Effect of partial substitution of Rh catalysts with Pt or Pd during the partial oxidation of methane in the presence of sulphur

S. Cimino [a,*], L. Lisi [a], G. Russo [b], R. Torbati [b]

[a] Istituto Ricerche sulla Combustione, CNR, Italy
[b] Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, Italy

ABSTRACT

The effect of the partial substitution of $Rh/La–Al_2O_3$ monolith catalysts with either Pt or Pd during the catalytic partial oxidation of methane in the presence of H_2S under self-sustained high-temperature conditions was investigated. The catalysts were fully characterized by BET, SEM-EDS, SO_2-TPD and in situ DRIFT spectroscopy of adsorbed CO at room temperature, which was used to study changes on the surface state of Rh before and after exposures to sulphur species at temperatures and conditions close to those expected under actual CPO of methane. Both steady state and transient operation of the CPO reactor were investigated particularly with regards to poisoning/regeneration cycles and low-temperature light-off phase.

The partial substitution of Rh with Pt was shown to reduce the detrimental effect of S, which strongly inhibits the steam reforming reaction on monometallic Rh catalyst. DRIFT experiments indicate that sulphur acts as a selective poison by preferentially adsorbing on smaller well-dispersed Rh crystallites while larger metallic Rh sites are mostly unaffected; the presence of Pt or Pd does not directly influence the way S adsorbs on highly dispersed Rh sites.

© Elsevier B.V. All rights reserved.

1. Introduction

The production of syngas (CO and H_2) via the catalytic partial oxidation (CPO) of methane is an attractive and feasible alternative to steam reforming reaction in the 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 by Fischer–Tropsch synthesis. Furthermore, CPO of various hydrocarbons has been proposed as a preliminary conversion stage for hybrid gas turbine catalytic burners [1,2].

Recent results on the effect of sulphur addition during the CPO of methane over Rh-based honeycomb catalysts tested under self-sustained high-temperature condition [3,4] demonstrated that sulphur inhibits the steam reforming (SR) reaction by directly poisoning the active Rh sites. The effect of sulphur poisoning was also found to be completely reversible and the catalyst immediately regained its initial activity when the sulphur was removed from the feed [4]. Furthermore, under the typical operating conditions of methane CPO, i.e. at high temperatures (>800 °C) and short contact times, the sulphur storage capacity of the support did

not show any beneficial effect on the sulphur tolerance of the catalyst [4]. Contrary to what was observed when the CPO of methane was carried out in the low- to moderate-temperature regime (300–800 °C), where nature of the support material played a crucial role in the partial oxidation reaction [5].

Many studies have been published on the partial oxidation of methane over noble metals but only few studies have been done very recently in the presence of sulphur compounds [3,6]. Although there has been no direct study on the improvement on the sulphur tolerance of Rh-based catalysts conducted under CPO conditions, it has been reported that the addition of Pt [7] or Pd [8] to Rh improves the activity of the catalyst during the steam reforming of sulphur-containing fuels. In addition the partial substitution of Rh with Pt or Pd will be highly economical due to high cost of Rh metal. Accordingly, the purpose of this work is to investigate the enhancement in sulphur tolerance of Rh-based catalyst by partially substituting Rh with either Pt or Pd under self-sustained steady state operation at high temperatures and short contact times as well as during low-temperature light-off phase. This work uses in situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of adsorbed CO at room temperature to investigate changes on the surface state of rhodium before and after exposure to sulphur species at temperatures and conditions close to those expected under actual CPO of methane. Furthermore, an attempt is made to identify sites responsible for

the loss in the catalytic activity by comparing the results with the activity data.

2. Experimental

2.1. Catalyst preparation

Commercial honeycomb monoliths with straight and 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 and washcoated with 3% La_2O_3-stabilised γ-Al_2O_3 (SCFa140-L3 Sasol) by a modified dip-coating procedure [2,4]. Monometallic Rh catalysts were prepared via incipient wetness impregnation onto washcoated monoliths using an aqueous solution of Rh $(NO_3)_3$ (Aldrich) to achieve the desired loading of $\sim$1.0% (w/w). After impregnation, the catalysts were dried at 120 $°C$ and calcined in air at 550 $°C$. Bimetallic Rh–Pt and Rh–Pd catalysts were prepared by sequentially impregnating calcined Rh (loading 0.5 wt.%) monolith samples with a solution of H_2PtCl_6 or $Pd(NO_3)_2$. The target Rh/Pt and Rh/Pd weight ratio was 1 with a total metal loading of 1.0 wt.%. 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. Furthermore a 1.0 wt.% Rh supported on α-Al_2O_3 powder was also prepared by the same procedure. 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 the microwave-assisted digestion of samples in nitric/hydrochloric acid solution.

BET specific surface area of samples was evaluated by N_2 adsorption at 77 K using a Quantachromm Autosorb 1-C which was also used for CO chemisorptions experiments. Prior to CO adsorption measurement, the sample was heated under He at 120 $°C$ for 30 min and then at 800 $°C$ under a flow of pure H_2. After 1 h at this temperature, the sample was evacuated and cooled under vacuum to 40 $°C$ where CO adsorption was performed.

Temperature programmed desorption (TPD) experiments were performed to examine the extent of catalyst sulphation. The sample, typically 0.1 g (300–400 μm), was placed in a fixed bed quartz flow reactor and its temperature was monitored by a K-type thermocouple embedded in the catalytic bed. Prior to the TPD measurements, the catalysts were sulphated in situ by flowing 80 ppm SO_2 in air at 300 $°C$ for 1 h, during which the samples were exposed to approximately 23 mg S/g of catalyst. Following sulphur poisoning, the sample was heated from 300 to 1000 $°C$ in a stream of N_2 (20 L min^{-1}) at 10 $°C$ min^{-1} and the evolution of SO_2 was monitored by an on-line SO_2/H_2S continuous gas analyser (ABB AO2020 series).

The nature of metal species was investigated by DRIFT spectroscopy using CO as a probe molecule. DRIFT experiments were performed on a Perkin Elmer Spectrum GX spectrometer with a spectral resolution of 4 cm^{-1} and averaged over 50 scans. For each experiment approximately 0.03 g of finely ground powder sample was placed into the ceramic cup of a commercial high-temperature Pike DRIFT cell equipped with a ZnSe window and connected to mass-flow controlled gas lines. The sample was then treated in the following way: (i) prior to the experiments the sample was reduced with a 2% H_2/N_2 mixture for 1 h at 800 $°C$ and then cooled down to room temperature under the same mixture. The sample was purged with Ar for about 15 min before a

background spectrum was recorded; (ii) CO was adsorbed at room temperature (2% CO/N_2 mixture, 100 cm^3 min^{-1}) for 30 min and any excess CO was removed by flushing with Ar (100 cm^3 min^{-1}) prior to recording the IR spectra; (iii) the sample was then flushed with Ar at 800 $°C$ for 15 min followed by exposure to 20 ppm H_2S/2% H_2–N_2 (100 cm^3 min^{-1}) mixture for 30 min; (iv) after sulphation at 800 $°C$, the sample was cooled down to room temperature under the same reaction mixture followed by purging with Ar for approximately 15 min before CO adsorption. All spectra were ratioed against the background spectra collected on the adsorbate-free sample at room temperature. The effect of the regeneration of S-poisoned catalyst by reduction under a mixture of 2% H_2/N_2 at high temperatures was also investigated.

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 set up were already reported elsewhere [2,4].

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 and based on the volume of the catalytic honeycomb) 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 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 in N_2 mixture.

Catalytic light-off temperatures were determined by ramping-up the external furnace from 200 $°C$ to the light-off temperature at a rate of $\sim$5 $°C$/min under transient conditions using methane–air mixtures at fixed feed ratio (CH_4/O_2 = 1.8), in the absence and presence of 20 ppm H_2S.

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

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

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

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

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