several ways in which the compressive strength and surface area of the shell material are affected by composition and calcination temperature. Substitution of high surface area γ -alumina (CP-7) for low surface area α -alumina (I-64) increases the surface area of the material almost in direct proportion to the level of substitution. On the other hand, the compressive strength of the calcined material decreases rapidly as the level of substitution increases. The compressive strength of the calcined material also depends on both the particle size and concentration of the limestone incorporated in the formulation. For a mixture of α -alumina and -44/+210 μm particles of limestone, the maximum compressive strength of the calcined tablets was achieved with 10 wt.% limestone. Much stronger tablets were produced by reducing the limestone particle size to -37/+44 μm and limiting the concentration to 5 wt.%. This trend invites future exploration. Another important factor is the concentration of the finest size of α -alumina particles (A-16SG) in the shell formulation since the compressive strength of the calcined mixture is proportional to this concentration.

The compressive strength of the shell material increases with calcination temperature over the range from 600 to 1100°C, whereas the surface area generally decreases, especially above 900°C. These effects as well as the dependence of compressive strength on particle size indicate that the compressive strength is actually dependent on the degree of sintering of the material for it is well known that finer size particles sinter more readily than coarser particles and also that sintering converts micropores to macropores with an attendant loss of surface area.

CONCLUSIONS

A promising material for use in steam reforming hydrocarbons and separating the reaction products thereof can be made in the form of small spherical pellets, each pellet consisting of a core capable of absorbing CO_2 surrounded by a shell that supports a catalyst.

Furthermore, the core-in-shell pellets that had been developed previously for desulfurizing hot coal gas can be adapted for this application by introducing a nickel catalyst into the porous shell of each pellet. These pellets consist of cores made of limestone or dolime particles encased in shells made largely of alumina particles with some limestone particles. The shells are strengthened through sintering at high temperatures (e.g., 1100°C). A nickel catalyst can be introduced by soaking the particles in either an aqueous or organic solution of nickel nitrate followed by calcination at 600°C to decompose the nickel nitrate, and subsequent reduction with hydrogen at 550-600°C to form elemental nickel. This procedure leads to a dispersion of very fine nickel particles within the pellet shells and within the adjacent border of core material. Catalyst/sorbent pellets prepared with the original core and shell formulation have adequate compressive strength and readily absorb CO₂, but their catalytic activity is somewhat limited because the shells are composed largely of α -alumina with a relatively small surface area. By replacing a portion of the α -alumina with γ -alumina having a large surface area, the catalytic activity of the catalyst/sorbent material is improved noticeably. However, this replacement also reduces the compressive strength of the pellets. Since the compressive strength depends not only on the relative amounts of γ -alumina and α -alumina but also on several other factors, it may be possible to find an optimum combination of factors that will provide the necessary physical strength and catalytic activity. The factors that bear further consideration include the relative concentrations and particle size distributions of the α -alumina, γ -alumina, and limestone particles plus the calcination temperature and time used for shell sintering.

By conducting steam reforming of methane or propane in a bed of the improved catalyst/sorbent pellets that have been developed to date, hydrogen can be produced and separated from CO₂ in a single stage. Furthermore, the sorbent can be regenerated easily by

increasing its temperature and/or treating it with an inert gas. In laboratory tests of methane reforming conducted at 600°C and 1 atm, a product with 96 mole% H₂ (dry basis) has been produced while also achieving a H₂ yield of 95%. Similar results have been achieved by reforming propane at 560°C. In addition, the combined catalyst/sorbent has been regenerated and reused multiple times without seriously degrading its catalytic properties or absorption capacity.

These results are very relevant to the development of more efficient and less costly technology for producing hydrogen from coal with all of its implications for energy utilization with less environmental pollution.

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