High purity hydrogen from catalytic partial dehydrogenation of kerosene using saccharide-templated mesoporous alumina supported Pt–Sn

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A B S T R A C T

Hydrogen is an element of high economic interest, having significant perspectives for future use in applications as an energy vector. Nowadays H2 is produced mainly from hydrocarbons in large scale steam reforming plants. However, local integrated generation of hydrogen directly from fuel cells is emerging as a promising technology, with the advantages of being adaptable to the transport sector and avoiding the problems associated with the storage of gaseous hydrogen. Partial dehydrogenation of transport fuels is attracting increasing interest in this context. Partial dehydrogenation of jet fuel requires the development of specific catalysts, amongst which Pt–Sn supported on a high surface γ-Al2O3, shows good activity and selectivity, leading to production of high purity hydrogen. A strong influence of the textural properties of the support and the chloride content on the hydrogen productivity is observed.

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1. Introduction

In the last two decades, fuel cells have reached a place in the vanguard of power generation technologies, but the means to a sustainable and economically feasible hydrogen supply must be developed. Many options for hydrogen storage have been proposed, liquid or high pressure hydrogen storage [1], metal hydride storage [2], generation by aluminium hydrolysis [3], adsorption on different supports [4,5] and thermo-chemical cycles [6]. A promising alternative is hydrogen generation following chemical storage and subsequent on-board consumption, because it avoids some of the technical and safety issues associated with molecular hydrogen storage. Hydrogen can be released from a vast number of compounds including ammonia, formic acid, or hydrazine [7,8], but hydrocarbons are attractive due to their cost and availability. Several processes are currently in use for hydrogen production, like thermal and catalytic cracking, water electrolysis, coal and biomass gasification, hydrocarbon reforming and hydrocarbon dehydrogenation [9,10]. Transportation fuels, like diesel or kerosene, can be considered a source of stored hydrogen, and this option has been studied as a new way to obtain hydrogen in specific scenarios, like on-board generation of hydrogen as fuel cell feedstock for power generation. Different catalytic processes have been proposed [11–16] to derive hydrogen from diesel and kerosene. Partial dehydrogenation (PDH) of hydrocarbon based fuels is attractive because of their availability, and the potential integration of a PDH process with current technologies. Further, the absence of oxygen in kerosene, for example, implies that the hydrogen stream produced will be free of CO, which could therefore be used directly to feed an on-board proton exchange membrane fuel cell, potentially without further purification or treatment. On the other hand, Partial dehydrogenation of kerosene fuel has great potential for implementation in future development of the aircraft electrification [15,16], the hydrogen generated on-board being used in a fuel cell auxiliary power unit, and the partially dehydrogenated product being returned to the fuel tank [15].

Much has been published about the use of Pt and Ni as active phases for catalytic systems in reforming and dehydrogenation of hydrocarbons, using many types of supports [13,15–19]. In these cases, the use of mild conditions produces less cracking on the hydrocarbon molecules, one of the main pathways for coke

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formation. The formation of Pt–Sn alloy phases supported over alumina has been reported as being active for dehydrogenation reactions, and also for the PDH of hydrocarbon mixtures [15] and ultra low sulfur kerosene (ULSK) [16].

We describe below the development and characterization of novel porous alumina supports for Pt–Sn by using glucose and sucrose as templates and AlCl₃ as alumina source, and the catalytic performance in partial dehydrogenation of ULSK.

2. Experimental

2.1. Catalyst preparation

The method used for support synthesis was based on the work of Xu et al. [20]. In this work, AlCl₃·6H₂O was dissolved in water, and glucose or sucrose was added with a molar ratio Al:sugar:H₂O 1:1:7.5. Afterwards, a solution of NH₃ (30 wt%) was added dropwise to adjust the pH to 5 while stirring at 500 rpm. Sucrose, glucose and aluminium chloride were purchased from Sigma–Aldrich. After stirring for 5 h, the resulting gel was heated at 80 °C until dry and calcined at 550 °C for 6 h, using a ramp rate of 2 °C min⁻¹. The active phase was added to the support by incipient wetness impregnation using a solution of H₂PtCl₆·6H₂O/Alfa Aesar) and SnCl₂·2H₂O (Acros) as precursors, to give a ratio 1 wt%. Pt and 1 wt% Sn (Pt:Sn = 0.61 molar ratio). The tin precursor was dissolved in 1 M HCl and then mixed with the platinum salt solution. The solution turned red-orange, due to the formation of Pt–Sn–Cl complexes [21]. After drying the impregnated materials overnight at 80 °C, they were thermally treated at 120 °C for 2 h and then at 560 °C for 2 h. These support materials are denoted ALUGLUPtSn and ALUSUC respectively, while the suffix PtSn refers to the catalyst as prepared. A reference catalyst was prepared using a commercial alumina (Sasol type SCFa140, labelled JM ref.) and containing the same amount of Pt and Sn and prepared in the same way. Part of the catalyst samples was further steam-treated in a tubular oven (H₂O/N₂ at 550 °C for 2 h), in order to study the influence of dechlorination on catalyst performance. These dechlorinated catalysts are given the further suffix D (i.e. ALUGLUPtSnD).

2.2. Characterization

Structural investigation of the samples was performed by X-ray diffraction, using a PANalytical XPert diffractometer, using Cu Kα radiation (λ = 0.15418 nm, 40 kV, 25 mA) with an acquisition time of 30 min. Phase identification was performed using HighScore software by PANalytical.

Adsorption–desorption N₂ isotherms at −196 °C were carried out with an ASAP2020 system from Micromeritics. Samples were outgassed at 200 °C for 8 h under a vacuum of 0.5 mbar. Specific surface area was calculated using the BET method and the pore size distribution using the BJH method and the ASAP2020 implemented software.

Transmission electron microscopy (TEM) imaging was performed using a Jeol 1200 EX II microscope working at 100 kV. Samples were dispersed in ethanol and dropped over Cu grids.

The chemical composition was determined by wavelength dispersion X-ray fluorescence spectroscopy (WD-XRF) using a PANalytical AxiosMax apparatus working at 4 KW. Data analysis and semi-quantitative calculations were performed using the SuperQ software of PANalytical.

The metal dispersion was calculated from H₂ chemisorption isotherms using an ASAP 2010C apparatus. 100 mg of sample were reduced under a H₂ flow for 2 h at 350 °C prior to analysis, and evacuated for a further 2 h. H₂ chemisorption isotherms were obtained by measuring the adsorbed amount of H₂ for pressures varying from 10 to 600 mmHg at 35 °C. After completing the initial analysis, the reversibly adsorbed gas was evacuated and the analysis repeated to determine the chemisorbed molecules only.

The surface acidity of materials was studied by NH₃ temperature-programmed desorption (NH₃-TPD), using an Autochem 2910 automatic system from Micromeritics. Samples were heated to 550 °C in a He flow then cooled to 100 °C. Then a flow of pure NH₃ was passed through the samples for 1 h, which were then flushed with He at 100 °C for 1 h. NH₃ was thermally desorbed up to 600 °C with a heating ramp of 10 °C min⁻¹ and detected using a TC detector.

H₂ temperature-programmed reduction (H₂-TPR) was performed in an Autochem 2910 apparatus. Prior to the analysis, the sample was heated to 550 °C for 30 min, under a 30 ml min⁻¹ flow of He. After cooling to 50 °C, a 30 ml min⁻¹ flow of H₂/5%N₂ mixture was flowed over the sample, which was heated at 10 °C min⁻¹ up to 700 °C, recording the H₂ consumption with a TC detector.

In order to determine the amount of carbon deposited on used catalysts, thermogravimetric analyses were performed using a SETARAM Labsys TG/DTA/DSC system, working in dynamic-air flux mode. Before the analysis, samples were outgassed overnight to eliminate any residue of volatile products in the samples. The thermal programme (20–700 °C), used a ramp of 5 °C min⁻¹, under a flow of synthetic air of 50 ml min⁻¹.

2.3. Catalytic performance on kerosene PDH

The PDH reaction on ultra low sulfur kerosene (S < 3 ppm), ULSK, was performed in a stainless steel fixed-bed tubular reactor. Before the reaction, the catalyst was reduced at atmospheric pressure with a H₂/Ar flow (4/6, v/v) at 350 °C for 2 h. A vapour flow of ULSK, together with a 7 vol% of H₂ (to simulate a recycle), was fed with a volumetric pump to the reactor containing pelletized catalyst (d = 1–0.85 mm) at T = 450 °C and P = 10 bar. These flows were regulated in order to obtain a contact time τ = 2 s (calculated at STP). After condensing the dehydrogenated kerosene at room temperature and −20 °C using a double condenser, hydrogen production rate (NI H₂ h⁻¹ kgcat⁻¹) was calculated from measurement of the gas out-flow with a digital mass flow metre (Brooks S86051 Smart II mass flow metre), and the data processed with LabView 8.2 instrumentation software. Hydrogen production rate was calculated using Eq. (1):

\[ \text{H}_2 \text{ production rate} = \frac{\text{Gas Flow} \times (\text{H}_2 \text{ Concentration/100})}{m_{\text{cat}}} \]  

(1)

Hydrogen net productivity is easily calculated by subtracting the recycled amount (7%) from the mass flow metre reading and adjusting the sensitivity factor by comparison with a volumetric flow metre installed downstream. A scheme of the reaction rig is shown in Fig. 1. Hydrogen purity was analysed with a gas chromatograph Agilent 7890A with a dual column HP-Plot Molsieve 5A with TC to analyse the hydrogen and HP-Plot/Q with FI detector to analyse the light hydrocarbons produced. The performance was compared with as prepared and dechlorinated catalysts.

3. Results and discussion

3.1. Catalyst activity

The hydrogen productivity plots for as–prepared and dechlorinated samples of ALUGLUPtSn and ALUSUCPtSn catalysts are shown in Fig. 2. Different profiles are observed depending on the nature of the support and its residual chlorine content. Data on catalytic performance and the projected time until productivity drops to 1000 NI h⁻¹ are collected in Table 1. The deactivation factor (DF) and the lifetime are calculated on the basis of a linear interpolation.
Fig. 1. Simplified reactor scheme used for PDH of kerosene. MFC, mass flow controller; G/L sep, gas liquid separator; MF, mass flow sensor; GC, gas chromatograph.

Fig. 2. Hydrogen productivity plots. Reaction conditions: $T = 450^\circ\text{C}$, $P = 10\text{bar}$, $\tau = 2\text{s}$. Left: as prepared. Right: after dechlorination treatment.

Fig. 3. Evolution of hydrogen purity versus time. Reaction conditions: $T = 450^\circ\text{C}$, $P = 10\text{bar}$, $\tau = 2\text{s}$.

of the $H_2$ productivity data in the range of 120–240 min of time on stream. The lifetime has been calculated from the productivity plots using a linear interpolation, taking the values between 120 and 240 min. The deactivation factor (DF) is the rate of loss of productivity per kg of catalyst, and is derived from the slope of the interpolation line. The value of lifetime to $1000\text{Ni h}^{-1}$ is taken directly from the plot.

Regardless of use of the dechlorination step, the ALUGLU based catalysts have the highest hydrogen productivity. Particularly, ALUGLU presents a hydrogen productivity close to $2000\text{NI h}^{-1}\text{Kcat}^{-1}$ at 360 min of TOS. The ALUSUC based catalyst on the other hand, shows greater resistance to deactivation, more than double lifetime, but lower productivity, close to $1000\text{NI h}^{-1}\text{Kcat}^{-1}$ at 360 min of TOS. In both materials, the dechlorination treatment decreases the productivity but gives a small improvement in the stability of catalyst activity with time.

The composition of the gas stream was been determined at periodic intervals, and the results are expressed as hydrogen purity in Fig. 3. In all cases the hydrogen purity exceeds 98%, although catalysts using the ALUSUC support show a tendency to higher purity values (>99 vol.%). In both cases, hydrogen purity is higher

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_2$ conc. (vol.%)$^a$</th>
<th>Lifetime to 1000NI (h)</th>
<th>Lifetime to 0NI (h)</th>
<th>Deactivation factor (NI h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALUGLU/PtSn</td>
<td>97.6</td>
<td>15.0</td>
<td>24.1</td>
<td>109</td>
</tr>
<tr>
<td>ALUSUC/PtSn</td>
<td>98.8</td>
<td>2.1</td>
<td>47.8</td>
<td>22</td>
</tr>
<tr>
<td>JM-Ref</td>
<td>97.2</td>
<td>3.5</td>
<td>11.0</td>
<td>134</td>
</tr>
<tr>
<td>ALUGLU/PtSn D</td>
<td>97.9</td>
<td>6.8</td>
<td>16.8</td>
<td>99</td>
</tr>
<tr>
<td>ALUSUC/PtSn D</td>
<td>99.1</td>
<td>0.5</td>
<td>24.4</td>
<td>36</td>
</tr>
</tbody>
</table>

$^a$ Value at TOS = 240 min.

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than that obtained with the catalyst prepared using a commercial alumina support. The composition of the gaseous outstream is summarized in Table 2. All the compositions give an average value of 98.5 vol.%, H₂ Small amounts of light hydrocarbons are detected, mainly methane. The dechlorination treatment slightly increases the hydrogen purity.

The presence of chloride species can play an important role in the Pt–Sn couple and their catalytic activity in reforming and dehydrogenation reactions. On the one hand, Cl is known to complex with Pt–Sn [21], and increase the interaction between the active phase and the support. On the other hand, Zhang et al. [22] concluded that the dechlorination process decreases the interaction between Pt and Sn, and destroys the initial matching between the metallic functions and the acid function of the fresh catalyst. This effect could lead to a strongly reduced catalyst activity after the dechlorination treatment.

3.2. Characterization

X-ray diffraction profiles of synthesized materials are shown in Fig. 4. Only diffraction lines assigned to γ-alumina (ICSD#01-077-0396) at 37.7, 45.8 and 66.9° (2θ) and metallic Pt (ICSD#01-087-0644) at 38.6, 45.0, 65.5 and 78.3° (2θ) are detected. Diffraction lines are broad, indicating the small size of the crystallites. Using the Scherrer equation, an average value of 4 nm is obtained for Pt domain size, using the main diffraction line at 38.7°. Pt–Sn phases are not directly detected by XRD, and this is consistent with observations of their formation in situ using operando Mössbauer spectroscopy [24]. Adsorption–desorption isotherms of fresh catalysts are plotted in Fig. 5. The isotherms are of type IV in the IUPAC classification, showing a hysteresis loop. Extensive use has been made of surfactants to generate high surface area and control pore dimensions, [25,26] while the use of glucose [20] and sucrose is attractive both from economic and environmental viewpoints. Acidic pH due to hydrolysis of Al(OH)₃⁺ species promotes sucrose hydrolysis to fructose and glucose, enhancing the pore size and the distribution, as observed in Fig. 5. Pore size distributions in the ALUGLI and ALUSUC materials are different, but both are centred at around 10 nm. In case of ALUSUC, a bimodal pore size distribution is observed, due to the presence of glucose and fructose. No evident changes in the shapes of the adsorption isotherms, mean pore sizes or pore size distribution are observed after impregnation, only a reduction of surface area and pore volume (Table 3). The use of glucose and sucrose thus leads to two alumina based supports with different textural properties, which strongly affect the catalytic performance, as shown in Fig. 2 and Table 1.

TEM micrographs of ALUGLUPtSn and ALUSUCPtSn are shown in Fig. 6. Both materials show the same structure, nanosized agglomerated particles of alumina with a size between 3 and 5 nm, and the porosity of the support is clearly visible. Dark spots are observed, that could be assigned either to alumina particles or Pt clusters. The pore and metal particle size that can be measured are consistent with the values shown in Table 3.

The chemical composition has been studied using X-ray fluorescence in order to quantify the amount of chloride present on the as prepared and treated catalysts. In both ALUGLUPtSn and ALUSUCPtSn, the total amount of Cl is around 1.2 wt%. After steam treatment, this value decreases to 0.5–0.6 wt%. For reference, the amount of chloride ion present in as prepared ALUGLU and ALUSUC supports was also measured, and an average Cl value of 0.3 wt% was determined. These values are in line with those described elsewhere [22].

NH₃–TPD profiles of ALUGLU and ALUSUC materials are shown in Fig. 7. These profiles are characterized by two main peaks, one

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centred close to 200 °C, which signals the presence of Bronsted type acid sites, and a second peak between 300 and 400 °C assigned to Lewis type acid sites. Incorporation of the active phase on the support decreases the number of acid sites, probably due to partial coverage of the sites and interaction with metal species. Total acidity values are provided in Table 3. After dechlorination, the total acidity decreases for ALUGLUPtSn D to 292 μmol NH₃ g⁻¹ and for ALUSUCPtSn D to 256 μmol NH₃ g⁻¹, compared with initial values of 327 and 273 μmol NH₃ g⁻¹, respectively. The acidity decrease can probably be explained as a combination of two phenomena: sintering and phase transformation. These phenomena start at as low as 600 °C in the case of commercial γ-alumina, followed by structural transformations [27,28], which provoke a decrease of the number of Lewis acid sites and weakens the interactions between the support and the active phase [22], and elimination of Cl [23].

Dechlorination decreases the hydrogen productivity of the catalysts in partial dehydrogenation of ULSK as shown in Fig. 2, but increases stability due to an acidity modification, as noticed. From the acidity data in Table 3, it may be concluded that a medium acidity is required for higher hydrogen productivity, higher or lower values giving less productivity but lower deactivation rates. It is of interest to relate the relative acidity of the supports to the hydrogen purity described above: the ALUGLU catalysts produce slightly lower hydrogen purity, probably a result of increased cracking reactions due to the higher number of acid sites; similarly the lower surface acidity of ALUSUC based catalysts leads to a higher purity hydrogen product.

In the TPR analysis performed on the fresh catalysts, two broad peaks are observed (Fig. 8). For ALUGLUPtSn, a first peak with a maximum at 220 °C (shoulder at 180 °C) is seen, and a second peak with a maximum at 600 °C and ending at 640 °C. The reduction of Pt(IV) takes place normally in a temperature range of 150–300 °C depending on the strength of the interaction with the support.

In the present case, the first peak is interpreted as including a contribution from the first reduction peak of Sn(IV) and the reduction of Pt(IV) [16,17]. The reduction of Sn(IV) normally leads to two thermal reduction peaks at 200–300 °C and 380–600 °C so that the shoulder at 180–200 °C and the second broad peak at 600 °C could be attributed to the reduction of Sn species [17,29,30]. The profile obtained for ALUSUCPtSn is similar, but with a shift of the peaks to 300 °C and 550 °C, respectively, indicating the Sn(IV) species to be more easily reduced. These different reducibility patterns are related to the textural properties of the support [31], in particular to the lower pore volume of the ALUSUC catalyst (0.37 cm³ g⁻¹) than that of ALUGLU (0.54 cm³ g⁻¹). The lower surface area and pore volume facilitates reduction of Sn species but
favours a stronger interaction between Pt and Sn, which is reflected in the increase of the Pt reduction peak temperature from 220 to 300 °C. This increment in Pt reduction temperature may affect the nature of the final alloy and the resulting catalyst performance, giving lower hydrogen productivity as is observed for ALUSUC based catalyst.

The TGA analyses performed on the spent catalysts show a weight loss in the range 320–480 °C, attributable to the combustion of the carbon coke formed during the PDH reaction. As a representative example, TG and DTA plots of spent ALUSUCPtSn are presented in Fig. 9. The values of mass loss in percentage are in the range of 3–7% and the carbon amount formed appears to correlate with the deactivation factor for each catalyst. From the DTA analysis, two different peaks ascribable to the combustion of different types of carbon may be distinguished. The peak at 360 °C is related to the carbon coke formed on the active metal phase of the catalyst and the second peak at 460–480 °C results from the combustion of the carbon coke formed on the acid sites of the alumina support [32,33].

The TGA plots of spent catalysts (Fig. 10) indicate similar behaviour in all cases, but with lower weight losses for the dechlorinated materials. There is a direct correlation with the acidity and coke formation, less intense peaks being observed for the dechlorinated catalyst and a slight displacement of the maximum temperature in the second peak to higher temperatures, probably related the support acidity. The degree of graphitization of the coke deposited could affect the rate and extent of deactivation [34]. Further studies are underway to improve understanding of the deactivation effects due to carbon deposition.

4. Conclusions

γ-Alumina supported PtSn catalysts are active in the partial dehydrogenation of ultra low sulfur kerosene (ULSK) under mild pressure (10 bar) and temperature (450 °C). The materials synthesized using glucose and sucrose templates, and used as support for the Pt–Sn active phase, provide greater H2 productivity than is obtained by impregnation of a commercial alumina support. The hydrogen productivity, catalyst deactivation rate and catalyst lifetime are strongly dependent on catalyst textural properties. Mild acidity, easily reducible active phases and high surface area in a Pt–Sn based mesoporous alumina catalyst appear favourable to PDH of ULSK.

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