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Hydrogen generation via catalytic partial dehydrogenation of gasoline and diesel fuels

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ABSTRACT

Partial dehydrogenation (PDh) of fuels is a novel method to generate high purity hydrogen on-board, in order to directly feed a fuel-cell based power unit. In this work, the PDh of diesel and gasoline has been studied in order to investigate the possibility of applying such a system to vehicles. The studies have been performed with a Pt–Sn/γ-Al_2O_3 catalyst using a series of diesel and gasoline surrogates. The reactivity of the fuels has been studied, identifying different reaction mechanisms, in relation to the chemical composition and the process conditions. The PDh of a gasoline surrogate provides an average hydrogen production of 1800 NL h^{-1} $kg_{cat}{}^{-1}$ with a purity of over 99% vol. and an extrapolated catalyst lifetime of over 300 h. With diesel, PDh gave an average hydrogen production of 3500 NL h^{-1} $kg_{cat}{}^{-1}$, a purity of over 99% vol. and a lifetime of only 29 h. These preliminary results open up interesting perspectives for future applications of the partial dehydrogenation technology to feed on-board fuel-cells.

1. Introduction

The control of greenhouse emissions to the atmosphere has become mandatory and in the future will become more and more restrictive [1,2]. The combustion of fossil fuels for the transportation is a major contribution to the greenhouse gases and emissions of other pollutants and it is estimated that about 24% of the world-wide CO_2 emissions are caused by land, maritime and aeronautic transports [2,3]. A way to reduce these emissions is to drive this sector in the direction of "more electrified vehicles" (MEV) and currently the most promising technology to do so is with fuel-cells [4–6]. The implementation of a fuel-cell system on-board a vehicle, in particular as an auxiliary power unit (APU) on fossil fuels based vehicles, would increase energy efficiency and reduce of the fuel consumption.

A new fuel processing technology by partial dehydrogenation (PDh) of liquid hydrocarbons is gathering growing interest for hydrogen generation purposes. PDh leads to high purity, CO-free hydrogen, without denaturing the starting hydrocarbons which can be recycled to the fuel tanks. On-board hydrogen production via partial dehydrogenation of kerosene has emerged as an innovative way to produce hydrogen for aviation applications with an increasing number of publications on this subject. The most promising catalyst for this reaction uses Pt alloys supported on mesoporous materials. As first reported by Resini et al. [7], catalytic reaction of kerosene at 350 °C, 5 bar pressure over 5% wt. Pt-1% wt. Sn/γ-Al_2O_3 and 5% wt. Pt-1% wt. Sn-1% wt. Na/γ-Al_2O_3, obtained by impregnation of alumina pellets produces high purity H_2 (90–96% vol.), containing mainly impurities of CH_4 and light hydrocarbons. Better results in terms of purity and hydrogen productivity were subsequently reported by Lucarelli et al. [8,9] also using bimetallic Pt–Sn catalysts. In previous work we have described the possibility of further increasing the process performance either by enhancement of the Pt–Sn/γ-Al_2O_3 system by modification of the support [10] or by the modification of the active phase by addition of a third metal component [11], or by pretreatment of the kerosene feed [12].

Considering the encouraging results obtained in PDh of kerosene, we decided to carry out a feasibility study of the partial dehydrogenation of gasoline and diesel fuels. Since no previous example of partial dehydrogenation of gasoline and diesel were found in the literature we decided, in a first stage, to use fuel surrogates but without presence of sulfur components, in order to better understand the reactivity and explain the mechanisms of reaction and catalyst deactivation, while avoiding sulfur components well known to have a significant impact on catalyst deactivation. This

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Table 1
Fuel surrogate compositions.

Gasoline A	Gasoline B	Diesel A	Diesel B
N-heptane 13.5%	*N*-heptane 15%	*N*-hexadecane 23.5%	*N*-hexadecane 24%
Iso-octane 37.5%	*Iso*-octane 38%	Iso-octane 19%	*Iso*-octane 19%
Cyclohexane 9%	Cyclohexane 10%	Butyl-cyclohexane 27%	Butyl-cyclohexane 27%
Cyclohexene 6%	Cyclohexene 7%	Butyl-benzene 23%	Butyl-benzene 23%
Toluene 30.5%	Toluene 30%	1-Me-napthalene 7.5%	Tetralin 7%
Ethanol 3.5%			

experimental work has as objective the evaluation of the feasibility of the hydrogen production on-board vehicles that rely on gasoline and diesel for their propulsion.

2. Experimental

2.1. Catalyst preparation

The catalyst used for partial dehydrogenation reactions was prepared via incipient wetness impregnation, using the same procedure than in our previous work [10]. The alumina support was prepared via sol–gel method using $AlCl_3$ (Sigma–Aldrich) a sucrose non-surfactant template, NH_4OH for pH regulation and de-ionized water. The mole ratio used for the synthesis of the γ-Al_2O_3 support was 1:0.5:75 for Al:sucrose:H_2O. The resulting gel was heated at 60 °C until dry and calcined at 600 °C for 6 h. Aqueous solutions of $H_2PtCl_6{\cdot}6H_2O$ (*Alfa Aesar*) and $SnCl_2{\cdot}2H_2O$ (*Acros*), in a ratio 1% wt. Pt and 1% wt. Sn (mol. ratio Pt/Sn = 0.61) were used to co-impregnate the alumina support. The tin precursor was first dissolved in 1 M HCl and then mixed with the platinum salt solution upon which the solution turns red–brown due to the formation of a $[PtCl_2(SnCl_3)_2]^{2-}$ complex. It is reported that the procedure of Pt–Sn co-impregnation leads to a higher amount of PtSn alloy formation that favors catalyst stability [13,14]. After drying the impregnated catalyst overnight at 80 °C, it was thermally treated in air at 120 °C for 2 h and then at 560 °C for 2 h (ramp rate 2 °C min^{-1}).

2.2. Fuel surrogates

The composition of the four fuel surrogates used in this work is given in Table 1. The two gasoline surrogates A and B are based on the formulation proposed by Pera et al. [15] and comprises a five component mixture of *n*-heptane, *iso*-octane, cyclohexane, cyclohexene and toluene. The difference between gasoline A and B is that the former also contains ethanol. The two diesel surrogates are formulated on the basis of the studies carried out by Pitz et al. [16]. Both are a mixture of *n*-hexadecane, *iso*-octane, butyl-cyclohexane and butylbenzene but differ by the compound representative of the bi-cyclic hydrocarbons class: 1-methyl-naphthalene for diesel A and tetralin for diesel B.

2.3. Catalyst characterization

Adsorption–desorption of N_2 was carried out at −196 °C with an *ASAP2020* system from *Micromeritics*. Samples were out-gassed at 200 °C for 8 h under a vacuum of 66.7 Pa. Specific surface area was calculated using the BET (Brunauer, Emmett and Teller) method and pore size distribution using the BJH (Barrett, Joyner, Halenda) method using the *ASAP2020* implemented software; pore volume values are relative to the condensation point at $P/P^0 = 0.99$. The acidity of the materials was studied by NH_3 temperature programmed desorption (NH_3-TPD), using an *Autochem 2910* automatic system from *Micromeritics*. Samples were heated to 550 °C in a He flow of 30 ml min^{-1} (ramp rate 5 °C min^{-1}) then cooled to 100 °C. A flow of 20 ml min^{-1} NH_3 was passed over the samples for 1 h, then replaced with He at 100 °C for 1 h. NH_3 was thermally desorbed up to 600 °C with a heating ramp of 10 °C min^{-1} and the signal was recorded using a TC (thermal-conductivity) detector. The apparatus was calibrated using $Ni(NH_3)_6Cl_2$. H_2 temperature programmed reduction (H_2-TPR) war performed in an *Autochem 2910* apparatus. The samples were oxidized in synthetic air (30 ml min^{-1}; 500 °C, 5 °C min^{-1}). After cooling to 50 °C, a 30 ml min^{-1} flow of H_2 (5%)/N_2 mixture was passed over the sample, which was then heated at 10 °C min^{-1} up to 700 °C, recording the H_2 consumption with a TC detector. H_2 chemisorption was performed in an *Autochem 2910* apparatus. The samples were heated in air flow (30 ml min^{-1}; 500 °C, 5 °C min^{-1}) and then reduced with a H_2(5%)/N_2 mixture at 350 °C. Desorption of physisorbed hydrogen was carried out in N_2 flow at 380 °C for 1 h. Pure H_2 pulse adsorption was recorded at 40 °C. The stoichiometry assumed for the dispersion calculation was $Pt/H_2 = 2$ and for the particles size calculation the shape considered was a hemisphere. The amount of chemisorbed hydrogen is determined from the hydrogen pulse peaks. Thermogravimetric analyses of used catalysts were performed using a *Netzsch* STA409TP TG/DTA system, working in dynamic-air flux mode. Before the analysis, samples were out-gassed overnight to eliminate any residue of volatile products in the samples. The thermal program (1 h standby at 60 °C then heating up to 800 °C), was performed in a flow of synthetic air of 50 ml min^{-1}, with a ramp of 5 °C min^{-1}. CNHS elemental analysis on spent catalysts was performed with a *ThermoFinnigan Flash EA1112* automatic analyzer.

2.4. Catalytic tests

The PDh reactions on fuel surrogates were performed in a stainless steel fixed-bed tubular reactor. Before the reaction, the catalyst was oxidized in synthetic air flow (55 ml min^{-1}) at 500 °C and reduced in a H_2/Ar flow (55 ml min^{-1}–4:6 v/v) at 350 °C and atmospheric pressure for 2 h. In order to start the reaction the fuel was fed with a volumetric pump (*Shimatzu* LC20AD—0.53 ml min^{-1}) to the evaporator and then vaporized fuel, for the reactions carried out with recycle simulation, was mixed with a 7% vol. of H_2 before entering the reactor containing pelletized catalyst (d = 1–0.85 mm; $V_{cat.bed}$ = 1.8 cm^3; mass average ≈1 g). These flows were regulated in order to obtain a contact time τ = 2 s (calculated at standard temperature and pressure). A scheme of the reaction rig is shown in Fig. 1. After condensation of the partially dehydrogenated fuel, hydrogen production (NL h^{-1} kg_{cat}^{-1}) was calculated from measurement of the gas out-flow with a digital mass flow meter (*Brooks 5860S1 Smart II* mass flow meter), and the data processed with *LabView 8.2* instrumentation software. Hydrogen production was calculated following the Eq. (1):

$$H_2 \text{ production rate} = \frac{\text{Produced gas outflow (NL/h)} - \text{Hydrogen recycle (NL/h)}}{m_{cat}\,(\text{kg})} \quad (1)$$

Hydrogen purity was analyzed with an *Agilent 7890A* gas chromatograph equipped with a dual column system. A *HP-PLOT molesieve 5A column* connected to a Thermal Conductivity Detector (TCD) was used to analyze the composition of the gas produced by the reaction (hydrogen, methane, propane) and *a HP-PLOT/Q*