

Carbon dioxide reforming of methane with Pt catalysts using microwave dielectric heating

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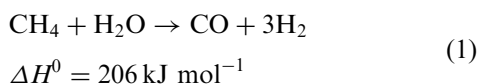
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Microwave heating was applied to the catalytic reforming reaction of methane with carbon dioxide over platinum catalysts. It was found that CO₂ and CH₄ conversions and the product selectivity (H₂/CO) were generally higher under microwave conditions than that obtained with conventional heating at the same measured temperature. The effect of microwave heating was attributed to the formation of hot spots with higher temperature than that measured in the bulk catalyst bed.

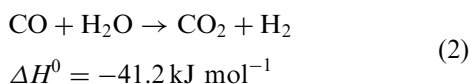
KEY WORDS: carbon dioxide; methane; catalytic reforming; microwave heating; Pt catalysts.

1. Introduction

Synthesis gas (syngas), which is a mixture of CO and H₂, is an important feedstock for the chemical industry. The established commercial method employed for synthesis gas production is the steam reforming of methane:

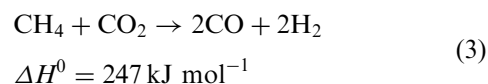


which is achieved by the use of a nickel/ α -Al₂O₃ catalyst at temperatures around 900 °C and at pressures of 15–30 atm [1,2]. The product mixture can then be introduced to a methanol synthesis reactor. Demand for this process has increased markedly due to the rapid expansion of MTBE (methyl *tert*-butyl ether) use in the automotive fuel sector. Alternatively, the initial syngas mixture can be further modified with water to enhance the hydrogen concentration by the water-gas shift reaction over a catalyst such as Cu/ZnO/Al₂O₃ [3].



This latter mixture is then suitable for use in an ammonia synthesis industrial reactor. A critical parameter for subsequent reaction of the synthesis gas is the H₂/CO ratio that must be adjusted close to unity for some syntheses such as the manufacture of oxo-alcohols and acetic acid [4].

These latter issues have stimulated research into the formation of synthesis gas by the carbon dioxide reforming of methane (dry reforming). The carbon dioxide reforming of methane, in fact, has been of interest for a long time, dating back to as early as the 1920's [5], but it is only in recent years that interest in it has rapidly increased for both environmental and commercial reasons. This reaction can be represented as



This process has many desirable advantages over steam reforming [6,7]: (a) Synthesis gas has an H₂/CO ratio of unity without further, post-reformer reactions. (b) The use of CO₂ means that it is an attractive route toward CO₂ mitigation in stationary anthropogenic sources. (c) It allows the conversion of methane, previously a waste component of oil reserves, into an economically attractive feedstock.

This process can also be used as a chemical energy storage and an energy transmission system [8,9]. In this system, solar energy is used to drive the endothermic forward reaction, and the energy thus stored can be transported via pipelines such as syngas and liberated at will by the reverse reaction at any location or time. The highly endothermic reaction could be an option to store solar energy in hot regions.

A number of studies have been made on this reaction, but there is still no process for the CO₂ reforming currently considered to be commercially feasible. The major obstacle preventing commercialization of the process is that, owing to the endothermic nature of the process, high temperatures are required to reach high

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conversions. These conditions are conducive to carbon deposition, and a catalyst capable of operating at such severely deactivating conditions has not been well developed. So, the main concern of many CO₂-reforming studies is to develop suitable catalysts and optimize the lifetime stability of the catalysts used.

Numerous materials have been tested as potential catalysts for reforming of CH₄ with CO₂, and most of them have been focused on Group VIII metals on a variety of supports. The metals studied include Co, Ni, Ru, Rh, Pd and Pt. La and Zr have also been used. Oxides such as CeO₂, Al₂O₃, La₂O₃, MgO, CaO, SiO₂, TiO₂ and ZrO have been employed as support materials. Among the catalysts examined, nickel-based catalysts, as well as supported noble metal catalysts, have been found to exhibit promising catalytic activities in terms of methane conversion and selectivity to synthesis gas. Encouraging stability results have been obtained using noble metal-based catalysts [10]. However, it was observed that carbon deposition cannot be avoided over nickel-supported catalysts and for a CO₂/CH₄ molar ratio of unity [10,11].

With regard to the reactors used for the research, most of the investigations were carried out in conventional fixed-bed tubular reactors or fluidized bed reactors, while some special reactors have also been investigated, such as membrane reactors [12,13] and hot-wire thermal-diffusion column reactors [14].

Microwave radiation has been shown to have the potential to increase the reaction rate of some heterogeneous reactions, and a difference between the reaction site temperature and the bulk catalyst temperature has been observed [15–17]. It provides a new way to induce the heterogeneous catalytic reforming of CH₄ with CO₂. The aim of this study was to investigate the reforming of methane with carbon dioxide under microwave conditions. Catalysts of platinum supported on γ -alumina at several loading levels with different promoters were examined. The effects of temperature, feed gas compositions and heating methods were investigated. The reaction was also carried out with conventional heating for comparative purposes.

2. Experimental

2.1. Materials

The following chemicals were purchased from Aldrich Chemicals: carbon dioxide (99.8%), methane (99.0%), cerium nitrate hexahydrate ([Ce(NO₃)₃ · 6H₂O], 99.99%) and lanthanum nitrate hexahydrate ([La(NO₃)₃ · 6H₂O], 99.999%). Hydrogen hexachloroplatinate hexahydrate (chloroplatinic acid) (H₂PtCl₆ · 6H₂O with 40.18 (wt)% Pt) was supplied by Alfa of Johnson Matthey. Activated aluminum oxide (99% Al₂O₃) was also purchased from Alfa, Johnson Matthey, in white powder pellets with a surface area of 90 m² g⁻¹.

2.2. Catalyst preparation

All catalysts used in this study were prepared by a wet impregnation technique. For the monometallic catalyst with Pt supported on γ -Al₂O₃, the alumina pellets were ground and sieved to give grains having diameters between 157 and 178 μ m. The grains were first mixed with an aqueous solution of H₂PtCl₆ · 6H₂O, which was calculated to produce a desired content of Pt on the support and allowed to stand at room temperature for a period of 6 h. The paste was then dried in a furnace at a temperature of 60 °C over a period of 18 h. Once dried, the sample was calcined in a flow of air at 500 °C for a period of 2 h. Before use in reactions, the catalyst precursor was reduced with hydrogen for a period of 1 h at a temperature of 400 °C.

For the supported platinum catalyst with promoters CeO₂ or La₂O₃, a two-step co-impregnation was used. The promoter CeO₂ or La₂O₃ was first impregnated onto the γ -Al₂O₃ using Ce(NO₃)₃ · 6H₂O or La(NO₃)₃ · 6H₂O solution in the concentration on the basis of the calculation. The sample was then dried at 60 °C over a period of 18 h, calcined in a flow air at 500 °C for a period of 2 h. Platinum was then impregnated onto CeO₂/ γ -Al₂O₃ or La₂O₃/ γ -Al₂O₃ using H₂PtCl₆ · 6H₂O solution by the same procedure for the platinum impregnation described above.

2.3. Catalyst characterization

The composition of catalysts used in this study before and after reactions was analyzed by X-ray powder diffraction technique with a PW1710 X-ray diffractometer (Philips Electronic Instruments) using CuK α radiation of wavelength 1.54 Å.

2.4. Experimental procedures

All reactions were carried out in a laboratory-scale, continuous-flow reaction system with a tubular packed-bed reactor (i.d. 10 × 150 mm) placed either in a cylindrical microwave cavity or in a conventional tubular furnace [16]. During the operation, the product mixture from the reactor outlet was led to an ice-water trap through the tube wrapped by a heating tape, so as to condense the water produced, which was removed regularly. The effluent gas was then analyzed using a 16-channel quadrupole mass spectrometer (QMS-200D, European Spectrometry Systems), which was connected to the atmospheric pressure part of the system via a set of differentially pumped needle valves. The mass spectrometry data, together with the temperature measurements, were logged by a real-time, computerized data acquisition system (Sensorlab V.5, Fisons Instruments, Vacuum Generators Quadrupoles). Mass flow controllers (ASM model AFC-260) were used to control

the flow rates of the feed gases in known proportions prior to reaction.

The temperature in the microwave cavity was monitored using an Accufibre optical fiber thermometer (Model 10, LUXTRON), which had its tip at the center of the catalyst sample. The optical sensor (900-LP-12SS, LUXTRON) with a closed-end sheath (960-SS-12C) was made of sapphire, which was transparent to microwaves. Before the catalytic studies were carried out, the optical sensor was calibrated against a thermocouple. The microwaves were generated at 2.45 GHz using an Electro-Medical Supplies Ltd generator (0–200 W) and relayed by means of a coaxial cable to a tunable cylindrical microwave cavity placed around the reactor. A directional coupler was inserted into the microwave guide system so that the amount of microwave power reflected from the cavity could be measured. In the conventional heating system of a tubular furnace, a chromel–alumel thermocouple was used to measure the temperature.

Experiments were carried out under atmospheric pressure in the temperature range of 450–800 °C at 50 °C intervals. The compositions of the feed gases were varied by changing the molar ratio of CO₂/CH₄ between 3.0:1.0 to 1.0:3.0, while the total flow rate was maintained at 60 ml min^{−1} and the flow rate of argon at a constant of 6 ml min^{−1}. All the catalytic reactions were carried out using 0.50 g of catalyst.

The reaction product mixture leaving the reactor contained mainly CH₄, CO₂, CO and H₂, with some H₂O being observed sometimes. The conversion of carbon dioxide and methane are defined respectively as the percentage of carbon dioxide and methane that have reacted.

$$\text{CO}_2 \text{ conversion, \%} = 100 \times [(\text{CO}_2)_{\text{in}} - (\text{CO}_2)_{\text{out}}]/(\text{CO}_2)_{\text{in}} \quad (4)$$

$$\text{CH}_4 \text{ conversion, \%} = 100 \times [(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}]/(\text{CH}_4)_{\text{in}} \quad (5)$$

The product's selectivity is represented as the molar ratio of H₂/CO. The comparisons of the activities of these catalysts were primarily characterized by the conversion and the product selectivity criteria.

3. Results and discussion

3.1. Characterization of catalyst

X-ray diffraction (XRD) measurements were performed after the catalyst was reduced in an H₂ flow at 400 °C for 1 h and after reactions with either microwave or conventional heating. The XRD analyses results of catalyst Pt(8%)/CeO₂(20%)/γ-Al₂O₃ showed that before reaction the peaks corresponding to CeO₂ were

observed, the 2θ diffraction angles which were located at 28.45°, 47.57°, 56.20° and 33.12° [18]. After reaction with conventional heating, all the XRD peaks of CeO₂ were reduced somewhat and some new peaks were observed. According to literature data [18], these new diffraction peaks at 2θ = 33.56°, 41.42°, 59.98° and 23.54° can be assigned to cerium aluminum oxide (or cerium aluminate), CeAlO₃. After the reaction was carried out under microwave conditions, the XRD analysis of the catalyst used showed that these new peaks of CeAlO₃ were pronounced, while the CeO₂ peaks became even weaker. As the reaction of CeO₂ with Al₂O₃ to form CeAlO₃ needs a fairly high temperature (about 1000 °C) [19], the acceleration in reaction rate indicated that the catalyst temperature under microwave conditions was higher than that with conventional heating even though the measured temperature was in the same range.

3.2. Conversions of CO₂ and CH₄ as a function of temperature

It was observed that the concentrations of both reactants (CO₂ and CH₄) and products (CO, H₂ and H₂O) could be maintained at a constant level as long as the temperature was kept constant. When the temperature was raised, the reactant gases (CO₂ and CH₄) were noted to decrease in concentration, whilst the concentration of the product gases CO and H₂ was increased; the concurrent increased production of water was also noted.

Figure 1 shows, as a function of temperature, the conversions of CO₂ and CH₄ over the catalyst Pt(8%)/CeO₂(20%)/γ-Al₂O₃ at a feed molar ratio (CO₂/CH₄) of 1.0:1.0 with both microwave and conventional heating. The equilibrium conversions of CO₂ and CH₄ are also plotted in the figure, which were obtained from the thermodynamic analysis results [20], where two reactions were considered, namely, the carbon dioxide reforming of methane, the main reaction, and the reverse water-gas shift reaction, the secondary reaction.

It can be seen that as the temperature increased the conversions of CO₂ and CH₄ were increased, but the effect flattened out at temperatures above 700 °C. It was also observed that the conversions of CO₂ and CH₄ approached the thermodynamic equilibrium values with conventional heating, but conversions higher than the calculated equilibrium data were obtained under microwave conditions. It was noted that the conversion difference between the experimental and the theoretical data was reduced with increasing temperature, and finally merged at the higher temperatures, where the conversion exceeded 80%.

The microwave enhancement in reaction rates has been observed previously in the catalytic decomposition

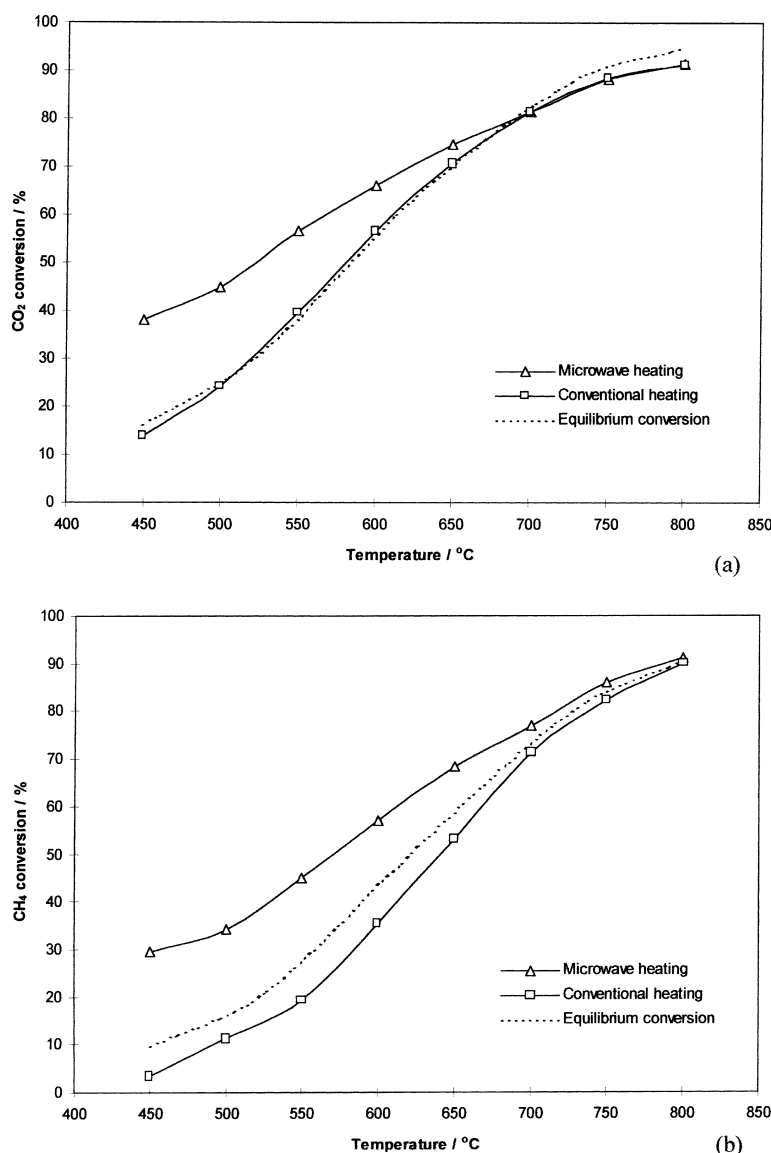


Figure 1. (a) CO₂ and (b) CH₄ conversions as a function of temperature over catalyst Pt(8%)/CeO₂(20%)/γ-Al₂O₃.

of H₂S and the reduction of SO₂ with methane over a MoS₂/γ-Al₂O₃ catalyst, and the equilibrium shift noted for the former reaction has also been observed. These results have been attributed to the formation of hot spots having higher temperatures compared to the measured average temperature in the bulk catalyst bed. In the CO₂-reforming reaction system catalyzed by Pt/CeO₂/γ-Al₂O₃ catalysts, the hot spots could also be created as the operating conditions were very similar to those in the previous studies. Such hot spots with higher temperature could consequently result in a higher conversion of CO₂ and CH₄ than that expected at the measured temperature.

Clearly, the reliable temperature measurement must be established for comparative studies on microwave and conventional effects on reactions. However, the direct measurement of temperature under microwave heating conditions in which there are strong electro-

magnetic fields is problematical. The use of optical fiber technology may overcome this problem, but such measurements are still only capable of providing average temperatures.

In our previous studies on the microwave-assisted catalysis, the temperature difference between the hot spots and the bulk catalyst bed was estimated on the basis of the reaction results, where the equilibrium that was set up was characteristic of the hot-spot temperature and not the average temperature of the catalyst bed as a whole, provided that the rate-determining step for both forward and back reactions occurred between adsorbed species that were fully accommodated to the active catalyst temperature. For the catalytic decomposition of H₂S [16], where an apparent equilibrium shift was also observed, the hot-spot temperatures were found 100–200 °C higher than the temperature measured by the optical thermometer. In the study on the

reduction of SO_2 with CH_4 [21], it was found that some regions of the catalyst reached temperatures which were approximately 200°C in excess of the measured temperature. In the present study, it was noticed that, when the temperature was increased, in particular, above 700°C , the difference between the conversions under microwave and conventional heating became small for both CO_2 and CH_4 conversions and the temperature difference between the hot spots and the bulk catalyst bed was in the range of 0 to 100°C . These results could not be explained simply by a constant difference in the effective temperature of reactions. Since the introduction of the microwave field with heterogeneous catalysts is complex, it is difficult to locate the hot spots and determine their exact temperatures.

3.3. Effect of temperature on product selectivity

Figure 2 shows the product selectivity in terms of the H_2/CO molar ratio at different temperatures, over catalyst $\text{Pt}(8\%)/\text{CeO}_2(20\%)/\gamma\text{-Al}_2\text{O}_3$ at a feed molar ratio of 1.0:1.0 (CO_2/CH_4) at 650°C with both microwave and conventional heating. The theoretical results under equilibrium conditions are also shown in the figure for comparison.

In general, the H_2/CO ratios increased when the temperature was raised. With conventional heating, the H_2/CO ratio was lower than the equilibrium values when the temperature was below 650°C , but close to the theoretical data above this temperature level. In contrast, under microwave conditions, the H_2/CO

ratio was higher than the equilibrium value in the lower temperature range and merged with the conventional heating data in the higher-temperature range.

The fact that the H_2/CO ratio was less than 1.0 indicated that the reverse water-gas shift reaction (2) was occurring simultaneously with the CO_2 -reforming reaction (3), depending upon the process conditions.

The variation of H_2/CO ratios depends on the degree of competition for the reaction systems. According to thermodynamic analysis, both the main reaction (1), *i.e.*, the CO_2 reforming of CH_4 , and the secondary reaction (2), *i.e.*, the reverse water-gas shift reaction, are endothermic. With the temperature rising, both equilibrium constants (K_p) increased, but the K_p of the CO_2 -reforming reaction increased at a greater rate than that for the second reaction. This indicated that increasing temperature was more favorable to the first reaction to produce hydrogen and carbon monoxide, which gave a ratio close to unity.

As the microwave effect on the reaction was attributed to the formation of hot spots, its effect on the H_2/CO ratio should be similar to that from the thermal temperature effect. When microwave heating was employed, the reaction could occur at a higher temperature than that measured, so a higher H_2/CO ratio could be reached that could be even higher than the equilibrium value predicted at the measured temperature level. At temperatures above 700°C , the microwave hot-spot effect appeared to be less, although the two curves must come together at very high temperature when the H_2/CO ratios from both microwave and conventional heating must approach unity.

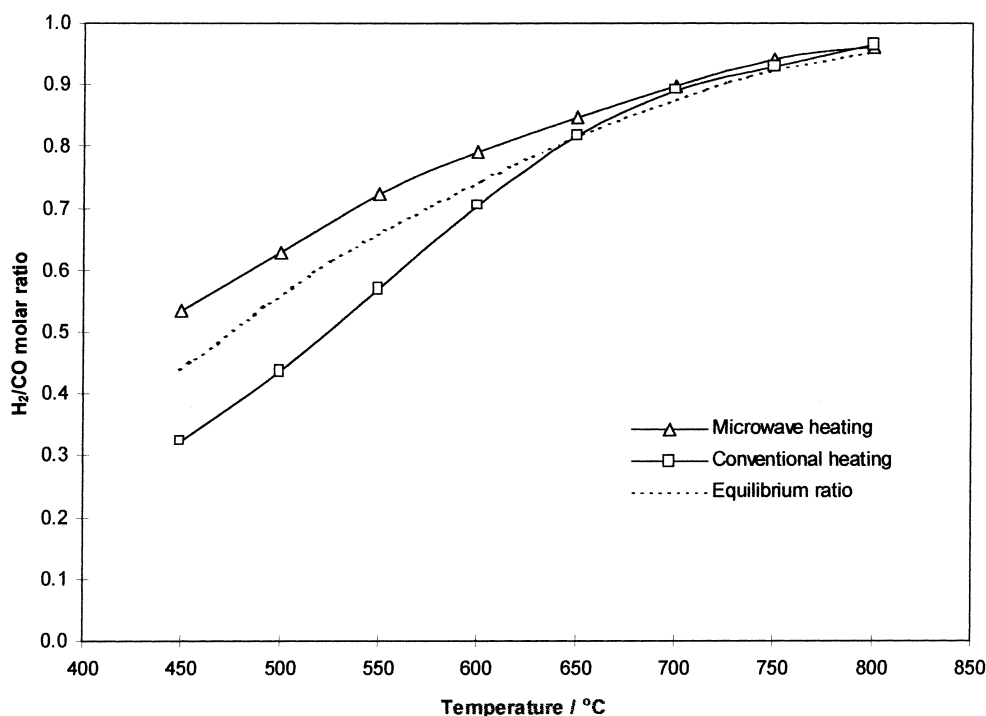


Figure 2. Products selectivity as a function of temperature over catalyst $\text{Pt}(8\%)/\text{CeO}_2(20\%)/\gamma\text{-Al}_2\text{O}_3$.

3.4. Effect of feed gas molar ratio (CO_2/CH_4)

The effect of varying the feed molar ratios of CO_2/CH_4 on the conversions and product selectivity was investigated over the catalyst $\text{Pt}(8\%)/\text{CeO}_2(20\%)/\gamma\text{-Al}_2\text{O}_3$ in a range of feed molar ratios (CO_2/CH_4) from 1.0:3.0 to 3.0:1.0 at 650°C with both microwave and conventional heating. The results are illustrated in figures 3 and 4.

As the CO_2/CH_4 ratio was increased, there was greater conversion of CH_4 , while the CO_2 conversion decreased, with either conventional or microwave heating. An equal conversion of CO_2 and CH_4 was obtained at a CO_2/CH_4 ratio of about 1.2:1.0 with both microwave and conventional heating. This indicated that more CO_2 was being consumed due to the secondary reaction. When the ratio of CO_2/CH_4 was less than 1.2:1.0, CO_2 conversion was higher than CH_4 conversion as CO_2 was less than the stoichiometric ratio. On the other hand, when CO_2 was in excess of that required, its conversion became lower than that of methane and the secondary reaction between CO_2 and H_2 could take place to produce the by-products.

It is interesting to note that the conversions of CO_2 and CH_4 were always higher under microwave conditions than those obtained with conventional heating and an almost constant difference was observed. On the basis of the hot-spot assumption, it could be concluded that there was almost a constant difference in the reaction temperature when the reaction was carried out with the two different heating methods at a same measured temperature level. The variation of CO_2/CH_4 ratios had little effect on the temperature difference.

With increasing CO_2 in the feed, there was a decreasing H_2/CO ratio in the product (see figure 4) indicating that the contribution of the reforming reaction was decreasing, while the reverse water-gas shift reaction was making a large contribution to the overall process. It was also observed that the H_2/CO ratio was higher under microwave conditions than that with conventional heating. This was mainly due to the higher temperature thought to occur under microwave conditions, which could benefit the CO_2 reforming reaction to give a higher H_2/CO ratio. When the higher CO_2/CH_4 ratio was used, the conversion of CH_4 by both heating methods was high ($> 90\%$); thus the effect of any higher temperature resulting from microwaves on the conversion was not significant and the H_2/CO ratios for the two different heating methods came close to the same value. Therefore, in all experiments where the reforming reaction itself was of primary interest, a stoichiometric feed composition of $\text{CO}_2/\text{CH}_4 = 1.0 : 1.0$ was applied.

3.5. Effect of varying Pt loading

Results showing the influence of Pt loading for catalysts on the performance of $\text{Pt}/\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ under microwave conditions are presented in figure 5. The experiment was carried out at different temperature levels with a feed CO_2/CH_4 ratio at 1.0:1.0 and Pt contents at levels of 3 (wt)%, 5 (wt)%, 8 (wt)% and 12 (wt)%. The loading of CeO_2 was kept constant at 20% throughout.

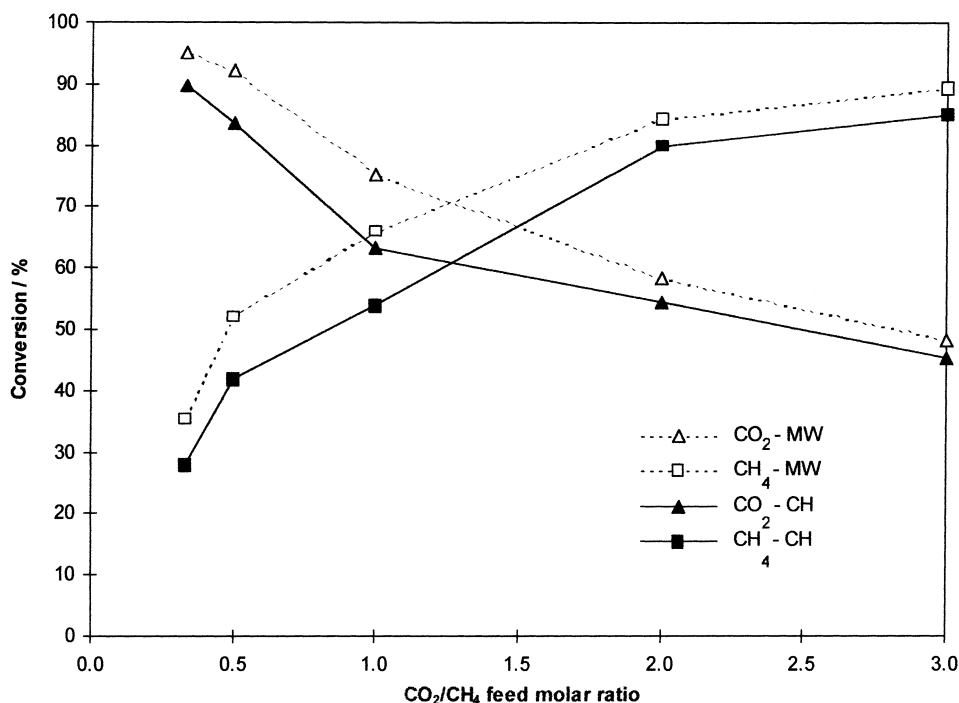


Figure 3. CO_2 and CH_4 conversions at different molar ratios of CO_2/CH_4 over catalyst $\text{Pt}(8\%)/\text{CeO}_2(20\%)/\gamma\text{-Al}_2\text{O}_3$ at 650°C .

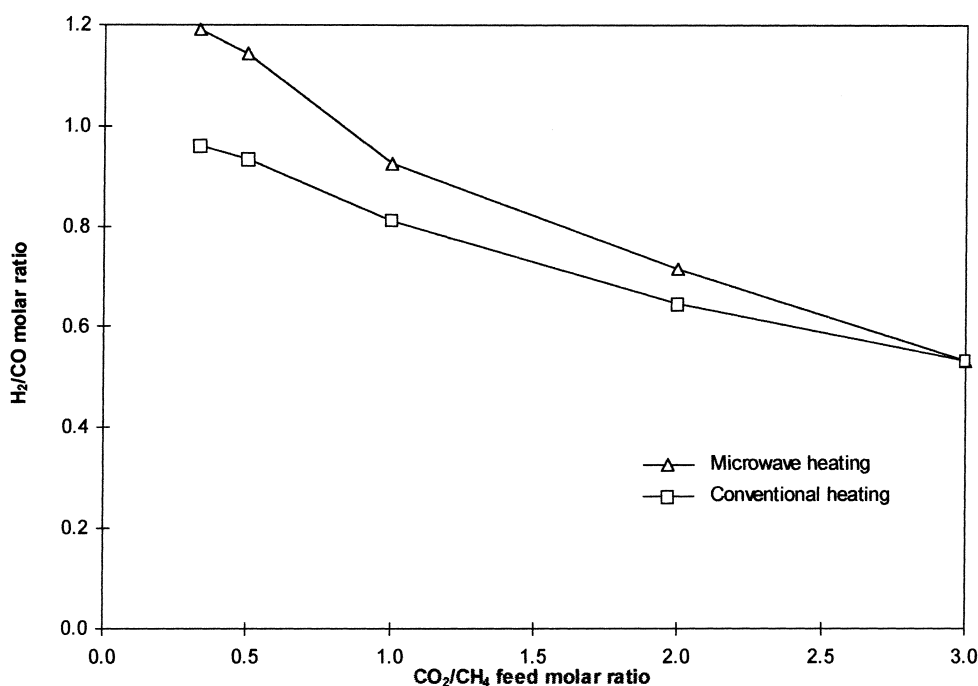


Figure 4. Product selectivity at different molar ratios of CO₂/CH₄ over catalyst Pt(8%)/CeO₂(20%)/ γ -Al₂O₃ at 650 °C.

As a general observation, both CO₂ and CH₄ conversions varied with the Pt loading when the temperature was lower than 700 °C under microwave conditions, and the catalyst with 5 (wt)% Pt caused the highest conversion. In the higher-temperature range (>700 °C), there was a little effect on the conversion by varying the Pt loading.

As discussed above, the main feature of using microwave heating is the possible creation of hot spots. In the microwave CO₂-reforming reaction system, where the conversions of CO₂ and CH₄ were higher than the equilibrium conversion, the variation of Pt loading may affect the formation of the hot spots that consequently influence the reaction results. It was observed that this effect, reflected in the conversion, was reduced at temperatures where the conversions were also high. For example, at a temperature of 800 °C, the conversions of both CO₂ and CH₄ were above 90% where both microwave and Pt loading effects were negligible.

It is interesting to note that as the Pt loading was increased the H₂/CO ratios decreased, in particular in the lower-temperature range (see figure 5(c)). If the reaction occurred under equilibrium control, changes in temperature shifted the position of equilibrium and the competition situation between the main reaction and the secondary reaction was also changed, which resulted in the variation of the product's selectivity. Varying the Pt loading may affect the microwave influence on reaction temperature and result in changes in the H₂/CO ratios. In the higher-temperature range, where the temperature difference appeared to be reduced, the change in the H₂/CO ratios was decreased. The decrease in the

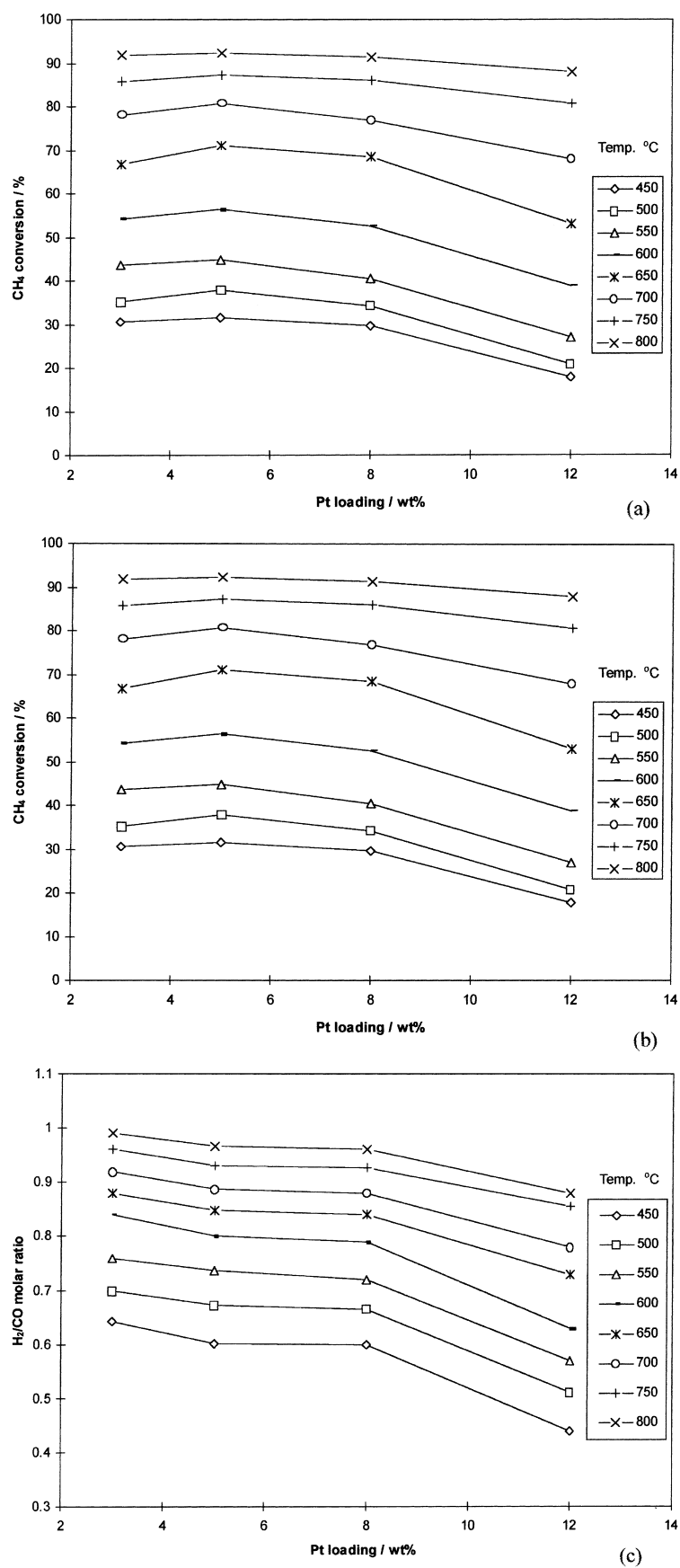
H₂/CO ratios as the Pt loading was increased also indicated that Pt catalyzed the reverse water–gas reaction preferentially.

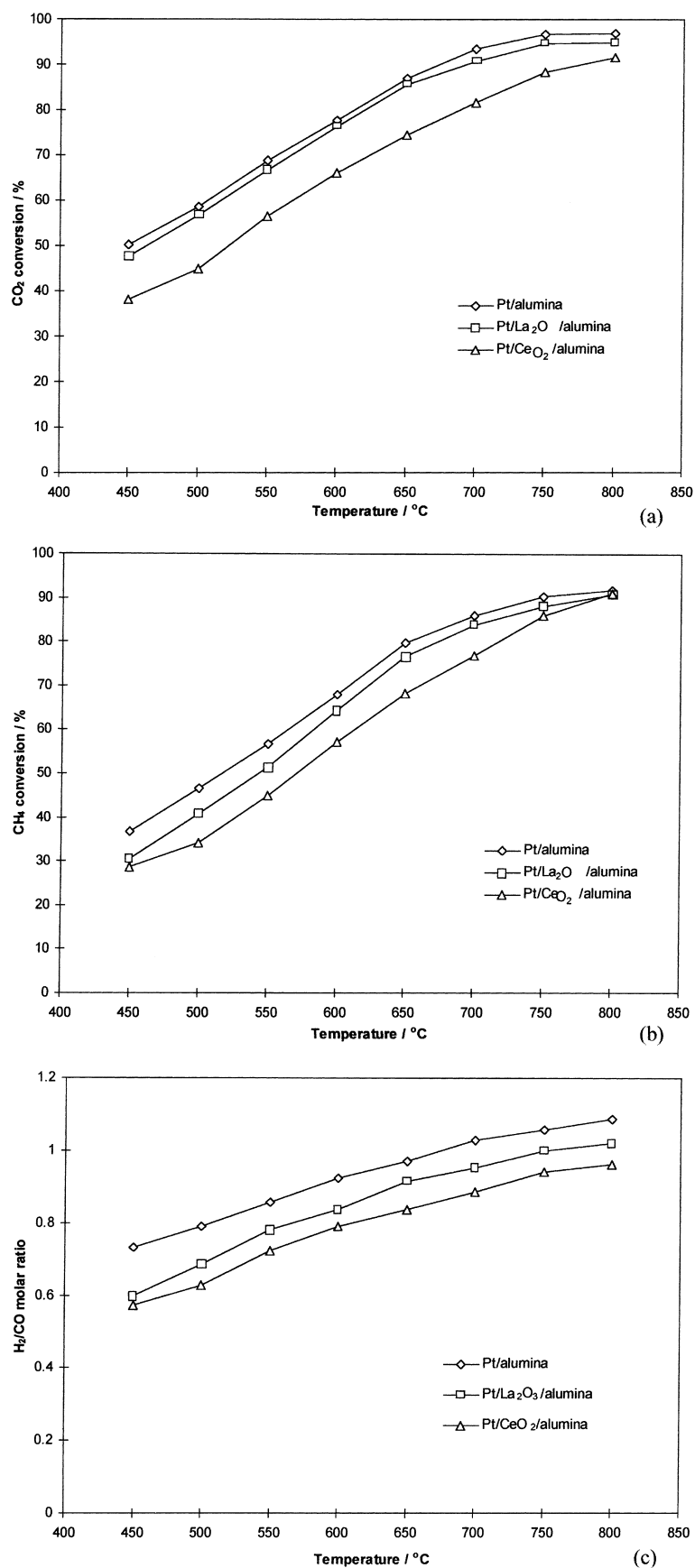
Experiments were also carried out using conventional heating under identical conditions to those using microwave heating. It was observed that the Pt loading had very little effect on the CO₂ conversion with conventional heating. As described above, the CO₂ conversion was close to the equilibrium value at every temperature level studied, so the reaction was almost under equilibrium control. However, the CH₄ conversion was affected by varying the Pt loading with conventional heating. With increasing Pt loading, the CH₄ conversion was decreased slightly. This observation, together with the variation in H₂/CO ratios when the Pt loading was changed, gave a clue to the existence of other secondary reactions in addition to the reverse water–gas shift reaction, especially at high temperatures. For example, at temperatures above 750 °C, H₂/CO ratios greater than one were obtained indicating a possible decomposition of methane.

3.6. Comparison of promoters

In figure 6, results are presented for catalysts containing La₂O₃ or CeO₂ at different temperatures under microwave conditions with a feed molar ratio (CO₂/CH₄) of 1:1.

It was observed that the conversions of CO₂ and CH₄ increased with temperature for all three catalysts used under microwave conditions. The performance of the three catalysts in terms of conversion and product

Figure 5. Performance of catalyst Pt/CeO₂(20%)/γ-Al₂O₃ at different Pt loadings using microwave heating.

Figure 6. Performance of catalyst Pt(8%)/ γ -Al₂O₃ with different promoters using microwave heating.

selectivity showed the following order, but the differences were reduced in the higher-temperature range:

$$\begin{aligned} [\text{Pt}(8\%)/\gamma\text{-Al}_2\text{O}_3] &> [\text{Pt}(8\%)/\text{La}_2\text{O}_3(5\%)/\gamma\text{-Al}_2\text{O}_3] \\ &> [\text{Pt}(8\%)/\text{CeO}_2(20\%)/\gamma\text{-Al}_2\text{O}_3] \end{aligned}$$

Since the reaction was strongly dependent on the reaction temperature and microwave heating could create a higher reaction temperature than that measured, it is important to note the overall reaction results, which could be a combination effect from both the microwave influence and the different promoters. Firstly, the promoter may result in different activity levels over the catalysts at the same reaction temperature. Secondly, the promoter may alter the dielectric properties of the catalyst, which, in turn, may affect the formation of hot spots. With conventional heating, the effect from promoters could be compared if the reaction is carried out at the same temperature level. This, therefore, could be useful to understand the results obtained under microwave conditions.

Using conventional heating under identical conditions to those under which the microwave heating experiments were carried out, the results of the conversions and the product selectivity were obtained.

With conventional heating, it was found that the CO_2 conversion for the three catalysts was in the following order:

$$\begin{aligned} [\text{Pt}/\gamma\text{-Al}_2\text{O}_3] &> [\text{Pt}/\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3] \\ &> [\text{Pt}/\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3] \end{aligned}$$

The product selectivity H_2/CO for the three catalysts was also found to follow the same order as the CO_2 conversion, but the CH_4 conversions differed from them. The CH_4 conversion for the three catalysts was in the following order:

$$\begin{aligned} [\text{Pt}/\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3] &> [\text{Pt}/\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3] \\ &> [\text{Pt}/\gamma\text{-Al}_2\text{O}_3] \end{aligned}$$

This difference in conversions of CO_2 and CH_4 also indicated the occurrence of secondary reactions, the promoted catalysts having different selectivity for the products. Since the order of product selectivity was not the same in all cases, the choice of promoters should be made depending on the requirements for the process.

3.7. Catalyst bed temperature versus microwave power

In the microwave supply system, the microwave power output from the generator is displayed on the output power meter, whilst the reflected power is monitored on the reflected power meter. If the system is free of leakage, the power absorbed by the catalyst bed can be calculated from the two meters' readings.

$$\text{Absorbed power (W)} = \text{Output power (W)}$$

$$- \text{Reflected power (W)}$$

Figure 7 shows the effects of forward, reflected and absorbed microwave power on the temperature of the catalyst bed with different catalysts. In general, the

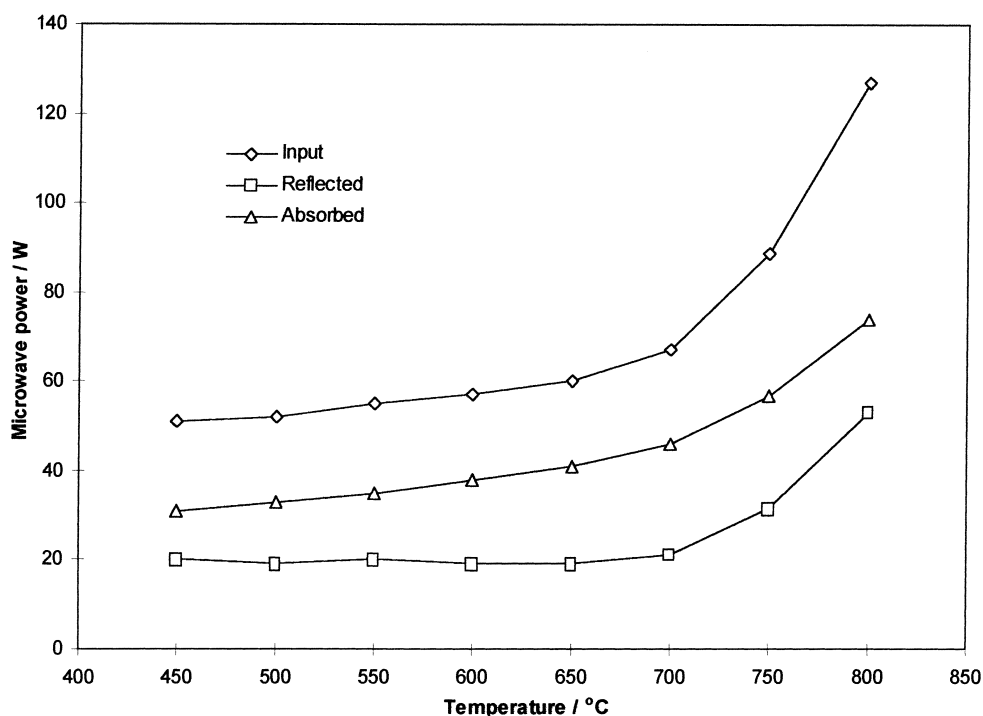


Figure 7. The relation between microwave power and temperature over catalyst $\text{Pt}(8\%)/\text{CeO}_2(20\%)/\gamma\text{-Al}_2\text{O}_3$.

microwave power had to be increased to increase the catalyst bed temperature, while the output power and reflected power strongly depended on the properties of the catalyst used and the interface between the catalyst and the microwave field.

It can also be seen that the temperature increased almost linearly with increasing power level but with a low gradient when it was below 700 °C. However, if the temperature was above 700 °C, the heating efficiency was markedly reduced and high power levels were needed to increase the temperature. This observation, together with the phase change shown in the XRD analysis and the conversion efficiency change in this temperature range, indicated that changes were occurring in the catalyst bed, which might reduce the microwave effect on the reaction temperature.

4. Conclusions

The application of microwaves in the CO₂ reforming of CH₄ was investigated for a range of catalysts at different temperature levels and different feed compositions. All the experiments were carried out with conventional heating for comparison.

The conversions of CO₂ and CH₄ and the product selectivity in terms of the H₂/CO ratio increased with rising temperature using both microwave and conventional heating, and the conversions and the selectivities were generally higher under microwave conditions than that obtained with conventional heating at the same measured temperature level. The product selectivity was decreased when the feed molar ratio (CO₂/CH₄) was increased. The CO₂ conversion was decreased but the CH₄ conversion was increased with CO₂/CH₄ rising using both heating methods.

Varying the platinum loading had only a small effect on the CO₂ and CH₄ conversions with both heating methods, but the H₂/CO ratio was affected significantly. Changing the catalyst promoters influenced both the conversions and the product selectivity, but the catalyst with the highest conversion and highest H₂/CO ratio was simply platinum-supported on γ -alumina. Comparing the input and reflected microwave power levels

showed that, for all the catalysts used, the absorbed power varied over a small range but the input and reflected power at a certain temperature level were different for each catalyst. This was a reflection of the efficiency for each catalyst to absorb microwave energy.

The effect of microwaves on the process, compared to that of conventional heating, was attributed to the formation of hot spots at higher temperature than that measured in the bulk catalyst bed.

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