Bimetallic Ni-Rh catalysts with low amounts of Rh for the steam and autothermal reforming of *n*-butane for fuel cell applications☆

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A B S T R A C T

Mono-metallic nickel and rhodium catalysts and bimetallic Ni-Rh catalysts supported on La-Al_2O_3, $CeZrO_2$ and $CeMgO_x$ were prepared and evaluated for catalyzing the steam and autothermal reforming of *n*-butane. The binary Ni-Rh supported on La-Al_2O_3 catalysts with low weight loading of rhodium exhibited higher H_2 yields than Ni or Rh alone. The Ni-Rh/$CeZrO_2$ catalyst exhibited higher performance and no coke formation, compared to the same metals on other supports. A $NiAl_2O_4$ spinel phase was obtained on all Ni and Ni-Rh catalysts supported on La-Al_2O_3. The presence of rhodium stabilized the spinel phase as well as NiO_x species upon reforming while Ni alone was mostly reduced into metallic species. Extended X-ray absorption fine-structure analysis showed evidence of Ni-Rh alloy during preparation and even further after an accelerated aging at 900 °C in a H_2/H_2O atmosphere.

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1. Introduction

New fuel processing technologies are being developed to reform infrastructure fuels such as natural gas and liquefied petroleum gas (LPG) to provide H_2 at the point of application for use with fuel cell systems for distributed power generation. In these technologies, the selection and development of a catalyst for the fuel reforming is an important problem. In the industrial production of H_2, nickel catalysts are preferred over precious metal (Rh, Pt, Pd) catalysts for cost reasons, despite the lower stability. For use in distributed fuel processor–fuel cell systems, however, nickel catalysts are unsuitable due to excessive carbon buildup, as well as due to the tendency to sinter and to form inactive oxidized nickel during shutdown, startup, and turndown cycling [1]. Most R&D efforts to develop new reforming catalysts for these systems have focused on precious metals, primarily Rh, Pt, or Pd, which exhibit higher reforming rates than Ni. Furthermore, the precious metal catalysts are less prone to deactivate due to coke formation, sulfur poisoning, and interactions with the oxide support. Since precious metals

are expensive, the efforts focus on the addition of small amounts of such metals to nickel-based materials, which may result in a catalyst that provides sufficiently high activity and low coke formation with only a little added cost. Particularly, Ni-Rh catalysts have been reported to have high activity for steam reforming of jet fuel [2] and ethanol [3], as well as for partial oxidation [4], carbon dioxide reforming [5] and autothermal reforming of methane [6].

The choice of the support for these materials is limited because of the high temperature and the presence of steam. The most widely used support for reforming nickel catalysts is modified alumina [7]. The addition of La to Ni/Al_2O_3 has been shown beneficial for the carbon dioxide reforming of methane due to an increase in the nickel metallic dispersion and a lower coke formation [8]. It was also shown that ceria, and particularly ceria-zirconia, are more promising supports for nickel catalysts as compared to alumina-based supports [9]. In a recent combinatorial study with more than 5000 diverse oxides for the reforming of methane, $NiCeZrO_x$ demonstrated superior activity and stability among non-precious metal catalysts [10].

In the present work, we are investigating bimetallic formulations of nickel and rhodium as a means of limiting the rhodium loading compared with that of rhodium-only precious metal catalysts, without sacrificing the desirable performance characteristics of the latter. The objectives of this research were (1) to investigate

whether synergistic effects occur between nickel and rhodium for both the steam and autothermal reforming of *n*-butane, and (2) to determine if reducible supports, such as $Ce_{0.42}Zr_{0.58}O_2$ or $CeMgO_x$, are better at promoting the gasification of carbon (which would otherwise be deposited in the catalyst bed as coke) than refractory supports, such as $La-Al_2O_3$. X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure (EXAFS) spectroscopy were used to determine the nature of the interaction between nickel and rhodium before and after reforming and accelerated aging. We also investigated the reduction behavior by means of temperature-programmed reduction (TPR). Scanning electronic microscopy (SEM) was used to determine the extent and type of coke formed on the catalyst, if any, after reaction.

2. Experimental

2.1. Preparation of catalysts

Rhodium and nickel were deposited on selected oxide supports using the incipient wetness technique. A sufficient amount of a solution containing rhodium nitrate ($Rh(NO_3)_3 \cdot 2H_2O$, Alfa Aesar, Johnson Matthey Co., 31.36 wt% purity) and/or nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Aldrich Chemical Company Inc., 99.999%) was added to $La-Al_2O_3$ (3.1 wt% La, HIQ X-160, 160 m^2/g, Alcoa World Alumina), $Ce_{0.42}Zr_{0.58}O_2$ (Rhodia), or $CeMgO_x$ (prepared by co-precipitation of cerium and magnesium carbonate). The samples were then dried overnight at 100 °C and calcined by heating from room temperature to 700 °C at a rate of 5 °C/min and then holding at 700 °C for 1 h. The catalyst after calcination is referred to as "fresh". The catalyst samples used in this study are labeled as following: metal (Ni, Rh) composition (wt%) support (LA for $La-Al_2O_3$, CZ for $Ce_{0.42}Zr_{0.58}O_2$ and CM for $CeMgO_x$). For instance, 9.83 wt% Ni–0.17 wt% $Rh/La-Al_2O_3$ is labeled Ni9.83Rh0.17LA.

2.2. Catalyst activity studies

The activity and stability of the catalysts for steam and autothermal reforming of *n*-butane (99.5% Linde Gas) were investigated using a microreactor apparatus, which consisted of a 12.7 mm-OD stainless steel tube heated by a temperature-programmed furnace. For these studies, 0.6 g samples (~1 cm^3) of the catalyst, sieved to −20/+40 mesh, were used. The samples were reduced in 4%H_2/He at 700 °C for 1 h, prior to any catalytic tests. For the steam reforming experiments, the *n*-butane and nitrogen feed rates were 38 and 357 mL/min (STP), respectively, and the liquid water feed rate was 0.34 mL/min, providing a steam-to-carbon (H_2O:C) ratio of 3.0 and a gas hourly space velocity (GHSV) of 51,000 h^{-1}. For the autothermal reforming experiments, the *n*-butane feed rate was also 38 mL/min, the air feed rate was 357 mL/min (STP), and the liquid water feed rate was 0.22 mL/min, providing an H_2O:C of 2.0, an O_2:C ratio of 0.50, and a gas hourly space velocity (GHSV) of 42,000 h^{-1}. The temperature profile in the catalyst bed was measured using an Omega K-type multiprobe thermocouple with the probes separated by 6.35 mm. Samples of the product gas were analyzed for H_2, CO, CO_2, and C_1–C_8 hydrocarbons using a gas chromatograph (Hewlett Packard Model 6890, customized by Wasson) equipped with a mass spectrometer.

2.3. Aging

To simulate the effect of catalyst aging in use, a hydrothermal treatment was used. Freshly prepared samples of the catalysts were exposed to a flowing gas mixture of 33% H_2, 17% steam and 50% He at 900 °C for 100 h. This treatment was meant to simulate accelerated aging of the catalyst under conditions representative of what

the catalyst would experience during steam reforming (i.e., high temperatures and humid, reducing atmospheres) [11].

2.4. Characterization

Temperature-programmed reduction (TPR) studies were conducted using a commercial catalyst characterization system (Zeton Altamira, Model AMI-100), equipped with a thermal conductivity detector (TCD), with a continuous flow of 25 mL/min of 3% H_2 in Ar at a heating rate of 5 °C/min from room temperature to 800 °C. The amount of sample used for each measurement was ~100 mg. Prior to TPR, the samples were flushed with He at 200 °C to remove any moisture and adsorbed gases.

X-ray absorption spectroscopy was conducted at the Advanced Photon Source at Argonne National Laboratory (ANL). Catalyst samples were pressed into thin self-supporting wafers, 4 mm diameter, and mounted in a cylindrical steel holder designed to hold six samples for parallel treatment and measurement. The amount of catalyst used to press the wafer was chosen to optimize the edge step vs support absorbance. For the Rh *K*-edge the samples consisted of about 60 mg of powder. EXAFS spectra of the samples were obtained at the Rh *K*-edge (23,220 eV) and the Ni *K*-edge (8333 eV), with data points integrated over 1 eV (Rh) and 0.35 eV (Ni) for 0.05 to 0.10 s per data point. The XANES data were recorded during heating of the samples in 4% H_2 in He from room temperature to 800 °C at a heating rate of 2 °C/min. The EXAFS data were recorded at room temperature. Prior to EXAFS measurements, the samples were reduced in a flowing gas mixture consisting of 4% H_2 in He at either 200 or 750 °C temperatures for 30 min and then cooled to room temperature. The reason for the reduction step was to reduce the samples for a better determination of the Rh-Rh coordination number. All spectra were recorded in the transmission mode using a cryogenically cooled double-crystal Si (1 1 1) monochromator with a platinum-coated mirror for Rh *K*-edge and a rhodium-coated mirror for Ni *K*-edge to minimize the presence of harmonics. Rhodium and nickel foils were used for energy calibration. The data were analyzed using the following software programs: *ATHENA* to remove the background and to fit the XANES data, *FEFF version 8.28* to model the EXAFS data, and *ARTEMIS* to fit the EXAFS function [12,13]. For each spectrum, the Fourier transforms of k^2-weighted EXAFS oscillations were obtained using a Hanning-type window in the interval $k = 3$–15 $Å^{-1}$. XANES references were obtained from standard compounds: Rh^0, Rh_2O_3, RhO_2, Ni^0, NiO, NiO_2, Ni_2O_3 and $NiAl_2O_4$. The calculations from FEFF for the EXAFS functions for Rh-Rh and Rh-O were calibrated to Rh foil and Rh_2O_3, respectively. Self-consistent fields were used and an additional 1.5 eV of broadening was included; these two steps greatly improved the fit quality. The *R*-factors reported in Tables 1 and 2 are a measure of the goodness of fit defined as the magnitude of the difference between the fit (or theory) and the data and scaled by the magnitude of the data. For the EXAFS fits in Table 2, an *R*-factor smaller than 2% typically indicates a good fit. For the XANES linear combination fit (Table 1), we established that an *R*-factor larger than 0.1% indicates a poor fit (for the XANES fit an acceptable *R*-factor depends on the absorption edge and the fit range).

A Hitachi S-4700-II field emission scanning electron microscope (SEM) was used at the Electron Microscopy Center in the Material Science Division at Argonne.

3. Results and discussion

3.1. Temperature-programmed reduction

Temperature-programmed reduction of fresh samples of Ni, Ni-Rh, and Rh supported on $La-Al_2O_3$ was performed and the TCD