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Catalysis Today 84 (2003) 17–25

CATALYSIS TODAY

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Effect of pressure on the carbon deposition route in CO_2 reforming of $^{13}CH_4$

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Abstract

In production of synthesis gas (syngas) from natural gas, carbon deposition is the major cause of catalyst deactivation, specifically on Ni-based catalysts. Because the rate of carbon formation is greater than the rate of carbon gasification, carbon accumulates in the catalyst bed. In order to better understand the carbon deposition process at high pressure during dry reforming, we have tested a series of noble metal and Ni-based catalysts at pressures of one, and 14 bar using ^{13}C-labeled methane. The source of the carbon deposition during the reactions was then studied using temperature-programmed oxidation (TPO). The results indicated that the source of carbon is different for the reactions conducted at low pressure compared to those performed at higher pressure over noble metal catalysts. At high pressure a significant amount of carbon formed on the catalysts and both methane and carbon dioxide equally contributed to carbon deposition. However, at low pressure the amounts of carbon formed on these catalysts were insignificant and came predominantly from $^{12}CO_2$. It was also found that at high pressure the total amount of carbon was higher regardless of catalyst type or composition.
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Keywords: Synthesis gas; Dry reforming; Catalysis

1. Introduction

The production of synthesis gas by CO_2 reforming of methane has recently been a topic of great interest. The increase in interest, of late, has primarily been driven by environmental concerns over CO_2 as a greenhouse gas. This reaction has also been suggested as a candidate for solar energy storage [1], as a method of recovering excess heat from gas turbine exhaust [2], and as a source of CO and H_2 for flame stabilization in low temperature methane fired gas turbines [3]. The intent in this last work is to reduce NO_x emissions by reducing the flame temperature. The CO_2 reforming of methane may also be useful for conversion of methane sources already high in CO_2, such as some coal bed methane and methane from sewage treatment plants or landfills. The combination of CO_2 reforming with other methane reforming reactions can also be used to tailor the H_2/CO ratio of the product synthesis gas to that needed for a given application. The three basic reactions that can be used to produce synthesis gas from natural gas are steam reforming, dry reforming and partial oxidation. Each has its advantages and likewise has drawbacks. Steam reforming is endothermic ($\Delta H^\circ = 206$ kJ/mol) and produces an H_2/CO ratio of about 3/1, which is good for hydrogen production, but is too high for fuel synthesis. Methanol and Fischer–Tropsch synthesis both use a H_2/CO ratio of 2/1. CO_2 reforming of methane results in a H_2/CO ratio of 1/1 and is also endothermic ($\Delta H^\circ = 247$ kJ/mol) requiring more energy than steam reforming. Partial oxidation

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0920-5861/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/S0920-5861(03)00296-7

reaction is exothermic ($\Delta H^\circ = -35.7\,\text{kJ/mol}$) and has the correct H_2/CO ratio for fuel synthesis, but requires a pure oxygen source, adding to the cost. The catalysts used in partial oxidation can also be susceptible to sintering due to hotspots created by the exothermic nature of the reaction. In addition to the individual drawbacks, all of these processes must be run with O/C ratios of greater than one to prevent coking of the catalyst. This makes the processes more expensive in practice than would be expected under optimized conditions for the stoichiometric reactions. The propensity of these processes to form carbon at low O/C ratios is even more pronounced at high pressures where, in industry, they would need to be run to minimize reactor size and energy use. Clearly, creating new catalysts that inhibit carbon formation would make all of these reactions more efficient for producing cheaper and environmentally cleaner energy.

Numerous research groups have focused their efforts on reducing carbon formation during dry reforming of methane [3–11]. For the most part, they have carried out their work at atmospheric pressure, but several have also looked at carbon formation at high pressure. Tomishige et al. have investigated the effect of pressure on dry reforming over a $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst that, under atmospheric pressure, is very resistant to carbon deposition [12,13]. Song et al. have reported preliminary results of high-pressure studies over Ni/Na–Y and Ni/Al_2O_3 catalysts [14] as well as ruthenium catalyst on the same support [15]. The effect of pressure are very similar in all cases, both methane and CO_2 conversion rates decreased, the H_2/CO ratio decreased, and the rate of carbon deposition increased with increasing pressure. Our earlier studies on Pt/ZrO_2, $Pt/Ce–ZrO_2$, and Rh/Al_2O_3 catalysts have given a similar result [16].

The higher rate of carbon deposition on reforming catalysts at high pressure leads naturally to the question of whether the source of carbon at elevated pressures is the same as at one atmosphere. It is known that the predominant sources of carbon on methane reforming catalysts are CO disproportionation and methane decomposition. Understanding which of these carbon sources is the major contributor at high pressure is necessary information in developing a catalytic process that will minimize carbon formation under industrial reaction conditions. Therefore, we have studied reforming of ^{13}C-labeled methane (99 atm% ^{13}C) with $^{12}CO_2$ and compared the relative contributions of methane and CO_2 as the sources of carbon formation at low and high pressures.

2. Experimental

The Pt/ZrO_2 and Ce-promoted catalysts were prepared as described by Stagg and Rasasco [17]. The 1 wt.% metal loaded Rh/Al_2O_3 catalyst was purchased from Alfa Aesar. The Ni/La_2O_3 catalyst was synthesized by first precipitating the La_2O_3 support from $La(NO_3)_3$ using $(NH_4)_2CO_3$ as the precipitating agent. The resulting fine powder was then heated in air for 6 h at 900 °C. The nickel was added to the support by the incipient wetness method, using a $Ni(NO_3)_2$ solution. The impregnated nickel catalyst was then calcined in air at 900 °C for 6 h. Prior to reaction the catalysts were reduced at 600 °C for 1 h in a 30 cm^3/min flow of pure H_2. The reforming reaction was performed in a fixed bed reactor. The reactor containing a quartz thermocouple well was a 0.3 m long ceramic tube (6.35 mm o.d., 4.0 mm i.d.), which was sealed inside a stainless steel tube at high pressure. The reactor was loaded with 0.012–0.100 g of catalyst (−28/+48 mesh) mixed with 0.030 g silica and held in place by quartz wool. The reactions were carried out at 800 °C, and at 1 and 14 bar, using a 20 cm^3/min flow of a 1:1 $^{13}CH_4/^{12}CO_2$ mixture. Temperature-programmed oxidation (TPO) of deposited carbon after the reaction was performed by heating the sample from 50 to 950 °C at a rate of 20 °C/min in flow of 2% oxygen in helium (40 cm^3/min). The exit gases were analyzed using a thermal conductivity detector and a quadrupole mass spectrometer.

3. Results and discussion

3.1. Thermodynamic calculations

In methane reforming processes, CH_4 decomposition (1) and CO disproportionation (2):

$$CH_4 \rightarrow C + 2H_2 \quad (f\mathrm{H}_{298} = 75\,\text{kJ/mol}) \tag{1}$$

$$2CO \rightarrow C + CO_2 \quad (f\mathrm{H}_{298} = -172\,\text{kJ/mol}) \tag{2}$$

are the two major reactions that contribute to carbon formation. To see which carbon forming reaction

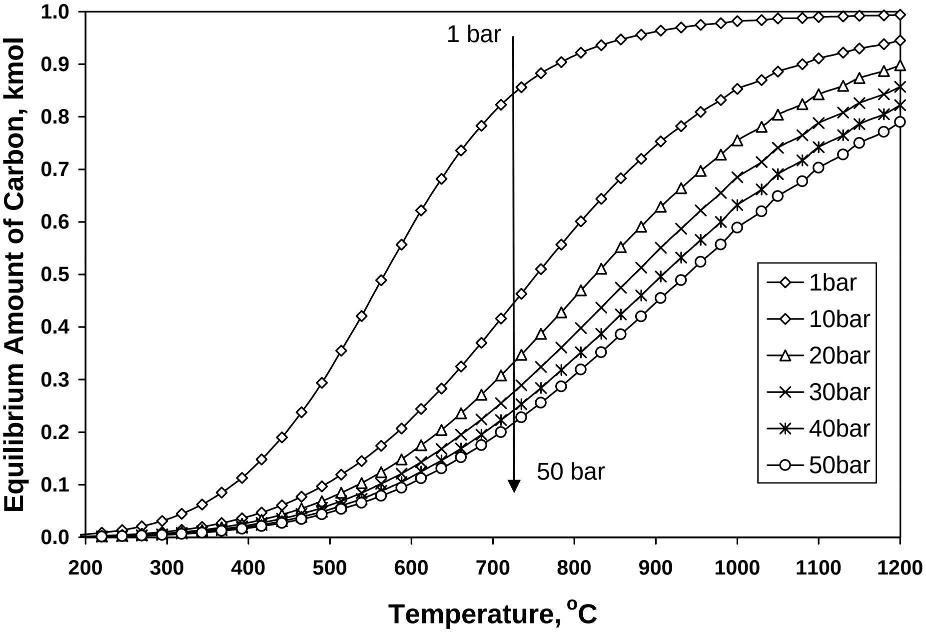

Fig. 1. Effects of temperature and pressure on equilibrium amount of carbon for methane decomposition reaction.

contributed most as a function of temperature and pressure, thermodynamic calculations were performed on the individual reactions as shown in Figs. 1 and 2. Calculations on the CH_4 decomposition reaction showed that as the temperature increased the equilibrium amount of carbon increased. However, increasing the pressure decreased the amount of carbon deposited by this reaction. The same calculation

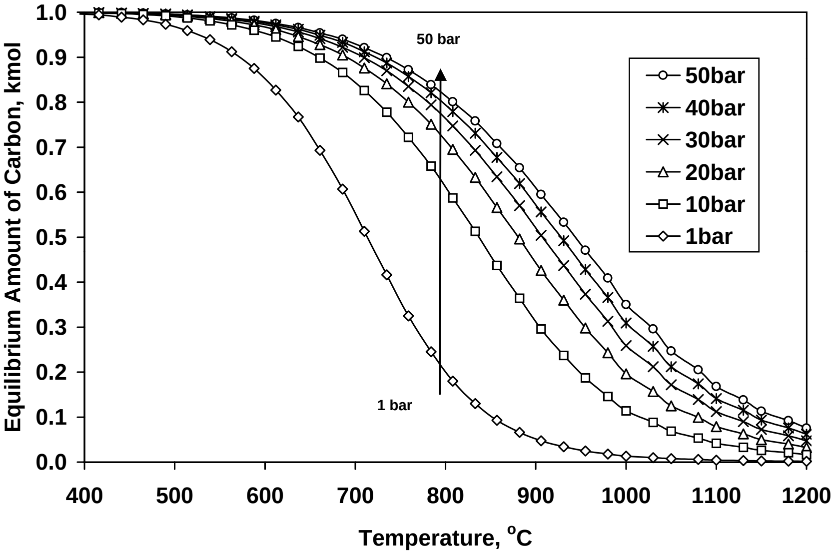

Fig. 2. Effects of temperature and pressure on equilibrium amount of carbon for CO disproportionation reaction.

performed on the CO disproportionation reaction indicated that the equilibrium amount of carbon decreased with increasing temperature, but increased with increasing pressure. A similar result was obtained for the endothermic reaction of CO_2 with CH_4, containing a mixture of CH_4, CO_2, H_2O, CO and H_2, indicating that the equilibrium amount of carbon decreases with increasing temperature and increases with increasing pressure. These results suggest that the CO disproportionation becomes a larger contributor to carbon deposition on dry reforming catalysts used at high pressure. Higher pressure also affects the equilibrium amount of water produced during the dry reforming reaction. At atmospheric pressure water disappears at temperatures above 900 °C, but at higher pressures this temperature increases to more than 1200 °C. The high concentration of water is mainly due to the reverse water gas shift (RWGS) reaction, which also resulted in a lower H_2/CO ratio. Both carbon and water are by-products of dry reforming and as with the reaction of water, the equilibrium amount of carbon also increases with increasing pressure. These calculations were performed using Gibbs energy minimization method [18], assuming carbon as a pure substance and water in the gas phase.

3.2. ^{13}C-labeled studies

The products formed during the reaction of an equimolar mixture of $^{13}CH_4$ and $^{12}CO_2$ over Pt/Ce–ZrO_2 catalyst were monitored by a quadrupole mass spectrometry and are shown in Fig. 3. Note that for both CO and CO_2 the amount of these species-containing ^{13}C is nearly equal to those containing ^{12}C. In particular, the presence of $^{13}CO_2$ in the reaction products suggests considerable back reaction by either CO disproportionation or water gas shift reaction. It is also known that on oxide surfaces and high temperature the oxygen exchange between CO and CO_2 is very fast [19]. This specific experiment was done with a flow rate of 20 cm^3/min at 800 °C and 14 bar, but this result is typical, regardless of which catalyst is used. This is consistent with the reactions being near equilibrium. The only difference found in any of

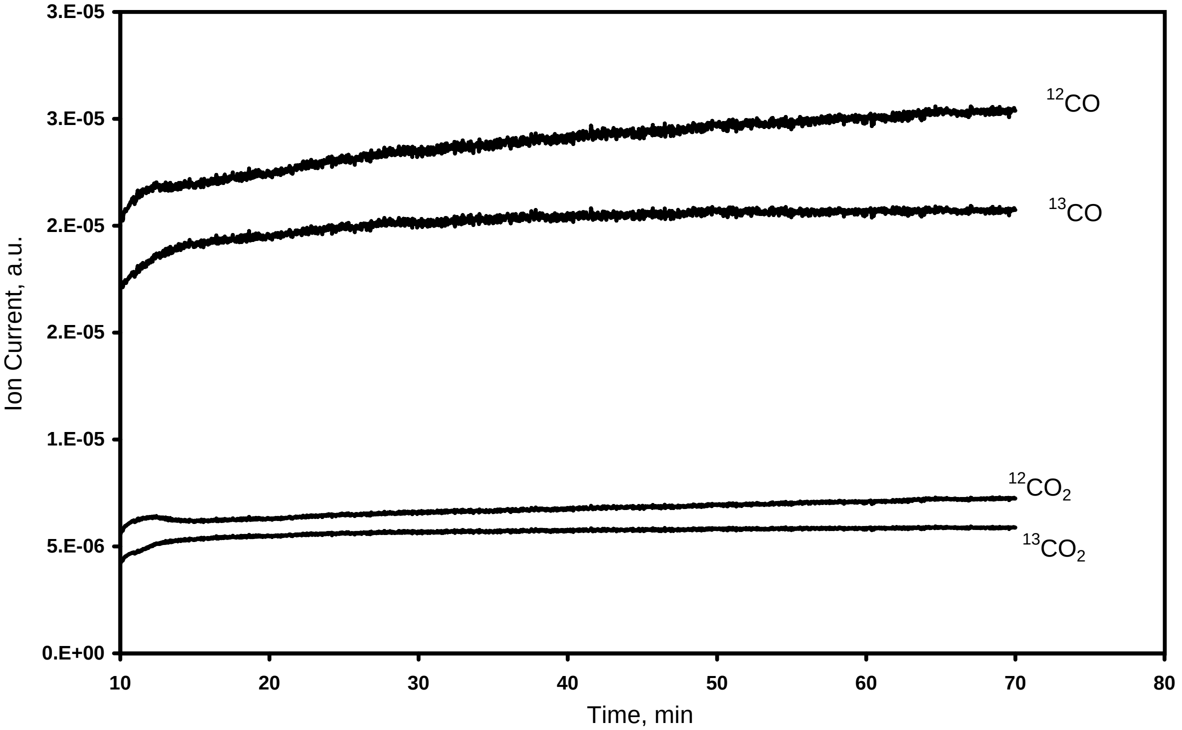

Fig. 3. Reforming of $^{13}CH_4$ over a Pt/Ce–ZrO_2 catalyst at 800 °C, 14 bar, and 1:1 $^{12}CO_2$/$^{13}CH_4$.

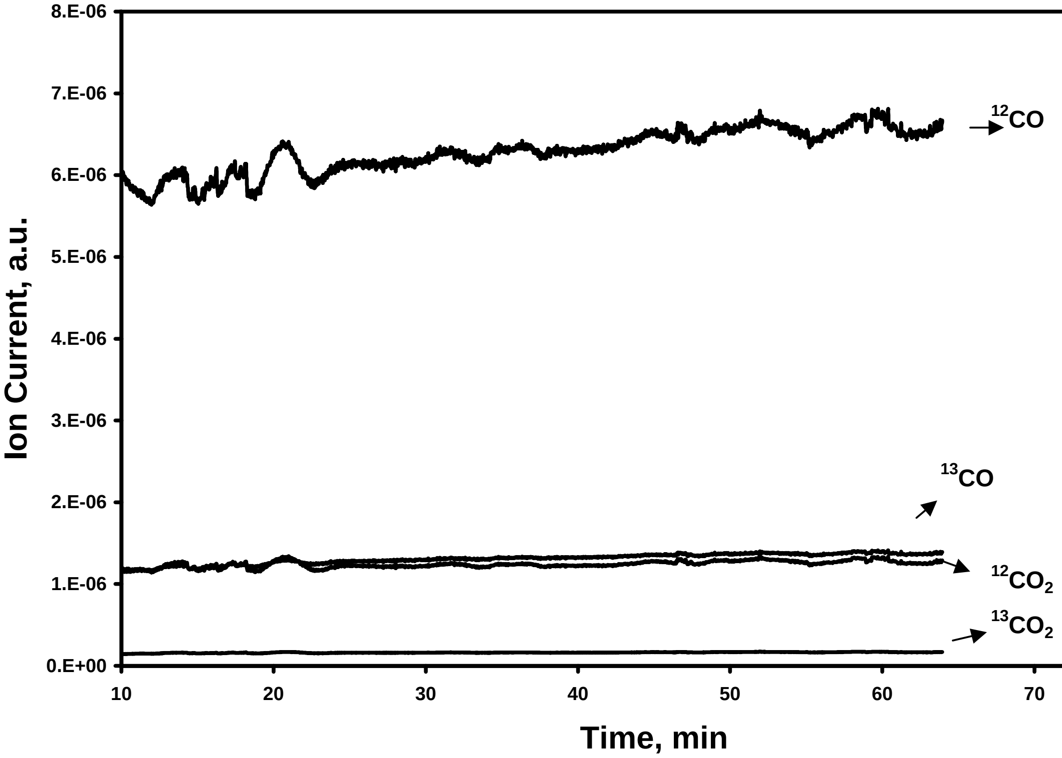

Fig. 4. Reforming $^{12}CH_4$ over a Pt/Ce–ZrO_2 catalyst at 800 °C, 14 bar, and 1:1 $^{12}CO_2/^{12}CH_4$.

these reactions is that both methane and CO_2 conversions are higher when the reactions are conducted at 1 bar compared to at 14 bar, however the approximate ratios for $^{13}CO/^{12}CO$ and $^{13}CO_2/^{12}CO_2$ were 0.84 and 0.85, respectively. As a comparison, the reaction products for the same reaction, but done using $^{12}CH_4$ are shown in Fig. 4. As expected, the occurrence of ^{13}C-containing species is considerably less and the ratios of $^{13}CO/^{12}CO$ and $^{13}CO_2/^{12}CO_2$ are 0.21 and 0.13, respectively. These ratios were 0.007 and 0.013 when CO_2 injected into the mass spectrometer. The natural abundance (ATOM%) for ^{13}C and ^{12}C are 1.108 and 98.892, respectively.

Temperature-programmed oxidation (TPO) of the carbon deposited on the catalysts was also performed and the results for the Pt/ZrO_2 catalyst, reacted at 1 bar, are shown in Fig. 5. Two major peaks, one occurring near 380 °C and the other near 830 °C are visible in the $^{12}CO_2$ signal. Note that no significant amounts of ^{13}C-containing species were detected, indicating that at 1 atm pressure the carbon formed on this catalyst comes mostly from CO_2. The occurrence of multiple peaks in TPO results has been analyzed in a similar study by X-ray photoelectron spectroscopy (XPS) [20]. It was concluded that the different peaks present in the TPO were the result of carbon deposited at two different locations on the catalyst surface. The first peak in each TPO therefore may be formed on a catalyst site that assists in the oxidation of carbon and the second peak may be formed on a catalyst support that does not assist in oxidation of the carbon. The same catalyst was also reacted at 800 °C and 14 bar and the result of the TPO analysis after reaction is shown in Fig. 6. It is clearly seen that at high pressure both CO_2 and CH_4 contribute equally as sources of carbon formation on the Pt/ZrO_2 catalyst, as indicated by the approximately equal peak areas in both the $^{12}CO_2$ and $^{13}CO_2$ signals, occurring at 660 °C. This result

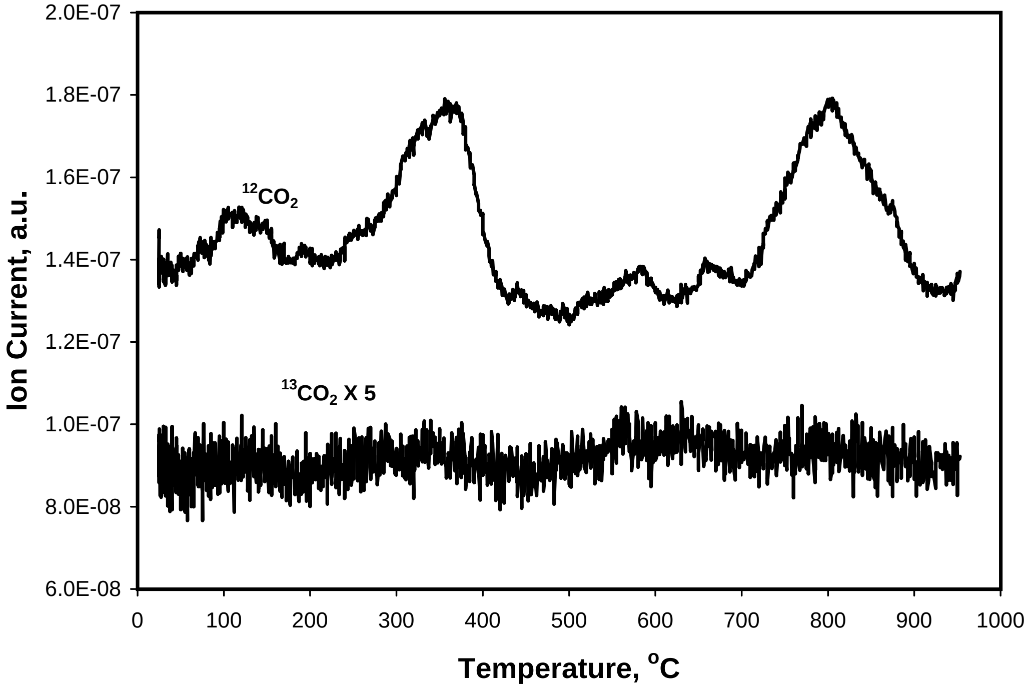

Fig. 5. Temperature-programmed oxidation of deposited carbon on Pt/ZrO_2 catalyst reacted at 800 °C, 1 bar, and 1:1 $^{12}CO_2$/$^{13}CH_4$.

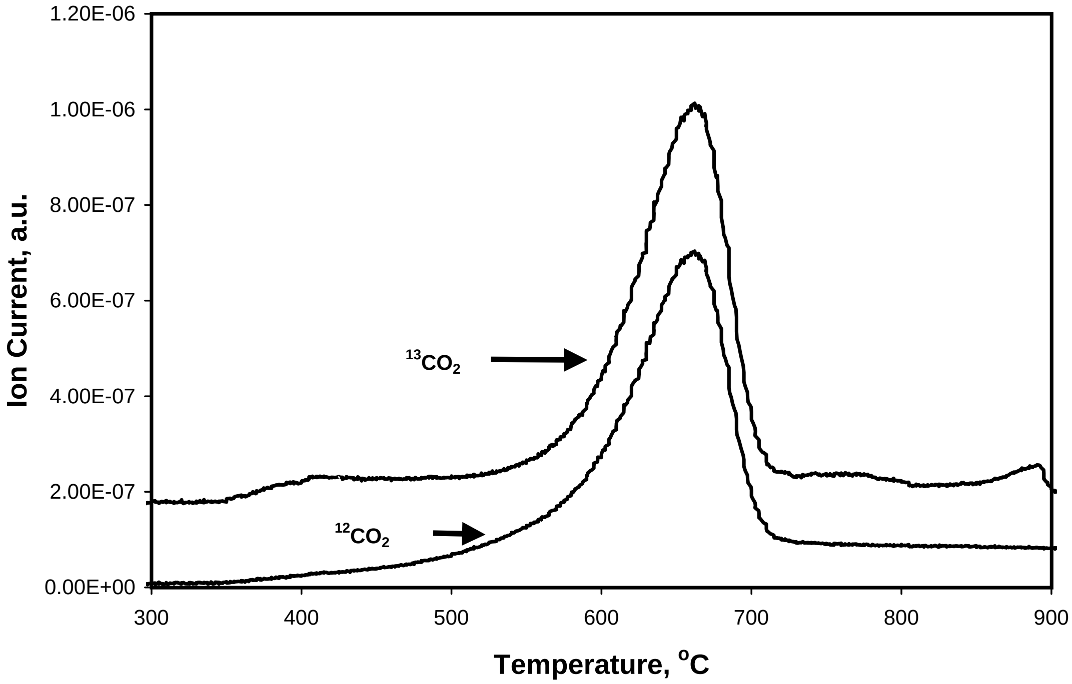

Fig. 6. Temperature-programmed oxidation of deposited carbon on Pt/ZrO_2 catalyst reacted at 800 °C, 14 bar, and 1:1 $^{12}CO_2$/$^{13}CH_4$.

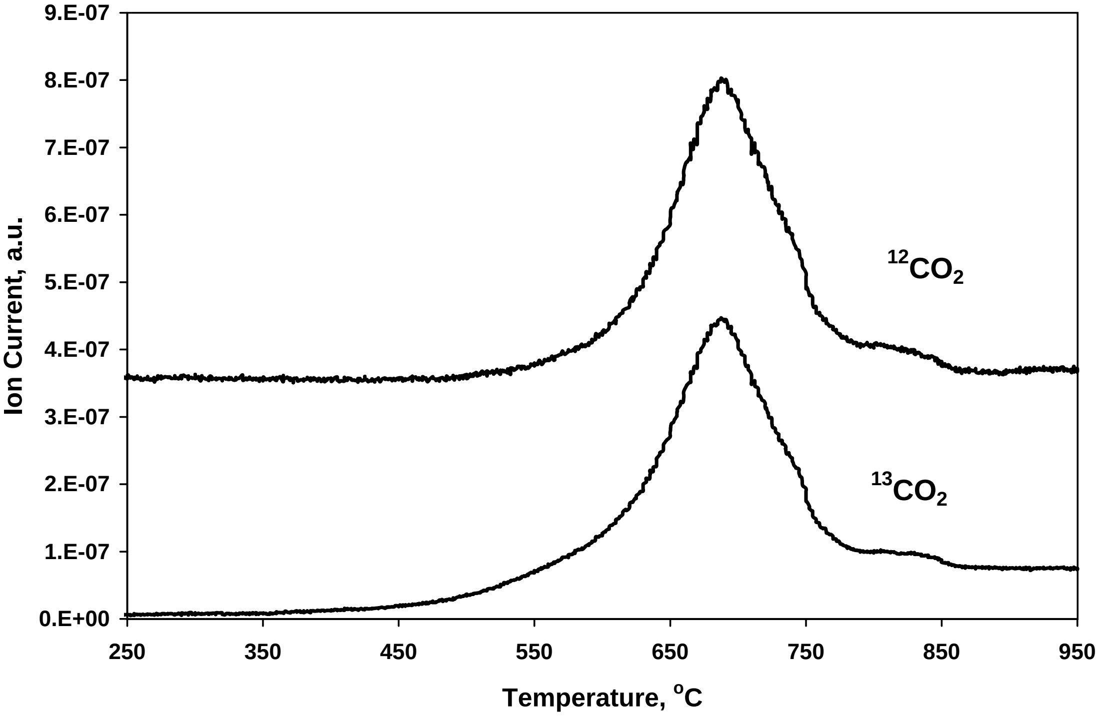

Fig. 7. Temperature-programmed oxidation of deposited carbon on Pt/Ce–ZrO$_2$ catalyst reacted at 800 °C, 14 bar and 1:1 $^{12}CO_2/^{13}CH_4$.

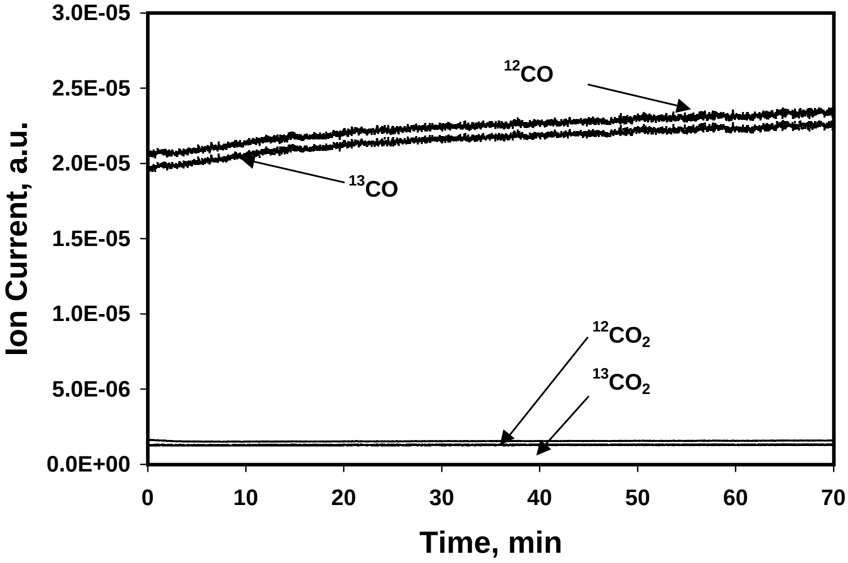

Fig. 8. Reforming of $^{13}CH_4$ over Rh/Al$_2$O$_3$ at 800 °C, 1 bar, 20 cm^3/min, and 1:1 $^{13}CH_4/CO_2$.

consistent with CO disproportionation being the more predominant reaction at high pressures because of the high levels of CO in the product combined with the increased contact time over the catalyst at 14 bar.

Identical experiments were carried out using Pt/Ce–ZrO_2 catalyst. Again, the monitoring of reaction products by a quadrupole mass spectrometer and the top (shown in Fig. 7) showed essentially identical results to those obtained for the Pt/ZrO_2 catalyst at 14 bar. The amount of carbon formed on the catalyst at 1 bar was significantly lower than that formed at 14 bar. The TPO results obtained for the Pt/Ce–ZrO_2 catalyst reacted at 1 bar again show that at low pressure CO_2 is the predominant source of carbon deposited on the this catalyst. There is also some small signal from $^{13}CO_2$. Where in the TPO of the Pt/ZrO_2 catalyst, reacted at 1 bar, no significant ^{13}C contribution to carbon formation was found.

Two additional catalysts, 1 wt.% Rh on Al_2O_3 (Fig. 8) and 3 wt.% Ni on La_2O_3 (Fig. 9), were also studied and tested at the same conditions as the Pt/ZrO_2 and Ce-promoted Pt/ZrO_2 catalysts. As with the previous catalysts, when the reactions were conducted at low pressure over 1 wt.% Rh on Al_2O_3, the TPO results showed that the main source of carbon was from CO_2, although, as with the Pt/Ce–ZrO_2 catalyst, small amount of carbon originated from $^{13}CH_4$. The low-pressure reactions also resulted in multiple peaks in the TPO, indicating either different carbon forms and/or carbon found on different locations on the catalyst. Again, when the reaction were carried out at 14 bar the TPO results showed approximately equal amounts of carbon coming from $^{12}CO_2$ and $^{13}CH_4$, and producing a single predominant peak. Even though the carbon formation route at high pressure seems unaffected by the catalyst, catalyst composition may still be modified to reduce overall carbon formation. While our study is not quantitative, we made a rough estimate of the amount of carbon formed under a given reaction condition by simply measuring the intensity or peak area of the TPO signals. For the reactions carried out under similar conditions, the Rh catalyst appeared to form the least amount of carbon and the Ni catalyst formed the greatest amount of carbon of the catalysts tested in this study. Indeed, in order to get a reasonable signal to noise ratio for the CO_2 produced during a TPO experiment, the reaction

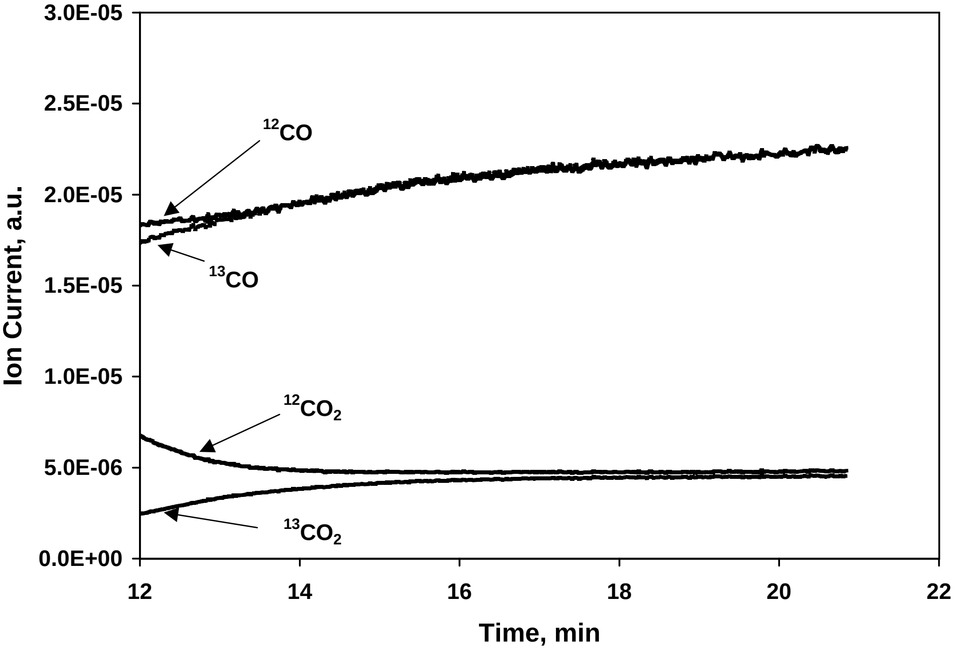

Fig. 9. Reforming of $^{13}CH_4$ over Ni/La_2O_3 at 800 °C, 14 bar, 20 cm^3/min, and 1:1 $^{13}CH_4/CO_2$.

time at 1 bar was extended from 1 to 2 h so that enough carbon deposited on the catalysts. Conversely, reactions over Ni-supported catalysts were done for only ten minutes so that during the TPO experiments sufficient oxygen remains in the gas phase for completing the oxidation of carbon to CO_2.

4. Conclusions

CO_2 reforming of $^{13}CH_4$ was studied over Ni-, Pt-, and Rh-supported catalysts at 800 °C and at pressures of one and 14 bar. The amount of carbon deposited on Pt- and Rh-supported catalysts at 1 bar and reaction time of 1–2 h were insignificant compared to that produced at 14 bar. At low pressure, CO_2 appears to be the major source of carbon deposited on these catalysts, which is in good agreement with the results obtained by Tsipouriari et al. for Rh-supported catalyst [21]. However, at 14 bar and on the Ni-supported catalysts the deposited carbon comes from both methane and CO_2, depending on reactant partial pressure. These data along with thermodynamic calculation data are consistent with CO disproportionation being the main route for carbon formation.

Acknowledgements

The authors thank the Natural Gas Processing and Utilization Team of NETL for funding this work and Professor D.E. Resasco and his research group for providing the Pt/Ce–ZrO_2 and Pt/ZrO_2 catalysts used in this study.

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