



Rh-based catalysts for syngas production via SCT-CPO reactors

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ARTICLE INFO

Article history:

Available online 19 May 2009

Keywords:

Syngas production
Methane catalytic partial oxidation
Short time contact
Fixed bed reactor
Rhodium catalyst
Alumina carrier
Egg-shell/egg-yolk catalyst type

ABSTRACT

Short contact time catalytic partial oxidation (SCT-CPO) of natural gas is a promising technology for syngas production, representing an appealing alternative to existing processes. This process is likely to become more important in the future due to its advantages in thermodynamics, mildly exothermic overall reaction, H₂/CO ratio of 2, ideal for downstream processes. The present work refers to an experimental study of syngas production from CH₄ and O₂ via a SCT-CPO reactor made of a fixed bed of Rh/Al₂O₃ spheres, with Rh deposited in egg-shell or egg-yolk configuration. In the WHSV range from 120 to 470 NI h⁻¹ g_{cat}⁻¹, five different fixed bed structures were investigated. The best performances in term of CH₄ conversion and H₂ selectivity, together with no coke formation, were obtained with an physical mixture of egg-shell and egg-yolk catalysts at WHSV values of 150–300 NI h⁻¹ g_{cat}⁻¹.

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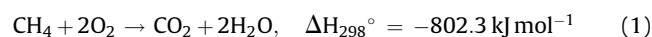
1. Introduction

Partial oxidation is presently considered an alternative to steam reforming for the generation of H₂ from fossil fuels in decentralized applications [1]. An important recent example is the generation of H₂ for stationary or mobile fuel cells [2]. The catalytic partial oxidation (CPO) of CH₄ to CO/H₂ mixtures has been discussed in the literature and several catalysts were proposed, including non-noble [3–5] and noble metals-based ones [6–9]. The extensive work on short contact time (SCT) reactors available in literature [10–28] showed that Rh has high activity and selectivity, superior to that of other noble metals, avoiding or at least partially limiting coke formation [29]. The use of Rh leads to the conversion of CH₄/O₂ mixtures to CO and H₂ at contact times of few milliseconds under adiabatic conditions (e.g., at temperatures higher than 800 °C [22]).

It is widely accepted that with metal catalysts CH₄ is first oxidized to CO₂ and H₂O in the initial part of the catalytic bed until O₂ is exhausted [30]; then, in the following part of the bed, the reforming reactions of remaining CH₄ with steam and CO₂ initially formed [6–8] occur. However, at extremely high temperatures and very short contact time, syngas may be formed directly [7,8,11–13]. The main chemical

reactions involved in the catalytic process are represented in Eqs. (1)–(6):

Methane total oxidation (MTO):



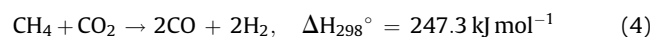
Methane partial oxidation (MPO):



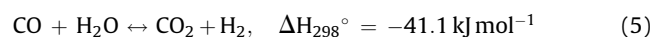
Methane steam reforming (MSR):



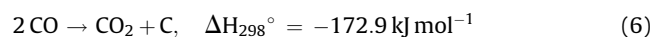
Methane dry reforming (MDR):



Water gas shift equilibrium (WGS):



Coke formation (Boudouard reaction):



The effect of catalyst preparation and pretreatment, as well as of Rh precursors and of the carriers over the morphology of Rh nanoparticles was also investigated [31–40]: both metallic Rh particles and highly dispersed Rh species were found to be active towards CPO; their relative amount can change following the exposition to the high temperature of the CH₄ CPO conditions [37]. The exposition of the catalysts to high temperatures induced a reconstruction of the surface, since its heterogeneity was largely

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eliminated and the reorganization of isolated atoms and the smaller aggregates into bigger metallic particles occurred [38,39]. Recently, Rh embedded into porous Al_2O_3 has been shown promising stability performances [41,42].

The present work deals with the experimental activities on SCT-CPO of CH_4 on a fixed bed reactor of Rh-supported alumina particles; a set of experimental data, related to CH_4 conversion (ξ_{CH_4}), H_2 and CO selectivity (σ_{H_2} and σ_{CO}), mainly focusing on the effects of weight hourly space velocity (WHSV), is presented and discussed. The goal of this work was the design of an optimal fixed bed structure, in order to attain a very thermally stable system under extreme working conditions, avoiding sintering and coking problems, using two different kinds of 1 wt.% Rh on Al_2O_3 catalysts, alone or in combination: one catalyst carrying Rh on the external support surface (egg-shell) and the other with Rh embedded into the support pores (egg-yolk).

For the egg-shell catalyst, the metallic active phase is distributed only on a thin external surface layer (about 50 μm thick) of $\gamma\text{-Al}_2\text{O}_3$ carrier spheres, but not in the internal pores. Such a situation is congruent with a low contact time process which is controlled by external mass transfer phenomena [43]: the reaction takes place on the catalyst surface, easily and quickly accessible by the reagents, which would have limited possibility to diffuse and react inside the pores. Anyway, the idea to study also an egg-yolk configuration, i.e., to embed Rh nanoclusters in porous Al_2O_3 , was born to limit the sintering of Rh clusters under the severe MPO environment [40,41]. Moreover, the porous structure of Al_2O_3 wrapping Rh nanoparticles should control the diffusion rate of the reactant molecules inside the carrier: Knudsen type diffusion mechanism of the reactant molecules has been proposed for microporous $\gamma\text{-Al}_2\text{O}_3$ [44]. In this case, a diffusion rate of a reactant molecule is faster as its molecular weight becomes smaller.

2. Experimental

The egg-shell Rh catalyst, hereafter named catalyst "A", was prepared by Rh deposition over commercial $\gamma\text{-Al}_2\text{O}_3$ spheres 1 mm in diameter (Sasol Germany GmbH). Rh was deposited by incipient wetness impregnation technique, using 10 wt.% aqueous solution of $\text{Rh}(\text{NO}_3)_3$. The catalysts spheres were then calcined in air for 6 h at 600 °C [45]. The egg-yolk Rh catalyst, hereafter named catalyst "B", was synthesized starting from the preparation of stabilized Rh nanoparticles under Ar atmosphere at room temperature (T_{room}). Briefly, an aqueous solution containing NaBH_4 (the reducing agent) and the cationic surfactant HEAC16Br (used as protective agent for Rh metal particles) was quickly added under vigorous stirring to an aqueous solution of $\text{Rh}(\text{NO}_3)_3$. The obtained suspension was then stirred for 2 h to decompose the excess of reductant and finally $\text{Al}(\text{NO}_3)_3$ was added. When the complete dissolution of the salt was achieved, the precipitation of $\text{Al}(\text{OH})_3$ was performed dropping the resulting system into NH_4OH solution. The formed gel was matured and then filtered. Several washing cycles were applied to remove the bromide ions from the surfactant [41]. The obtained precipitate was suspended in 2-propanol and refluxed for 5 h in order to stabilize the textural framework of the support. After filtration, the solid was dried at 120 °C overnight and calcined firstly at 500 °C for 5 h and then for 5 h at 900 °C. The carrier after calcination was composed of 50 wt.% $\gamma\text{-Al}_2\text{O}_3$ and 50 wt.% $\theta\text{-Al}_2\text{O}_3$ [41]. Finally, the material was pressed, crushed and sieved to collect the fraction between 425 and 850 μm .

The morphology of as-prepared A and B catalysts was observed by FESEM (SEM FEI Quanta Inspect 200 LV apparatus) and HRTEM microscopy (Philips CM200 UT apparatus). The catalysts' BET surface area was measured by means of N_2 adsorption with an automated gas sorption analyzer (Micromeritics ASAP 2010C). Metal dispersion was estimated by H_2 chemisorption at 35 °C

using a Micromeritics ASAP 2020C instrument. Prior to the experiments, the two catalysts were reduced at 750 °C for 2 h flowing H_2 (5%)/Ar (40 ml min^{-1}) and degassed at 750 °C for 5 min and at 400 °C for 3 h. The chemisorbed H_2 was determined by extrapolation to zero pressure of the linear part adsorption isotherm after removing the so-called reversible hydrogen adsorption ("double isotherm" procedure) and assuming a chemisorption stoichiometry Rh:H = 1:1.

The catalytic activity of the as-prepared catalysts was tested in a tubular reactor (Inconel[®] 601) composed of two coaxial pipes (the internal one 15 mm i.d. and 2 mm wall thickness) with a resulting jacket which contributed to the reactor thermal insulation [45]. The internal tube was covered with an oxidized layer of FeCrAlloy[®] to avoid contacts between reactive gases and the Inconel[®] surface wall [45], just to prevent any catalytic effect towards CPO reactions of Ni, present in the Inconel[®] alloy. The catalyst particles were arranged in a fixed bed placed between two porous inert regions. The upstream region was constituted by a quartz particles bed (to improve the CH_4/O_2 mixture by static mixing) followed by high thermal conductivity SiC particles (to provide both a shield for the radiant energy emerging from catalyst bed and, the pre-heating of the reagents fed at room temperature, thus exploiting the heat developed during the catalytic process). The downstream zone was a bed of low thermal conductivity quartz particles so as to reduce heat loss and allow a slower cooling of the outlet stream. The inlet (T_{in}) and outlet (T_{out}) catalyst bed temperatures were monitored by two suitably located thermocouples. The gas stream composition at the reactor outlet was monitored by a multiple gas analyzer (ABB) able to measure simultaneously H_2 (thermal conductivity module Caldos 17), $\text{CO}/\text{CO}_2/\text{CH}_4$ (infrared module Uras 14) and O_2 (paramagnetic module Magnos 106). The CPO reaction ignition was performed by heating the reactor, placed in a tubular oven, up to 920 °C and by feeding a T_{room} mixture of pure CH_4 and O_2 at O_2/CH_4 ratio equal to 0.5 (stoichiometric condition for MPO, reaction (2)). The feedstock stream was pre-heated by the hot particles bed region upstream the catalyst bed and once ignited, the reactor remained thermally self-sustained by the heat released from the exothermic reactions. The start-up procedure took about 1 min and then the O_2/CH_4 ratio was gradually increased to the operative desired value and maintained till to reach steady-state conditions. The chosen O_2/CH_4 ratio was 0.575, a value slightly above the stoichiometric one, which a previous research demonstrated to be the best one to maintain the T_{reactor} in a proper range [45]. The feed flow rate was adjusted to obtain a WHSV between 120 and 470 $\text{Ni h}^{-1} \text{g}_{\text{cat}}^{-1}$. The as-prepared A and B catalysts were tested into the reactor in the following fixed bed structures (1.5 g of catalyst were always present in the bed, for a total length of about 2 cm):

- i. A catalyst fixed bed only;
- ii. B catalyst fixed bed only;
- iii. A + B catalysts, 50 wt.%–50 wt.%, i.e., 1st bed A catalyst, 2nd bed B one;
- iv. B + A catalysts, 50 wt.%–50 wt.%, i.e., 1st bed B catalyst, 2nd bed A one;
- v. A/B catalysts mix, 50 wt.%–50 wt.%, i.e., a bed of a random A and B catalysts mixture.

3. Results and discussion

The characterization parameters of the basic catalysts are reported in Table 1. BET surface area values of the two catalysts are high and very similar, notwithstanding the complete different preparation methods used. This might suggest that the calcination step is able to reduce the differences related to the two preparation

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