

# Catalytic activity of molybdenum carbide for hydrogen generation via diesel reforming

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## Abstract

The activity of a bulk molybdenum carbide catalyst for the steam (SR) and oxidative-steam reforming (OSR) of hexadecane has been studied with and without the presence of aromatic coke precursors and sulfur compounds. It is shown that this catalyst can be stable under very low steam:carbon ratios at temperatures as low as 885 °C under OSR conditions, and 965 °C under SR conditions. Using benzo-thiophene as a model sulfur compound at concentrations as high as 500 ppmw, the degree of deactivation was found to be dependent on the sulfur concentration but was minimal at concentrations below 100 ppmw. Experiments confirmed that the sulfur poisoning is reversible and characterization studies suggested the formation of sulfur entities, which lead to carbide oxidation and subsequent coking. There was minimal effect of the aromatic species on the catalyst stability.

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## 1. Introduction

Electric power generation using fuel cells has huge potential since they provide efficiency as well as superior environmental and operational benefits over conventional technologies [1]. Gasoline, diesel and jet fuels are prospective candidates for fuel cell hydrogen, because they have an existing infrastructure for manufacturing and distribution, and provide high energy density compared to other fuels [2]. Although these fuels are rich in hydrogen, they also contain sulfur compounds as well as coke precursors. Unfortunately, the typical metal reforming catalysts are prone to deactivation by coking, as well as sulfur poisoning [3–5]. Whereas coking can be controlled with excess steam (and/or oxygen injection), the high sulfur levels in these fuels will require sulfur removal upstream of the reformer [6], if conventional reforming catalysts are employed. Therefore, the successful reforming of these fuels will largely depend on the development of a catalyst, which is resistant to both sulfur and coking.

The interest in Mo<sub>2</sub>C 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 [7]. Later, Sehested et al. [8] showed that these catalysts could also be stabilized, even at atmospheric pressure, by operating a reforming reactor with very high recycle ratios. Mo<sub>2</sub>C was also studied for its performance in water–gas shift reactions [9–11].

In previous work in our laboratory we have demonstrated that bulk molybdenum carbide (Mo<sub>2</sub>C) catalysts are essentially coke resistant at low steam/carbon (S/C) ratios and, in a net carburizing environment, are resistant to oxidation by steam and oxygen during 2,2,4-trimethyl-pentane (TMP) reforming [12]. Our earlier studies have also shown that the bulk carbide has a high resistance to sulfur in methane and TMP reforming [12,13]. Based on these promising results we have extended our investigation of bulk molybdenum carbide catalysts to study the effect of sulfur contamination on the reforming of diesel fuel. The goal of the present work was to determine the feasibility of using Mo<sub>2</sub>C catalysts to reform diesel type fuels, specifically, using benzothiophene and aromatic-doped hexadecane as a model for retail diesel fuel. In this paper, we discuss the results of a sys-

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tematic study to determine the effect of operating parameters on the product distribution and conversion efficiency of hydrocarbon mixtures in both steam reforming (SR) and oxy-steam reforming (OSR). In addition, we have also examined the conditions under which the  $\text{Mo}_2\text{C}$  catalysts remain stable to coking and oxidation. The results of this study are presented here in terms of the effect of fuel additives on catalytic activity, correlating these observations with characterization of post-reacted catalysts.

## 2. Experimental

### 2.1. Materials

The catalysts consisted of bulk molybdenum carbide (Alfa Aesar, Lot # F29P01), which were pelletized and then ground to an average particle size of 2 mm. The catalysts had a BET area of  $<5 \text{ m}^2 \text{ g}^{-1}$  and XRD showed the presence of  $\beta\text{-Mo}_2\text{C}$ , although XPS detected the presence of surface oxides. This catalyst was chosen since our previous work [14] proved that the high surface area  $\text{Mo}_2\text{C}$  prepared by TPR method [15] offer no advantage in high temperature reforming. All the experiments were performed in a 12 mm fixed-bed tubular (quartz) reactor. Hexadecane (HD) was chosen as a surrogate for diesel type fuels and the liquid feed consisting of water and HD was vaporized ( $450^\circ\text{C}$ ) 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 temperatures above  $850^\circ\text{C}$  and the hot product gas leaving the reactor was cooled ( $-20^\circ\text{C}$ ) to separate water and unconverted liquid hydrocarbons from the product gas. The dry overhead product gas from the condenser was analyzed using an gas chromatograph (SRI 8610C) to monitor  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  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  $\text{Mo}_2\text{C}$  catalyst was supported on a layer of quartz wool, and then pre-treated to remove surface oxygen by flowing a 20%  $\text{H}_2$ -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  $\text{Co K}\alpha$  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 with time. Oxygen was never observed in the effluent during any of the experiments at any of the temperatures tested. Condensate from the reactor was considered as unconverted/reformulated hydrocarbon. The data were analyzed in terms of hydrogen yield and carbon conversion, where hydrogen yield was defined as the

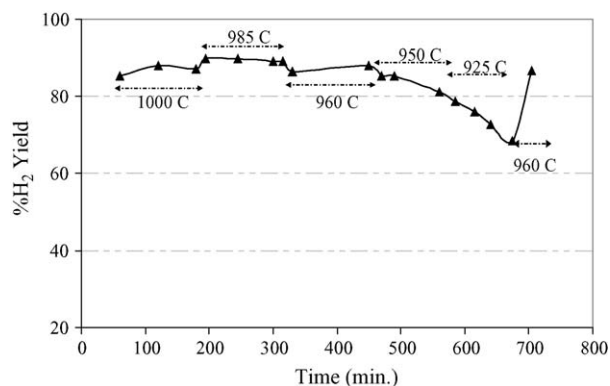


Fig. 1. Hydrogen yield as a function of time at different temperatures during hexadecane SR over bulk  $\text{Mo}_2\text{C}$  at a S/C value of 1.3,  $P=1$  bar and a GHSV of  $4000 \text{ h}^{-1}$ .

ratio of molar hydrogen concentration in the product to that in the reactants (HD + water) and carbon or HD conversion is the molar ratio of carbon from C1 compounds ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ) in the products to that of the total carbon fed in HD.

## 3. Results and discussion

### 3.1. HD steam reforming

Earlier studies on TMP reforming have shown that  $\text{Mo}_2\text{C}$  tends to oxidize at higher steam-to-carbon (S/C) ratios ( $>1.3$ ) [12]. Based on this observation, HD steam reforming was carried out over the bulk  $\text{Mo}_2\text{C}$  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. Fig. 1 shows the results from this experiment and it can be seen that the catalyst exhibits stable SR activity at temperatures  $>960^\circ\text{C}$ , yielding approximately 90%  $\text{H}_2$ . Lower temperatures produce lower hydrogen yields and adversely affect the stability as can be seen in the figure.

Fig. 2 shows the effect of S/C ratio on the hydrogen yield for HD steam reforming, at a fixed reactor temperature of  $965^\circ\text{C}$  and a space velocity of  $4000 \text{ h}^{-1}$ . While higher hydrogen yields can be obtained at higher S/C ratios, at  $\text{S/C} > 1.4$ , the measured stability ratio (defined as the ratio of carburizing gases ( $\text{CO}$ ,  $\text{H}_2$ ) to that of oxidizing gases ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ) [1,12]) values were  $<6$ , which according to our previous studies on TMP leads to  $\text{Mo}_2\text{C}$  oxidation [12]. Based on these observations, stability tests

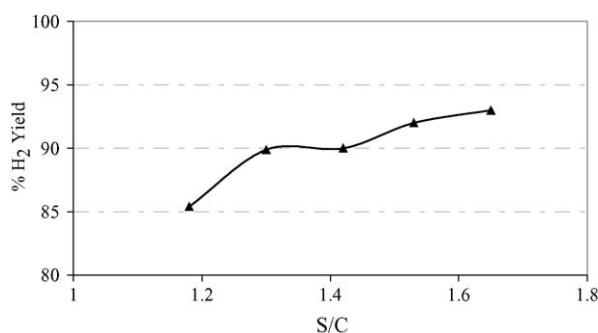


Fig. 2. Effect of S/C ratio on hydrogen yield during the hexadecane SR over bulk  $\text{Mo}_2\text{C}$  at  $T=965^\circ\text{C}$ ,  $P=1$  bar, and  $\text{GHSV}=4000 \text{ h}^{-1}$ .

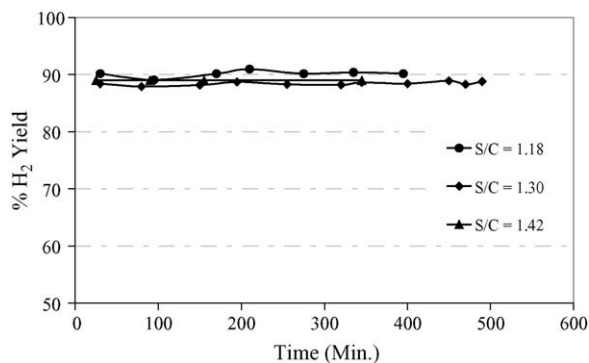


Fig. 3. Long-term performance ( $H_2$  yield) of bulk  $Mo_2C$  for SR of hexadecane at different S/C ratios at  $T = 965\text{ }^\circ\text{C}$ ,  $P = 1\text{ bar}$ , and  $GHSV = 5500\text{ h}^{-1}$ .

carried out at  $S/C > 1.4$  resulted in a slow degradation due to oxidation (XRD). The effect of space velocity was also studied and it was noticed that  $GHSV > 6000\text{ h}^{-1}$  leads to deactivation due to the adverse effect of higher mass velocity (which is a measure of the mass transfer coefficient and is defined as the rate of molar feed per unit surface area of the catalyst bed) on catalyst stability, as reported by LaMont and Thomson [16]. In light of the above observations, optimal hydrogen enrichment in the effluent mixture seems possible by operating at a S/C ratio of 1.3, GHSV of  $5500\text{ h}^{-1}$  and  $965\text{ }^\circ\text{C}$ . Stability tests at different S/C ratios conducted at this temperature and space velocity showed no deactivation (Fig. 3).

### 3.2. HD oxidative steam reforming

The oxidative steam reforming activity of the bulk  $Mo_2C$  catalyst for hydrogen generation from HD was also tested. In our earlier studies, OSR of TMP showed that the total atomic molar concentration of oxygen per gram of catalyst has to be maintained constant for stable activity [12]. Preliminary experiments were hence conducted to identify these conditions for HD reforming by lowering the S/C ratio while increasing the  $O_2/C$  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  $885\text{ }^\circ\text{C}$ . Fig. 4 shows the effect of the  $O_2/C$  ratio and it can be seen that hydrogen yield approaches  $\sim 93\%$  at the optimal conditions. Product distribution as a function of this ratio is also presented in the

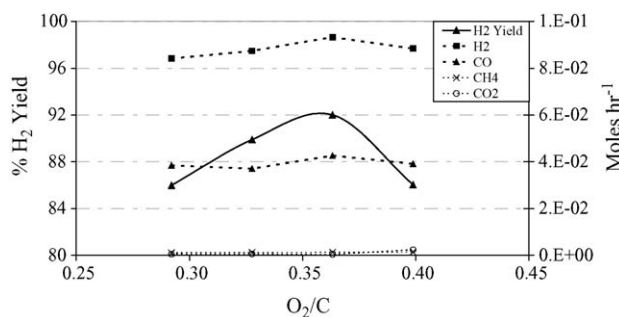


Fig. 4. Hydrogen yield and molar flow rate of the products as a function of  $O_2/C$  ratio during OSR of hexadecane over a bulk  $Mo_2C$  catalyst at a temperature of  $885\text{ }^\circ\text{C}$ , S/C of 0.71,  $P = 1\text{ bar}$ , and  $GHSV$  of  $3500\text{ h}^{-1}$ .

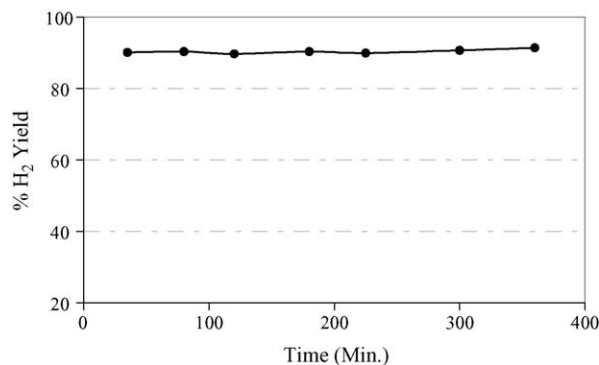


Fig. 5. Long-term performance ( $H_2$  yield) of bulk  $Mo_2C$  for OSR of hexadecane at the optimal conditions of  $S/C = 0.71$ ,  $O_2/C = 0.36$ ,  $GHSV = 4500\text{ h}^{-1}$  and  $T = 885\text{ }^\circ\text{C}$ ,  $P = 1\text{ bar}$ .

same figure. Any deviation from these values resulted in the activity drop. The effect of GHSV on catalytic activity during OSR of HD was also tested and it was found that the activity drops at values  $> 5000\text{ h}^{-1}$ , and the catalyst becomes unstable. Again, this is due to mass velocity effects. At the optimal conditions suggested above, the activity was stable for more than 6 h (Fig. 5) and analysis of the spent catalyst showed no oxidation or coking. Under these conditions, the stability ratio was calculated to be greater than 6.0.

### 3.3. Effect of aromatic compounds

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. Figs. 6 and 7 show the hydrogen yield as a function of time under both SR and OSR conditions for 2% di-ethyl benzene and methyl naphthalene, respectively. For both aromatics, the catalyst was stable under SR optimal conditions, with no signs of either coking or oxidation. However, a 25% drop in the hydrogen yield was noticed for both aromat-

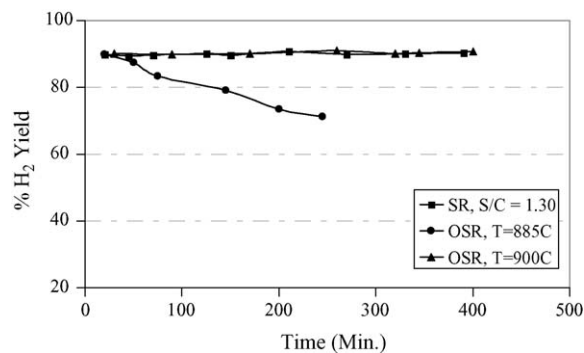


Fig. 6. Hydrogen yield vs. time at different temperatures during OSR and SR of hexadecane containing 2 wt.% of Diethyl-benzene (mono-aromatic compound) at the optimal conditions.

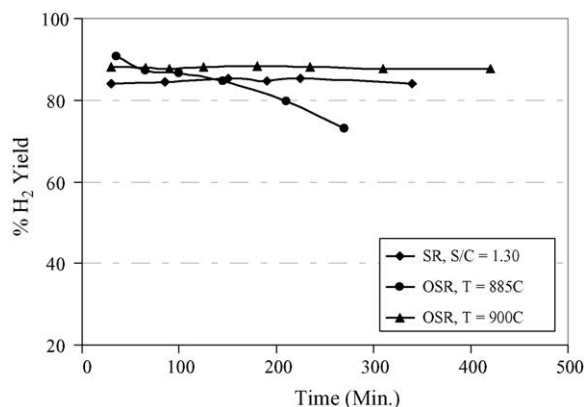


Fig. 7. Hydrogen yield vs. time at different temperatures during OSR and SR of hexadecane containing 2 wt.% of methyl-naphthalene (di-aromatic compound) at the optimal conditions.

ics, after just 250 min on stream when operated at the optimal OSR conditions (885 °C, S/C 0.71, O<sub>2</sub>/C 0.36), although stable activity was observed when the temperature was increased to 900 °C. XRD analysis showed both oxidation and coking on the spent catalyst from the experiment performed at 885 °C, but neither was observed for the experiment at 900 °C. These results indicate that once coking takes place, the catalytic active sites become blocked, leading to a depletion of carburizing gases at the surface and subsequent oxidation. This type of phenomena was also observed by LaMont and Thomson [16] in an earlier study of the effect of mass velocity during dry methane reforming.

### 3.4. Effect of sulfur compounds

The dependencies of product distribution and hydrogen yield on the concentration of sulfur poison were investigated during SR and OSR of HD over the bulk Mo<sub>2</sub>C catalyst. Typically the reactions were started with sulfur bearing feeds (benzothiophene mixed with HD) and after a significant drop in the activity, the feed was switched back to the original sulfur-free mixture. This process was repeated for different benzothiophene concentrations, ranging from 125 to 500 ppm by weight and the results from these experiments are discussed below. A series of blank experiments were also run at SR and OSR conditions to determine the degree to which the HD and benzothiophene reacted in the gas phase. In the absence of air (SR), the hydrogen yield was approximately 3.5%, but under the OSR conditions, the yield jumped to approximately 8.8%. The high yield under OSR conditions and the fact that all of the oxygen was consumed, indicates that partial oxidation takes place in the gas phase and is likely completed upstream of the catalyst bed.

Fig. 8 shows the hydrogen yield as a function of time during the steam reforming of HD over the bulk Mo<sub>2</sub>C catalyst at the optimal conditions. It can be observed that, when the feed containing 500 ppmw of benzo-thiophene was supplied to the reactor, the hydrogen yield dropped sharply. Obviously the presence of sulfur in the feed resulted in a serious loss of reforming activity, which could not be restored (not shown) by reverting

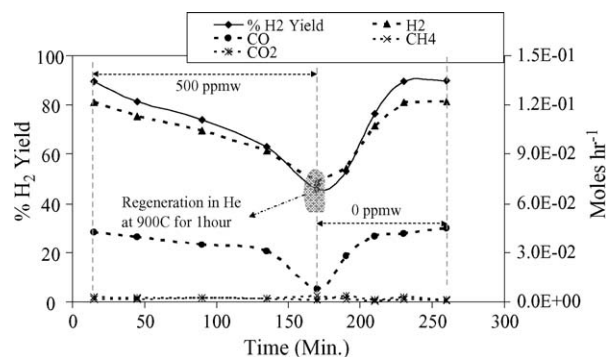


Fig. 8. Hydrogen yield and products composition as a function of time during hexadecane steam reforming experiments in presence of 500 ppmw of benzo-thiophene at  $T = 965$  °C,  $S/C = 1.3$ ,  $P = 1$  bar and  $GHSV = 5500$  h<sup>-1</sup>.

back to the sulfur-free feed. At this juncture, the catalyst was subjected to a regeneration treatment in presence of helium at 900 °C for 1 h. As can be seen, the Mo<sub>2</sub>C catalyst regained complete activity in terms of hydrogen yield. This experiment reveals that the poisoning is completely reversible when subjected to a thermal treatment. The product composition as a function of time from the above experiment is also shown in Fig. 8. Although it is not readily obvious from Fig. 8, during deactivation, there was a 15% increase in the methane production; an indication that increased cracking of HD occurs over the deactivated catalysts.

Experiments were also conducted in the presence of lower concentrations of benzo-thiophene and results similar to that observed from the above experiment were obtained and parallel trends were observed in hydrogen yield and catalytic regeneration. An interesting result to note from the above set of experiments is that in all cases, while hydrogen yield drops with time, the rate of loss depends on and is directly proportional to the concentration of benzo-thiophene in the feed gas (Fig. 9). These results may be an indication that the active reaction zone shifts down the catalytic bed after the surface becomes completely deactivated, similar to the observations made during our earlier TMP studies [12].

Fig. 10 shows the hydrogen yield and product distribution as a function of time during the oxidative steam reforming of HD over the bulk Mo<sub>2</sub>C catalyst at the optimal conditions. Similar to the SR experimental results, in the presence of sulfur,

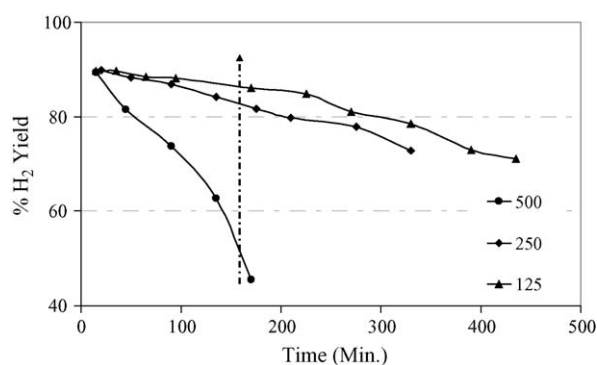


Fig. 9. Hydrogen yield vs. time at different benzo-thiophene concentrations (125–500 ppmw) at  $T = 965$  °C,  $S/C = 1.3$ ,  $P = 1$  bar and  $GHSV = 5500$  h<sup>-1</sup>.

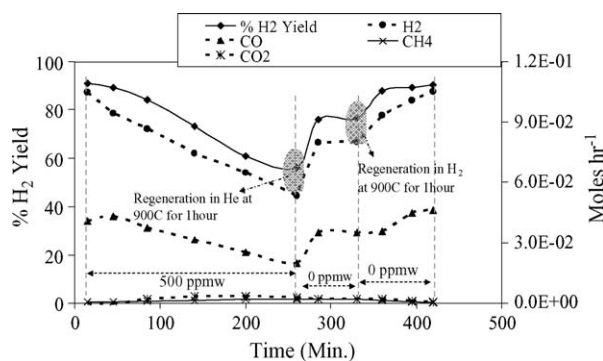


Fig. 10. Hydrogen yield and products composition as a function of time during hexadecane oxidative-steam reforming experiments in presence of 500 ppmw of benzo-thiophene at the optimal conditions of  $S/C=0.71$ ,  $O_2/C=0.36$ ,  $GHSV=4500\text{ h}^{-1}$ ,  $T=885\text{ }^\circ\text{C}$ , and  $P=1\text{ bar}$ .

the catalyst deactivated with time and the rapidity and degree of deactivation was also similar. However, unlike the SR experiments, complete improvement in the activity was not observed when the catalyst was subjected to regeneration treatment at  $900\text{ }^\circ\text{C}$  in helium. This experiment reveals that the poisoning is partially reversible even after the thermal treatment. However, regeneration in 20%  $H_2$ -in-helium at  $900\text{ }^\circ\text{C}$  was able to restore the original activity completely, suggesting that this fraction of the sulfur removal occurs via a chemical reaction. Similar results were also observed when the benzo-thiophene concentration was lowered to 250 ppmw. These results differ from those observed during the OSR experiments performed over sulfur laden TMP [12]. In that case, it was not possible to regain complete activity even after regeneration in hydrogen at  $1000\text{ }^\circ\text{C}$ .

However, as can be seen in Fig. 11, at concentrations of 125 ppmw there was no detectable drop in  $H_2$  yield even after 300 min on stream. Interestingly, the deactivation at this lower concentration (125 ppmw) is zero compared to that of SR, probably due to a slower inhibition of the carburization kinetics resulting in a slower shift of the active reaction zone down the catalytic bed. In other words, the deactivation as a function of sulfur concentration is not linear as would be expected from a moving deactivation zone. Rather, it appears to be a combination of both sulfur saturation and changes in the kinetic pathways on the catalytic surface.

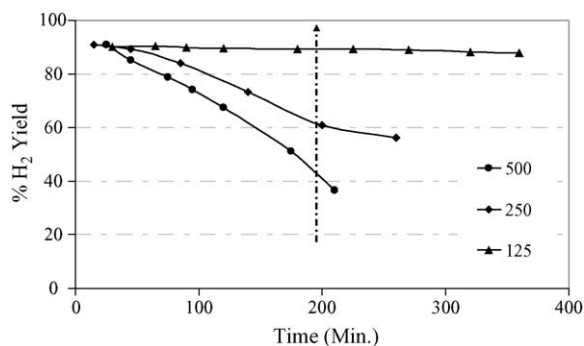


Fig. 11. Hydrogen yield vs. time at different benzo-thiophene concentrations (125–500 ppmw) at the optimal conditions of  $S/C=0.71$ ,  $O_2/C=0.36$ ,  $GHSV=4500\text{ h}^{-1}$ ,  $T=885\text{ }^\circ\text{C}$ , and  $P=1\text{ bar}$ .

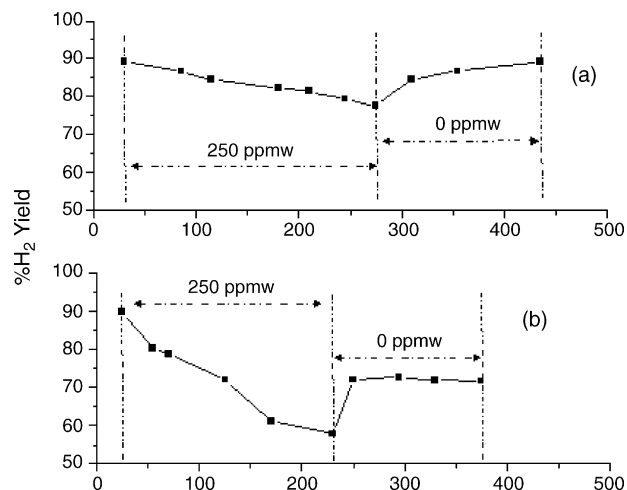


Fig. 12. SR (a) and OSR (b) of hexadecane at the optimal conditions; switching to pure hexadecane after catalytic deactivation at low benzo-thiophene concentration (250 ppmw).

As described earlier, switching to pure HD after significant deactivation due to 500 ppmw of benzo-thiophene in the feed showed no improvement in the reforming activity during both SR and OSR. However, this was not true for all sulfur concentrations. At 250 ppmw during SR, the catalyst regained total activity just by changing the feed to pure HD without any regeneration treatment and these results are shown in Fig. 12. However, only partial revival in the activity was possible in OSR experiment performed at the same concentration, indicating that the severity of catalyst surface changes is dependent on the concentration and/or the type of sulfur species in the gas.

### 3.5. Characterization

From the results of SR and OSR experiments, it is clear that in presence of sulfur-laden fuels (benzo-thiophene), adsorption of sulfur species occur on the catalytic surface, resulting in a loss of activity. It also appears that the presence of molecular oxygen in the feed gases results in surface interactions that are different than those which occur in the absence of molecular oxygen. In an effort to clarify these issues, a series of blank experiments were also conducted to determine the nature of the sulfur species that are produced in the gas phase, with and without molecular oxygen. From these experiments, it was determined that, in the absence of oxygen, benzo-thiophene reacts above the catalytic bed to form light hydrocarbons and  $CS_2$ , similar to what was previously observed for thiophene in TMP reforming and dimethyl-sulfide in dry methane reforming studies [12,13]. When molecular oxygen was added to the feed, all of the oxygen was consumed prior to the feed reaching the catalyst bed and the primary sulfur species were  $SO_2$  and  $CS_2$ , in contrast to what was observed in a similar experiment using thiophene as a model sulfur compound during isooctane reforming studies [12]. The interaction of these sulfur species was investigated using XRD and XPS analysis techniques and the results are discussed below.

Fig. 13 shows the XRD patterns obtained from the spent deactivated catalysts used in the SR and OSR studies along

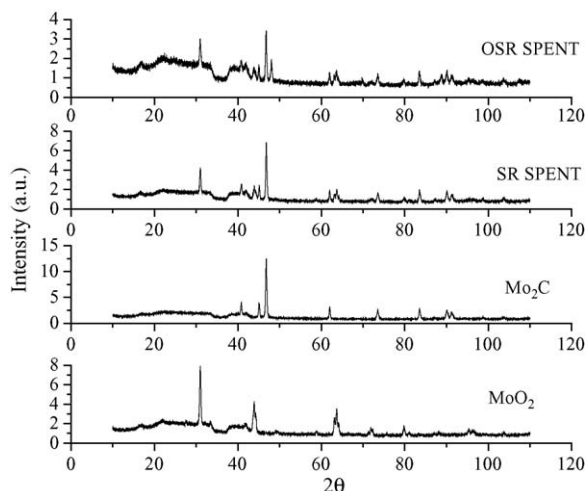


Fig. 13. XRD analysis of spent catalysts from SR and OSR experiments. Diffraction patterns of  $\text{Mo}_2\text{C}$  and  $\text{MoO}_2$  are shown for comparison.

with the XRD patterns of fresh  $\text{Mo}_2\text{C}$ , and  $\text{MoO}_2$ . As can be seen, the crystal structure of the spent catalyst from both SR and OSR experiments in the presence of 500 ppmw benzo-thiophene reveals the presence of  $\text{MoO}_2$  in the bulk phase, but no peaks representing that of  $\text{MoS}_2$  are present. The presence of other forms of oxide (e.g.,  $\text{Mo}_2\text{O}_5$ ,  $\text{MoO}$ ,  $\text{Mo}_4\text{O}_{11}$ , etc.) cannot be ruled out by XRD analysis since they may exist as small particles or amorphous solids. The most remarkable thing to notice in these samples is the absence of sulfide in the bulk phase (no sign of sulfur species in XRD analysis, Fig. 13) despite the fact that these catalysts were subjected to very harsh conditions (high levels of sulfur, 500 ppmw). The absence of sulfur derivatives in the bulk phase is probably due to the fact that most of the experiments were run for relatively short time periods (<10 h), which may not be enough for these compounds to appear in the bulk phase. On the basis of these results it appears that the deactivation in the case of SR and OSR catalysts is due to the oxidation of the active carbide phase (bulk) into the inactive oxide phase. As pointed out by D'arujati et al. [17], the avoidance of carbide oxidation requires the presence of carburizing gases. Thus it is possible that the interaction of sulfur entities with the catalytic surface somehow interferes with the protective action of these gases, leading to oxidation and subsequent catalyst deactivation.

Catalyst deactivation due to surface modification was investigated by XPS analysis. Fig. 14 presents the S 2p spectrum of the spent catalysts (500 ppmw benzo-thiophene, no regeneration) from the SR and OSR experiments. The S 2p spectrum of the spent SR and OSR samples show two peaks having apparent maxima at 161.9 and 162.6 eV. The peaks indicate one S  $2p_{3/2}$  component at binding energy (BE) of 161.9 ( $\pm 0.2$ ) and a second at 162.6 ( $\pm 0.2$ ). Spevack and McIntyre [18,19] and Niemantsverdriet et al. [20–22] extensively studied the reactivity of Mo oxide ( $\text{MoO}_3$ ) films and their sulfidation. Characterization of  $\text{MoS}_3$  and Mo–S clusters by XPS was also studied [20,23]. It appears from these studies that different sulfur species in a BE range between 161.6 and 163.1 eV can be detected with assignments ranging from basal  $\text{S}^{2-}$  in  $\text{MoS}_2$  to  $\text{S}_2^{2-}$  species in different environments (162.6 eV for  $\text{S}_2^{2-}$  in  $\text{MoS}_3$ ). Therefore,

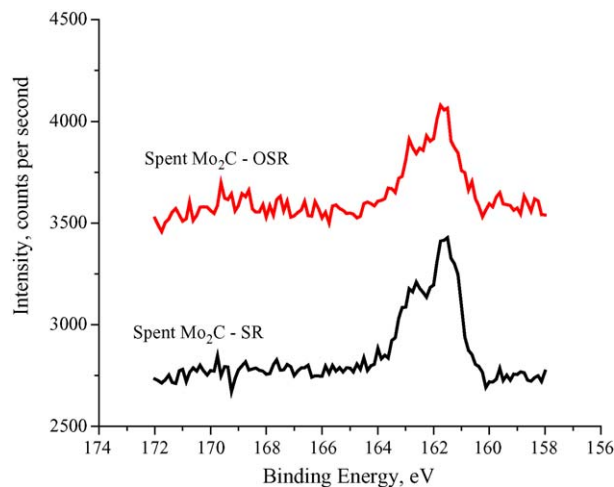


Fig. 14. S 2p XPS spectrum of spent SR and OSR catalysts after exposure to 500 ppmw of benzo-thiophene.

the second species detected on the sample is probably  $\text{S}_2^{2-}$ . Considering the second species, the presence of SH groups that point at a similar BE cannot be ruled out. Also, Mo 3d signal with Mo  $3d_{5/2}$  BE 228.1 ( $\pm 0.1$ ) eV and the first S 2p signal with S  $2p_{3/2}$  BE 161.9 are characteristic of the presence of  $\text{MoS}_2$ . Indeed, in the literature,  $\text{MoS}_2$  has been characterized by the Mo  $3d_{5/2}$  BE at 229.0 ( $\pm 0.6$ ) eV and a S  $2p_{1/2,3/2}$  BE (apparent maximum) of 161.3–162.2 eV [18–20]. Adsorbed sulfur strongly bound to the Mo (1 1 0) plane is also located at 161.6 eV [24], whereas elemental sulfur has a higher BE ( $\sim 164$  eV [20,21,23]).

Fig. 15 shows the Mo 3d spectrum of the two spent reforming catalysts discussed above along with that of a fresh  $\text{Mo}_2\text{C}$  catalyst. The Mo 3d spectra are complex and show various components. The first one is the low BE component whose Mo  $3d_{5/2}$  peak appears at 228.1 ( $\pm 0.1$ ) conveying the presence of molybdenum carbide/metal in accordance with the carbidic carbon at 284.0 ( $\pm 0.3$ ) [20]. Mo 3d spectrum of the fresh  $\text{Mo}_2\text{C}$  indicates the presence of  $\text{MoO}_3$  on the surface corresponding to the BE values of 232.5 eV and 235.6 eV, although  $\text{Mo}_2\text{C}$  is anticipated.

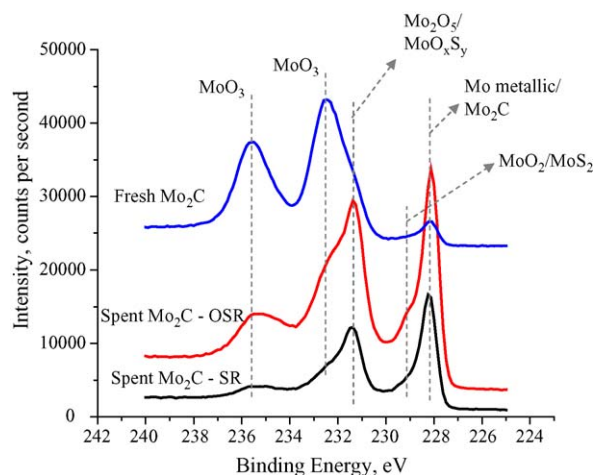


Fig. 15. Mo 3d XPS spectrum of fresh ( $\text{Mo}_2\text{C}$ ) and spent OSR and SR catalysts after exposure to 500 ppmw of benzo-thiophene.

Table 1  
XPS results on the catalysts

Summary of XPS analysis (in at.%) of fresh and spent catalysts				
Catalyst	Mo	C	O	S
Mo <sub>2</sub> C-fresh	17.57	18.78	62.53	–
Mo <sub>2</sub> C-SR-500	18.76	51.62	28.45	1.17
Mo <sub>2</sub> C-OSR-500	18.44	35.87	45.01	0.68

This is normal since the fresh sample used for the XPS analysis was not treated and the catalyst supplied from the manufacturer was passivated in 1% O<sub>2</sub> as this procedure is known to protect the bulk sample from oxidizing in the presence of atmospheric oxygen. It can be noticed that the same fresh sample used for XPS analysis does not show any peaks characteristic of MoO<sub>2</sub> or MoO<sub>3</sub> as can be seen in the XRD pattern of fresh sample in Fig. 13. Similarly, the presence of MoO<sub>3</sub> can also be seen on the surface of the spent catalysts, in addition to MoO<sub>2</sub> at a BE value of 229.2 eV, in agreement with the results from the XRD analysis, which showed strong oxidation in the bulk phase. The most interesting results, however can be seen at the BE value of 231.4(±0.2) eV, which corresponds to either MoO<sub>x</sub>S<sub>y</sub> or Mo<sub>2</sub>O<sub>5</sub> [21,25,26]. Since sulfur was observed in the S 2p spectrum of both the spent catalysts, this peak definitely corresponds to that of MoO<sub>x</sub>S<sub>y</sub> or a combination of MoO<sub>x</sub>S<sub>y</sub> and Mo<sub>2</sub>O<sub>5</sub>, (Fig. 14). Indeed, in a study of the sulfidation of MoO<sub>3</sub>, Weber et al. [21] found a Mo 3d<sub>5/2</sub> BE at 231.3 eV and attributed it to an oxysulfide intermediate phase.

A summary of the quantitative results from the XPS analysis of these samples is shown in Table 1. Of particular significance is the presence of increased quantities of carbon on both the spent catalysts. It appears that under both the reforming conditions, sulfur interactions with the catalyst surface acts as a precursor to oxidation as well as excessive coking. One mechanism may be the formation of sulfates on the catalyst surface, which could induce surface acidity and subsequent coking. What is also likely is that once the carbide suffers oxidation, coking of the resulting oxide becomes more prevalent.

#### 4. Conclusions

Bulk molybdenum carbide seems to be a promising catalyst for reforming higher hydrocarbons typical of diesel fuel, without the necessity of employing a pre-reforming step. It has been shown that bulk Mo<sub>2</sub>C catalysts can successfully steam reform hexadecane at very low steam-to-carbon ratios, without coke formation and the catalyst appears to be stable over the time period tested. Furthermore, the presence of aromatic compounds as high as 2 wt.% had little or no effect on activity or stability. The same conclusions can also be drawn for OSR of hexadecane except that temperatures are lower (885 °C versus 965 °C) and required slightly higher temperatures to be resistant to coking from aromatic coke precursors. Based on the experimental results it can also be concluded that the presence of sulfur during hexadecane reforming results in minimal to complete deactivation, depending on the sulfur concentration and the reforming conditions (SR or OSR). In all cases benzo-thiophene

was shown to decompose in the gas phase, above the catalyst bed, with the primary sulfur species being CS<sub>2</sub> and/or SO<sub>2</sub>. Characterization of the spent catalysts by XRD and XPS showed that deactivation during reforming was due to a combination of carbide oxidation, coking and the formation of sulfur compounds. XPS examinations of the surface of deactivated OSR and SR catalysts showed the presence of sulfur compounds (as an oxysulfide and/or MoS<sub>2</sub>/MoS<sub>3</sub>), in addition to a high concentration of carbon, indicating coking of the active sites. It is possible that coking was due to either increased surface acidity induced by the presence of oxysulfides and/or to the blocking of active sites by sulfur species which results in carbide oxidation and subsequently higher coking rates over the resulting oxides. Regeneration of deactivated SR and OSR catalysts in inert and/or H<sub>2</sub> gases was found to completely restore catalytic activity. Since it is well known that most sulfide species are easily removed by chemical/thermal treatment [27], it is possible that reversibly adsorbed species were removed by this treatment. Based on the observations made during this study, we conclude that although Mo<sub>2</sub>C shows promising results for diesel reforming, it still suffers from stability due to sulfur poisoning and hence further studies involving the addition of dopants to make it sulfur tolerant are recommended.

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