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Partial oxidation of methane and the effect of sulfur on catalytic activity and selectivity

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ABSTRACT

Partial oxidation of methane into syngas was conducted over fresh and sulfided catalysts at a temperature range of 450–750 °C. The temperature dependence of conversion, H_2/CO ratio, and the CO_2 concentration were measured for both fresh and sulfided catalysts. Regardless of metal type, metal loading, support type, and the methods of preparation it appears that all the fresh catalysts were very active and conversions of higher than 70% with H_2/CO ratio of about 2 were observed at 750 °C. Pulse sulfidation appears to be reversible for some of the catalysts but not for all. Under pulse sulfidation conditions, the Rh(0.5%)/Al_2O_3 and $NiMg_2O_x$-1100 °C (solid solution) catalysts were fully regenerated after reduction with hydrogen. Rh catalyst showed the best overall activity, less carbon deposition, both fresh and when it was exposed to pulses of H_2S. Sulfidation under steady-state conditions, flowing H_2S/Ar mixture over the catalysts, significantly reduce catalyst activity. The catalysts were characterized before and after reaction with H_2S using temperature-programmed oxidation (TPO) and reduction (TPR), X-ray diffraction, and XPS.

1. Introduction

Catalytic partial oxidation is an alternative process to steam reforming, the industrial process for production of synthesis gas from natural gas. Partial oxidation (POX) is a more energy efficient and less expensive process than steam reforming. The POX process is capable of producing syngas with a H_2/CO ratio of about 2, which makes it favorable for methanol and hydrocarbon synthesis [1–4]. Unfortunately, most catalysts used for the POX process are poisoned, and therefore deactivated, in the presence of sulfur compounds [5].

It is well reported that noble metal catalysts (Ir, Ru, Rh, Pt, Pd, etc.) exhibit high activity, along with long-term stability, while minimizing the levels of coking [1,3]. Furthermore, the cost of these metals, in addition to the limited supply, has caused the researchers to concentrate their efforts on more readily available catalysts, particularly, Ni-based supported catalysts. However, Ni supported catalysts can be deactivated rapidly via carbon formation and sulfur poisoning. It has been reported earlier on the formation of carbon from methane over Ni–MgO in the presence of CO_2 and CO, demonstrating that carbon formed from both methane and CO_2 possibly via CO disproportionation [6].

In this paper, we are reporting on the catalytic activity and the effects of sulfur poisoning on the performance of reforming catalysts used for partial oxidation of methane into syngas.

Deactivation of reforming catalysts by sulfur has been widely studied and it is well understood that the sulfur significantly alters catalyst performance [7,8]. Sulfur poisoning and regeneration of poisoned supported noble metal catalysts have been studied for many applications including methane reforming and combustions. Deng and Nevell studied the sulfur poisoning and recovery of supported Pd, Rh, and Ir catalysts for methane oxidation. They reported that all of these catalysts were significantly affected by sulfur poisoning [9]. They reported the formation of sulfate (S^{6+}), using XPS, which its concentrations decreased with increasing temperature. Nasri et al. reported that noble metal catalysts demonstrated different activity for methane combustion when they were exposed to H_2S [10]. They studied alumina-supported Pt, Pd, and Rh catalysts and found that the order of reactivity for the fresh and reduced catalysts is Pd > Rh > Pt but for the regenerated catalysts is Rh > Pt > Pd. Miller and Koningsberger reported that Pt catalysts supported on acidic and alkaline supports lose most of their activity due to loss of exposed Pt sites when they are exposed to hydrogen sulfide, forming adsorbed sulfur species (Pt–S) which physically block the active sites [11].

It is reported that the catalytic activity of Rh catalyst is significantly affected by the type of support, metal sintering, carbon deposition, and the presence of sulfur impurities either in feed or in

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the support and the small amount of sulfur can deactivate Rh via coordination to active metal centers [12]. It was shown that sulfate impurity in Al_2O_3 support had a negative effect on the performance of Rh/γ-Al_2O_3 during dry reforming of methane. However, the catalytic activity was significantly improved by removing SO_4^{2-} from the support. Furthermore, studying the effects of sulfur on catalytic activity, the Rh–Ce coated foam monoliths showed that the CH_4 conversion and selectivity to H_2 decreased due to sulfur poisoning of the active sites [13]. They also reported that the effect was reversible and the catalyst regained its activity when the sulfur was removed from the feed.

Two types of Pt–S bond distances of 2.34 and 2.53 Å have been reported when the catalysts were exposed to severe operating conditions (19 atm and 2000 ppm sulfur) [14]. This study showed that only one type (2.31 Å) appears to be similar to the bulk Pt–S, concluding that the loss of catalytic activity in the presence of sulfur (H_2S) is due to sulfur-poisoning-induced agglomeration of platinum and formation of platinum sulfide (PtS) [14].

Effects of sulfur poisoning on alumina-supported Pd catalysts during methane oxidation was studied by Yu and Shaw [15]. They reported the formation of surface sulfite, sulfate, and aluminum sulfate at lower temperatures, which were removed at higher temperature (600 °C) under reducing conditions with hydrogen, producing Al_2O_3, SO_2, and H_2O. Meeyoo et al. reported that the presence of trace amount of H_2S and SO_2 deactivated Pd and Rh whereas slightly enhanced the activity of platinum catalyst during oxidation of methane [16]. This was explained by the formation of aluminum sulfate, which increased catalyst acidity, and contributed to the higher activity of the catalyst for methane oxidation [17].

Catalyst poisoning via sulfur has been contributed to several factors, including strong bonding to the active sites, forming metal sulfides on the surface, which are stable and prevent the reactants to be adsorbed on the catalytic sites [18]. Sulfating of the catalyst supports is another factor that can change the crystalline structure and the nature of the support [19]. Reaction of H_2S with metal oxide surfaces appears to influence catalytic properties, H_2S coordination on TiO_2 generates strong acid sites while H_2S adsorption on alumina does not significantly change its acidity, replacing O^{2-} by S^{2-} in MgO, ZrO_2, and CeO_2 influence their redox properties [17]. Similar claim has been made when molybdenum carbide was exposed to dimethyl sulfide during dry reforming of methane, resulting in a slow surface oxidation [18]. During the sulfidation of oxides, CeO_2 contains the highest amount of sulfur and that attributed to the labile character of oxygen ion in CeO_2 [20]. Oxidative adsorption of SO_2 on ceria produced two types of sulfates, surface and bulk, which the later is more difficult to remove by reduction with hydrogen.

Even though noble metal catalysts are affected by sulfur to a lesser degree than Ni-based catalysts sulfur compounds nonetheless deactivate the noble metal catalysts and the extent of deactivation is very much dependent on metal type [16]. One particular study showed that H_2 regeneration of supported Pt catalyst was unable to fully recover the catalyst activity after it has been poisoned by sulfur, which resulted in agglomeration of Pt particles [14].

The reaction mechanisms for partial oxidation of methane to syngas have been debated widely in the literature [21–23]. The direct route for syngas production involves initial formation of CO and H_2 [24,25] where as in indirect route part of methane is converted into water and carbon dioxide [26–28], which followed by steam reforming and water–gas-shift reactions [27,28]. At the catalyst entrance where the concentration of oxygen is relatively high, it may contribute to higher concentration of adsorbed oxygen. Therefore, in the presence of higher adsorbed oxygen, the main products are H_2O and CO_2 [23]. This mechanism is also supported by the recent report that in front of the catalyst bed Rh/Al_2O_3 catalyst is mainly in oxidized state where as at the end of the bed it is in reduced or metallic state [29,30]. Furthermore, at lower concentration of adsorbed oxygen the adsorption of CH_4 is fast and the main products are CO and H_2 [23]. Similar arguments on the reaction mechanisms, concerning thermodynamic and kinetic analysis of POX reaction of methane, are reported in the literature as well [31].

In this paper, we are reporting partial oxidation of methane over fresh and sulfided catalysts, comparing the results with commercially available catalyst at a temperature range of 450–750 °C; including catalyst characterization before and after reaction with H_2S using temperature-programmed oxidation and reduction, X-ray diffraction, and XPS.

2. Experimental

2.1. Catalysts preparation

Catalysts $NiMg_2O_x$-1100 °C, NiMgO/GDC2-900 °C, and FeCrAl#11 ($NiMg_2O_x$-1100 °C supported on metal foam) were prepared in our lab and tested with three commercially available catalysts. The catalysts Rh(0.5 wt.%) on Al_2O_3, Pd/Ru(0.12% each) on Al_2O_3, and GDC–NiO (50:50) were purchased and tested for partial oxidation of methane, investigating the effects of sulfur poisoning on the catalyst activity and selectivity. The $NiMg_2O_x$-1100 °C (solid solution) and FeCrAl#11 catalysts were prepared as we reported earlier [32]. The catalysts NiMgO/GDC2-900 °C is a mixture (50:50) of gadolinium-doped cerium oxide (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$) with $NiMg_2O_x$-1100 °C (solid solution) and calcined at 900 °C. The sulfided catalysts were first reduced by flowing hydrogen and then sulfided either by pulsing or flowing H_2S over the reduced catalysts at 850 °C. The details of experimental conditions are shown in Table 1.

2.2. Partial oxidation reaction

Samples of 100 mg fresh catalyst (20–28 mesh) was loaded in the center of a fixed-bed quartz reactor tube (6.35 mm o.d.,

Table 1
Experimental conditions used for testing the catalysts; fresh (F) and sulfided (S)

Catalyst	Mass (g)		Space velocity ($cm^3\,g^{-1}\,h^{-1}$)		Reduction temperature (°C)		Total POX time (min)	
	F	S	F	S	F	S	F	S
$NiMg_2O_x$-1100 °C	0.10189	0.10369	17,666	17,359	775	748	156	143
Rh(0.5%)/Al_2O_3	0.09131	0.09131	19,713	19,713	772	745	152	154
FeCrAl#11	0.29912	0.29912	6018	6,018	791	743	137	140
Pd(0.12%) Ru(0.12%)/Al_2O_3	0.10458	0.1006	17,212	17,893	694	716	133	114
NiO (50%)/GDC	0.10019	0.10755	17,966	16,736	734	692	120	117
NiMgO/GDC2-900 °C	0.10481	0.10256	17,174	17,551	751	746	134	122

4 mm i.d., and 279.4 mm long) and held in place with quartz wool, below which quartz chips were placed to reduce the void space. Above the catalyst bed, a quartz thermocouple well with a thermocouple used to measure the catalyst temperature. The catalyst was reduced, heated in flowing hydrogen (20 cm^3/min) from room temperature to 775 °C at 10 °C/min and held in hydrogen flow for 2 h. The hydrogen flow was replaced with argon and the catalyst was heated to reaction temperature (e.g., 750 °C) in about 30 min. The reactants, a mixture of methane and oxygen, are then introduced at the specified flow rate (Table 1) and in a molar ratio of $CH_4/O_2 = 2/1$ at 1 atm.

The experiment consisted of varying the temperature at which the partial oxidation was occurring to determine the effect of reaction temperature on the activity of the catalyst before exposure to H_2S. Methane conversion and the ratio of H_2 to CO were determined for each sample between 2 and 4 h on stream.

The reaction products including un-reacted methane and oxygen (oxygen was detected at lower temperatures) were analyzed by an on-line gas chromatograph (GC) with a thermal conductivity detector (TCD). The products were separated using a 3.66 m × 3.2 mm o.d. stainless steel HayeSep C (80/100 mesh) column (Argon carrier gas) and a 1 m × 3.2 mm o.d. stainless steel molecular sieve 5A column (helium carrier gas) at isothermal oven temperatures of 50 and 120 °C, respectively. Certified calibration gas mixtures were used to determine the response factors, which are needed for determining the gas compositions of reaction products.

2.3. Catalyst sulfidation

Before partial oxidation reaction, a sample of 500 mg catalyst was sulfided in a flow of approximately 30 cm^3/min H_2S/Ar mixture (20 vol.% H_2S) for 2 h at 850 °C, this process is referred to as steady-state sulfidation. Pulse sulfidation was done by pulsing 100 μL of H_2S/Ar mixture over 100 mg of catalyst at 850 °C (helium used as carrier gas at 40 cm^3/min) and the effluent gases were monitored by a mass spectrometer. Total of 6000 μL of H_2S passed over each catalyst during pulse sulfidation. When no more H_2S adsorbed, the flow of H_2S/Ar gas mixture stopped and the catalysts reduced with hydrogen again before conducting partial oxidation reaction of methane.

2.4. Temperature-programmed reduction (TPR)

The temperature was raised from 30 to 750 °C in 1 h while passing H_2 over the catalyst at 45 cm^3/min. The temperature held constant for an additional hour, after which the catalyst was cooled to the initial reaction temperature under 10 cm^3/min of argon. The gases were monitored either with a quadrupole mass spectrometer or with a thermal conductivity detector, depending on the sensitivity desired. The same method was used to remove the sulfur from sulfided catalysts, producing H_2S.

2.5. Temperature-programmed oxidation (TPO)

TPO used to determine the amount of carbon deposited on the catalyst during POX reaction. Flow of 40 cm^3/min O_2/He mixture (2 vol.% O_2) passed over each catalyst while raising the temperature from 30 to 950 °C at 20 °C/min. The same method used to remove sulfur from sulfided catalysts, producing SO_2. Furthermore, higher (>10 mg) amounts of carbon were completely oxidized with pure oxygen at high temperature (>900 °C) and the CO_2 was measured using a CO_2 Coulometer.

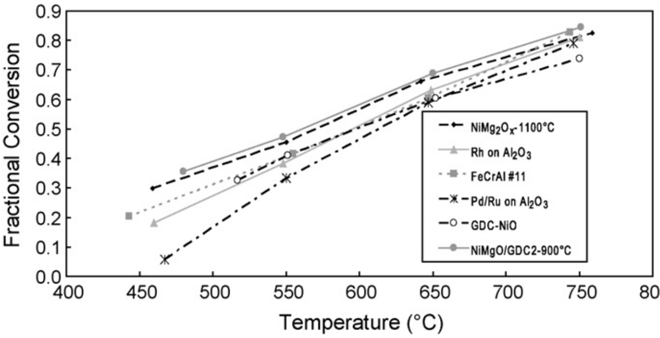

Fig. 1. Methane conversion during POX reaction over fresh reforming catalysts, $CH_4/O_2 = 2/1$, at 1 atm.

3. Results and discussion

The temperature dependence of methane conversion, H_2/CO ratio, and the CO_2 concentration is depicted in Figs. 1–3. Regardless of metal type, metal loading, support type, and the methods of preparation all fresh catalysts were very active and conversions of higher than 70% were observed at temperature of 750 °C. However, there were some differences at lower temperatures. The lowest activity was observed for Pd/Ru/Al_2O_3, possibly due to low metal loading of Pd and Ru(0.12 wt.% each). The highest conversion observed was for NiMgO/GDC2-900 °C, indicating that higher concentrations of highly active Ni sites are present on the surface of this catalyst contributing to the higher activity of the Ni-based catalyst.

As shown in Fig. 2, higher H_2/CO ratios were obtained at lower temperatures. Thermodynamic calculations show that partial

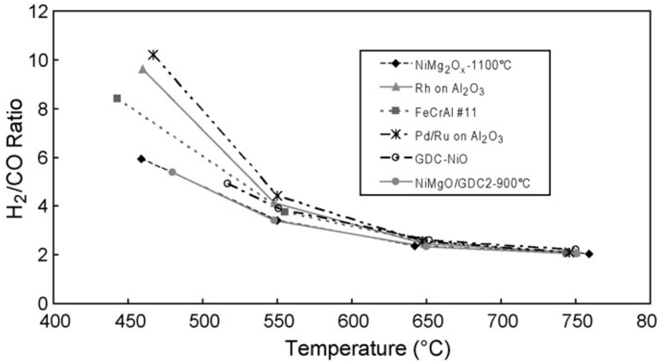

Fig. 2. H_2/CO ratios over fresh reforming catalysts, $CH_4/O_2 = 2/1$, at 1 atm.

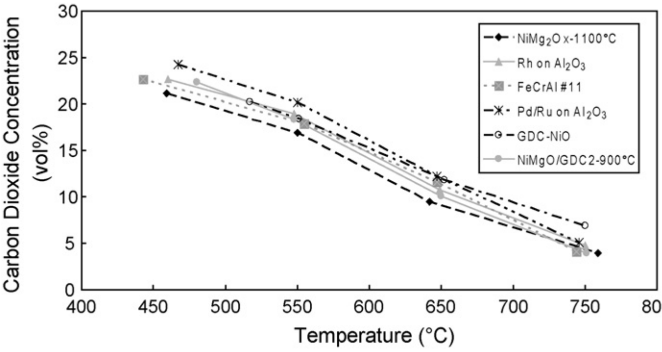

Fig. 3. Carbon dioxide produced during POX reaction over fresh reforming catalysts $CH_4/O_2 = 2/1$, at 1 atm.

oxidation is thermodynamically favorable in the temperature rage of this study and if the POX reaction is the only one occurring, the concentration of both hydrogen and carbon monoxide should be increased with increasing temperature [32]. However, significantly higher concentrations of hydrogen and CO_2 were observed at lower temperatures. Therefore, at lower temperatures, POX reaction is more complicated and several other reactions can take place. For example, CO can react on the catalyst surface producing CO_2 and carbon (Boudard reaction) or CO can react with H_2O producing hydrogen and CO_2 via water–gas-shift reaction. Furthermore, as the temperature increased to 750 °C a stoichiometric H_2/CO ratio of 2:1 was obtained for all the catalysts as predicted by the equilibrium calculation [32]. At higher temperatures both CO_2 and H_2O are the primary product of combustion, which can contribute to the further reforming of methane and therefore changing the product distribution [29–31]. At lower temperatures, less active Pd–Ru/Al_2O_3 catalyst produced higher H_2/CO ratio than those with higher activity such as $NiMg_2O_x$-1100 °C and NiMgO/GDC2-900 °C. A similar result was obtained for CO_2 concentration (Fig. 3), less active catalyst produced more CO_2 at lower temperature and as the temperature increased, the CO_2 concentration was reduced to less than 5%. This could be resulted from reverse WGS reaction, which is favorable at higher temperatures, and/or lower reactivity of CO_2 and H_2O with methane at lower temperatures.

The relative amount of carbon deposited on the catalyst was measured by temperature-programmed oxidation of carbon into CO_2. The peak areas were integrated and the highest amount of carbon was observed for GDC–NiO and the lowest for Rh/Al_2O_3. The order for carbon deposition is GDC–NiO $\gg$ FeCrAl#11 $>$ $NiMg_2O_x$-1100 °C $>$ Pd–Ru/Al_2O_3 $>$ Rh/Al_2O_3 as shown in Fig. 4. The amount of carbon deposited on GDC–NiO catalyst was significantly higher than the amount observed for the other catalysts therefore the TPO method for complete oxidation of carbon and measuring the amount of carbon was not adequate. Therefore, the carbon was completely oxidized with pure oxygen at high temperature ($>$900 °C) and the CO_2 was measured using a CO_2 Coulometer.

3.1. Fresh and sulfided catalysts

The above reforming catalysts were evaluated for partial oxidation of methane before and after exposure to hydrogen sulfide. The catalysts were sulfided either by pulsing 100 μL of H_2S/Ar mixture (20% H_2S) or by flowing it over the catalyst as described earlier. Once the catalysts were saturated with H_2S, the samples were reduced again and the POX reactions were repeated. Methane conversions and H_2/CO ratios were determined at several reaction temperatures. All the reactions were conducted at similar reaction conditions (flow rate, reactor volume, pressure, and temperature) in a 4-mm i.d. quartz reactor, except for the FeCrAl#11 that was tested in a 12.2-mm i.d. quartz reactor.

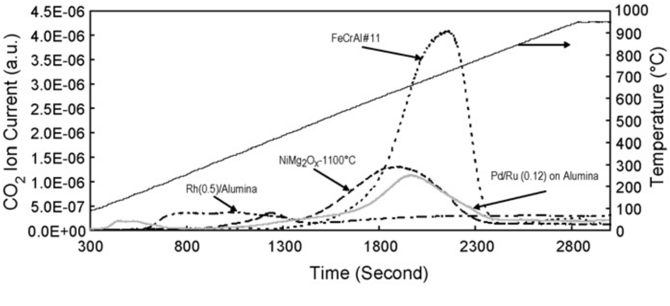

Fig. 4. Carbon dioxide produced during temperature-programmed oxidation of carbon deposited on fresh catalysts.

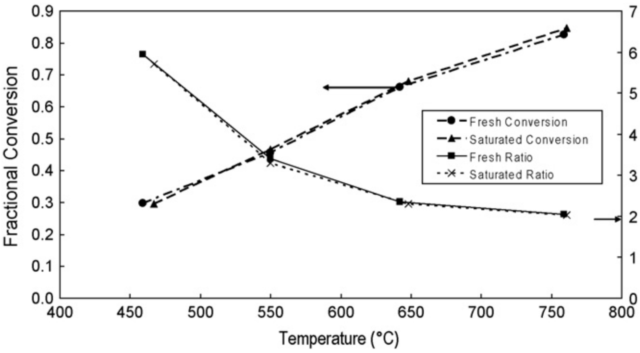

Fig. 5. Methane conversions and H_2/CO ratios for fresh and pulsed sulfided $NiMg_2O_x$-1100 °C catalyst, CH_4/O_2 = 2/1, at 1 atm.

Three catalysts $NiMg_2O_x$-1100 °C, Rh/Al_2O_3 and FeCrAl#11 ($NiMg_2O_x$-1100 °C supported on metal foam) were sulfided by pulsing H_2S and then reduced with hydrogen before partial oxidation of methane. It appears that both $NiMg_2O_x$-1100 °C and Rh/Al_2O_3 maintained their catalytic activities and selectivities at 750 °C even after they were exposed to H_2S as shown in Figs. 5 and 6. However, the sulfided Rh/Al_2O_3 catalyst showed a significantly lower H_2/CO ratio at lower temperature. Under similar conditions FeCrAl#11 was significantly deactivated when exposed to pulses of H_2S. Under steady-state sulfidation condition where 20% H_2S/Ar mixture passed over the catalysts almost all the catalysts were siginificantly deactivated at lower temperatures except for Rh/Al_2O_3. This can be explained by the higher bond strength of sulfur on Ni-based catalysts. Furthermore, it has been reportd that surface nickel–sulfur bonds are significnaly more stable than the bulk nickel–sulfur bonds [7]. Metal dispersion also plays an important role in the extend of catalytic deactivation by sulfur. For example, smaller particles (higher dispersion) are more resistant to sulfur piosioning than larger ones and this is explained by the changes in electronic properties of the small particles [8].

The Rh/Al_2O_3 catalyst was sulfided via both pulse and at steady-state conditions as explained earlier. As shown in Figs. 7 and 8, catalyst with pulse sulfidation has higher catalytic activity than the catalyst that was sulfided under steady-state. Furthermore, the catalyst with lower activity produced higher concentrations of H_2S and SO_2 during TPR and TPO as shown in Figs. 9 and 10. Significantly, higher amount of sulfur was removed from the samples sulfided under steady-state conditions compared to that of pulse sulfidation. It appears that pulse sulfidation produces less stable sulfides, which can be easily removed with hydrogen at higher temperatures. Under steady-state conditions, the sulfides are more difficult to remove and the peaks during reduction

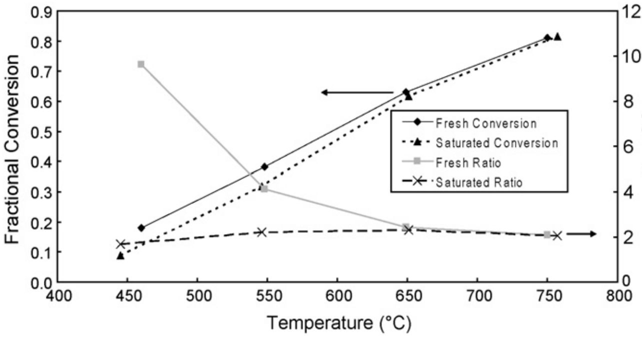

Fig. 6. Methane conversions and H_2/CO ratios for fresh and pulsed sulfided Rh(0.5%)/Al_2O_3 catalyst, CH_4/O_2 = 2/1, at 1 atm.

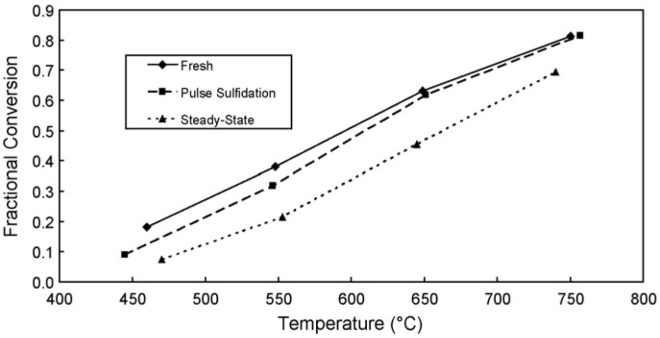

Fig. 7. Methane conversion during partial oxidation over fresh and sulfided Rh(0.5%)/Al_2O_3 catalysts, $CH_4/O_2 = 2/1$, at 1 atm.

(producing H_2S) and oxidation (producing SO_2) were shifted to higher temperatures, respectively.

At the highest reaction temperature (750 °C), the H_2/CO ratios are at equilibrium and they are essentially identical for three samples (Fig. 8). However, as the reaction temperature decreases larger differences begin to appear. Particularly, the more active fresh sample produces higher H_2/CO ratio of 9.5 at 450 °C where as the sufided catalysts produced significantly lower H_2/CO ratio. This explains that at higher temperature, some of the sulfur is removed from the catalyst surface during partial oxidation but at lower temperature, it remains on the catalyst surface which significantly alters catalyst activity and selectivity.

The amount of carbon deposited on fresh and sulfided Rh/Al_2O_3 catalysts during the POX reaction was also determined. The fresh samples produced significantly (more than twice) higher amount of carbon, presumably due to higher reactivity of fresh samples. The results seem to show that higher conversion causes more carbon deposition, as in the fresh case, but addition and subsequent removal of sulfur may change the catalyst structure that resulted in less carbon deposition. There was no significant changes for the Rh/Al_2O_3 as it was observed for PdRu/Al_2O_3 and $NiMg_2O_x$-1100 °C, causing more carbon deposition on the sulfided catalyst than on the fresh one.

3.2. Ru(0.12 wt.%)/Pd(0.12 wt.%) on Al_2O_3

The Ru/Pd catalyst, when fresh, appeared to be an active catalyst for partial oxidation of methane (Fig. 1). The CH_4 conversion over the catalyst was comparable to the others, though slightly lower at lower temperatures. The H_2/CO ratio was also similar to the other catalysts, however when the catalyst exposed to H_2S it was significantly deactivated at lower temperatures (450 and 550 °C), but it began to regenerate, although not fully, at higher temperatures (650 and 750 °C). At the highest temperature, the catalyst only had half of its original activity in converting CH_4 into syngas. More carbon deposited on the sulfided than on the fresh catalyst.

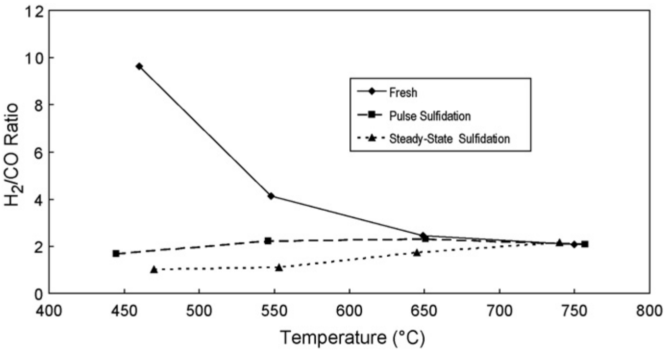

Fig. 8. H_2/CO ratios for POX of methane over fresh and sulfided Rh(0.5%)/Al_2O_3 catalysts, $CH_4/O_2 = 2/1$, at 1 atm.

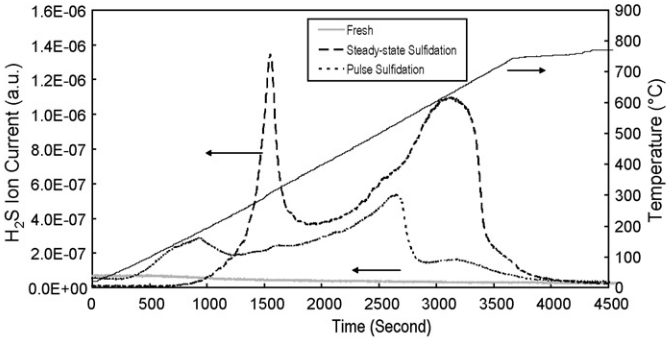

Fig. 9. Hydrogen sulfide produced during temperature-programmed reduction (TPR) of fresh and sulfided Rh(0.5%)/Al_2O_3 catalysts.

3.3. GDC–NiO

The GDC–NiO catalyst is also active as fresh, while having slightly less CH_4 conversion than the other catalysts, particularly at the highest temperature (Fig. 1). The H_2/CO ratio, however, is very similar to the other catalysts, specifically at higher temperatures (Fig. 2). The major difference between the GDC–NiO and the others was that the amount of carbon deposited on the fresh catalyst was significantly higher than the other catalysts. Furthermore, the GDC–NiO was completely deactivated when it was exposed to H_2S (CH_4 conversion <1%) with both methods of sulfidation. Due to lack of activity no significant amount of carbon deposited on the sulfided catalyst during POX reaction. Attempt to remove the sulfur either by reducing it with H_2 or by oxidizing it with O_2 did not regenerate the catalyst and no significant catalytic activity was observed before or after removing the sulfur.

3.4. NiMgO/GDC2-900 °C

The catalyst tested at different reaction temperatures under POX reaction conditions and the fresh sample as shown in Figs. 1–3 is very active and CH_4 conversion of more than 80% was observed for this catalyst, even at a low temperature (487 °C) a conversion of 35% was observed. However, exposure to H_2S significantly deactivated the catalyst and methane conversion of less than 10% was obtained at higher temperature (750 °C). Due to lack of catalytic activity, little or no carbon deposited on the sulfided catalyst during POX reactions. However, there were two distinct CO_2 peaks during TPO of deposited carbon over fresh catalyst. The

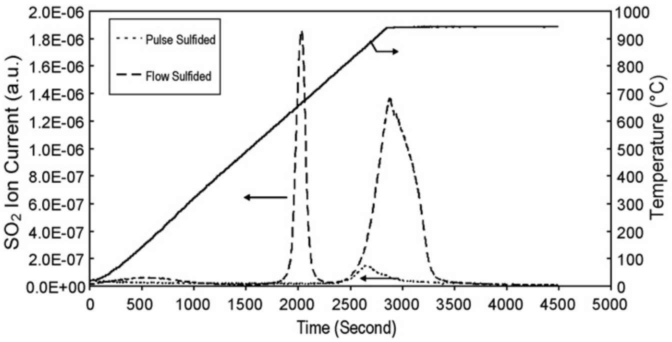

Fig. 10. Sulfur dioxide produced during temperature-programmed oxidation (TPO) of sulfided Rh(0.5%)/Al_2O_3 catalysts.

first of these appears at 385 °C and the second, a larger peak, at about 615 °C, indicating two types of carbon or the carbon is located near the active sites that is catalyzed reacting with O_2 at lower temperature where as the other deposited on the support reacting at a higher temperature.

3.5. Sulfur removal

Temperature-programmed reduction and oxidation were used to remove the sulfur as H_2S and SO_2, respectively. The amount of sulfur removed from the catalysts depends on the severity of sulfidation. Sulfur adsorbed during pulse sulfidation appears to react with H_2 more easily than the sulfur species produced during steady-state sufidation. The GDC–NiO contained the highest amount of sulfur followed by NiMgO/GDC2-900 °C and FeCrAl#11 catalyst. The Pd–Ru/Al_2O_3 and the Rh/Al_2O_3 appeared to have the same amount of sulfur. Aside from the actual amount of sulfur removed, estimated from the total areas under each H_2S peak, the TPR also shows the relative difficulty in removing sulfur species. Peaks that occur at higher temperatures require additional energy for the sulfur to be removed, possibly due to bulk sulfidation and diffusion limitation in reacting H_2 or O_2 with sulfur in the bulk. However, lower temperature peaks are more likely to be resulted form the surface that has fewer problems with diffusion. Furthermore, due to complex nature of the sulfur clusters (Rh_xS_y) the position of the peaks may also be associated with the chemical reactivity of the sulfur compounds. Therefore, further studies are needed to identify the nature of these peaks.

The GDC–NiO catalyst required higher temperature, with no sulfur removal until about 700 °C, followed by the NiMgO/GDC2-900 °C, which had several peaks at varying temperatures. FeCrAl#11 seemed to have numerous peaks as well. The remaining catalysts had multiple peaks, but each had some sulfur that was removed relatively easily at lower temperatures. For example, reduction of sulfur into H_2S from Rh/Al_2O_3 sample has four peaks at 325, 440, 560, and 630 °C. All the reactive sulfur was removed at temperatures less than 850 °C. It appears that not all the sulfur is removed by reacting with hydrogen even under POX reaction conditions. Therefore, the sulfur was removed by TPO.

Oxidation of sulfur into SO_2 produced two peaks, one at 290 °C and the other at 850 °C. However, temperature of higher than 850 °C is required to remove the sulfur completely. Similar results obtained for Pd–Ru/Al_2O_3 catalyst with H_2S peaks appeared at about 295 and 590 °C where as the SO_2 peaks observed at 280 and 850 °C. Comparing the results of Pd–Ru/Al_2O_3 with Ru/Al_2O_3, it appears that most of the sulfur is associated with Ru and this was confirmed by the XPS analysis showing no significant amount of Pd on the surface where as the concentration of Ru was about 3 at.% on the sulfided sample. Due to low concentrations of Pd and Ru no sulfided phases of these elements were detected by X-ray diffraction (XRD). However, XRD detected MgS, Ni_3S_2 for sulfided $NiMg_2O_x$-1100 °C, and Ce_2S_3, $MgGd_2S_4$ for sulfided catalysts containing GDC. Most of the catalyst supports, except alumina that showed no bulk sulfur compounds by XRD, were very reactive and formed various sulfur species when they were exposed to H_2S.

4. Conclusions

Under pulse sulfidation, Rh/Al_2O_3 appears to be the best catalyst and it has a high activity as fresh and when it is exposed to H_2S. Furthermore, this catalyst produces the least amount of carbon during POX reaction. The $NiMg_2O_x$-1100 °C catalyst also showed higher activity and it was fully regenerated after pulse sulfidation and reduction with hydrogen. The reactivity of both fresh and sulfided catalyst is similar to rhodium, only slightly higher for both fresh and regenerated samples. However, during POX reaction it produces significantly higher amount of carbon than the rhodium catalyst.

The catalyst activity and selectivity was greatly affected by the exposure to H_2S, specifically when they were sulfided under steady-state conditions. In fact, the majority of the catalysts were completely deactivated at lower temperatures, while only regaining a portion (<50% maximum) of their original activity at higher temperatures. The only catalyst that seemed to be tolerant, although not completely, to sulfur is the Rh/Al_2O_3, which yielded CH_4 conversion of about 50% of the original at the lowest and 85% at the highest temperature. There was no significant structural changes observed for Rh/Al_2O_3 as it was for Pd–Ru/Al_2O_3 and $NiMg_2O_x$-1100 °C, which resulted in more carbon deposition on the sulfided than on the fresh catalyst.

The catalysts were not immediately poisoned by the sulfur, but poisoned over time under severe conditions and this may enable for periodic regeneration of the catalyst before complete deactivation, therefore, extending the practical life of the catalysts when low levels of H_2S are present in feed streams.

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