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Meng Kong
Zhejiang University

Karl O. Albrecht
Pacific Northwest National Laboratory

Brent H. Shanks
Iowa State University, bshanks@iastate.edu

See next page for additional authors

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Abstract
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Keywords
carbon dioxide, catalysts, chemical shift, porous shells, shell materials, side reactions, spherical pellets, water gas shift (WGS) reaction

Disciplines
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Comments

Authors
Meng Kong, Karl O. Albrecht, Brent H. Shanks, and Thomas D. Wheelock

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Development of a Combined Catalyst and Sorbent for the Water Gas Shift Reaction

Meng Kong,† Karl O. Albrecht,‡ Brent H. Shanks,§ and Thomas D. Wheelock*‡§

†Institute of Catalysis, Key Lab of Applied Chemistry of Zhejiang Province, Zhejiang University, Hangzhou, Zhejiang 310028, China
‡Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99352, United States
§Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States

ABSTRACT: A combined catalyst and sorbent was developed for reacting CO with steam to produce H2 in a single reaction stage at 600 °C by employing the water gas shift (WGS) reaction. The combined material was in the form of spherical pellets where each pellet consisted of a CaO core for absorbing byproduct CO2 surrounded by a porous shell of Al2O3 which supported a Ni catalyst. The best results were achieved by incorporating 5 wt % limestone in the shell material to suppress coking. By employing the best core-in-shell pellets and supplying a 3:1 mol ratio of steam to CO at 600 °C, more than 97% of the CO was converted to H2 by the WGS reaction and less than 1% was converted to CH4 by a side reaction. Also, none of the CO was converted to coke.

INTRODUCTION

The water gas shift (WGS) reaction shown below is frequently employed for the production of hydrogen (H2) by reacting steam (H2O) with carbon monoxide (CO) that is produced either by reforming hydrocarbons or by gasifying coal or biomass.

CO(g) + H2O(g) ↔ H2(g) + CO2(g) \[\Delta H_{25^\circ C} = -41 \text{ kJ/mol}\] (1)

Because this is an exothermic reaction, it becomes thermodynamically limited at high temperature. Therefore, a two-stage industrial process has been widely used in which a mixture of gases is first reacted over a Fe3O4/Cr2O3 catalyst at 350–500 °C and then over a Cu/ZnO/Al2O3 catalyst at about 200 °C.1

An attractive alternative under development is a single-stage process which conducts the preceding reaction in the presence of a CO2 absorbent such as CaO so that the following reaction takes place simultaneously:

CO2(g) + CaO(s) ↔ CaCO3(s) \[\Delta H_{25^\circ C} = -175 \text{ kJ/mol}\] (2)

By removing CO2 from the reaction mixture, the equilibrium is shifted to the product side, which makes it possible to conduct the WGS reaction at a higher temperature with other catalysts. Han and Harrison2,3 showed that by conducting the WGS reaction in a fixed bed reactor packed with either calcined limestone or dolomite a large CO conversion could be achieved at 550 °C and 15 atm total pressure with no other catalyst present. Although it had been known previously that MgO would catalyze the WGS reaction, the similar results obtained with both materials provided an indication that the catalytic activity of CaO was similar to that of MgO.

The catalytic activity of CaO for the WGS reaction was verified by Müller et al.4 who extended the work of Han and Harrison. The catalytic activity of two natural and two synthetic CaO-based sorbents was determined. The starting materials included both natural limestone and dolomite, a commercially available calcium magnesium acetate (CMA), and a dispersion of CaO on Ca12Al14O33 (mayenite). Each material was first calcined at 800 °C to prepare the CaO and then subjected to a five cycle test of the WGS reaction. During each cycle, the WGS reaction was conducted at 650 °C followed by sorbent regeneration at 800 °C. The process was complicated by the loss in catalytic activity as CaO was converted to CaCO3, a noncatalyst. In addition, the catalytic activity of CaO itself declined gradually from cycle to cycle. Among the four materials tested, the catalyst/sorbent derived from CMA was the most stable and most productive over five cycles. Although the absorption capacity of the calcined limestone was the highest initially, it was the lowest after five cycles.

The observed decline in catalytic/sorbent activity of CaO as it is converted to CaCO3 and then regenerated has also been observed in other studies and has been attributed to sintering of the material which is favored by the higher regeneration temperature.5,6 Recent studies7–9 have shown that the CO2 absorption capacity of CaO can be stabilized partially by incorporating within it a small amount of material such as MgO or Al2O3 which has greater high temperature stability. This has been accomplished either by intimate physical mixing of fine particles7,8 or by coprecipitating the materials.9

Although calcined limestone may provide both the catalyst and sorbent needed for a single-stage process for producing H2 from CO, the material is soft and tends to decrepitate when subjected to a cyclic process of reaction and sorbent regeneration. This problem can be overcome by encapsulating the limestone in a porous protective shell made of partially sintered alumina which can also support a Ni catalyst.10 This
application was demonstrated successfully by reforming CH₄ with steam to produce H₂.¹²

Interestingly, Ni supported on Al₂O₃ was also shown previously to catalyze the WGS reaction at 450 °C.¹² In addition, the activity and stability of the catalyst was improved by employing CeO₂ as a promoter. However, the catalyst with or without CeO₂ was also observed to cause some conversion of CO into CH₄ by reactions such as the following:

\[
\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{25^\circ C} = -206 \text{ kJ/mol}
\]

Furthermore, Ni has also been shown to catalyze the decomposition of CO by the Boudouard reaction.¹³

\[
2\text{CO(g)} = \text{C(s)} + \text{CO}_2(g) \quad \Delta H_{25^\circ C} = -172 \text{ kJ/mol}
\]

Both CH₄ and carbon are undesirable byproducts which may be suppressed by using a large excess of H₂ and steam, but that may not always be economical. In two cases, coking was suppressed by impregnating an Al₂O₃-supported Ni catalyst with CaO.¹⁴,¹⁵ However, in both cases, the catalyst was used for CO₂ reforming of CH₄.

In developing a single-stage process for producing H₂ from CO, consideration had to be given to finding not only an appropriate combination of catalyst and sorbent for the WGS reaction but also a combination that would either avoid or suppress the preceding side reactions. The potential catalysts selected for testing included Al₂O₃, CaO, and Ni because all of these had been shown previously to catalyze the WGS reaction. To compare their relative catalytic activity, pellets were prepared with the different materials and tested in a fixed bed tubular reactor supplied with CO and steam. The Al₂O₃ and CaO were tested separately, and they were also made into core-in-shell pellets for testing. These pellets were made with CaO cores encased in Al₂O₃ shells. For some tests, the Al₂O₃ was impregnated with Ni, and for a few of these tests, CaO was added to the Al₂O₃ to suppress coking.

The results were analyzed by using four different reaction models based on different combinations of the preceding series of reactions. For example, when the WGS reaction 1 was conducted in the presence of CaO so both reactions 1 and 2 took place, the results were explained by Model I consisting of both reactions. On the other hand, when the WGS reaction was conducted in the presence of Al₂O₃, some carbon or coke was also produced, so the results were explained by a combination of reactions 1 and 4 or Model II.

**THERMODYNAMIC ANALYSIS**

A thermodynamic analysis of the basic reaction system composed of reactions 1 and 2, i.e., reaction Model I, is revealing. For the system supplied initially with 1.0 mol of CO and 3.0 mol of H₂O in chemical equilibrium at 1.0 atm, the resulting gas composition is indicated in Table 1. The values are based on published reaction equilibrium constants.¹,¹⁶ Two cases are illustrated. In one case, an active CaO sorbent is present to absorb CO₂ while in another case CaO is not present, which would correspond to a fully loaded sorbent. It can be seen that by having active CaO present, virtually all of the CO is converted to H₂ and CO₂ which is largely absorbed over the 480–600 °C temperature range. In contrast, without an active CaO sorbent present, the CO is incompletely converted to H₂ and CO₂ in equal concentrations.

<table>
<thead>
<tr>
<th>temp. °C</th>
<th>CO₂ absorption</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>CO conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>maximum</td>
<td>0.00</td>
<td>0.00</td>
<td>100.00</td>
<td>92.8</td>
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<td>3.79</td>
<td>48.11</td>
<td>48.11</td>
<td></td>
</tr>
<tr>
<td>520</td>
<td>maximum</td>
<td>0.00</td>
<td>0.10</td>
<td>99.90</td>
<td>90.7</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>4.88</td>
<td>47.56</td>
<td>47.56</td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>maximum</td>
<td>0.00</td>
<td>0.20</td>
<td>99.80</td>
<td>89.1</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>5.76</td>
<td>47.12</td>
<td>47.12</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>maximum</td>
<td>0.20</td>
<td>0.79</td>
<td>99.01</td>
<td>86.3</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>7.35</td>
<td>46.32</td>
<td>46.32</td>
<td></td>
</tr>
</tbody>
</table>

Also presented in Table 1 are values of the CO conversion for the case where no CaO is present to absorb CO₂. As expected, the conversion of CO into H₂ by the WGS reaction decreases with increasing reaction temperature, but even at 600 °C, the equilibrium conversion of 86% is relatively large. Of course, with a CaO sorbent present, the CO conversion would be nearly 100% at any of these temperatures.

**EXPERIMENTAL METHODS AND MATERIALS**

**Materials.** Pellets made of limestone and/or alumina (Al₂O₃) were prepared for testing as catalysts or sorbents by pelletizing the powdered materials. The limestone came from two different sources. Columbia River Carbonates in Washington State supplied Microna 3 limestone, with a mean particle size of 3.2 μm and a CaCO₃ content greater than 97% according to the supplier. Coarser limestone with 97% CaCO₃ was obtained from the Ames, Iowa, quarry of Martin Marietta Aggregates. This material was ground and screened to a size of −212/+63 μm.

Three different particle sizes of alumina were employed. Two sizes of α-Al₂O₃ were supplied by Almatis AC, Inc. One of these, designated as A16-SG, had a mean particle size of 0.4 μm, while another designated as T-64 alumina consisted of −325 mesh, or −44 μm size, particles. A third size designated as DD-290 by its supplier, the Engelhard Corp., was an amorphous, noncrystalline alumina with a mean particle size of 9.8 μm and a surface area of 275 m²/g.

The catalysts being tested were supported on a bed of “inert” SiC pellets supplied by Saint-Gobain Norpro. In later tests of combined catalyst and sorbent pellets, the pellets were interspersed with smaller SiC pellets having a diameter of 0.1 cm.

**Preparation Methods.** Spherical pellets were prepared for catalyst testing by employing a revolving conical drum pelletizer having a maximum diameter of 25 cm. The pellets were prepared by placing a measured quantity of limestone or alumina powder in the rotating drum and spraying it with deionized water intermittently so that the material balled up as the drum revolved at 30 rpm. After sufficient pellets in the 3.96 to 4.76 mm (−4/+5 mesh) size range had been prepared, they were recovered by screening and then subjected to a hardening operation to improve their sphericity and uniformity which required rolling them in the pelletizer at the following speed and time settings: 10 rpm for 10 min, 30 rpm for 20 min, 60 rpm for 30 min, and 90 rpm for 30 min.

Core-in-shell pellets were prepared by first using the preceding process to produce the core material but in the
pellets were calcined in air at 900 °C prepared from Microna 3 limestone. After preparation, the reactor with 13.7 g of CaO pellets which initially had been products. This was demonstrated by charging the quartz tubular reactor with 13.7 g of CaO pellets which were previously calcined at 900 °C. One reactor was made of quartz and had an inside diameter of 5.17 cm and length of 42 cm. The lower part of the reactor was filled with a 20 cm deep bed of 3 mm diameter SiC pellets. On top of these pellets was placed a smaller bed of catalyst pellets for testing. The remaining space was filled with more SiC pellets to mix and preheat the reactants.

A second reactor was made of stainless steel and had an inside diameter of 1.27 cm and length of 61 cm. This reactor was employed for testing core-in-shell pellets during the final stage of the project. The lower part of the reactor was filled with a 25 cm deep bed of SiC pellets. Above this bed was the reactor midsection occupied by the core-in-shell pellets being tested. The midsection was occupied by a mixture consisting of 13.7 g of core-in-shell pellets and 8.2 g of 0.1 cm diameter SiC pellets which created a bed depth of 10–11 cm. The SiC pellets were interspersed among the other pellets to reduce gas channeling and to improve heat transfer. Above the midsection was placed a 10 cm deep bed of 0.32 cm diameter extruded SiC pellets to mix and preheat the reactants.

During a catalyst test, either reactor was supplied with a controlled mixture of steam and CO usually in a 3:1 mol ratio. Water was supplied by a metering pump, and CO was metered by a Brooks mass flow controller. The mixture was heated to vaporize the water and preheat the mixture before it reached the reactor. Samples of the reactor effluent were periodically drawn with GasTight syringes and analyzed with a gas chromatograph (GC) equipped with both a thermal conductivity detector and flame ionization detector to determine the concentrations of H2, CO, CO2, and CH4. The critical reaction temperature was measured with a thermocouple inserted in the middle of the catalyst bed.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Performance of CaO Pellets.** Pellets made entirely of CaO were unique since they could serve both as a catalyst for the WGS reaction and the CaO carbonation reaction in series. This combination made it possible for the CO2 produced by the first reaction to react with CaO to form CaCO3. For about the first 70 min, the overall rate of the combined reactions appeared to be controlled by the WGS reaction because the CO2 concentration remained close to zero, whereas both the CO and H2 concentrations changed due to slowing of the WGS reaction as the available CaO surface area declined. After this initial period, the CO2 concentration increased rapidly as its rate of absorption decreased until the sorbent became nearly saturated. At this point, only the WGS reaction continued at a reduced rate, possibly catalyzed by the reaction product, and the H2 concentration became equal to the CO2 concentration.

While these results indicate that CaO alone is an excellent catalyst for the WGS reaction and a good absorbent for the CO2 produced, it does have some disadvantages. For use in a continuously operating system, the sorbent has to undergo a repeated cycle of absorption and regeneration, and it has been observed that the absorption capacity of the CaO declines as the cycle is repeated, probably as a result of a decrease in surface area.6 However, several promising methods have been proposed for stabilizing the sorbent.7–9

Another shortcoming of pelletized CaO is that the pellets are relatively fragile and break apart in use. This problem has been overcome by encapsulating each pellet in a relatively thin layer of partially sintered Al2O3 which can also serve as a catalyst for the water gas shift reaction or as a support for other catalysts such as Ni.11

**Catalytic Performance of Alumina Pellets.** The catalytic activity of calcined Al2O3 pellets was determined by conducting a series of tests in which samples that had been calcined at either 600 or 900 °C were used to catalyze the WGS reaction. For these tests, the quartz tubular reactor was charged with 13.7 g of the prepared and calcined pellets and heated to 600 °C. For each test, a mixture of steam and CO in a 3:1 mol ratio was supplied to the reactor at a constant flow rate corresponding to the feed rate of 7.4 mmol/min. The Ni catalysts were prepared by impregnating the Al2O3 catalyst support with either an aqueous or an organic solution of nickel nitrate hexahydrate (99.999% pure) supplied by Sigma-Aldrich. The nitrate was decomposed at 500 °C, and the resulting NiO was then reduced to Ni by treatment with H2 at 550 °C. The Ni catalysts were unique since they could serve both as a catalyst for the WGS reaction and a good absorbent for the CO2 produced by the first reaction to react with CaO to form CaCO3. For about the first 70 min, the overall rate of the combined reactions appeared to be controlled by the WGS reaction because the CO2 concentration remained close to zero, whereas both the CO and H2 concentrations changed due to slowing of the WGS reaction as the available CaO surface area declined. After this initial period, the CO2 concentration increased rapidly as its rate of absorption decreased until the sorbent became nearly saturated. At this point, only the WGS reaction continued at a reduced rate, possibly catalyzed by the reaction product, and the H2 concentration became equal to the CO2 concentration.

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either 7.4 or 3.6 mmol/min. Each test was conducted for 120 min or longer, and during the test, samples of the gaseous product were collected and analyzed. The results of these tests are presented in Table 2 where the average gas composition on an H₂O-free basis is listed. Because the catalytic properties of the material did not change significantly after an initial 20 min period of operation, each reported gas concentration represents an average of the concentration measured during the subsequent 100 min of stable operation. While the first four tests were conducted with pellets made entirely of Al₂O₃, the last two tests were made with pellets which also contained 10 wt % CaO.

The results of this series of tests can be explained by reaction Model II consisting of the WGS reaction 1 and the Boudouard reaction 4. Because more CO₂ was produced than H₂ in five of six tests, it meant that in these tests some CO was converted to CO₂ and C by the second reaction, although most of the CO₂ was produced by the first reaction. The indicated conversions of CO to H₂ and C are based on a material balance around the reaction system. Because much more CO was converted to H₂ than to C, the rate of the first reaction was greater than the rate of the second reaction which suggests that Al₂O₃ is a better catalyst for the first reaction.

Although the results appeared to be affected only slightly by the Al₂O₃ precalcination temperature, they were affected noticeably by both the reactant feed rate and the presence of CaO. A comparison of the results with pellets precalcined at 900 °C showed that the incorporation of 10 wt % CaO in the Al₂O₃ increased the average CO conversion to H₂ by 36% at the highest feed rate and 46% at the lowest feed rate. On the other hand, while the conversion of CO to C did not seem affected by the presence of CaO, this conversion did increase noticeably when the CO feed rate was reduced. Therefore, the rates of both reactions seemed to be affected by the feed rate, while only the rate of the first reaction was affected by CaO.

**Catalytic Performance of Ni on Al₂O₃.** The catalytic activity of calcined Al₂O₃ pellets impregnated with a Ni catalyst was determined by conducting a series of tests in which samples of pellets were used to catalyze the WGS reaction under different reaction conditions. For these tests, no CaO was present. For each test, the quartz tubular reactor was first charged with 13.7 g of pellets which was then treated with H₂ at 750 °C for 2 h to reduce the Ni catalyst. The temperature of the reactor was then lowered to the temperature selected for catalyst testing, and a mixture of steam and CO in a 3:1 mol ratio was supplied to the reactor at a rate of 7.4 mmol/min.

The first set of tests in the series was conducted to determine the effect of Ni concentration on the conversion of CO into different products at 600 °C. The pellets were free of CaO while the Ni concentration ranged from 0.8 to 6.5 wt % among tests. Each test was conducted for approximately 300 min, and during this time there was little variation in the product gas concentrations, which was indicative of a stable catalyst. The average product gas concentrations and corresponding conversion of CO into different products based on these concentrations are presented in Table 3. Also shown are the results of an earlier test conducted with similar Al₂O₃ pellets which had neither Ni nor CaO present.

Because a small portion of the CO was converted to CH₄ when Ni was employed as a catalyst, it became necessary to employ Model III for analyzing the present results. This model includes the methanation reaction 3 in addition to the water gas shift 1 and Boudouard 4 reactions. With this model, it is possible to determine the conversion of CO into H₂, C, and CH₄.

The present results show that with a Ni catalyst supported on Al₂O₃ much more CO was converted to both H₂ and C than was observed before, either with Al₂O₃ by itself or with 10 wt % CaO, but the results also indicate that a small quantity of CO was converted to CH₄ with the Ni catalyst. Because neither C nor CH₄ are desirable byproducts when the water gas shift reaction is used to produce H₂, some means for suppressing the two side reactions would be required.

Interestingly, the present results indicate that increasing the Ni concentration of the catalyst had the effect of slightly reducing the conversion of CO to both H₂ and C while increasing the conversion of CO to CH₄ (Table 3). The effect of increasing Ni concentration on the slight reduction in the conversion of CO into H₂ and C was surprising. To investigate this result further, the surface area of the Ni catalyst was determined by first reducing samples of the different catalysts at 800 °C for 2 h followed by measuring the quantity of H₂.

Table 2. Results of Conducting the WGS Reaction in the Presence of Al₂O₃ Pellets at 600 °C Using a 3:1 mol ratio of H₂O/CO

<table>
<thead>
<tr>
<th>calcin. temp., °C</th>
<th>feed rate mmol/min</th>
<th>catalyst promoter</th>
<th></th>
<th>concentration (dry basis), mol %</th>
<th>CO conv., %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO</td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
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<td>43.25</td>
<td>27.45</td>
<td>29.30</td>
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</tbody>
</table>

“a100 min average. b10 wt %.

Table 3. Effect of Ni Catalyst Concentration on the Conversion of CO into Different Products at 600 °C Using a Feed Rate of 7.4 mmol/min

<table>
<thead>
<tr>
<th>Ni wt %</th>
<th>CO (dry basis), mol %</th>
<th>H₂</th>
<th>CO₂</th>
<th>CH₄</th>
<th>H₂</th>
<th>C</th>
<th>CH₄</th>
<th>total</th>
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</thead>
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<td>0.8</td>
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<td>7.97</td>
<td>41.18</td>
<td>49.70</td>
<td>1.35</td>
<td>71.22</td>
<td>14.10</td>
<td>2.12</td>
<td>87.00</td>
</tr>
</tbody>
</table>

dx.doi.org/10.1021/ie402607a
chemisorbed at 40 °C. The results are presented in Table 4 where it can be seen that the surface area of the Ni present increased from 0.04 to 0.35 m²/g for the different catalyst samples. Because a change of this magnitude in the surface area of the Ni catalyst would likely affect the reaction kinetics, it was concluded that in this case the WGS reaction was controlled by thermodynamic equilibrium rather than by reaction kinetics. A second set of tests was conducted in the series to determine the effect of temperature on the performance of the reaction system which employed an Al₂O₃-supported Ni catalyst (Table 5). The experimental conditions were virtually the same as for the previous set, and only the reaction temperature was varied among tests. All of the tests were conducted with a Ni concentration of 0.8 wt %.

Table 4. Surface Area of Ni Supported by Al₂O₃ Determined by H₂ Chemisorption at 40 °C

<table>
<thead>
<tr>
<th>concentration Ni, wt %</th>
<th>H₂ uptake, μmol/g</th>
<th>surface Ni, μmol/g</th>
<th>Ni area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1.01</td>
<td>2.02</td>
<td>0.04</td>
</tr>
<tr>
<td>3.7</td>
<td>4.96</td>
<td>9.92</td>
<td>0.19</td>
</tr>
<tr>
<td>6.5</td>
<td>9.02</td>
<td>18.04</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The results of these tests indicate that the main effect of increasing the reaction temperature is to reduce the conversion of CO either to H₂ or to CH₄ while increasing the conversion of CO to C. The pellet samples. Because a change of this magnitude in the surface area of the Ni catalyst would likely affect the reaction kinetics, it was concluded that in this case the WGS reaction was controlled by thermodynamic equilibrium rather than by reaction kinetics.

A second set of tests was conducted in the series to determine the effect of temperature on the performance of the reaction system which employed an Al₂O₃-supported Ni catalyst (Table 5). The experimental conditions were virtually the same as for the previous set, and only the reaction temperature was varied among tests. All of the tests were conducted with a Ni concentration of 0.8 wt %.

Table 5. Effect of Reaction Temperature on the Conversion of CO into Different Products while Using a Catalyst with 0.8 wt % Ni and a Feed Rate of 7.4 mmol/min

<table>
<thead>
<tr>
<th>temp., °C</th>
<th>CO (dry basis), mol %</th>
<th>H₂ conversion, %</th>
<th>CO₂ conversion, %</th>
<th>CH₄ conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>5.03</td>
<td>38.77</td>
<td>52.72</td>
<td>3.89</td>
</tr>
<tr>
<td>550</td>
<td>6.08</td>
<td>40.66</td>
<td>51.35</td>
<td>2.41</td>
</tr>
<tr>
<td>600</td>
<td>9.01</td>
<td>41.36</td>
<td>48.84</td>
<td>0.96</td>
</tr>
<tr>
<td>650</td>
<td>9.85</td>
<td>42.01</td>
<td>47.91</td>
<td>0.28</td>
</tr>
<tr>
<td>700</td>
<td>11.96</td>
<td>41.22</td>
<td>46.73</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The results of these tests indicate that the main effect of increasing the reaction temperature is to reduce the conversion of CO either to H₂ or to CH₄ while increasing the conversion of CO to C. In the sections which follow, the catalytic performance of core-in-shell pellets with CaO cores and Al₂O₃ shells is described. It also shows how their performance can be improved by adding either CaO or Ni or both to the shell material.

Performance of Core-in-Shell Pellets. The catalytic performance of pellets having cores prepared from Microna 3 limestone and shells made of Al₂O₃ was tested in the quartz tubular reactor. For the first test, no CaO was present in the shell material, whereas for the second test the shell material contained 10 wt % CaO. In later tests, a Ni catalyst was added to the shell material.

For most of these tests, 13.7 g of precalcined pellets was placed between deep layers of SiC pellets and heated to 775 °C in argon for 2 h. The reactor temperature was then reduced to 600 °C, and a mixture of steam and CO in a 3:1 mol ratio was supplied to the reactor at a rate of 7.4 mmol/min. As the test proceeded, the composition of the reactor effluent was determined, which for the first test provided the results in Figure 2.

These results are generally similar to those in Figure 1 for pellets made entirely of CaO because in both cases each pellet combined a catalyst for the WGS reaction with a sorbent for CO₂. However, the pellets made entirely of CaO had nearly twice the CO₂ absorption capacity as the core-in-shell pellets. Consequently, a much longer time was required to saturate the sorbent with CO₂ in pellets made entirely of limestone. The diffusional resistance of the pellet shells would also have played a role and very likely accounted for the lower H₂ concentration observed with core-in-shell pellets during the initial 50 min or more of the test.

As in the case of pellets made entirely of CaO, the results obtained with core-in-shell pellets were consistent with reaction Model 1, but the conversions of CO and CO₂ based on this model changed more rapidly over time because of the smaller CaO content of the core-in-shell pellets. The second performance test of core-in-shell pellets was conducted to determine the effect of adding 10 wt % CaO to the Al₂O₃ shell material. Otherwise, the core-in-shell pellets and other experimental conditions were the same as for the previous test. While the results of the second test (Figure 3) were similar to those obtained in the previous test, the addition of CaO to the shell resulted in a higher concentration of H₂ and lower concentration of CO in the product gas because of an increase in CO conversion due to an increase in catalytic activity of the shell material.

Core-in-Shell Pellets with a Ni Catalyst. The catalytic performance of core-in-shell pellets impregnated with a Ni catalyst was determined by first preparing the pellets as before, but without CaO in the shell, and then calcining them at 900 °C. The pellets were subsequently recarbonated by treatment...
with CO₂ at 600 °C for 3 h. Next, the pellets were immersed in an aqueous solution of nickel nitrate for several hours, dried at 120 °C, and recalcined at 800 °C for 3 h.

To determine the catalytic performance of the material, the quartz tubular reactor was charged with 13.7 g of core-in-shell pellets placed between deep layers of SiC pellets. The pellets were subsequently treated with H₂ at 750 °C to reduce the NiO which then resulted in a Ni content of 0.8 wt %. A subsequent test of the pellets conducted by supplying the reactor with a 1:3 mol ratio of CO to steam at a rate of 7.4 mmol/min, while maintaining the reactor at 600 °C, produced the results in Figure 4. Although the results were generally similar to those produced with core-in-shell pellets which did not have the Ni catalyst (see Figure 2), they differed in several respects. After only 50 min on stream, the CO concentration had risen to 60 mol % in Figure 2 but only 14 mol % in Figure 4 which showed that much more CO was converted when the Ni catalyst was present. Furthermore, after 100 min on stream, the concentration of CO₂ exceeded the concentration of H₂ when the Ni catalyst was present but not when it was absent. In addition, even with a Ni catalyst present, the concentration of CH₄ in the reactor effluent was always less than 0.1 mol % and, therefore, played a negligible role.

The results obtained with the Ni catalyst can be explained by employing different reaction models for the initial and final stages of the process. During the early part of the test, the results were produced by a combination of the WGS reaction and the CaO carbonation reaction, Model I. During the subsequent part, the results were produced by a combination of the WGS reaction and the CO decomposition reaction, Model II. The conversions of CO and CO₂ were determined by employing these models, and the resulting values are reproduced in Figure 5. Initially, both the CO conversion by the WGS reaction and the CO₂ conversion by the carbonation reaction were greater than 90%. However, as the sorbent became loaded, both reactions slowed, although at different rates. After only 100 min, the rate of conversion of CO₂ by reaction with CaO had decreased to zero, apparently due to the complete conversion of the CaO to CaCO₃. At about the same time, the rate of conversion of CO into H₂ was approaching a nearly constant value such that 62% of the CO in the reactor feed was being converted into H₂. Also at this time, part of the CO supplied to the reactor began to be decomposed into elemental carbon and CO₂. Eventually, the rate of CO decomposition became relatively constant so that about 13% of the CO fed was being decomposed. By this time, 75% of the CO being supplied was either being converted to H₂ or being decomposed. Although these results showed that the catalytic performance of core-in-shell pellets for the WGS reaction was improved greatly by impregnation with a Ni catalyst, they also showed that further modification was required to avoid catalyzing the decomposition of CO.

**Best Core-in-Shell Pellets.** The best core-in-shell pellets tested were generally similar to pellets that had been developed previously for reforming methane with steam. Therefore, they differed in several respects from the core-in-shell pellets described above. Most of these differences such as the use of Iowa limestone in a larger particle size (≈ 212/63 μm) and the use of a 5 wt % lignin in water solution for pelletizing the materials probably had little effect on the final results. While the Ni concentration of 6.1 wt % was higher than necessary, the results presented above indicate that this also would have had little effect. Therefore, the feature which seemed to account for the improved performance of the present core-in-shell pellets was the addition of 5 wt % limestone to the shell material. The limestone had been added to the pellets fortuitously before the later work described above had shown that CaO would inhibit the Boudouard reaction. Another feature which may have contributed to the best pellet performance was the interspersion of smaller 0.1 cm diameter SiC pellets among the larger core-in-shell pellets for testing. This addition would have reduced gas channeling and improved heat transfer.

Before testing the best core-in-shell pellets, the bed was first heated to desorb any CO₂ present in the core material, in effect regenerating the material. This involved passing a mixture of CO and steam in a 1:3 mol ratio through the reactor at a rate of 3.6 mmol/min while the bed temperature was raised to 850 °C. Although the WGS reaction could have taken place, the resulting partial pressure of CO₂ was so low that it did not interfere with the desorption of CO₂. Under these conditions, the desorption of CO₂ was complete when the CO₂ concentration in the reactor effluent remained constant which usually took 1.0–1.5 h at 850 °C. The use of CO and steam for regenerating the sorbent ensured that the Ni catalyst remained in a reduced state.

After the sorbent had been regenerated, the flow of gas was stopped, and the bed of pellets was cooled to the desired reaction temperature. When this temperature was reached, a test was initiated by reintroducing the reactants in the same ratio and flow rate as before. While the test continued, samples of reactor effluent were collected periodically and analyzed.

The results of a typical performance test conducted at 600 °C with a freshly regenerated sample of core-in-shell pellets are
The measured product gas composition was very similar to the calculated equilibrium composition shown in Table 1 for maximum CO₂ absorption. Therefore, the gas composition appeared to be largely controlled by thermodynamic equilibrium. As the test continued, less CO₂ was absorbed, and for the next 40 min, its concentration increased rapidly until it reached a level of 44–46 mol % where it remained for the rest of the test. Meanwhile, the H₂ concentration fell to a level of 49–51 mol % where it remained. During this seemingly steady-state period, the H₂ and CO₂ concentrations differed from the thermodynamic equilibrium values by only a few percent. Throughout the test, the H₂ concentration exceeded the CO₂ concentration, and the CH₄ concentration was negligible. Therefore, the process fit reaction Model I consisted of the WGS reaction and the carbonation of CaO. During the period when the CO₂ concentration increased rapidly, the rate of reaction was probably controlled by the rate of CO₂ diffusion through the carbonate layer that was increasing in thickness within the sorbent. Most importantly, there was little CO decomposition and carbon formation.

The best core-in-shell pellets with the Ni catalyst were utilized for a series of tests of the WGS reaction conducted at four different temperatures ranging from 480 to 600 °C. The results presented in Table 6 show that small but increasing amounts of CH₄ were produced as the temperature was reduced. Therefore, to explain these results, the methanation reaction 3 was considered together with both the WGS reaction 1 and the carbonation reaction 2. The three reaction combination became Model IV which was used for calculating the conversion of CO to both H₂ and CH₄ and for calculating the conversion of CO₂ into CaCO₃. Table 6 lists the gas composition and conversions for two different absorption periods at each temperature. The “fast” period represents the results observed during the initial period when the process seemed to be controlled by thermodynamic equilibrium, whereas the “slow” period represents average results during the final 60–70 min period. It should be noted that gas concentrations are presented on an H₂O-free basis. As the reaction temperature was raised from 480 to 600 °C, the H₂ concentration observed during the fast absorption period rose from 96.6% to 98.2%, which was matched by an increase in CO conversion from 97.3% to 99.0%. However, this change in temperature caused very little change in the H₂ concentration during the slow absorption period which remained around 50 mol %. Again, it is noteworthy that, for any given temperature, the change from fast to slow CO₂ absorption produced only a small decrease in CO conversion into H₂.

### SUMMARY AND CONCLUSIONS

To develop a useful combined catalyst and sorbent for conducting the WGS reaction and separating the products in a single stage, consideration was given to several promising catalytic and sorbent materials. These materials included calcium oxide (CaO), alumina (Al₂O₃), mixtures of Al₂O₃ and CaO, and Ni supported by Al₂O₃ both with and without CaO. The powdered materials were made into pellets for testing, and in some cases, pellets made of CaO were encased in shells made largely of partially sintered Al₂O₃ which could support a Ni catalyst. Although the catalytic activity of the materials varied widely, each was found to catalyze the WGS reaction to some extent, but some also catalyzed the conversion of CO into undesirable byproducts, i.e., methane and carbon.

Preliminary tests of CaO pellets derived from limestone were unusual because the CaO proved to be both an excellent catalyst for the WGS reaction and an excellent absorbent for CO₂; the principal byproduct. Furthermore, the CaO did not catalyze undesirable side reactions, but pellets made entirely of CaO were fragile, which was overcome by encasing the pellets in porous Al₂O₃ shells. However, the performance of the CaO as a catalyst and sorbent suffered to some extent.

Other preliminary tests conducted at 600 °C with pelletized Al₂O₃ produced only modest conversions of CO into H₂ by the WGS reaction and much smaller conversions of CO into carbon by the Boudouard reaction. Subsequent tests with Al₂O₃ pellets containing 10 wt % CaO produced greater conversions of CO into H₂ but not greater conversions of CO into carbon.

### Table 6. Results of Conducting the WGS Reaction at Different Temperatures with the Best Core-in-Shell Pellets and a Ni Catalyst

<table>
<thead>
<tr>
<th>temp, °C</th>
<th>absorption period</th>
<th>CO (dry basis), mol %</th>
<th>CO₂</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO conv. % to H₂</th>
<th>CO₂ conv. % to CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>fast</td>
<td>2.1</td>
<td>0.75</td>
<td>96.6</td>
<td>0.6</td>
<td>97.3</td>
<td>96.6</td>
</tr>
<tr>
<td></td>
<td>slow</td>
<td>2.5</td>
<td>46.0</td>
<td>50.9</td>
<td>0.6</td>
<td>94.8</td>
<td>12.1</td>
</tr>
<tr>
<td>520</td>
<td>fast</td>
<td>2.3</td>
<td>1.1</td>
<td>96.3</td>
<td>0.3</td>
<td>97.4</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>slow</td>
<td>3.7</td>
<td>47.8</td>
<td>48.2</td>
<td>0.3</td>
<td>92.5</td>
<td>6.6</td>
</tr>
<tr>
<td>550</td>
<td>fast</td>
<td>1.5</td>
<td>0.8</td>
<td>97.4</td>
<td>0.3</td>
<td>98.2</td>
<td>97.4</td>
</tr>
<tr>
<td></td>
<td>slow</td>
<td>5.2</td>
<td>43.9</td>
<td>50.6</td>
<td>0.3</td>
<td>90.3</td>
<td>13.3</td>
</tr>
<tr>
<td>600</td>
<td>fast</td>
<td>0.9</td>
<td>0.7</td>
<td>98.2</td>
<td>0.1</td>
<td>99.0</td>
<td>98.3</td>
</tr>
<tr>
<td></td>
<td>slow</td>
<td>6.3</td>
<td>43.2</td>
<td>50.2</td>
<td>0.2</td>
<td>88.7</td>
<td>13.3</td>
</tr>
</tbody>
</table>

A series of performance tests conducted with Al₂O₃ pellets impregnated with Ni in different concentrations showed Ni on Al₂O₃ to be an excellent catalyst for the WGS reaction but also, to a lesser extent, a catalyst for both the carbon producing and CH₄ producing reactions. Increasing the Ni concentration from 0.8 to 6.5 wt % had little effect on the results, which indicated that the process was largely controlled or limited by thermodynamic equilibrium and not reaction kinetics.

When pellets with CaO cores and Al₂O₃ shells were impregnated with 0.8 wt % Ni, the catalytic performance of the material for the WGS reaction at 600 °C increased greatly. At first, only the WGS reaction appeared to be catalyzed, but after the CaO was fully carbonated, the Boudouard reaction became active and 13% of the CO was converted into CO₂ and carbon.

Before all of these results were known, tests had been conducted with a series of core-in-shell pellets that were generally similar to those described above except for the addition 5 wt % limestone to the shell material that supported a Ni catalyst. This addition proved extremely important because, with WGS reaction testing of the material at temperatures ranging from 480 to 600 °C and during an operating period when most of the CO₂ was absorbed, more than 97% of the CO was converted to H₂, less than 1% was converted to CH₄, and none was converted to carbon.

**REFERENCES**


**NOTE ADDED AFTER ASAP PUBLICATION**

This paper was published ASAP on May 29, 2014, with an error in the reaction product of equation 3. The corrected version was reposted on June 2, 2014.