



Pt on Fecralloy catalyses methane partial oxidation to syngas at high pressure



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ABSTRACT

μ -Gas-to-Liquids technology (μ -GTL) can potentially reduce natural gas that is flared throughout the world. Integrating syngas production (at high pressure) together with Fischer–Tropsch in the same vessel addresses both investment costs and operating costs challenges related to μ -GTL. Pt on a Fecralloy woven metal support effectively oxidizes methane in the presence of O₂/Ar mixtures. Both CO and H₂ selectivity are higher over the Fecralloy compared to either a commercial Pt-gauze or a Pt/Rh gauze at 900 °C and 20 bar. The catalyst activity is stable over 1 h but the 80–300 nm Pt particles agglomerate and form popcorn shape particles that are as large as 1150 nm.

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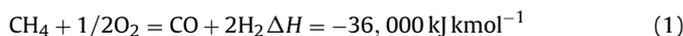
1. Introduction

The World Bank launched the Global Gas Flaring Reduction partnership in 2002 as part of the World Summit on Sustainable Development. They estimated that petroleum companies flare as much as \$35 billion per year of natural gas (NG). Building pipeline infrastructure is uneconomic for remote reservoirs or for reservoirs with a short life expectancy. The economics of converting low volumes of gas to Fischer–Tropsch fuels, methanol, DME (gasoline), ammonia, or ethylene might be attractive if the investment costs can be maintained at the standard for large scale units. Investment in gas-to-liquids processes (Fischer–Tropsch fuels, for example) is 100,000 \$ per bbl of oil produced.

Most NG conversion technologies rely on producing syngas (H₂ and CO) in the first step via steam methane reforming (SMR), auto-thermal reforming (ATR) or partial oxidation (POX). Our final goal is to combine CPOX with the Fischer–Tropsch process in one single vessel in order to reduce both investment and operating costs. According to the thermodynamic analysis, the best conditions to

produce syngas are at ambient pressure and high temperature (<900 °C) whereas the thermodynamics of the Fischer–Tropsch step favour high pressure (<20 bar) and low temperature (>320 °C). From a thermodynamic perspective, the CPOX reaction is more efficient at low pressure and it is a challenge to convert CH₄ to CO and H₂ selectively at high pressure. Newitt and Haffner [1] pioneered high pressure methane partial oxidation in 1932. Much later, Lott and Sliepcevic [2] designed a bench process to study hydrocarbon partial oxidation at 200,000 psi.

In CPOX, molecular O₂ partially oxidizes CH₄ to CO and H₂. It requires 1/2 mole of O₂ per mole of CH₄ (Eq. (1)), whereas complete combustion of CH₄ requires 2 moles of O₂ per mole of methane (Eq. (2)). Complete combustion is 20 times more exothermic than partial oxidation



The most common industrial reforming catalysts are based on Ni that cost less than noble metals. However, methane cokes on Ni more rapidly than noble metals and according to XPS analyses surface carbon species, such as carbide species and carbon filaments that form on the surface, may alter the catalyst structure [3]. Together with Ni other CPOX catalysts include Co supported on

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ZSM-5 [4], Ni/Ru system with addition of steam [5], Ni/Co/Ru [6], Ni-Pt/La_{0.2}Zr_{0.4}Ce_{0.4}O_x [7]. Noble metal catalysts remain the best candidates for CPOX because they are most stable and CO and H₂ yields are higher [8] and because carbon does not dissolve in those elements [9].

Methane pyrolyses on reduced metal sites forming hydrogen and carbon adspecies. Carbon reacts with oxygen to form CO [10]. Both Pt and Rh are active noble catalysts but Rh selectivity is higher [11,12]. Basini et al. [13] studied the thermal decomposition on the surface of Rh based catalyst and reported differences between gas and solid temperatures. Methane combusted or oxidized partially in the front end of the catalytic bed while near the end of the bed, less energetic reactions – steam reforming, CO₂ reforming and the water gas shift – predominated. To take advantage of the spatial differences across the catalyst bed, Smith et al. [14] segment the reactor by placing catalysts optimized for each reaction in different parts of the bed: at the reactor inlet, they placed combustion catalysts and after they place a reforming catalyst

Thermodynamics and reaction kinetics depend on pressure. Reaction rates increase with pressure while maintaining the GHSV constant over Pt while the rate is less prominent for Rh [15]. Cerium oxides (CeO₂, Ce₂O₃) improve noble metal stability and the oxygen adsorption rates [16].

Partial oxidation reactors are smaller than steam reformers but operate less efficiently [15]. Their main advantage is that they can react higher hydrocarbon feedstocks and NO_x and SO_x emissions are lower. Many reactor types have been adapted to partially oxidize methane: fixed beds [17,18], fluidized beds [19,20], membranes [21,22], monoliths [23,24], and gauzes [25], chemical looping technology [26,27] and cyclic fixed beds [28].

New reactor classes for CPOX include microliths and coated metal plate reactors. We develop woven Fecralloy[®] metal fibres (FA) as a catalyst support. Fecralloy resists temperatures and have excellent thermal properties [29]. Catalyst can be added to FA by slurry deposition of impregnated alumina [30], by spraying an atomized solution of precursor [31], electro-synthesis [32] or by growing the support on the existing Al₂O₃ on the surface of the FA [33].

We deposited Pt over a FA microlith to partially oxidize CH₄ to syngas at high pressure in air. We evaluated the activity of spray-coating the Fecralloy woven construction at 1 bar and 20 bar at 1173 K. We compared conversion and selectivity of three FA compositions together with two commercial gauzes (Pt and Pt/Rh). At high pressure, the thermodynamic equilibrium selectivity to coke is about 5% but experimentally the Fecralloy produced as much as 40% coke at ambient pressure and 20 bar.

2. Experimental

2.1. Catalysts synthesis

We synthesized several catalysts and tested two commercial gauzes. The FA has a mass fraction of 20% chromium, 5% aluminum, yttrium >0.1%, 0.3% silicon, 0.08% manganese, 0.03% copper, 0.03% carbon and the balance iron. This metallic support resembles a woven fabric (Fig. 1) with a wire diameter of 10 μm. The first commercial sample was a 52 mesh 99.9% Pt gauze (wire diameter – d_w – 0.1 mm from Sigma–Aldrich) and the second was an 80 mesh 90% Pt on 10% Rh gauze (d_w =0.076 mm from Alfa Aesar). The catalysts we prepared are based on a Fecralloy woven (FA) support coated with alumina or alumina-ceria solutions. In the first step, air oxidized 2.5 g of FA at 1000 °C in a furnace for 3 h. The furnace ramped the temperature from ambient to the set point at 5 °C min⁻¹. In the second step, we placed the oxidized FA on a hot plate at 300 °C and sprayed 7.5 mL of a 0.44 mol L⁻¹ Al(NO₃)₃·9H₂O solution on both



Fig. 1. Optical microscope image of FA tissue provided by Eratec.

sides. An IR camera monitored the surface temperature of the FA. The solution for the alumina-ceria supports contained 0.07 mol L⁻¹ cerium(IV) ammonium nitrate and 0.44 mol L⁻¹ aluminium nitrate mixture. The catalyst calcined for 4 h at 600 °C with the same temperature ramp as the initial FA oxidation step in the oven. In the final two steps, platinum salt solutions were sprayed on the FA+support and they calcined at 1000 °C for 4 h (with a 5 °C min⁻¹ ramp). We sprayed 2.5 mL of a chloroplatinic acid hexahydrate (PtH₂Cl₆·6H₂O) solution on each side of the coated FA. The concentration of the Pt salt was 0.051 mol L⁻¹ and 0.13 mol L⁻¹ for the 1%Pt/FA and the 5%Pt/FA, respectively. The final weight ratio of Al₂O₃:CeO₂ was 79:21. All the reagents were certified high purity chemicals by Sigma–Aldrich and were used without further purification.

2.2. Catalyst characterization

An X-ray Philips X'pert diffractometer (XRD) recorded the diffraction patterns of the FA, FA+support and FA catalysts with Cu Kα (1.5406 Å) radiation at 50 kV and 40 mA at room temperature. The diffraction angle varied from 0° and 90°, with an incidence of 1°.

2.3. Catalytic partial oxidation – CPOX

The high-pressure CPOX reactor was a 8 mm quartz tube that was placed in a stainless steel tube (Fig. 2). The FA catalyst bed consisted of 10 disks x 8 mm ID stacked on top of each other with a total bed height of 25 mm. We loaded a single 8 mm diameter disk for tests with the pure Pt metallic gauze and the Pt/10%Rh gauze.

The gas manifold included CH₄, 30%O₂ in Ar and Ar. Bronkhorst mass flow controllers (MFC) dosed the gas flows to the reactor and maintained the O₂ at 21%. A spring-loaded back-pressure valve maintained the reactor pressure at 20 bar.

A type-K thermocouple monitored the temperature at top of the catalyst bed (effluent side). Horn et al. [34] and de Smet et al. [35] tested alternative strategies to measure bed temperatures with thermocouples but an IR camera is better to identify radial and axial non-uniformities. The gas entered the quartz tube cold and traveled 150 mm before reaching the FA. The time it takes for the gas to reach the FA is insufficient to heat it to the reaction temperature. Preheating the gas increases the reaction rates in the bed and increases the conversion (and selectivity). Under some conditions, the temperature exceeded 1173 K.

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