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The Effect of Support on Sulphur Tolerance of Rh Based Catalysts for Methane Partial Oxidation

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Abstract The presence of sulphur containing compounds, naturally occurring in natural gas or added as odorants, can adversely affect the performance of noble metals based catalysts for the partial oxidation of methane to syngas. In this paper the effect of SO_2 addition on the catalytic partial oxidation of methane was investigated on Rh (1 wt.%) catalysts prepared by incipient wetness impregnation method on two different commercially available high temperature γ-alumina supports stabilized either with 10% SiO_2 or 3% La_2O_3. Based on the results of catalytic activity measurements and in-situ FT-IR spectroscopic characterisation, as well as TPR/TPD studies, it has been shown that the presence of sulphur can severely suppress the formation of synthesis gas by inhibiting the reforming reactions during the catalytic partial oxidation of methane. The results also demonstrated that the support plays a crucial role in the partial oxidation reaction. In the presence of a sulphating support such as La_2O_3–Al_2O_3 the partial oxidation reaction was much less inhibited than a less sulphating support such as SiO_2–Al_2O_3. The sulphating support acts as a sulphur storage reservoir, which minimises the poison from adsorbing on or near the active Rh sites where reactions take place.

Keywords Catalytic partial oxidation · Methane · Synthesis gas · Rhodium · Sulphur poisoning

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1 Introduction

The catalytic partial oxidation of methane (CPO) to syngas (CO and H_2) 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, CPO 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 methane CPO to syngas, and Rh-based catalysts have been shown to be the most active and selective towards CO and H_2 [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 [4]. 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 [5]. Based on the kinetic model for steam reforming over rhodium catalysts, it has been demonstrated that the turnover frequency is proportional to the specific perimeter of the metal particles, i.e. the total length of the metal-support interface per unit surface area. The kinetics can be explained by a bi-functional reaction mechanism [5] in which the hydrocarbon is activated by the rhodium, while water adsorbs on the support to form surface hydroxyl species. Sulphation of the support inhibits steam reforming by preventing (i) the formation of hydroxyl species adjacent to the metal-support interface and (ii) migration of more remote hydroxyl species to the interface where they can interact with adsorbed hydrocarbon [6]. 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 [7, 8].

Although desulphurisation units can be used to significantly reduce the sulphur content in the feed, its inclusion increases the complexity, size and cost of the fuel processing system. Therefore it will be more desirable to develop catalysts that are intrinsically sulphur tolerant and are not readily poisoned by the amounts of sulphur commonly found in fuels such as natural gas.

Whilst alumina is the most widely used commercial catalyst support for catalytic partial and total oxidations, due to its mechanical stability, moderately high surface area and good metal stabilising effect, it has the drawback of accumulating large amounts of S which can lead to catalyst deactivation. Silica 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_2O_3-stabilised γ-Al_2O_3 and 10% SiO_2–Al_2O_3 materials (respectively type SCFa140-L3 and type Siralox 10-360 from Sasol) were prepared by the incipient wetness impregnation method using an aqueous solution of Rh$(NO_3)_3$ (Aldrich). The samples (hereafter labelled as R-LA and R-SA) were dried at 120 °C for 8 h and calcined in air at 550 °C for 2 h (referred to as fresh); part of the samples was further calcined in air at 800 °C for 4 h to investigate the effect of thermal ageing. In order to investigate and compare the extent of sulphation, the fresh catalysts were S treated by flowing 100 ppm SO_2 in air at 300 °C for 2 h, during which the catalysts were exposed to approximately 14 mg S per gram of catalyst.

2.2 Catalyst Characterisation

The actual Rh content in each catalyst was quantitatively determined by inductively coupled plasma spectrometry on a Agilent 7500 ICP-MS instrument, after MW-assisted dissolution of samples in nitric/hydrochloric acid solution. The BET surface area of the catalysts was determined by N_2 adsorption at 77 K with a Quantachrome Autosorb 1-C which was also used for hydrogen chemisorption experiments. Prior to H_2 adsorption measurement, the sample was heated under He at 120 °C for 30 min and then at 400 °C under a flow of pure H_2. After 2 h at this temperature, the sample was evacuated and cooled under vacuum to 40 °C where H_2 adsorption was performed. In this study the use of H_2 chemisorption to determine metal dispersion was found not to be suitable, particularly in the case of R-SA sample: due to the occurrence of spillover phenomena, the experimental H/Rh values are much larger than those expected for true H_2 adsorption on the metal (Table 1).

Temperature programmed reductions (TPR) experiments were carried out with Micrometrics TPD/TPR 2900 apparatus equipped with a TCD detector on both fresh and S-poisoned catalysts. 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 basic KOH trap to remove any water, CO_2 and acidic sulphur compounds such as H_2S or SO_2.

Temperature programmed desorption (TPD) experiments were performed using 200 mg of sulphated catalyst. The sample was heated from ambient to 1,000 °C in an He stream (25 cm^3 min^{-1}) at 10 °C min^{-1}. The reaction products were monitored with a quadrupole mass spectrometer (QMS 200—Pfeiffer).

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 equipped with a ZnSe window connected to a vacuum pump or gas lines. The disk was treated in the following way: (i) outgassed at 300 °C for 2 h and then cooled to room

Table 1 Characteristics of La_2O_3 and SiO_2 stabilised alumina supported Rh catalysts

Name	Commercial support	Stabilizer (w/w%)	Rh loading (w/w%)		Surface area (m^2/g)		Dispersion (%)
	Sasol		Nominal	ICP	550 °C	800 °C	Fresh
R-LA	SCFa140-L3	3% La_2O_3	1.0	0.96	150	133	61
R-SA	Siralox 10-360	10% SiO_2	1.0	1.05	312	259	118

temperature where background spectra of the sample were recorded; (ii) reduced at 300 °C with a 2% H_2/N_2 mixture for 2 h, 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 min and IR spectra were recorded after evacuation. Spectra were also recorded under reaction conditions by dosing 100 $cm^3\ min^{-1}$ 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 powder samples (250–300 μm) in a fixed bed quartz flow reactor using a standard feed of composition $CH_4/O_2/N_2 = 1/0.6/98.4$, at GHSV = $7.5 \times 10^4\ h^{-1}$ and total $P = 1.2$ atm. During temperature programmed experiments, the reactor was externally heated under feed mixture from 300 to 800 °C at 10 °C min^{-1}. The sample temperature was measured using a K-type thermocouple inserted in the catalytic bed. The activity measurements over fresh samples were repeated twice in order to allow for catalyst activation under reaction at high temperature.

Exit gases passed through a $CaCl_2$ water trap and analyzed continuously for H_2, CO, CO_2, CH_4 concentrations by a Hartmann & Braun Advance Optima analyser. Carbon balance was always closed within ±4%; O_2 conversion was estimated by closing mass balances for H and O.

To examine the effects of sulphur in the reaction mixture, 100 ppm or 20 ppm SO_2 was added to the reactor feed at 500 °C for 1 h. In fact it has been recently reported that S-poisoning impact on CPO performance of Rh-based catalysts is not dependent on the type of sulphur species introduced (i.e. thiophene, sulphur dioxide, benzothiophene, dibenzothiophene) but only on their quantity [9].

Before adding the SO_2, the partial oxidation reactions were allowed to stabilise 15 min at 500 °C. Following sulphation at 500 °C under reaction mixture, the sample was cooled down on bypass and the light-off ramp was repeated in order to determine the extent of catalyst deactivation. The sample was then cooled and the temperature programmed activity measurement was repeated in order to determine the extent of catalyst recovery from sulphur poisoning.

3 Results and Discussion

3.1 Characterisation

Table 1 illustrates catalysts denomination, metal loading, total surface areas and their dispersions after calcination at 550 °C.

The actual noble metal loading is close to the nominal one for both catalysts. Reduction of surface area is observed upon calcinations at 800 °C for both samples although it is proportionally less pronounced for R-LA due to the stronger inhibiting effect of surface lanthanum oxide towards γ-alumina phase transition. Nevertheless the R-SA catalyst still retained a specific surface area which was almost twice that of R-LA sample following thermal ageing at 800 °C. The high metal dispersion values obtained (>100%) for R-SA sample is related to the spillover phenomenon, as discussed in the Experimental section.

TPR experiments were conducted to investigate the reducibility of rhodium oxide supported on La_2O_3 or SiO_2 stabilised aluminas. Figure 1 illustrates the reduction profiles of the fresh and thermally aged catalysts while the corresponding amount of hydrogen taken up by the sample is reported in Table 2.

Fresh catalysts calcined at 550 °C show a shoulder and a peak maximum at 125 and 270 °C for R-LA and 130 and 335 °C for R-SA, 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 [10, 11] to the reduction of rhodium oxide particles having no interaction with the support, while the higher temperature peak, accounting for significantly more

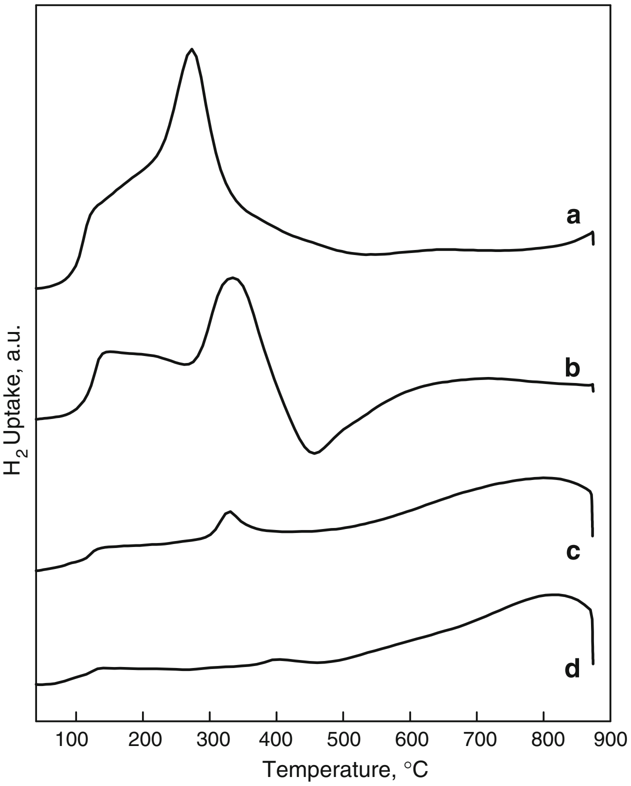


Fig. 1 H_2-TPR traces of R-LA (**a**,**c**) and R-SA (**b**, **d**) catalysts after calcination in air at 550 °C (**a**, **b**) and thermal ageing in air at 800 °C (**c**, **d**)

Table 2 TPR analysis of the R-LA and R-SA samples before and after S ageing (100 ppm SO_2 in air at 300 °C for 2 h)

Catalyst	H_2 uptake mmoles H_2/g		H_2 uptake—S aged mmoles H_2/g	
	550 °C	800 °C	Up to 310 °C	Total
R-LA	0.16	0.15	0.15	1.0
R-SA	0.13	0.11	0.15	0.6

hydrogen uptake, could be related to the reduction of Rh which has interacted strongly with the alumina.

The hydrogen consumption for the R-LA catalyst corresponds to the full reduction of Rh^{3+} to Rh^0. Interestingly the TPR profile of the fresh R-SA 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 R-SA 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 [12] 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 h 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 (around 800 °C for both samples). The increase in the reduction temperature is possibly caused by the formation of surface spinel type $Rh(AlO_2)y$ species, which are reduced at high temperatures [13]. A large decrease in the amount of surface rhodium in Rh/Al_2O_3 catalyst has been reported after high temperature ageing in an oxidising atmosphere due to a strong interaction between Rh_2O_3 and the support that can lead to severe catalyst deactivation [10, 11]. However, the integration of the TPR profile of the thermally aged catalysts reveals only a limited decrease of accessible Rh_2O_3 in the sample (Table 2). This would then argue against any significant deep penetration of Rh into the alumina under the conditions of this study. In particular for the R-LA catalyst this could be due to the presence of La^{3+} in the γ-Al_2O_3 which can block the defect sites in the surface of the alumina thus reducing the interaction of Rh with the support [11, 14]. The aged R-SA catalyst showed a very similar TPR trace, indicating comparable metal interaction with the support, which also led to the disappearance of the spillover effect. In addition the aged R-SA sample showed a slightly more pronounced decrease in the amount of hydrogen uptake with respect to the fresh catalyst.

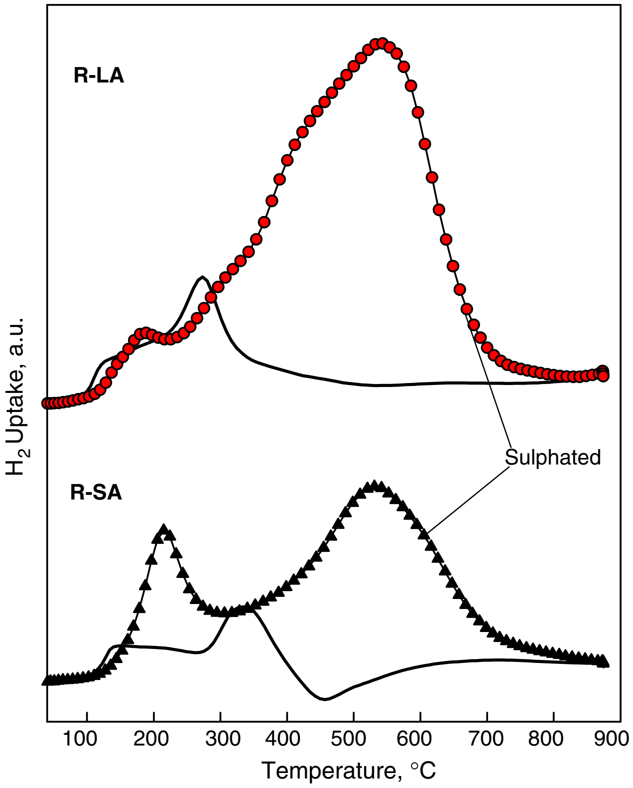


Fig. 2 H_2-TPR profiles of S aged Rh catalysts compared with TPR profiles of the corresponding fresh samples

Figure 2 shows a comparison of the H_2 uptake profiles for the fresh and sulphated catalysts and Table 2 illustrates a summary of the amount of hydrogen consumed before and after S ageing.

For sulphated R-LA sample it can be seen that the initial part of the reduction profile closely follows the trace of the fresh oxidised sample up to approximately 300 °C, indicating that Rh_2O_3 species are largely unaffected. Indeed integration of the H_2 uptake profile up to this temperature accounts for the total reduction of Rh^{+3} to Rh^0 (Table 2). The remaining H_2 consumption is characterized by an intense peak centered at 535 °C with a shoulder at 400 °C, which can be attributed to the reduction of bulk $Al_2(SO_4)_3$ species which is completed by 800 °C. H_2-TPR of sulphated Rh supported on pure γ-alumina (not shown) displayed a similar profile. In fact the reduction of lanthanum sulphates/oxysulphates which may be formed during sulphation would occur in the same temperature range [15], and could be therefore masked by the larger contribution of the $Al_2(SO_4)_3$ reduction.

The TPR profile of the S aged R-SA catalyst shows two distinct peaks of comparable maximum values respectively centered at 220 and 535 °C. The first peak can be assigned to the reduction of Rh^{+3} species since H_2 uptake up to 300 °C accounts once again for the total reduction of Rh^{+3} to metallic Rh^0 (Table 2). However the presence of a single and well defined peak centered at 220 °C instead of a more complex profile with a maximum at 330 °C recorded on the fresh oxidized catalyst, suggests the presence of Rh^{+3} sulphated species rather than only Rh_2O_3. The formation of $Rh_2(SO_4)_3$ species has been reported for the SiO_2 supported Rh sample treated in SO_2/air mixtures [16].

With regards to the second peak at 535 °C ascribed to the reduction of bulk $Al_2(SO_4)_3$, the R-SA catalyst stores approximately half as much S than the corresponding R-LA sample (Table 2). The Siralox material used as a support in this study is an amorphous silica-doped alumina, the surface of which is enriched with silica [17], hence reducing the amount of surface alumina which is susceptible to sulphation. Under oxidizing conditions sulphur dioxide is readily oxidized over the noble metal to form sulphur trioxide [16], which can then spill-over to the carrier and further react with alumina to form aluminum sulphate species, thus restoring the Rh_2O_3 sites. However in the case of pure silica [16] or silica type materials the extent of sulphur storage is significantly reduced.

He-TPD experiments were also carried out to compare desorption temperature for the S aged R-LA and R-SA catalysts: the corresponding Mass Spectrometry (MS) signals are shown in Fig. 3. The only detected MS-signal which was directly attributed to desorption of sulphur compounds was that of SO_2 (ms 64), whereas no signal for H_2S (ms 34) or SO_3 (ms 80) was detected. The same mass of catalyst was used in all experiments so the larger peak areas indicate larger amount of desorbing species per unit mass. On the R-LA catalyst SO_2 evolution profile is characterized by a small peak at approximately 600 °C and a sharp peak at ca. 950 °C. It is of interest to note that the intense SO_2 peak at ca. 950 °C is accompanied by a simultaneous large desorption of O_2 which can be attributed to the decomposition of bulk $Al_2(SO_4)_3$. On the other hand, the SO_2 desorption peak at 600 °C, accompanied by a much lower O_2 desorption, can be assigned to the decomposition of sulphate species (SO_x) on the Rh surface or at the metal support interface which can result in the oxidation of Rh metal particles. Similar TPD profiles were also obtained on Rh/Al_2O_3 only catalyst, thus excluding any major contribution from the La_2O_3 stabilizer.

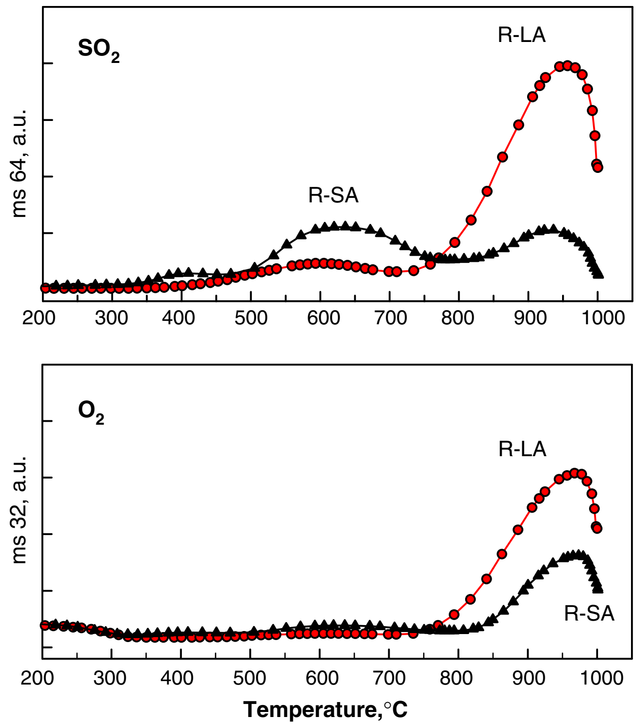


Fig. 3 Mass Spec. traces for SO_2 and O_2 during He-TPD on Rh catalysts following S ageing (100 ppm SO_2 in air at 300 °C)

The R-SA catalyst stores significantly less sulphur than the corresponding R-LA sample: the two main SO_2 desorption peaks have similar areas and a further small peak appears around 400 °C, implying that a significant reduction in the formation of bulk $Al_2(SO_4)_3$ due to the presence of surface SiO_2 is accompanied by a larger accumulation of SO_x species on or close to the noble metal, which is in good agreement with the results obtained in TPR experiments.

FTIR experiments were also carried out to investigate the effect of SO_2 addition to the reaction mixture on Rh sites. The FT-IR spectrum of CO adsorbed at room temperature on a fresh R-LA catalyst pre-reduced in situ under H_2 at 300 °C is shown in Fig. 4a. The dominant features of this spectrum are the doublet bands at 2,089 and 2,016 cm^{-1} corresponding to gem-dicarbonyl species on isolated Rh atoms [18] generated by the reaction of CO

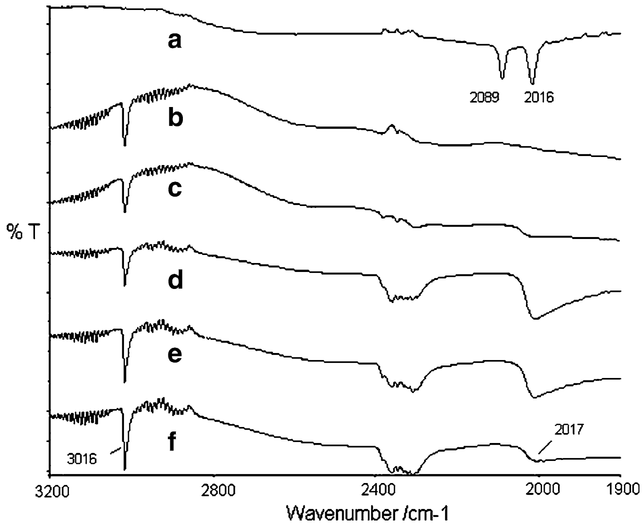


Fig. 4 FT-IR spectra of fresh R-LA: (**a**) CO adsorption at room temperature after pre-reduction with H_2 at 300 °C. FT-IR spectra under CPO reaction ($CH_4/O_2/Ar$ = 2/1/97) at (**b**) 300 °C, (**c**) 400 °C, (**d**) 500 °C and during progressive exposure to 40 ppm SO_2 under reaction at 500 °C: (e) 60 min, (f) 120 min

with Rh particles and hydroxyl groups of the support. The presence of these bands is related to highly dispersed Rh metal particles on the catalyst surface [18]. Similar bands were also observed for the R-SA sample, in agreement with other authors who did not detect any shift of gem-dicarbonyl bands for differently supported Rh samples [19].

Following CO evacuation at 300 °C, the sample was exposed to a flow of simulated CPO feed ($CH_4/O_2/Ar = 2/1/97$, 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 T $\geq$400 °C was verified by the decrease in the intensity of the methyl band at 3,016 cm^{-1} and a concomitant increase in the adsorbed CO band at 2,017 cm^{-1} assigned to carbonyl hydride on reduced Rh [20] (Fig. 4b–d). Similar results were also obtained for the R-SA catalyst (not shown).

The rate of deactivation of the catalysts in the presence of 40 ppm SO_2 in the feed stream was then measured at 500 °C as a function of time on stream (Fig. 4e, f). The detrimental effect of SO_2 in the reaction mixture on the catalytic activity of R-LA started to appear after approximately 50 min and was evident after 120 min as confirmed by the increase in the intensity of the methyl band at 3,016 cm^{-1} and a simultaneous decrease in the adsorbed CO band at 2,017 cm^{-1} with increasing exposure to gas phase SO_2. The rate of loss in the intensity of adsorbed CO band on the R-SA catalyst (not shown) was however much faster (started after about 30 min) indicating a lower tolerance of Rh to sulphur poisoning when supported on a less sulphating support. However, the presence of sulphate species, characterized by bands in the range 1,045–1,360 cm^{-1} [21] could not be detected, either due to low surface concentration and/or to limited sensitivity of the DTGS (Deuterated TriGlycerine Sulphate) detector used in this study.

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. Figure 5 illustrates the CO spectra obtained at room temperature over a fresh R-LA catalyst following: (a) reduction at 300 °C, (b) partial oxidation test at 500 °C and (c) partial oxidation test (for 2 h) at 500 °C in the presence of 40 ppm SO_2.

The CO spectrum obtained at room temperature, after exposure to the reaction mixture at 500 °C (Fig. 5b), is quite similar to the freshly reduced sample (Fig. 5a) showing the typical gem-dicarbonyl CO species associated with highly dispersed metallic Rh sites. The higher intensity of the gem-dicarbonyl bands is most probably caused by further reduction of Rh particles during the partial oxidation reaction at 500 °C, which agrees with the enhancement in activity reported on Rh catalysts after exposure to high temperature CPO reaction conditions, also observed on our catalysts following the first ramp during the temperature programmed reaction tests (see *activity measurements*). The band at 2,172 cm^{-1} is assigned to the gas phase CO [22], which was already observed prior to evacuating the IR cell; this would imply an insufficient time of the evacuation process. However, exposure to the reaction mixture containing SO_2 at 500 °C, resulted in a significant decrease in the intensity of the doublet bands of adsorbed CO (Fig. 5c). The decrease in intensity could either be due to the blockage or the oxidation of Rh sites by sulphur. We tend to favour the latter, since during the activity measurement following sulphation the initial part of the catalytic activity was very similar to that of the fresh oxidised sample.

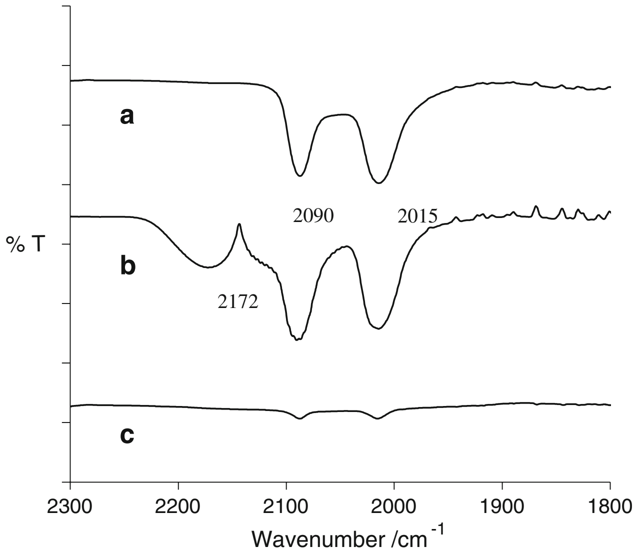


Fig. 5 FT-IR spectra of CO adsorption at room temperature over R-SA catalyst following: (**a**) reduction of fresh catalyst at 300 °C, (**b**) reaction with) at 500 °C for 30 min ($CH_4/O_2/Ar = 2/1/97$), (**c**) SO_2 ageing (40 ppm) under reaction at 500 °C for 120 min

The spectra of CO adsorbed at room temperature over a R-SA catalyst (not shown) followed a similar behaviour to those obtained over the R-LA catalyst. Both catalysts showed some residual Rh^0 species on their surface which are responsible for the low CPO activity measured at the end of the sulphation period over both samples. The presence of metallic Rh species could be related to a partial regeneration of the catalyst during cool down in Ar from 500 °C to room temperature following exposure to the SO_2 reaction mixture.

3.2 Activity Measurement

Figure 6 illustrates the effect of addition of 20 ppm SO_2 at 500 °C for 1 h (exposures to ca. 4 mg S/g Cat.) in the reaction mixture on methane concentration as a function of time on stream over R-LA and R-SA catalysts following sample activation at 800 °C under reaction mixture. The partial oxidation reaction of methane was allowed to reach a steady state at 500 °C (15 min) before the addition of 20 ppm SO_2 into the feed stream. Before the addition of SO_2 both samples show similar methane (75–77%) and complete oxygen conversion levels; the corresponding measured selectivities to H_2 and CO are above 95% and 75% respectively, on both catalysts, with a H_2 to CO molar ratio of about 2.6. This ratio is lower than the equilibrium value at 500 °C (=4.7), which indirectly indicates the absence of solid carbon formation predicted by thermodynamics up to 575 °C; moreover it suggests local hot spots formation in the catalyst bed caused by the exotherm of the reaction since the equilibrium value for H_2/CO is about 2.7 at 550 °C.

The addition of 20 ppm of SO_2 into the feed caused a small rise in measured bed temperature (ca. 10 °C) and after approximately 30 min ($\sim$2 mg S/g) in the presence of SO_2 the CH_4 conversion for the R-SA sample began to decrease indicating that the catalytic partial oxidation reaction was being inhibited by sulphur. On the contrary on R-LA catalyst there was no significant deactivation or change in syngas production during the 1 h period in the presence of 20 ppm SO_2. This apparent support effect can be explained by the higher sulphur storage capacity of La_2O_3–Al_2O_3 support, which retains the sulphur thus delaying the poisoning of the Rh surface particles as confirmed by the TPR/TPD measurements.

With regards to R-SA catalyst, it is very interesting to note that the decrease in CH_4 conversion was not accompanied by a decline in oxygen conversion which, on the other hand, remained complete (Fig. 6) during the entire experiment. In terms of products distribution this implies a progressive decline in H_2 and CO selectivities, as shown in Fig. 7, in favour of total oxidation products (CO_2 and H_2O) which also explains the rise in temperature observed during the experiment. Furthermore, the simultaneous decrease in CO and H_2 selectivity is not consistent with water-gas shift being inhibited but indicates the following: the presence of sulphur species on R-SA would cause the oxidation of Rh active sites (Rh^{+3} possibly as sulphates or sulphites) thus preventing the formation of synthesis gas by most probably inhibiting the indirect reaction pathway which proceeds through the reforming of residual methane with water (and CO_2).

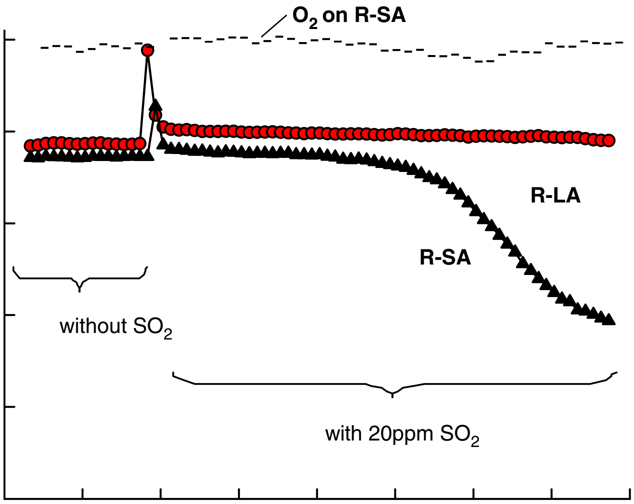


Fig. 6 Effect of addition of 20 ppm SO_2 in the reaction mixture at 500 °C on CH_4 conversion as a function of time on stream

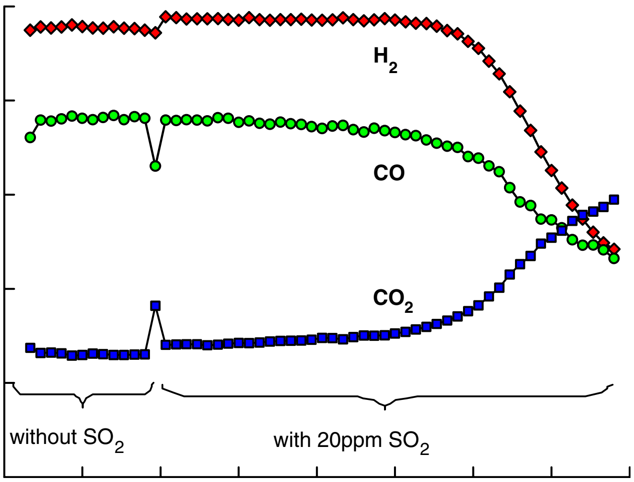
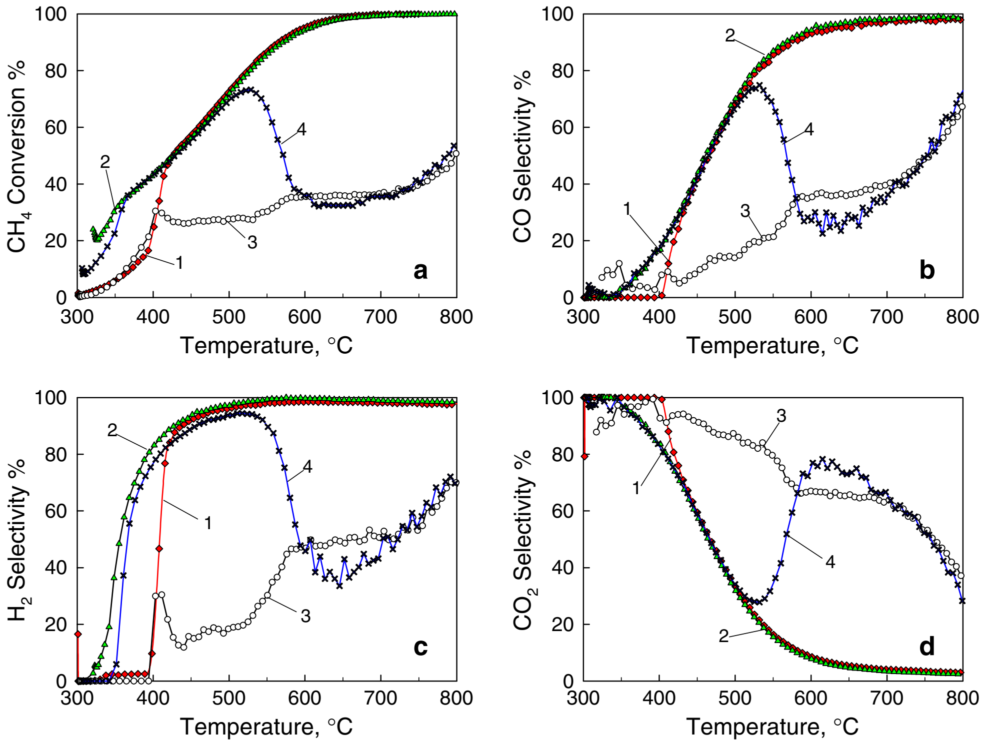


Fig. 7 Effect of SO_2 addition on the performance of R-SA during the addition of 20 ppm SO_2 at 500 °C as a function of time

In order to investigate the extent of catalyst deactivation and regeneration following severe sulphur poisoning, the catalysts were subjected to temperature programmed reaction cycles from 300 up to 800 °C at 10 °C min^{-1} before and after exposures to 100 ppm SO_2 in the reaction mixture for 1 h at 500 °C, where the catalysts were exposed to about 20 mg S/g Cat.

Figure 8a illustrates methane conversion as a function of catalyst temperature over R-LA catalyst. During the initial ramp over the fresh oxidised catalyst, methane conversion increased slowly with temperature up to about 400 °C where there was a sudden light-off, followed by a more steady increase in methane conversion (Ramp 1). The corresponding selectivity plots for Ramp 1 in Fig. 8b–d clearly indicate that the first catalytic event at low temperature on the oxidized Rh (Rh_2O_3) catalyst was the total oxidation of methane, accompanied by an exotherm and high production of CO_2 (and water) at the beginning of the test. The steep increase in methane conversion occurs when some of the metal oxide is reduced to Rh metal thus allowing methane to dissociate more readily on the catalyst surface and to start forming partial oxidation products

Fig. 8 Methane conversion and selectivities for CO, H_2 and CO_2 as a function of temperature over R-LA catalyst: (1) fresh; (2) activated in ramp 1; (3) after sulphation in reaction at 500 °C for 1 h with 100 ppm SO_2; (4) after regeneration in ramp 3



instead of combustion. Therefore, when the catalyst was exposed to the reaction condition at high temperatures (800 °C), reduced or partially reduced Rh sites were obtained which resulted in higher methane conversion at lower temperatures, as seen in Ramp 2—Fig. 8a. Indeed light-off was achieved as soon as the reaction mixture was dosed to the catalytic bed at 300 °C, with a relatively rapid transient formation of total combustion products (until molecular oxygen was completely consumed) and a progressive shift towards H_2 and CO products with increasing temperature, as predicted by equilibrium.

During sulphation at 500 °C under reaction mixture with 100 ppm SO_2 (not shown), also the R-LA sample underwent marked decrease in methane conversion as opposed to what was reported in Fig. 6 during exposure to only 20 ppm SO_2. The activity began to drop after exposures to approximately 6 mg S/g Cat. and this was accompanied by a shift in products towards CO_2 and H_2O at the expense of partial oxidation products. Following harsh sulphation at 500 °C the sample was cooled down and the light-off was repeated, Ramp 3—Fig. 8a. Even though the catalytic activity is severely affected, it is interesting to note that the initial part of the light-off curve is very similar to that obtained during the first ramp over the fresh oxidised sample (Ramp 1), showing a distinct ignition temperature at about 400 °C. This is likely to be due to the oxidation of metallic Rh particles by SO_2 during sulphation which delays the methane dissociation.

However, major differences between the fresh and sulphur poisoned catalyst arose following the light-off temperature where, unlike the fresh sample, the poisoned catalyst was no longer able to convert methane to partial oxidation products, even after all the molecular oxygen in the feed was consumed. During Ramp 3 methane conversion increased only marginally in the temperature range of up to 720 °C showing two distinct plateau regions: the first at approximately 430 °C extending up to approximately 530 °C, from where on methane conversion increases slowly, probably due to temperature activated desorption of S close to or directly bonded to Rh active sites; the second in the range between 570 and 720 °C where a new poisoning effect appears which blocks CH_4 conversion at 35% irrespective of a temperature increase of up to 150 °C. Above this temperature methane conversion began to increase steadily but at 800 °C the catalyst only recovered 50% of its initial methane conversion, most likely caused by the slow decomposition of stable $Al_2(SO_4)_3$.

After Ramp 3 to 800 °C, the sample was cooled and the activity measurement repeated in order to determine the extent of catalyst recovery from sulphur poisoning—Ramp 4, Fig. 8a. The catalyst almost completely regained all its initial low temperature activity (similar to Ramp 2) up to 530 °C, before showing a rapid decline in methane conversion, which reaches a plateau of 35% at approximately 600 up to 720 °C before increasing again at higher temperatures. Interestingly the corresponding selectivity profiles for CO and H_2 (Fig. 8b, c—Ramp 4) follow an identical pattern to that of methane conversion: at approximately 530 °C there is a sharp fall in the selectivity for H_2 and CO (mirrored by the CO_2 trace) before increasing again at higher temperatures (>700 °C).

Since the catalyst recovered all its initial low temperature activity following regeneration (Ramp 3), this indicates that surface Rh sites regained their initial reduced active state and that they were free from any sulphur poisoning. Thus, the sudden decline in methane conversion at 530 °C, which is accompanied by a decrease in selectivity for both CO and H_2, must be caused by the presence of residual sulphur on the support which can migrate back onto the Rh metal sites and thereby poisoning the partial oxidation reaction. It is also worth noting that the above temperature (530 °C) corresponds to the peak maximum temperature obtained during the TPR profile of the SO_2 aged R-LA (and R-SA) catalyst which was assigned to the reduction of bulk $Al_2(SO_4)_3$. The changes in H_2 and CO formation over the catalyst are most likely to be due to poisoning of steam (and dry) reforming reaction which is known to occur on supported Rh catalysts [5]. Indeed even in the presence of unconverted methane, water and CO_2, no further syngas is produced regardless of any temperature increase. Similar results were also obtained on Rh/Al_2O_3 only sample (not shown), thus ruling out any major contribution from the La_2O_3 stabilizer. The above results are in agreement with the latest findings on Rh-Ce coated monoliths operated under self-sustained high temperature conditions [23].

Figure 9a–d shows the methane conversion and the corresponding selectivities for CO, CO_2 and H_2 over R-SA catalyst before and after sulphur poisoning. Following catalyst conditioning (Ramp 2) methane conversion plots for R-LA and R-SA samples are superimposed. Furthermore after sulphation the methane conversion profile for the R-SA sample follows a very similar trend to that of R-LA sample with the exception that it has a slightly higher light-off temperature (Ramp 3). However, during Ramp 4 it appeared that the R-SA catalyst did not recover its low temperature activity as much as the R-LA sample, following the regeneration step. This is because the SiO_2–Al_2O_3 support can not act as an effective S trap, as confirmed by TPR/TPD. As a result, sites on Rh will become the major targets for selective chemisorption by sulphur species which will lead to higher concentrations of SO_x species on Rh as well as sites surrounding the precious metal: this results in a more rapid and severe deactivation in the low temperature region than for the La_2O_3–Al_2O_3 supported material. Nevertheless, above the temperature decomposition threshold of the rhodium sulphate species, which depends on the specific conditions, the situation is somehow reverted with the R-SA catalyst which is able to produce more syn-gas than the R-LA sample. This is shown in Fig. 9b, c by the higher values of CO and H_2 selectivities measured above 550 °C during both ramp 3 and ramp 4 on R-SA sample with respect to the corresponding values for R-LA (Fig. 8b, c). Moreover, the CO selectivity for R-SA sample >550 °C shows a further

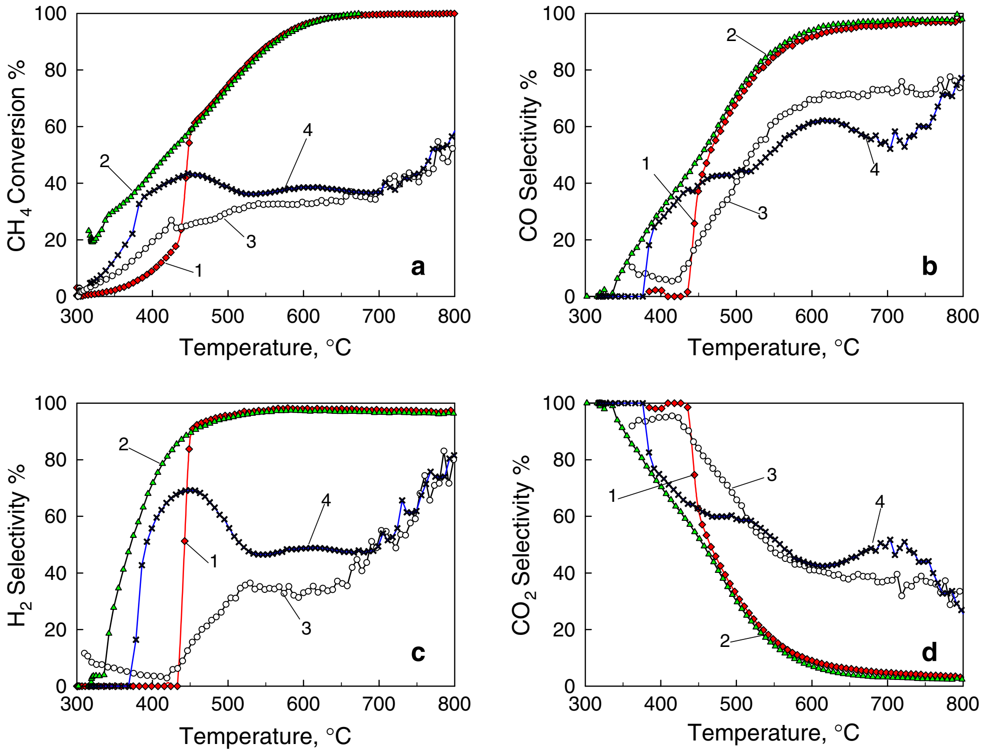


Fig. 9 Methane conversion and selectivities for CO, H_2 and CO_2 as a function of temperature over R-SA catalyst: (1) fresh, (2) activated in ramp 1; (3) after sulphation in reaction at 500 °C—1 h with 100 ppm SO_2; (4) after regeneration in ramp 3

relative maximum centred at approximately 600 °C mirrored by the CO_2 trace (Fig. 9d). On the whole, the lower amount of sulphur stored as $Al_2(SO_4)_3$ on R-SA seems to cause a slightly lower inhibition on the catalytic partial oxidation reaction at higher temperatures (500–700 °C).

Overall the results illustrate that on the less-sulphating support, S accumulates to a greater extent directly on and around the active Rh sites where reactions take place [4], whilst a sulphating support such as La_2O_3–Al_2O_3 can act (temporarily) as a sink for sulphur species thus limiting and delaying its accumulation on the Rh sites. Temperature programmed reaction cycles demonstrated that Rh sites can be almost completely regenerated at relatively low temperatures; however, as temperature increases above a threshold level, sulphur species stored on the support surrounding the Rh particles can spill back onto the metal thus re-oxidizing it and consequently inhibiting the catalytic partial oxidation reaction. Most affected appears to be the indirect reaction path to syn-gas involving steam reforming of residual methane.

4 Conclusions

The effect of SO_2 addition on the performance of methane catalytic partial oxidation reaction was investigated over Rh catalysts supported on commercial γ-Al_2O_3 stabilized by either La_2O_3 or SiO_2. The extent of catalyst sulphation was also found to be highly dependant on the nature of the support material. In the presence of a sulphating support such as La_2O_3–Al_2O_3, the partial oxidation reaction was much less inhibited than a less sulphating support such as SiO_2–Al_2O_3. The sulphating support acts as a sulphur getter and keeps the sulphur away from the active metal sites and this minimises the build-up of S on or close to the active Rh sites where reactions take place. TPR/TPD experiments illustrated that, although the SiO_2–Al_2O_3 supported Rh catalyst stores significantly less bulk aluminium sulphate species due to the presence of surface silica, the catalyst accumulates more S on or close to the precious metal. During methane CPO reaction, sulphur poisoning appears to mostly affect the indirect reaction path to syn-gas involving steam reforming of residual methane thus shifting products distribution towards CO_2 and water. Once sulphur is removed from the feed, Rh sites can be almost completely regenerated at relatively low temperatures. However, as temperature increases above a threshold level of 530 °C, sulphur species stored on the support, as $Al_2(SO_4)_3$ surrounding the Rh sites, can spill back onto the metal thus re-oxidizing it and consequently inhibiting the CPO reaction in favour of the total oxidation of methane.

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