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Report Title

ABSTRACT

The objective of this project is to investigate the feasibility of using molybdenum carbide catalysts for the reforming of transportation fuels (gasoline and diesel) in the presence of sulfur. Using trimethyl pentane (TMP) and hexadecane (HD) as model fuels and thiophene and benzothiophene as model sulfur compounds, all of the original objectives of the project were successfully accomplished. We have found that the steam reforming (SR) of sulfur-free TMP can be carried out over bulk Mo_2C catalysts at essentially stoichiometric feed conditions without coking, as long as the temperatures are at about 1000 C. However, the stable operating temperature can be lowered to 900 C, by adding molecular oxygen (oxidative-steam reforming (OSR)). The activity of a bulk molybdenum carbide catalyst for the steam (SR) of sulfur free hexadecane was found to be stable under very low steam:carbon ratios at temperatures as low as 885 oC under OSR conditions, and at 965 oC under SR conditions. For both TMP and HD, the degree of deactivation in the presence of sulfur was dependent on the sulfur concentration but was minimal at concentrations below 100 ppmw. While deactivation was completely reversible in the case of TMP steam reforming, spent catalysts from OSR could only be partially reactivated. However, sulfur poisoning was totally reversible for HD under both SR and OSR conditions

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List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Praveen K. Cheekatamarla and William J. Thomson, "Catalytic activity of molybdenum carbide for hydrogen generation via diesel reforming", Journal of Power Sources, In Press, Corrected Proof, in press, Available online 18 October 2005.

Cheekatamarla P. K., and W.J. Thomson, “Hydrogen Generation from 2,2,4-trimethyl pentane reforming over molybdenum carbide at low steam-to-carbon ratios”, Journal of Power Sources, in press Available online 23 June 2005
(2005)

Cheekatamarla P. K., and W.J. Thomson, “Poisoning effect of Thiophene on the Catalytic Activity of Molybdenum Carbide During Tri-methyl Pentane Reforming for Hydrogen Generation”, Applied Catalysis A, 287 (2005) 176-182

Number of Papers published in peer-reviewed journals: 3.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

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Number of Papers not Published: 0.00

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED	
Robert McCauley	0.25	No
FTE Equivalent:	**0.25**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED	
Praveen Cheekatamarla	1.00	No
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
William J. Thomson	0.20	No
FTE Equivalent:	**0.20**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Personnel receiving masters degrees

NAME	
Robert McCauley	No
Total Number:	**1**

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

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Inventions (DD882)

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REPORT DETAILS

PROBLEM STATEMENT

Based on the success of a previous project which illustrated the efficacy of bulk Mo_2C catalysts for steam and dry reforming of methane at stoichiometric feeds and in the presence of sulfur, this project was undertaken to investigate the feasibility of utilizing bulk Mo_2C catalysts for the reforming of transportation fuels; specifically, gasoline and diesel. The selected approach was to utilize model compounds; TMP for gasoline and HD for diesel, and to investigate the effect of model sulfur compounds (thiophene for gasoline and benzothiophene for diesel). In addition, preliminary experiments were also conducted into the feasibility of using supported Mo_2C for both catalytic steam reforming of TMP and as a reversible sulfur trap. Furthermore, as well as the feasibility of adding either CO or H2 into the feed was also investigated, in an attempt to lower the stable operating temperature.

SUMMARY OF IMPORTANT RESULTS

As a result of this project, it can be concluded than bulk Mo_2C catalysts can effectively reform gasoline and diesel type fuels in the presence of sulfur and at much lower steam/C ratios than are necessary for Ni or noble metal catalysts. The following lists the specific results obtained during the course of this project.

TMP Reforming is stable under the following conditions:

- Under OSR conditions with Steam/C = 0.71, O2/C = 0.12, at temperatures >900 ^{o}C, GHSV < 6000 h^{-1} and with thiophene concentrations less than 100 ppmw
- Under SR conditions with Steam/C = 1.3, at temperatures >1000 ^{o}C and with thiophene concentrations less than 100 ppmw

HD Reforming is stable under the following conditions:

- Under OSR conditions with Steam/C = 0.71, $O_2/C = 0.36$, at temperatures >885 ^{o}C, GHSV < 5500 h^{-1} and with benzothiophene concentrations less than 100 ppmw
- Under SR conditions with Steam/C = 1.3, at temperatures > 965 ^{o}C and with benzothiophene concentrations less than 100 ppmw

Sulfur Poisoning

- At sulfur concentrations less ≤ 100 ppm, there are no visible effects over a 10 hour period in either the steam or oxidative steam reforming of TMP or HD.

- At higher sulfur concentrations, the extent of deactivation was proportional to the sulfur concentration.

- Deactivation due to sulfur poisoning during SR or OSR of HD and SR of TMP could be reversed be exposing the catalyst to an inert gas at operating temperatures (~ 900 C).

- Deactivation due to sulfur poisoning during OSR of TMP could only be partially reversed and then only in hydrogen at temperatures ~ 1000 C.

Aromatics

- There was a negligible effect of aromatic coke precursors during SR or OSR of HD

Supported Catalysts

- A preliminary investigation into supported Mo2C catalysts did not show any advantage of supported catalysts versus bulk catalysts.

REPORT DETAILS

Trimethylpentane (TMP) Reforming

STEAM REFORMING (SR) In order to determine the optimum reforming operational conditions, experiments were conducted to evaluate the effects of temperature, steam-to-carbon (S/C) ratio, and gas hourly space velocity (GHSV) on the initial (15 min time-on-stream) catalytic activity. Consistent with our previous data with methane reforming [1], it was observed that higher operating temperatures are favorable for higher conversions, and necessary to avoid oxidation of the catalyst, particularly above 1000 ^{o}C. While higher initial conversions and hydrogen yields could be obtained at higher S/C ratios (1.5 – 2.0), the conversions dropped significantly after 45 min of operation. This was also attributed to catalyst oxidation, which was subsequently confirmed by XRD analysis of the spent catalysts (MoO_2). At S/C ratios close to 1.0, the catalyst did not oxidize, but deactivated due to coking. Consequently an optimum S/C ratio of 1.3 was determined and was employed in all subsequent experiments. 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 [2]. The effect of space velocity was also evaluated, at GHSV values of 1000 – 6000 h^{-1}. The product gas composition reached near equilibrium concentrations at all the space velocities tested, but 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 and these results are shown in Fig. 1. As can be seen from Fig. 1, stable reforming activity was observed with no signs of deactivation, even after operating for more than 5 h. Thus bulk Mo2C catalysts offer significant activity at lower steam-to-carbon ratios (1.3) as compared to ratios above 2 over many noble metal catalysts suggested in the literature.

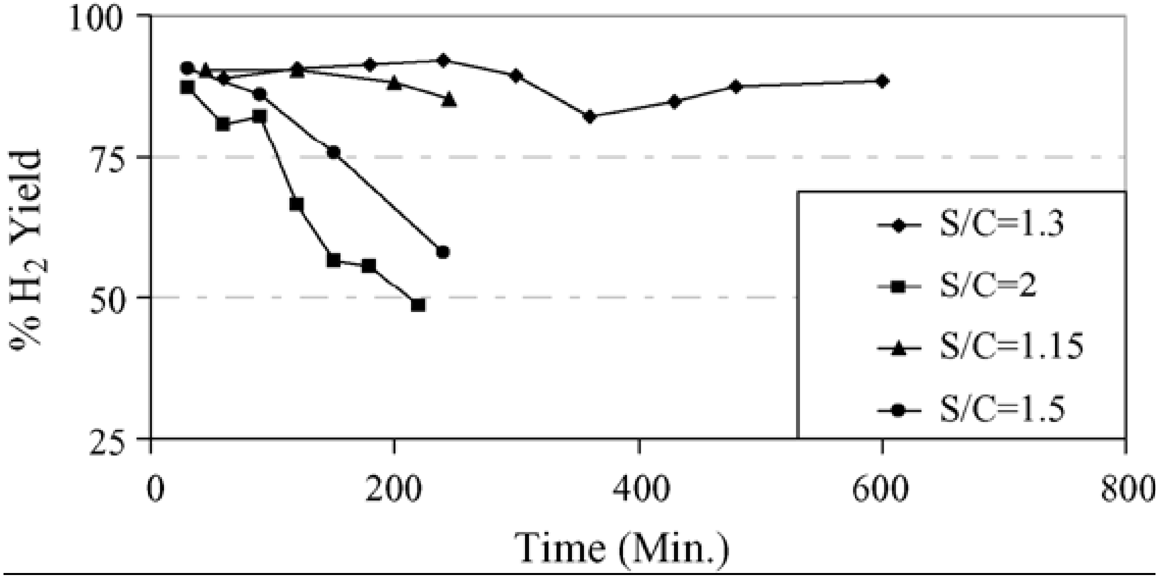

Fig. 1. Long-term catalytic activity of Mo2C for TMP steam reforming at a temperature of 1000 ◦C and GHSV of 1500 h−1.

OXIDATIVE STEAM REFORMING (OSR) In an effort to decrease the operating temperature and still maintain catalytic stability and activity, steam-oxygen reforming experiments were also conducted. Based on the optimum S/C ratio during steam reforming of TMP, molecular oxygen was initially 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 as well as the hydrogen yield and also resulted 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 oxygen (atomic) concentration per gram of catalyst (TOC) as was derived during SR; viz., 0.0149 mol of "O" per gram of catalyst. This was achieved by lowering the S/C ratio as the feed oxygen concentration was raised, and using this criterion, the S/C, O2/C and temperature values were systematically varied in an effort to optimize the hydrogen yield and carbon conversion at the lowest possible temperature. Oxygen was never observed in the effluent during any of the experiments at any of the temperatures tested and it is believed that the oxygen is consumed in the gas phase, upstream of the catalyst bed. 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 andO2/C = 0.12. The optimum conditions for both SR and OSR were then employed in a longer term experiment and, as can be seen in Fig. 2, stable activity was maintained for more than 50 hr on stream.

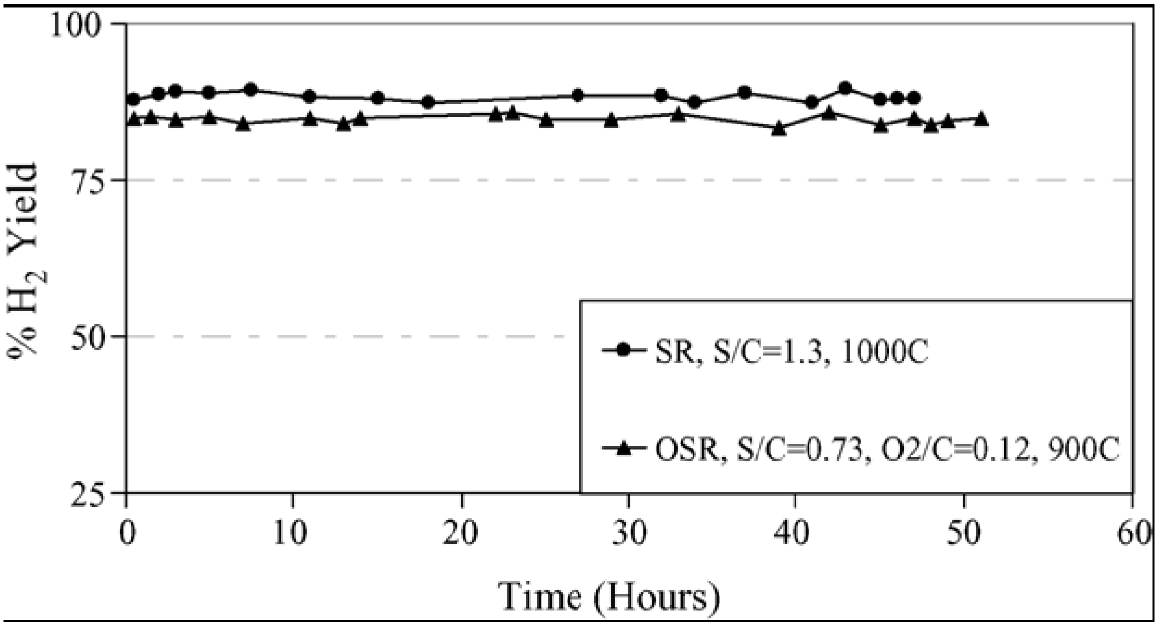

Fig 2. Long term catalytic stability for steam and oxidative steam reforming of TMP. GHSV = 1500 h^{-1}

SULFUR RESISTANCE In order to evaluate the effect of sulfur on catalyst stability during TMP reforming, thiophene was added to TMP at concentrations between 50 and 1000 ppmw and activity was monitored as a function of time during both SR and OSR. When the catalyst was exposed to 1000 ppmw of thiophene at the optimum conditions for SR (S/C = 1.3, 1000 °C), both the hydrogen yield and carbon conversion dropped sharply. It was found that the activity could not be restored by reverting back to the sulfur-free feed, and could only be partially restored when regenerated in an inert gas (helium). However, when the catalyst was exposed to 20% hydrogen at 800 °C for 1 hour, the Mo_2C catalyst regained complete activity in terms of both carbon conversion and hydrogen yield. Similar results were obtained at thiophene concentrations down to 250 ppmw. This experiment reveals that the poisoning is completely reversible in the presence of a reducing environment when poisoning occurs at thiophene concentrations greater than 250 ppmw. However, at thiophene concentrations less than or equal to 250 ppmw, the catalyst regained total activity just by changing the feed to pure TMP and the results for a thiophene concentration of 250 ppmw are shown in Fig. 3.

Similar experiments with thiophene were conducted during OSR As in the case of SR, deactivation occurred at the higher thiophene concentrations, in this case, above 50 ppmw. However, unlike SR, the catalyst could not be regenerated, even in hydrogen at thiophene concentrations above 550 ppmw. At 250 ppmw, the catalyst could only be partially regenerated in hydrogen. On the other hand, no detectable reduction in activity

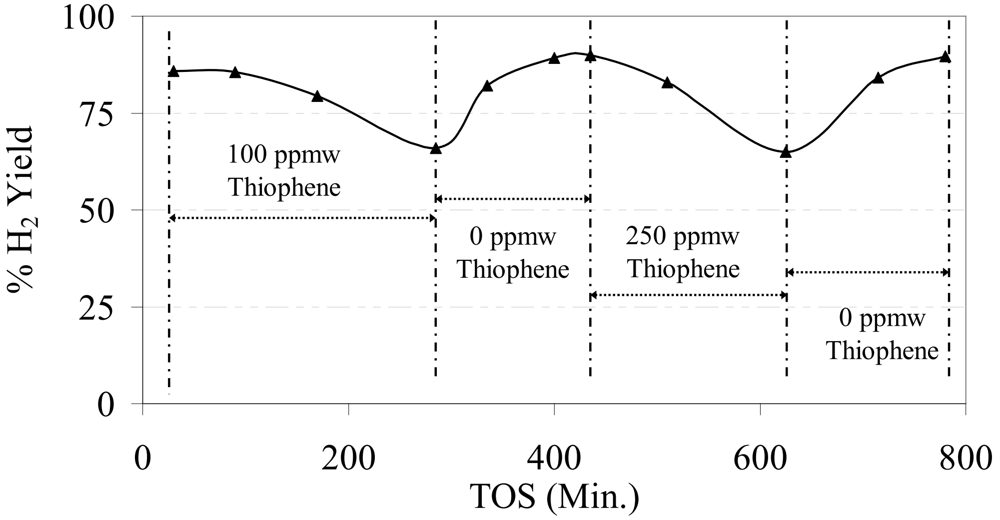

Figure 3: TMP steam reforming at the optimal conditions; switching to pure TMP after catalytic deactivation at low thiophene concentrations (up to 250 ppmw).

was observed at 50 ppmw, after 300 minutes on stream. Figure 4 shows these results at 100 and 50 ppmw thiophene concentrations. Unlike SR, deactivation due to sulfur poisoning was much slower under OSR conditions.

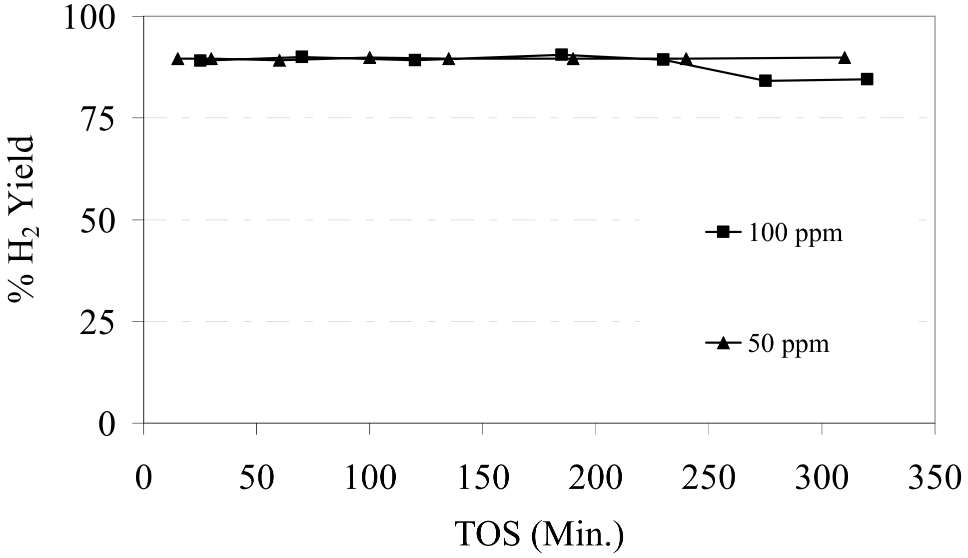

Figure 4: Hydrogen yield during OSR at low thiophene concentrations. S/C=0.73, O_2/C=0.12 & T=900 C

Hexadecane (HD) Reforming

STEAM REFORMING (SR) The starting point for HD reforming was to utilize the stable conditions found during SR of TMP. Based on this observation, HD steam reforming was carried out over the bulk Mo_2C catalyst at a S/C ratio of 1.3 and the hydrogen yield was measured as a function of time while varying the reactor temperature. These experiments demonstrated that the temperature had to be greater than 965 ^{o}C in order to have stable activity; i.e., prevent catalyst oxidation. Both the S/C ratio and the GHSV were also varied and it was found that S/C ratios greater than 1.4 resulted in catalyst oxidation and that GHSV values greater than 6000 h^{-1} also resulted in oxidation due to the effect of mass velocity as reported by LaMont and Thomson [1]. In light of the above observations, optimal hydrogen enrichment in the effluent mixture was obtained by operating at a S/C ratio of 1.3, GHSV of 5500 h^{-1} and a temperature of 965 ◦C. Stability tests at different S/C ratios conducted at this temperature and space velocity also showed no deactivation at S/C ratios between 1.18 and 1.42 (Fig. 5).

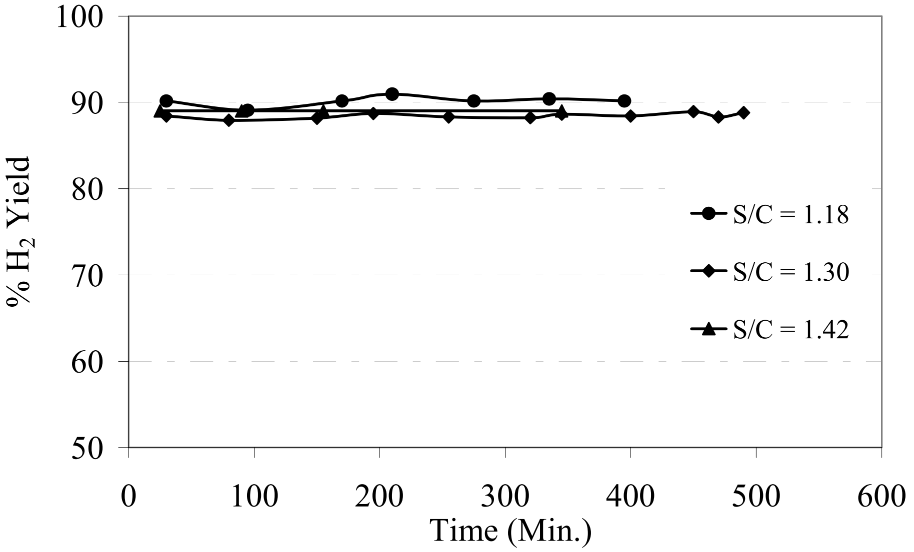

Figure 5: Long-term performance (H_2 yield) of bulk Mo_2C for SR of hexadecane at different S/C ratios at T = 965ºC, P=1bar, and GHSV = 5500 hr^{-1}.

OXIDATIVE STEAM REFORMING (OSR) The oxidative steam reforming activity of the bulk Mo_2C catalyst for hydrogen generation from HD was also tested. In the TMP reforming studies, OSR stability required that the total atomic molar concentration of oxygen per gram of catalyst had to be maintained constant. As with TMP, the optimum conditions for SR of HD were found by lowering the S/C ratio while increasing the O2/C ratio as a function of temperature. These experiments showed that the hydrogen yield can be maximized and stabilized at an O_2/C of 0.36, S/C of 0.71 and a temperature of 885 ◦C. Fig. 6 shows the effect of the O_2/C ratio and it can be seen that the hydrogen yield approaches ~ 93% at the optimal conditions. The product distribution as a function of this ratio is also shown in Figure 6.

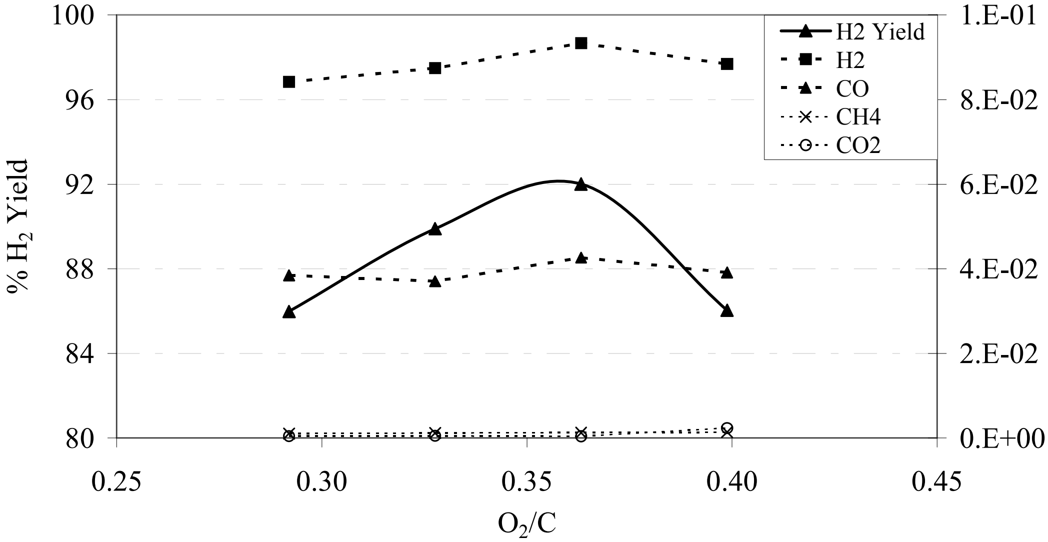

Figure 6: Hydrogen yield and molar flow rate of the products as a function of O_2/C ratio during OSR of hexadecane over a bulk Mo_2C catalyst at a temperature of 885ºC, S/C of 0.71, P=1bar, and GHSV of 3500 hr^{-1}.

The effect of GHSV on catalytic activity during OSR of HD was also tested and it was found that the catalyst became unstable at values >5000 h−1, and a value of 4500 h^{-1} was chosen to evaluate longer term performance. At the optimal conditions suggested above, the activity was stable for more than 6 hrs, as can be seen in Fig 7.

It is well known that essentially all diesel fuels consist of both mono and di-aromatic compounds, at various concentrations, and they are known coke pre-cursors. Experiments were hence carried out to check the effect of these compounds during SR and OSR of HD at the optimal conditions described in the above sections. Di-ethyl benzene and methyl naphthalene at a concentration of approximately 2 wt.% (wt.% analysis, Exxon) were chosen as model compounds to evaluate the effect of mono and di-aromatics, respectively. Under the predetermined optimal SR conditions, there was no effect of these coke precursors on catalyst stability. Although, at the optimal conditions for OSR (885 ^{o}C) there was evidence of slight but continuous deactivation due to coking, when the temperature was raised slightly to 900 ^{o}C, the catalyst remained stable for over 7 hours.

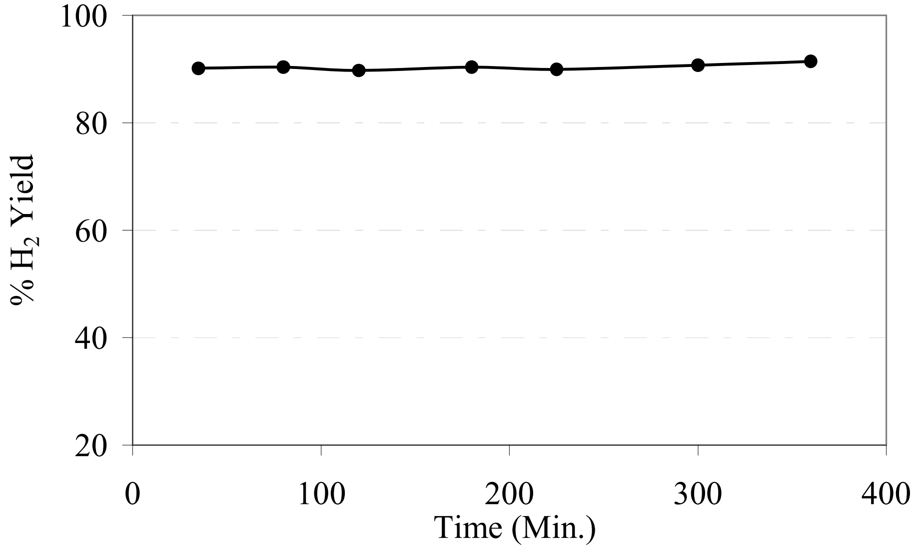

Figure 7: Long-term performance (H_2 yield) of bulk Mo_2C for OSR of hexadecane at the optimal conditions of S/C=0.71, O_2/C=0.36, GHSV=4500hr^{-1} and T=885°C, P=1bar.

<u>*SULFUR RESISTANCE*</u> The dependencies of product distribution and hydrogen yield on the concentration of sulfur poison was investigated during SR and OSR of HD over the bulk Mo_2C catalyst. Typically the reactions were started with sulfur bearing feeds (125 – 500 ppmw benzothiophene mixed with HD) and after a significant drop in the activity, the feed was switched back to the original sulfur-free mixture to determine whether activity could be restored. If not, then attempts to regenerate the catalysts were made by exposing the catalysts to either helium or hydrogen at reforming temperatures. It was found that during SR, the catalyst activity decreased at a rate proportional to the benzothiophene concentration at concentration levels of 125 ppmw or higher. Whereas the catalyst activity could not be recovered by merely switching to a sulfur-free feed, it could be completely regenerated by exposing it to helium for 1 hr at 900 oC.

The sulfur resistance of the catalyst was somewhat different under OSR conditions. As can be seen in Fig 8, after poisoning in 500 ppmw benzothiophene, the catalyst could only be partially regenerated by exposure to helium. However, when it was then regenerated in 20 % H2, complete regeneration was obtained. This indicates that some degree of the poisoning occurs via a surface reaction as opposed to a strictly adsorption phenomenon. The severity of sulfur poisoning during OSR was also less than during SR. Whereas deactivation was observed at 125 ppmw benzothiophene during SR, the catalyst was stable at this sulfur level during OSR (Fig 9).

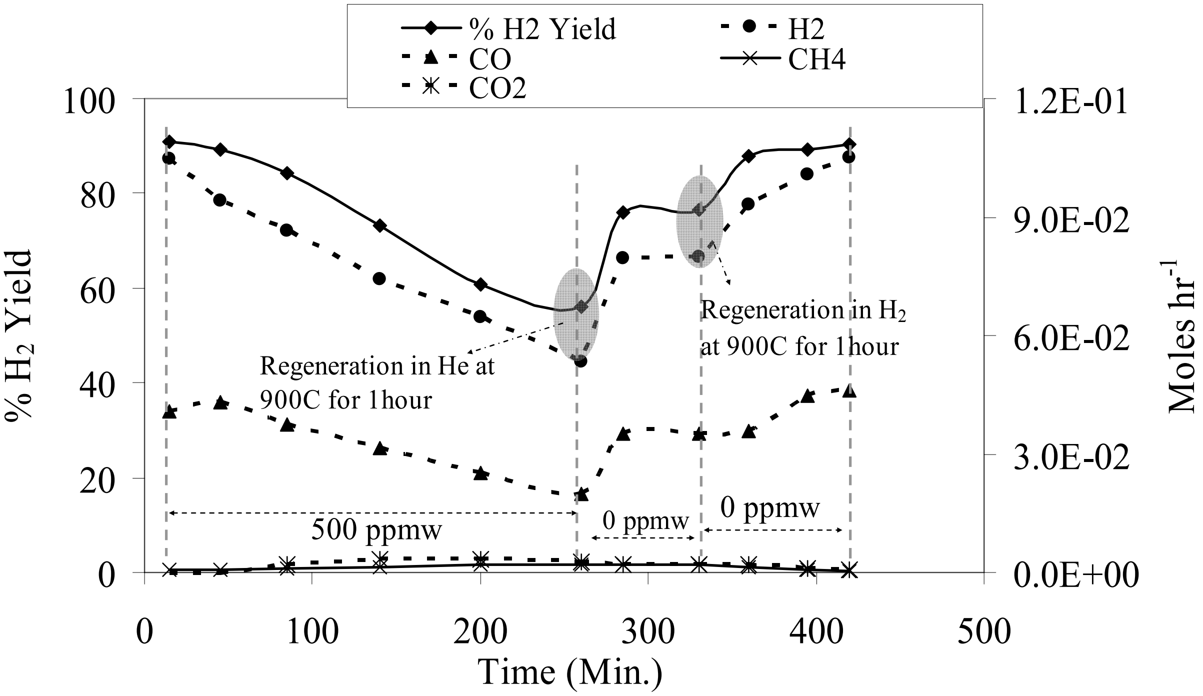

Figure 8: Hydrogen yield and products composition as a function of time during hexadecane oxidative-steam reforming experiments in presence of 500 ppmw of benzothiophene at the optimal conditions of S/C = 0.71, O_2/C = 0.36, GHSV = 4500hr^{-1}, T = 885ºC, and P = 1bar.

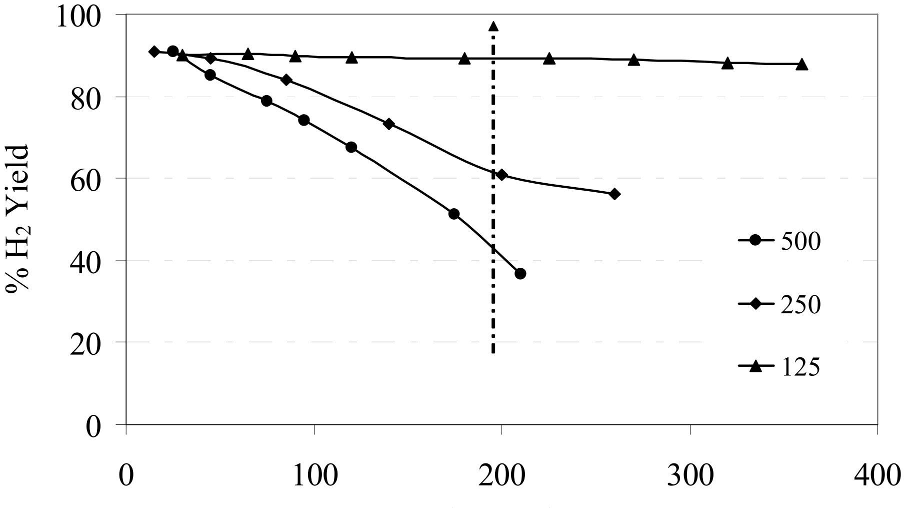

Figure 9: Hydrogen yield vs. time at different benzothiophene concentrations (125 – 500 ppmw) at the optimal conditions of S/C = 0.71, O_2/C = 0.36, GHSV = 4500hr^{-1}, T = 885ºC, and P = 1bar

Effectiveness of Supported Catalysts

Preliminary experiments were also conducted to determine whether Mo_2C catalysts supported on various supports would give higher activities, hopefully at lower temperatures. The steam reforming of TMP was chosen for this effort and experiments were conducted with MgO, ZrO_2 and Al_2O3 supports. Only the Al_2O_3 support had good activity and so a catalyst consisting of 30% Mo_2C /Al_2O_3 was evaluated and compared to the results previously obtained with bulk Mo_2C catalysts. As can be seen from Figure 10, there was no apparent advantage for the supported catalyst, resulting in almost identical results for the bulk catalyst.

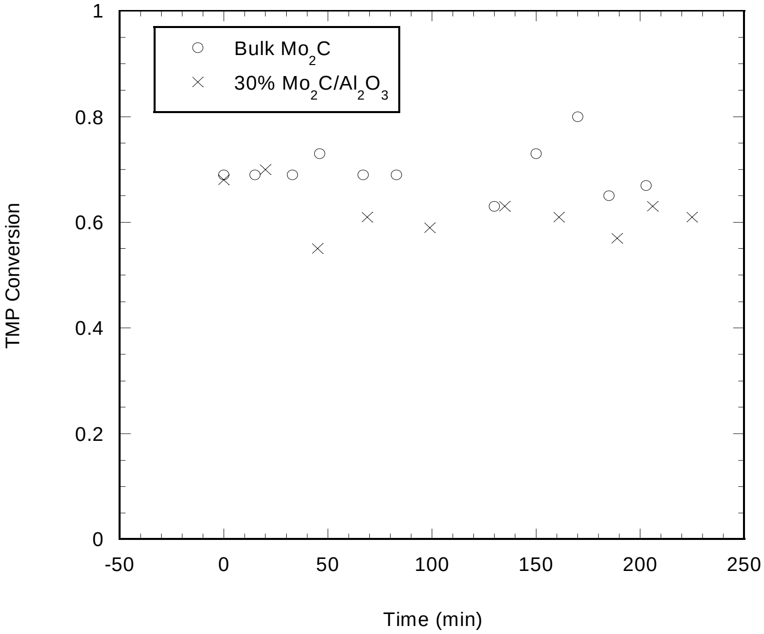

Fig 10: Comparison of bulk and supported catalysts for TMP steam reforming. S/C = 1.3, WHSV = 1.6 h^{-1}, 1000 ^oC

Mo_2C as a Reversible Sulfur Trap

After observing that sulfur tended to adsorb reversibly during catalytic reforming of methane, TMP and HD, we conducted experiments to measure the sulfur adsorption capacity of Mo_2C materials. We found that bulk Mo_2C materials had adsorption capacities of 0.002 mmol/g but that when Mo_2C was supported on Al2O3, the capacity increased by a factor of four, to 0.008 mmol/g. In fact, stable operation during the SR of TMP reforming was maintained for 90 min ???? in the presence of 500 ppmw thiophene, before deactivation began to occur. It remains to be seen as to whether this would be a viable sulfur adsorbent.

Stability Improvement with Co-fed CO and

Based on our earlier work, we know that Mo_2C catalysts are prone to oxidation at lower temperatures and that the presence of carburizing gases (CO and H2) as well as low mass velocities serve to lower the temperatures at which stable operation will occur. Thus, as part of this study, we investigated the effect of co-feeding CO and H2, choosing the steam reforming of methane as the more difficult reforming process. In the absence of co-fed CO or H2, temperatures greater than 950 ^{o}C were required to obtain stable operation. Low concentrations of CO and H2 in the feed did not lower the stability temperature significantly and it took concentrations of47% CO (or H2) before a significant effect was observed. At these feed concentrations the lowest stable operating temperature was found to be 950 ^{o}C, but there was a negative effect on activity, where the methane conversion dropped from 90% to 57%.

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[2] D.C. LaMont, A.J. Gilligan, A.R.S. Darujati, A.S. Chellappa, W.J. Thomson, Appl. Catal. A: Gen. 255 (2003) 239.