

Short communication

Hydrogen generation from 2,2,4-trimethyl pentane reforming over molybdenum carbide at low steam-to-carbon ratios

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Abstract

Because of the need for an efficient and inexpensive reforming catalyst, the objective of this work is to determine the feasibility of employing Mo_2C catalyst for the steam reforming and oxy-steam reforming of the higher hydrocarbons typical of transportation fuels such as gasoline. It is shown that bulk Mo_2C catalysts can successfully reform 2,2,4-trimethyl pentane (isooctane) to generate H_2 , CO and CO_2 at very low steam/carbon ratios, without coke formation, eliminating the need for pre-reforming. Maximum hydrogen generation was observed at a S/C ratio of 1.3 and 1000°C during SR reactions and S/C of 0.71, O_2/C of 0.12 at 900°C during oxidative steam reforming reactions.

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1. Introduction

The reforming of higher hydrocarbons (e.g. gasoline or diesel) for fuel cell hydrogen is a challenging proposition, not only because of sulfur problems, but also because coking problems can be severe. Therefore, the successful reforming of these fuels will largely depend on the development of a catalyst, which is resistant to both sulfur and coking. Based on previous work in our laboratory [1,2], we have demonstrated that bulk carbide catalysts are coke resistant at low steam-to-carbon ratios, and are resistant to oxidation by steam and have a high resistance to sulfur in methane reforming.

While the reforming of higher hydrocarbon mixtures can be a difficult undertaking, hydrogen production from the steam reforming of methane (natural gas) is a widespread commercial reality in oil refineries and ammonia plants. Reforming in this case is carried out over a supported nickel catalyst, using excess steam to control coking ($\text{H}_2\text{O}/\text{CH}_4 \sim 3$). Noble metals can also be used, but they are

expensive and also prone to sulfur poisoning. Typically, the reforming of heavier hydrocarbon requires more extensive feedstock purification upstream of the reformer as well as steam/carbon ratios between 2 and 3, which translates to very high steam/hydrocarbon ratios [3].

Another means of dealing with the coke and sulfur problems is to use autothermal reforming. In this process, a mixture of air and steam is fed to the reformer so that the partial oxidation and reforming reactions are in thermal balance, coke deposition is minimized, and a portion of the sulfur is converted to sulfur oxides. This approach has been successfully applied to methane reforming at somewhat lower temperatures (800°C) [4] but serious coking problems were observed when applied to the autothermal reforming of propane [5]. A group at Argonne National Laboratory has been utilizing autothermal reforming for higher hydrocarbon fuels over a proprietary noble metal catalyst [6]. Springmann et al. [7] reported that steam reforming of higher hydrocarbons resulted in heavy coke formations, particularly when the steam/carbon ratio dropped below about 1.8. Palm et al. [8] also used noble metal catalysts to study the autothermal reforming of simulated diesel fuels at temperature of 545°C and reported steady conversions of 96% for 20 h on stream.

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The interest in Mo₂C catalysts for oxidative fuel reforming was prompted by a number of publications emanating from a group at Oxford, who claimed that bulk molybdenum and tungsten carbide catalysts were capable of methane reforming under stoichiometric feed conditions without coking problems, as long as the operating pressure was 8 atm [9]. Later, Sehested et al. [10] showed that these catalysts could also be stabilized, even at atmospheric pressure, by operating a reforming reactor with very high recycle ratios. Mo₂C was also studied for its performance in water-gas shift reactions [11–13].

Although considerable work was done on the performance of bulk Mo₂C catalysts for dry methane reforming (DMR), partial oxidation of methane (POM), and steam methane reforming (SMR) reactions, there have been no published studies related to the reforming of higher hydrocarbons such as gasoline. The goal of the present work is to determine the feasibility of using Mo₂C catalysts to reform gasoline type fuels, using 2,2,4-trimethyl pentane (isooctane) as a simulant. In this paper, we discuss the results of a systematic study to determine the effect of operating parameters on the product distribution and conversion efficiency of TMP in steam reforming (SR) and on oxidative steam reforming. In addition, we have also examined the conditions for Mo₂C stability (coking and oxidation resistant). The data presented in this study is a first step towards understanding the behavior of Mo₂C as a catalyst for reforming higher hydrocarbons such as gasoline in stationary fuel cell applications.

2. Experimental

2.1. Materials

The catalysts consisted of bulk molybdenum carbide (99.9%, Alfa Aesar, Lot # F29P01), which were palletized and then ground to an average particle size of 2 mm. The catalysts had a BET area of <5 m² g⁻¹ and XRD showed the presence of β -Mo₂C, although XPS detected the presence of surface oxides. This low surface area catalyst was chosen, in light of previous work [9] which demonstrated that high surface area molybdenum carbides, prepared by TPR methods [10], had no advantage in high temperature reforming and could lead to coking on excess carbon deposited during catalyst synthesis. All the experiments were performed in a 12 mm fixed-bed tubular (quartz) reactor. TMP was chosen as a surrogate for gasoline type fuels and the liquid feed consisting of water and TMP was vaporized (350 °C) and mixed along with helium and/or oxygen in a pre-heater containing a silicon carbide bed to enhance mixing. Oxygen for the oxidative steam reforming experiments was supplied by an oxygen cylinder and calibrated syringe pumps and mass flow controllers were used to control the flow rates. The reactor with the catalyst bed was operated at $T \geq 900$ °C and the hot product gas leaving the reactor was cooled (–20 °C) to sep-

arate water and unconverted liquid hydrocarbons from the product gas. The dry product gas from the condenser was analyzed using a gas chromatograph manufactured by SRI Instruments to monitor H₂, CO, CO₂, CH₄ and O₂ concentrations. Blank experiments in the absence of catalyst were also conducted in order to determine the importance of gas phase reactions.

2.2. Methods

For each experiment, 2 g of fresh Mo₂C catalyst was supported on a layer of quartz wool. For the activity tests, the catalyst was first pre-treated to remove surface oxygen by flowing a 20% H₂-in-helium gas across the reactor bed until reforming temperatures were reached. Fresh (as is, no pre-treatment) and spent catalysts were characterized by Powder X-ray diffraction (XRD) on a Philips diffractometer using Co K α radiation with an iron filter. X-ray Photoelectronic Spectroscopic (XPS) data were obtained using a Kratos Axis 165 with an Al anode as the X-ray source. These studies were performed on fresh and spent catalysts to identify the changes in surface properties after subjecting the catalysts to activity tests. The experiments reported in this document were performed under the following conditions: Steam-to-carbon (S/C) of 1–3, Oxygen-to-carbon (O₂/C) of 0.1–1, pre-heater temperature = 350 °C, space velocity (GHSV) = 1000–7000 h⁻¹. Condensate from the reactor was considered as unconverted/reformulated hydrocarbon.

The data were analyzed in terms of hydrogen yield and carbon conversion. Hydrogen yield was defined as the ratio of molar hydrogen concentration in the product to that in the reactants (TMP + water) and carbon or TMP conversion was defined as the molar ratio of carbon from C1 compounds (CO, CO₂, and CH₄) in the products to that of total carbon from TMP. H₂O conversion was calculated based on an oxygen balance between feed and products.

3. Results and discussion

Preliminary experiments were carried out to identify the optimal operating conditions for reforming TMP over bulk Mo₂C catalyst. Initial experiments were conducted at the conditions, which were suggested in the previous work done by our group, viz., at low mass velocity, high temperature, and low space velocity [1]. A series of blank experiments in presence of silicon carbide were also run at the conditions of (steam reforming) SR and (oxidative-steam reforming) OSR to determine the degree to which the TMP reacted in the gas phase. In the absence of air (SR), the hydrogen yield was approximately 4.6%, but under the OSR conditions, the yield jumped to approximately 9.2%. Because the products of the partial oxidation and reforming reactions are the same (H₂ and CO), the increase in yield indicates that partial oxidation did take place in the gas phase.

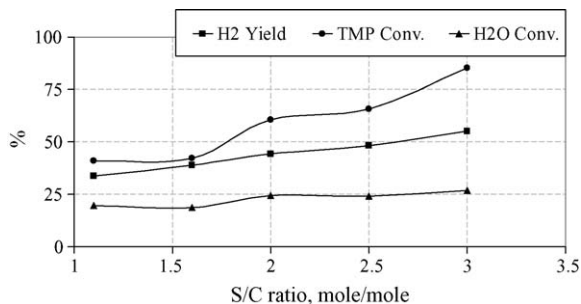


Fig. 1. Effect of S/C ratio on the catalytic activity of Mo₂C for TMP steam reforming at a temperature of 1000 °C and GHSV of 6000 h⁻¹.

3.1. TMP steam reforming

Fig. 1 shows the effect of steam-to-carbon (S/C) ratio on the initial (15 min time-on-stream) catalytic activity for steam reforming at 1000 °C and a space velocity of 6000 h⁻¹. While higher initial conversions and hydrogen yields can be obtained at higher S/C ratios, the conversions dropped significantly after 45 min of operation. This is indicative of catalyst oxidation, which was subsequently confirmed by XRD analysis of the spent catalysts (MoO₂). Similar experiments (not shown here) were also conducted by varying the reactor temperature at a fixed S/C ratio and space velocity. Consistent with our previous data with methane reforming [14], it was observed that higher operating temperatures are favorable for higher conversions, particularly above 1000 °C.

Fig. 2 shows the effect of space velocity on the steam reforming activity of the carbide catalyst at 1000 °C and a S/C = 2. The product gas composition (primary axis) reached near equilibrium concentrations (not shown here) at all the space velocities tested. However, the conversion and hydrogen yield values increased as the space velocity decreased, as expected.

The results from the above set of experiments suggest that the SR activity of Mo₂C can be improved by operating at lower space velocities, and higher temperatures. In view of the above observations, long-term experiments were carried out by varying the S/C ratio at a S.V. of 1500 h⁻¹

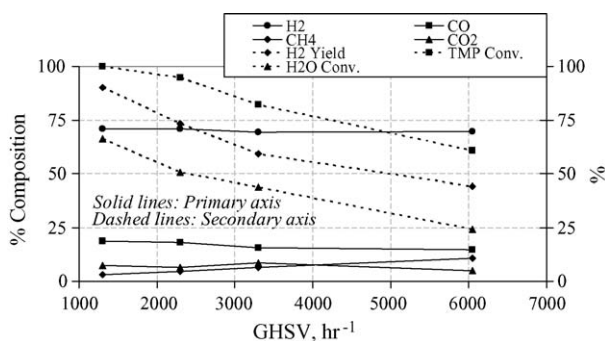


Fig. 2. Effect of gas hourly space velocity (GHSV) on the catalytic activity of Mo₂C for TMP steam reforming at a temperature of 1000 °C and S/C ratio of 2.

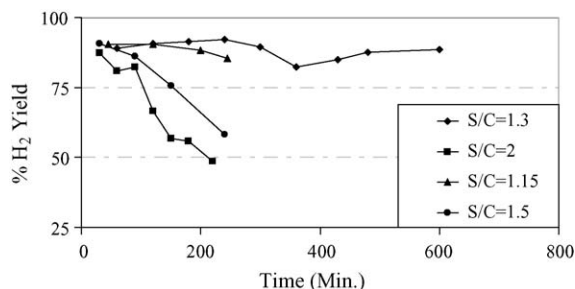


Fig. 3. Long-term catalytic activity of Mo₂C for TMP steam reforming at a temperature of 1000 °C and GHSV of 1500 h⁻¹.

and these results are shown in Fig. 3. The first experiment was conducted at a S/C value of 2 and there was a 50% drop in the hydrogen yield after 4 h of operation. The spent catalyst from this experiment was found to be partially oxidized, probably due to extra steam in the gas stream. Similar results were obtained at a S/C value of 1.5, however, the degree of oxidation decreased. The S/C value was further decreased to near stoichiometric amounts (1.15) and the results clearly show a decrease in the rate of deactivation compared to that observed at higher S/C ratios. Although the spent catalyst from this experiment showed no sign of oxidation, coke formation was observed. These results suggest that the optimal operating value for S/C lies between 1.15 and 1.5. That is, where there is a kinetic balance between the carburizing and oxidizing gases, as observed in our previous studies during dry methane reforming (DMR) reactions [1]. Our earlier studies have shown that stoichiometric feeds during DMR are kinetically net oxidizing and deactivation will eventually occur if reforming kinetics are limiting. Exposure of the catalyst to various mixtures of reforming gas compositions, following the oxidation state of Mo₂C by dynamic X-ray diffraction showed that oxidation can be prevented, even at low pressures, by insuring that a “stability ratio”, $R_S = \frac{P_{CO} + P_{H_2}}{P_{H_2O} + P_{CO_2}}$, is greater than about 0.8 [1]. Thus, TMP steam reforming was conducted at a S/C ratio of 1.3 and as can be seen in Fig. 3, stable reforming activity was observed with no signs of deactivation, even after operating for more than 5 h Bulk Mo₂C thus offers significant activity at lower steam-to-carbon ratios (1.3) compared to ratios above 2 over many noble metal catalysts suggested in the literature [3–8].

Based on the results obtained from the experiments shown in Fig. 3, the stability ratio, defined as the ratio of carburizing gases (CO, H₂) to that of oxidizing gases (H₂O, CO₂) [1] was calculated for each experiment. It was found that the catalyst oxidizes when this ratio is below a value of 6 for TMP while operating under steam reforming conditions.

3.2. Oxidative steam reforming of TMP

In an effort to decrease the operating temperature and still maintain the catalytic stability and activity, steam-oxygen reforming experiments were also conducted. Initially oxygen

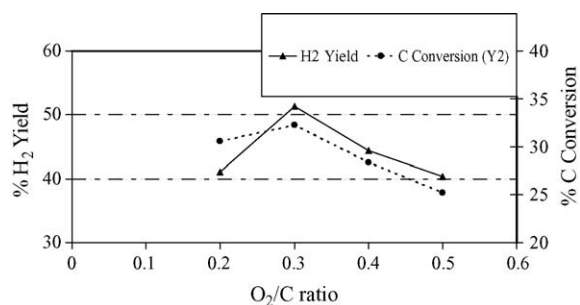


Fig. 4. Effect of O₂/C ratio on the activity of bulk Mo₂C catalyst during oxidative steam reforming at S/C value of 1 and temperature of 900 °C.

was added in different proportions to the feed to produce O₂/C ratios of 0.3 and 0.2, while the S/C ratio was held at 1.3. However, the higher overall oxygen concentrations lowered the activity, yielding lower amounts of hydrogen and resulting in reduced stability due to catalyst oxidation.

Consequently, it was decided that oxygen should be added to the feed stream while maintaining the same total concentration of atomic oxygen per gram of catalyst (TOC). This value was calculated based on the stable results from steam reforming experiments discussed above, which was set at 0.0149 mol of “O” per gram of catalyst. This was achieved by lowering the S/C ratio as the oxygen concentration was raised, and using this criterion, experiments were carried out in order to study the effect of oxygen addition (expressed as O₂/C ratio) on catalytic activity. Fig. 4 shows the results obtained from an experiment carried at S/C = 1 and 900 °C while maintaining the TOC at 0.0149. Oxygen was never observed in the effluent during any of the experiments at any of the temperatures tested. Note that the highest performance was obtained at an oxygen ratio (O₂/C) of 0.3. However, long-term experiments carried out at these conditions showed deactivation after 2 h on stream. But when the temperature was raised to 925 °C, the catalyst demonstrated stable activity for more than 5 h of operation.

In an effort to optimize the hydrogen yield and carbon conversion, the S/C, O₂/C and temperature values were systematically varied. Temperatures below 900 °C had too low an activity, but at 900 °C, the hydrogen yield and carbon conversion were in excess of 85% when S/C = 0.73 and O₂/C = 0.12. These conditions were then employed in a longer term experiment and, as can be seen in Fig. 5, stable activity was obtained for over 5 h. Analysis of the spent catalyst from this experiment showed no signs of either oxidation or coking. Under these conditions, the stability ratio was calculated to be greater than the previously determined value of 6.0.

3.3. Stability of Mo₂C

Based on the results obtained during the SR and OSR tests discussed above, stability of the bulk Mo₂C catalyst was tested under the optimal reaction conditions found in the preliminary tests and the results are shown in Fig. 6. As can

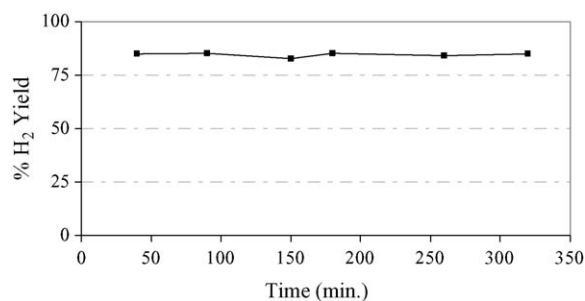


Fig. 5. Long-term activity of the bulk Mo₂C catalyst for TMP oxidative steam reforming at S/C of 0.73, O₂/C of 0.12 and temperature of 900 °C.

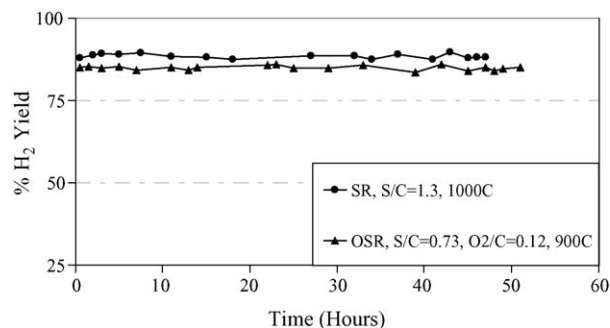


Fig. 6. Long-term activity of the bulk Mo₂C catalyst for TMP reforming (SR and OSR) at the optimal conditions in Figs. 3 and 5, respectively.

be seen, the catalyst showed stable activity even after testing for more than 50 h on stream.

4. Conclusions

Bulk molybdenum carbide seems to be a promising catalyst for reforming higher hydrocarbons for hydrogen generation in fuel cell applications, without the necessity of employing a pre-reforming step. Maximum hydrogen generation was observed at a S/C ratio of 1.3 and 1000 °C during SR reactions and S/C of 0.71, O₂/C of 0.12 at 900 °C during oxidative steam reforming reactions. In contrast with noble metal and Ni based catalysts, much lower steam/carbon ratios can be used and the catalyst appears to be stable over the time period tested.

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