Improving sulphur tolerance of methane combustion catalysts
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1. Introduction
The catalytic partial oxidation of methane (POM) to syngas (CO and H₂) is of great practical importance in utilisation of the world’s abundant natural gas reserves. The syngas can then be converted to clean fuels such as sulphur-free diesel or gasoline and oxygenates through Fischer-Tropsch and methanol synthesis processes. Furthermore, POM has been recently proposed as a preliminary conversion stage for hybrid gas turbine catalytic burners. In this case a fuel-rich/air mixture is first catalytically converted to both partial and total oxidation products which are subsequently oxidized with excess air to complete the combustion in a homogeneous flame [1]. Many catalysts have been investigated for the POM to syngas, and Rh-based catalysts have been shown to be the most active and selective towards CO and H₂ [2, 3]. However, the presence of sulphur containing compounds naturally occurring in natural gas or added as odorants necessary for safety reasons can result in a sulphur concentration totalling approximately 10 ppm, which can adversely affect the catalytic performance. Sulphur chemisorbs onto and reacts with the active catalytic sites, thus preventing reactant access. In addition sulphation of the support component can also occur, which consequently will have an impact on the metal-support interaction. Indeed sulphation of the support is implicated as the main cause of deactivation for steam reforming over supported rhodium catalysts [4]. Similar mechanism has also been proposed for the partial oxidation of methane over alumina supported Rh catalyst where hydroxyl groups on the support are involved in methane conversion [5,6]. Although Al₂O₃ is the most widely used commercial catalyst support for catalytic partial and total oxidations, it has the drawback of accumulating large amounts of S which can lead to catalyst deactivation. Silica (SiO₂) type supports, however, do not readily form stable sulphates and are more S tolerant. The aim of the present work is to investigate the influence of the support material on the sulphur poisoning tolerance of rhodium catalysts for the partial oxidation of methane.

2. Experimental
2.1. Catalyst Preparation
Rhodium (1 wt.%) catalysts supported on 3% La-stabilised γ-Al₂O₃ (type SCFa140-L3, from Sasol) and 10% SiO₂-Al₂O₃ (Siralox type 10-360, from Sasol) materials were prepared by the incipient wetness impregnation method using an aqueous solution of Rh(NO₃)₃ (Aldrich). The samples were dried at 120°C for 8 h and calcined in static air at 550 °C for 2 h (referred to as fresh). To investigate the effect of thermal ageing, samples were further calcined in air at 800 °C for 4 h. Monolith samples were prepared by applying washcoats onto cordierite monoliths (Corning 400cpsi) using a dip-coating procedure already described elsewhere [1]. The powder of Rh/La-Al₂O₃ and Rh/SiO₂-Al₂O₃ to be deposited on the monolith, was dispersed in water, giving a slurry using Disperal or Ludox (10% wt. solids), respectively, as a binder. Monolith samples of 9 mm in length with 9 open channels were loaded with approximately 25% w./w. of catalyst and calcined in air at 550°C for 2 h.

2.2. Catalyst characterisation
The BET surface area of the catalysts was determined by N₂ adsorption at 77 K, using a Quantachrome Autosorb 1-C. The surface areas of the catalysts fresh and aged, respectively,
are 150m$^2$/g and 133m$^2$/g for 1 wt.% Rh/La-Al$_2$O$_3$, 312m$^2$/g and 259m$^2$/g for 1 wt.% Rh/SiO$_2$-Al$_2$O$_3$. In this study the use of H$_2$ chemisorption to determine metal dispersion was found not to be suitable, particularly in the case of SiO$_2$-Al$_2$O$_3$ supported Rh catalysts: due to the occurrence of intense spillover phenomena, the experimental H/Rh values are much larger than those expected for true H$_2$ adsorption on the metal.

TPR experiments were carried out with Micrometrics TPD/TPR 2900 apparatus equipped with a TCD detector. The sample (100 mg) was heated at 10 °C min$^{-1}$ between room temperature and 900 °C in flowing 2%H$_2$/Ar mixture (25 cm$^3$ min$^{-1}$). The exit gas from the reactor was passed through cold KOH trap to remove any water and CO$_2$.

FTIR experiments were performed on a Perkin Elmer Spectrum GX spectrometer with a spectral resolution of 4 cm$^{-1}$. A 15-30 mg amount of sieved catalyst, <100 mesh, was pressed into self-supporting disk and placed in the IR cell. The disk was treated in the following way: (i) outgassed at 300 °C for 2hrs and then cooled to room temperature where background spectra of the sample were recorded; (ii) reduced at 300 °C with a 2% H$_2$/N$_2$ mixture for 2 hrs, after which time the cell was cooled down to room temperature and evacuated; (iii) CO was adsorbed at room temperature (2%CO/N$_2$ mix) for 30 minutes and IR spectra were recorded after evacuation. Spectra were also recorded under reaction conditions by dosing 100cm$^3$ min$^{-1}$ of a CH$_4$/O$_2$/Ar mixture (2/1/97) at 300, 400 and 500 °C, respectively.

To examine the effects of sulphur in the reaction mixture, 40 ppm SO$_2$ was added to the reactor feed. Before the SO$_2$ was added, the partial oxidation reactions were allowed to (30 min) stabilise at 500 °C.

Catalytic tests were carried out on monoliths, pseudo-isothermally, to compare the intrinsic activity of the monolith catalysts under controlled fluid dynamics. Monoliths were positioned inside quartz reactor (d = 10mm), externally heated by a three zone electrical tubular furnace. The central monolith channel was blocked for catalyst wall temperature measurement with a K-type thermocouples. Standard feed composition was CH$_4$/O$_2$/N$_2$ = 1/0.6/98.4, at GHSV 3.5 x 10$^5$ h$^{-1}$ based on monolith volume, with a corresponding F/W = 1.76 x 10$^6$ Ncc/(g·h).

3. Results and discussion

TPR experiments were conducted to investigate the reducibility of rhodium oxide supported on La stabilised alumina (SCFa140-L3) and Siralox (SiO$_2$-Al$_2$O$_3$) materials. Fig. 1 illustrates the reduction profiles of the fresh and thermally aged catalysts. When fresh both catalysts show two peak maxima at 125 °C and 270 °C for 1%Rh/La-Al$_2$O$_3$ and 130 °C and 335 °C for 1%Rh/SiO$_2$-Al$_2$O$_3$ which would indicate the existence of two different states of oxidised rhodium on the sample. The lower temperature TPR peak (125 °C) has previously been attributed [7, 8] to the reduction of rhodium oxide particles having no interaction with the support, while the higher temperature peak which accounts for significantly more hydrogen uptake could be related to the reduction of Rh which has interacted strongly with the alumina.

The hydrogen consumption for the La-Al$_2$O$_3$ supported Rh catalyst corresponds to the full reduction of Rh$^{3+}$ to Rh$^0$. Interestingly the TPR profile of the fresh Rh/SiO$_2$-Al$_2$O$_3$ catalyst passes through a negative between 400 and 500 °C, probably caused by some H$_2$ desorption. The experiment was repeated twice and the same profile was obtained. The
desorption of hydrogen from the sample could explain the very high H/Rh ratio obtained for the Rh/SiO$_2$-Al$_2$O$_3$ catalyst during H$_2$ chemisorption experiments. This finding agrees fairly well with the results obtained from the study of H$_2$ chemisorption on a ceria-supported Rhodium catalyst [9] where it was shown that at room temperature, in the presence of highly dispersed Rh, ceria chemisorbs large amounts of hydrogen by the spillover process. At higher temperature the reverse reaction i.e., the so-called back-spillover process can occur. Thermal aging at 800°C for 4 hrs in air produces Rh species which are more difficult to reduce, thereby causing a broadening of the reduction peak and a shift in the peak maximum to much higher temperature. A large decrease in the amount of surface rhodium in Rh/Al$_2$O$_3$ catalyst has been reported after high temperature aging in an oxidising atmosphere due to a strong interaction between Rh$_2$O$_3$ and the support that can lead to severe catalyst deactivation [7, 8]. However, the integration of the TPR profile of the thermally aged Rh/La-Al$_2$O$_3$ catalyst again corresponds to the full reduction of accessible Rh$_2$O$_3$, which accounts essentially for all Rh$^{3+}$ in the sample. This would then argue against any significant sintering of Rh or deep penetration of Rh into the alumina under the conditions of this study. This could be due to the presence of La$^{3+}$ in the γ-Al$_2$O$_3$ which can block the defect sites on the surface of the alumina thus reducing the interaction of Rh with the support [8, 10]. The aged Rh/SiO$_2$-Al$_2$O$_3$ catalyst showed a similar TPR trace, indicating comparable metal interaction with the support, which also led to the disappearance of the spillover effect.

In order to investigate the extent of sulphation, the fresh catalysts were S poisoned in air at low temperatures (300 °C) for 2 h using 100 ppm SO$_2$, during which the catalysts were exposed to approximately 14 mg S per gram of catalyst. The amount of S accumulated on the catalyst was then measured by TPR (Fig. 2), using the following stoichiometric equation:

$$\text{SO}_4^{2-} + 8\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{O}^{2-} + 3\text{H}_2\text{O}$$

It is assumed that almost all of the hydrogen is consumed in the reduction of sulphate and only minimal amount of H$_2$ is used in the reduction of the metal. Table 1 illustrates the amount of hydrogen consumed and S stored on the two catalysts. The Siralox supported Rh catalyst stores significantly less S than the corresponding alumina supported catalyst. The Siralox material is an amorphous silica-doped alumina, the surface of which is enriched with silica [11], hence making the catalyst less susceptible to S poisoning. The TPR profile of the S aged Rh/SiO$_2$-Al$_2$O$_3$ catalyst shows two distinct peaks centered at 220 and 535°C. The peak at 220°C could be assigned to the reduction of sulphate species on the Rh surface, whilst the peak at 535 °C can be attributed to the reduction of bulk Al$_2$(SO$_4$)$_3$. However, on Rh/La-Al$_2$O$_3$ catalyst, in addition to the low and high temperature reduction peaks, there is a distinct shoulder at approximately 330 °C, which could be ascribed to the reduction of sulphate species held at the Rh-Al$_2$O$_3$ interface.

Preliminary experiments were carried out to compare the fresh catalytic activity of the two monolith samples (Fig. 3). Under pseudo-isothermal conditions, the Rh/SiO$_2$-Al$_2$O$_3$ (Siralox)
monolith sample shows slightly lower activity for methane conversion compared to the Rh/La-Al2O3 (SCF) monolith sample. Although both samples show comparable selectivity to CO and CO2, the Siralox sample has a lower selectivity for H2. The effect of addition of SO2 in to the reaction feed, on the catalytic performance and the ease of regeneration of catalysts after their exposure to SO2 is currently under investigation.

Since the two catalysts have comparable activities for methane conversion, FTIR experiments were carried out to investigate and characterise the nature of the metal species on the two catalysts both before and after exposures to gas phase SO2. The FT-IR spectrum of CO adsorbed at room temperature on a fresh Rh/SiO2-Al2O3 catalyst pre-reduced in situ under H2 at 300 °C is shown in Fig. 4a. The dominant features of this spectrum are the doublet bands at 2089 and 2016 cm\(^{-1}\) corresponding to gem-dicarbonyl species on isolated Rh\(^{+}\) species [13]. Following CO evacuation at 300 °C (Fig. 4b), the sample was exposed to a flow of simulated POM feed (CH4/O2/Ar = 2/1/97, volume ratio) at 300, 400 and 500 °C, respectively. The reaction at each temperature was allowed to stabilize (30 min.) prior to recording the IR spectra. The occurrence of the partial oxidation reaction at higher temperature was verified by the decrease in the intensity of the methyl band at 3016 cm\(^{-1}\) and a concomitant increase in the adsorbed CO band at 2017 cm\(^{-1}\) as the temperature was increased (Fig. 4 c-e). Similar results were obtained for the fresh La-Al2O3 supported Rh catalyst (not shown). In order to examine the influence of SO2 in the reaction mixture, the partial oxidation reaction of methane was first allowed to reach a steady state at 500°C (30 min.), before the addition of 40 ppm of SO2 in to the feed stream. The rate of deactivation of the catalysts in the presence of SO2 for the partial oxidation reaction of methane was then measured as a function of time (Fig. 5). The detrimental effect of SO2 in the reaction mixture on the catalytic activity of Rh/La-Al2O3 was confirmed by the increase in the intensity of the methyl band at 3016 cm\(^{-1}\) and a simultaneous decrease in the adsorbed CO band at 2009 cm\(^{-1}\) with increasing exposure to gas phase SO2 (Fig. 5 b-j). The loss in the catalytic activity for the Rh/SiO2-Al2O3 catalyst was also confirmed by the decrease in the intensity of the adsorbed CO band at 2015 cm\(^{-1}\) with increasing exposure to gas phase SO2 (not shown). However, unlike the alumina supported Rh catalyst, there was no evident change in the intensity of the methyl band at 3016 cm\(^{-1}\). In conjunction with FTIR spectroscopy, CO adsorption at room temperature was used as a probe to investigate the nature of the metal species present on the catalyst. Fig. 6-1 and Fig. 6-2 illustrate the CO spectra obtained at room temperature following various reactions over a fresh Rh/La-Al2O3 and Rh/SiO2-Al2O3 catalysts, respectively.
The interaction of CO at room temperature following reduction at 300°C, results in the formation of gem-dicarbonyl CO species (doublet bands: ~2090 and 2015 cm⁻¹) associated with isolated Rh⁺ sites (Fig. 6-1a). The CO spectrum obtained at room temperature, after exposure to the reaction mixture at 500°C (Fig. 6-1b), is very similar to the freshly reduced sample (Fig. 6-1a), with the exception of the band at 2172 cm⁻¹ which is assigned to the gas phase CO [12]. The permanence of this band (2172 cm⁻¹), already observed prior to evacuating the IR cell, would imply an insufficient time of the evacuation process. However, exposures to the reaction mixture containing SO₂ at 500 °C, results in a significant decrease in the intensity of the doublet bands formed following the adsorption of CO at room temperature (Fig. 6-Ic). The decrease in intensity is likely to be due to the blockage of Rh sites by sulphur. The effect of regeneration of S poisoned catalyst by reduction at 500°C for 1 h was also investigated. The spectrum of CO adsorbed at room temperature following reduction at 500 °C (Fig. 6-1d) shows the appearance of a new band at ~ 2060 cm⁻¹, assigned to linear CO species [12] adsorbed on Rh⁰ sites. The decrease in the intensity of the doublet bands, following reduction at 500 °C, may suggest a decrease in the concentration of isolated Rh⁺ sites, formed as a result of CO-assisted oxidation of metallic Rh. Hence reductions at high temperatures (≥500 °C) could minimise the influence of CO-assisted oxidation of metallic Rh particles. The spectra of CO adsorbed at room temperature over a fresh Rh/SiO₂-Al₂O₃ catalyst (Fig 6-II) following various reactions are similar to those obtained over the La-Al₂O₃ supported Rh catalyst (Fig. 6-I), with the exception that the intensity of the doublet bands does not decrease following exposures to the SO₂ reaction mixture (Fig 6-IIC), indicating no evidence of sulphur poisoning of the sites for CO adsorption. On the contrary, under these conditions, it appears that the catalyst has more sites for CO adsorption, since the bands at ~2095 and 2020 cm⁻¹, associated with isolated Rh⁺ sites, are more intense than the freshly reduced catalyst (Fig. 6-Ia). The most plausible explanation for the absence of S poisoning based on the CO adsorption studies could be due to the regeneration of the catalyst during cool down in Ar from 500 °C to room temperature following exposure to the SO₂ reaction mixture. Although both SiO₂-Al₂O₃ and La-Al₂O₃ supported Rh catalysts were exposed to similar amounts of SO₂ (40ppm SO₂ for 115 min.), it appears that once the SO₂ addition is stopped the Rh/SiO₂-Al₂O₃ catalyst can quickly recover its activity, indicating that the adsorbed sulphur species are weakly held compared to the Rh/La-Al₂O₃ catalyst.
Based on the results of FT-IR spectroscopic characterisation, as well as TPR and CO adsorption studies on the reaction of partial oxidation of methane to syngas over SiO$_2$-Al$_2$O$_3$ and La-Al$_2$O$_3$ supported Rh catalysts, it has been demonstrated that both the extent of catalyst sulphation and recovery are highly dependent on the nature of the support material. Preliminary results indicate that by dispersing Rh on a SiO$_2$-Al$_2$O$_3$ (Siralox) type material, the catalyst stores significantly less sulphur than the corresponding Al$_2$O$_3$ support. Also based on the FTIR studies it is shown that the Rh catalysts can be more easily regenerated when dispersed on a non sulphating supports such as Siralox. Thus, the extent of sulphation and the stability of the sulphate are important factors influencing the desulphation process. The intrinsic activity of fresh Rh catalyst is only slightly affected by the presence of a more S tolerant support.

5. References