



Deactivation due to sulfur poisoning and carbon deposition on Rh-Ni/Al₂O₃ catalyst during steam reforming of sulfur-doped n-hexadecane

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ABSTRACT

Deactivation by sulfur poisoning and carbon deposition of steam reforming catalyst used for hydrogen production from diesel or jet fuel creates a significant barrier to commercialization of fuel cell technologies. Steam reforming of n-hexadecane on a rhodium/nickel catalyst supported on γ -alumina, a formulation previously proposed for steam reforming of logistic fuel, was used to study the deactivation mechanisms. The steam reforming activity was measured in terms of H₂ yields and showed that the catalysts were stable in the absence of sulfur but deactivated over a period of 10 h when sulfur was present at high loading. Stability and activity were higher with higher amounts of Rh content when Ni was kept constant. TEM-EDS of used catalysts revealed preferential adsorption of sulfur on the surface of Ni crystallites; EDS and XRD analysis showed no bulk sulfide formation. Excessive carbon deposition was observed during steam reforming of sulfur-containing fuel. Blocking of reactant species on the surface of the catalyst due to the formation of aromatic/polymeric carbon on the support was also seen, although higher Rh content inhibited this phenomenon.

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1. Introduction

Petrochemical fuel reserves are limited, and their combustion leads to CO₂ formation; thus, researchers are striving to introduce alternative fuel sources and use existing sources more efficiently. For selected applications, fuel cells are highly efficient and offer operational and environmental benefits in both stationary and mobile settings. Application in a hybrid system consisting of a conventional internal combustion engine (ICE) for propulsion and a fuel cell powered auxiliary power unit (APU) presents one possible option that could potentially reduce greenhouse gas emissions and provide high fuel efficiencies [1]. One of the challenges involved in implementing this system is on-board storage of hydrogen, since H₂ has low energy density and also lacks a well developed distribution network. It is therefore desirable to produce hydrogen on-board using fuel already present on the vehicle, i.e. gasoline, diesel or jet fuel [2].

Steam reforming, in which fuel and water are converted to H₂ and CO₂ over a selective catalyst, provides a method to produce hydrogen. Generally, reforming catalysts consist of a base metal (Ni, Co, etc.) promoted by a noble metal (Pt, Pd, Rh, Ru, etc.)

supported on stabilized supports (alumina, ceria, ceria promoted alumina, zeolite, etc.). Studies reveal that Ni based catalysts promoted with Rh supported on alumina are fairly active [3,4] for reforming of hydrocarbon mixtures and simple fuels.

Much recent work has focused on the development of sulfur-tolerant catalysts [3,5–9]. Studies have been conducted using catalysts designed for reforming of low molecular weight hydrocarbons [10–16] and reveal that sulfur is adsorbed on the same sites as those involved in carbon formation [17]. Studies with catalyst surfaces [18–23], including single-crystal metal surfaces, have established that sulfur inhibits the chemisorption of small molecules (H₂, CO, NO, C₂H₄, etc.), and thus leads to deactivation in the catalyst effectiveness for CO methanation, alkane hydrogenolysis, olefin hydrogenation, and the water–gas shift reaction. Controlled pre-sulfiding of the metal catalyst may result in carbon-free operation by ensemble control [24,25].

Sulfur compounds present in the logistic fuels are known to undergo cracking to give H₂S, and sulfur is deposited as a consequence of H₂S decomposition [22]. Sulfur binds to the metal site forming stable compounds with all transition metals [23], leading to sulfur poisoning.

Another major challenge in steam reforming is deactivation associated with carbon deposition, since the high temperatures associated with steam reforming favors the formation of carbon. Though carbon deposition can be somewhat controlled using

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excess steam, the economics of the process does not allow operating at high steam to carbon ratios. There are several mechanisms of carbon deposition [26], including (i) chemisorption as a monolayer or physisorption in multilayers that block access of reactants to metal surface sites, (ii) encapsulation of a metal particle and complete deactivation of that particle, (iii) deposition in pores such that access of reactants is denied, and (iv) formation of carbon whiskers [27]. Barbier et al. [28] and Coughlin et al. [29] concluded that graphitization of coke deposited on the metal was one of the main reasons for deactivation. Graphitic carbon formation on Ni surface was first reported by Dent et al. [30]. Irrespective of the type of coke, carbon deposition always involves an initial step of dehydrogenation and formation of unsaturated species which are able to migrate, either in the gaseous phase or in the adsorbed phase. There is a tendency for coking to increase as unsaturation, molecular weight, and aromaticity increase, and thus olefins and aromatics are major coke precursors.

Diesel and jet fuel are complex hydrocarbon mixtures characterized by the presence of sulfur, ranging from a few ppm in diesel to as high as 3000 ppm in jet fuel. Even though desulfurization can be used to remove most of the sulfur from a traditional fuel, small quantities that remain can lead to deactivation after many hours on stream. The present work using n-hexadecane doped with thiophene was designed to gain insights into carbon deposition and sulfur poisoning during steam reforming.

2. Experimental

Catalysts were prepared with different active metal compositions in order to understand the deactivation mechanism of Rh-Ni/ Al_2O_3 catalysts. Each catalyst was used during steam reforming of n-hexadecane doped with thiophene to produce a set of used catalysts that could be evaluated for chemical and structural changes. The sole purpose of testing this set of catalysts was to gain information about the deactivation mechanism on 0.5Rh-Ni/ Al_2O_3 catalyst; it was not our intention in this work to formulate a more active or more stable catalyst.

2.1. Catalyst preparation

Four different catalyst formulations were prepared with varying levels of nickel and rhodium loading. Two monometallic catalysts contained 2.5% and 10% Rh and Ni, respectively. Two bimetallic catalysts, each containing 10% nickel, were prepared with Rh loadings of 0.5% and 2.5%. The catalysts were designated based on the active metal present as Ni/ Al_2O_3 (10Ni), Rh-Ni/ Al_2O_3 (both 0.5Rh10Ni and 2.5Rh10) and Rh/ Al_2O_3 (2.5Rh). The catalysts were prepared using parameters (catalyst precursor and calcination temperature) which were optimized previously in our laboratory for the present application, and based on information available in the literature [31,32]. These compositions were used to allow experimental analysis of used catalysts; there was no attempt to optimize formulations since our goal in the current work was to understand the role of sulfur in catalyst deactivation, rather than to optimize a specific sulfur-tolerant catalyst formulation.

All catalysts were prepared by a co-impregnation technique using tetrahydrofuran (THF) as the solvent, based on a recipe developed in previous work [33,34]. Catalysts were prepared by impregnating γ -alumina (Grace Davison) with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Rh}(\text{CH}_3\text{COCHCOCH}_3)_3$ dissolved in THF at the required concentration, followed by drying at 120 °C for 1 h and calcination in air at 800 °C for 3 h. These catalysts were then used in steam reforming for 10 h using procedures described below. In the further discussion, the term *used catalyst* refers to post reaction catalyst.

2.2. Steam reforming reactor configuration

A schematic of the experimental set-up used to conduct steam reforming of the fuel is shown in Fig. 1. A quartz reactor tube was used to minimize coke formation, and confirmed through experiment that coking on the inner walls of the quartz tube was negligible. Quartz wool was used to support the catalyst on either side. The temperature of the preheater and the reactor were maintained using single-zone tube furnaces controlled by tem-

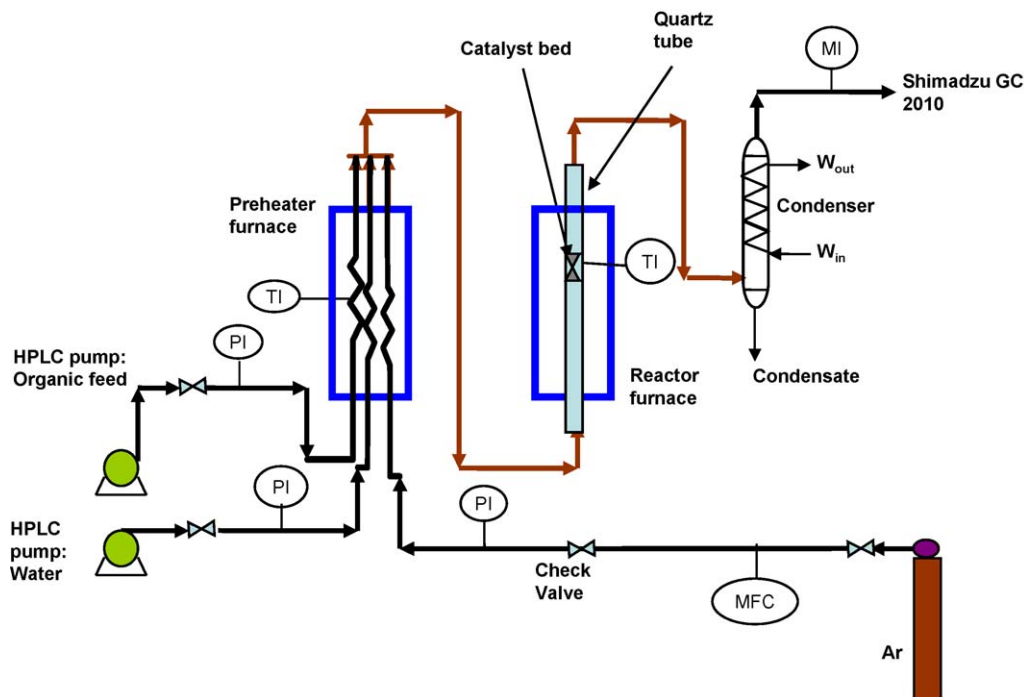


Fig. 1. Schematic of the experimental set-up used for steam reforming.

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