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Development of ceria-supported sulfur tolerant nanocatalysts: Pd-based formulations

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Abstract

The conversion of logistics fuels (JP-5, JP-8, Jet-A and diesel) to hydrogen by steam reforming is attractive but poses great challenge since these fuels contain sulfur up to about 3000 ppm leading to catalyst deactivation due to sulfur poisoning. In this paper, we report the fabrication of nominally doped nanoscale ceria-supported palladium catalyst matrices for their performance evaluation in sulfur-laden fuel streams. Systematic structural and microstructural characterization of the catalysts was carried out before and after the steam reforming and simulated experiments in sulfur containing streams (50 ppm \( < S < 1000 \text{ ppm} \)) over a wide range of temperature and duration, to speculate and understand the deactivation mechanism and the sulfur tolerance aspects. Steam reforming of toluene as a model fuel without or with 50 ppm sulfur (as thiophene) was carried out at 825 °C and steam to carbon (S/C) ratio of 3. It was found that the addition of metal oxide additives yielded more stable and sulfur-tolerant formulation.

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Keywords: Nanoscale doped-ceria supports; Noble metals; Metal oxides; Logistic fuels; Steam reforming; Electron microscopy; Sulfur-tolerance; Coking phenomenon

1. Introduction

The level of sulfur contamination in various logistic fuels is typically in the range 0.3–1% by weight (equivalent to 3000–10,000 weight parts per million). The sulfur content in jet fuel currently averages about 0.05% worldwide, well below the specification allowance of 0.3%. Recent legislations enforced by the United States EPA have placed stringent restrictions on other more heavily used hydrocarbon fuels such as gasoline and diesel. In June 2006, the EPA released a mandate that requires refineries to produce ultra-low-sulfur diesel by allowing a maximum sulfur level of 15 ppm. Gasoline also received a mandate in 2004 that requires the sulfur content to be less than 30 ppm [1]. Thus, the fuel processors are required to generate hydrogen-rich reformate for extended periods of time in the presence of sulfur and deliver hydrogen with little or no sulfur to the fuel cell stack. If not sequestered, it leads to the formation of \( \text{H}_2\text{S} \) which is detrimental to the anode in the fuel cell stack [2–4] in addition to emitting unpleasant odor. Not much experimental data is available on catalyst development or testing in actual jet fuels under the preferred experimental conditions (long testing time, higher temperatures and pressures, high gas space velocity, etc.). Currently available catalysts deactivate quickly and/or are poisoned due to large sulfur contents in the simulated/surrogate fuels.

Two areas of utmost priorities with respect to using jet fuel-operated fuel cells are, desulfurization and development of sulfur-tolerant reforming catalysts for jet fuels. The development of robust desulfurizers and new reforming catalysts therefore, is a critical path in the development of processors for jet fuels and their eventual utilization in fuel cells. They are envisaged to provide auxiliary power to the research and commercial flights by NASA (cabin comfort, lighting, air conditioning, taxiing and idling on the runway prior to take-off, etc.), and to the Army for military applications, where distributed power generation in the field is needed [5].

From this point of view, JP-8 is the fuel of choice because of the ‘one-fuel’ policy of the military. Most of the logistic (liquid) fuels contain sulfur in the range of 1500–3000 ppm. In
order to use the hydrogen-rich reformat as the feed in SOFC, the sulfur level should be 0.1 ppm or lower [6]; higher sulfur-containing fuel feeds quickly reduce the cell performance to unacceptable levels. For example, with standard Ni-YSZ anodes at 800 °C, the anode overpotential increases about 20% (at current densities of 0.24 to 0.70 A/cm²) after 3 h of exposure to humid hydrogen fuel with 5 ppm H₂S, and rises to >1 V at 30 ppm H₂S [7]. Lower temperatures worsen the effect: the threshold level of S for the onset of loss of performance, as indicated by an increase in electrode impedance, decreases from 2 ppm H₂S at 1000 °C to 0.5 ppm and 0.05 ppm H₂S at 900 and 750 °C, respectively [8]. For low levels of sulfur exposure (<15 ppm), the effects are reversible with the standard Ni/YSZ anode [8]. The recovery appears to be thermally activated, requiring less time at higher temperatures after elimination of sulfur from the fuel stream. As a benchmark, natural gas contains ~10 ppm of added sulfur-containing impurities as odors [9].

This paper highlights the results of an investigation that was carried out to develop sulfur-tolerant formulations, containing small levels of palladium; the performance of rhodium-bearing analogs has been reported elsewhere [10]. High surface area nanoscale ceria supports were synthesized via hydrothermal process onto which small amounts of noble metals were effectively dispersed by rotary-evaporation technique. Steam reforming of a model C-7 hydrocarbon (toluene with or without metal oxides (loading: 1–5 wt.%) was incorporated on the nanoscale ceria support powders (BET surface area ~80 m²/g), using corresponding water soluble precursors (palladium (II) nitrate (99.95%), rhodium (III) nitrate-2H₂O (99.99%), ytrrium (III) nitrate-6H₂O (99.995%) and copper (II) nitrate 6H₂O (99.999%), all from Alfa-Aesar) and thoroughly homogenized using a rotary evaporator for 4 h. The concentrated semi-solid slurry retrieved from rotovap was kept in a vacuum oven until completely dry. The resulting cakes consisting of soft agglomerates were crushed manually and, pulverized in a ball mill using isopropyl alcohol (IPA) and zirconia spheres (5 mm diameter) as the milling media. The resulting material was again dried at room temperature and ambient pressure in a fume hood and sieved through 325 mesh screen. Each formulation was calcined in air for 2 h at 700 °C. The gross composition of the catalysts employed in this study is listed in Table 1. Formulations with the prefix 1 are GDC-based and those with prefix 2 are ZDC-based.

2.2. Catalyst and second phase loading

Palladium (loading: 0.5–1 wt.%) with or without metal oxides (loading: 1–5 wt.%) was incorporated on the nanoscale ceria support powders (BET surface area ~80 m²/g), using corresponding water soluble precursors (palladium (II) nitrate (99.95%), rhodium (III) nitrate-2H₂O (99.99%), ytrrium (III) nitrate-6H₂O (99.995%) and copper (II) nitrate 6H₂O (99.999%), all from Alfa-Aesar) and thoroughly homogenized using a rotary evaporator for 4 h. The concentrated semi-solid slurry retrieved from rotovap was kept in a vacuum oven until completely dry. The resulting cakes consisting of soft agglomerates were crushed manually and, pulverized in a ball mill using isopropyl alcohol (IPA) and zirconia spheres (5 mm diameter) as the milling media. The resulting material was again dried at room temperature and ambient pressure in a fume hood and sieved through 325 mesh screen. Each formulation was calcined in air for 2 h at 700 °C. The gross composition of the catalysts employed in this study is listed in Table 1. Formulations with the prefix 1 are GDC-based and those with prefix 2 are ZDC-based.

2.3. Characterization

The catalyzed powders were characterized with respect to the dispersion of the active metal, crystallinity, morphological features and, the temperature-programmed reduction characteristics. X-ray powder diffraction (XRD) signatures on the calcined as well as on the post steam-reformed sample were collected on a Philips diffractometer (PW 3050/60 X’pert Pro), using monochromatic Cu Kα1 radiations (λ = 1.54056 Å) and Ni filter. The scanning and transmission electron microscopy was carried out using Phillips XL30-FEG and JEOL 2011 instrument for SEM and TEM, respectively. Both these instruments are equipped with the capability of doing energy dispersive X-ray spectroscopy (EDS) as well. Temperature-programmed-reduction (TPR), chemisorption, and BET surface area analysis were all conducted using the Micromeritics AutoChem 2910.

2.4. Fuel reforming experiment

Fig. 1 illustrates the components involved in the experimental set-up of the reactor system. The organic feed (toluene, C₇H₈) and water were pumped into the system via a ChromTech Isocratic Pump (Series II, high pressure liquid chromatography (HPLC) pump). Air, nitrogen, and argon, provided by Airgas,

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Dopant in ceria matrix</th>
<th>Active metal</th>
<th>Oxide additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A/2A</td>
<td>Gd₂O₃ (10 mol%)/ZrO₂</td>
<td>Pd (1 wt.%)</td>
<td>None</td>
</tr>
<tr>
<td>1J/2J</td>
<td>Gd₂O₃ (10 mol%)/ZrO₂</td>
<td>Pd (1 wt.%)</td>
<td>Y₂O₃ (5 wt.%)</td>
</tr>
<tr>
<td>1L/2L</td>
<td>Gd₂O₃ (10 mol%)/ZrO₂</td>
<td>Pd (1 wt.%)</td>
<td>CuO (5 wt.%)</td>
</tr>
</tbody>
</table>

Table 1
Nominal composition of the ceria-based catalysts investigated in this study
Inc., were regulated to provide the required flow rates using an Alicat Scientific Mass Flow Controller (model # MC-500SCCM-D, P-D control, local mode). Each feed entered the system through individual 1/8-in. OD stainless steel tubing from Swagelok. Each feed stream was passed through heating coils placed in the pre-heater furnace (Hoskins Mfg. Co.), which was set to a temperature of 550 °C, and temperature was controlled by an Omega Monitor/Controller. The feed lines were connected through a 4-way Swagelok cross, mixing the feeds just after the pre-heater.

The reactor was an 18-in. long (i.d.: 0.68-in. and o.d.: 1-in.) stainless steel tube, complete with custom seals and couplings from Swagelok. The coupling at the top of the reactor tube has a thermocouple port through which a 12-in. long K-type thermocouple (0.0625-in o.d.) from Omega was inserted. The rolled strip (detailed give below) was placed in a stainless steel tube (i.d.: 0.68-in. and o.d.: 1-in.) with the tip of the thermocouple in the closest proximity of the foil. The reactor tube was placed vertically inside a PID-controlled tubular furnace. The reforming reactions were run at 825 °C with a steam-to-carbon ratio of 3:1. The gaseous product emitting out at the top of the reactor tube were led into a Shimadzu gas chromatograph (GC-2010) for the composition analysis, after proper conditioning and removal of excess water via condensation. A ShinCarbon ST, 100/120 mesh, Silcosteel Micropacked column (length = 2 m, i.d. = 1.0 mm, catalog #19808), used for separating permanent gases, such as CO and CO2, and light hydrocarbons mixtures, was connected to the pulse discharge ionization detector (PDID) for analysis of N2, H2, CO, CO2, and CH4. A 30 m long RT-QPLOT column of inner diameter 0.53 mm was connected to a flame ionization detector (FID) for analysis of heavier hydrocarbons: C3H2, C2H4, C3H6, C4H6, C5H8, C6H8, and C4H10. An initial temperature of 40 °C was held for 6 min, followed by a ramp of 30'/min to 180 °C, held for 10 min and then a second ramp to 230 °C at 50'/min. Once this temperature was reached, it was held constant for 3 min. Each catalyst was tested for steam reforming of toluene (Fisher Scientific, Certified A.S.C.) at atmospheric pressure, 825 °C, S/C = 3:1, and a GHSV = 11,000 h⁻¹. Prior to testing, catalysts were pre-treated by reduction for 2 h at 500 °C using 5% H2–N2 gas mixture.

To gauge the sulfur-tolerance of the catalysts, experiments were performed with fuel simulating a sulfur-laden stream. The toluene feed was doped with thiophene (99%, Alfa Aesar) to a concentration equivalent to 50 ppm of sulfur. Thiophene was used as a simulant for the organosulfur compounds (primarily substituted thiophenes) typically present in jet fuel. A level of 50 ppm was chosen assuming that this would be achievable if high sulfur jet fuel was desulfurized prior to reforming.

The stoichiometry of the steam reforming (SR) reaction, assuming the water gas shift reaction also occurs, can be written as:

\[
C_7H_8 + 14H_2O \rightarrow 18H_2 + 7CO_2
\]  

The composition of the gas was measured by the GC, with the known flow rate of the inert gas (nitrogen or argon) providing an internal standard through which the product gas flow rates could be calculated. Hydrogen yields were calculated according to the stoichiometry of the reaction,

\[
H_2 \text{ yield} = \frac{(F_{H_2})}{(n_{H_2})(F_{C_7H_8})} \]  

Fig. 1. Schematic of the reforming reactor set-up used in the present work.
Experimental set-up shown in Fig. 3 was designed and fabricated in this research.

2.5. Sulfur-tolerance evaluation

In order to test sulfur tolerance of the catalysts, an experimental set-up shown in Fig. 3 was designed and fabricated. About 1 g of the dry and free flowing catalyst powder was packed into a 1-in. long Swagelok cylindrical filter (porosity 80 μm). Folded glass wool was used as the cushion for the catalyst powder and also as the top lid. This facilitated an unrestricted gas flow across the sample without any pressure build-up. In order to simulate the actual experimental conditions in a reformer, the catalyst was activated and brought in-situ to a state it would exist, prior to and during reforming. The gas cylinders containing pure nitrogen, pure hydrogen and nitrogen containing 1000 ppm H2S were connected to a manifold (FCV-1) via flow meters for each of these gases entering the reaction chamber (R-1). After leaving the reaction chamber, the gas was passed through a bottle (V-1) containing dilute silver nitrate solution in order to precipitate out uncaptured H2S, prior to letting the exhaust gas into the open atmosphere.

All the sulfidation experiments were performed in a fume hood. The sample was subsequently allowed to cool naturally to room temperature under nitrogen atmosphere. Upon retrieval from the reactor, the samples were evaluated using XRD, SEM/EDS, TEM/EDS, TPR/Chemisorption, and BET surface area measurements to assess and quantify the influence of temperature-time-sulfur exposure process parameters. The amount of sulfur captured by the catalyst was also determined by chemical analyses.

3. Results and discussion

Catalysts, usually in the form of a powder, can be supported or unsupported. Supports are used to provide large surface area to the catalyst and are typically inert to the process and are only present as a surface area promoter. Alumina (Al2O3) is a common support for a number of catalysts in oil refining due to its high thermal and chemical stability. Ceria (CeO2) is commercially used in automotive catalytic converters as a support for the three-way catalyst for reducing harmful emissions from the tail pipes of automobiles. Cerium oxide is well known for its high oxygen storage capacity (OSC), and oxygen mobility and facile reducibility due to its easy CeIII ⇄ CeIV equilibrium [11–14]. Ceria when used as a support for a precious metal, results in the transfer of oxygen to the supported metal while the support is then re-oxidized by the water present in the steam reforming reaction. In streams containing SO2, ceria-based catalysts loaded with nominal amounts of transition metal oxides (Cu, Ni, Co) have shown to be surprisingly active in reducing SO2 exhaust emissions implying certain level of sulfur tolerance [15–18]. Thus, while most supports are inert to the on-going reaction and are configured to be surface area promoters, a ceria support allows enhanced activity in a simultaneous bi-functional role. CeO2-based materials are quite active and highly stable catalysts in reducing as well as oxidizing atmospheres in high temperature regimes compared to other conventional support systems. This in conjunction with a preparative technique that provides nanoscale particles results in a high surface area catalyst with the possibility of high activity for the reforming of sulfur-laden fuels. The gadolinium oxide and zirconium oxide dopants in ceria provide higher temperature stability and an increased oxygen storage capacity (OSC). An increase in OSC results in an increase in oxygen vacancies which contributes to an increase in reducibility of the ceria as well [19] with a concomitant increase in ionic conductivity [20]. Even though CeO2 is more active as a reforming catalyst than Ce2O3, as ceria is reduced from CeO2 to Ce2O3, the latter could contribute
positively toward the much sought after sulfur tolerance of the catalyst. It turns out that in a reducing environment, Ce₂O₃ has a higher sulfidation equilibrium constant than does CeO₂. This translates into the propensity of formation of either cerium oxysulfide (partial sulfidation) or cerium sesquisulfide (complete sulfidation). Thus, in the temperature range of 600–850 °C, following reactions are encountered:

Reduction: \[ \text{CeO}_2 (s) + (2 - n) \text{H}_2 (g) \rightarrow \text{CeO}_n (s) + (2 - n) \text{H}_2 \text{O} (g) \]

Sulfidation: \[ \text{CeO}_n (s) + \text{H}_2 \text{S} (g) + (2n - 3) \text{H}_2 (g) \rightarrow \text{Ce}_2\text{O}_2\text{S} (s) + 2(n - 1) \text{H}_2 \text{O} (g) \]

This reaction pathway might help mitigate sulfur-led poisoning and deactivation in the long run. Such a sacrificial role may allow the precious metal to remain active longer resulting in higher catalyst life on-line. As an additional benefit, it has been reported that H₂S adsorption on ceria is partially reversible [19]. The thermodynamics of the CeO₂–H₂S reaction, however, do not allow the reduction of H₂S to below 200 ppm at about ~627 °C; even at a temperature of 827 °C, H₂S level cannot be reduced to below 100 ppm. This requires ceria to be in a reduced form, CeOₙ (n < 2) to achieve the desired sulfur removal levels. These cyclic redox characteristics of ceria are well known and have been advantageously exploited in many catalytic processes. After reduction of the CeO₂ to Ce₂O₃, oxygen ion vacancies are created by the removal of oxygen. As sulfur is introduced to the reduced state, sulfidation occurs rapidly. This initial sulfidation is an irreversible step. However, any additional surface sulfidation beyond this point is reversible [21–23]. In the light of these characteristics, ceria was selected as the catalyst support system in this work.

3.1. Morphological and structural features of the catalyst supports

It is well known that the preparatory history (viz., synthesis ad processing) and physical attributes (such as surface area, particle size, agglomeration, porosity, etc.) of the catalyst supports play a crucial role in explaining the observed behavior of a catalyst. For example, low catalytic activity can be ascribed to small surface area, large particle size or large particle size distribution and uneven porosity in the support. Fig. 4 shows the TEM image of the as-synthesized GDC and ZDC powders (scale bar = 1 nm).

The nanoscale features of the particles are clearly seen. In the case of GDC powder, the lattice spacing (~ 0.167 nm) is also evident which suggest that even in the as-prepared stage the powder is mostly crystalline. Similar nanoscale features were present in the ZDC powder prepared by the hydrothermal process adopted in this work.

The comparative X-ray diffraction patterns in Fig. 5 show the systematic evolution of crystalline structure in the GDC powder as a function of calcination temperature; the numbers 4, 7 and 10 refer, respectively, to 400, 700 and 1000 °C, the temperature at which the as-prepared (GDC-0) powder was...
calcined for 2 h each. It can be seen that while the peak positions remain unchanged, the peak width gradually decreased with increase in calcination temperature, indicative of the expected and systematic particle growth with temperature. Calculation using Scherrer’s equation for the (211) reflection of GDC yielded values of 9.1, 18.3 and 73.2 nm as the crystallite size of the powder calcined at 400, 700 and 1000 °C, respectively. The inset shows the XRD pattern of nanoscale ZDC calcined at 700 °C for 2 h. These patterns conform to the standard ICDD cards.

3.2. Evaluation of Pd-catalyzed formulations

3.2.1. Catalysts 1A (Pd/GDC) and 2A (Pd/ZDC)

The catalysts 1A and 2A are, respectively, GDC and ZDC formulations loaded with a nominal amount of palladium,
The TEM images of 1A calcined at 700°C for 2 h are shown in Fig. 6. As can be seen, the material possesses nanofeatures with particle size in the range of 5–10 nm. The EDS signature collected on 1A (not shown) identified all the constituents present.

Catalyst 1A (Pd/GDC) and 2A (Pd/ZDC) were used: (i) as powder in more severe sulfidation test (1000 ppm H$_2$S/N$_2$) at 825°C for 4 h and (ii) in the form of foil supported system for steam reforming of toluene without and with 50 ppm sulfur (as thiophene) in the stream at 825°C for 20 h.

The TEM images of the catalyst 1A calcined in air and after sulfur exposure are shown in Fig. 7 (a and b, respectively). Two distinct features can be readily discerned. First, there is noticeable grain growth as a result of sulfidation. Second, the particle edges sharpened and assumed more defined geometrical motifs compared to those in the virgin catalyst. This leads to the likelihood of a surface-limited gas–solid interaction between hydrogen sulfide and the catalyst. The sulfur up-take by 1A is corroborated by a representative EDS signature (analysis performed on various regions of the sample exposed to 1000 ppm H$_2$S at 825°C; Fig. 7c).

The morphological features of catalyst 1A after steam reforming of toluene in sulfur-free and sulfur-laden stream are compared in Fig. 8. Again, several interesting features can be highlighted. First, the TEM images in Fig. 8(a–b) show that while the nanofeatures of the catalyst grains are preserved, the particle size has increased. As seen from Fig. 6, the virgin catalyst sample consists of particles with size ranging between 5 and 10 nm; steam reforming causes the particle size to increase by about three-fold (~15–30 nm). This could be an artifact of grain growth as a result of long dwell time (~20 h) at high temperature (825°C) under the reforming conditions.

In addition, sintering leading to agglomeration can also be seen (Fig. 8c and d). In particular, in image 8d, the beginning of the formation of necks between adjacent particles, which is the precursor to the onset of sintering, is clearly visible. The phenomena of sintering and particle agglomeration result in surface area reduction leading to a concomitant lowering of the catalytic activity. Palladium containing catalysts such as 1A seem to be particularly vulnerable to sintering. This could be due to the fact that the stability of palladium in a hydrogen-rich atmosphere is quite low.

Fig. 8. Post-reforming TEM images of catalyst 1A (Pd/GDC) with: (a) 0 ppm and (b) 50 ppm sulfur in the stream (scale bar: 5 nm). Images c (scale bar: 20 nm) and d (scale bar: 5 nm) show the evidence of sintering, agglomeration and particle coalescence after 20 h in S-free stream.
It has also been reported that at high temperatures palladium tends to migrate to produce a more favorable arrangement with a lower surface area [24]. The particle size increase can be attributed to the expected grain growth at high temperatures. This corresponds well in terms of increase in particle size and texturing observed in XRD patterns. Although the sulfur poisoning is expected to be more severe in samples exposed to 1000 ppm H₂S as opposed to 50 ppm during the reforming reaction, it still reinforces the fact that deactivation may be linked in some way to sulfur poisoning during steam reforming even if at a slower rate. It is worth mentioning here that the semi-quantitative elemental analysis results from EDS yield sulfur content that is more than what could have theoretically been possible if it is assumed that only palladium was sulfided. Thus, it is most likely that GDC was also sulfided during the H₂S reaction; both Gd₂O₃ and CeO₂ are capable of forming thermodynamically stable oxysulfides – Gd₂O₂S and Ce₂O₂S. This assumption is strengthened by the work of Karljalainen et al. [15] wherein, based on thermodynamic modeling and reliable phase diagrams, it was reported that sulfur tends to react more readily with ceria under reducing conditions to form Ce₂O₅S than it does with precious metals to form corresponding sulfides.

On the contrary, the ZDC-supported formulation (catalyst 2A, Pd/ZDC) did not seem to undergo drastic morphological variations after steam reforming under the same experimental conditions. The post-reforming (toluene without sulfur) TEM images shown in Fig. 9, exhibit small (~10 nm) particle size and less of agglomeration and/or sintering. This is in excellent agreement with the crystallite size (~11 nm) calculated from the XRD pattern collected on the same sample and shown in Fig. 10, using Sherrer equation [25]. For comparison, the diffraction pattern of the fresh sample is also shown, which indicates that but for some grain growth, the chemical structure of the catalyst remains intact after steam reforming.

Furthermore, similar benign trend were observed when the catalyst 2A was subjected to sulfidation experiments at 825 °C in gas streams containing 1000 ppm H₂S for 4 h. While some grain refining was evident, sintering and agglomeration were found to be less pronounced. This can be seen from the TEM
image shown in Fig. 11. Moreover, in contrast to the catalyst 1A (Fig. 7), the EDS analysis of the post-sulfidation samples of 2A did not show the presence of sulfur. Thus, in the light of the foregoing discussion it is safe to assume that a zirconia-doped ceria support offers a higher sulfur tolerance than the gadolinia analog.

Fig. 12 shows a comparison of the reforming activity of the catalysts loaded with palladium on both GDC and ZDC supports in sulfur-free and sulfur-laden streams. It can be seen that under identical experimental conditions, the Pd-supported catalysts perform better in non-sulfur bearing stream than in sulfur-laden stream. Moreover, in the initial periods (up to ~5 h) of reforming, ZDC-based catalyst showed superior performance, in terms of hydrogen yield, in the stream laden with 50 ppm sulfur. In the later case, both 1A and 2A, nevertheless, demonstrated the attainment of steady-state in about 6 h on stream with hydrogen yield hovering around 15%. Slight activation of the Pd/GDC formulation observed in the case of sulfur-laden stream is likely due to the prevailing non-steady state condition in the initial hours (~0–2 h) of reforming.

3.2.2. Catalysts 1J (Pd, Y2O3/GDC) and 2J (Pd, Y2O3/ZDC)

Catalysts 1J and 2J contain Pd as the precious metal and Y2O3 as the oxide additive and both showed improvements over catalysts 1A and 2A, the corresponding Pd-only analogs; the presence of oxide additive improved the catalytic activity (~60% H2 yield versus ~35% in Pd-only formulation) and stability in non-sulfur fuel streams. This is shown in Fig. 13.

In comparison to the A-series, Catalyst 1J showed slightly better performance in sulfur-free fuel feeds whereas 2J showed slightly better performance over 1J.

However, the performance edge of the ZDC-based formulation (2J) over its GDC analog was marginal. The hydrogen yield was also higher with J-series compared to the A-series in sulfur containing streams, 1J performing better than 2J (15% versus 25% H2 yield). A noteworthy effect of the addition of Y2O3 to the catalytic formulation is the increase in the noble metal (Pd) dispersion in ceria matrix. Calculations based on the results of CO chemisorption on the A- and J-series catalysts showed that the Pd dispersion in J-series was more than three times higher than in the A analogs; for example, the Pd dispersion increased from 2.5 to 7.8% in the presence of Y2O3, thereby increasing the surface area of metals from 0.115 to 0.350 m2/g of the sample. Calculations based on these chemisorption experiments also revealed that metal oxide addition resulted in reducing the particle size of the active metal.
from 44 nm in the A-series to 14 nm in the J-series. The enhanced dispersion of the precious metal attributed to the metal oxide addition seems to have enabled the catalyst to remain highly active in the non-sulfur feed with little deactivation. The deactivation that did occur could be attributed to the migration and sintering of palladium at the intergranular region (EDS evidence). The TEM images of the as-prepared 1J sample and that subjected to sulfidation in 1000 ppm H₂S at 825 °C for 4 h are compared in Fig. 14.

An additional feature of the oxide phase addition to the catalyst formulations is the occurrence of coking-related deactivation that was not noticed with the ‘noble-metal only’ formulations (A series). Both samples in J-series showed signs of coking in sulfur-free as well as sulfur-laden fuel stream. This is corroborated by the TEM-EDS analyses conducted on the post-reforming specimen.

The morphological features of the post fuel-reformed (feed without and with 50 ppm sulfur) 1J samples are compared in Fig. 15; grain growth leading to some sintering is evident in the later case.

3.2.3. Catalysts 1L (Pd, CuO/GDC) and 2L (Pd, CuO/ZDC)

The formulations 1L and 2L are similar to the J-series Pd-loaded matrices but with another oxide additive, viz., CuO. The L-series catalysts significantly outperformed the other Pd-supported catalysts, particularly in the first 2 h on stream. Surprisingly, 1L outperformed all other catalysts in the first 2 h in the presence of sulfur as well, giving as high as 95% H₂ yield. However, this was followed by a very rapid deactivation where H₂ yield declined steadily to around 30% before the reforming reaction ended. A plausible explanation for this behavior could be as follows. Copper oxide underwent rapid reduction to elemental copper which was immediately consumed by H₂S to form the corresponding sulfide; it is also feasible that copper oxide by itself reacted with gaseous H₂S leading to the formation of the corresponding sulfide (CuS). The reason for such a rapid deactivation due to sulfur poisoning could be explained from another angle. In the temperature-programmed-reduction (TPR) conducted on the formulations developed in this research, majority of the systems exhibit a hydrogen consumption hump at temperatures in the range of 300–350 °C – characteristic of reduction of nanoscale ceria. At this juncture it should be mentioned that the TPR spectrum for the L-series of catalysts did not exhibit the hydrogen consumption hump in the vicinity of 300 °C. This would suggest that in this particular case, the ceria support might remain unreduced (CeO₂).
stated earlier that the stoichiometric cerium oxide does not have high sulfidation equilibrium constant. This facilitates sulfur to directly attack the other active species (either the noble metal or the oxide additive). This theory might also support the observed high spike in H₂ yield, by taking into cognizance the impact of the additional stability and activity provided by CeO₂ in the initial stages of reforming reaction versus the deactivation that is promoted by reduced form of ceria (Ce₂O₃) in other formulations, whereby during longer times on stream and under more reducing environment (i.e. the high H₂ yield regime), CeO₂ does in fact get reduced.

The average particle size in the post-reformed 1L sample calculated from the XRD data is approximately 30 nm and the corresponding surface area is ~ 25 m²/g. This loss of surface area is confirmed by the TEM images of the pre- and post-reforming samples shown in Fig. 16; the latter shows evidence of significant grain growth combined with agglomeration and sintering.

Fig. 17 shows a comparison of the activity of L-series catalysts with that of A- and J-series analogs in sulfur-free and sulfur-laden atmospheres. It can be seen that generally the addition of an oxide phase contributed to a definite increase in activity and stability versus the Pd-only loaded catalysts. However, the role played by different additives is different and strongly dependent on the type of oxide employed. The addition of yttrium oxide seemed to have contributed more to the activity of the catalyst while the copper oxide addition seemed to show significant enhancement in long-term stability. However, the reason for the unusual behavior of 2L sample, at this time, is unknown, and experiments are underway to collect detailed structural, microscopic and quantitative data to help explain the observation. Similarly, it is also unknown if the catalyst truly behaves in the manner shown or that there were some unknown experimental variables that contributed to this.

4. Conclusions

Nanoscale powders of doped ceria support were developed and used to synthesize a large number of novel sulfur-tolerant catalyst formulations. The morphological and fuel reforming characteristics of a number of palladium-supported catalyst systems were studied and attempts were made to correlate the two. High hydrogen yield, sulfur-tolerance and relatively higher stability during long dwells on stream in sulfur-laden fuel feeds were some of the salient features. The performance enhancement was attributed to the high dispersion of the noble metal.

Metal oxide additives were also shown to have certain beneficial effects on the catalyst performance. Addition of Y₂O₃ along with a nominal loading of palladium showed an increase in yield over its noble metal-only counterpart. This has been attributed to the increased metal surface area available for reaction. Addition of a different oxide (CuO) also proved to be effective in increasing yield over its metal-only loaded counterpart. In addition to the increased hydrogen yield, the copper oxide containing formulations also displayed an enhanced stability. Based on the experimental data, it was concluded that the increased yield in this case was due to an increase in metal dispersion on the catalyst surface while the increased stability was most likely due to the oxide acting as a sacrificial sulfidation site, taking the sulfur species away from the active metal and/or the ceria support. Addition of CuO, demonstrated substantial improvement in terms of hydrogen yield, albeit not without deactivation. The H₂ yield from catalyst 1L decreased drastically from 90 to 27% in this case, the hydrogen yield steadily decreased throughout the duration of the experiment. It appears that longer times on-stream are needed to better determine the long term behavior of CuO containing catalysts. The J-series catalysts containing Y₂O₃ also demonstrated higher activity than the A series. While these catalysts did not reach the same level of activity as did the CuO-promoted catalysts, they demonstrated improved stability over time. Some deactivation did occur, but compared to 1L there was, relatively, not a drastic loss of performance. In the light of these results, it is expected that more robust catalytic formulations that show tolerance to even higher level of sulfur in the stream without compromising the hydrogen yield and, the stability and integrity of the system could be designed. These efforts are now underway.

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References


