Sn-modified Ni catalysts for aqueous-phase reforming: Characterization and deactivation studies

J.W. Shabaker, D.A. Simonetti, R.D. Cortright, J.A. Dumesic *

Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI 53706, USA

Received 19 August 2004; revised 6 January 2005; accepted 16 January 2005
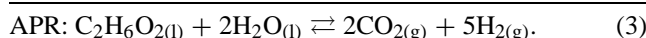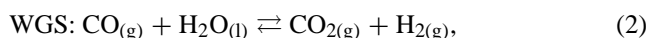
Abstract

The catalytic deactivation of R-NiSn catalysts was explored during hydrogen production by aqueous-phase reforming (APR) of ethylene glycol. X-ray photoelectron spectroscopy and CO and H_2 adsorption microcalorimetry were combined with previous characterization to show that R-NiSn catalysts are composed of a Ni core surrounded by a Ni_3Sn alloy after heat treatments above 533 K. Adsorption studies (CO, H_2, and N_2), XPS, X-ray diffraction, and thermogravimetric analysis show that R-Ni_{15}Sn catalysts deactivate by interaction with water under APR reaction conditions, rather than coking or $Ni(CO)_4$ formation. Over the first 48 h on stream, deactivation proceeds rapidly by the sintering of small Ni particles and by the formation of NiSn surface alloys with lower catalytic activity and higher selectivity for the production of hydrogen by APR of dilute feed solutions. After several days on stream, R-Ni_{15}Sn catalysts deactivate at a slower rate because of oxidation and dissolution by water, leading to Ni effluent concentrations near 50 wppm after 240 h on stream. The first-order deactivation constant can be improved from $k_d = 0.0020$ h^{-1} to less than 0.0001 h^{-1} between 140 and 240 h on stream with the use of rigorous heat treatments at 623 K in H_2 to form resilient NiSn alloys prior to reaction and/or with the use of energy-efficient stoichiometric feeds (water/ethylene glycol = 2).
© 2005 Elsevier Inc. All rights reserved.

Keywords: Ethylene glycol; Reforming; Hydrogen production; Nickel–tin catalysts; Microcalorimetry; XPS; Catalyst deactivation

1. Introduction

The production of hydrogen is a major limitation in the widespread use of fuel cells for the generation of electricity. Aqueous-phase reforming (APR) produces hydrogen in a single liquid-phase reactor at temperatures near 500 K. This process can use low-cost, renewable oxygenated hydrocarbons derived from biomass (e.g., sorbitol, glycerol, ethylene glycol) that are environmentally benign [1–3]. The APR reaction proceeds through a carbon monoxide intermediate:

Reforming: $C_2H_6O_{2(l)} \rightleftarrows 2CO_{(g)} + 3H_{2(g)}$, (1)

WGS: $CO_{(g)} + H_2O_{(l)} \rightleftarrows CO_{2(g)} + H_{2(g)}$, (2)

APR: $C_2H_6O_{2(l)} + 2H_2O_{(l)} \rightleftarrows 2CO_{2(g)} + 5H_{2(g)}$. (3)

Early work proved that high activity, selectivity, and stability for hydrogen production could be achieved with Pt-based catalysts [4–6]. Further studies have detailed the development of inexpensive Sn-promoted Raney Ni catalysts with similar activity and selectivity for aqueous-phase reforming of oxygenated hydrocarbons as Pt/Al_2O_3 [7–9]. Although these Raney Ni-based catalysts deactivate much more slowly than supported Ni catalysts, which have been shown to sinter rapidly under APR process conditions [8], they partially deactivate over a period of days during the aqueous-phase reforming of dilute solutions of oxygenated hydrocarbons at temperatures near 500 K. In addition to sintering in the aqueous environment, Ni-based catalysts are vulnerable to oxidation (by dissolved oxygen or water) and metal loss by leaching into the reactor effluent. Finally, Ni-based catalysts are vulnerable to strong interactions with feed molecules and reaction intermediates of the APR process that may lead to catalyst deactivation by coking.

In this paper we report the results of characterization of R-NiSn catalysts by X-ray photoelectron spectroscopy (XPS), adsorption studies, and thermogravimetric analysis (TGA) to assess the state of the fresh and spent catalysts. We then present the results of long-term catalytic stability tests to quantify the deactivation of R-NiSn catalysts and suggest process conditions that stabilize their performance considerably during aqueous-phase reforming.

2. Experimental

2.1. Catalyst preparation

We prepared Raney Ni–Sn (R-Ni$_x$Sn) catalysts by reducing Raney Ni 2800 (R-Ni) (Grace Davison) at 533 K for 2 h (heating at 0.5 K min^{-1}) in flowing H$_2$, adding appropriate amounts of a 9.4 wt% Sn (tributyltin acetate) solution in ethanol to reduced R-Ni under a N$_2$ atmosphere, and subsequently heating the mixture in a sealed Parr acid digestion bomb to 423 K for 2 h (heating at 0.5 K min^{-1}). The catalysts were then washed and stored under de-ionized water. Before characterization or collection of reaction kinetics data, all catalysts were reduced in flowing H$_2$ (100 cm^3(STP) min^{-1}) for 2 h at 533 K, unless noted otherwise. We passivated some catalysts for characterization by flowing 2% O$_2$/He mixtures at 300 K. The composition of each fresh catalyst was verified by atomic absorption spectroscopy (AAS/ICP) after digestion in acids.

2.2. Reaction kinetics measurements

Reaction kinetics measurements were performed to quantify catalyst deactivation with a reactor system described elsewhere [5]. The Raney catalysts were loaded without sieving (particle diameters are 45–90 μm) or pelletizing to operate in the kinetic regime [5]. De-aerated aqueous solutions containing 5–63 wt% ethylene glycol were fed to the reactor at a flow rate of 0.08 cm^3 min^{-1}. Reaction kinetics measurements were made at temperature of 483 K and system pressures near the bubble-point of the feed solution. Each reaction condition was maintained for at least 6 h to ensure that steady state had been achieved, as determined by online gas chromatography. The liquid-phase effluent from the reactor was collected during reaction kinetics measurements, and this liquid was analyzed via gas chromatography (FID detector), total organic carbon (TOC), and atomic absorption (AAS/ICP) measurements. The "normalized CO$_2$ activity" (current CO$_2$ production rate/initial CO$_2$ production rate) was used to assess catalyst stability.

2.3. Catalyst characterization

Freshly reduced catalysts were characterized by N$_2$ adsorption at 77 K (BET method) and the irreversible extent of CO adsorption at 300 K. Spent catalysts were similarly characterized by adsorption studies after drying in air at 300 K (after runs with 5 wt% ethylene glycol feed solutions) or at 373 K (after runs with 63 wt% ethylene glycol feed solutions) and subsequent reduction at 523 K for 2 h (0.5 K min^{-1}). X-ray diffraction studies were conducted with a Cu-K$_\alpha$ source and a Scintag PADV diffractometer operating at 40.0 mA and 35.0 kV. The Scherrer equation was used to estimate the Ni crystal size. Fresh catalysts were reduced and passivated in flowing 2% O$_2$/He before XRD, and spent catalysts were dried under air as described above.

The procedure for microcalorimetry has been described in detail elsewhere [10]. Briefly, passivated R-NiSn catalysts were reduced for 2 h at 523 K in a quartz flow cell under H$_2$ (200 cm^3(STP) min^{-1}, ultrahigh purity) after heating at 1.3 K min^{-1}. The cell was then sealed and evacuated for 5 min before introduction of flowing He (200 cm^3(STP) min^{-1}, ultrahigh purity). The cell was then purged with He for 1 h at 523 K before the sample was torch-sealed inside a Pyrex NMR tube for transport to the microcalorimeter. Microcalorimetry of CO and H$_2$ adsorption was performed at 300 K on separate samples of each catalyst with a Setaram BT2.15D heat-flux calorimeter.

Before we collected XPS spectra, samples were treated in a high-vacuum pretreatment cell. Samples were dropped onto Ta sample plates in slurry form. Each sample plate was manually loaded onto a heater stage in a pretreatment cell and dried there under flowing H$_2$ or N$_2$ for 2 h at 333 K. Once dry, most samples were treated at elevated temperature in flowing H$_2$ (100 cm^3(STP) min^{-1}, ultrahigh purity). The pretreatment cell was then evacuated to < 0.3 Torr with a dry diaphragm pump, and the reduced or oxidized sample was transferred into a UHV system with a base pressure below 10^{-10} Torr via a turbopump-evacuated load-lock without exposure to air. The XPS system irradiated the sample with a 400-W Mg (K$_\alpha$) X-ray gun, and photoelectrons were collected with an Omicron EA 125 Channeltron energy analyzer. The spectrometer was calibrated to the Ag 4s$^{1/2}$ line at a binding energy of 97.0 eV. Surface compositions were measured with the use of the Ni 2p^3, Sn 3d^5, C 1s, O 1s, and Al 2p peak areas and sensitivities published elsewhere [11].

Thermogravimetric analysis was accomplished with a Netzsch TG 209 apparatus. Approximately 20 mg of each catalyst was loaded into an Al sample boat and placed on the balance. The sample zone was then sealed and purged with N$_2$ (40 cm^3(STP) min^{-1}) for 30 min before it was heated to 493 K (10 K min^{-1}) and held for 1 h. The dried sample was then heated to 823 K (10 K min^{-1}) and held for 10 min. After cooling to 278 K under flowing N$_2$, the flowing gas was switched to air (40 cm^3(STP) min^{-1}) and allowed to purge for 30 min. The sample was then heated directly to 823 K (10 K min^{-1}) in air and held for 10 min.