

Stability Tests of a 5 kWeq LPG Hydrogen Generator for PEFC

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This paper presents the experimental activities on a pre-commercial hydrogen generator unit HYGen II, for Polymer Electrolyte Fuel Cell (PEFC) in residential applications. The unit is able to convert light hydrocarbons (methane, propane, LPG, butane) with a nominal hydrogen production of 5 Nm³h⁻¹ and a maximum hydrogen production of 8.5 Nm³h⁻¹. Stability tests with a proprietary Pt/CeO₂ catalyst for the C₃H₈ autothermal reforming (ATR) step, coupled with commercial catalyst for intermediate water gas shift (ITWS) and preferential oxidation (PROX), have been carried out. Propane conversion of 99.8 % associated with total oxygen conversion, in absence of byproducts has been evidenced. A CO concentration below to 10 ppm was observed in the first 140 h of operation. Subsequently, a performance decrease in the ITWS step determined a rapid increase in the CO concentration.

1. Introduction

There are several ways to produce hydrogen gas from carbonaceous fuels like steam reforming, partial oxidation and autothermal reforming (natural gas, oil and/or alcohol). Most of these processes are designed for large scale industrial production and are not suitable for a compact hydrogen generator, as required for both mobile and stationary applications (1). Hydrogen production from hydrocarbons is a sufficiently simple process: difficult cold start-up, low transient response capability, high weight/electric power ratio are the related problems (2). The integration between the chosen fuel cell and the fuel processor, depending on the required extent of the gas clean-up treatment, is a key issue. The produced hydrogen rich gas must contain a low level of harmful impurities: high carbon monoxide levels require additional purification stages. Besides, hydrogen not consumed at the anode can be utilized in other sections of the integrated system to maximise thermal efficiency. In the steam-reforming based fuel processor, i.e., hydrogen is fed to the reformer burner and supplies most, if not all, of the energy requirements for the endothermic steam-hydrocarbon reactions. In systems that do not require energy to process the fuel (such as autothermal reforming and partial oxidation) other uses must to be found for anodic exhaust to maximise the efficiency: the utilisation of every stream's energy in the system must be maximized. Therefore, considerable effort goes into the optimization of heat exchangers, condenser, and other energy-exchange devices (3). The total systems evaluation, taking into account the different fuel processing schemes and the related feasibility, shows that with the autothermal reforming process a good compromise (volume and weight low, higher performance in the transient regime, easy start-up, etc.) can be reached (4-6).

Based on previous experimental tests with a subscale (2 kWe) hydrogen generator unit (7), a more compact and reliable 5 kWe unit (HYGen II), for residential applications has been developed and tested (8).

The prototype is based on three catalytic reaction steps: the Autothermal Reforming (ATR), the Intermediate Water Gas Shift (ITWS) and the Preferential Oxidation (PROX). The system has been engineered, focusing the design of every single component and the integration of the system, to meet the requirements of small size and volume, improving thermal and mass transfer and system efficiency. An automation system, to monitor the operating conditions and to control the plant equipment, has been developed (9). Experimental tests, using propane as fuel, have been carried out with a proprietary Pt/CeO₂ catalyst for the autothermal reforming step coupled with commercial catalysts for intermediate water gas shift and preferential oxidation. The main aim of the tests has been to define the operating parameters, in order to assure high activity and stability for prolonged start-up and shut-down cycles, indicating the drawbacks of the system for a future commercial unit. Validation of heat/mass balance and reactors/system performance (in steady state and transient response), in terms of fuel conversion, hydrogen content and efficiency, has been derived.

2. Prototype Concept and Design

HYGen II can reach a nominal hydrogen production of 5 Nm³h⁻¹ (from methane, propane, LPG, butane) with a maximum hydrogen production of 8.5 Nm³h⁻¹. The net size (mm) of the fuel processor, shown in Fig. 1, is 636 (width) x 868 (length) x 1350 (height).



Figure 1. View of the 5 kWeq fuel processor (HYGen II).

The diagram of the integrated system is reported in Fig. 2; the processing unit is coupled with a heat exchanger, a static mixer, a water reservoir, manual/automatic valves, pressure regulators/transducers, flow meters, and ancillaries.

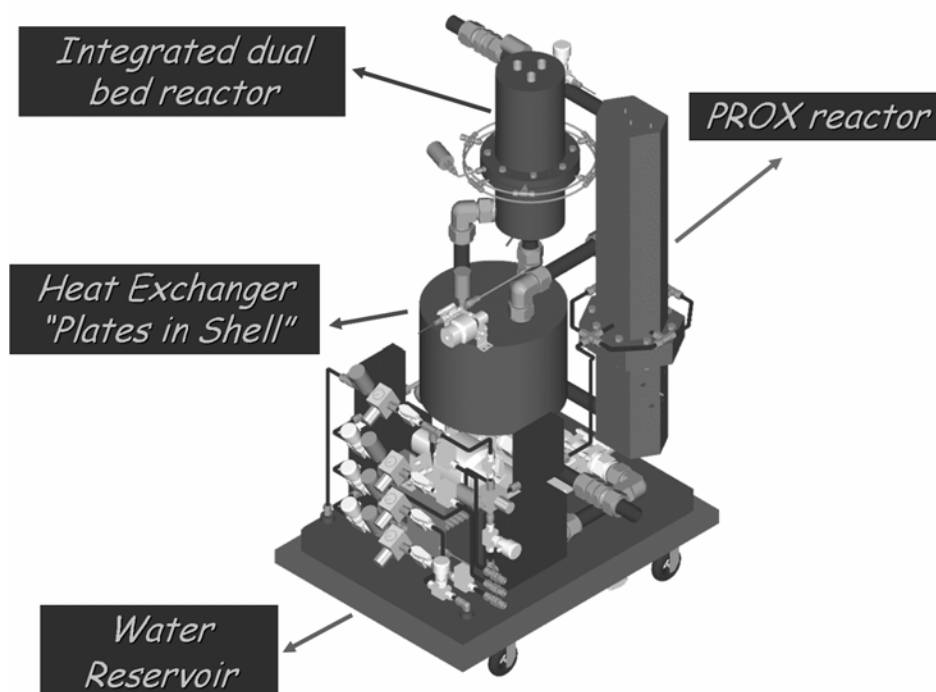


Figure 2. Diagram of the 5 kWe fuel processor (HYGen II).

A new design concept, related to earlier developments (7) was applied in the integration of the two catalytic processes, autothermal reforming and intermediate water gas shift: a combined dual bed reactor geometry has been realized.

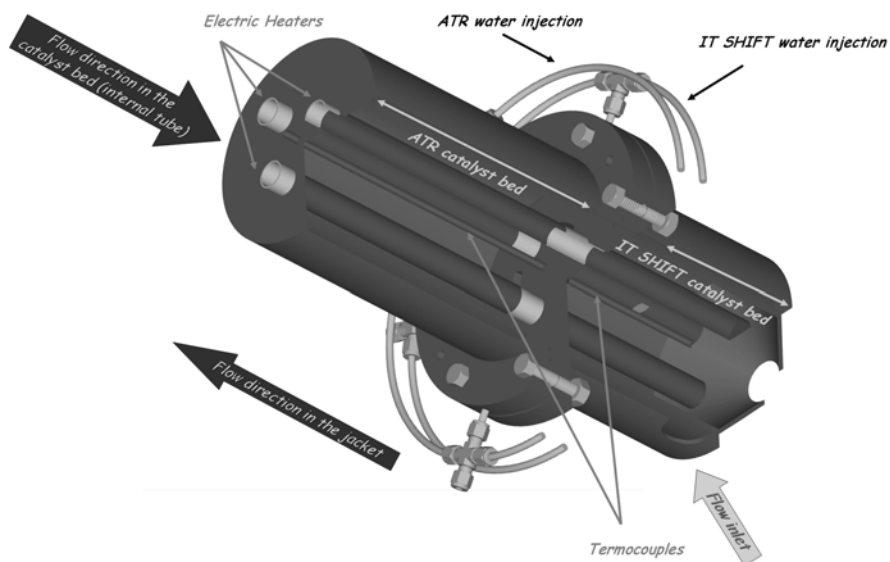


Figure 3. Cut away view of the integrated dual bed reactor.

The integrated reactor, showed in Fig. 3, consists of two coaxial tubes: the gas flows into the jacket and then reaches the internal tube, where the catalyst beds, with a volume of 2.8 (ATR) and 1.3 litres (ITWS), respectively, are introduced.

Previous studies on momentum-based modeling in a packed bed reactor (10), have shown that a coaxial geometrical configuration can assure a constant distribution of reagent flow on the ATR catalyst bed and, consequently, can optimize process' performances. The configuration of the coupling zone (ATR and ITWS catalytic beds) in a single reactor, has been designed and analyzed by a modeling approach (11), showing an optimized flow distribution.

The PROX reactor is a shell and tube system (Fig. 4); the design has been developed at CNR-ITAE in order to obtain isothermal conditions along the reactor; a single-stage multi-tube reactor geometry has been adopted.

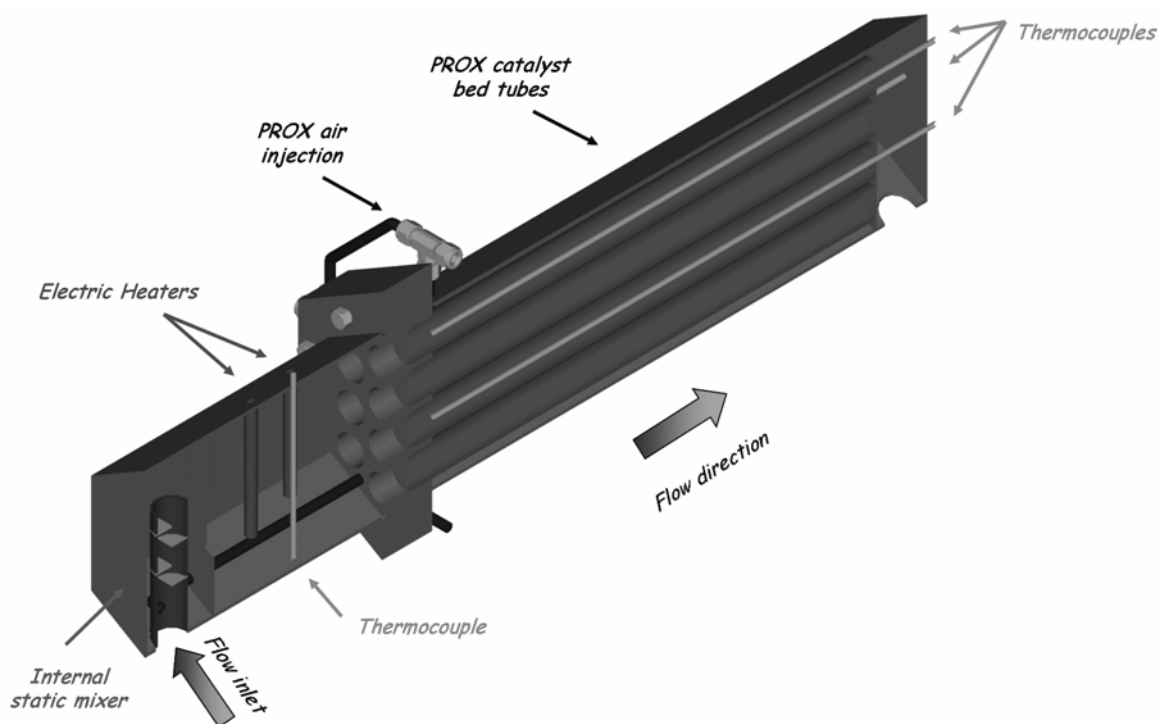


Figure 4. Cut away view of the single stage-multi tube PROX reactor .

The single-stage multi-tube reactor was filled with 4.38 litres of commercial catalysts in pellet form.

The reactor consists of ten parallel and cylindrical tubes: the product gas mixture coming from the previous water gas shift step, enters into a static mixer where it is mixed with air and then reaches the heating zone, that consists of an inert bed heated by electrical heating elements only during the start-up step. Here the PROX reagent mixture is heated to reach the light-off temperature and then distributed uniformly into the tubes. The air required for the reaction is fed from four injections into the satellite system. When the air flows through the cooling jacket, an optimal reaction temperature is reached.

Simulation studies (12, 13) showed that it is possible to achieve sufficient carbon monoxide conversion varying the reagent inlet temperature in the range 373-433 K and that an optimal temperature control can be achieved using a configuration with a cocurrent air flow in the interspace.

Reactant and product gas mixture were analyzed by gas chromatography and mass spectrometry.

The prototype includes a fully automated data acquisition and control system, based on Field Point distributed I/O hardware. Control of plant parameters (fluxes, temperatures, absolute pressures, electro valves state, electric heaters) and storage of process data, at user-defined intervals, were realized by coupling the management software and the measurement hardware. The integrated software and hardware platform can control the unit in two operation modes: a semi-automatic control, to test the performance of the prototype with manual procedures, and a fully automatic screening..

Based upon the above considerations, the control instrumentations (flow meters/regulators, thermocouples, absolute pressure transmitters, power solid state relays with analog control) have been identified. Furthermore, the plant has been provided with electronically controllable components, such as electro-valves and contactors, obtaining automation and control of the processes.

The safety system consists of different action cycles for these events: P_{\max} (Maximum Pressure), P_{\min} (Minimum Pressure), T_{high} (High Temperature), T_{low} (Low Temperature), as synthetically reported in Table I.

TABLE I. Safety levels.

Safety levels	Monitoring Instrumentations	Controlled parameter
Manual	Manometer, Monitor	Pressures, Temperatures
Active	Electrovalves	Pressures, Temperatures
Passive	Safety valves, Gas sensor	Pressures, Leakages

Two action cycles were defined for each controlled parameter: a pre-alarm (visual and sound signal) and an alarm, that modifies the working configuration of the system to isolate any malfunctions and/or to switch on the shut-down phase.

The management of the action cycles is based on the following control levels:

- manual level: monitoring of temperatures and pressures is carried out by the operator;
- active level: operative when the controlled parameters reach a value out of the set up ranges. The monitoring is carried out by the management system software;
- passive level: activated by controlled fluid, maintains temperatures and pressures in the fixed ranges. The monitoring is carried out by safety valves and gas sensors; the management system also protects against danger sources related to elements not easily identifiable, such as high pressure or leakage.

3. Catalysts

The reaction conditions and the catalyst formulation, that can assure high activity, good thermal, mechanical and chemical stability have been derived from previous micro-scale tests (14, 15).

ATR catalyst is a CNR-ITAE proprietary catalyst; the Pt/CeO₂ sample, prepared by combustion synthesis, presents Pt as solid-solution with CeO₂ and dispersed on support with particle size of about 50 Å, as revealed by TEM analysis reported in Fig. 5.

The operating parameters such as temperature, O₂/C₃H₈ and H₂O/C₃H₈ molar ratio and gas hourly space velocity (GHSV) have been previously evaluated.

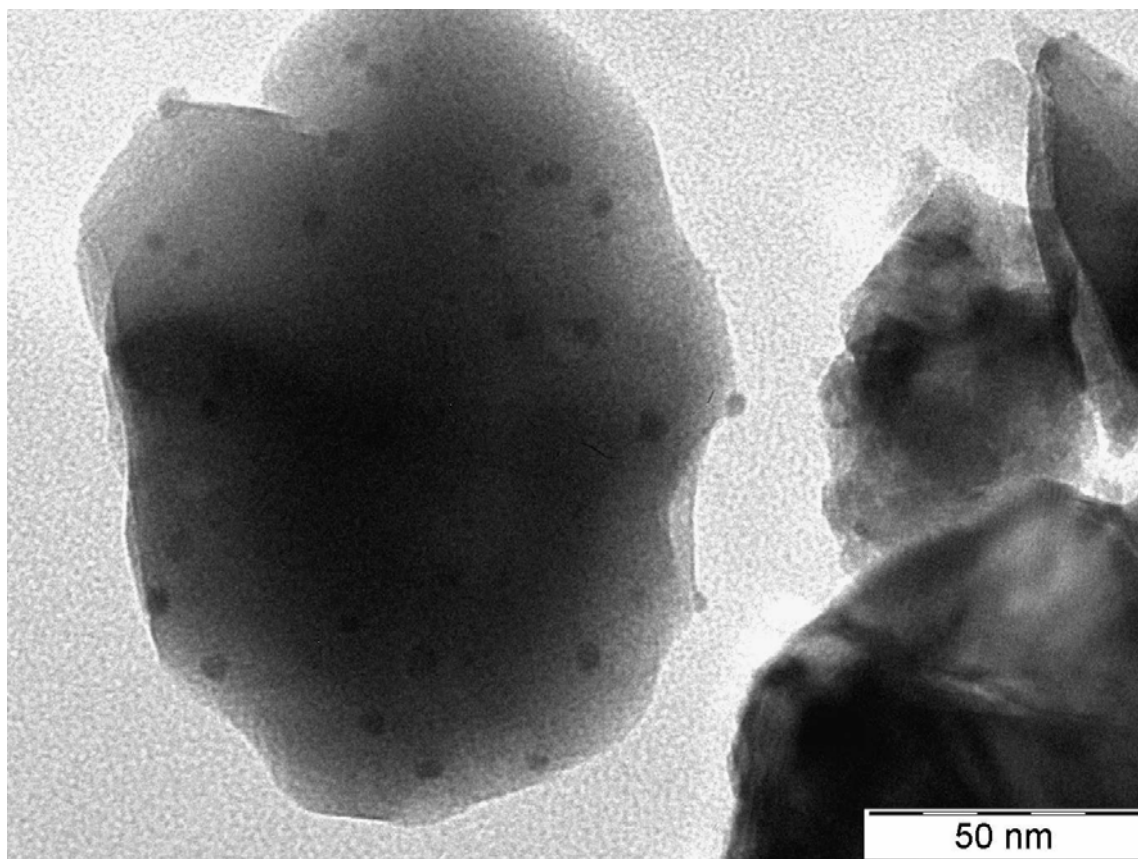


Figure 5. TEM image of “as prepared” Pt/CeO₂ catalyst.

The catalyst, pressed into pellets 3x3 mm, operates at 650°C (light-off temperatures of 300 °C) under atmospheric pressure with GHSV of 5000 h⁻¹, O₂/C₃H₈ and H₂O/C₃H₈ ratios of 2.0 and 3.0, respectively.

Two commercial catalysts have been selected for the ITWS and PROX reactions, and used in their manufactured shapes and sizes. The ITWS catalyst (pellets form 3x3 mm), supplied by NexTech Materials, operates at 330°C (light-off temperature of 260 °C) under atmospheric pressure with GHSV = 30 000 h⁻¹ and H₂O/CO ratio of 3.0. The choice of the operating temperature for the ITWS step is a compromise between thermodynamics requirements, that severely restricts the CO conversion at higher temperatures (16) and the need to achieve an optimized heat integration.

The PROX catalyst (pellets form 3x3 mm), supplied by Engelhard, operates at 130°C (light-off temperature of 90 °C) under atmospheric pressure with a gas hourly space velocity of 4000 h⁻¹ and O₂/CO ratio of 2.0.

4. Results and Discussion

During the start-up, nitrogen is sent to the system and heated by electric heaters, located inside the integrated reactor. When the temperatures of the ATR, ITWS and PROX catalytic beds reach about 300°C, 260°C and 120 °C respectively, nitrogen is stopped and the air-propane-steam mixture is sent to the system. At regime conditions, the reagent mixture is preheated by the reaction’s products in the jacket of the integrated

reactor. External heating is supplied only during the start-up; on regime operations the global heat balance is smoothly exothermic in order to compensate for the heat transfer losses. During shut-down, the air-propane-steam mixture is stopped and nitrogen is sent as a purge. The electrical modulation of the power solid state relays is automatically regulated to reach and maintain the temperatures set, relieved by thermocouples.

The tests have been carried out with daily cycles of 6 h continuous test for a total of 310 h, at a constant flow rate of the gaseous feed in order to analyze the performance of the system in a steady state; at the end of each test the reactor has been maintained at ambient temperature. The main operating conditions of each reaction step are summarized in Table II.

TABLE II. Operating conditions used during the test, P=1 atm..

Reactions	Experimental conditions
ATR	GHSV = 5000 h ⁻¹ , T= 650°C, O ₂ /C ₃ H ₈ = 2.0, H ₂ O/C ₃ H ₈ = 3
ITWS	GHSV = 30 000 h ⁻¹ , T=330°C, H ₂ O/CO = 3
PROX	GHSV = 4000 h ⁻¹ , T= 130°C, O ₂ /CO = 2

Sending the air-propane-steam mixture into the dual bed reactor, a rapid increase in temperature of the ATR bed was observed that stabilised within some minutes at 650 °C, while the ITWS bed temperature quickly reached 330 °C by the exothermic CO conversion.

Fuel conversion and product compositions in the stream from the integrated reactor are shown in Fig. 6.

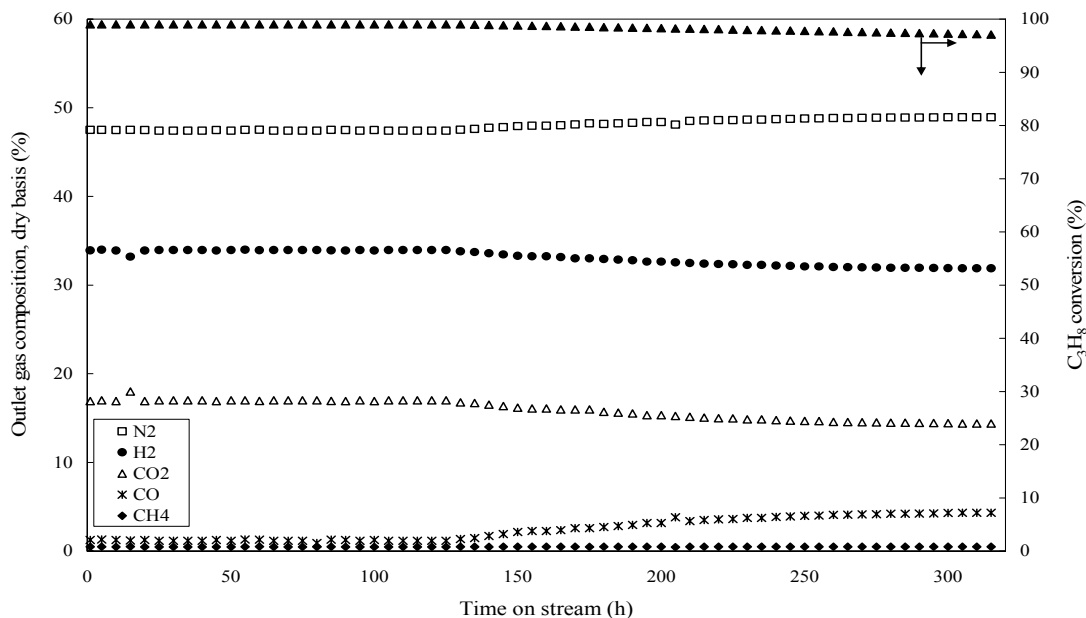


Figure 6. ATR-ITWS performances.

The results show steady performance of the catalyst over 100 h, characterized by a high fuel conversion (99.8%), with a H₂ and CO concentration in the product stream of about 34% and 1%, respectively; CH₄, only by-product of the reforming reaction, was recorded as traces. A light decrease in the C₃H₈ conversion was observed increasing the time of test, associated with a decrease in the H₂ and CO₂ output, while the CO content increased up to 5%.

During the tests, pressure drops in the reactor were recorded, showing stable values: suggests the absence of carbon deposition phenomena. Besides, the temperature along the ATR catalytic bed, measured by thermocouples placed inside the reactor, showed a non uniform distribution, particularly during start-up: this probably caused a sintering phenomena in some parts of the catalytic bed, and can explain the low decrease of the propane conversion after 100-120 h. Besides, the presence of catalyst dust, observed in the ITWS reactor at the end of the long-term tests, denotes a poor mechanical resistance of shift catalyst, that can negatively influences the ITWS (directly) and PROX (indirectly) performances, as shown from the decreasing of H_2 and CO_2 amounts (Fig. 6) coupled with a large CO increasing (Fig. 7).

A good start-up time (from ambient temperature to light-off temperature) of about 20 minutes was also noted.

The performance of the parallel CO preferential oxidation step carried out under an excess of oxygen ($O_2/CO=2$) is shown in Fig. 7.

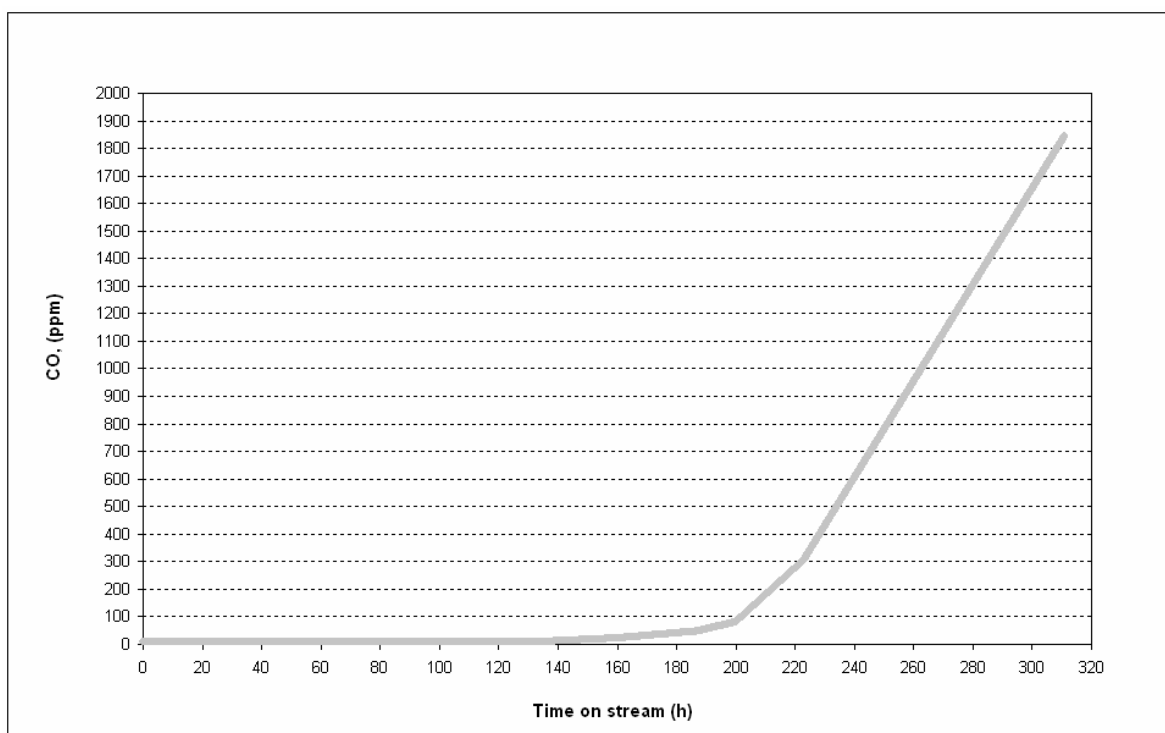


Figure 7. CO concentrations in the product gas from the preferential oxidation reactor.

The experimental O_2/CO ratio, higher than the stoichiometric value, was used considering that the CO content of the ITWS exit can fluctuate incidentally during transient period.

A concentration below to 10 ppm was observed along the initial 140 h of test; after that a rapid increase in the CO content was observed, strictly related to the decrease in the performance of the ITWS step, as previous reported.

The spent ATR catalyst was characterized by means of XRD and TEM analysis. The related XRD pattern, compared with the “as prepared” sample was depicted in Fig. 8.

The observed reflection peaks of CeO_2 in “as prepared” and spent samples present analogous peaks broadening, suggesting that the CeO_2 particle size remains unchanged

after the catalytic tests. Besides, the shift to high degree, observed in both samples, confirms the presence of Pt as solid-solution.

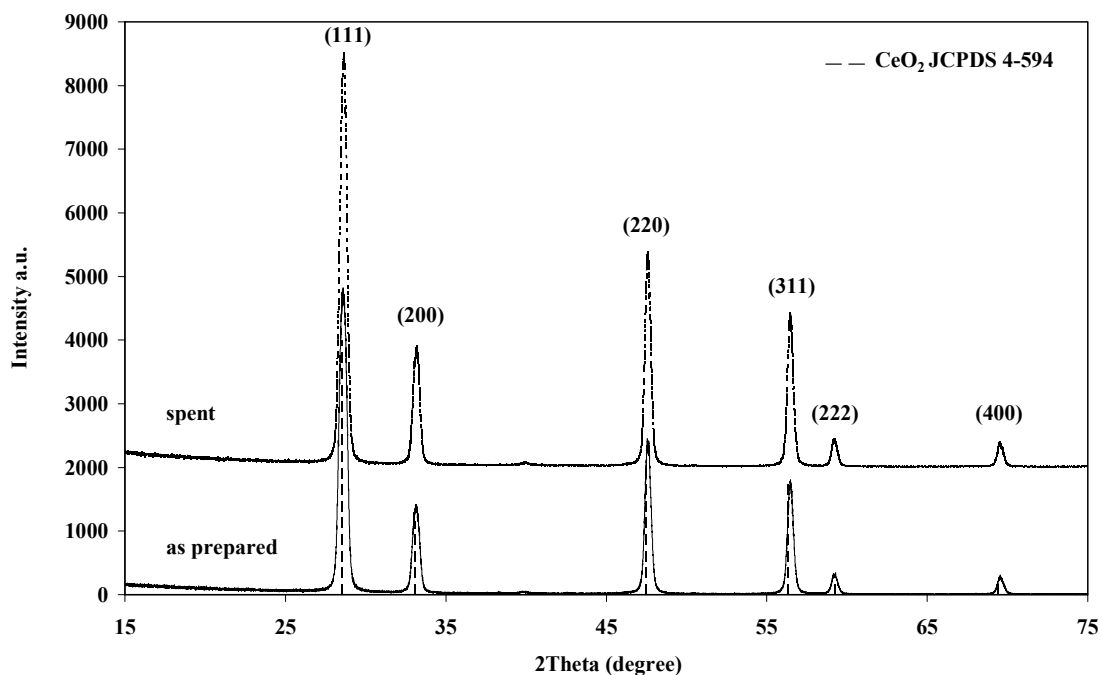


Figure 8. X-Ray diffraction patterns of “as prepared” and spent ATR catalyst.

TEM investigation, carried out on spent catalyst (Fig. 9), shows Pt particle size of about 65 Å, that confirms a little growth of the particle related to the “as prepared” one and the absence of carbon deposition.

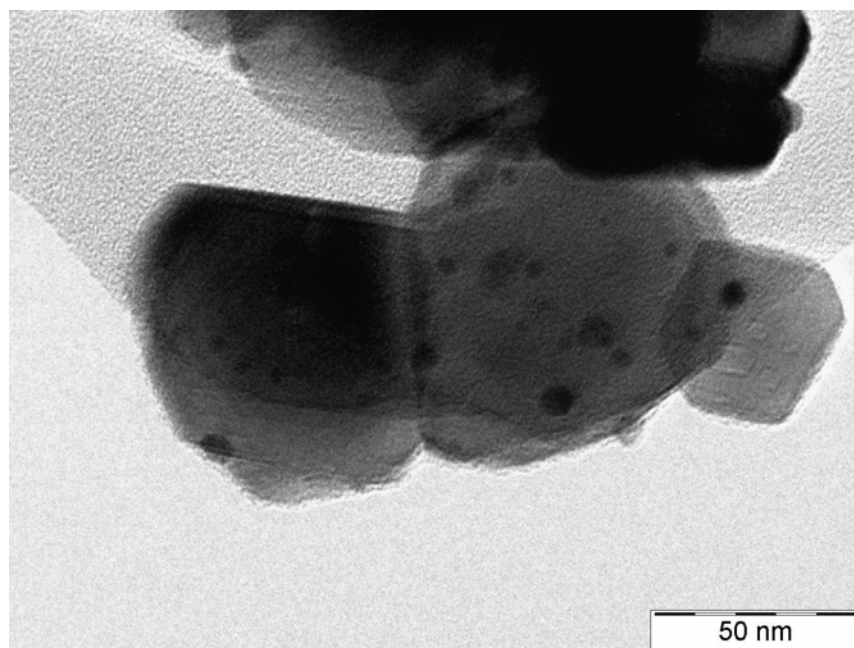


Figure 9. TEM image of spent ATR (Pt/CeO₂) catalyst after catalytic tests.

5. Conclusions

Performance of a precommercial 5 kWe hydrogen generation has been investigated experimentally. The proposed prototype satisfies some of the requests of a proper hydrogen generator, like good propane conversion and H₂ production, small unit size, improved thermal and mass transfer, very simple system management.

The ATR proprietary catalyst has shown a good catalytic activity and stability during several hours of operation with absence of by-product and carbon deposition.

A management unit to monitor operating conditions and control plant equipment has been successfully designed. The main drawbacks indicated in experimental tests include the drop of ITWS performances after 100-120 h and the subsequent CO increase in the PROX output stream.

Additional tests with other ITWS catalysts will be carried out in order to verify the performances in terms of chemical stability (for prolonged start-up and shut-down cycles) and to overcome limiting factors of the unit.

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