In-Situ Infared Study of Catalytic Ignition of Methane on Rh/Al$_2$O$_3$

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Abstract

Catalytic partial oxidation (CPO) of methane to syngas has received considerably interest recently as a way to utilize remote natural gas resources. Despite this interest, the mechanism of methane CPO is not completely understood. For example, there is disagreement in the literature if syngas is formed directly from oxidation or whether an indirect mechanism is responsible. Investigation of the catalytic ignition of methane CPO can provide insights on the mechanism of CPO, particularly on the role of the chemical and physical state of the noble metal catalyst. In this work, ignition of methane CPO on Rh/Al$_2$O$_3$ catalysts was studied using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

The ignition temperature was found to change with the catalyst state, and is lowest on freshly reduced catalysts. Ignition temperature decreased with an increase in oxygen concentration in the reactant mixture, which is the opposite trend noted for Pt/Al$_2$O$_3$. To investigate this phenomenon, the oxidation state of rhodium was investigated by using CO as a probe molecule. Prior to ignition, ppm of CO were adsorbed on the working catalyst, and the DRIFTS signal was obtained. From this signal, the oxidation state of rhodium could be inferred. As the reactant mixture flowed over the catalyst and the temperature is raised towards the ignition temperature, the oxidation state of the catalyst changes significantly. An oxidized rhodium state, Rh^{n+}, progressively forms as temperature is increased while Rh$^+$ and Rh^o decrease. In addition, a greater amount of Rh^{n+} is found when the oxygen concentration in the feed is higher. From these results, it is hypothesized that ignition of methane CPO on Rh/Al$_2$O$_3$ is related to the accumulation of the Rh^{n+} state.

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Introduction

CH$_4$ conversion into higher hydrocarbons has become extremely attractive recent years because of abundant natural gas resources and steadily depleting oil reserves. CH$_4$ steam reforming is a traditional way to utilize natural gas resources through syngas. But this method has its own drawbacks such as energy intensive, unsuitable hydrogen to CO ratio and poor selectivity of CO. Catalytic partial oxidation of CH$_4$ has attracted interest as a potential replacement for steam reforming. The interest in this reaction is that the products of CPO has a more preferable ratio of 2:1 which can be used directly as feedstock for methanol or higher hydrocarbons production. In addition, because of its exothermic property, CPO is a more rapid process with a higher reaction rate and can run auto thermally without external heating once ignited.

While the potential of CPO reaction for syngas generation is considerable, the reaction mechanism is not well understood yet. For example, some experimental work shows that CPO proceeds directly from CH$_4$ and O$_2$ reaction to syngas, while other researchers insists that combustion of CH$_4$ occurs first followed by reforming reactions and water gas shift reaction. Thus, a complete understanding of the reaction mechanism is necessary and the ignition process study is helpful for this purpose. Moreover, ignition process study can provide a reasonable estimate of the energy required to initiate the reaction.

The goal of the present investigation was to investigate the surface intermediates and the surface states of rhodium during methane adsorption and ignition process of methane partial oxidation as the temperature is raised to ignition temperature using in situ DRIFTS coupled by mass spectrometer. Interaction of several catalysts and catalysts states with CH$_4$ and CH$_4$/O$_2$/He were examined.
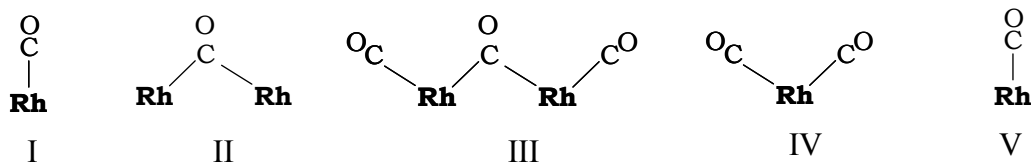
Experimental

Rh/Al$_2$O$_3$ powder catalysts are prepared by impregnating the γ-Al$_2$O$_3$ (powder S$_{BET}$ = 121 m^2/g) with aqueous solutions of Rh(NH$_3$)$_4$(NO$_3$)$_2$.2H$_2$O. There are four different catalysts were investigated in this research, freshly reduced, aged, sintered, and oxidized catalysts. The average particle sizes of the prepared Rh catalysts were determined by means of a transmission electron microscope (TEM) and H$_2$ pulse chemisorption.

The methane adsorption experiments were performed on different states of the catalyst. After pretreatment of the catalyst, a mixture of 50%-vol. CH$_4$ in helium with a flow rate of 520 cc/min was introduced to the DRIFTS cell at 323K and the catalyst temperature was slowly increased while IR spectra were collected every 10K at a resolution of 4 cm^{-1} with 20 co-added scans. Reaction ignition experiments are also performed in same DRIFTS cell with a total flow rate in the range of 300 to 650 cc/min. CH$_4$/O$_2$/He were introduced into the DRIFT cell at 323 K and then the temperature was slowly increased (10 K/min) while IR spectra were periodically collected. The catalyst

ignition temperature was measured when the thermocouple temperature increased rapidly beyond the controller set point. All data points were reproducible to within $\pm$ 3 K.

The oxidation states of rhodium during the reaction were characterized using CO as a probe molecule. The temperature of the catalyst was increased slowly under reaction mixture to a certain temperature, which was lower than ignition temperature. The reaction mixture was flowed for 3min and then switched to He for 3min. After evacuation, the catalyst was cooled to 373K quickly. At this temperature, ppm CO in helium was pulsed into the reactor through a six-way valve and the spectra were recorded immediately with 5 scans. The cooling time was short (close to 2 min) and the change of the catalyst state during this process is assumed to be negligible. The different carbonyl species are listed below. The structures and the corresponding Rh oxidation states are also explained. The positions of different carbonyls and the metal oxidation states, which indicate, would be very useful for the study in this research.

The single band at 2045 - 2062 cm^{-1} is assigned to CO molecules adsorbed on the rhodium atoms on the surface of rhodium metal crystallites. The corresponding formula is species I with oxidation state of Rh^0. Single band showing up at 1905 –1925cm^{-1} is assigned to CO molecule bridged between two neighboring Rh atoms figured as species III with oxidation state of Rh^0. Yao and Rothschild [1] have suggested that the broad band peaking between 1850 and 1900 cm-1 should be assigned to a mixture of bridged species II and III. The II species exhibit near 1850 cm^{-1} while species III absorb near 1925 cm^{-1}. Both oxidation states are Rh^0. Infrared band at 2095 and 2027 cm^{-1} were assigned to the symmetric and antisymmetric stretching modes for adsorbed species IV (gem-dicarbonyl). These two bands did not shift with increasing CO coverage. The Rh oxidation state of this species is +1. The peaks at 2100 cm^{-1} or slightly above are assigned to species V. While the oxidation states of Rh on which this carbonyl formed are not clear enough because all of states except Rh^0 are possible to show up at this area, thus called $Rh^{n+}(1 \leq n \leq 3)$.

Ignition Temperatures

Light off experiments have been performed with a fresh 2%Rh/Al$_2$O$_3$ catalyst using 40CH$_4$/xO$_2$/He mixtures (with x such as $1.16 \leq \dfrac{CH_4}{O_2} \leq 8$). The flow rate was 650 sccm with each ratio. It has been observed that the ignition temperature was lower for higher amounts of oxygen as shown in **Figure 1**. These results are quite the contrary of the one obtained with platinum where the ignition temperature was higher for higher

amounts of oxygen. In this latter case it has been shown that oxygen is mainly covering the surface until the ignition temperature. A competition between the two reactants was assumed with the heat of adsorption of oxygen being a key factor for ignition of the surface reaction [2].
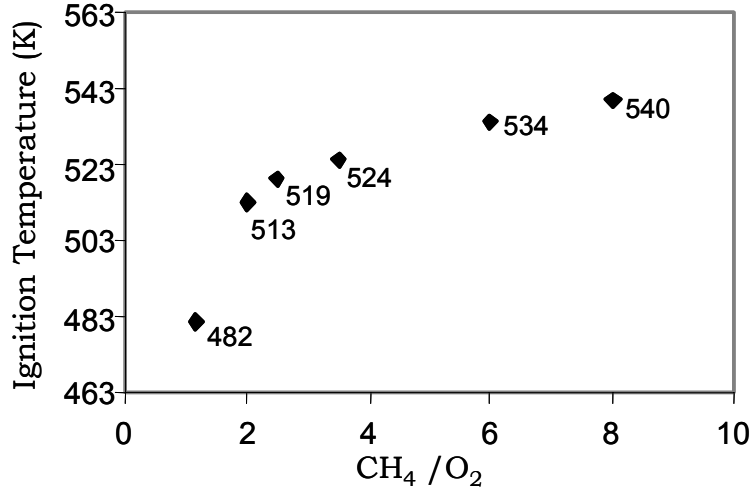

Figure 1 Evolution of the ignition temperature with CH$_4$/O$_2$ ratio

Similar light off experiments using $\dfrac{CH_4}{O_2} = 2$ have also been performed on aged, oxidized and sintered 2%Rh/Al$_2$O$_3$ catalysts. The aged catalyst was obtained after exposing the fresh catalyst to a number of successive oxidation-reduction-light-off cycles performed with the AMI instrument. The oxidized catalyst has been obtained after treatment in oxygen at 773K for 1h. The sintered catalyst has been obtained after exposure of the fresh catalyst to He at 1073K for 2 hours. It has been observed the following trend for the ignition temperature: fresh < aged ≈ oxidized < sintered. The ignition temperatures, dispersions and particle sizes for the catalysts are listed in table 1.

Table 1 Reaction ignition temperatures on different states of catalysts and related characterization results

Catalyst	Dispersion	Particle sizes (nm)	Ignition temperatures (K)
Reduced aged	74%	1.8	598
Reduced fresh	37%	2.9	513
Reduced sintered	28%	4.2	623
Oxidized	27%	0.8	596

Attempting to explain these results based on metal dispersion and particle size is not easy to do, at least between the oxidized and the other three catalysts. The four catalysts show indeed different dispersion i.e. different number of accessible sites with the oxidized catalyst having the lowest dispersion then the sintered then the fresh one and then the aged catalyst. These results are quite surprising especially for the aged catalyst having the highest dispersion while one might expect the dispersion to decrease due to

sintering (as in the case of platinum). The strong interaction between the support $\gamma\text{-Al}_2\text{O}_3$ and the rhodium resulting from the several oxidation-reduction-light-off cycles may be a possible explanation. For the oxidized catalyst it can be seen from the TEM results that the rhodium is not agglomerating as would be suggested by the hydrogen chemisorption measurement but it is rather dissolving in the support as also mentioned by others authors in the literature [3].

Initial states of catalysts

The surface state characterization of four different catalysts has been done using CO adsorption followed by FTIR. The IR spectra obtained are represented in **Figure 2**. It can be observed that they are different according to the surface state of the catalysts. The spectrum of the sintered catalyst (Fig. 2a) is dominated by a band at 2065 cm^{-1} due to the linearly adsorbed CO species (species I) on reduced Rh. Additional broad IR bands at 1870 and 1940 cm^{-1} indicate the presence of bridged CO species (species II and III) also adsorbed on reduced rhodium [4].
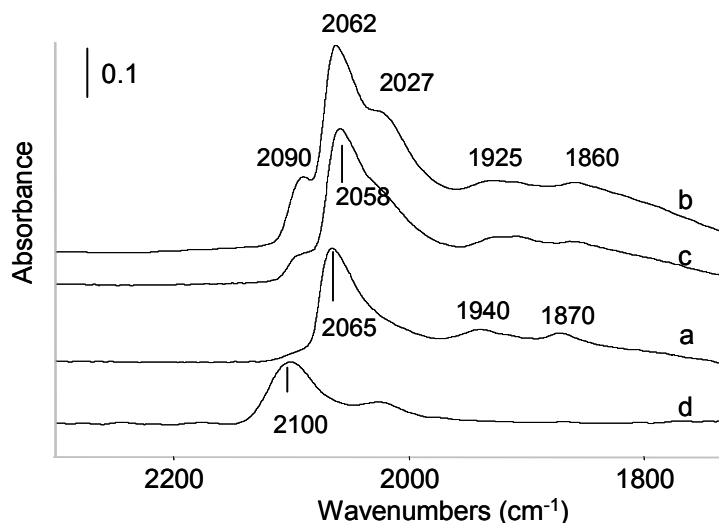

Figure 2 IR spectrum of adsorbed CO on (a) sintered (b) fresh (c) aged and (d) oxidized 2%Rh/Al$_2$O$_3$

On the fresh catalyst (Fig. 2b) the adsorption of CO led to species I at 2064 cm^{-1} and species II and III at 1925 and 1860 cm^{-1} respectively, formed on reduced rhodium. Also appearing on this catalyst are gem dicarbonyl species $Rh^+(CO)_2$ (species IV) characterized by the doublet of IR bands at 2027 and 2090 cm^{-1} (assigned to the symmetric and antisymmetric stretching modes respectively). Similar CO species were also observed on the aged catalyst (Fig. 2c) with a lower intensity for species IV. The positions of the IR bands were the same except for species I which is located at 2058 cm^{-1}. The evolution of the position of the IR band of the linearly adsorbed CO on Rh^0 for the three considered surface states catalysts is in total agreement with the results of the particle size measurements where the following order was obtained: $D_{aged} < D_{fresh} < D_{sintered}$. The position of the IR band of the linearly adsorbed CO species may indeed be

an indicator of the particle size [5] with a blue shift expected as the particle size increases. The intensity of the IR spectrum of the adsorbed CO on the oxidized catalyst (Fig 2d) is much lower than the ones obtained with the other surface state. This is also in agreement with the TEM result where it has been shown that the oxidizing treatment at high temperature leads rhodium to dissolve into the support. The IR spectrum is dominated by a band at 2100 cm^{-1} assigned to CO adsorbed on Rh^{n+} sites ($1<n<3$) (species V) [4]. An additional band at 2025 cm^{-1} indicates the presence of the gem dicarbonyl species (species IV). The antisymmetric stretching mode expected from this species is certainly hidden by the intense asymmetric band at 2100 cm^{-1}. The tail of this band may also cover any weak signal due to species I.

Interaction of methane with Rhodium

The interaction of methane with the different surface state of $2\%Rh/Al_2O_3$ in the absence of gas phase oxygen has been investigated in the 323 - 573K range using a 50% CH_4/He mixture at a flow rate of 300 SCCM.

The IR results obtained after admission of CH_4/He on the fresh catalyst are shown in **Figure 3**. A weak IR band at 2010 cm^{-1} appears at 423K. As the temperature is increased, this IR band, ascribed to the linearly adsorbed CO species (species I) on the reduced Rh, increases while a broad weak IR band centered at 1850 cm^{-1}, assigned to species II, is progressively formed.
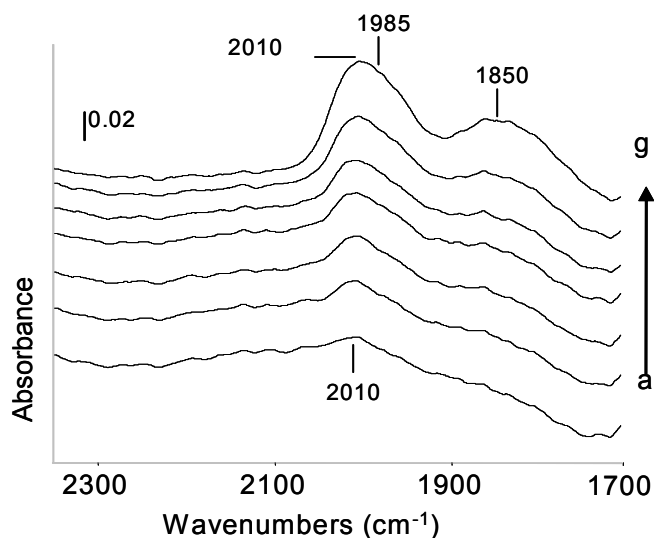

Figure 3 Evolution with the temperature of the IR spectra of adsorbed species formed when interacting 50%CH_4/He with the fresh catalyst: (a) 423, (b) 433, (c) 443, (d) 453, (e) 463, (f) 483, (g) 513 K

Figure 4 shows the IR spectra of the adsorbed species when interacting CH_4/He with the aged catalyst. A weak IR band appears at 2000 cm^{-1} from 383K, i.e. at a lower

temperature than that on the fresh catalyst. This IR band is assigned to the linearly adsorbed CO species (species I) on the reduced Rh. As the temperature is increased, this IR band increases and shifts to 2010 cm^{-1} at 553K while a broad weak IR band centered at 1860 cm^{-1}, assigned to species II, is progressively formed. **Figure 5** shows the IR spectra of the adsorbed species when interacting CH$_4$/He with the sintered catalyst. A weak IR band appears at 2000 cm^{-1} from 473K, i.e. at a temperature higher than that on the fresh catalyst. The same behavior as the one on the previous catalysts is observed for the evolution of this IR spectrum with temperature. **Figure 6** shows the IR spectra of the adsorbed species when interacting CH$_4$/He with the oxidized catalyst. A weak IR band appears at 2100 cm^{-1} from 463K, nearly the same temperature as on the sintered one. As the temperature is increased this IR band slightly increases while a band assigned to species I appears at 2035 cm^{-1} with a shoulder at 2085 cm^{-1} which does not result from the shift of the band at 2100 cm^{-1} but which is rather assigned to the antisymmetric stretching mode of species IV. It is indeed reported that the IR bands of the gem dicarbonyl species do not shift with the increase in intensity, i.e. the increase of its amount on the surface [4] The IR band at 2100 cm^{-1} would be rather assigned to species V. The second component of the doublet expected from this species is probably masked by the tailing of the band at 2035 cm^{-1}. From 523K also appears a broad band centered at 1850 cm^{-1} and assigned to species II.
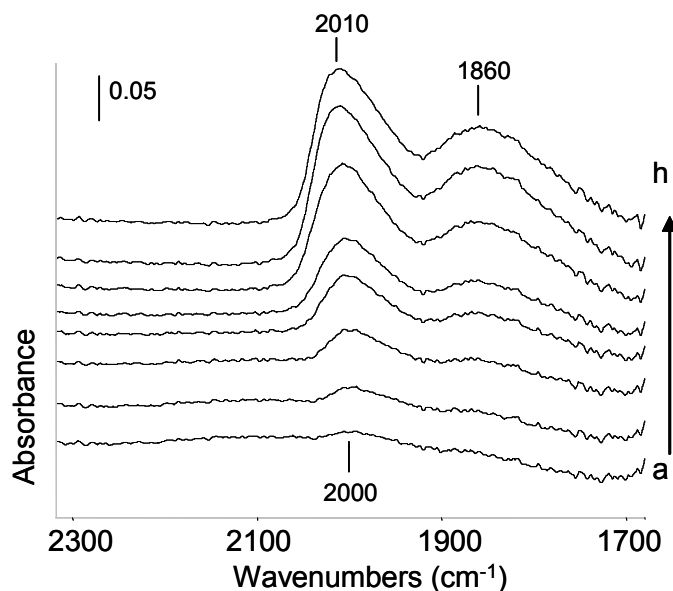

Figure 4 Evolution with the temperature of the IR spectra of adsorbed species formed when interacting 50%CH$_4$/He with the aged catalyst: (a) 383, (b) 393, (c) 413, (d) 433, (e) 453, (f) 493, (g) 533, (h) 553 K
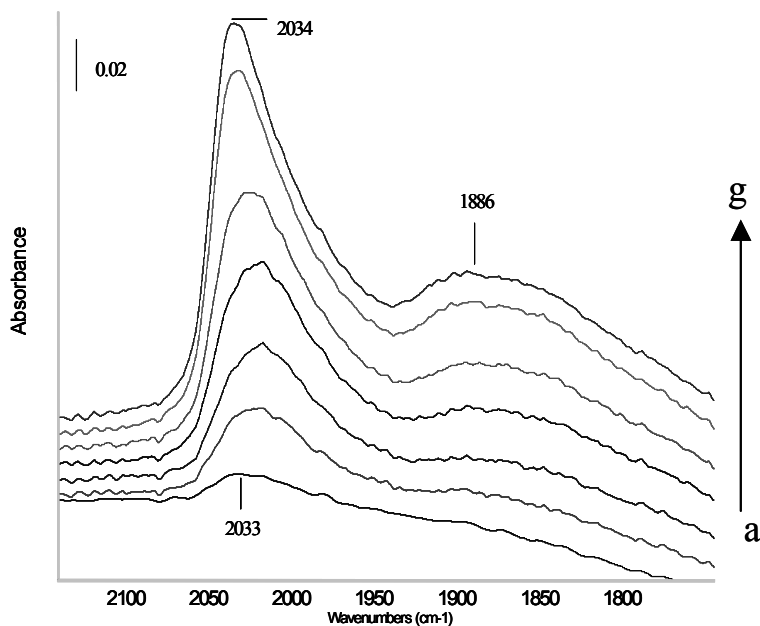
Figure 5 Evolution with the temperature of the IR spectra of adsorbed species formed when interacting 50%CH₄/He with the sintered catalyst: (a) 383, (b) 393, (c) 413, (d) 433, (e) 453, (f) 493, (g) 533, (h) 553 K.
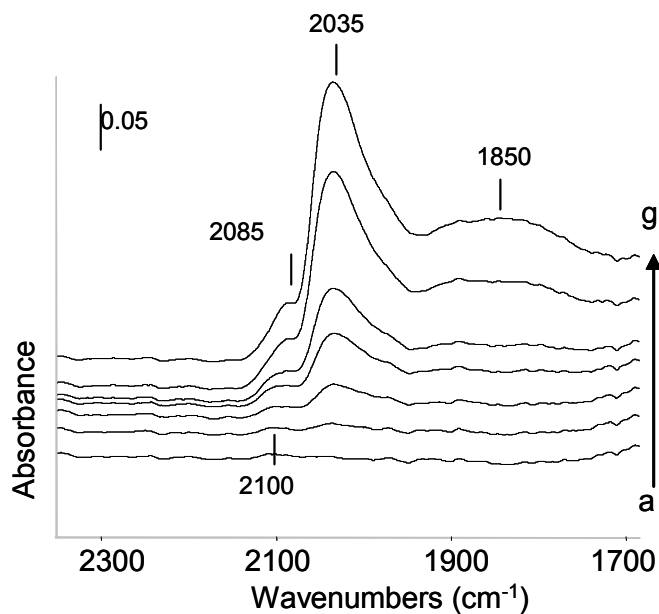

Figure 6 Evolution with the temperature of the IR spectra of adsorbed species formed when interacting 50%CH₄/He with the oxidized 2%Rh/Al₂O₃ catalyst: (a) 463, (b) 473, (c) 483, (d) 493, (e) 503, (f) 523, (g) 543 K.

The following remarks can be made from the results obtained during the interaction of methane with the different catalyst states: i) the dissociative adsorption of

methane on rhodium is an activated process since it occurs only at high temperature which is in agreement with the data reported in the literature [6]; ii) the temperature at which the dissociative adsorption of methane occurs is different according to the catalyst state considered: the temperature is the lowest on the aged catalyst while it is the highest on the sintered catalyst, i.e. highly dispersed rhodium will activate the dissociative adsorption of methane much more easily than larger particles of rhodium.

Surface state characterization during interaction of CH$_4$/O$_2$/He mixtures with rhodium catalyst

Chracterization of the Rh surface state in the course of the light-off process has been performed using CO adsorption followed by obtaining an FTIR spectrum at 373K. **Figure 7** shows the IR spectra of adsorbed CO obtained with the 40%CH$_4$/11.4%O$_2$/He (CH$_4$/O$_2$ = 3.5) mixture where the temperatures at which CO was adsorbed were 438, 463, 488 and 513 K.
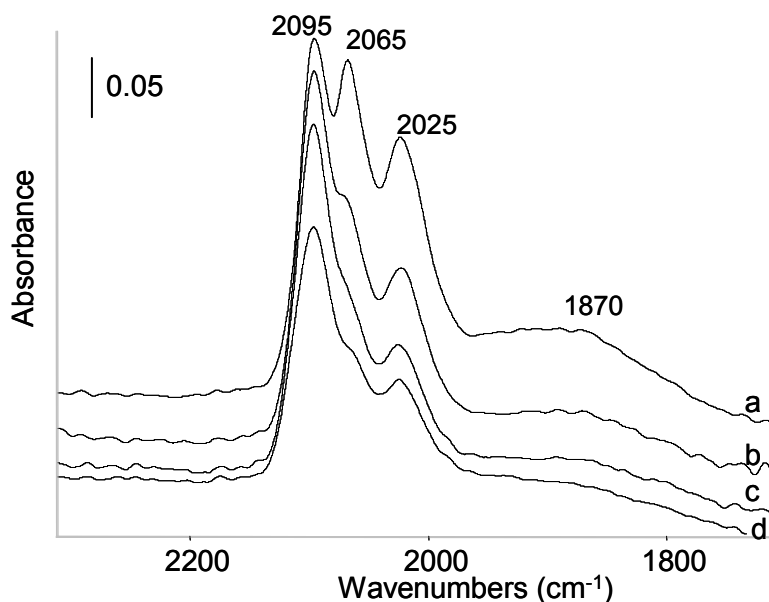

Figure 7 IR spectra of adsorbed CO on the surface of fresh 2%Rh/Al$_2$O$_3$ at 373 K after increasing temperature from room temperature to (a) 438 (b) 463 (c) 488 and (d) 513 K under 40%CH$_4$/11.4%O$_2$/He mixture

The spectrum of the adsorbed CO after reaching 438K (Fig. 7a) reveals strong bands at 2025, 2065 and 2095 cm^{-1} and a broad band centered at 1870 cm^{-1} associated with the bridged CO species. As mentioned above, the 2065 cm^{-1} band can be assigned to the linearly adsorbed CO on reduced rhodium while the 2025 and 2095 cm^{-1} bands can be assigned to the two components of the doublet of the gem dicarbonyl species. For this latter species it is apparent that the band at 2095 cm^{-1} is markedly more intense than the one at 2025 cm^{-1} while the integrated areas should be nearly the same [4]. This indicates the presence of a species near 2095 cm^{-1}, which is probably species V.

The spectrum of the adsorbed CO after reaching 463K (Fig. 7b) shows CO species similar to that after reaching 438K. While the intensity of the bands of the gem dicarbonyl species, the bridged CO species and the linear CO species has decreased, the intensity of the band of the species V seems to be stable or has even increased. The same trend is observed for the evolution of the bands of the adsorbed CO species after reaching 488 (Fig. 7c) and 513K (Fig. 7d) under the reaction mixture. The bridged CO species has completely disappeared and species V seems to increase more as the temperature reached while flowing the reactant mixture is higher. Similar experiments have been performed using different mixture compositions where the partial pressure of oxygen was varied. The ratios of CH_4/O_2 were 1.16, 2 and 8 with fixed methane partial pressure.

In order to evaluate the decrease of the intensities of the linear and gem dicarbonyl CO species and the increase of the intensity of species V in the course of the light-off process, a deconvolution of the bands in the 1950 - 2150 cm^{-1} range using the GRAM software has been realized. This is done assuming that the number of IR bands resulting from the CO adsorption is four and the integrated area of the two components of the gem dicarbonyl are equal for all conditions. **Figures 8, and 9** show the evolution with the reached temperature of the integrated area of species V and the linearly adsorbed CO species combined with the gem dicarbonyl CO species, respectively. It can be seen that the intensity of the linear CO species and the gem dicarbonyl CO species is decreasing with the reached temperature while the intensity of species V is increasing which confirm the above observation.
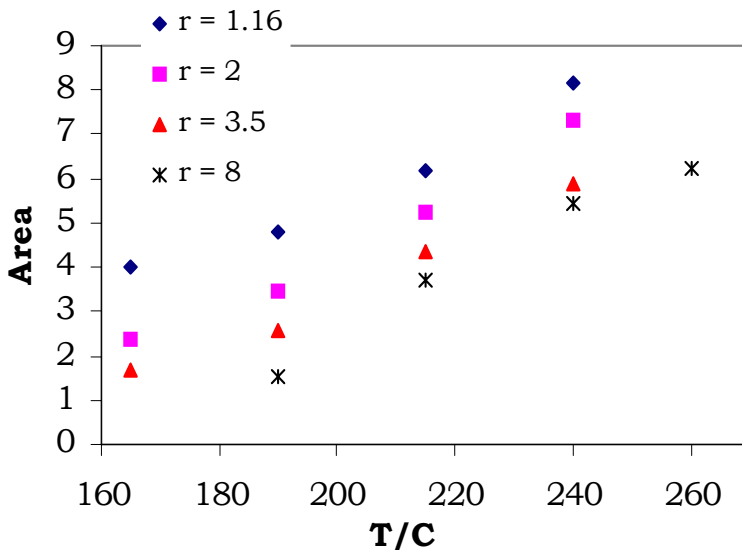

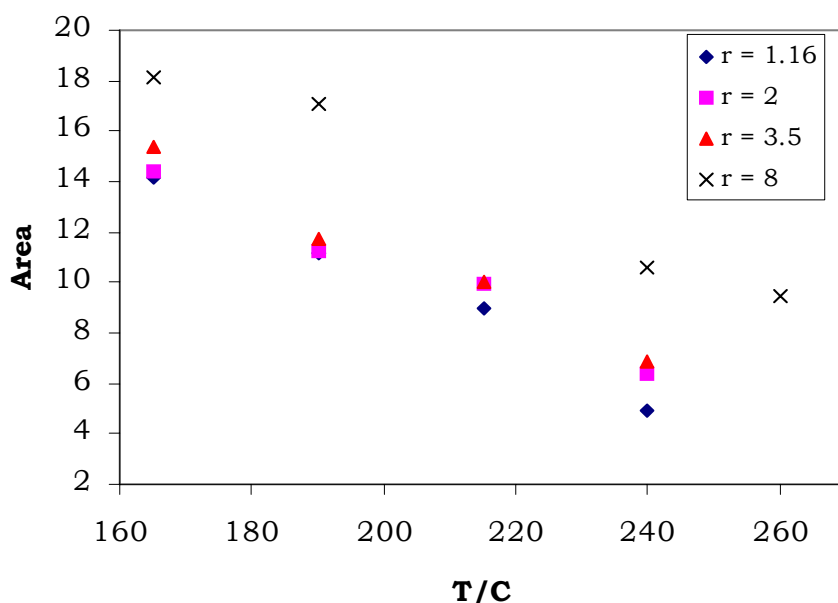**Figure 8 Evolution of the integrated area of Rh^{n+} with reached temperatures for the different CH_4/O_2 ratio**

Figure 9 Evolution of the combined integrated area of Rh^0 and Rh $^{+1}$ with reached temperatures for the different CH$_4$/O$_2$ ratio

After deconvoluting the IR bands in the 1950 - 2150 cm^{-1} region, the following observations can be made from the integrated areas obtained in figures 8 and 9: i) whatever the mixture considered the linear CO species and gem species are present and as the temperature is increased the sum of their integrated area is decreasing; iii) the species V is increasing with the reached temperature and the higher the amount of oxygen in the mixture the higher is its integrated area for any temperature.

Two points should be mentioned regarding the use of CO adsorption as a means to characterize the surface state of rhodium catalyst. The first one is that a surface reaction occurs after the injection of the CO pulse evidenced by the immediate formation of a small IR band at ~1450 cm^{-1} assigned probably to carbonate species. The reaction of CO with the oxygen present on the surface may be the cause. Because the CO pulse contains enough CO molecules to compensate for this consumption and the amount of adsorbed oxygen is small, this should not affect significantly our IR spectra. The second point concerns the fact that the CO-assisted oxidative disruption of Rh metallic crystallites can also occur [7, 8] leading to the formation of gem dicarbonyl CO species so that the amount detected on the surface can not automatically be related to the species initially present in the sample. However it is reported in the literature that this phenomenon is retarded by decreasing the number of OH groups on the support and by the use of a low partial pressure of CO [7,8]. The conditions used in our experiments (a temperature of 373K to prevent higher amount of OH, the pulse of CO for a lower partial pressure and the immediate recording of the IR spectrum) should minimize this effect.

According to results from methane activation, partial oxidation ignition and CO adsorption experiments conducted in *in-situ* DRIFTS cell, it was found that reaction

ignition on $2\%Rh/Al_2O_3$ is affected by the oxidation states of the catalysts and that methane activation occurred on selected state of catalysts.

As the temperature is raised in the presence of methane, the formation of CO detected by IR on the catalysts indicated that the active sites for methane dissociation to form CO are reduced metal Rh. For methane dissociation on catalysts without chemisorbed O, the initial states of the three catalyst after the same treatment respectively are sintered catalysts with biggest particles size now have biggest metal crystallites size, thus stronger Rh^0-O^{2-} and Rh-Rh bond which is harder to break up and need more energy. With temperature increasing after CH_4 admission, CH_4 start to dissociate on the available Rh crystallite metal sites when activation energy is provided. Dissociated products from CH_4 start to disintegrate the Rh metal crystallites little by little evidenced by the baseline decreasing. With temperature increasing, enough energy is provided to break Rh-Rh and Rh^0-O^{2-} bonds. CH_4 dissociated produces thus have the opportunities to contact with neighboring O species to form CO. Big crystallite particles of sintered catalyst retard the CH_4-assisted disintegration of Rh particles, thus need more energy, therefore CO formed later on sintered catalysts. It is easiest to form CO on aged catalysts with smallest particle size. Same reason, the formation of CO on Fresh catalyst is in between.

As the temperature is raised towards the ignition temperature under the reactant mixture, the oxidation state of the catalyst changes significantly. An oxidized rhodium state, Rh^{n+}, progressively forms as temperature is increased while Rh^+ and Rh^o decrease. In addition, a greater amount of Rh^{n+} is found when the oxygen concentration in the feed is higher. Thus, it is hypothesized that ignition of methane CPO on $2\%Rh/Al_2O_3$ is related to the accumulation of the Rh^{n+} state.

Conclusions

Study of the catalytic ignition of methane on Rh/Al_2O_3 using in situ IR provided a means to study the CPO reaction mechanism. The ignition temperature was found to be lowest on freshly reduced catalyst, highest on sintered catalyst and in between for aged catalyst. This trend is hypothesized to be due to the ease of methane activation on these three samples. In situ IR studies of these three catalysts during their interaction with methane found that methane dissociation (as judged by the appearance of CO in the IR spectrum) occurred at lower temperatures on the freshly reduced catalysts, followed by the aged catalysts and then the sintered catalyst. This may be caused by particle size: catalysts with the smallest Rh particle size had the lowest ignition temperature. It has also been shown that the ignition temperatures increased with decreased concentration of oxygen in the reactant mixture. This trend may be due to differences in the catalyst state. In-situ IR studies showed rhodium was progressively oxidized as the reaction temperature was increased, therefore, ignition of methane CPO on $2\% Rh/Al_2O_3$ may be related to the presence of oxidized Rh.

Acknowledgements

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