In Situ Infrared Study of the Catalytic Ignition of Methane on Pt/Al$_2$O$_3$

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Abstract

The ignition process of the catalytic partial oxidation of methane has been studied by diffuse reflectance infrared spectroscopy (DRIFTS) over Pt/Al$_2$O$_3$ catalyst in a freshly reduced (D_{Pt} = 1.8 nm), oxidized (D_{Pt} = 2.1 nm) and aged (D_{Pt} = 5.1 nm) state. The ignition temperature is found to change with the catalyst state following the order oxidized > freshly reduced > aged. Whatever the catalyst state it is shown that the surface is mainly covered by oxygen till ≈ 50 K below the ignition temperature. The ignition is linked to the desorption of the adsorbed oxygen species from the surface leaving sites for the methane adsorption. This is in agreement with the measurements of the heat of adsorption of oxygen on Pt in the literature where it is reported that the oxygen-metal bond strength is lower on bigger reduced particle.

Introduction

Catalytic partial oxidation (CPO) of alkanes at millisecond contact times has been found to be an efficient means for producing syngas [1,2]. In a millisecond contact time reactor, a pre-mixed fuel and oxygen mixture is flowed at high flow rates through a noble metal catalyst. The catalyst is heated until catalytic ignition occurs, at which time autothermal operation is possible. CPO could also be considered as a means for producing hydrogen in mobile applications for powering proton exchange membrane fuel cells (PEMFC) [3]. Of particular interest to this application is the dynamic behavior of the CPO reactor, as hydrogen would need to be produced on-demand due to problems related to its on-board storage. The process by which the catalyst is ignited is of special interest, since a fast light off would be required so that the automobile could be powered as soon as the ignition key was turned by supplying only a low degree of external preheating.

Catalytic ignition has been studied before in both the combustion and partial oxidation regimes [4-8]. Most studies have focused on accurately measuring the temperature at which either surface or surface-initiated gas phase ignition occurs. Mass spectrometry was usually used for monitoring gas phase species concentrations. There is a lack of information about how the surface species change as the temperature is raised towards the ignition temperature. This work uses in situ diffuse reflectance infrared spectroscopy (DRIFTS) to study the mechanism of the catalytic partial oxidation of methane on Pt/Al$_2$O$_3$ as the catalyst is ignited.

Experimental

A Pt/Al$_2$O$_3$ catalyst has been prepared by impregnating the support (γ-Al$_2$O$_3$ S$_{BET}$ = 80-120 m^2/g) with an aqueous solution of H$_2$PtCl$_6$, 3H$_2$O to yield a nominal metal loading of 10%.

After drying for 12h at room temperature and then for 24h at 383 K the solid was treated for 10h in O_2 at 773 K.

Prior to each experiment, the catalyst sample was pretreated in the DRIFT cell according to the following procedure: oxygen (T = 773K, t = 1h) → helium (T = 773K, t = 10 min) → H_2 (T = 773K, t = 1h) → helium (T = 773K, t = 10 min) → helium (room temperature). This resulted in a freshly reduced catalyst. Some reduced samples were further treated in oxygen at 773K for 1h, resulting in an oxidized catalyst. A number of successive oxidation-reduction-reaction cycles resulted in the so-called aged catalyst.

The average particle size of the freshly reduced, oxidized and aged catalysts was determined by means of a JEOJEM 2010F transmission electron microscope (TEM). The results are shown Table 1.

Table 1: Average Pt particle size for the different state of the 10% Pt/Al_2O_3 catalyst

Catalyst state	Particle size (nm)
Freshly reduced	1.8
Oxidized	2.1
Aged	5.1

For each experiment 0.03g of catalyst was placed into the ceramic cup of a commercial high-temperature high-pressure diffuse reflectance cell (Spectra-Tech) with ZnSe window. The ceramic cup, porous on the bottom, can be heated up to 1173 K and permits the flow of the gases through the sample. A Chromel-alumel thermocouple was inserted into the powdered sample and used to measure its temperature, while an external controller adjusted the power applied to the heater to maintain a desired temperature. The cell residing in a Nicolet NEXUS 870 infrared spectrophotometer bench with a liquid nitrogen cooled MCT detector was connected to a control panel which allowed to prepare and analyze gas mixture at atmospheric pressure.

Gases of commercial purity, N_2 (99.995%), CH_4 (99%) and O_2 (99.996%) were used without further purifications for experiments. N_2 was used as carrier gas. Flow rates in the range of 200 SCCM to 650 SCCM were used.

The experiments were performed according to the following procedure: after the pretreatment of the solid, mixtures of CH_4/N_2 for methane adsorption or $CH_4/O_2/N_2$ (2:1:2) for light-off experiments were introduced in the IR cell at 323 K and then the temperature was slowly increased (≈5 K/min) while IR spectra were periodically recorded. For the light-off experiments the catalyst ignition temperature was determined by the temperature where the thermocouple temperature increased rapidly beyond the controller set point.

Results and Discussion

1- Surface ignition temperature

The surface ignition temperature has been measured during the light-off experiments. The $CH_4/O_2/N_2$ mixture initially at 323 K and atmospheric pressure was continuously fed into the cell at a flow rate of 650 SCCM. The catalyst was heated up by increasing the temperature of the ceramic cup. The surface ignition temperature was then determined by the suddenly

rapid increase of the temperature. The ignition temperature was 567 K for the aged catalyst, 597 K for the freshly reduced catalyst and 623 K for the oxidized catalyst.

*2-Surface state of the catalyst before the ignition temperature*

a- Interaction of the catalyst with CH$_4$/N$_2$ mixture

The interaction of CH$_4$ with reduced and oxidized Pt/Al$_2$O$_3$ in the absence of gas-phase oxygen has been investigated in the 323-623 K range.

After admission of the mixture over the reduced catalyst (Figure 1) at 323 K, an IR band is observed at 2065 cm^{-1} ascribed to the linear CO species adsorbed on a reduced surface of Pt [9]. This IR band increases with exposure time while a broad weak IR band at 1830 cm^{-1} assigned to multibound CO species is progressively formed.

Increasing the temperature up to 623 K shows that the multibound CO species disappears because of its low heat of adsorption [10] while the IR band of the linear CO species is still present and has shifted to 2036 cm^{-1}. As no formation of carbon-containing reaction products have been observed on reduced non-supported catalysts when interacting with CH$_4$ [11], the involvement of oxygen sites of the support must be assumed.

An IR band at 1540 cm^{-1}, observed immediately after CH$_4$ admission at 323 K is ascribed to surface carbonate adsorbed on the Al$_2$O$_3$ support. Formate also adsorbed on the support, characterized by the IR band at 1590 cm^{-1} and 1460 cm^{-1} are progressively formed with time on stream. The intensity of these carbonaceous species increases with the increase of the temperature.
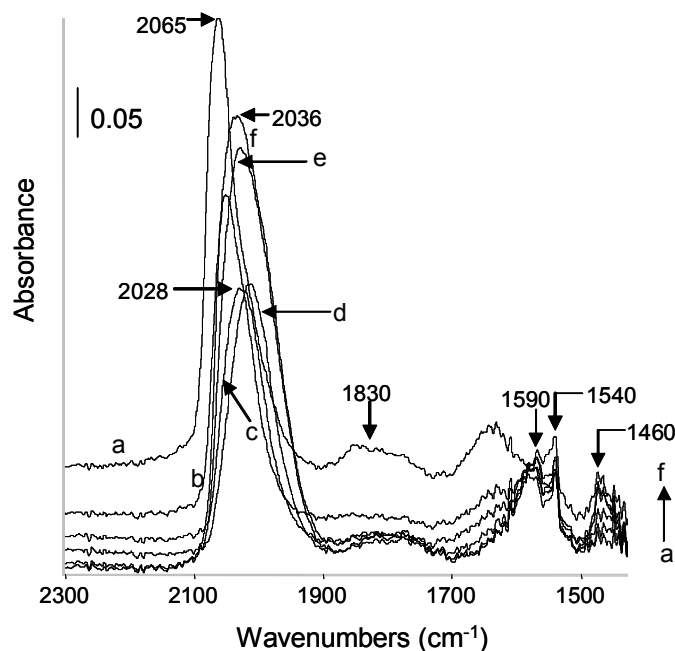
Figure 1: Evolution of the IR spectrum of the adsorbed species when interacting CH$_4$/N$_2$ with the fresh reduced catalyst (a) 323 K, (b) 418 K, (c) 463 K, (d) 503 K, (e) 543 K, (f) 623 K
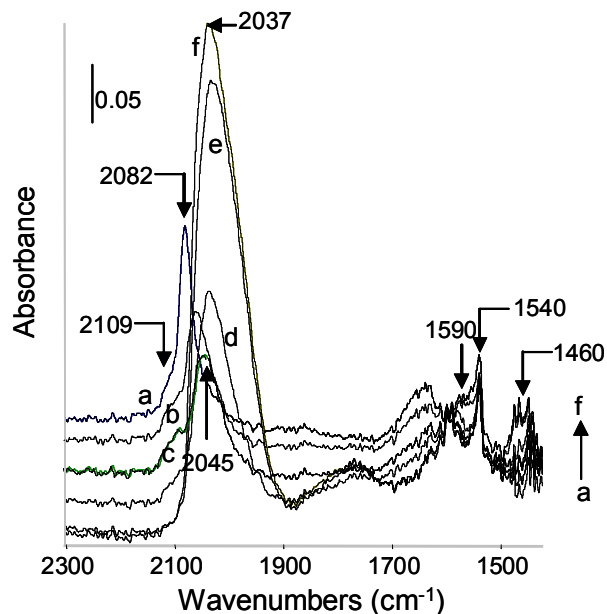
Figure 2: Evolution of the IR spectrum of the adsorbed species when interacting CH_4/N_2 with the oxidized catalyst (a) 318 K, (b) 388 K, (c) 428 K, (d) 473 K, (e) 558 K, (f) 600 K

Figure 2 shows the IR spectra of the adsorbed species when interacting CH_4 with the oxidized catalyst in the 323-600 K range. At 323 K, a weak IR band is observed at 2082 cm^{-1} assigned to the linear adsorbed CO species while it was observed at 2065 cm^{-1} with a higher intensity for the reduced catalyst as seen above. This is due to the presence of the oxygen on the surface **[12]** coming from the oxidative treatment. Moreover a shoulder is detected at 2109 cm^{-1} ascribed to linear CO species adsorbed on Pt^{2+} **[13]**. This indicates that some Pt^0 sites were converted into Pt^{2+} during the oxidative treatment at 773 K.

Increasing the temperature to 600 K shows an increase of the intensity of the IR band of the linear CO species along with a shift to 2037 cm^{-1} as on the reduced catalyst while the disappearance of the Pt^{2+} sites is observed. Apparently, in the absence of gas-phase oxygen, CH_4 reduces the surface catalyst.

As on the reduced catalyst, adsorbed carbonate and formate on the support are progressively formed with time on stream and increase with the rise of the temperature.

b- Interaction of the catalyst with $CH_4/O_2/N_2$

Figure 3 shows the IR spectra of adsorbed species during the light-off experiment performed on a freshly reduced catalyst from 323 K to 597 K, the temperature of the ignition of the surface reaction. It can be observed that a weak IR band is immediately formed at 2078 cm^{-1} and increases with time on stream at 323 K. The position of the IR band shows that adsorbed oxygen is immediately present on the surface **[12]** and even on such surface state methane could adsorb and form the linear adsorbed CO species. Burch and Loader **[14],** pulsing a $CH_4/O_2/N_2$ mixture ($0.2 < \dfrac{CH_4}{O_2} < 5$) over a reduced 2% Pt/Al_2O_3 catalyst at 573 K, also showed by measuring the carbon balance that CH_4 was first adsorbed on the surface
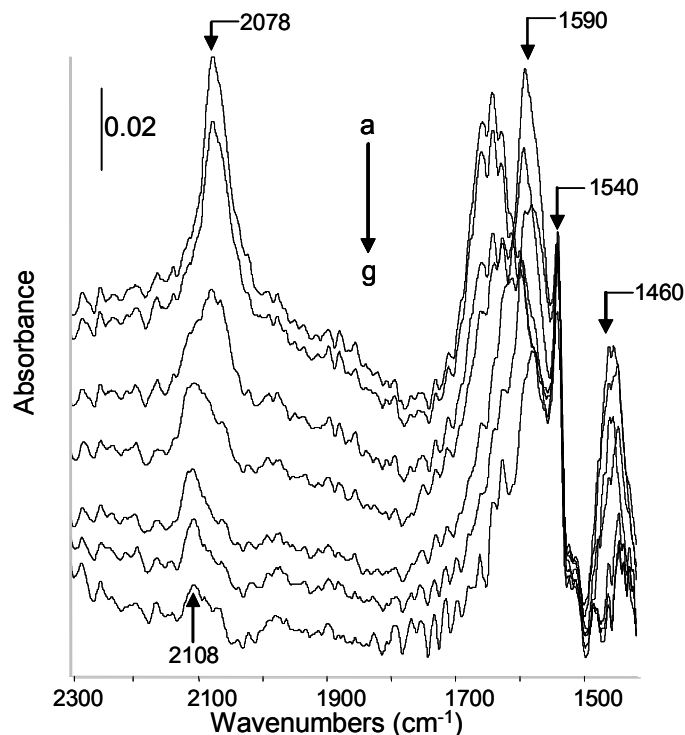
Figure 3: Evolution of the IR spectrum of the adsorbed species when interacting $CH_4/O_2/N_2$ with the freshly reduced catalyst (a) 323 K, (b) 343 K, (c) 378 K, (d) 418 K, (e) 498 K, (f) 553 K, (g) 590 K

without reacting with oxygen. Adsorbed carbonaceous species formate (IR bands at 1590 cm^{-1} and 1460 cm^{-1}) and carbonate (IR band at 1540 cm^{-1}), are also observed on the support.

With an increase in temperature, the IR band of the linear CO species at 2078 cm^{-1} decreases without any significant shift and disappears at 430 K while the band at 2108 cm^{-1} ascribed to linear CO species adsorbed on Pt^{2+} [13] appears at 373 K and remains constant up to 500 K. Above that temperature the intensity of this band decreases and almost disappears at 597 K. Thus in the presence of gas-phase oxygen, adsorbed oxygen is mainly covering the surface of the catalyst and it has converted some Pt^0 into Pt^{2+}.

The intensity of the IR bands of carbonate and formate increase up to 500 K and then starts to decrease but these adsorbed species are still present at 600 K. Gas-phase CO_2 is detected from 520 K. This could be due to the desorption of adsorbed species from the support, but the gas-phase CO_2 could also indicate that surface reaction is occurring even below the ignition temperature, as seen by Schwiedernoch et al. [8]. Using a mass spectrometer to analyze the gas-phase composition during a light-off experiment on a Rh/Alumina catalyst, they observed that a small amount of methane and oxygen was consumed above 600 K leading to some water and carbon dioxide formation.

On the aged and oxidized catalysts at 323 K under N_2, before the introduction of the $CH_4/O_2/N_2$ mixture, a weak IR band at 2045 cm^{-1} has been observed, which is ascribed to adsorbed carbon monoxide formed after the ignition temperature of previous light off experiments. Even after the oxidation-reduction treatment and the oxidative treatment at 773 K for the aged and oxidized catalysts respectively, the adsorbed CO still remains. Paal et al. [15] have also found that even after treatment at 773 K some carbon-containing species are left on

a platinum catalyst. The IR band of the remaining adsorbed CO is almost constant from 323 K to the ignition temperature during the interaction of the catalysts with the reactants mixture. As seen above on the freshly reduced catalyst the IR band of CO formed is weak and so it cannot be said if in the presence of gas-phase oxygen the decomposition of methane on a surface on which O_2 and CO are initially present is permitted or prevented. However carbonate and formate were formed on the support and displayed similar trends as on the fresh reduced catalyst. Gas phase CO_2 was detected from 483 K and 573 K for the aged and oxidized catalysts respectively indicating that surface reaction is occurring below the ignition temperature.

3- Oxygen-metal bond strength

Up to this point it can be said that whatever the catalyst state the surface is mainly covered by adsorbed oxygen until the ignition temperature in the presence of the $CH_4/O_2/N_2$ mixture. While in the absence of gas-phase O_2 the methane can decompose to form CO and can even reduce an oxidized surface, it is seen that in the presence of gas-phase O_2 the adsorption and decomposition of CH_4 is blocked until $\approx$ 50 K below the ignition temperature (except for the freshly reduced catalyst where decomposition is also initially observed at low temperature).

The ignition of the surface reaction of the partial oxidation of methane is then linked to the available adsorption sites for methane. Veser and Schmidt **[4]** proposed a model based on a Langmuir-Hinshelwood mechanism with competitive adsorption of the reactant gases to predict the catalytic ignition temperature of the oxidation of alkanes. The model showed that the oxygen desorption was mainly controlling the surface ignition. In their numerical study of the transient behavior of the partial oxidation of methane Schwiedernoch et al. **[8]** also considered that the adsorption-desorption equilibrium for oxygen was slowly shifting towards desorption with the increase of temperature leading to more and more vacancies on the surface.

With this model, catalysts with stronger oxygen-metal adsorption strengths will have a higher ignition temperature. Therefore, our results imply that the oxygen-platinum adsorption strength is strongest in the order: oxidized (T= 623 K) > freshly reduced (T= 597 K) > aged (T= 567 K). According to the particle size measurement shown in table 1 it seems that the bond strength of adsorbed oxygen is lower for the bigger particle size obtained with the aged catalyst. Briot et al. **[16]** have found by calorimetric measurement that the heat of adsorption of adsorbed oxygen on the aged catalyst with a particle size of 12 nm was lower than that of the fresh catalyst with an average particle diameter of 2 nm. As for the difference observed between the oxidized and freshly reduced catalyst, although the particle size is almost the same, Drozdov et al. **[17]** have found from the measurement of the heat of adsorption of oxygen, that oxygen is bound more weakly on platinum metal than on the bulk oxide. Thus the oxygen-metal bond strength is a key factor in the ignition of the catalytic partial oxidation of methane.

Conclusion

In a DRIFT cell the ignition temperature of the catalytic partial oxidation of methane using a $CH_4/O_2/N_2$ mixture (2:1:2) at a flow rate of 650 SCCM has been measured using a 10% Pt/Al_2O_3 catalyst in different surface states. The results obtained were 597 K, 623 K and 567 K on the freshly reduced (D_{Pt} = 1.8 nm), oxidized (D_{Pt} = 2.1 nm) and aged (D_{Pt} = 5.1 nm) catalysts respectively. The DRIFT study showed that adsorbed oxygen was mainly covering the surface until the ignition temperature, as suggested in the literature. The ignition temperature is thought to be linked to the desorption of the adsorbed oxygen from the surface, which is necessary to allow methane adsorption. Our results are in agreement with oxygen heat adsorption measurements in the literature where the oxygen-metal bond strength is lower for bigger particles of Pt and higher for bulk Pt oxide from oxidized treatment at high temperature.

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