Development of sulfur-tolerant ATR catalysts for portable auxiliary low-power units

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Abstract

Fuel Cell technologies provide the opportunity for electric power generation in diverse applications such as recreational yachts, vehicles, etc. where portable, low-cost/volume/weight power sources are required. An LPG Auto Thermal Reformer (ATR) with a High-Temperature Polymer Electrolyte Membrane (HT-PEM) fuel cell looks very attractive as an auxiliary power unit because of simple thermal integration efforts and less requirements concerning the choice of the materials for key system components. However, for safety reasons LPG is odorized by sulfur compounds and even small amounts of sulfur (higher than 1 ppm) can have detrimental effects in the fuel cell anode, the Water Gas Shift (WGS) catalyst and possibly to the reforming catalyst. The present paper describes work towards downstream reformate desulfurization for a 500 W_e ATR-HT-PEM system. Besides conventional wet chemistry-based catalyst development technologies, many advanced technologies have been employed including liquid and solid phase high-temperature synthesis as well as aerosol-based technologies for the development of mixed metal oxide catalytic structures including precious metals (PGM). These catalysts together with a commercially available ATR catalyst have been compared under varying realistic reforming conditions with regard to fuel conversion and hydrogen production (temperature, space velocity, steam-to-carbon and oxygen-to-carbon ratio, sulfur content and PGM content). Specific synthesis techniques led to significant enhancement of performance in the presence of sulfur compared to the commercial catalyst, thereby enabling the LPG/ATR technology to be integrated in such systems.

Introduction

The present paper describes development actions within an EC co-funded research project (PURE) in the framework of FP7-JTI-FCH. This project concerns the realization of an electric power generator based on an LPG Auto Thermal Reformer (ATR) with a High-Temperature Polymer Electrolyte Membrane (HT-PEM) fuel cell. An ATR-HT-PEM systems look very attractive to be used as an auxiliary power unit because of simple thermal integration efforts and less requirements concerning the choice of the materials for the key components of the system. LPG is odorized by sulfur compounds for safety reasons. In Europe, LPG is odorized by ethyl mercaptan (C_2H_5SH) at levels up to 50 ppm for transportation. During reforming sulfur compounds are converted mostly to hydrogen sulphide (H_2S) and in some cases to smaller amounts of carbonyl sulphide (COS). Even small amounts of sulfur (higher than 1 ppm) can have detrimental effects in the fuel cell anode, the Water Gas Shift (WGS) catalyst and possibly to the reforming catalyst. A common practice is to remove the sulfur compounds immediately after the introduction of the fuel into the system. For LPG this is quite difficult since higher hydrocarbons may adsorb competitively to the sulfur compounds. In addition, sulfur removal upstream of the reformer requires bulky sulfur traps which are not suitable for portable and transport related applications. Reformate desulfurization downstream of the reformer provides certain advantages being quite straightforward with less system energy and hardware requirements. On the other hand, desulfurization downstream of the reformer requires a sulfur tolerant reforming catalyst.

This paper focuses on the development of a sulfur-tolerant ATR for the PURE system. The sulfur effects on the reformer depend on the temperature, the sulfur content and the catalyst type. In general the higher the temperature the less the sulfur poisoning [1]. A catalyst with notable deactivation at 700 ºC may demonstrate significant resistance to sulfur at 900 ºC. Obviously, the higher the sulfur content of the feed the higher its effect on the catalyst`. However, it is possible to increase the sulfur tolerance by modifying the composition and/or morphology of the reformer catalyst. In general, precious metals (PGMs) exhibit better sulfur tolerance than base metals such as Ni. Increasing oxygen mobility may lead to better sulfur tolerance as well [2].

The authors have applied advanced liquid and solid phase combustion as well as aerosol-based synthesis techniques to realize catalytic structures of high surface area and porosity for maximizing reforming performance and sulfur tolerance. Several materials were synthesized and evaluated with respect to their reforming performance. As a first step, these materials were benchmarked against a state-of-the-art, commercially available catalyst. Subsequently, following a defined testing protocol, the behavior of the best performing materials was evaluated in the presence of sulfur. The first results obtained called for further catalyst optimisation. The optimized materials went through a thorough performance assessment. This assessment concerned the performance of systems with different catalyst types, synthesis techniques and PGM content under different space velocity, water content and sulfur content concentrations. The assessment revealed two types of reforming catalysts with significant sulfur tolerance.

In this paper, the material synthesis technologies employed by APTL for the production of the reforming catalyst are presented first. A description of the performance evaluation setup is then provided. As a next step, a number of candidate catalytic systems are presented with respect to their reforming performance. Finally, the evaluation concerning sulfur tolerance of the selected materials is presented under varying operating conditions.

Material synthesis technologies and catalytic systems produced

The following material synthesis technologies have been employed for the realization of the PURE reforming catalyst. These are [3], [4]:

Solid State Synthesis (SSS): It concerns a synthesis route that involves co-firing of a mixture of the corresponding component oxides under air.

Solid Phase Self-propagating High-temperature Synthesis (SPSHS): It is based on the heat released from the reaction of a metal powder ("fuel") with oxygen ("oxidizer") in the presence of the corresponding mixture of metal oxides. The reactants are dry-mixed and poured in a molybdenum boat. Initial ignition is achieved with the aid of a tungsten wire. The local ignition creates a flame front that propagates through the whole mass of the reactants that react spontaneously.

Liquid Phase Self-propagating High-temperature Synthesis (LPSHS): It is based on the reaction of nitrate salts ("oxidant") with soluble organic substances that contain aminogroups ("fuel") such as glycine or urea to form ammonium nitrate that is explosive, and in addition, stable chelates with the metal ions in solute on, preventing selective precipitation before combustion. Citric acid can also be employed and in this case the ammonium ions are added as NH_4OH.

Aerosol Spray Pyrolysis (ASP) particle synthesis: ASP is a one-step aerosol-based process where a precursor solution is atomized into fine droplets which are heated when entering a tubular reactor[5]. Every droplet is a microreactor which undergoes evaporation of the solvent and precipitation of reactants when exposed to different temperature profiles and forms a single particle. The synthesized powders are collected in a filter at the reactor exit. The chemistry of the precursor solution as well as the aerosol spray pyrolysis process parameters (e.g. temperature profile, aerosol flow, gas type) can control the particle synthesis at the molecular level (bottom up synthesis), thus leading to controllable porous particle morphologies.

The first three catalyst synthesis technologies were employed during the first round of catalyst production where catalysts with and without PGM (Rh-based and Ni-based catalysts) were realized. The use of SSS, SPSHS and LPSHS led to the development of several catalytic structures based on alumina, cerium or magnesium/silicon oxides and different perovskite and spinel structures. An alumina-based catalyst containing Rh was also synthesized by ASP in a second round of catalyst production (optimization steps). A commercially available catalyst containing Rh was used as reference. Table 1 summarizes the synthesized catalytic systems.

Table 1. Overview of the synthesized catalytic systems

Catalyst	Material	Synthesis	Description
precious metal doping	Cordierite	-	Reference
	Alumina-based oxide	-	"Alumina-based"+1%Rh
			"Alumina-based"+0.5%Rh
	Alumina-based oxide	ASP	"Alumina-base"+2%Rh
	"Cerium-based" oxide	LPSHS	CeZrGd – oxide + 2%Rh
	Perovskite	LPSHS	LaAl-perovskite+1%Rh
Ni-metal doping	Spinel	SPSHS	MgAl-oxide+20%Ni (Mg fuel)
			MgAl-oxide+20%Ni (Al fuel)
	"magnesium/silicon"-oxide	SSS	MgO/SiO$_2$+10%Ni
	"Cerium-based" oxide	LPSHS	CeZr-oxide+10%Ni
	Perovskite	LPSHS	LaAl-perovskite+5%Ce+15%Ni

Three of the most characteristic catalytic materials are presented below. In Figure 1 an image of the conventionally synthesized (wet-chemistry) "Alumina-based" oxide + 1% Rh catalyst obtained by Scanning Electron Microscopy (SEM) is presented. One can notice irregularly shaped particles with increased grain size. Smaller particles are organized into large aggregates.
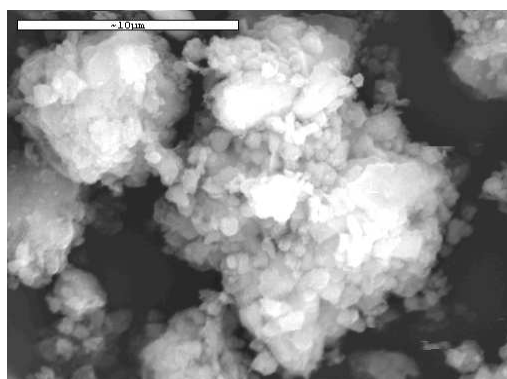

Figure 1. SEM picture of "Alumina-based" substrate+1%Rh

In Figure 2, the LaAl-perovskite/Ce/Ni is shown. The existence of irregularly shaped particles riddled with pores is evident. This is a typical morphology of particles synthesized via LPSHS with the use of glycine as fuel. In Figure 3, the TEM image of the ASP synthesized alumina-based catalyst is presented. The ASP technique was employed to develop specific nano-structured morphologies where catalytic nanoparticles are incorporated into the pores of nanoporous alumina oxide particles; the porous particle acts as a support, which on the one hand offers high surface area for catalytic nanoparticle dispersion and on the other hand its pore cavity acts as protection from catalyst aggregation and associated catalytic surface area loss which can occur during e.g. high temperature conditions.
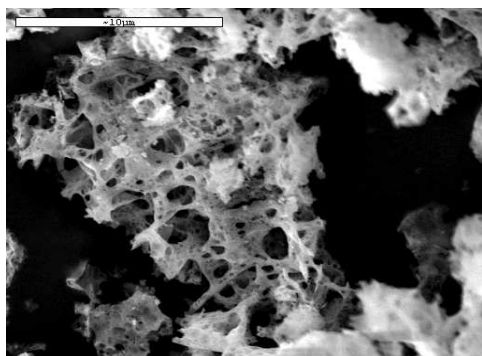
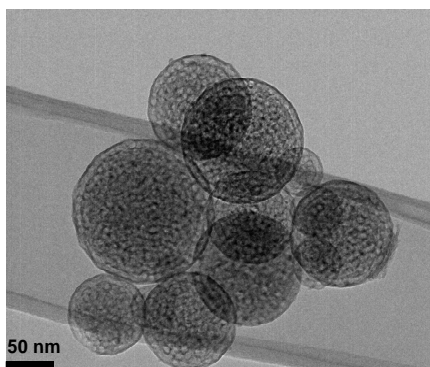Figure 2. SEM picture of the LaAl-perovskite+5%Ce+15%Ni structure.

Figure 3. TEM image of the porous alumina particles with 2%Rh.

Experimental setup

Figure 4 presents the setup used for measuring the performance of the synthesized reforming catalysts. The reactants feed is introduced upstream of the reactor together with sufficient water vapor flow. The reactor is placed in a furnace to efficiently control the temperature of the catalytic bed. Downstream of the reactor, water condensates in a water trap. The product effluent is then analyzed by a mass spectrometer (OMNISTAR™ gas analysis system) measuring the H_2 and propane concentration. CO and CO_2 concentrations are measured by dedicated analyzers.
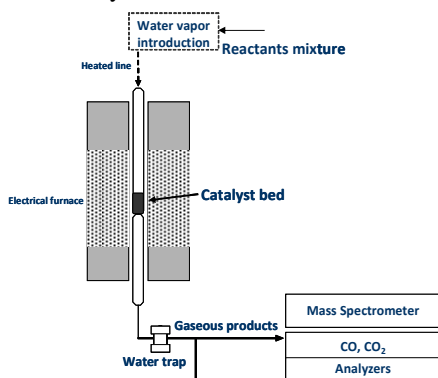

Figure 4. The reforming performance evaluation set-up

The first step of every evaluation assessment test is an in-situ reduction process with 5% H_2 in N_2 at 750 °C. The reforming performance is then tested at constant temperature in the range of 550 to 700 °C. The feed

comprises 6 % C_3H_8 (laboratory grade), 30-60 % water vapor and the balance is air. For reasons of comparison, the Space Velocity (SV) was initially kept constant (100,000 h^{-1}). This means that different masses of the catalyst were used at each test due to the differences in the bed bulk densities.

Results

Assessment of reforming potential without sulfur

A typical reforming test (reformate composition) is shown in Figure 5. The results refer to the "Alumina-based" catalyst with 1% Rh (C_3H_8=6%, water vapor=32 %, balance=air). In this case, at low ($\approx$ 560 °C) temperature the C_3H_8 concentration downstream of the reformer is as low as 0.14 %, while at higher temperatures it becomes insignificant. H_2 concentration starts from 33% ($\approx$ 560 °C) and increases to 37% on a dry basis at $\approx$ 700 °C. The CO concentration increases from 5.2 to 8.4% as temperature increases.
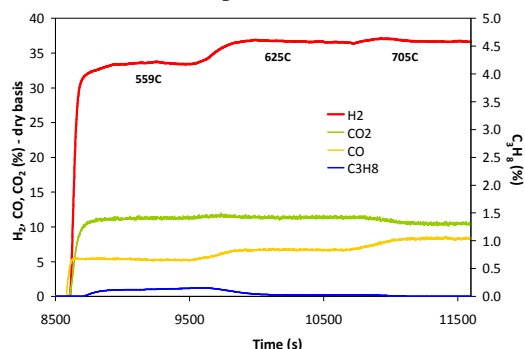

Figure 5. Reforming performance evaluation test for the "Alumina-based" catalyst with 1% Rh.

Three values are considered for the comparison of the reforming efficiency: Fuel conversion, H_2 yield (H_2 in the reformate / H_2 in propane feed) and H_2/CO ratio. Figure 6 presents the reforming results for the catalytic systems presented in Table 1.
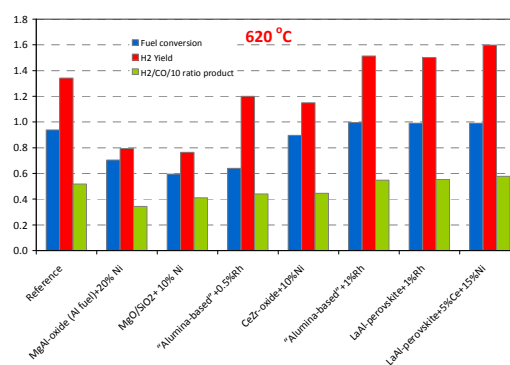

Figure 6. Reforming performance of the different catalytic systems at 620 °C.

Results for the 620 °C case are presented. Conversion is essentially complete for the reference, the alumina based (with 1 % Rh) and the perovskite (with and without Rh) catalysts. Evidently, these systems demonstrate the best performance compared to the other alternatives. Conversion was generally increased with temperature (not shown). For the best performing

systems, H_2/CO ratio is higher than 5 at 620 °C and remains higher than 4 at 700 °C showing, as expected, a decrease as temperature inrceases.

It is useful to compare the above materials on the basis of produced H_2 per g of catalyst (powder mass) employed. From Figure 7, it is obvious that the best performing materials with respect to this parameter are the perovskite catalysts and the "Alumina-based" catalysts. All other materials demonstrate inferior to the reference catalyst performance .
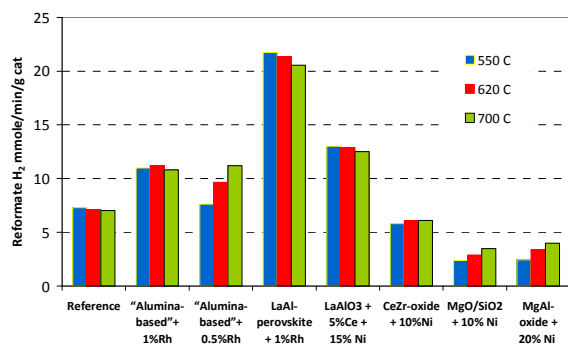

Figure 7. H_2 flowrate in reformate per g of catalyst powder for the different materials synthesized.

Sulfur tolerance tests

For the sulfur tolerance tests, hydrogen sulfide (H_2S) was used as a model sulfur compound in the ATR feed gas. H_2S is the compound mostly used in the literature for studying the thermodynamics of catalyst poisoning. As already stated, LPG is odorized by ethyl mercaptan (C_2H_5SH). Ethyl mercaptan and more complex heterocyclic sulfur compounds as THT and DBT (Dibenzothiophene, $C_{12}H_8S$) may not behave the same as H_2S. However, most of sulfur compounds are transformed to H_2S while the heterocyclic compounds are more stable than H_2S and this leads to less poisoning effects of the catalyst (reaction of sulfur with the reduced metal). Therefore, the tests with H_2S could be considered as representative of the worst case scenario conditions.

As in the case of the reforming performance evaluation tests, the first step is an in-situ reduction process with 5% H_2 in N_2 at 750 °C. Then, the temperature is set to 620 °C and the same as previously feed (6% C_3H_8, air and water vapour) is employed. The system is stabilized at the defined temperature and the reformate composition is measured (H_2, C_3H_8, CO, CO_2). As a next step, H_2S is also introduced into the feed. An H_2S bottle (202 ppm H_2S in N_2) and a dedicated mass flow controller are used for this step. The introduction of the H_2S stream leads to the increase in the space velocity by approximately 25% (dilution effect). The H_2S concentration is 33 ppm in the reactors feed. It should be noted that catalyst deactivation by sulfur poisoning is strongly connected to sulfur concentration. The concentration of 33 ppm is more than 10 times higher than what is expected in the actual operation of the system. In the actual system, the maximum concentration of sulfur in the ATR reactor feed will be 3 ppm and about 2 ppm in the reformate

due to dilution. The higher H_2S concentration was used for acceleration of tests.

A characteristic test for the sulfur tolerance evaluation is depicted in Figure 8 and concerns the reference catalyst. The introduction of H_2S leads to rapid decrease of the produced H_2. A small part of this decrease is caused by the dilution with the stream containing the H_2S (~ 25 %), but the major part is due to the deactivation of the catalyst. This is also evident by the rapid increase of the propane concentration in the reformate. A certain amount of the reduced metal is reacted with the sulfur forming metal sulfide. Sulfidation stops after a certain time period and the H_2 and propane concentrations are reaching a plateau. The same is also true for the CO and the CO_2. As a next step, H_2S concentration in the feed is zeroed. H_2 concentration is increased but the respective value before the exposure to sulfur atmosphere is not re-established, thereby indicating a measurable permanent catalyst deactivation effect. Comparing fuel conversion and H_2 production before and after the addition of sulfur are used as metrics of the catalyst deactivation.
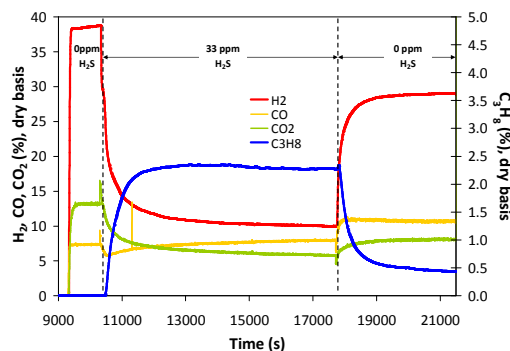

Figure 8. Effect of H_2S in the reformate composition; reference catalyst, T=620 C.

Initial tests revealed that the catalysts without Rh suffered from substantial deactivation due to the exposure to sulfur. Therefore, further testing and development concentrated on the reference, the alumina and the perovskite catalysts containing Rh plus a CeZrGd/Rh catalyst. These catalytic systems have been tested for reforming potential and sulfur tolerance under different space velocities expressed (from 37,000 to 100,000 h^{-1}) or $m^3/kg/h$ (from 100 to 320) and constant temperature (≈620 °C). The Rh concentration also varied in the different systems. Table 2 summarizes the materials tested as well as the experimental conditions per test.

Table 2 Overview of the synthesized catalytic systems tested for sulfur tolerance and the respective experimental conditions.

Catalyst	Substrate	Synthesis	Description	Rh (%)	SV (h-1, '000s)	SV (m3/kg/h)
Rh doping	Cordierite	-	Reference		100	100
	Alumina oxide	Wet Chem.	Alumina based	1 and 2	72 and 100	100 and 140
	Alumina oxide	ASP	Alumina based	2	100	320
	Perovskite	LPSHS	LaAl-perovskite	1 and 2	37 and 100	100 and 270
	Oxide based	LPSHS	CeZrGd	2	100	250

The test results are presented in the following paragraphs. Figure 9 shows the effect of the exposure to 33 ppm of sulfur concentration on the Fuel Conversion

(FC) performance of the materials under evaluation. It should be noted that this plot summarizes all results irrespectively of the SV and the mass of the catalyst samples. All materials demonstrate higher FC after exposure than the reference sample with one exception: the LaAl perovskite/2% Rh/1.3 g. It should be noted though that this sample had much less catalyst mass than the rest of the samples. The increase in the Rh concentration leads to better performance after exposure. In general the increase in the catalyst mass and the Rh content leads to better performance of the exposed samples. One should notice the very good performance of the ASP synthesized catalyst. The performance of this material can be compared to the performance of the LaAl perovskite/3.5 g sample although its mass is more than three times less than that of the perovskite catalyst.
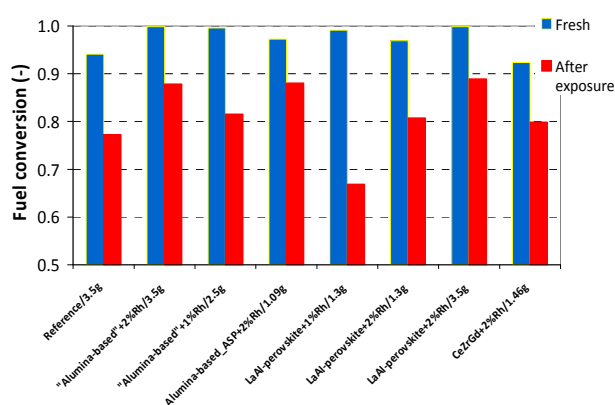

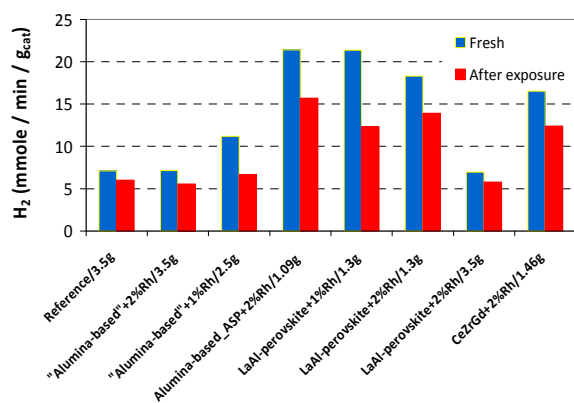Figure 9. Effect of sulfur (33 ppm) exposure on Fuel Conversion.

Figure 10. Effect of sulfur (33 ppm) exposure on H_2 production rate.

Figure 10 presents the effect of sulfur exposure on H_2 production rate. This rate is expressed in terms of mmole/min of H_2 per g of catalyst in order to better illustrate the potential of the different systems as each sample may have a different catalyst mass. One can notice that the reference, the alumina based catalyst and the LaAl perovskite catalyst demonstrate almost the same performance in terms of H_2 production if compared at the same catalyst mass basis. Nevertheless, the ASP as well as the perovskite catalysts demonstrate very high potential and look promising even in case a

small catalyst mass is used. Furthermore one can notice the superior performance of the ASP and the perovskite catalysts compared to the conventionally prepared alumina catalysts as well as the CeZrGd catalyst.

The results presented up to now demonstrate that the most of the tested catalysts reveal a good performance at fresh and after exposure to 33 ppm state. Deactivation of catalyst was present in all cases although some types of catalysts revealed a higher potential for less deactivation. From the systems presented so far the LaAl perovskite and the Alumina catalysts revealed somewhat better performance. Although the ASP prepared alumina-based catalyst demonstrated higher potential than the conventionally prepared catalyst the production of higher amounts of such catalytic structures was not yet readily available to APTL. Therefore, further testing only concerned the LaAl perovskite and the conventionally prepared alumina-based (Wet chem.) catalyst.

As already stated, the presented results concerned a feed containing only 32 % steam, which should be considered low for ATR application. Such low water concentration was used as a pro-active measure for the protection of the gas analysis setup downstream of the ATR. Therefore, and as a next step, increased water-vapor concentration must be studied. As a consequence, the best performing systems were tested under 62 % of water vapor content. Figure 11 and Figure 12 present the respective results where the SV is kept constant for all samples at 100 m^3/kg/h. From Figure 11, it can be seen that for the fresh catalysts the increase in the water content leads to lower FC in both the reference and the alumina catalyst. In the case of the LaAl perovskite, the increase in steam content from 32 to 62 % did not bring any significant loss in the FC. Moreover, the deactivation of the catalysts is, in all cases, more pronounced in the presence of higher stean content. Nevertheless, the LaAl perovskite after exposure demonstrates 16 % higher FC than the exposed reference catalyst.
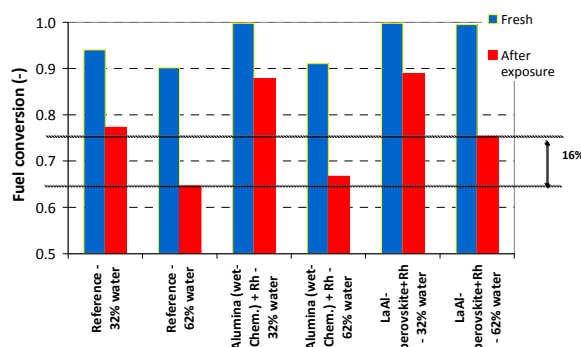

Figure 11. Effect of water content on the FC of fresh and after exposure systems (SV=100 m^3/kg/h).

While the increase in the steam content leads to decreased FC, the opposite is true for H_2 production (Figure 12). The deactivation caused by sulfur is more or less at the same level for the reference and the alumina (wet chem.) catalysts. A quite high H_2 production rate is demonstrated for the fresh LaAl

perovskite/ 2% Rh catalyst. After exposure, this is decreased by 22 % but is still higher by almost 40% than the H_2 production rate of the commercial catalyst.
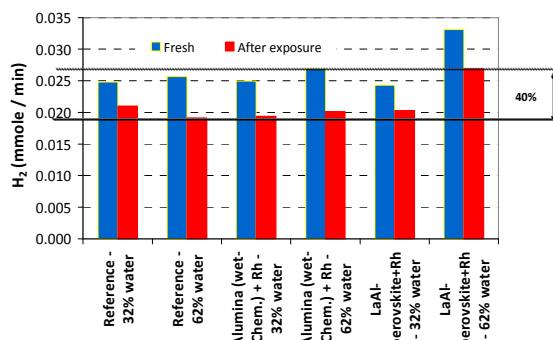

Figure 12. Effect of water content on the H_2 production of fresh and after exposure systems (SV=100 m^3/kg/h).

As already stated, the catalyst deactivation is strongly dependent on the sulfur concentration to which the catalytic system is exposed. The more the sulfur content in the feed the higher the catalyst deactivation. The reference as well as the LaAl perovskite systems have been exposed to lower sulfur content (10 ppm versus 33 ppm) at constant SV (=100 m^3/kg/h) and steam content of 62%. The results are presented in Figure 13 and Figure 14. Figure 13 reveals that in the case of 10 ppm of sulfur exposure, the FC is 17% higher for the LaAl perovskite c.f. the reference catalyst.
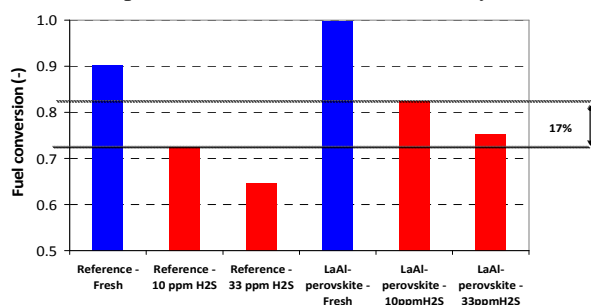

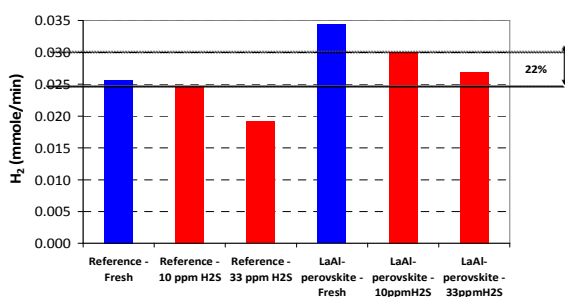Figure 13. Effect of sulfur concentration on catalyst deactivation (FC): SV=100 m^3/kg/h, Water=62%.

Figure 14. Effect of sulfur concentration on catalyst deactivation (H_2 production rate): SV=100 m^3/kg/h, Water=62%.

Figure 14 demonstrates that in the case of 10 ppm sulfur, the H_2 production rate for the LaAl perovskite is 22 % higher than the one of the reference catalyst. More importantly, one can see that the exposed LaAl perovskite demonstrates higher H_2 production rates than even the fresh reference catalyst, a statement which is true for both levels of sulfur exposure (10 and 33 ppm).

Conclusions

The following summarize the conclusions from the ATR material synthesis and evaluation results described above:

- PGM (Rh) inclusion is necessary to enable sulfur tolerance. The more the Rh content the higher the tolerance to H_2S exposure.
- Very active Rh-based ATR catalysts have been developed employing advanced material synthesis technologies (LPSHS for the perovskite and ASP for the alumina-based catalyst).
- The increase in the water content leads to lower FC and to an increase in the H_2 production rate.
- The decrease in the sulfur concentration leads to substantial decrease in the catalyst deactivation.
- 40 % improvement in terms of hydrogen production is realized with the LaAl perovskite catalyst compared to the reference one when 33 ppm sulfur exposure results are considered (22 % in case of 10 ppm exposure).

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