Partial Oxidation and Combined Reforming of Methane on Ce-promoted Catalysts

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Introduction

Significant attention has been given to the partial oxidation and reforming of various hydrocarbon sources for the production of synthesis gas. This work has stemmed from the concern about the world dependence on petroleum oil. Many hydrocarbon sources are currently being investigated including bio-based feedstocks, such as ethanol, sunflower oil, and biomass derived oils. However, the most common feedstock is still methane due to its abundance and inexpensive nature.

Many of the natural gas reservoirs are located in remote regions making the recovery and transportation cost prohibitive. The conversion of natural gas into transportation fuels such as gasoline and diesel helps top overcome these costs. The so-called gas-to-liquids technology (GTL) is based on the conversion of natural gas to a synthesis gas prior to the liquid production through the Fischer-Tropsch Synthesis (1). The syngas generation is the most capital and energy intensive part of the production plant (2). Therefore, the economic viability of GTL technology depends on optimizing the process for syngas production. Autothermal reforming (ATR) fulfills the requirements to a syngas with H_2/CO ratio of 2, the ratio necessary for GTL plants. ATR combines non catalytic partial oxidation with steam reforming in one reactor. The ATR technology requires the addition of CO_2 or CO_2-rich gas, in order to adjust the syngas composition to the desired H_2/CO ratio (3).

Catalyst stability in the presence of O_2, CO_2, and H_2O can be a significant issue. It is well established that mixed oxide supports result in improved catalytic performance for the dry reforming reaction due to the ability of the support to participate in the reaction (4). Similar studies for the partial oxidation reaction have shown that the addition of Ce to ZrO_2 results in a catalyst which exhibits minimal deactivation compared to Pt/Al_2O_3 and Pt/ZrO_2 catalysts (5). The mechanism of reaction was shown to proceed through combustion of methane followed by combined steam and CO_2 reforming.

Several studies have been performed on the dry reforming reaction in the presence of oxygen (6,7). The results showed that the conversion of methane increased as the amount of oxygen in the feed increased, but the selectivity towards H_2 decreased. The decrease in H_2 selectivity was more pronounced at lower temperatures where the formation of CO_2 and H_2O were favored. Minimal deactivation was observed on the Pt/ZrO_2 catalyst at low space velocities and with a significant amount of diluent in the feed (6).

This paper focuses on the partial oxidation and combined partial oxidation and reforming reactions over Pt supported on ZrO_2 and $CeZrO_2$. Specifically, we have investigated the effect of the metal loading and effect of the addition of oxygen and water on the activity, stability, and syngas ratio produced. A general reaction mechanism is discussed.

Experimental

ZrO_2 and cerium (18 wt%)-doped ZrO_2 were all obtained from Magnesium Elektron, Inc. Prior to the addition of the metal the supports were calcined at 800°C in stagnant air for 4 hours. Pt was added to the supports using incipient wetness impregnation of an aqueous solution of H_2PtCL_6•$6H_2O$. The metal loading was 0.5 wt% and 1.5 wt%. All of the catalysts were dried overnight at 110°C, and then reduced *in-situ* in H_2 (30 cm^3/min) at 500°C for 1.5 h, prior to reaction.

Partial oxidation experiments were carried out in a quartz flow reactor at 800°C using a CH_4:O_2 ratio of 2:1 and a total flow rate of 100 cc/min. The catalysts were diluted with a 3:1 ratio of SiC to catalyst to help reduce any heat effects. 20 milligrams of catalyst was used for the reaction on the 1.5 wt% catalysts while 60 mg was used for the runs with the 0.5 wt% catalyst, in order to maintain the same metal content in the reactor. For the experiments in the presence of oxygen, the composition of the feedstock was such that the C:O ratio was 1:1. The reactions were performed at 800°C with a total flow rate of 100 cc/min.

Results and Discussion

The surface area of the Ce promoted ZrO_2 support was 48 m^2/g while that of the ZrO^2 was 29 m^2/g. Transmission Electron Microscopy (TEM) was used to determine the dispersion of the 0.5 wt% catalysts. The catalysts were reduced at 500°C and then heated to 800°C in He. The dispersion of the 0.5 wt% Pt/ZrO_2 catalyst was approximately 21% while the dispersion of the 0.5 wt% Pt/$CeZrO_2$ catalyst was near 30%. The dispersion of the 1.5 wt% catalysts was measured using dehydrogenation of cyclohexane after reduction at 500°C. The dispersion after reduction at 500°C before heating to 800°C was measured to be 29% for the 1.5 wt% Pt/ZrO_2 catalyst and 34% for the 1.5 wt% Pt/$CeZrO_2$. TEM of a 1.5 wt% Pt/ZrO_2 catalyst after heating to 800°C showed that the dispersion was closer to 15%. These results are in agreement with previous studies which have shown that the sintering of the Pt/ZrO_2 catalyst during the heating from 500°C to 800°C is much greater than the sintering on the Pt/$CeZrO_2$ catalyst. Based on the dispersion results, it appears as if the metal particle sizes for the 0.5 wt% and the 1.5 wt% catalysts are similar after heating to 800°C.

Table 1. Methane Conversion During the Partial Oxidation Reaction at 800°C and a 2:1 CH_4:O_2 Feed Ratio

	% Methane Conversion		
Catalyst	After 1 hour	After 12 hours	After 24 hours
0.5 wt % Pt/ZrO_2	49	26	13
0.5 wt % Pt/$CeZrO_2$	39	40	37
1.5 wt % Pt/ZrO_2	51	34	13
1.5 wt % Pt/$CeZrO_2$	49	46	37

Table 1 shows the methane conversion during the partial oxidation reaction at 800°C and a 2:1 ratio of CH_4:O_2. The 0.5 wt% Pt/$CeZrO_2$ catalyst had an initial activity that was approximately 10% less than the 1.5 wt% Pt/$CeZrO_2$ and both of the unpromoted ZrO_2 catalysts. However, this material was the most stable of the 4 catalysts studied. Both of the ZrO_2 catalysts exhibited significant deactivation during the reaction which has been ascribed to carbon deposition. The loading of the metal was found not to have any effect on the long term activity of the catalyst which is most likely due to the similarity in the metal particle size after heating to 800°C and reaction for 24 hours.

Figure 1 shows the CO and CO_2 selectivity for the same 24 hour experiment for the $CeZrO_2$ and ZrO_2 catalysts containing 0.5 wt% Pt. Similar profiles were obtained for the 1.5 wt% samples. The CO selectivity for the ZrO_2 catalyst decreased significantly during the 24

hour experiment while the CO_2 selectivity increased. After approximately 10 hours of reaction the CO_2 selectivity became greater than the CO selectivity. In contrast, the CO and CO_2 selectivities of the $CeZrO_2$ catalyst were very stable with CO always being greater than CO_2. Similarly, the H_2:CO ratio remained at 2.6 during the 24 hour reaction for the Ce containing catalysts, while it was initially 2.6 for the ZrO_2 samples, but decreased to 0.8 by the end of the reaction.

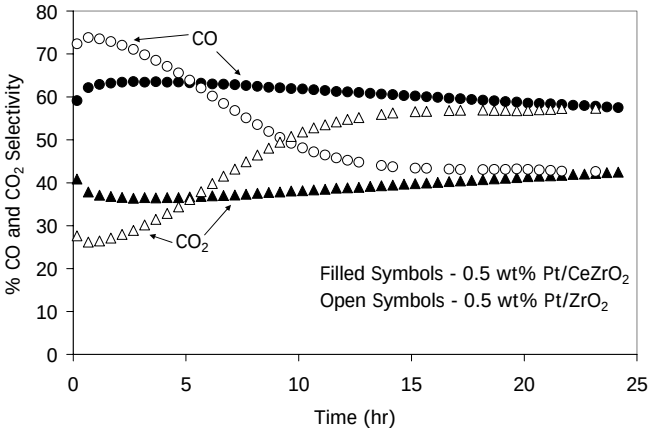

Figure 1. CO and CO_2 selectivity for the 0.5 wt% $Pt/CeZrO_2$ and the 0.5 wt% Pt/ZrO_2 during the partial oxidation reaction at 800°C and a 2:1 CH_4:O_2 feed ratio.

Previous studies (5) on a $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst have suggested that the reaction mechanism proceeds via the combustion of methane followed by the combined steam and dry reforming. The observed initial H_2:CO ratio greater than 2 is evidence for the occurrence of the steam reforming reaction and the two step mechanism. The decrease in the CO selectivity and the H_2:CO ratio with the simultaneous increase in CO_2 selectivity is attributed to carbon formation inhibiting the second step of the reaction mechanism. The stability of the Ce-promoted materials is ascribed to the ability of the support to minimize carbon deposition on the Pt particle due to increased oxygen release capability.

The catalysts were exposed to reactions with both CO_2 and O_2 at 800°C with a CH_4:CO_2:O_2 feed ratio of 4:2:1. Reactions were performed such that the C:O ratio remained at 1:1. Figure 2 shows the conversion for the 0.5 wt% catalysts for 10 hours of reaction. The conversion of methane and the deactivation observed on the 0.5 wt% Pt/ZrO_2 is almost identical to that observed for the partial oxidation reaction. The H_2:CO product ratio was initially 1.18 but decreased to 0.95 during the experiment. A significant amount of water was collected using a condenser placed after the reactor. The formation of water could be due to the occurrence of the reverse water gas shift reaction, which also explains the H_2:CO ratio being less than 1. The water could also be formed by the combustion reaction. The partial oxidation studies demonstrated that combustion does occur in the presence of O_2 and that the ZrO_2 catalysts are prone to carbon deposition which can decrease the ability to do combined CO_2 and steam reforming. In order to determine the relative importance of each reaction, combustion and reverse water gas shift, in the overall process a complete mechanistic study is currently being performed.

The 0.5 wt% $Pt/CeZrO_2$ catalyst was very stable in the presence of oxygen and the H_2:CO ratio produced was constant throughout the experiment at 1.25. Higher oxygen contents resulted in an increase in the product ratio and the formation of water.

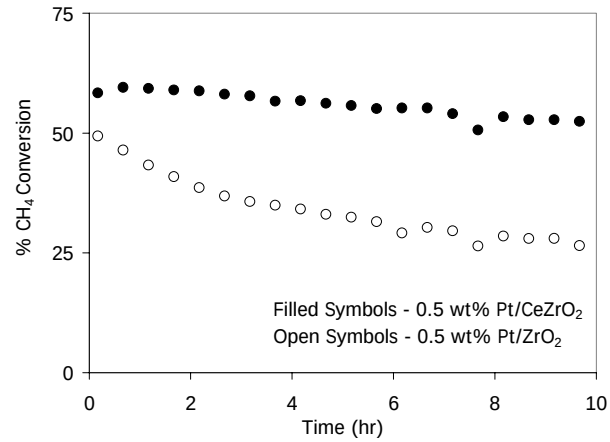

Figure 2. CH_4 conversion for the 0.5 wt% $Pt/CeZrO_2$ and the 0.5 wt% Pt/ZrO_2 during the combined dry reforming and partial oxidation reaction at 800°C and a CH_4:CO_2:O_2 feed ratio at 4:2:1.

Additional reaction studies on the 0.5 wt% and 1.5 wt% $Pt/CeZrO_2$ catalysts have shown that the catalysts are very stable in the presence of water. Switching the feed composition while the reactor was online resulted in the same conversion and product ratio as would be obtained by the individual reactions. Thus, the product ratio can be accurately predicted prior to switching the feed and a variety of syngas ratios can be generated without altering the catalyst performance.

Conclusions

The studies reported here have shown that increasing the Pt metal loading did not have any effect on the long term activity of the catalyst. The initial activity of the 1.5 wt% $Pt/CeZrO_2$ was higher than the 0.5 wt% $Pt/CeZrO_2$ catalyst. However, the deactivation on the 1.5 wt% catalyst was more pronounced resulting in the same activity after 24 hours. The similar long term activity is most likely due to the similar particle size after heating to 800°C. Significant deactivation is observed in the presence of O_2 and water on the Pt/ZrO_2 catalysts which is ascribed to the formation of carbon deposits that hinder the reforming reaction. In the presence of oxygen, the reaction mechanism is believed to proceed through combustion followed by combined dry and steam reforming as opposed to through direct partial oxidation. The Ce-promoted catalysts are very stable in the presence of oxygen and water and are promising for the ATR reaction. Detailed mechanistic studies in the presence of oxygen and water are currently underway.

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