Recent advances in catalytic oxidation and reformation of jet fuels

Teresa A. Wierzbicki^{a,b}, Ivan C. Lee^c, and Ashwani K. Gupta^{d,*}

^a Department of Mechanical Engineering, 2181 Martin Hall, Campus Dr., University of Maryland, College Park, MD 20742, USA, E-mail: twierz@umd.edu

5 ^b Sensors and Electron Devices Directorate, U.S. Army Research Laboratory, 2800 Powder Mill Rd., Adelphi, MD 20783, USA, E-mail: teresa.wierzbicki.civ@mail.mil

^c Sensors and Electron Devices Directorate, U.S. Army Research Laboratory, 2800 Powder Mill Rd., Adelphi, MD 20783, USA, E-mail: ivan.c.lee2.civ@mail.mil

10 ^d Department of Mechanical Engineering, 2181 Martin Hall, Campus Dr., University of Maryland, College Park, MD 20742, USA, E-mail: ak Gupta@umd.edu ; Phone: 301-405-5276

* Corresponding author

15 Abstract

20 This paper provides a review of progress in catalytic conversion of JP-8 fuel and its surrogates made over the last decade. The effect of different types of catalyst and support materials, as well as different preparation methods, is discussed in detail. The derivation of kinetic models for computational studies is also examined. Particular attention is given to the development of sulfur tolerant catalysts and the mechanisms by which catalyst poisoning occurs, as this is an important obstacle to overcome for systems using sulfur-laden fuel. Suggestions for further research are offered.

Keywords

25 Catalytic combustion and fuel reformation; JP-8; surrogate fuel; sulfur tolerance; kinetic
modeling; hybrid combustion

1. Introduction

30 Jet propellant-8 (JP-8) is a conventional petroleum-derived jet fuel used
extensively as a logistic fuel by U.S. military. JP-8 contains a wide distribution of alkane,
cycloalkane, and aromatic compounds, ranging from C₈ to C₁₆, as well as up to 3000 ppm
by weight of sulfur [1]. Alternative jet fuels derived from methods such as Fischer-
Tropsch synthesis and extraction from bio-matter have also been developed and shown to
35 possess similar characteristics and performance as conventional JP-8 [2-8]. These
alternative fuels tend to only contain paraffin species and negligible sulfur compounds.
The complex nature of this JP-8, together with the fact that every batch has a different
composition [1], makes it difficult to draw many meaningful conclusions from
experimental work, and makes it almost impossible to develop a detailed kinetic model.
40 As such, many researchers prefer to use surrogate fuels, which typically contain 1 – 3
different components (although more intricate ones can have more) that are
representative of the fuel being studied. For JP-8, most surrogates contain a paraffin
(typically dodecane), an aromatic (such as benzene, toluene, or xylene), and occasionally
a cycloalkane, as these are the three primary classes of hydrocarbon found in the fuel [9].

45 The use of a catalyst during the conversion of liquid hydrocarbons offers several
benefits. First, the primary function of a catalyst is to lower the activation energy needed
to initiate combustion, thus allowing the reaction to ignite at a lower temperature,
reducing the need for input power at startup. Stemming from this, catalytic reactions tend
to proceed at lower temperatures than purely gas-phase reactions, which is favorable for
50 portable power generation applications. Catalysts are also very active in determining the
product selectivity of the reaction, so a system can be tailored to fit the individual needs
of the user. To evaluate the effectiveness of a catalyst for JP-8 conversion, the effects of
different types of hydrocarbons must be taken into consideration. To this end, extensive
studies have been performed to examine the influence of different classes of

hydrocarbons on catalytic performance and to optimize the reactor or operating conditions to meet the researchers' respective goals [10-16]. Small-scale catalytic systems utilizing logistic fuels can be used in a multitude of applications, including portable power generation [17,18] and fuel processing for fuel cells [19].

Several review papers exploring this topic have already been published [20-24]. These papers primarily concentrate on either a specific class of catalyst or a specific application. The current review provides a broader view of the topic, focusing on the characteristics of suitable catalysts, the development of kinetic models, and the investigation of sulfur-tolerant catalysts for use with JP-8 and its surrogates. Suggestions for further studies are also presented.

2. Catalysts

2.1 Catalyst materials

2.1.1 Supported metals

The most common type of catalyst for oxidation or reformation of jet fuels and other liquid hydrocarbons is a supported metal, in which a support (either inert or catalytic) is coated with an active metal species. Depositing the metal particles on the support allows for greater particle dispersion and thus higher catalytic activity. Different metals have different catalytic properties. Santos et al [25] compared the activity of Pt, Pd, Ir, Rh, and Au catalysts supported on TiO₂ for toluene oxidation. They reported the following trend in activity: Pt > Pd ≫ Rh ≅ Ir ≫ Au. This was explained in terms of the oxidation method of toluene on noble metals—each metal has a dissociative chemisorption energy for O₂. At a given temperature the specific activities of each metal as a function of oxygen chemisorption energy form a volcano plot; metals with very low or very high chemisorption energies have low activities due to lowered capability for adsorption/desorption from the catalyst surface, and metals with a median value have high activities due to a functional balance of adsorption/desorption. The volcano plot for

toluene and ethanol from this study is presented in Figure 1. Pt and Rh catalysts were also compared in terms of activity for CPOX of decane to form H₂ and olefins in an earlier study [26]. For this application, Rh had significantly higher H₂ and olefin production; Pt produced hardly any H₂. Kim [27] studied Cu, Fe, Mn, V, Mo, Co, Ni, and Zn catalysts supported on γ -Al₂O₃ for the oxidation of benzene, toluene, and xylene (BTX). It was found that Co, Ni, and Zn catalysts showed negligibly low fuel conversion at all reaction temperatures examined; Fe, V, and Mo catalysts had mid-range values for fuel conversion at high temperature (350 °C); and Cu and Mn catalysts had the highest conversions, reaching > 98% at 350 °C.

While the type of metal is clearly very influential in determining the activity of the catalyst, its characteristics on the support, including metal loading (wt. %) and particle size, are equally important. Kim [27] further optimized the most active catalyst from the previously described study, Cu/ γ -Al₂O₃, by varying the Cu loading from 1 to 100 wt. %. It was determined that the optimal Cu loading for oxidation of BTX was 5 wt. %. As the loadings increased, the surface area of the catalyst decreased, causing a loss in catalytic activity; 1 wt. % Cu had the highest surface area, however, it also had the lowest conversion due to the reduced number of Cu active sites. Other studies have also been conducted to analyze the effect of metal loading on product formation [28,29]. High catalytic activity typically corresponds to high catalyst surface area, as it provides more active sites upon which reactions can occur. High surface area results from high metal dispersion and small particle sizes. However, the relationship between particle size and catalytic activity is quite complex—the effect of particle size is often dependent upon other factors (e.g. metal/support material, reaction conditions, and preparation method). Pérez-Cadenas et al [30] found that for the total oxidation of xylene, Pd catalysts with smaller particles exhibited higher activity, whereas the opposite was true for Pt. The difference in particle sizes was a consequence of different metal-support interface properties caused by different pretreatment temperatures of the catalyst supports prior to metal deposition, so the authors purported that the inconsistency in activity trends was likely due to a structural sensitivity effect. This structure sensitivity was also observed by Santos et al [20] for both Pt and Pd catalysts (the activity of each increased with

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4 increasing particle size). There are many complexities pertaining to the relationship
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6 between particle size and catalytic activity for other noble metals, leading to discord
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8 115 within the literature. For Au catalysts there appears to be a general consensus that smaller
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10 Au particles are more desirable for total oxidation of volatile organic compounds (VOCs)
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12 [20,31-33].
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14 The addition of a second or third metal onto the catalyst has been shown in many
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16 studies to be beneficial in improving catalytic activity and product selectivity. The
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18 120 interactions between metal atoms in bimetallic catalysts often improves performance
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20 above either monometallic catalyst, and can offer increased resistance to poisoning,
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22 sintering, and coking [34,35]. The addition of Au to Pt and Pd has been shown to greatly
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24 promote the total oxidation of toluene [20,31,32,36]. Kim et al [37] studied the effects of
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26 Fe, Co, and Mo addition on Ni catalysts supported on MgO/Al₂O₃. It was found that the
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28 125 Ni/Fe/MgO/Al₂O₃ catalyst exhibited the best stability and activity for autothermal
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30 reforming of iso-octane; the addition of Fe, Co, and Mo significantly increased the
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32 surface area of the catalyst, as confirmed by BET analysis, but the catalyst with Fe had
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34 the highest. Colby et al [38] found that the addition of Ce to Rh catalysts physically
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36 130 dispersed the particles. X-ray diffraction (XRD) analysis revealed that catalysts without
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38 Ce experienced increased crystallinity, indicating larger crystallite, and thus particle,
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40 sizes, as well as the existence of low-index surface planes, (i.e. (100), (110), and (111)
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42 formations), which lowers the catalytic activity relative to smaller Rh clusters. With the
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44 addition of Ce, however, the Rh did not undergo increased crystallinity, allowing the Rh
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46 135 particles to remain amorphous, which is indicative of higher dispersion and smaller
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48 particle sizes. XRD patterns for both catalysts are shown in Figure 2. Bimetallic catalysts
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50 also provide greater resistance to sulfur poisoning than monometallic catalysts; this will
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52 be discussed further in Section 4.1.
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56 140 2.1.2 Other catalyst materials 57 58 59 60 61 62 63 64 65

Although supported noble metal catalysts are the most active and thus most commonly used catalysts for heavy hydrocarbon conversion, for certain applications the high price of noble metals can be prohibitive. Some experimental work has been reported in the literature using non-supported metal catalysts. Doroftei et al [39] developed an Sr-manganite (SrMnO_3) powder catalyst for the combustion of aliphatic and aromatic compounds. The researchers found that, although combustion was initiated at a lower temperature ($\sim 100^\circ\text{C}$) for the aromatics, the maximum conversion observed was only approximately 50%, compared to the aliphatics, which lit off at a higher temperature ($\sim 150^\circ\text{C}$) but reached $> 90\%$ conversion. They concluded that the mobility of lattice oxygen is a large contributing factor to the overall activity of the catalyst, a phenomenon also observed by Santos et al [40] for the oxidation of toluene over cryptomelane ($\text{KMn}_8\text{O}_{16}$) and other manganese oxide catalysts. It has been seen that lattice oxygen in Mn_xO_y catalysts actively participates in the oxidation of VOCs, meaning that oxidation occurs via a redox mechanism [41]. The mobility of the lattice oxygen (i.e. how easily it can be removed from the lattice structure) plays a large role in the selectivity to CO_2 ; higher mobility promotes higher CO_2 formation. Thus, catalysts with high concentrations of mobile surface lattice oxygen tend to exhibit the highest oxidation activity [41].

Marin-Flores et al [42] investigated MoO_2 as a catalyst for CPOX of iso-octane. They found that the bulk MoO_2 structure gradually transformed into Mo_2C over the duration of the reaction. This occurred via diffusion of the surface carbon formed from the dissociative adsorption of the fuel into the bulk structure, filling oxygen vacancies. Mo_2C has also been used as a catalyst in the literature. A bulk molybdenum carbide (Mo_2C) catalyst was developed for use with diesel fuel [43]. The catalyst showed good stability for steam reforming (SR) and oxidative steam reforming (OSR) of alkane and aromatic species, and, although it succumbed to sulfur poisoning, the poisoning was shown to be reversible, indicating that Mo_2C may be a good replacement for noble metal catalysts for the SR and OSR of diesel fuel.

2.2 Role of support

For supported metal catalysts, the support material and its interaction with the catalyst metal plays a significant role in the catalytic combustion processes. The nature and properties of the support can influence the particle size, shape, and dispersion of the metal [28,44], as well as the amount that becomes anchored to the surface [20]. Additionally, the geometry of the support can influence the flow within the catalytic structure and thus affect the product selectivity [26,31,45,46]. When reducible oxides are present in the support, it may also participate in the catalytic reaction pathways; surface lattice oxygen vacancies provide sites for oxygen adsorption and activation, thus contributing to the overall catalytic activity [20,40,47]. The binding energy between the support and the metal can also contribute to the catalytic properties and thus affect the activity and product selectivity [48,49]. Additionally, the nature of the support can affect the adsorption/desorption of the reactants—if the adsorption energy of the support is too strong, coke can form on the surface of the catalyst, causing either deactivation or oscillations in CO₂ formation and apparent fuel conversion [50]. In addition to the support materials described in detail below, other support materials described in the literature include carbon-coated supports [30,51], cordierites [29,52], yttrium-stabilized zirconia (YSZ) [13], hopcalite [53], hydrotalcite [54], MCM-41 [20,33], and metal oxides such as SiO₂ [27,28,44,55], TiO₂ [20,27,28,56], ZrO₂ [56,57], and MgO [37,48].

2.2.1 Alumina and ceria supports

Alumina (Al₂O₃) and ceria (CeO₂) are the most common catalyst support materials for oxidation of hydrocarbon fuels found in the literature. Al₂O₃ is a desirable material for a catalyst support due to its high thermal and chemical stability. Linsmeier and Taglauer [44] examined the metal-support interactions of Rh/Al₂O₃ and Rh/TiO₂. They discovered via low-energy ion scattering (LEIS) that the Rh particle was completely encapsulated by the TiO₂ support during high-temperature reductive treatment (HTR), which resulted in the destruction of Rh active sites to significantly reduce the catalytic activity. This was not the case for the Al₂O₃ support—Rh/Al₂O₃ did not exhibit strong metal-support interactions, allowing the Rh particles to remain active. Similarly, Kim [27] found that catalysts on Al₂O₃ supports demonstrated higher activity for the oxidation

of BTX than those on TiO₂ and SiO₂ supports. From a more fundamental viewpoint, alumina has been shown to play an important role in the water-gas shift (WGS) reaction (Equation 1), a crucial reaction in any reforming or oxidation process.

It has been proposed [58] that the alumina support activates the H₂O molecule, decomposing it into OH and H on the Al₂O₃ surface. CO adsorbed onto the metal then diffuses towards the OH on the support to form COOH, which is an important step in the formation of CO₂ via the WGS reaction.

Ceria has a high oxygen storage capacity (OSC) and oxygen mobility, is easily reducible, and is thermally stable enough to operate in high-temperature oxidative environments. There exists a synergistic relationship between the ceria support and the noble metal dispersed upon it—oxygen from the CeO₂ support gets transferred to the metal particles to react with the fuel, and is then replenished by either O₂ (in the reactant stream) or H₂O (during steam reforming) [59]. Different doping agents can be used on the ceria support to improve the catalytic activity. It has been found that integrating Cu by up to 3.6 wt. % in the support structure increases the activity as well as facilitates ~100% selectivity to CO₂ during the oxidation of naphthalene [47]. CeO₂ also has a distinctive advantage over Al₂O₃ for resistance against sulfur poisoning of the catalyst. When a sulfur-laden fuel is oxidized, the CeO₂ is easily sulfided, leaving the noble metal catalyst available for oxidation/reforming reactions and thus extending the lifespan of the catalyst [60,61,62]. This finding was confirmed in a study by Xie et al [48], in which the sulfur tolerances of Rh/Al₂O₃ and Pt/Al₂O₃ were compared to those of the noble metals supported on CeO₂. Although the Al₂O₃ allowed for significantly higher surface area and metal dispersion, the CeO₂-supported catalysts demonstrated higher hydrogen production rates (HPR) and lower carbon deposition over 55 h on stream than the Al₂O₃-supported catalysts. The mechanism by which this occurs will be further discussed in Section 4.2. Despite their inferior sulfur tolerance to ceria, alumina is still a desirable support material due to its thermal and chemical stability and increased surface area. As such, several sulfur resistance studies have been performed on catalysts with CeO₂-doped Al₂O₃ supports [63,64,65,66,67]. It was found that the addition of CeO₂ to the Al₂O₃ support

facilitated higher H₂ and CO₂ production, with suppressed olefin production [66]. It also allowed the catalyst to remain active for longer times on stream [67].

2.2.2 Zeolites

Zeolites are a common fluid catalytic cracking (FCC) catalyst for hydrocarbon fuels, and are often used as a support material for noble metal catalysts. Zeolite structures are unique in that only molecules of a certain size can penetrate the crystal structure, allowing for greater control in product selectivity. They also facilitate the removal of aromatic species from logistic fuels via ring contraction and opening processes [68]. When a noble metal is deposited onto the support surface, the properties of the zeolite structure change. Zhang et al [69] saw via transmission electron microscopy (TEM) that Rh nanoparticles dispersed evenly within the zeolite framework without significantly altering the parent zeolite shape. However, the addition of Rh blocked some of the micropores in the zeolite framework, thus decreasing the surface area. Despite this, it was found that the Rh increased the adsorption activity for benzene, indicating that zeolite-supported Rh may be an effective catalyst for logistic fuel conversion. Tidahy et al [70] found that zeolite-based Pd catalysts exhibited a higher activity than Pd/ZrO₂ in the oxidation of toluene by enabling significantly higher surface areas and thus smaller particle sizes and more favorable Pd dispersion. Zeolites stabilized with rare earth metals, such as Ce, La, and Y, have been found to be thermally stable, meaning that at high temperatures the zeolite structure does not break down. At typical liquid fuel reforming temperatures, Y offers the best thermal stability. Y-zeolites coated in Rh have been shown to exhibit superior durability in the reformation of JP-8 to a conventional Rh/Al₂O₃ catalyst [68].

2.2.3 Perovskites

Support structures are often modified to optimize the catalytic activity or product selectivity. Perovskite (ABO₃) supports have a multitude of formulations and thus are

frequently modified to tailor the results for specific applications. Sekine et al [71] found that perovskite-supported Ni catalysts exhibited significantly higher activity than Ni/ α - Al_2O_3 and Ni/ La_2O_3 for the steam reforming of toluene. They also found that partial substitution of Sr into the La sites increased the activity further, with the Ni/ $\text{La}_{0.7}\text{Sr}_{0.3}\text{AlO}_{3-\delta}$ catalyst exhibiting the most desirable behavior. A summary of their findings is given in Table 1. Likewise, Erri et al [72] studied different compositions of Ce- and Ni- substituted LaFeO_3 catalysts for the autothermal reforming of JP-8. It was determined that the amount of Ni substitution had little effect on conversion, but the Ni-rich catalyst ($\text{LaFe}_{0.4}\text{Ni}_{0.6}\text{O}_3$) showed significant coking. All catalysts yielded >90% fuel conversion. In a subsequent study, it was found that a substitution of 1 wt. % Ru or 2 wt. % K on a Ce- and Ni-doped perovskite ($\text{La}_{0.6}\text{Ce}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$) catalysts exhibited higher resistance to sulfur poisoning than those without Ru or K for autothermal reforming of JP-8 with sulfur content up to 220 ppm [73]. This is clearly seen in Figure 3, which shows the fuel conversion rates for perovskites with and without Ru/K substitutions as a function of fuel sulfur content. LaCoO_3 perovskites modified with Ru have also been shown to exhibit increased catalytic stability (in terms of activity and H_2 yield) during oxidative reforming of diesel [74], and those with Fe superior conversion of n-hexadecane, as well as oxidation of soot [75,76], compared to unmodified catalysts.

In addition to their good modifiability, perovskites also offer higher resistance to coking and sulfur poisoning than more conventional supported metal catalysts. Due to their superior thermal stability, perovskite-supported catalysts are able to operate at higher temperatures (>1000 °C), inhibiting coke formation without the risk of sintering [77,78,79]. Similar to ceria, as discussed in Section 2.2.1, perovskite crystal structures contain oxygen vacancies and have good oxygen ion mobility within the crystal lattice, which enhances the catalyst performance [80]. This is apparent even when the perovskite is not the bulk material. Perovskites may appear as a defect phase in a pyrochlore crystal structure ($\text{A}_2\text{B}_2\text{O}_7$). Studies have shown that a lanthanum zirconate pyrochlore ($\text{La}_2\text{Zr}_2\text{O}_7$) doped with Rh and Sr ($\text{La}_{(2-x)}\text{Sr}_x\text{Rh}_y\text{Zr}_{(2-y)}\text{O}_{(7-\xi)}$) will develop a defect SrZrO_3 perovskite phase, which improves catalytic performance [81,82,83]. This phenomenon

seems to occur regardless of the second metal, as long as Sr is present, as it was also observed for $\text{La}_2\text{Zr}_2\text{O}_7$ doped with Sr/Ru [83] and Sr/Ni [84].

2.3 Catalyst Preparation and Pretreatment

While the material of the catalyst is very important to the functionality of the catalytic system, the method of catalyst preparation is often an equally important factor to consider. The preparation method has a large influence on the crystalline and lattice structures, and, for supported metals, on the metal particle size, shape, and dispersion. All of these factors in turn dictate the catalyst surface area and thus the number of active sites, which controls the catalytic activity and therefore the overall performance of the catalytic system.

2.3.1 Pretreatment atmosphere

Catalyst pretreatment in different atmospheres (i.e. reducing, oxidative, or inert) also has a significant influence on catalytic performance, as the chemical state of the metal, which is effected by the pretreatment, plays an important role in catalytic activity. Huang et al [85] examined $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts pre-reduced in an H_2 environment at various temperatures in the context of o-xylene oxidation. The researchers found that the pretreated catalysts exhibited significantly higher conversion rates than the fresh (un-pretreated) catalyst, with those reduced at 300 °C/400 °C having the highest rates. When the pre-reduced catalyst was further pretreated in an oxidative environment at various temperatures, the activity decreased sharply with increasing pretreatment temperature. These findings are shown in Figures 4 and 5. Similar results were found by Liu et al [86]. They studied $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalysts pretreated with H_2 , N_2 , He, and air, and found that catalytic activity increased when pretreated in a reductive environment (H_2) and decreased in an oxidative environment (air), further supporting the conclusion that the chemical state of Pd is an exceptionally important factor in overall catalytic activity [85,86]. The inert environments (N_2 and He) did not alter the chemical state of the Pd, but

rather modified the crystal structure of the Pd species, resulting in increased catalytic activity [86]. Wen et al [87] determined that the pretreatment atmosphere also affects the Pd dispersion; when the Pd/Pr₆O₁₁ catalyst was pretreated with either H₂ or O₂ gas, the formed surface species (surface hydroxyl or active oxygen species) prevented the Pd particles from migrating and sintering. The general consensus within the available literature is that a reductive atmosphere (i.e. H₂ gas) is the most favorable catalyst pretreatment environment for increasing catalytic activity [20,31,85,86,87].

Pretreatment can also be used to alter and purify the catalyst active species. Zheng et al [63] fabricated an Rh/CeO₂-Al₂O₃ catalyst via wet impregnation utilizing a solution of RhCl₃, which resulted in Cl⁻ remaining as an impurity in the supported catalyst. When the catalyst was pretreated with ammonia (soaked in NH₄OH solution, followed by filtering and calcination), this Cl⁻ was removed, which improved the Rh dispersion and catalytic activity.

2.3.2 Calcination temperature

Calcination also plays a large role in the structure and stability of the catalyst. The temperature at which the catalyst is calcined can dictate the overall catalytic activity by affecting the dispersion and surface area of the metal particles. Lu et al [49] conducted a study in which the effect of different calcination temperatures on the performance of a Pt/CeGdO catalyst was examined. Their findings are reported in Table 2. The researchers found that increasing calcination temperature caused an increased sintering tendency of the Pt, and thus a decrease in the metal surface area, which in turn reduces the catalytic activity, a phenomenon that has also been observed in other studies [27,20,31,53,71]. As seen in Table 2, the catalysts calcined at 600 °C and 800 °C had comparable fuel conversions and product selectivities despite the lower surface area of the 800 °C catalyst. However, further durability studies using iso-octane doped with 300 µg/g of sulfur revealed that calcination at 800 °C improved the catalyst's resistance to sulfur poisoning. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of CO adsorption and CO/H₂S revealed that strongly electron-deficient Pt sites

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4 were immune to sulfur poisoning, and calcination at 800 °C facilitated uniform formation
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6 345 of these sites, resulting in superior performance [49]. Similarly, Tidahy et al [57] found
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8 that when their Pd/ZrO₂ catalysts were calcined at 600 °C (as opposed to 400 °C), a
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10 higher amount of easily-reducible PdO sites were formed, which results in greater
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12 catalytic activity despite lower Pd surface area.
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15 16 350 17 18 **3. Modeling Work** 19

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21 Despite the abundance of detailed reaction mechanisms for homogenous
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23 combustion of jet fuel surrogates [88-93], very little information is present in the open
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25 literature on the modeling of catalytic systems. It has been shown that simulations of
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27 355 homogenous reactions using the existing kinetic mechanisms cannot accurately predict
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29 the product concentrations of catalytic reactions, indicating that the catalyst plays a major
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31 role in product selectivity [13], which emphasizes the need for accurate catalytic models.
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33 Due to the complexity of the fuels and of the heterogeneous reactions occurring on the
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35 catalyst surface, it is remarkably difficult to construct an accurate, detailed chemical
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37 360 mechanism for higher hydrocarbon fuels. However, several derivation and approximation
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39 methods have been shown to yield reasonably accurate results. Khan et al [94] derived a
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41 kinetic power law model to predict the reaction rate data for CPOX of a synthetic diesel
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43 fuel (a mixture of seven different paraffinic, olefinic, and aromatic compounds) to within
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45 365 15% accuracy. Shigarov et al [55] accurately predicted the temperature and species (H₂,
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47 CO, and CO₂) profiles for the autothermal reforming of n-decane by building a
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49 mathematical model around the assumption that n-decane follows two parallel reaction
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51 routes, complete oxidation and steam reforming. Rabe et al [95] successfully modeled the
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53 deactivation due to sulfur poisoning of an Rh/Al₂O₃ catalyst using Langmuir-
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55 370 Hinshelwood kinetic model, which assumes that fuel/oxidizer molecules adsorb onto the
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57 catalyst surface, and then the two adsorbed species undergo a bimolecular reaction. The
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59 Mars-van Krevelen kinetic model, in which reactions between lattice oxygen and
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61 reactants occur, was validated for combustion of toluene, benzene, and ethyl acetate over
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63 a supported Pd catalyst by He et al [96]. Equilibrium simulations have also been shown to
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be relatively accurate for lower fuel to oxygen ratios [97]. However, Gawade et al [98] found that some kinetic models are only valid under certain operating conditions (i.e. steam reforming or combustion). This phenomenon demonstrates the need for more detailed mechanisms for catalytic modeling.

Recently, the prevalent method for overcoming the lack of detailed kinetic models for catalytic oxidation of heavy hydrocarbons has been to break the mechanism into two parts: a simplified mechanism for cracking and/or dissociative adsorption of the fuel at the catalyst front face, followed by either a homogenous or heterogeneous mechanism for lower alkanes, about which there exists abundant information. As the first step is often based on empirical observations of the global reaction, these models are typically presented alongside experimental results for validation.

Thormann et al [99] developed a heterogeneous kinetic model for the steam reforming of hexadecane over an Rh/CeO₂ catalyst. Based on experimental observations of turnover frequencies for hydrocarbons of varying lengths, the researchers chose the first step in this mechanism to be the dissociative adsorption of C₁₆H₃₄ onto the catalyst surface (Equation 2) and chose appropriate kinetic parameters:

The suffix (s) denotes a surface species. For the second stage of the simulation, a detailed kinetic mechanism for steam reforming of methane was utilized. The model predicted the mole fractions of hexadecane, H₂, and H₂O fairly accurately, but not CO and CO₂. This implies that the conversion of hexadecane was well modeled, but the surface reactions pertaining to the equilibrium of CO and CO₂ were inaccurate. These results are shown in Figure 6.

Hartmann et al [100] also developed a two-stage reaction mechanism to simulate the partial oxidation of iso-octane on Rh. In the experimental studies, the researchers observed hybrid reaction behavior, with mostly heterogeneous reactions happening near the front face of the catalyst, and mostly homogenous reactions occurring throughout the remainder of the catalyst. A schematic of this is shown in Figure 7. Based on experimental observations of species profiles, the surface reaction mechanism consisted

of partial oxidation of C₁ – C₃ species, plus two lumped reactions for the dissociative adsorption and destruction of iso-octane:

This was followed by a detailed kinetic mechanism for the homogenous oxidation of iso-octane. This mechanism was used in a two-dimensional model to analyze the species profiles within the catalyst, allowing the researchers to more thoroughly understand the effects of mass transfer in the different zones (heterogeneous and homogeneous) of the catalyst. They found, through the modeling study, that combustion products (H₂O, CO₂, CO, and H₂) were formed primarily in the heterogeneous reaction zone, and the homogenous reaction zone olefins were formed from gas-phase fuel cracking. These findings are consistent with those of an earlier study using a similar two-part model [31], which was derived to mimic experimental observations [46]. In later papers the research group stated that the developed model could be used to optimize reactor design for maximum H₂ production and minimize coke formation [101] and to better understand the relationship between flow rate, chemical heat release, and thermal heat losses in CPOX of iso-octane [102]. This modeling approach was also employed to accurately predict the formation of soot precursors from iso-octane partial oxidation over Rh [103]. These results are seen in Figure 8.

4. Sulfur tolerance

425 Sulfur tolerance is exceptionally important for catalysts to be used with petroleum-based fuels. Often, the sulfur naturally present in the fuel will poison the catalyst by adsorbing onto the surface active sites and not desorbing, thus reducing the number of available active sites for oxidation and reforming reactions to occur and thus deactivating the catalyst. Sulfur can also facilitate higher occurrences of carbon deposition, which decreases catalytic activity [65,104,105].

4.1 Development of sulfur-tolerant catalysts

A comprehensive summary of sulfur-tolerant catalysts discussed in this paper is found in Table 3. It can be seen that there is a general consensus in the literature that Rh is an ideal catalyst for use with sulfur-laden fuels, as it tends to exhibit stable activity for extended periods of time for fuels containing up to 1096 ppm sulfur [21,48,59,60,64-68,95,104,105]. Addition of Rh to other supported metals (i.e. in a bi- or trimetallic configuration) has also been shown to improve sulfur resistance and increase catalytic activity [33,52,59,61,62,66,104,105,106,107]. The beneficial effects of bi- and trimetallic catalysts, particularly those containing Rh, are illustrated in Figure 9 and Table 4 [60-62]. In addition to Rh, successful resistance to sulfur poisoning has also been reported in the literature using noble metals such as Ru [21,48,60], Pt [21,48,49,53], and Au [20,33], as well as Mo₂C [43]. Monometallic Pd [21,33,48,60,105] and Ni [21,64-66,104,105] have been generally found to exhibit poor resistance to sulfur poisoning.

A common catalyst utilized for combustion of sulfur-laden liquid fuel is bimetallic Rh-Ni. This configuration has been shown in the literature to have higher sulfur tolerance than monometallic Rh catalysts [67], due to the Ni serving as sacrificial sulfur adsorption sites, leaving the Rh sites free for reforming and oxidation reactions. Strohm et al [67] studied the deactivation of Rh, Ni, and Rh-Ni catalysts with different Ni loadings on CeO₂-Al₂O₃ supports via the steam reforming of Norpar-13, an industrial solvent containing normal paraffins with an average carbon number of 13. The Norpar-13, which naturally contains 4 ppm of sulfur, was doped with additional sulfur to obtain higher concentrations. Their findings are summarized in Table 5. The deactivation of an Rh monometallic catalyst is shown in Figure 10. It is clearly seen that after approximately 18 hours on stream significant deactivation begins to occur, resulting in the fuel conversion dropping to 4% after 44 hours. However, as shown in Figure 11, the addition of Ni greatly increases the lifespan of the catalyst. The following section will explore the mechanisms by which this occurs.

4.2 Sulfur deactivation mechanisms

Lakshapatri and Abraham [104,105] proposed a mechanism by which sulfur causes catalyst deactivation on Rh-Ni catalysts. They found via transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) analysis that sulfur preferentially adsorbs onto Ni sites, and since no bulk sulfides were formed, they determined that the decomposition of the sulfur-containing compounds occurs exclusively on the Ni surface. The researchers also postulate that sulfur adsorbed onto the Rh sites migrates to the Ni, since the Rh-S bond is significantly weaker than Ni-S. As the Ni surface becomes saturated with S, the overall catalytic activity decreases, causing graphitic carbon and unsaturated/aromatic hydrocarbons to accumulate on the surface, thus further deactivating the catalyst. A schematic representation of this mechanism is shown in Figure 12. It was observed that the deactivation was significantly less severe for catalysts with higher Rh loadings. A similar mechanism was proposed by Chen et al [64]; they determined via X-ray absorption near-edge structure (XANES) analysis that the initial deactivation of an Rh-Ni catalyst was caused by metal sulfide formation on the surface of the Ni particles, followed by accumulation of carbon deposits once the steam reforming activity has been sufficiently reduced. Coupled with the fact that severe deactivation was not observed for sulfur-free fuels, these mechanisms suggest that coke deposition, which contributes to the decrease in catalytic activity, is not the cause of catalyst deactivation, but merely a consequence of the deactivation via sulfur poisoning on the catalyst surface [95].

Azad and Sundararajan [60-62] studied the contribution of the CeO₂ support to the sulfur deactivation of mono-, bi-, and trimetallic noble metal supported catalysts. The researchers postulated that, while the sulfidation of the noble metals was a key contributor to catalyst deactivation, it was not the primary mechanism. This was justified by the high hydrogen yields that were sustained for over 50 h. This, in conjunction with the favorable thermodynamics of the CeO₂-H₂-H₂S system (Equations 5-6), allowed the researchers to deduce that the ceria support formed an oxysulfide, allowing the noble metals to remain unobstructed for fuel reforming.

7 This proposition was confirmed by performing an experiment on the support alone, with
8 no noble metal coating. Deactivation of the catalyst eventually occurred when the noble
9 metal became sulfide, a process whose rate is dependent on the sulfur affinity of the
10 metal. In the monometal study [60], it was seen that Pd adsorbed sulfur competitively
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14 495 with the ceria support, allowing it to deactivate quickly, with no steady hydrogen
15 production period, whereas Ru and Rh were more resistant to sulfidation, enabling a long
16 hydrogen production period before sulfur spillover from the support to the metal
17 occurred. In the case of bimetallic catalysts [61], the researchers proposed that
18 cooperative synergy exists between the two metals, allowing sulfur spillover from the
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23 500 metal with higher sulfidation resistance to lower, thus facilitating a longer duration of
24 steady H_2 production than with monometallic catalysts. This also holds true for
25 trimetallic catalysts, but to a greater degree due to the additional noble metal [62].
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29 Schematic illustrations of the proposed mechanisms for mono-, bi-, and trimetallic
30 catalysts are shown in Figure 13.
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34 5. Recommendations for Future Work

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40 Much progress has been made in recent years to develop and optimize catalysts
41 for use with jet fuels and other heavy hydrocarbons. However, there are still some
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43 510 challenges and unanswered questions that are evident from the literature. Suggestions are
44 made for further work regarding the following areas:
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- 48 • ***In-situ* spectroscopy and microscopy:** Studies of catalytic oxidation and
49 reformation would provide valuable information on the active sites and deactivation
50 mechanisms. Such information will help us to identify important chemical properties
51 for the design of new catalyst formulations. As discussed earlier, such properties
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53 515 include the oxidation state and metal sulfidation of supported metal oxide catalyst.
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55 Therefore, carefully planned in-situ experiments with advanced spectroscopy and
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57 electron microscopy could be utilized to monitor the transformation of catalyst during
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the catalyst pretreatment, reaction initiation, time-on-stream operation and catalyst deactivation.

- **Hybrid reaction mechanism:** There is much interaction between heterogeneous and homogenous reactions during the oxidation of heavy hydrocarbon fuels. The current consensus amongst the literature is that, during reformation processes, the sole function of the catalyst is to ignite the reaction. Then, once all of the bulk oxygen is consumed, gas-phase reactions dominate throughout the rest of the catalyst. However, it is unknown if the catalyst will continue to contribute to the chemistry occurring downstream of the ignition zone system for operating conditions where there is less than 100% oxygen conversion (i.e. fuel-lean combustion). Future work can be done to investigate this. It would also be of interest to study how different classes of hydrocarbons (e.g. paraffins, olefins, cycloalkanes, and aromatics) affect the hybrid combustion mechanism.

- **Modeling:** It is clearly evident from the literature that there is still much research needed regarding the modeling of catalytic systems for heavy hydrocarbon fuels. Despite progress over the last few years, with the development of two-part models that can mimic experimental conditions with reasonable accuracy, the current models utilize assumptions that may make them unusable for reactors other than the ones after which they were designed. Of particular interest is the interaction between heterogeneous and homogeneous reactions that occur on and near the catalyst surface. Further studies may seek to clarify and quantify those interactions and thus expand the current hybrid combustion models. The development of more robust models will also be beneficial for the analysis of catalyst deactivation via sulfur poisoning and carbon deposition.

- **Sulfur tolerance:** Although much progress has been made in recent years in the development of sulfur-tolerant catalysts, there is a need to develop a catalyst that is universally functional for the long-term oxidation or reforming of sulfur-laden fuels. As can be seen in Table 3, the resistance to sulfur poisoning of catalysts described in the literature is dependent on a multitude of different factors, such as fuel components (i.e. alkanes and aromatics), catalytic processes (i.e. oxidation, SR, ATR, or CPOX), and reaction conditions (i.e. reactor temperature and space velocity). Additionally, it

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4 550 is clear from the literature that, while the mechanisms of long-term sulfur
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6 deactivation are fairly well understood, the influence of sulfur during the ignition
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8 process has not been studied to any great extent. Since logistic and transportation
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10 fuels tend to contain non-negligible amounts of sulfur, it is important to understand
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12 each stage of the combustion/reformation process before new technologies can be
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14 555 developed.

15 16 17 18 19 20 **6. Conclusions**

21
22 A comprehensive survey of recent progress in catalytic conversion of jet fuels and
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24 560 their surrogates has been provided. Much progress has been made in the last decade to
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26 further the understanding of the effects of catalyst/support materials and preparation
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28 methods thereof on catalytic processes associated with fuel oxidation and reformation.
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30 Great strides have also been made in the realm of computer simulations of catalytic
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32 systems, although there is still much room for growth and improvement on that front.
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34 565 Sulfur poisoning is a problem that has been a major obstacle to the development of
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36 commercially viable catalysts for use with JP-8 and other logistic fuels. As such, an
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38 immense amount of research has gone into the development of sulfur tolerant catalysts, to
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40 varying degrees of success. Suggestions for further research are presented at the end of
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42 the work.

43 44 45 46 47 48 49 **Acknowledgments**

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Heterogeneous
chemistry only

Coupled heterogeneous &
homogeneous chemistry

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

(a)

(b)

(c)

Table 1

Catalyst	Conversion (%)	Selectivity (%)				H ₂ Yield (%)	Amount of Carbon Deposition (g/g _{cat})
		CO	CH ₄	CO ₂	C ₆ H ₆		
Ni/LaAlO ₃	25.8	33.8	0.9	62.9	2.4	27.6	800
Ni/La _{0.9} Sr _{0.1} AlO _{3-δ}	58.5	31.9	8.5	58.8	0.8	49.5	235
Ni/La _{0.7} Sr _{0.3} AlO _{3-δ}	58.2	33.3	3.3	62.3	1.1	48.4	57
Ni/La _{0.5} Sr _{0.5} AlO _{3-δ}	52.3	32.7	3.6	63.2	0.5	46.7	52
Ni/α-Al ₂ O ₃	6.3	44.6	0	54.5	0.9	5.6	431
Ni/La ₂ O ₃	14.0	35.7	0	59.0	5.3	14.0	6

Table 2

Calcination Temperature (°C)	S_{BET} (m ² /g)	Pt Dispersion (%)	Iso-Octane Conversion (%)	Product Composition (mol %), dry			
				H ₂	CO	CO ₂	CH ₄
600	57	63	99.7	71.7	12.4	15.6	0.3
800	39	59	99.1	72.4	12.1	15.3	0.2
1000	10	15	80.0	69.1	11.7	16.2	3.0
	<i>Equilibrium</i>		100	72	13	15	Trace

Table 3

1st Author (pub. year)	Ref. No.	Catalyst (loading)	Support	Fuel	Sulfur Content (ppm)	Sulfur Tolerance?
Azad (2007)		Rh (0.5-1%) Rh (0.5-1%)-Pd (0.5-1%) Rh (0.5-1%)-CuO (1-5%)	Gd ₂ O ₃ -doped CeO ₂ (GDC) ZrO ₂ -doped CeO ₂ (ZDC)	Toluene	50	<ul style="list-style-type: none"> Rh/GDC had stable H₂ yield of ~45% after 10 h, Rh/ZDC had ~60% after 8 h Rh-Pd/GDC had stable H₂ yield of ~70% after 18 h, Rh-Pd had ~75% after 20 h No significant deactivation seen for Rh or Rh-Pd H₂ yield of Rh-CuO catalysts slowly decreased from ~80% to ~60% over 22 h
Azad (2010)		Ru (1%) Pd (1%) Rh (1%)	Gd ₂ O ₃ -doped CeO ₂	H ₂ S Kerosene	1000 260	<ul style="list-style-type: none"> Pd adsorbed ~2600 ppm S after 24 h soak in H₂S, Rh ~2200, Ru ~2000 (amount proportional to soak time) Pd showed steady deactivation over 60 h Ru had constant H₂ yield until 51 h, Rh until 55 h (Ru max = 79%, Rh max = 87%)
Azad (2011)		Ru (0.5%)-Pd (0.5%) Ru (0.5%)-Rh (0.5%) Rh (0.5%)-Pd (0.5%)	Gd ₂ O ₃ -doped CeO ₂	H ₂ S Kerosene	1000 260	<ul style="list-style-type: none"> Rh-Pd adsorbed ~1200 ppm S after H₂S soak, Ru-Rh ~1050 ppm, Ru-Pd ~750 ppm Constant H₂ yield for 68 h (Ru-Pd), 75 h (Rh-Pd), and 88 h (Ru-Rh) All had > 85% H₂ yield at steady state before deactivation
Azad (2010)		RPR323: Ru (0.33%)-Pd (0.5%)-Rh (0.33%) RPR322: Ru (0.33%)-Pd (0.5%)-Rh (0.5%) RPR232: Ru (0.5%)-Pd (0.33%)-Rh (0.5%) RPR223: Ru (0.5%)-Pd (0.5%)-Rh (0.33%)	Gd ₂ O ₃ -doped CeO ₂	H ₂ S Kerosene	1000 260	<ul style="list-style-type: none"> RPR322/RPR223 adsorbed ~400 ppm S after H₂S soak, RPR232 ~350, and RPR333 ~300 Constant H₂ yield for 86 h (RPR333), 89 h (RPR223), 92 h (RPR322), and 109 h (RPR232) Max H₂ yield: 78.3% (RPR333), 82.5% (RPR322), 84.5% (RPR223), and 89.1% (RPR232)

Cheekatamarla (2006)		-	Mo ₂ C	Benzothiophene-doped hexadecane	125 250 500	<ul style="list-style-type: none"> Steam reforming: all three fuels showed deactivation (immediate decrease in H₂ yield) Oxidative steam reforming: fuel with 125 ppm S showed no signs of deactivation after 6 h, but fuels with 250/500 ppm S did Rate of decrease of H₂ yield was proportional to S concentration
Chen (2010)		Rh (2%) Ni (10%)	CeO ₂ -Al ₂ O ₃	3-methylbenzothiophene-doped Norpar-13	350	<ul style="list-style-type: none"> Ni catalyst began to deactivate immediately Rh retained ~90% of initial HPR after 55 h
Klinghoffer (2011)		Pt-Rh (-)	Cordierite	JP-8	125	<ul style="list-style-type: none"> Deactivation observed at beginning of study, but conversion/H₂ concentration stabilized after ~250 h on stream Steady-state conversion ~25% lower with sulfur present
Kuchеров (2009)		Au (2%, 4%) Pd (3%) Au (1%)-Pd (3%) Au (2%)-Rh (9%)	MCM-41 (2% Au, Au-Rh) TiO ₂ (4% Au, Pd, Au-Pd)	Dimethyldisulfide (DMDS)	1000	<ul style="list-style-type: none"> At 155 °C deactivation of Au/MCM-41 began after 6 h, but at 500 °C no deactivation occurred DMDS conversion on Au/TiO₂ decreased slowly over 4 h, but remained steady for Au-Pd Pd showed poor oxidative activity up to 200 °C Au-Rh had stable, mostly complete conversion
Lakhapatri (2009)		Rh (2.5%) Ni (10%) Rh (0.5%)-Ni (10%) Rh (2.5%)-Ni (10%)	γ-Al ₂ O ₃	Thiophene-doped n-hexadecane	1000	<ul style="list-style-type: none"> 1000 ppm S decreases H₂ yield of Rh (0.5%)-Ni (10%) catalyst by 50% Higher Rh (2.5%, as compared to 0%/0.5%) decreased surface carbon deposition by ~80% in presence of sulfur, thus helping prevent deactivation
Lakhapatri (2011)		Ni (10%) Pd (1.5%) Rh (1.0%) Ni (10%)-Pd (1.5%) Ni (10%)-Rh (1.0%)	γ-Al ₂ O ₃	Thiophene-doped Jet-A	1000	<ul style="list-style-type: none"> Rh-containing catalysts have highest H₂ yield and resistance to sulfur poisoning, particularly bi- and trimetallic catalysts Ni-Rh-Pd catalyst did not show significant carbon deposition until 20 h on stream H₂ yield of Ni-Rh-Pd decreased by 40% over 45

		Rh (1.0%)-Pd (1.5%) Ni (10%)-Rh (1.0%)-Pd (1.5%)				h on stream
Lee (2008)		Rh (2.50%) Rh (2.13%)	γ -Al ₂ O ₃ Sm-NaY zeolite/ γ -Al ₂ O ₃	JP-8	1096	<ul style="list-style-type: none"> Al₂O₃-supported catalyst degraded more rapidly than zeolite Steady product selectivities after 10 h on stream for zeolite-supported catalyst
Lu (2008)		Pt (1.5%)	CeGdO	Thiophene-doped iso-octane	300	<ul style="list-style-type: none"> Catalyst was able to sustain > 95% conversion and constant H₂ concentration over 100 h study with no degradation
Rabe (2009)		Rh (proprietary)	Al ₂ O ₃	Gasoline (C _{7.285} H _{12.289})	6	<ul style="list-style-type: none"> H₂ concentration decreased 20% after 3.5 h Unconverted HC increased by ~50% after 3.5 h, and H₂O by 100% Onset of reaction function of TOS (sulfur influences ignition process)
Strohm (2006)		<i>See Table 5</i>	<i>See Table 5</i>	<i>See Table 5</i>	<i>See Table 5</i>	<i>See Table 5</i>
Szynkowska (2009)		Pd (1%) Pt (1%) Au (1%)	Hopcalite (70% MnO ₂ , 30% CuO)	Thiophene	N/A	<ul style="list-style-type: none"> Au did not significantly improve catalytic activity (compared to support alone) >90% conversion for Pd and ~100% for Pt Pt and Pd promoted total oxidation
Xie (2010)		Rh (2%) Ni (10%) Rh (2%)-Ni (10%)	CeO ₂ -Al ₂ O ₃	3-methylbenzothio- phene-doped Norpar-13	350	<ul style="list-style-type: none"> At 550 °C Rh-Ni had highest initial H₂ production rate (HPR), and degraded slower (50% decrease in HPR after 10 h) than Rh (5 h) and Ni (3 h) At 800 °C HPR of Rh-Ni was initially highest but began to deactivate after ~25 h, while Rh HPR was mostly stable for 55 h
Xie (2011)		Rh (2%) Ni (10%)	CeO ₂ -Al ₂ O ₃	3-methylbenzothio- phene-doped Norpar-13	350	<ul style="list-style-type: none"> After 55 h Ni catalyst accumulated 1.23 g/g_{cat} carbon, and the Rh 0.13 g/g_{cat} Ni formed more aromatic and quinone than Rh, and Rh more carboxyls and carbonates

Xie (2012)		Rh (2%) Pt (2%) Ru (2%) Pd (2%)	Al ₂ O ₃ (all) CeO ₂ (Rh and Pt) SiO ₂ (Rh) MgO (Rh)	3-methylbenzothio- phene-doped Norpar-13	350	<ul style="list-style-type: none"> • HPR of Ru, Pt, Pd/Al₂O₃ decreased by > 94% after 55 h, and Rh/Al₂O₃ by 44% • After 55 h Ru, Pt, Pd, and Rh had ~1.6, ~1.2, ~1.8, and ~0.35 g/g_{cat} carbon, respectively • Rh/Al₂O₃ and Rh/CeO₂ had significantly higher HPR and significantly lower carbon deposition than Rh/SiO₂ and Rh/MgO • Pt/CeO₂ had higher HPR and significantly lower carbon deposition than Pt/Al₂O₃
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Table 4

Catalyst	Monometallic			Bimetallic			Trimetallic RPR			
	Ru	Pd	Rh	Ru-Pd	Ru-Rh	Rh-Pd	333	322	232	223
Max H ₂ yield (%)	79	84.4	87	86	88	89	78.3	82.5	89.1	84.5
Duration (h) of steady level H ₂ yield	51	-	55	68	88	75	86	92	109	89
Time (h) to deactivate to 20% H ₂ yield	66	59	68	92	114	96	102	123	129	106

Table 5

Catalyst	S concentration of Norpar-13 (ppm)	Time on Stream (h)	Initial/Final Conversion (%)	Carbon (wt. %)
2% Rh/CeAl	4	72	100/96	3.11
2% Rh/CeAl	15	57	100/70	2.94
2% Rh/CeAl	35	25.5	100/76	3.07
2% Rh/CeAl	33	44	100/4	7.64
2% Rh/Al	15	10	100/98	3.89
2% Rh/CeAl	100	10	100/59	2.99
2% Rh-2% Ni/CeAl	100	10	98/92	3.06
2% Rh-5% Ni/CeAl	126	16	99/66	2.96
2% Rh-10% Ni/CeAl	100	32	100/65	24.7
2% Rh-10% Ni/CeAl	126	9	100/75	8.21
2% Rh-20% Ni/CeAl	126	42	98/78	34.4
2% Rh-5% Ni/CeAl	104	19	100/71	4.89
5% Ni/Al	33	4.5	80/5	13.7
5% Ni/CeAl	104	3.5	98/35	14.9
10% Ni/CeAl	104	5	95/98	59.9

1. Catalytic activities of $\text{Ni/La}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$ catalysts for steam reforming of toluene and the amounts of carbon deposition on these catalysts after the reaction for 180 min: $\text{W/F} = 3.4 \text{ g h mol}^{-1}$, $\text{S/C} = 2.0$, reaction temperature: 873 K, and Ni loading: 5 wt% [71].
2. Effect of the calcination temperature of Pt/CeGdO catalysts on conversion and product composition for the SR of iso-octane [49]
3. Summary of sulfur tolerance studies
4. Performance summary of the mono-, bi- and trimetal supported catalysts [62]. RPR333, RPR322, RPR232, and R223 (where first R refers to the noble metal Ru and the second R to Rh and P for Pd) respectively, represent 1/3wt% Ru + 1/3wt% Pd + 1/3wt% Rh), (1/3wt% Ru + 1/2wt% Pd + 1/2wt% Rh), (1/2wt% Ru + 1/3wt% Pd + 1/2wt% Rh), (1/2wt% Ru + 1/2wt% Pd + 1/3 wt% Rh), with the remaining GDC support material (Nanoscale support material consisting 10 mole% gadolinia- (Gd_2O_3 -) doped CeO_2).
5. Results of reforming of model fuels doped with sulfur over various catalysts [67]