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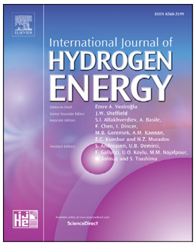

Water-gas shift of reformate streams over mono-metallic PGM catalysts

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ABSTRACT

Mono-metallic Pt and Rh catalysts supported on both CeO_2 and TiO_2 were prepared and tested for water-gas shift activity in a Flowrence, high throughput reactor system. The feed composition mimicked a typical fuel processor, steam methane reformer outlet stream. The Pt/CeO_2 catalyst showed the best metal activity of ~3.8 E-07 moles CO converted·gPt^{-1} s^{-1}, at a Pt loading of 0.5 wt%, activity decreasing with increasing metal loading. Furthermore, the Pt/CeO_2 catalyst produced almost no methane while the Rh based catalysts led to substantial methanation.

Introduction

Hydrogen and fuel cell technologies are reaching the point where commercial implementation at a meaningful scale is to be anticipated within the remainder of this decade. Although automotive applications are well established as demonstrators and with some early production models announced for the next few years, this very large-scale market will remain constrained by the absence of consumer access to hydrogen fuel. At the other end of the applications spectrum, small (0.03 kW–10 kW) fuel cells are likely sooner to transition to commercial use, and whereas the smaller power packs in the range 0.03–0.5 kW (or perhaps even to 1 kW) will likely in many cases employ liquid methanol as fuel (viz. in direct methanol fuel cells, DMFC), (trans)portable power applications in the 1–10 kW range will likely run on hydrogen-rich streams – either pure bottled hydrogen (where storage conditions and supply permit) or locally produced, hydrogen-rich, syngas streams derived from reformed 'hydrocarbon' fuels, notably liquid fuels for reason of their high energy density and availability, or existing networks of natural gas.

The generation of a hydrogen-rich gaseous synfuel from conventional liquid fuels or natural gas is achieved via a number of catalytic stages (typically five) in a process termed a fuel processing. Generically, the process involves desulphurisation, reforming, water gas-shift conversion and a CO clean-up step (either preferential oxidation or selective methanation) at which point the synthetic gaseous feed is suitable for conversion to electric power in a fuel cell. Finally, the fuel cell off-gas, still containing approximately 20% of the hydrogen, is passed to a catalytic combustion stage both for

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purposes of a final conversion of all components to carbon dioxide and water waste as well as for the generation of heat required to drive the initial endothermic steam reforming step.

The need for platinum group metals (PGM's)

All the conversion stages of the fuel processor are catalytic, although, in some cases, the desulphurization step may employ a sorbent instead. Whereas well established base-metal catalysts exist for almost all the catalytic stages (as typically employed in commercial hydrogen and syngas plants), these base-metal catalysts require lengthy and delicate activation procedures (reduction) and even then, remain susceptible to re-oxidation and de-activation by oxygen ingress – in some cases, these materials may also be pyrophoric [1–3]. It is therefore generally anticipated that, for portable and standby fuel cell applications, fuel processor catalysts will be formulated from platinum group metals, both for reason of the nobility (stability with respect to oxidation) and their high activity relative to base-metal catalysts in lower temperature windows, the latter also essential for the development of the small fuel processing footprint desired for small (1–10 kW) power modules [1,4].

PGM's are known to be active for reforming, water-gas shift (WGS) [4,5] preferential oxidation (PrOx) and selective methanation (SelMeth) [5], with Pt, Pd, Ru, Rh and Ir each showing different performance for the various reactions. In addition, various metal-oxide carrier (support) materials show promise, including Al_2O_3, SiO_2, CeO_2, ZrO_2, TiO_2 and others such that, inclusive of synergistic effects amongst both the active PGM's and the various metal-oxide supports, a very large combinatorial space exists for catalyst formulation and optimization [4,6]. Indeed, this compositional space together with the need for formulations which ensure 'freedom-to-operate', suggests that a capacity for the evaluation of large experimental arrays is essential to any programme aimed at developing performance leading PGM-based fuel processor catalysts.

Water-gas shift is commercially undertaken in a two-stage process, viz. (i) high temperature shift (HTS) employing a robust iron-chromia catalyst at elevated temperatures of 375–450 °C and utilising enhanced kinetics for CO conversion, and (ii) low temperature shift (LTS) employing a temperature and poison-susceptible copper-zinc catalyst at mild temperatures of 190–230 °C and utilising improved thermodynamics (i.e. higher equilibrium conversion of CO) [7]. A crucial prerequisite for the techno-economic success of fuel processors for small (trans)portable fuel cell systems and standby power applications is the development of improved WGS catalysts with improved activity in the low-to-medium temperature shift range and that do not require controlled and elaborate pre-reduction processes (as opposed to copper-zinc catalysts), that are non-pyrophoric and oxidation-tolerant on exposure to air (as opposed to both HTS and LTS catalysts).

Of the many catalysts that have been studied and reported in literature over the last number of years, precious metal (mainly Pt, Rh, Ru, Au and Pd) deposited on partially reducible metal oxides (ceria, zirconia, titania, iron oxide and mixed oxides of ceria) have been found to most closely fulfil these requirements [1,8–16]. These catalyst formulations generally offer significant advantages, especially for mobile and (trans) portable applications, in that they are satisfactorily active in the medium shift range of 250–350 °C, which in turn allows for the feasibility of single stage reactors and less complex heat management systems [17]. In addition, the avoidance of pre-reduction requirements also allows for quicker and less complex start-up and cycling procedures. Other transition metals, such as cobalt and nickel that have been investigated as WGS catalysts have been largely discounted due to their high methanation activity, especially below 350 °C [1].

However, apart from their relatively high cost which remains a significant obstacle, some of the technical drawbacks of PGM or noble metal catalysts in WGS applications at low temperatures include (i) lower catalytic activity below 250 °C compared to copper-based materials, (ii) mild yet undesired methanation activity below 300 °C [1], and (iii) formation of strongly-bound formate and carbonate species on the surface, ultimately leading to catalyst deactivation [18]. Unquestionably, deactivation remains a critical issue for PGM-based WGS catalysts, and much efforts are now directed towards improving their durability [17,19,20].

In 2007, researchers from the Honda Motor Company reported results of a combinatorial catalysis study of over 250 000 materials and claimed that catalysts containing a combination of a) one noble metal like Pt or Rh, b) one group 11 metal like Cu, Ag or Au, and c) one partially reducible oxide like CeO_2, ZrO_2, TiO_2, La_2O_3, V_2O_5 or mixed metal oxides thereof, form improved WGS catalysts in terms of both activity and stability in the low–medium temperature shift range [21]. Suppression of methanation activity by the inclusion of basic oxides like ZnO, MgO, CaO, SrO and BaO in the catalyst support have been claimed in a further study [22]. Moreover, the addition of alkali ions has been shown to facilitate the decomposition of formate species [23], whilst the addition of acidic oxides of Nb, Mo, Ta and W has been shown to facilitate the decomposition of carbonates to CO_2 [24], thus improving catalyst stability and preventing deactivation by surface coverage of unreactive species.

This study will focus on the long-term performance (i.e. > 600 h) of various monometallic loadings of Pt and Rh supported on TiO_2 and CeO_2 for the WGS reaction using a typical reformate fuel processing stream and study, in particular, the effect of PGM metal loading on metal specific activity. Catalyst performance will be evaluated in a temperature range of 225–350 °C and relevant space velocities.

Experimental

Catalyst preparation

Monometallic Pt and Rh supported catalysts have been prepared on both CeO_2 and TiO_2, as per a similar method previously described by Luchters et al. [25]. All catalysts have been prepared by the wet impregnation (WI) technique using the Chemspeed Isynth robot. Stock solutions of chloroplatinic acid, H_2PtCl_6, and rhodium nitrate, $Rh(NO_3)$, obtained from Sigma–Aldrich, of sufficient concentration – so as to ultimately prepare catalysts of 5 wt% PGM by one impregnation