Sulphur inhibition on the catalytic partial oxidation of methane over Rh-based monolith catalysts

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ABSTRACT

The effect of sulphur addition (2–58 ppm) during the catalytic partial oxidation (CPO) of methane was investigated on Rh-based honeycomb catalysts tested under self-sustained high temperature condition. Both steady state and transient operation of the CPO reactor were investigated particularly with regard to poisoning/regeneration cycles and low temperature light-off phase. The analysis of products distribution in the effluent and a heat balance demonstrates that sulphur reversibly adsorbed on Rh selectively inhibits the steam reforming (SR) reaction path to syngas production. The extent of SR inhibition is greater when operating in air and diminishes at lower CH_4/O_2 feed ratios. The poisoning effect has been shown to be independent from the type of sulphur bearing compound and only indirectly affected by the type of catalyst support (La_2O_3 or SiO_2 stabilized alumina) through the value of Rh dispersion.

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1. Introduction

The depletion of worldwide reserves of crude oil has resulted in an increased interest in the use of natural gas to meet the world's energy demand. Even though the world has large deposits of natural gas, most of this is located in remote areas and consequently it must be transported across vast distances to reach its markets [1]. Conversion of methane to more useful and easily transportable liquid fuels is therefore of high interest. The catalytic partial oxidation (CPO) of methane over precious metal catalyst has been shown to be an attractive way to obtain syngas (CO and H_2) which can be converted to clean fuels such as sulphur-free diesel or gasoline by Fischer–Tropsch synthesis [1–3]. Moreover the production of H_2 rich gas streams from commercial hydrocarbon fuels by CPO or autothermal reforming (ATR) is of great interest for high temperature fuel cell applications [4–11].

Furthermore, CPO of various hydrocarbons has been proposed as a preliminary conversion stage for advanced combustion systems such as hybrid gas turbine catalytic burners [12,13]. In this case a fuel-rich/air mixture is first catalytically converted to partial oxidation products which are subsequently burnt with excess air to complete the combustion in a relatively cold and very

stable homogeneous flame, allowing strong reduction of NO_x emissions [12].

A number of catalysts have been tested for the CPO of hydrocarbons from methane up to diesel and jet-fuels and Rh-based catalysts have shown the highest activity and selectivity to syngas [1,14]. However, the presence of sulphur bearing compounds naturally occurring in the fuel, or added as odorants to pipe-line natural gas (approximately up to 10 ppm), can have a detrimental effect on the CPO activity. The adverse impact of sulphur compounds on catalytic performance is well known [15,16] and is the subject of much current research, particularly in the case of (autothermal) steam reforming of liquid fuels [4–11] and automotive catalysts [17,18]. However, studies on the effect of sulphur during the CPO of methane over Rh-based catalysts have so far remained scarce, as recently [19] pointed out by the group of L.D. Schmidt, who investigated the impact and features of poisoning by CH_3SH on Rh–Ce coated foam monoliths operated at short contact time. They found a marked negative effect on CH_4 conversion and H_2 selectivity by even small amounts of sulphur, mainly attributed to a partially reversible inhibition of the steam reforming reaction. Moreover, it was shown that Pt has greater tolerance than Rh–Ce to sulphur poisoning [19].

Recently we have reported results on the effect of SO_2 addition on the CPO of methane in the low to moderate temperature regime (300–800 °C) over Rh catalysts supported on La_2O_3 or SiO_2 stabilized γ-Al_2O_3 [20]: the presence of sulphur strongly inhibits

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the formation of syngas, by suppressing the reforming reactions normally active during CPO. The extent of catalyst poisoning was also found to be highly dependant on the nature of the support material [20].

In this work we set out to investigate the effects of sulphur addition during the CPO of methane at short contact times and self-sustained high temperatures over Rh catalysts supported on either La_2O_3–Al_2O_3 or SiO_2–Al_2O_3 coated monolith samples. Individual effects of feed ratio, nitrogen dilution and addition of two different sulphur surrogates such as SO_2 and H_2S will be discussed with regards to both steady state and transient operation of the CPO reactor during poisoning/regeneration cycles or low temperature light-off phase.

2. Experimental

2.1. Catalyst preparation

Commercial honeycomb monoliths with straight, parallel channels of roughly square section (cordierite, 600 cpsi by NGK) were cut in the shape of disks of 17 mm diameter and 10 mm long; a layer of stabilized γ-Al_2O_3 with nominal average thickness of 20 μm was firmly anchored onto the walls of the honeycomb channels by a modified dip-coating procedure [13]. The washcoat was made of either 3% La_2O_3-stabilized γ-Al_2O_3 or 10% SiO_2–Al_2O_3 (respectively type SCFa140-L3 and type Siralox 10-360 from Sasol). Rh was finally deposited onto washcoated monoliths by the incipient wetness impregnation method using an aqueous solution of Rh $(NO_3)_3$ (Aldrich) [13]; target loading of precious metal was ~0.75% (w/w) (monolithic substrate excluded). Reference powder catalysts with same composition were prepared by incipient wetness impregnations of the γ-Al_2O_3 powders used as washcoat for the monoliths. All the catalysts were calcined in air at 550 °C for 3 h.

2.2. Catalyst characterization

Actual metal content was quantitatively determined on selected fresh and used catalysts by inductively coupled plasma spectrometry (ICP) on an Agilent 7500 ICP-MS instrument, after microwave-assisted digestion of samples in nitric/hydrochloric acid solution.

BET specific surface area of samples, evaluated by N_2 adsorption at 77 K using a Quantachrome Autosorb 1-C after degassing under vacuum at 150 °C, was assigned only to the active washcoat layer (SSA of honeycomb substrate $\leq$1 m^2/g).

2.3. Catalyst testing

The catalytic honeycombs were stacked between two mullite foam monoliths (45 ppi, L = 12 mm) as heat shields and placed in a quartz tube inserted in an electric furnace that was used for pre-heating the feed mixture. Reactor temperatures were measured by means of K-type thermocouples (d = 0.5 mm) placed in the middle of the central channel of the catalyst, in close contact with the solid, as well as in the gas upstream and downstream of heat shields. Further details on the experimental setup were already reported elsewhere [13,21].

High-purity gases (CH_4, O_2, N_2, H_2S 206 ppm in N_2 and SO_2 185 ppm in N_2) calibrated via 5 Brooks 5850-series mass-flow controllers were pre-mixed and fed to the reactor at gas hourly space velocity (GHSV) comprised between 5 and 8×10^4 h^{-1} (standard conditions on the basis of honeycomb volume) corresponding to residence times as low as 14 ms at the average reactor temperature of 900 °C. Methane catalytic partial oxidation tests were run under self-sustained pseudo-adiabatic conditions at fixed pre-heating (250 °C) and an overall pressure of P = 1.2 bar,

either using simulated air as oxidant, or oxygen with N_2 added to obtain a fixed dilution level (10 or 20 vol.%) of the feed. The catalytic monoliths were tested after stabilisation upon exposure to standard reacting conditions.

The impact of sulphur addition on the catalytic performance was studied at CH_4/O_2 feed ratios in the range of 1.6–2 under both transient and steady state conditions. The sulphur level was varied between 2 and 58 ppm on a molar basis with respect to the total flow of gases by partially substituting the N_2 flow in the feed with an equal flow of H_2S or SO_2 in N_2 mixtures.

Catalytic light-off temperatures were determined by ramping-up the external furnace from 200 °C under flow conditions at CH_4/O_2 = 1.8 with air, at different sulphur levels (H_2S from 0 to 20 ppm vol.) over fresh, S-poisoned and regenerated (under reaction) catalysts.

Methane conversion, yields and selectivities to CO and H_2 were calculated according to the definitions:

$$x_{CH_4} = 100\left(1 - \frac{CH_4^{OUT}}{CH_4^{OUT} + CO_2^{OUT} + CO^{OUT}}\right)$$

$$Y_{CO} = 100\left(\frac{CO^{OUT}}{CH_4^{OUT} + CO_2^{OUT} + CO^{OUT}}\right), \qquad S_{CO} = 100\left(\frac{Y_{CO}}{x_{CH_4}}\right)$$

$$Y_{H_2} = \frac{100}{2}\left(\frac{H_2^{OUT}}{CH_4^{OUT} + CO_2^{OUT} + CO^{OUT}}\right), \qquad S_{H_2} = 100 \times 2\left(\frac{Y_{H_2}}{x_{CH_4}}\right)$$

based on the exit dry-gas mol fractions of CO, CO_2, CH_4 and H_2 independently measured by a continuous analyser with cross-sensitivity correction (ABB Advance Optima). No other hydrocarbons except from methane were detected in the products, whereas O_2 was always completely converted (TCD-GC analysis). Carbon and hydrogen balances were always closed within ±1.5% and ±3.5%, respectively. Sulphur species were not directly measured but preliminary TGA analysis excluded any significant sulphur capture effect by materials placed in the reactor before the catalyst (i.e. mullite and SiC foams) under representative operating conditions.

Thermodynamic equilibrium calculations were performed using CHEMKIN 4.1.1 software [22] excluding carbon formation on the catalysts.

3. Results and discussion

Table 1 illustrates catalysts denomination, metal loading, total surface areas and Rh dispersions measured by CO chemisorption after H_2 reduction at 800 °C. The commercial γ-aluminas stabilized either with La_2O_3 or SiO_2 are characterized by a specific surface area of 140 and 360 m^2/g, respectively. The addition of alumina binder and calcination in air at 800 °C, used to obtain the final washcoat, caused a reduction in the specific surface area for the SA washcoat only (down to 270 m^2/g), which was still twice that of LA sample due to its smaller average pore size (98 Å vs. 135 Å for LA). The actual noble metal loading is close to the nominal one for both catalysts. BET values for the final monolith catalysts after deposition of Rh are in line with the corresponding washcoat layers, therefore the higher metal dispersion value obtained for R-SA sample is justified by the larger surface area of the silica stabilized alumina support.

3.1. Pseudo-adiabatic catalytic tests

The effect of addition and removal of 8, 18 and 37 ppm H_2S to and from the reaction feed under CPO conditions over R-LA monolith operated at a fixed CH_4/O_2 feed ratio is illustrated in Fig. 1.