Cooperative Synergy in Nanoscale Ceria-Based Systems

Desikan Sundararajan1 and Abdul-Majeed Azad2, *

1 Green Systems, 6551 Westminster Ct., Liberty Twp, OH 45044, USA
2 Department of Chemical Engineering, The University of Toledo, 2801 W. Bancroft St., Mail Stop # 305, Toledo, OH 43606-3390, USA

Rapid industrialization and growth in global population have led to energy consumption all over the world at an unprecedented pace witnessed never before. This phenomenal industrial growth has compromised the ways energy is produced and used. To meet the rapidly increasing demand for energy, newer pathways ought to be discovered to improve the efficiency of energy production and utilization. In this context, fuel cells are seen as the near-term alternatives capable of providing clean and high efficiency energy. Clean power source utilizing vast logistic fuel reserves (natural gas, jet fuels, diesel and coal) would be the main driver in the 21st century for high efficiency. However, the jet and other logistic fuels are invariably sulfur-laden. Sulfur poisons and deactivates the reforming catalysts. Robust and reliable fuel processors are required to convert these fuels into high quality hydrogen (for PEMFCs) or hydrogen-rich reformate (for SOFCs) for extended periods, and deliver hydrogen with little or no sulfur to the fuel cell stack. Therefore, it poses great technical challenge and requires development of robust sulfur-tolerant catalysts. In this paper, the philosophy and technical rationale for the development of such formulations is highlighted, by selecting a non-traditional nanoscale ceramic support and recognizing its synergistic role towards improved on-stream performance in conjunction with the actively operating intermetallic cooperative phenomena among the noble metals present in them.

Keywords: Nanoscale Ceramic Powders, Ceria, Precious Metals, Ruthenium, Palladium, Rhodium, Sulfur-Tolerant Catalysts, Fuel Reforming, Hydrogen.

CONTENTS

1. Introduction ........................................ 739
2. Materials and Methods ............................... 741
3. Characterization ..................................... 742
4. Results and Discussion ............................... 743
4.1. A Priori Catalyst Activation........................ 743
4.2. Microstructural and Structural Artifacts of the Supported Formulations .................. 745
4.3. Propensity to Sulfur Tolerance...................... 746
4.4. Phase and Microstructural Evaluation of Post-Sulfided Samples ...................... 746
4.5. Steam Reforming Characteristics .................... 748
5. Conclusion ........................................ 761
References and Notes ................................ 761

1. INTRODUCTION

Our energy infrastructure dictates continued and increased use of fossil fuels for the next several years and maybe decades. The use of domestic resources, such as coal is especially attractive. Clean power source utilizing vast reserves of other logistic fuels (JP-8, Jet-A, kerosene and diesel) would be the main driver for high efficiency fuel cells. Hydrocarbon fuels such as diesel and jet fuel have logistics (well-established distribution network) and safety advantages for military applications compared to compressed hydrogen. Energy densities of both diesel and jet fuel JP-8 (11.8 and 11.1 kWh/Kg, respectively) are much higher compared to lower hydrocarbons (natural gas). Furthermore, diesel is a petroleum derived product that is a complex mixture of paraffins (n-, iso-, and cyclo-paraffins) and ring chained aromatic compounds (squaline, tetralin and methyl naphthalenes). Reforming of diesel to produce hydrogen from solid oxide fuel cell has great advantages, as the hydrogen density of diesel is very high. The reformate gas contains mainly CO, CO2, H2 and trace amount of H2S. The sulfur products can be removed by sulfur sorbents.

A direct application of this technology is by installing SOFC based auxiliary power unit (APU) in trucks to provide energy instead of relying on running diesel engine. Similarly, fuel cells running on jet fuel reformate are attractive to NASA for its uninhabited aerial vehicle and...
low emission alternative power missions. The US military has interest in fuel cells due to their lightweight, zero emission and low acoustic signatures in strategic zones. Jet fuels, such as Jet-A and JP-8 are already on board in many applications. If they can be reformed and used in solid oxide fuel cells (SOFCs), military missions can be made more effective. Hydrogen had been touted to be the ideal energy carrier of the future well over a century ago by Jules Verne.\(^1\)

Owing to the emergence of fuel cell technology, the demand for hydrogen production is constantly increasing. The growth rate in the hydrogen production industry has been in excess of 10% per year for the last four years. Fifty million metric tons of hydrogen, equal to about 170 million tons of oil equivalent, was produced in 2004. In 2007, the hydrogen produced amounted to 65 million metric tons.\(^2\) According to Freedonia Group Inc., the net worth of the fuel cell industry was approximately $1 billion in 2008, the estimated growth is projected to be $18 billion by 2015.\(^3\)

However, the infrastructure for fuel cell based H\(_2\) economy is years or even decades away. Therefore, hydrocarbon fuels must first be converted into a hydrogen-rich stream. The catalysts used for reforming heavy hydrocarbons are poisoned by sulfur invariably present in logistic fuels as organosulfur, up to 0.3–4% (3000–40,000 wppm);\(^4\) the level of sulfur in coal varies between 2.3% and 4.5% depending upon the quality of the bituminous coal.\(^5\) During reforming process, this sulfur is also likely to get transformed into H\(_2\)S; if not removed effectively, H\(_2\)S (\(<1\) ppm) deactivates the SOFC anode rapidly.\(^6\)

Thus, fuel processors are required to convert logistic fuels into hydrogen-rich reformate for extended periods in the presence of sulfur, and deliver hydrogen with little or no sulfur to the fuel cell stack. In order to facilitate continuous uninterrupted operation of logistic fuel processors, robust sulfur-tolerant catalysts ought to be developed.

In light of the recent quest for cleaner and greener energy, the use of hydrogen-rich reformates of logistic fuels such as Avgas (aviation gasoline), JP-5, JP-8 and military has interest in fuel cells due to their lightweight, zero emission and low acoustic signatures in strategic zones. Jet fuels, such as Jet-A and JP-8 are already on board in many applications. If they can be reformed and used in solid oxide fuel cells (SOFCs), military missions can be made more effective. Hydrogen had been touted to be the ideal energy carrier of the future well over a century ago by Jules Verne.\(^1\)

Owing to the emergence of fuel cell technology, the demand for hydrogen production is constantly increasing. The growth rate in the hydrogen production industry has been in excess of 10% per year for the last four years. Fifty million metric tons of hydrogen, equal to about 170 million tons of oil equivalent, was produced in 2004. In 2007, the hydrogen produced amounted to 65 million metric tons.\(^2\) According to Freedonia Group Inc., the net worth of the fuel cell industry was approximately $1 billion in 2008, the estimated growth is projected to be $18 billion by 2015.\(^3\)

However, the infrastructure for fuel cell based H\(_2\) economy is years or even decades away. Therefore, hydrocarbon fuels must first be converted into a hydrogen-rich stream. The catalysts used for reforming heavy hydrocarbons are poisoned by sulfur invariably present in logistic fuels as organosulfur, up to 0.3–4% (3000–40,000 wppm);\(^4\) the level of sulfur in coal varies between 2.3% and 4.5% depending upon the quality of the bituminous coal.\(^5\) During reforming process, this sulfur is also likely to get transformed into H\(_2\)S; if not removed effectively, H\(_2\)S (\(<1\) ppm) deactivates the SOFC anode rapidly.\(^6\)

Thus, fuel processors are required to convert logistic fuels into hydrogen-rich reformate for extended periods in the presence of sulfur, and deliver hydrogen with little or no sulfur to the fuel cell stack. In order to facilitate continuous uninterrupted operation of logistic fuel processors, robust sulfur-tolerant catalysts ought to be developed.

In light of the recent quest for cleaner and greener energy, the use of hydrogen-rich reformates of logistic fuels such as Avgas (aviation gasoline), JP-5, JP-8 and
Jet-A as the feed for PEMFCs and/or SOFCs for NASA and the Department of Defense, is attractive. Given the energy crisis in the US and especially in Southeast Asia in terms of its ever-rising demand, fuel cells running on clean hydrogen feeds derived from abundant logistic fuels, are attractive options, provided a strategy for effective desulfurization and sustained reforming via robust sulfur-tolerant catalysts is in place.

Much work has been done to better understand the sulfur poisoning of Ni- and Rh-based reforming catalysts.\textsuperscript{7-8} In presence of CeO\textsubscript{2}, Ru-supported Al\textsubscript{2}O\textsubscript{3} catalyst showed high sulfur resistance in the steam reforming of kerosene;\textsuperscript{9} sulfur tolerance increased from 0.1 to 50 ppm. Nevertheless, a highly active sulfur-tolerant catalyst for steam reforming of logistic fuels has not yet been developed.

Even though the key active metals used in the reforming catalysts are Pt, Pd, and Rh, no systematic study exists to compare their performance in the steam reforming of a given logistic fuel under identical experimental conditions. Nor is there a study where the definitive role of one precious metal over the other has been elucidated. Therefore, systematic investigation was undertaken to understand the role of precious metals in imparting sulfur-tolerance to the nanoscale ceria-based reforming catalysts in the process of hydrogen generation via steam reforming. The active metal dispersion in these sulfur-tolerant catalyst formulations was varied between 1 and 1.33 wt.%. The formulations contained either a single precious metal or a bi-metallic or a tri-metallic combination. These formulations were assessed in terms of their sulfur-tolerance, phase integrity and the quality of reformate from kerosene (a JP-8 surrogate) fuel at temperatures typically employed in reforming.

The rationale behind the choice of nanoscale ceria as support material in this work is as follows. While alumina (Al\textsubscript{2}O\textsubscript{3}) is a common support for a number of catalysts in oil refining due to its high thermal and chemical stability, there a great deal of rationale for using ceria supports in the present work. Ceria is commercially used in catalytic converters as a support for three-way catalyst for reducing harmful emissions from automobiles.\textsuperscript{10} It is well known for its high oxygen storage capacity (OSC) and easy reducibility due to its facile Ce\textsuperscript{III} ↔ Ce\textsuperscript{IV} equilibrium; CeO\textsubscript{2}-based materials are quite active and stable both in reducing and oxidizing atmospheres in high-temperature regimes compared to other conventional support systems.\textsuperscript{11-14} This, in conjunction with a preparative technique that provides nanoscale particle size distribution, results in a high-surface-area catalyst with the possibility of high activity for the reforming of sulfur-laden fuels. When used as a support for precious metal(s), it results in the transfer of oxygen to the supported metals while the support is then re-oxidized by the water present in the steam reforming reaction. Increased OSC leads to increase in oxygen vacancies which contribute to increased reducibility of ceria as well. Although, CeO\textsubscript{2} is more active as a reforming catalyst than Ce\textsubscript{2}O\textsubscript{3}, it can act beneficially towards sulfur tolerance as well as will be shown later.

Thermodynamically, in a reducing environment Ce\textsubscript{2}O\textsubscript{3} has higher sulfidation equilibrium constant than CeO\textsubscript{2}, suggesting the possibility of formation of either cerium oxysulfide (partial sulfidation) or cerium sesquisulfide (complete sulfidation). This mechanism might help mitigate sulfur-mediated poisoning and deactivation of ceria-based catalysts in the long run. This sacrificial role may also allow precious metal(s) to remain active longer, resulting in better catalyst life. Furthermore, H\textsubscript{2}S adsorption on ceria is partially reversible. The thermodynamics of the CeO\textsubscript{2}–H\textsubscript{2}S reaction, however, do not allow the reduction of H\textsubscript{2}S in the stream to below 200 ppm at about 627 °C. The reaction is endothermic and, though the equilibrium H\textsubscript{2}S level decreases with increasing temperature, even at 1100 °C, the H\textsubscript{2}S level cannot be reduced to below 100 ppm. On the other hand, the CeO\textsubscript{2}–H\textsubscript{2}S reaction is exothermic and the equilibrium H\textsubscript{2}S concentration increases with increasing temperature. Interestingly, however, H\textsubscript{2}S level could be reduced to below 1 ppm at 1000 °C.\textsuperscript{15} This requires ceria to be in a reduced form (CeO\textsubscript{2}; n < 2) to achieve the removal of sulfur to desired levels. Upon reduction, CeO\textsubscript{2} goes to Ce\textsubscript{2}O\textsubscript{3}, thereby creating oxygen ion vacancies, and thus sulfidation of ceria occurs rapidly. It has been reported that CeO\textsubscript{2} exhibits superior resistance to sintering when doped with zirconia or rare-earth oxides.\textsuperscript{16} In the light of these characteristics, doped ceria was used as a support matrix for the development of sulfur-tolerant catalytic formulations.\textsuperscript{17-19} For the same unique physical and chemical attributes, nanoscale 10 mole% gadolinia doped-ceria (GDC) was used as a support material for all the catalyst formulations prepared in this research.

This chapter would deal with the rationale of selecting ceria as the support and the choice of using one, two or three noble metals, in the development of a series of supported nanocatalysts. Their performance with regard to their suitability for the steam reforming of kerosene (a JP-8 surrogate) in terms of high hydrogen yield and excellent sulfur-tolerance over extended period of time on stream, would be assessed and compared. The unique feature of this series of ceria-based formulations pertaining to the presence of low levels of carbon monoxide and carbon dioxide and, higher level of methane in the reformate will also be analyzed. Finally, a plausible mechanistic correlation between the role of precious metals in the presence of one another by way of intermetallic cooperative phenomena, and the synergistic role of ceria support towards the improved on-stream performance of the developed formulations is proposed.

2. MATERIALS AND METHODS

Nanoscale support material consisting 10 mole% gadolinia (Gd\textsubscript{2}O\textsubscript{3})-doped CeO\textsubscript{2}—hereafter referred to as
GDC—was synthesized via ammonia precipitation using appropriate water soluble precursors for cerium and gadolinium (from Alfa-Aesar, MA) followed by hydrothermal treatment of the basic slurry thus obtained, in an autoclave at 240 °C, for 2 h. The resulting material was dried overnight and systematic structural and morphological characterizations were carried out to follow the crystallization and phase evolution pathways as a function of calcination temperature and time.

The catalysts were formulated by dispersing precious metals onto the GDC support material, using their respective water soluble precursors: ruthenium (III) chloride (99.999%), palladium (II) nitrate (99.95%), rhodium (III) nitrate hexahydrate (99.999%), all from Alfa-Aesar, MA. For this purpose, an aqueous slurry of GDC and the precious metal precursors in appropriate weight fractions, was homogenized in a rotary evaporator for 4–6 h and the thickened mass was dried overnight in a vacuum oven at 100 °C. The dried cake consisting of soft agglomerates was crushed using mortar and pestle, and pulverized in a ball mill using 2-propanol and 5-mm diameter zirconia media. The ball-milled slurry was dried again under ambient conditions and sieved through 325 mesh screen. Each formulation was calcined in air at 700 °C for 2 h.

A summary of the 10 catalyst formulations developed and investigated for their steam reforming characteristics is given in Table I. Throughout the discussion hereafter, they will be referred to as per the IDs assigned to them.

The experimental set-up for sulfidation experiments is shown in Figure 1. Steam-reforming experiments were carried out on powder samples (1 g) using kerosene as the fuel. Liquid chromatography-mass spectroscopy test established the sulfur content of this kerosene sample to be 260 ppm as determined by Paragon Laboratories, MI. A quartz tube, 19-in long and 1-in diameter was used as the packed-bed reactor. The catalyst was packed in a stainless steel filter (from Swagelok™) with 5 μm size pores. The filter containing the catalyst was placed in the center of the reactor and plugged with loosely packed quartz wool. The quartz reactor was then placed in a 1-in. ID split tube furnace equipped with a PID controller.

Water and fuel (kerosene) were pumped into the reactor with high precision HPLC pumps. Argon was used as a sweep gas for the reforming reactions. The steam to carbon ratio (S/C) was maintained at 3. The flow rates of water and fuel were adjusted to maintain a constant space velocity in the reactor at 65,000 h⁻¹. The feed stream containing sweep gas, water and fuel was first introduced into a pre-heater (vaporizer furnace) operated at 250 °C to ensure complete vaporization of the feed. All reforming reactions were carried out at 800 °C. The product stream coming out of the reactor was drawn into a condenser to separate the liquid and gas products. The liquid fraction consisted mainly of water and un-reacted fuel with traces of other liquid hydrocarbons. Shimadzu GC, Model 2010 equipped with pulsed discharge helium ionization detector (PDHID) and flame photometric detector (FPD) was used to analyze the composition of the gas reformate mixture. The FPD was useful in detecting sulfur species in the reformate stream. The schematic of the experimental set-up used in the steam reforming experiments is illustrated in Figure 2. The duration of the experiment was determined by the stability and activity exhibited by the catalysts on stream. The hydrogen yield was defined as:

\[
\text{%yield} = \left(\frac{F_i}{F_{i,0}}\right) \times 100 \quad (1)
\]

where, \(F_i\) is the moles of species \(i\) produced per min, \(v_i\) is the stoichiometric coefficient of species \(i\), and \(F_{i,0}\) is the molar flow rate of the reactant in moles/min.

The reforming tests were conducted over extended period of time and terminated as per a pre-determined criterion of arbitrarily selected hydrogen yield reducing to 20% of its highest level or the sulfur level reaching 50 ppm (as H₂S) in the exit stream. Concentration of other gases was also monitored simultaneously as a function of time. The GC was calibrated with respect to hydrogen, carbon monoxide, carbon dioxide and methane—the major constituents in a typical reformate—over a wide range of concentrations. GC was also calibrated with respect to H₂S concentration between zero and 1000 ppm.

### Table I. Formulations and IDs of steam reforming catalysts developed in this research.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Noble metal dispersion</th>
<th>Ru</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-metallic formulations</td>
<td></td>
<td>1 wt%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bi-metallic formulations</td>
<td></td>
<td>–</td>
<td>1 wt%</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td></td>
<td>–</td>
<td>1 wt%</td>
<td>–</td>
</tr>
<tr>
<td>Tri-metallic formulations</td>
<td></td>
<td>1/2 wt%</td>
<td>1/2 wt%</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td></td>
<td>1/2 wt%</td>
<td>–</td>
<td>1/2 wt%</td>
</tr>
</tbody>
</table>

#### 3. CHARACTERIZATION

All formulations (as-prepared, post-sulfided and post-reformed) were characterized by various characterization techniques to study their crystallinity, active noble metal dispersion, microstructural and morphological artifacts. Temperature programmed reduction (TPR) of the as-prepared catalysts samples was performed using Micromeritics Autochem 2910 (Norcross, GA). TPR...
analysis was particularly instrumental in determining the activation protocol for catalysts prior to sulfidation and reforming experiments. Reduction temperature and hydrogen uptake for each catalyst were used as a metric for catalyst activation based on the TPR studies. The total amount of sulfur retained by the catalysts was quantified by wet chemical techniques by NSL Analytical, Cleveland, OH.

Systematic microstructural analysis was performed by scanning electron microscopy (SEM-Phillips XL 30 FEG) and transmission electron microscopy (TEM-JEOL 3011). Both these techniques are equipped with the capability of performing energy dispersive X-ray spectroscopy (EDS) as well. The SEM is equipped with Rutherford’s back scattering electron mapping (RBSE) as well. The chemical state analysis of the active components in the post-reformed samples was performed by using X-ray Photoelectron Spectroscopy on the Kratos Axis Ultra XPS.

4. RESULTS AND DISCUSSION

4.1. A Priori Catalyst Activation

As is customary in all catalysis work, it is necessary to bring the catalysts to their most active form, prior to their use in reforming. An activation protocol was established by using the technique of temperature programmed-reduction (TPR) using the Micromeritics 2910 instrument (Norcross, GA). The amount of sample used in all the TPR experiments was kept constant (0.1 g). The TPR signals for the mono-metallic catalysts are compared in Figure 3. Some interesting features in terms of the location
Table II. Summary of the TPR characteristics of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total H₂ uptake for activation (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-metallic</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>21.26</td>
</tr>
<tr>
<td>Pd</td>
<td>20.09</td>
</tr>
<tr>
<td>Rh</td>
<td>22.94</td>
</tr>
<tr>
<td>Bi-metallic</td>
<td></td>
</tr>
<tr>
<td>RuPd</td>
<td>22.38</td>
</tr>
<tr>
<td>RuRh</td>
<td>23.91</td>
</tr>
<tr>
<td>RhPd</td>
<td>23.77</td>
</tr>
<tr>
<td>Tri-metallic</td>
<td></td>
</tr>
<tr>
<td>RPR333</td>
<td>23.52</td>
</tr>
<tr>
<td>RPR322</td>
<td>31.79</td>
</tr>
<tr>
<td>RPR232</td>
<td>31.98</td>
</tr>
<tr>
<td>RPR223</td>
<td>30.92</td>
</tr>
</tbody>
</table>

and magnitude of the TPR signals were discerned for the entire series. For example, while the peak position indicates the approximate temperature around which the reduction ought to be carried out to activate the catalyst, the area under the peaks signifies the amount of hydrogen required for the reduction of the corresponding noble metal(s) in the catalyst. As the TPR pattern for mono-metallic catalysts is representative of the location of reduction peaks for noble metals, TPR patterns of bi-metal and tri-metal catalysts are not shown.

As can be seen in Figure 3, two distinct peaks were present in the TPR profiles of all the catalysts: the first one occurred in the window of 140–170 °C, indicating that the reduction of any oxygen, adsorbed or chemically bonded

![TEM images of 1 wt% Ru (a), Pd (b) and Rh (c) supported GDC matrices. (Scale bar: 5 nm).](image1)

![TEM images the as-prepared RuPd (a), RuRh (b) and RhPd (c) catalysts. (Scale bar: 5 nm).](image2)
to the noble metal(s) was complete at or below 170 °C. There was a second hump-like peak around 300 °C which is possibly due to the reduction of the nanoscale cerium oxide (CeO₂) support to cerium sesquioxide (CeO₁.₅). Moreover, the amount of hydrogen up-take necessary to activate (reduce) the noble metal in a given catalyst was commensurate with the noble metal fraction in it, as can be readily seen from the TPR results summarized in Table II on all the ten catalyst formulations. Based on these results, an activation protocol was established for all sulfidation and reforming experiments; all the catalysts were reduced at 500 °C for 1 h in a 10% H₂-balance N₂ feed.

4.2. Microstructural and Structural Artifacts of the Supported Formulations

The morphological features of the as-prepared catalysts supporting one-, two- and three noble metals on 10 mole% Gd₂O₃-doped CeO₂ support, in terms of TEM images are shown in Figures 4–6, respectively. As can be seen, clearly all the formulations possess nanofeatures. The contrasting light and dark particle contours in these images belong to the GDC support and the noble metals, respectively. This further suggests that despite low concentration, the dispersion of the catalytic metals is highly uniform throughout the matrix. Thus, the preparatory technique utilized for making them is quite effective in yielding uniform distribution of the precious metals throughout the support.

The nanofeatures observed in the TEM images are also corroborated by the rather broad diffraction peaks in the XRD patterns of the powders calcined at 700 °C for 2 h. XRD signatures of the mono-metal supported catalysts are shown in Figure 7. The XRD-patterns for the bi- and tri-metal series were identical to that of the mono-metal series, and hence, not shown. The gross XRD patterns are typical of those for 10 mole% gadolina-doped ceria (GDC). The peaks for the noble metals were not discernable due to their low loading (≤1 1/3 wt%) which is below the detection limit of the XRD technique. The crystallite size estimated using

![Fig. 7. XRD signatures of mono-metal supported catalysts calcined at 700 °C for 2 h.](image-url)

![Fig. 6. TEM images of the as-prepared tri-metallic catalysts: (a) RPR333, (b) RPR322, (c) RPR232 and (d) RPR223. (Scale bar: 5 nm).](image-url)
Scherrer’s equation, yielded values in the range of 5–8 nm, which is in excellent agreement with those seen in the TEM images. These nanostructures ensure large surface area and the effectiveness of uniform noble metal dispersion in these formulations by the manufacturing technique adopted. This in turn lowers the loading and keeps the manufacturing cost low without compromising the reforming performance.

4.3. Propensity to Sulfur Tolerance

With respect to logistic fuels, sulfur tolerance of a reforming catalyst assumes prime importance. Recent studies have shown irreversible sulfur poisoning to be the main cause of deactivation of reforming catalyst in the case of logistic fuels, making it imperative that the catalysts designed for reforming of sulfur-laden fuels be evaluated for their sulfur tolerance and phase integrity under conditions of sulfur exposures for extended period. Packed beds of the catalyst powders (1 g) were exposed to stream containing 1000 ppm H₂S in nitrogen for 4 and 24 hours, and the post-sulfided samples were analyzed for sulfur pick-up. The cumulative results for the 10 formulations are shown in Figure 8, while Figure 9 compare the sulfur pick-up trend by one catalyst from each series during 4- and 24-h soak time.

The trend of sulfur pick-up by these formulations showed an interesting pattern. First and foremost, and as expected, it was found to be proportional to the soak-time: more sulfur was sorbed by sample in 24 h than in 4 h. Second, the amount of sorbed sulfur decreased progressively as the number of noble metals increased, without increasing their percentage appreciably. For example, it was found that the amount of sulfur scavanged by the bimetallic series was considerably lower than that in the case of single metal dispersion which decreased further in the case of trimetallic series.

Accordingly, in the 24 h soak experiments with the monometal series, RuGDC formulation picked up 2000 ppm H₂S while the Pd and Rh analog sorbed 2610 and 2190 ppm H₂S, respectively. Thus, among monometals, ruthenium-based formulation exhibited highest sulfur tolerance followed by the rhodium analog; palladium-based formulation was most susceptible to sulfur poisoning, meaning that the sulfidation susceptibility followed the pattern: Ru < Rh < Pd.

In the bimetal series, the amount of sulfur sorbed was 740, 1060, and 1240 ppm by RuPd (1/2 wt% Ru + 1/2 wt% Pd), RuRh (1/2 wt% Ru + 1/2 wt% Rh), and RhPd (1/2 wt% Pd + 1/2 wt% Rh), respectively. Similar trends were evident in trimetallic formulations too; the amount of sulfur sorbed by RPR333, RPR322, RPR232, and RPR223 was 290, 370, 320, and 360 ppm, respectively. Thus, RPR333 (1/3 wt% Ru + 1/3 wt% Pd + 1/3 wt% Rh) showed the smallest sulfur pickup. RPR322 (1/3 wt% Ru + 1/2 wt% Pd + 1/2 wt% Rh) and RPR223 (1/2 wt% Ru + 1/2 wt% Pd + 1/3 wt% Rh) showed higher sulfur sorption amongst the series. This could be attributed to the higher level (1/2 wt%) of palladium in them as opposed to 1/3 wt% in RPR333 and RPR232. Thus, the strong resistance to sulfidation by ruthenium followed by rhodium and then palladium (least resistant) is manifested in all the combinations. This systematic and interesting trend will be examined and correlated with steam-reforming capabilities of these formulations, later in the chapter.

4.4. Phase and Microstructural Evaluation of Post-Sulfided Samples

Phase and microstructural integrity of a catalyst is extremely important in steam reforming of logistic fuels. Hence, it is imperative to analyze these features in the post-sulfided samples.
Figures 10 through 12 show the TEM images of the catalysts in the three series after sulfidation for 24 h at 800 °C in a 1000 ppm H₂S-bal. N₂ stream. As can be seen from these TEM images, there is evidence of slight grain growth in the sulfided samples. Moreover, the particles show some agglomeration as well. In order to ascertain that the phase and microstructural integrity of the catalysts under sulfidation conditions was not compromised, the post-sulfided samples were subjected to X-ray diffraction, and the corresponding patterns are shown in Figures 13 and 14 for the mono and trimetal series (the XRD signature of the post-sulfided bimetal formulations was identical to these).

Both the patterns are identical; the peak sharpening is an indication of systematic crystallinity enhancement as a function of time at high temperature. In this case, the peak narrowing is an artifact of grain growth and crystallite size enhancement upon sulfidation. This corroborates the statement made above with respect to the microstructural features in the TEM images shown in Figures 10–12. Moreover, the crystallite texture is maintained; the crystallite size calculation and TEM images suggest that the grain growth in the sulfided samples is only minimal, indicating that no significant surface area reduction occurred. It can also be seen that no new phases could be discerned. This suggests that phase integrity was preserved in all the formulations sulfided at high temperature. Interestingly, neither the observed grain growth nor the agglomeration adversely affected their reforming performance, as was clearly seen in terms of hydrogen yield or life-time of these formulations on-stream, as discussed in the following section.
4.5. Steam Reforming Characteristics

All kerosene steam reforming experiments were carried out at 800 °C and atmospheric pressure (14.7 psi) keeping the steam-to-carbon ratio constant at 3.0. The experiments were terminated when the hydrogen yield in the reformate reached about 20% or the re-emergence of sulfur (as H₂S) in the reformate stream peaked to about 50 ppm.

Fig. 13. XRD patterns of catalysts sulfided for 24 h at 800 °C in 1000 ppm H₂S/bal. N₂.

Fig. 14. Comparative post-sulfidation XRD patterns of the trimetal-supported catalysts after exposure to 1000 ppm H₂S/bal. N₂ stream at 800 °C for 24 h.
Fig. 15. Composition of kerosene reformates using monometal catalysts: (a) Ru, (b) Pd and (c) Rh.

4.5.1. Monometal-Supported Catalysts

Figure 15 depicts the reformate compositions resulting from the steam reforming of kerosene on the monometal-supported catalysts, as a function of on-stream time. The performance trend in term of hydrogen yield in of these catalysts is characteristic of the precious metal on them, as seen from the data summarized in Table III.

Since the exact composition of the fuel (kerosene) was not precisely known, thermodynamic calculations were conducted on a close surrogate, which comprised of a mixture of 70% n-hexadecane and 30% toluene. This choice was based on similar assumptions used by others in the literature. Equilibrium conversions were estimated by Invensys Pro/II Simulation Software Version 8.3. The conditions chosen for simulation were identical to those employed in the reforming experiments: \( T = 800 \, ^\circ\text{C}, P = 1 \, \text{atm}, \) molar feed ratio of \( S/C = 3 \) and GHSV of 65,000 h\(^{-1}\). Assuming complete conversion of the fuel, the equilibrium concentrations thus obtained for \( \text{H}_2, \text{CO}, \text{CO}_2 \) and \( \text{CH}_4 \) were 78.34, 9.86, 11.27 and 0.53%, respectively. These simulation results are similar to those reported in the literature for \( n \)-hexadecane reforming. As can be seen, the reformate composition shown for the three catalyst systems in Figure 15 are in good agreement with the equilibrium data obtained from simulation. The hydrogen content in the reformate stream was slightly lower than the equilibrium conversion. It may be recalled that traces of un-reacted liquid fuel was seen in the condensate. This clearly suggests that fuel conversion was not complete as presumed in the thermodynamic calculations by the simulation technique.

Now, since kerosene contains 260 ppm of sulfur, it is imperative to understand the difference in performance of these catalysts in terms of their behavior towards sulfur as well. For that purpose, the sulfur level (as \( \text{H}_2\text{S} \)) in the exit stream as a function of the progress of the reaction was also monitored and is shown in Figure 16.

The hydrogen yield in the reformate with each of the three catalysts as a function of time on-stream is plotted in Figure 17.

Several interesting aspects emerge. First, the steady-state hydrogen concentration in the reformate is \( \sim 70\% \) in all but one case (viz., Pd-based catalyst) and stays that way for more than 50 h continuously. The Pd-based catalyst appears to deactivate quickly from the very beginning of the reforming process, as evidenced by the steadily declining level of hydrogen in the reformate. This suggests that in the case of Pd-supported GDC, the catalyst poisoning had begun very early on. The sulfur level in the exit drops to \( \sim 2 \) ppm at the end of 11 h.

### Table III. Performance summary of the mono-, bi- and tri-metal supported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mono-metallic</th>
<th>Bi-metallic</th>
<th>Tri-metallic (RPR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. ( \text{H}_2 ) yield (%)</td>
<td>79 84.4 87</td>
<td>86 88 89</td>
<td>78.3 82.5 89.1 84.5</td>
</tr>
<tr>
<td>Duration (h) of steady level</td>
<td>51 – 55 55</td>
<td>68 88 75</td>
<td>86 92 109 89</td>
</tr>
<tr>
<td>( \text{H}_2 ) yield</td>
<td>66 59 68 92 114 96</td>
<td>102 123 129 106</td>
<td></td>
</tr>
<tr>
<td>Time (h) to deactivate to 20% ( \text{H}_2 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cooperative Synergy in Nanoscale Ceria-Based Systems

Sundararajan and Azad

Fig. 16. Trend in H₂S concentration build-up in the exit stream with time on-stream.

on-stream, beyond which it shows steady increase with a concomitant decline in hydrogen concentration. The characteristic ‘tilted L-shaped’ locus of sulfur concentration with time is indicative of rapid and quantitative sulfur-poisoning of Pd-based catalyst. In the light of Figure 8, it can be inferred that the formation of thermodynamically stable PdS began from the very start. Therefore, at the first glance, it would appear that Pd-supported formulation is not a preferred reforming catalyst for a logistic fuel such as kerosene sulfur-laden to the extent of 260 ppm sulfur.

Nevertheless, the Pd-supported catalyst still continues to generate hydrogen at a reasonable albeit steadily diminishing rate. The distinct difference in slope seen in Figure 15(b) and in Figure 17 for hydrogen concentration is likely due to two somewhat different deactivation mechanisms. It is evident that the initial far quicker surface-dominated deactivation is followed by bulk sulfidation of the active metal in the later stages. The latter is diffusion-controlled and hence somewhat slower, at a given temperature (800 °C in this case) it would have a finite value of the limiting rate constant. Therefore, as seen from Figure 17, the rather high (> 84%) hydrogen yield calculated as per Eq. (1), in the early stage of steam reforming is due to the exceptionally high activity of the fresh Pd-supported catalyst. However, after about 4 h on-stream, it is believed that the surface sulfidation of palladium (hence more rapid decline in the yield) is completed which then changes to bulk sulfidation (diffusion controlled). Thus, for the remainder of the duration on-stream, the deactivation becomes more monotonic.

In contrast, the performance of the Ru- and Rh-based catalysts is superior, both in terms of hydrogen yield and on-stream stability over extended period. The steady-state hydrogen yield is about 80% or higher for about 51–55 h in both the cases. It takes another 15 h for the amount of hydrogen to fall below the pre-determined level of 20%.

A comparison between Figures 16 and 17 brings out an interesting correlation between hydrogen and sulfur level in the kerosene reformate. The initial period lasting about 3–5 h represents unsteady-state during which the sulfur level drops precipitously and then attains a low value which remains unaltered for about 50 h. This trend is reflected in the fluctuating hydrogen yield during the same period, followed by a corresponding flat region for the next 50 h or so, marking the attainment of steady-state with respect to hydrogen generation as well.

In the light of this, certain distinct behavioral features of Ru and Rh-based catalysts become evident. For example, in the case of Ru-supported GDC, the hydrogen production in the early stages of reforming is somewhat lower (~71.5%) which increases to about 79% once the catalyst stabilizes and steady-state is achieved. This is in direct correspondence to the drastic drop in sulfur level during the first few hours, leveling off to about 3 ppm H₂S (kerosene originally contains 260 ppm sulfur) for the remainder of the steady-state duration. A similar trend is seen in the case of Rh-supported GDC. However, in this case, the hydrogen level drops from ~87% in the early part of reforming to about 79% in the steady-state regime. Correspondingly, sulfur in the reformate levels off around 15 ppm. In both the cases, the decline in hydrogen yield beyond 54 h on-stream signals the onset of catalytic deactivation which is corroborated by the concomitant increase in sulfur level in the reformate.

With regard to steady-state hydrogen yield, the reforming capability of Ru- and Rh-based catalysts is almost identical. However, their sulfur-tolerance characteristics are different. In the case of Pd-supported catalyst, the quicker reduction and attainment of lower amount of residual sulfur in the reformate indicate better reforming capability together with superior sulfur tolerance. Moreover, as the hydrogen yield begins to decline probably due to sulfur-poisoning, the sulfur concentration in the exit stream increases rapidly and attains a new steady-state value of 50 ppm H₂S. This is in contrast to Rh-based where the steady-state sulfur concentration is somewhat higher (~15 ppm) than in Ru-based (~3 ppm) and increases...
steadily, once the catalyst deactivation has set in. In the light of the foregoing discussion, Ru-based formulation appears to be more sulfur-tolerant than the Rh-based analog.

4.5.2. Bimetal-Supported Catalysts

Figures 18 and 19 depict, respectively, the reformate compositions and hydrogen yield in the case of kerosene steam reforming on three bi-metal supported catalysts, as a function of time. Evidently, the hydrogen yield with bi-metallic formulations is higher than that with the monometal analogs. The performance in terms of duration over which hydrogen production is steady, was also superior (Table III). Furthermore, the hydrogen yield is characteristic of the combination of the precious metals.

Figure 19 clearly brings out the synergy of noble metals in the bi-metal formulations. The reformate compositions (Fig. 18) and hydrogen yield (Fig. 19) are in good agreement with the equilibrium data predicted by simulation, a procedure we alluded to previously in the case of monometal formulations. Hydrogen content in the reformate stream was slightly lower than the predicted equilibrium conversion, which clearly suggests that conversion of fuel was not complete as assumed in the thermodynamic estimations, since un-reacted liquid hydrocarbon fractions were seen in the condensate.

As stated in the case of the monometal series, better understanding of the difference in reforming pattern of different bimetal combinations could be obtained by comparing their behavior towards sulfur. The sulfur level (as H₂S) in the exit stream as a function of progress of the reaction is shown in Figure 20.

Several interesting features are worth-mentioning. For example, the sulfur level drops rather quickly in the early
stage of reformation, during which hydrogen yield is also somewhat lower, signifying that steady-state has not yet reached. This initial H\textsubscript{2}S drop coupled with high hydrogen generation rate (Fig. 19) is indicative of the likelihood of preferential sulfur sorption by the cerium oxide support matrix. As stated in the previous sections and supported by the literature, ceria establishes a facile thermodynamic equilibrium with sulfur. This is evidenced in Figure 19 by the establishment of the steady-state in the H\textsubscript{2} generation profile in the first 30–36 h window. During this period, it is believed that one of the noble metals with higher affinity for sulfur is being partially sulfided by the remnant sulfur, leaving the other noble metal to continue the reformatting activity. This minimizes sulfur poisoning of the more noble metal, sparing it to continue to produce hydrogen. This hypothesis is strengthened by the observed trend in sulfur tolerance and hydrogen generation by mono-metal supported catalysts and Figure 8 where the sulfur sorption characteristics of all catalytic formulations are compared.

During the second and longer steady-state period, the H\textsubscript{2}S concentration in the reformate becomes almost stagnant; this is seen as the most active phase of the catalyst where hydrogen yield is most optimum for an extended period. This is followed by a sudden decrease in H\textsubscript{2}S concentration. It is hypothesized that this is due to the sorption of sulfur by the second of the two noble metals. As the active sites on the second noble metal also begin to get sulfided, deactivation via sulfur poisoning ensues and the hydrogen yield starts to decline rapidly. A close examination of the profiles in Figure 19 with Figure 20, suggests that these two phenomena are almost synchronous. When both the noble metals in respective formulations have been fully poisoned by sulfur, rapid re-emergence of H\textsubscript{2}S ensues. Interestingly, the slope of the rise in sulfur concentration with time (Fig. 20), is identical in all the three cases, further fortifying the hypothesis laid out above.

From the foregoing discussion, it is amply clear that the choice of noble metal combination in the bimetallic formulations plays a vital and meaningful role in their performance. For instance, keeping with the inferior behavior of Pd-supported ceria catalyst in the mono-metal series, the bi-metal formulations containing Pd (RuPd and RhPd) exhibited relatively shorter span where hydrogen production was steady. Furthermore, the duration of steady hydrogen production was higher in the case of RhPd (75 h) than for RuPd (68 h). On the other hand, hydrogen generation was stable over the longest period (88 h) with RuRh that contained no Pd. It may be recalled that both RuRh and RhPd contain 1/2 wt% of Rh in each of them. Thus, the higher hydrogen yield and longer steady-state in the case of RuRh and RhPd could be attributed to the presence of the common noble metal rhodium in them.

The average sulfur levels in the steady-state regions (flat zones) of Figure 20 as computed from the GC signals were 43.9, 37.9 and 53.7 ppm for RuPd, RuRh and RhPd, respectively, which re-enforces the benign role of Ru and Rh towards sulfur tolerance. This could be explained by recalling the order of preference towards sulfur pick-up in the case of mono-metal catalysts: Pd > Rh > Ru. Thus, it could be stated that while Pd-alone formulations might not be very promising with regard to a steady and high hydrogen yield from logistic fuels, the combination of Pd and/or Ru with Rh endows great degree of synergy, resulting thereby into formulations that are stable over long durations on-stream and produce high quality reformate with high H\textsubscript{2} fraction.

### 4.5.3. Trimetal-Supported Catalysts

Figures 21(a–d) depicts the reformate gas compositions resulting from steam reforming of kerosene on four trimetal supported reforming catalysts as a function of time. In order to understand the synergy among the noble metals in the tri-metallic formulations, time dependence of H\textsubscript{2} yield in each case, is shown in Figure 22.

Three outstanding features of Figures 21 and 22 are worth-mentioning. First, hydrogen yield with tri-metallic formulations is notably higher than that obtained with the mono- or bi-metal analogs. Second, their performance in terms of the duration over which hydrogen production was steady, was far superior. Finally, the time taken by the catalysts in the tri-metallic series to deactivate (gauged by the decline in H\textsubscript{2} concentration in the reformate to 20% or below) was also progressively longer than that observed with other series. These features can be readily discerned quantitatively from the data summarized in Table III. Interestingly, the performance in term of hydrogen yield is very characteristic of the precious metal combination in each of the four formulations.

These features are well corroborated by the trend of sulfur level in the exit stream, shown in Figure 23.

For RPR333 (1/3 wt% Ru + 1/3 wt% Pd + 1/3 wt% Rh) and RPR223 (1/2 wt% Ru + 1/2 wt% Pd + 1/3 wt% Rh) the steady-state duration was 86 and 89 h, respectively. They also exhibited relatively higher levels of sulfur in the exit stream. The marginally higher on-stream stability of RPR223 could be attributed to the elevated level of ruthenium in it, compared to that in RPR333. At the same time, lower level of rhodium (1/3 wt%) in them could be the reason for somewhat lower H\textsubscript{2} yield too: 78.3% for RPR333 and 84.5% for RPR223. This speculation is strengthened by the fact that formulations with higher rhodium content, generally exhibited significantly longer steady-state regime: 92 h for RPR322 and 109 h for RPR232—both contain 1/2 wt% Rh.

Furthermore, we may recall that in the bi-metallic series, RuRh performed the best, which again contains 1/2 wt% Rh. RPR232 is essentially RuRh (1/2 wt% Ru + 1/2 wt% Rh) with the addition of 1/3 wt% of Pd. Thus intuitively,
RPR232 should outperform all the other formulations in the tri-metallic series. This turned out to be the case, as seen from the data presented in Figures 21 and 22. In the case of RPR232, the performance was optimal: the steady-state duration increased from 88 h for RuRh to 109 h in the case of RPR232. The equilibrium sulfur level in the case of RPR232 was also quite low, suggesting that incorporation of palladium helped in accentuating the sulfur pick-up by GDC, thereby making ruthenium and rhodium more facile to perform at their best in reforming, resulting in higher hydrogen yield. As a combination of these features, RPR232 also took the longest time to deactivate.

In view of the fact that all the formulations stayed active for considerable number of hours on-stream with sulfur-laden fuel, it is imperative to know their ultimate post-reformation fate. Thus, all the post-sulfided and post-reformed catalysts in the three series were subjected to systematic structural and microstructural investigation, but the
discussion here will be limited to the results on tri-metallic system alone, for the sake of illustrative brevity (those of the mono- and bimetallic systems can be accessed through Refs. [25–26]).

Figures 24(a–d) shows the TEM images of the post-reformed tri-metallic catalysts. It was found that apart from the expected peak sharpening (due to prolonged exposure to the fuel + steam) nothing unusual could be discerned from the XRD patterns of the post-reformed mono- or bimetallic catalysts25–26 which remain identical to those for as-prepared and the sulfided ones. No new phases in the XRD patterns (not shown here) could be identified, suggesting good phase integrity of the tri-metal series as well. Calculation with peak width showed that the grain growth in these cases was also nominal.

The TEM images of the post-reformed samples show anticipated grain growth similar to those seen in the case of post-reformed mono- and bi-metallic catalysts. The TEM images also show signs of slight agglomeration in the GDC support. However, as seen in the previous cases, neither grain growth nor particle agglomeration compromised the noble metal dispersion in them. The superior sulfur tolerance and reforming performance clearly suggest that there is no inferiorization of performance due to observed microstructural artifacts. It should be pointed out that this distinctive behavior of the mono-, bi- and trimetal-supported nanoscale ceria formulations with regard to their tolerance to sulfur in a real logistic fuel such as kerosene has been studied in such a systematic fashion perhaps for the first time. Thus, the excellent fuel reformation capability is intricately linked with their inherent sulfur-tolerance characteristics. Based on these experimental observations, in the following we shall attempt to propose a phenomenological mechanism that we believe is operative.

4.5.4. Cooperative Synergy Pathways

In early stages, the hydrogen produced during steam-reforming acts as a hydrodesulfurization (HDS) precursor converting the organosulfur into $\text{H}_2\text{S}$.27–29

$$\text{Pd} + \text{H}_2\text{S} \rightarrow \text{PdS} + \text{H}_2 \ (2)$$

Thiophene is used in the above example for illustrative purpose. Credence to this mechanism is derived from Figures 16, 20 and 23, where $\text{H}_2\text{S}$ was detected from the very beginning of the reaction. The hydrogen sulfide thus formed then partially reacts with nanoscale precious metals. To keep the discussion simple, we will focus on the case of single-metal supported system, but the arguments put forward at equally valid for bi- and tri-metal-supported systems as well.

Hence, in the case of palladium-bearing systems, the following reaction can be envisaged:

$$\text{Pd} + \text{H}_2\text{S} \rightarrow \text{PdS} + \text{H}_2 \ (2)$$

In the case of ruthenium, it binds sulfur as ruthenium sulfide, RuS₂.⁴⁰

\[
\text{Ru} + x\text{H}_2\text{S} \rightarrow \text{RuS}_x + x\text{H}_2
\]  

(3)

In the case of Ru-supported GDC catalyst, the sulfidation could be viewed as a two-stage process, accounting for the two steady-states observed in Figure 17. Ruthenium compounds exhibit at least eight oxidation states, but the +2, +3, and +4 are the most common. One would expect these to be the most prevalent ones under conditions existing in reforming.

One could anticipate the occurrence of one or all of the following reactions:

\[
\text{Ru} + \text{H}_2\text{S} \rightarrow \text{RuS} + \text{H}_2
\]  

(4a)

\[
3\text{RuS} \rightarrow \text{Ru}_2\text{S}_3 + \text{Ru}
\]  

(4b)

\[
\text{Ru} + 2\text{H}_2\text{S} \rightarrow \text{RuS}_2 + 2\text{H}_2
\]  

(5a)

\[
2\text{Ru} + 3\text{H}_2\text{S} \rightarrow \text{Ru}_2\text{S}_3 + 3\text{H}_2
\]  

(5b)

\[
2\text{RuS} \rightarrow \text{Ru}_2\text{S}_2 + \text{Ru}
\]  

(6a)

\[
\text{Ru}_2\text{S}_x + \text{H}_2\text{S} \rightarrow 2\text{RuS}_2 + \text{H}_2
\]  

(6b)

Transition of the atomic ratio of ruthenium to sulfur from 1:1 (in RuS) to 1:1.5 (in Ru₂S₃) to 1:2 (in Ru₂S₂) as outlined in the above scheme is substantiated by the observation made by Pecoraro and Chianelli²⁸ that the sulfides of ruthenium exhibit exceptional HDS activity. A similar conclusion was arrived at by Ishiguro et al.³¹ who examined the evolution of ruthenium sulfide nanoclusters on titania support.

On the other hand, as seen from the [H₂S] versus time profiles shown above, the drop in sulfur concentration in the case of Rh-supported GDC catalyst is somewhat slower (∼6 h) compared to ∼3 h in the case of Ru-supported GDC catalyst. This could be ascribed to the single-step process, where the most stable rhodium sulfide, Rh₂S₃ is partially formed.³²

\[
2\text{Rh} + 3\text{H}_2\text{S} \rightarrow \text{Rh}_2\text{S}_3 + 3\text{H}_2
\]  

(7)

At this juncture it is relevant to ask the question: is the sulfidation of the precious metals as outlined above is feasible is the key mechanism, responsible for the observed sulfur tolerance? The answer is no; while this scheme is feasible, it cannot possibly be the primary mechanism. Were this true, the sustained high hydrogen yields over long period would not be possible. Thus, it stands to reason that the outstanding performance of the formulations developed in this work is borne out of the fact that there is another mechanism for sulfur resistance.

It is well known that ceria itself is capable of forming an oxysulfide.³³–³⁶ Therefore, in reducing environments, due cognizance should be given to the highly favorable thermodynamics of CeO₂–H₂–H₂S system:

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

(8a)

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

(8b)

To clarify the debate whether this is happening in our case where the precious metals are supported on ceria matrix, an independent sulfidation experiment on GDC alone was performed using a stream of 90% H₂, 9.97% N₂ and 300 ppm H₂S at 800 °C for 16 h, simulating the reducing conditions and sulfur level prevailing in the case of original fuel (kerosene). The time dependence of the sulfur level in the exit stream is shown in Figure 25; the extent of sulfur picked up by GDC during the same period is shown in the inset.

As can be seen clearly, sulfur scavenging appears to be almost 100% from the very beginning of the simulated reaction, reaches steady-state rather quickly and its concentration in the exit stream hovers around 8 ± 1 ppm for the next 14 h. This unequivocally establishes that the primary sulfur tolerance in steam reforming of kerosene comes from the inherent and thermodynamically feasible sulfurizability of the ceria support matrix; by virtue of this the noble metals are spared sulfur attack and remain active in the reforming of the sulfur denuded fuel leading to high hydrogen yield.

At this juncture, it is worth pointing that the most extensively employed inert catalytic support, viz., α or γ-alumina is not endowed with such unique capability, which explains the short-term activity of such catalysts, even those which have far higher loading of noble metals.³⁷–³⁹ In the case of monometal series, the only exception appears to be the Pd-supported formulation, where it seems that the along with ceria, the precious metal also experienced preferential sulfur ingress leading to monotonous deactivation of the catalyst from the very
beginning of the process. On the other hand, in the case of bi- and trimetal series, the support and the combination of two and three noble metals accentuate the overall sulfur tolerance, which in turn led to the generation of a highly H₂-rich reformate. The duration of steady-state hydrogen yield was in turn an artifact of relative susceptibility of a given noble metal in the multiple metal formulations.

In the case of bimetallic formulations, this can be explained by invoking two mechanisms: preferential sulfurizability of one precious metal to comparison to other and the sulfur spill-over, in addition to the activation and initiation mechanisms identical to those elaborate in the case of monometallic catalysts. Thus, the increase in the duration of steady-state (during which the hydrogen yield remains high and sulfur level low) could be explained in the light of preferential sulfur pick-up by one noble metal followed by the transfer of sulfur to more sulfur susceptible counterpart.

The first aspect in a bi-metal system is a result of better dispersion, while the second aspect arises from the cooperative synergy between the two metals when exposed to identical chemical environment. This ability of say, NM₁, to pass the sulfur onto the more readily sulfurizable NM₂, allows the catalyst as a whole to remain active for a longer period of time. Thus, it is safe to assume that a sulfur ‘spill-over’ mechanism is operative in the case of bimetallic (NM₁ + NM₂) series. Under this mechanism, in the steady-state regime one of the two noble metals undergoes sulfidation first. At some point during this process, the sulfided metal begins transferring sulfur via ‘spill-over’ mechanism to the second metal which begins to then sulfide, allowing the first metal to remain active in reforming. Deactivation sets in when the second metal is completely sulfided and the more active one begins sulfiding. Due to sulfur pick-up by both the active metals in the catalyst, sulfur level in the exit drops and eventually when both metals are completely sulfided, the catalyst begins to deactivate; sulfur re-emerges in the exit and hydrogen production declines. In the light of this, it could be seen that a bi-metallic formulation could be very effective as a more sulfur-tolerant reforming catalyst compared to its mono-metal counterpart. This mechanistic picture is in total conformity with the experimental results discussed above, where clear evidence of superior reforming performance and sulfur tolerance of the bi-metallic catalysts over their monometallic analogs was seen.

The above scheme could be extended to the tri-metallic series as well. In this case, however, the cooperative synergy is further accentuated, resulting in even higher sulfur tolerance, still better hydrogen yield and significantly longer span of steady-state compared to any of the mono- or bi-metal series. Addition of a third precious metal, even in as small a weight fraction as 1/3 of 1%, to a bi-metallic formulation improvised the sulfur tolerance and reforming behavior significantly. In this case as well, systematic sulfidation of the noble metals occur in the steady-state regime. If the noble metals in the catalysts were to sulfide simultaneously, the catalyst would undergo deactivation rather quickly and hydrogen yield would decline immediately. On the contrary, the tri-metal supported catalysts remain active for a prolonged duration during which the hydrogen yield remains fairly high and almost constant. This experimental evidence could be explained if sulfur ‘spill-over’ mechanism is invoked again, akin to that in bi-metallic series. In this case, the initial successive sulfidation of the two of the three noble metals (NM₁ and NM₂) is followed by the sulfur spill-over to NM₃ with higher sulfur affinity. This spares NM₁ and NM₂ to remain unsulfided and active to perform the reforming process. Once NM₃ is fully sulfided, NM₁ and NM₂ begin to pick-up sulfur from the stream. At this stage, deactivation sets in. Upon completely sulfidation of all the three precious metals, the sulfur level in the exit re-emerges with a concomitant decrease in hydrogen yield.

The proposed mechanism is in complete agreement with the observed behavior in the sulfidation as well as reforming experiments over extended periods of time. It explains the role of noble metals—individually as well as in combination with others—in the reforming of sulfur-laden fuels. It also provides a good rationale for synergistic behavior of noble metals in the case of bi- and tri-metallic catalyst formulations.

This argument is strengthened further by systematic X-ray photoelectron spectroscopy (XPS) carried out on the virgin and sulfided GDC as well as on the post-reformed catalysts. The spectra are shown in Figures 26 and 27.

The XPS investigation indicates that the Ce³⁺ and Ce⁴⁺ species can be differentiated with distinct line shapes corresponding to various final states. As can be readily seen from this figures, the intensity of the peaks around ~914, 905, 897, 890 and 884 eV in the as-prepared sample, which correspond to Ce³⁺ oxidation state, decreased and those around ~886 and 880 eV in the sulfided samples increased; the later correspond to Ce in 3+ oxidation state.

![Fig. 26. Comparison of the XPS signature of virgin GDC sample with that sulfided at 800 °C for 16 h in a gas stream containing 300 ppm H₂S.](image)
This implies that in the sulfided sample, both Ce\(^{4+}\) and Ce\(^{3+}\) oxidation states coexist. The slight shifts seen in the peak positions of the virgin and the sulfided samples could be ascribed to differences in the local atomic environment of Ce in the gadolinia doped-ceria (GDC) as opposed to pure ceria (CeO\(_2\)), on which the XPS data are generally acquired and/or reported.\(^{40-42}\)

X-ray photoelectron spectra collected on the mono metal-supported catalysts after steam reforming of kerosene, are presented in Figure 27. The peak in Figure 27(a) at 284 eV corresponds to Ru(3d\(_{5/2}\)) in 4+ oxidation state.\(^{43}\) No peak at 280 eV corresponding to Ru(3d\(_{5/2}\)) in metallic state is present,\(^{33}\) suggesting that the noble metal did not undergo reduction to zerovalent elemental Ru during reforming of kerosene. Peaks at 336 and 342 eV in Figure 27(b) belong to Pd\(_{3/2}\) and Pd\(_{1/2}\), respectively,\(^{44}\) indicating that Pd in the post-reformed catalyst is in Pd (II) oxidation state. Similarly, the final oxidation state of rhodium in Rh-based sample is 3+, denoted by two peaks at 306.4 and 312 eV corresponding to Rh (3d\(_{5/2}\)) and Rh (3d\(_{3/2}\)), respectively.\(^{45}\)

These spectroscopic and microscopic data provide unequivocal evidence that the ceria support does participate in sulfur uptake from the fuel, thereby allowing the precious metals in Ru- and Rh-supported formulations to perform actively as the fuel reforming component. The increase in sulfur level in the exit stream and the decline in hydrogen yield at the end of steady-state regime, mark the eventual sulfidation of the precious metals.

Based on these self-supporting experimental evidences, a phenomenological mechanism operative in the steam-reforming of a sulfur-laden logistic fuel (such as kerosene) emerges. The mechanism essentially involves a sequential combination of the reactions shown in Eqs. (2) through (8), and can be summarized as follows:

As stated earlier, all the catalysts were made active by a prior hydrogen reduction step at 450 °C for 1 h. This pre-reforming protocol renders the precious metals active by reducing them to their elemental state. It was also observed
that hydrogen is produced in rather high concentration from the very beginning of fuel reforming. Under these conditions, it is correct to envisage the reduction of stoichiometric ceria (CeO₂) to CeO₁₋₂ (n < 2) as per Eq. (8a). Reduced ceria is more susceptible to sulfidation than its stoichiometric analog.

Therefore, the initial drastic drop in the H₂S level comes from the sulfidation of reduced cerium oxide in the catalyst via Eq. (8b).

It is also not incorrect to assume that in such a reducing environment, the organosulfur species in the fuel are degraded and form H₂S. The approach of a thermodynamic equilibrium in the CeO₂–H₂S–Ce₂O₂S phase field coincides with the arrival of the kinetic steady-state, which signals the on-set of a period of steady hydrogen generation, during which both H₂ and H₂S level in the exit stream remain practically constant. It is hypothesized that during this period, sulfur pick-up by the noble metal(s) occurs at steady albeit rather small rate, without significantly affecting the reforming propensity of the catalyst as a whole.

In the case of single-metal supported series, when the noble metal supported on ceria matrix also get completely sulfided, deactivation begins to set in. This is marked by the drop in hydrogen level and increase of sulfur levels in the stream at the end of steady-state. It should be emphasized that ceria by itself is not a reforming catalyst. Therefore, as soon as the active metal is poisoned by sulfide phase formation, the reforming capability of the catalyst plummets.

The proposed mechanism, thus, is in complete agreement with the observed behavior in the sulfidation as well as reforming experiments over extended periods of time for the formulations developed and tested here. It explains the role of noble metals—individually as well as in combination with others—in the reforming of sulfur-laden fuels. It also provides a good rationale for synergistic behavior of noble metals in the case of bi- and tri-metallic catalyst formulations.

Based on these self-supporting experimental evidences, a phenomenological mechanism operative in the steam-reforming of a sulfur-laden logistic fuel (such as kerosene) emerges. The mechanism essentially involves a sequential combination of the reactions shown in Eq. (2) through (8). This general multistage scheme is reflected in the sequence shown in Figures 28(a–c).

4.5.5. Mechanism of Formation of Lower Fractions of Carbonaceous Species in the Reformate

Yet another unique feature seen in the steam reforming of kerosene with mono metal-supported ceria catalysts in addition to exceptionally high hydrogen yield, is the unusually higher level of methane in the dehumidified reformate. Depending up on the nature of fuel, the typical constitution of the steam reformed reformate varies widely. In the case of natural gas, it comprises about 46% H₂, 7–10% CO, 6% CO₂, 2–3% CH₄ and 1% N₂ with balance water, while the average composition of coal syngas is about 29% H₂, 29% CO, 12% CO₂, 3% N₂ with balance water. As can be seen from Figures 15, 18, and 21, the steam-reformed kerosene reformates contain, on an average, about 9–10% CO, 9–10% CO₂ and 14–15% CH₄, in the flat (steady-state) regime. Once the catalyst degradation attended by a decline in hydrogen ensues, there is a slight upward trend in the concentration of CO, CO₂ and CH₄ as well. However the equilibrium conversion data calculated by simulation and reported above predicts the theoretical methane content in the reformate stream to be only 0.53%. A space velocity of 65,000 h⁻¹ was used in these experiments. Also the presence of small level of unreformed fuel in the condensate was detected. Hence, it is possible that incomplete conversion of the fuel at such a high space velocity yielded higher methane content in the reformate.

On the other hand, the higher level of methane in the reformate could be explained if one assumes that the catalysts used in this work are also capable of in-situ methanation of carbon monoxide and carbon dioxide in the presence of hydrogen. This would explain the lower level of carbon monoxide and carbon dioxide and, higher fraction of methane.

The possible pathways for the methanation reactions could be written as:

\[
4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \\
\Delta G_{1073 K}^{0} = -68.4 \text{ kJ (mol CO}_2\text{)}^{-1} \tag{9a}
\]

\[
3H_2 + CO \rightarrow CH_4 + H_2O \\
\Delta G_{1073 K}^{0} = -21.4 \text{ kJ (mol CO)}^{-1} \tag{9b}
\]

\[
7H_2 + CO + CO_2 \rightarrow 2CH_4 + 3H_2O \\
\Delta G_{1073 K}^{0} = -89.8 \text{ (mol[CO, CO}_2\text{])}^{-1} \tag{9c}
\]

It is evident that all these reactions are thermodynamically favored. In order to verify their practical feasibility, independent experiments were carried out under the conditions of catalytic reforming of kerosene in the same reactor at 800 °C and atmospheric pressure, without steam, using the formulations developed in this work. The molar ratios of CO₂:H₂, CO:H₂ and CO₂:CO:H₂ in the gaseous mixtures were maintained at 1:4, 1:3 and 1:1:7, respectively, as per the stoichiometry shown in Eqs. (9a–c).

In order to gauge the propensity of the catalyst to the change in composition and content of the mixture, the reactive components were varied while the reaction was in progress. For example, after flowing a stoichiometric mixture of CO₂+H₂ (Eq. (9a)) for the first 4 h, it was switched to the CO+H₂ mixture (Eq. (9b)) for the next 4 h and finally to CO+CO₂+H₂ mixture (Eq. (9c)) for the next 16 h. Composition of the mixture was continuously monitored during the experiment, by letting the exit...
stream after water removal via condensation into the GC. The results are shown in Figures 29(a–c).

By applying thermodynamic considerations to the steady-state kinetics at 800 °C and atmospheric pressure (101.325 kPa), we could compute the theoretical equilibrium concentration of the species in these mixtures, as shown below in the case of reaction (9a) for the purpose of illustration:

\[ 4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \]

\[ K_{eq} = \exp \left( \frac{-\Delta G^\circ_{1073 K}}{RT} \right) \]
\[ = \frac{\gamma_{H_2O} \cdot \gamma_{CH_4}}{\gamma_{H_2} \cdot \gamma_{CO_2}} = \frac{e_x^3 \cdot (5 - 2e_x)^2}{64 \cdot (1 - e_x)^3} \] (10)

Where \( e_x \) is the reaction fraction of each species at the steady-state.

At 800 °C, \( e_x \) is computed to be 0.862; the value of \( e_x \) for reaction (9b and c) is also calculated and is
The on-stream long-term stability of these catalysts is due to their superior sulfur-tolerance without the need of a priori desulfurization stage; in the case of a real fuel such as kerosene which is a surrogate of JP-8, this aspect has hitherto not been examined or reported in the literature. Fukunaga et al. have discussed the performance of bimetal-supported formulations in fuel reforming.

Some salient features of the tri-metal supported formulations are as follows:
(a) RPR232 (bi-metallic RuRh nominally doped with 1/3 wt% Pd) resulted in significant increment in the duration of steady H₂ production.
(b) RPR232 also resulted in the reduction in the overall H₂S concentration (< 10 ppm) in the reformate, making it the best formulation in the tri-metallic series.
(c) Performance enhancement shown by the tri-metallic formulations re-enforces the synergistic mechanism of various noble metals towards one another in fuel reforming.
REVIEW

Sundararajan and Azad Cooperative Synergy in Nanoscale Ceria-Based Systems

Table IV. Steady-state concentration (%) of the reactants and products of methanation process.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H₂ concentration</th>
<th>CO₂ concentration</th>
<th>CO concentration</th>
<th>CH₄ concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>9(a)</td>
<td>16.9</td>
<td>42.3</td>
<td>4.2</td>
<td>3.3</td>
</tr>
<tr>
<td>9(b)</td>
<td>25.3</td>
<td>47.3</td>
<td>–</td>
<td>3.9</td>
</tr>
<tr>
<td>9(c)</td>
<td>27.3</td>
<td>25.5</td>
<td>3.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

a combined Ni-based desulfurizer and a Ru-supported alumina catalyst in the steam reforming of kerosene containing 48–64 ppm sulfur at 730 °C. Even with the sulfur level reduced to about 0.05 ppm by desulfurization, the hydrogen level was ~70% with CO between 12–15% and CO₂ between 15–18% in the reformate. It can be reasonably argued that with pre-reforming desulfurization, the catalysts developed in this work would perform even better.

The catalysts are also capable of in-situ methanation of carbon monoxide and carbon dioxide in the presence of hydrogen—a feature also not reported in the literature with regard to fuel reforming. This aspect is unique and relevant in the context of eliminating CO and CO₂, thereby obviating the need of separate and elaborate stages for CO removal and, CO₂ sequestration and/or capture. Fukunaga et al. had employed a water-gas-shift reaction to remove CO from the stream.

The observed behavior of in-situ methanation is common to all the three formulations irrespective of the type of precious metal supported on the GDC matrix. Thus, it can be concluded that this is an artifact of the novel combination of the precious metal(s) with doped ceria support, both being endowed with nanofeatures. A recent study on methanation of carbon oxides used a catalyst that contains 9–16% Ru on γ-Al₂O₃. Methanation of CO in hydrogen rich gas mixture was also reported using catalysts containing 10% of several metals (Pt, Pd, Co, Ni, Ru) over SiO₂ support. Some studies using 7–10% NiO on TiO₂ and γ-Al₂O₃ for the methanation of carbon oxides in hydrogen-rich stream catalysts have also been reported.

As can be seen, these studies employ very high loading of Ni and other noble metals, all of which are quite expensive (in addition to Ni being prone to carburization) whereas the catalysts developed in this research contain 1% of the noble metal and are capable of performing in-situ methanation in addition to generating hydrogen in high yield.

5. CONCLUSION

New generation of noble metal(s)-supported ceria nanocatalysts were successfully developed. These catalysts exhibited superior performance in reforming of logistic fuels with regards to hydrogen production and sulfur tolerance. Steam reforming of kerosene at 800 °C and atmospheric pressure with steam-to-carbon (S/C) ratio equal to 3.0 on these formulations produced hydrogen-rich streams over long durations before deactivation sets in, which is rather slow and monotonic than sudden and precipitous. The experimental results were used to systematically study and understand various artifacts. The series possessed various key features such as: high sulfur tolerance, high activity towards hydrogen production, and capability of in-situ methanation. Independent investigations were carried out to understand the underlying mechanism behind each of these features. As a result of these independent investigations, several new and interesting aspects emerged.

The significance of ceria as a support material in reforming catalysts emerged. It was found that ceria plays a vital role in attributing sulfur-tolerance to the catalysts—a key feature required for logistic fuel reforming. A thorough comprehension of this paved the way to understand and elucidate the cooperative synergistic behavior among various noble metals. A plausible phenomenological mechanism for inter-metallic synergistic behavior was established, which could be used as an effective tool in tailoring and optimizing catalyst formulations. Independent experiments confirmed that the nanoceria-supported catalysts were capable of in-situ methanation leading to reduced formation of carbonaceous species, thereby minimizing the requirement of a water-gas-shift reactor in commercial-scale fuel reformers.

It is evident from the literature that development of robust catalysts for logistic fuel reformers is critical for extracting auxiliary power via SOFCs. Various aspects of ceria as a catalyst support clearly indicate that it will play an important role in catalytic processes in meeting future energy demands.

References and Notes

Cooperative Synergy in Nanoscale Ceria-Based Systems Sundararajan and Azad


REVIEW


Received: 11 January 2011. Accepted: 8 February 2011.