



Toward stable nickel catalysts for aqueous phase reforming of biomass-derived feedstock under reducing and alkaline conditions



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ABSTRACT

Nickel nanoparticles supported on carbon nanofibers (CNF) can be stabilized in aqueous phase processes at elevated temperatures and pressures by tuning the reaction conditions to control Ni oxidation and leaching. As a showcase, Ni/CNF was used for the production of hydrogen via aqueous phase reforming of ethylene glycol (EG). Under standard conditions ($T = 230$ °C, inert atmosphere, 1 wt.% EG), extensive catalyst deactivation occurred as a result of Ni particle growth. The extent of Ni particle growth was diminished either by using a more reducing environment by introducing additional H_2 into the reactor or by increasing the concentration of reactant. Deactivation of the Ni/CNF catalyst due to particle growth was almost completely prevented by addition of KOH to the reaction mixture. Stable H_2 production was achieved with high hydrogen selectivity (99%) during 50 h on stream by addition of KOH, while without KOH the catalyst lost 93% of its initial activity and the H_2 selectivity was lower (90%). The increased stability of Ni particles under both alkaline and reducing conditions is ascribed to the suppression of Ni leaching, which prevented subsequent particle growth via Ostwald ripening.

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1. Introduction

Environmental concerns and the diminishing fossil fuels supply have resulted in considerable research effort into the potential of biomass as a sustainable feedstock for the production of chemicals and fuels [1–6]. Catalytic reactions in the aqueous phase at elevated temperature and pressure, i.e., hydrothermal processes, are expected to play a key role in the sustainable conversion of biomass and biomass-derived feedstocks to chemicals and fuels [7]. Various catalytic processes such as hydrothermal gasification [8], hydrogenolysis [9], and aqueous phase reforming (APR) [10] have been proposed. Ni is a promising catalyst for these processes but exhibits poor stability under hydrothermal conditions, compared to the more expensive noble metal catalysts [11]. For example, Shabaker et al. [12] investigated Ni supported on Al_2O_3 , SiO_2 , or ZrO_2 for APR and showed that these catalysts lose about 90% of their initial activity within 2 days. Hence, improving the stability of non-noble-metal catalysts is an important issue in the field of biomass conversion and aqueous phase catalysis in particular.

Carbonaceous support materials such as activated carbon, carbon nanofibers (CNF) [13,14], and mesoporous carbon [15] are

stable under hydrothermal conditions and are therefore often preferred over conventional metal oxide supports. The use of carbon-coated metal oxide materials as supports has been explored as well [16]. Besides issues with the stability of the support, a major deactivation route for nanostructured catalysts is the loss of active (metal) surface area as a result of metal particle growth. The resulting loss of active surface area is detrimental to the productivity of the catalysts and thus will impede the application of Ni catalysts under hydrothermal conditions.

Strategies for the stabilization of supported metal nanoparticles with respect to sintering (particle growth due to particle migration and coalescence) generally involve careful control over catalyst properties such as metal–support interaction [17], particle size [18], particle location and spacing on the support [19], and particle confinement [20–23]. These strategies are applied with some success to catalysts designed for gas phase reactions. However, stabilizing the active Ni nanoparticles in the liquid phase is more cumbersome, since in the liquid phase, particle growth can proceed rapidly via Ostwald ripening (particle coarsening) [24]. Prevention of particle growth by Ostwald ripening is challenging for metals that, like Ni, may lead to substantial amounts of dissolved species in the aqueous phase. These species can be formed via (surface) oxidation and subsequent metal oxide dissolution (leaching). The driving force for the Ostwald ripening process is the reduction of the specific surface free energy, which is lower for larger particles.

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The presence of molecular or ionic dissolved species enables particle growth by mass transfer over a concentration gradient from smaller to larger particles. Additionally, in continuous processing this will lead not only to loss of active surface area due to particle growth but also to loss of the active metal via leaching and transport out of the reactor.

We showed previously that metal particle growth is the main deactivation mechanism for a Ni/CNF catalyst during aqueous phase reforming [11]. Now we report our successful attempts at stabilizing supported Ni nanoparticles under aqueous conditions, using aqueous phase reforming of ethylene glycol as a showcase, by tuning the reaction conditions. Gas phase atmosphere, reactant concentration, and pH are the key parameters investigated in this study. We will show that alkaline conditions effectively stabilize the Ni nanoparticles, resulting in stable catalytic performance, while at the same time increasing the activity and selectivity of the catalyst. The relation between catalyst stability and reaction conditions will be discussed.

2. Materials and methods

2.1. Catalyst synthesis

Carbon nanofibers were grown using a Ni/SiO₂ growth catalyst and syngas as the carbon source, as described elsewhere [25]. For the preparation of Ni/CNF, typically 4 g of surface-oxidized carbon nanofibers (sieve fraction 90–150 μm) were dried under vacuum at 80 °C for 2 h. After cooling to room temperature, the support was impregnated with 2.4 ml of a 5 M aqueous Ni(NO₃)₂·6H₂O (Acros 99%) precursor solution. This resulted in catalysts with a nominal Ni loading of 12.5 wt.%, which was verified by carbon burn-off experiments using thermogravimetric analysis (TGA).

The impregnated samples were then dried overnight at 120 °C. Next the samples were reduced for 2 h at 300 °C (heating ramp 5 °C/min) in a flow of 30 (v/v)% H₂/N₂ (100 ml/min). After reduction, the reactor was cooled to room temperature. To passivate the catalysts, prior to the characterization, air was allowed to diffuse into the reactor through a 26-cm-long tube with a 3-mm inner diameter.

2.2. Characterization

X-ray powder diffraction (XRD) was carried out using a Bruker-AXS D2 Phaser powder X-ray diffractometer with CoKα_{1,2} radiation (λ = 1.79026 Å) between 2θ 20° and 120°. The experimental data were fitted with a pseudo-Voigt function using a linear combination of the support (CNF) and metal contributions and a correction for instrumental broadening. Crystallite sizes were estimated from the Scherrer equation using a shape factor of 0.89.

Hydrogen chemisorption was performed on a Micromeritics ASAP 2020C instrument. Between 100 and 400 mg of catalyst was placed between quartz wool plugs in a quartz tube. The catalysts were reduced in H₂ (60 ml/min) at 300 °C for 2 h, after which the system was outgassed (*P* < 10⁻⁵ bar) at that temperature for 2 h. Subsequently the system was cooled to 150 °C and outgassed for another 0.5 h before the measurement was started. The monolayer H₂ uptake was found by extrapolating the linear part of the isotherm (150–600 mbar) to zero pressure. Particle sizes were calculated using the monolayer uptake, assuming complete reduction and a stoichiometry of 1 hydrogen atom per metal surface atom.

Transmission electron microscopy (TEM) analysis was carried out on an FEI Technai20F operated at 200 keV. The samples were ground to a fine powder in a mortar and a small amount of powder was supported on a thin carbon film on a copper grid.

Atomic absorption spectroscopy (AAS) was performed on an Analytik Jena ContrAA 700. The amount of leached metal was

measured in liquid samples taken after each reaction. These samples were filtered over a 0.45-μm syringe filter (Millipore), after which the pH of the filtrate was adjusted to 3 with sulfuric acid.

2.3. Catalyst testing

The Ni/CNF catalysts (sieve fraction 90–150 μm) were tested in the aqueous phase reforming of ethylene glycol (EG, degassed, 1–50 wt.%, 6 h, 230 °C). Batch reactors (10 ml) were used to study the effect of the nature and concentration of base additives (0–0.8 M) on the stability of the Ni particles. The reactors were filled with 100 mg of reduced catalyst, base additive, and the reactant solution (5 ml) in a glove box under N₂. The reactors were heated in an oil bath and stirred with a magnetic spinner at 1000 rpm under autogenous pressure (i.e., the saturation pressure of water and the pressure of the produced gases).

The effect of the initial gas phase composition on catalytic performance was investigated using an Autoclave Engineers 100-ml batch EZE seal batch autoclave equipped with a liquid sampling port. The passivated catalyst (2 g) was loaded into the reactor and activated in situ in flowing H₂ (50 ml/min) at 300 °C. After cooling down, the reactor was flushed and pressurized to 6 bar with H₂ or Ar and the reactant was introduced via a charge vessel. After the reactor was heated to 230 °C (12 °C/min), the stirring (1000 rpm) was started. The reactor was operated under autogenous pressure, which was monitored using a pressure transducer (Setra C206). The temperature was monitored using a K-type thermocouple placed in a thermowell. An example of the pressure and temperature profile is shown in Fig. S1. Liquid samples were taken to determine the EG concentration and monitor the formation of liquid phase products (methanol, ethanol, glycolic aldehyde, and glycolic acid) over time. The conversion was calculated based on the decrease in EG concentration (constant-volume approximation).

Catalyst activity and stability with time on stream (TOS) were measured in a fixed-bed continuous-flow reactor operated at 230 °C. The passivated catalyst (100 mg) was loaded into the reactor (stainless steel tube with inner diameter 4 mm) and SiC was used to minimize the reactor void volume. Blank experiments showed that the SiC and the reactor material had negligible activity. Prior to the catalytic experiment, the catalysts were activated at 300 °C for 1 h in a flow (30 ml/min) of 33% H₂/N₂, after which the system was thoroughly flushed with N₂. The degassed reactant solutions (10 wt.% EG, optionally with 0.5 M KOH) were introduced in upflow configuration using a syringe pump (ISCO Teledyne) at a flow rate of 3 ml/h. The corresponding WHSV was 3 g EG⁻¹ g cat⁻¹ h⁻¹. The reactor effluent was fed together with Ar sweep gas to a gas–liquid separator vessel. The system pressure was controlled at 29 bar using a back-pressure regulator.

As a result of carbon capture by the addition of base, the amount of CO₂ found in the gas phase was not representative of the amount of CO₂ produced in the process. Hence it was not possible to define selectivity to H₂ based on the amount of carbon detected in the gas phase and the reforming ratio (H₂/CO₂ ratio according to the reaction stoichiometry), as is normally done when studying APR. Therefore H₂ gas phase selectivities (*S*_{H₂}) were expressed based on the molar concentration of hydrogen in the gas phase relative to the total moles of hydrogen detected in the gas phase including the hydrocarbons CH₄, C₂H₆ and C₃H₈:

$$S_{H_2} = \frac{[H_2]}{[H_2] + 2[CH_4] + 3[C_2H_6] + 4[C_3H_8]} \times 100\%$$

Turnover frequencies (TOFs) were calculated based on the moles of H₂ and CH₄ produced and normalized by the number of nickel surface sites of the fresh catalyst as measured by H₂ chemisorption.

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