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



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T. van Haasterecht^a, C.C.I. Ludding^a, K.P. de Jong^a, J.H. Bitter^{a,b,*}

^a Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Universiteitsweg 99, 3584CE Utrecht, The Netherlands ^b Department of Biobased Chemistry and Technology, Wageningen University, Wageningen, The Netherlands

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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 H₂ 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 H₂ 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 H₂ 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 Al₂O₃, SiO₂, or ZrO₂ 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

* Corresponding author. Current address: Biobased Commodity Chemistry, Wageningen UR, Bornse Weilanden 9, 6708WG Wageningen, The Netherlands. *E-mail address*: Harry.Bitter@wur.nl (J.H. Bitter). stable under hydrothermal conditions and are therefore often preferred over conventional metal oxide supports. The use of carboncoated 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.



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 μ m) 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 CoK α 1,2 radiation (λ = 1.79026 Å) between 2 θ 20° and 120°. The experimental data were fitted with a pseudo-Voight 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 Micromeretics 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- μ m 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 $90-150 \ \mu m$) 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 CO_2 found in the gas phase was not representative of the amount of CO_2 produced in the process. Hence it was not possible to define selectivity to H_2 based on the amount of carbon detected in the gas phase and the reforming ratio (H_2/CO_2 ratio according to the reaction stoichiometry), as is normally done when studying APR. Therefore H_2 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 CH_4 , C_2H_6 and C_3H_8 :

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

Turnover frequencies (TOFs) were calculated based on the moles of H_2 and CH_4 produced and normalized by the number of nickel surface sites of the fresh catalyst as measured by H_2 chemisorption.

3. Results and discussion

3.1. Effect of the reaction conditions on the nickel particle size

The effect of the reaction conditions on the stability of the Ni/ CNF catalyst with respect to the Ni particle size was investigated for the APR of ethylene glycol (1–50 wt.% EG) at 230 °C. The reactions were initially carried out in a batch-stirred autoclave under either H₂ or an inert gas phase for 6 h and with KOH concentrations between 0 and 1.2 M.

3.1.1. Effect of gas atmosphere

The influence of the gas atmosphere (hydrogen versus argon) on the Ni/CNF catalyst during the reforming of 1 wt.% EG was investigated using XRD, TEM, and hydrogen chemisorption. The properties of the parent and spent catalysts are summarized in Table 1 (entries 1-3). We first discuss the results obtained from XRD analysis (Fig. 1). The parent catalyst showed diffraction lines at 52.1° and $60.9^{\circ} 2\theta$, corresponding to Ni (111) and Ni (200), respectively. In addition a broad contribution around $43^{\circ} 2\theta$, representing NiO, was observed as a consequence of the passivation treatment prior to the XRD analysis. After APR under inert atmosphere, which is the standard APR condition, a clear increase in Ni peak intensity and a narrowing of the Ni peak were observed in the spent samples. No evidence of an oxidic Ni phase was found for the spent samples. Since these samples were also exposed to air before measurement, this suggests either that the passivation layer was amorphous or that the amount of NiO was below the detection limit. The sizes of the metallic Ni crystallites of the parent and spent catalysts were calculated from line broadening analysis using the Scherrer equation. The crystallite size increased from 8 nm for the parent sample to 58 nm for the spent sample under the standard APR conditions. When the reaction was performed with an H₂ atmosphere of 6 bar, the Ni crystallite size increased to 36 nm, which is considerably less than for the sample tested under inert atmosphere. Increasing the H₂ pressure further to 20 bar resulted in a Ni crystallite size of 34 nm (entry 4), showing that a further increase in H₂ pressure only has a minimal effect on nickel particle growth.

We also investigated the available Ni surface sites of the parent and spent catalysts using H_2 chemisorption. Table 1 lists the total

Table 1

Effect of reaction conditions on properties of Ni/CNF catalysts (230 °C, 6 h).



Fig. 1. XRD profiles for parent and spent Ni/CNF catalysts after aqueous phase reforming of EG under different gas atmospheres (H_2 or Ar) and in the presence or absence of KOH (1 wt.% EG, KOH/EG molar ratio of 0.3, 230 °C for 6 h). The insert shows the deconvolution of the CNF and Ni contributions for spent Ni/CNF with KOH and Ar atmosphere.

amount (M_t) of chemisorbed hydrogen (also referred to as the saturation or monolayer amount) and the corresponding Ni particle size assuming spherical particles and an adsorption stoichiometry of Ni/H = 1.

The parent sample showed a total hydrogen uptake of 181 μ mol/g. After reaction using standard APR, the hydrogen uptake decreased to 17 μ mol/g, which amounts to a 91% loss of Ni surface sites. When the reaction was performed under an initial H₂ atmosphere, the H₂ capacity of the spent catalyst decreased to 34 μ mol/g and the loss in Ni surface sites was thus reduced to 81%.

Table 1 shows that besides a reduction in total hydrogen chemisorption capacity (M_t), the irreversible hydrogen uptake (M_{irr}) also decreased for the spent catalysts. The irreversible hydrogen uptake represents the more strongly adsorbing sites [25]. Since smaller particles have a higher M_{irr}/M_t ratio as a result of stronger metal– H binding, the M_{irr}/M_t ratio serves as an additional indicator of

Entry	[EG] (wt.%)	Base	Molar ratio (base/EG)	Gas phase	pН	Leaching		$d_{\rm XRD}({\rm nm})$	Chemisorption			
						Mass loss (%) ^a	[Ni] (ppmw)		$d_{\rm C} ({\rm nm})^{\rm b}$	$M_{\rm t}$ (µmol/g)	$M_{\rm irr}$ (µmol/g)	$M_{\rm irr}/M_{\rm t}$
1	Parent							8	5.9	181	61	0.34
2	1	None	0	Ar	3.5	0.26	6.4	58	61	17	2.3	0.14
3	1	None	0	H ₂	3.8	0.15	3.8	36	32	34	7	0.21
4 ^c	1	None	0	H ₂	4.3	n.a.	n.a.	34	n.a	n.a	n.a	n.a
5	1	KOH	3.1	Ar	11.0	<0.01	<0.1	12	7.6	142	40	0.28
6	1	KOH	3.1	H ₂	10.8	<0.01	<0.1	10	6.9	151	50	0.33
7	1	NaOH	3.1	Ar	11.6	n.a.	n.a.	12	n.a	n.a	n.a	n.a
8	1	$Ca(OH)_2$	3.1	Ar	12.4	n.a.	n.a.	14	n.a	n.a	n.a	n.a
9	1	$Mg(OH)_2$	3.1	Ar	8.7	n.a.	n.a.	21	n.a	n.a	n.a	n.a
10	10	None	0	Ar	4.2	n.a.	n.a.	34	64	17	0.8	0.05
11	50	None	0	Ar	4.0	n.a.	n.a.	21	n.a	n.a	n.a	n.a
12	10	None	0	H ₂	3.6	0.28	7.1	28	29	43	11	0.26
13	20	None	0	H ₂	4.0	0.26	6.6	24	23	47	12	0.25
14	50	None	0	H ₂	3.9	0.06	1.6	17	13	84	36	0.42
15	10	KOH	0.31	Ar	10.2	n.a.	n.a.	13	8.1	133	56	0.42
16	10	КОН	0.31	H ₂	8.1	<0.01	<0.1	10	8.1	132	39	0.30
17	Ni powder							-	3×10^3	3	<0.1	<0.01

n.a = not available.

^a Amount of Ni detected in the solution (100 ml) expressed as a percentage of the total amount of Ni (250 mg).

^b Average particle size calculated from the total H₂ uptake obtained from extrapolating the linear part of the total adsorption isotherm (100–600 mbar) to zero pressure and assuming hemispherical particle geometry and an H/Ni ratio of 1.

^c Initial H₂ pressure of 20 bars.

Table 2Gas phase composition (excluding Ar) sampled after 6 h.

Entry	Conditions	Composition (%)					S _{H2} ^c	Pressure ^d	
	[EG] (wt.%)	Base ^c	H_2	CO_2	CH_4	CO	C ₂₊	(%)	(bar)
1 ^a	10	None	37	23	38	0.6	1.9	31	33.4
2 ^a	10	KOH	89	9.7	1.7	0	0.04	96	47.2
3 ^a	1	None	48	31	19	0	1.8	52	31.3
4 ^a	1	KOH	97	0	3.2	0	0	94	40.5
5 ^b	1	KOH	90	5.4	4.3	0	0	_	35.1

Conditions: 230 °C, 1–10 wt.% EG, and optionally 0.5 M KOH.

^a The reaction was performed under: inert (Ar) gas atmosphere.

 $^{\rm b}\,$ The reaction was performed under: reducing (H_2) gas atmosphere.

^c Hydrogen gas phase selectivity with respect to the formation of gas phase

alkanes.

^d Total system pressure after 6 h.

particle growth [26]. The parent catalyst had an $M_{\rm irr}/M_{\rm t}$ of 0.34, whereas a reference Ni powder sample (Table 2, entry 17) had a negligible fraction of irreversible sites ($M_{\rm irr}/M_{\rm t} < 0.01$). The spent catalysts both showed a significant decrease in the $M_{\rm irr}/M_{\rm t}$ ratio to 0.21 for a H₂ atmosphere and to 0.14 for an Ar atmosphere. This indicates that Ni particle growth is responsible for the decrease in H₂ chemisorption capacity. Results from both XRD and chemisorption thus show that during APR with Ni/CNF, significant particle growth occurred, which could be reduced by performing the reaction with an initial H₂ gas phase.

3.1.2. Effect of base addition

Fig. 1 further shows the effect of the addition of 0.5 M KOH (KOH/EG molar ratio of 0.3) to the reaction mixture on the XRD patterns of the spent catalysts. With the addition of KOH, in contrast to APR under standard conditions, only very limited narrowing of the Ni diffraction lines was observed for the spent catalysts, irrespective of whether the reaction was performed with an Ar or H₂ gas phase. The Scherrer crystallite sizes were comparable for Ar and H₂, respectively 12 and 10 nm (Table 1, entries 5 and 6). This is only slightly larger than for the parent catalyst, especially considering that the parent sample also has a 3 nm NiO contribution after the passivation treatment. This indicates that only very limited growth of the Ni particles occurred in the presence of KOH compared to the spent catalyst used in reactions without KOH.

The absence of extensive crystallite growth in spent catalysts treated with KOH based on the XRD study does not exclude the possibility that Ni particles grow into aggregates with multiple small crystallite domains. Therefore the spent catalysts were also characterized using TEM. Fig. 2 shows representative TEM micrographs for the parent catalyst and the spent catalysts after the reforming of 1% EG both with and without KOH addition. The parent catalyst (Fig. 2a) showed a Ni particle size distribution in the range of 2–20 nm with a number-average particle size of 8 nm. After APR in the presence of KOH (Fig. 2b), a similar size distribution was obtained for the spent catalyst with a negligible increase in the average size to 9 nm.

In contrast, in the absence of KOH, significant growth of Ni particles was observed with TEM. The small Ni particles present in the parent catalyst had disappeared and larger particles of 20–50 nm were observed (Fig. 2c). Additionally, in other areas of the sample, the formation of very large Ni clusters of up to 200 nm was observed (Fig. 2d). The particle size distribution of this sample was very broad and bimodal. This is in qualitative agreement with the result obtained from XRD, which revealed a large increase in the average crystallite size. To get a more accurate quantitative picture, we preformed further characterization with H₂ chemisorption.

The higher stability for the catalysts treated in the presence of KOH was also evident from the H_2 uptake, i.e., 142 µmol/g and 151 µmol/g for the catalysts used in an Ar or H_2 atmosphere,

respectively (Table 1, entries 5–6). The decrease in H₂ uptake for these spent catalysts compared to the parent catalyst (16% and 27%) was thus much lower than for the same reaction without KOH (81% and 91%). Furthermore, for these catalysts, the $M_{\rm irr}/M_{\rm t}$ ratio was significantly higher (0.28 and 0.33) and close to the ratio of the parent catalyst (0.34). The particle sizes calculated from the total H₂ uptake are given in Table 1 and agree well with the results from XRD.

We also investigated the effect of other bases on the Ni crystallite growth (Table 1, entries 7–9). The addition of NaOH and Ca(OH)₂ resulted in Ni particles of 12 and 14 nm, respectively. The effect of these bases on the crystallite growth was therefore comparable to that of KOH, suggesting that the increase in pH is the most important factor (i.e., the cation does not play an essential role). The addition of Mg(OH)₂, however, resulted in a spent catalyst with considerably larger Ni crystallites (21 nm). This might be attributed to the low solubility of Mg(OH)₂, which has a solubility constant lower than Ca(OH)₂ by a factor of 10^5 .

3.1.3. Effect of reactant concentration

Fig. 3 shows the influence of the EG concentration on the Ni crystallite sizes, as determined by XRD. The most severe growth of Ni crystallites was observed with the lowest EG concentration under inert atmosphere. With increasing EG concentration, the increase in Ni crystallite size after reaction was less significant and the beneficial effect of using H_2 versus Ar atmosphere becomes smaller. These results are confirmed by hydrogen chemisorption (Table 1 entries 10–14), which shows that H_2 uptake of the spent catalyst increased for higher EG concentrations.

In the presence of KOH, an increase in EG concentration from 1 to 10 wt.% did not significantly affect the Ni crystallite size or the H_2 uptake of the spent catalysts (Table 1, entries 15, 16).

3.1.4. Particle size, leaching, and pH

To provide a possible explanation for the effect of the different reaction conditions on the extent of particle growth, we now discuss the influence of the pH of the solutions in relation to the amount of leached Ni species.

The concentration and relative amounts of leached Ni are given in Table 1. We have previously shown that leaching of metals from the stainless steel vessel wall also occurred, but its contribution to the total amount of leached Ni is insignificant (< 0.1 ppmw) and the presence of dissolved Ni species can thus be attributed to Ni leaching from the catalyst [11]. Concentrations of up to 7.1 ppm of leached nickel were observed, which represents only 0.28% of the total amount of nickel in the catalyst. Therefore leaching itself does not directly contribute to catalyst deactivation, but can play a role in the Ostwald ripening process. The extent of nickel leaching differed for the various reaction conditions applied. APR of EG solutions under standard conditions (neutral pH) resulted in an acidic reaction mixture (pH 3.5) containing substantial amounts (6.4 ppmw) of leached Ni (Table 1, entry 2). With KOH concentrations of 0.5 M in the feed solutions (pH 13.6), leaching of Ni was inhibited (<0.1 ppmw), and alkaline reaction mixtures were obtained, with pH ranging from 8.1 to 11.0, depending on the initial EG concentration (entries 5 and 6 and 15 and 16). Thus after reaction the pH was substantially lower than that of the feed solutions. This is attributed to CO₂ formation during APR ($C_2H_6O_2 + H_2O \rightarrow CO_2 + H_2$) [10], which reacts to form carbonic acid $(CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-)$ and thus decreases the pH. In addition, carboxylic acids are known to be formed as side products [11]. In this study we detected the formation of glycolic acid in significant amounts, up to 2 mmol/L; see Table S1. With the addition of KOH, these acids are neutralized and CO₂ is captured in the form of potassium (bi)carbonate [27]. The capture of CO_2 is also evident from the absence of CO_2 in the gas phase when KOH is present (Table 2).



Fig. 2. TEM micrographs and corresponding particle size distributions of (a) parent Ni/CNF catalyst, (b) spent catalyst after reaction with KOH:EG 3.1, and (c and d) spent catalyst after reaction without KOH (230 °C, 6 h, 1 wt.% EG).



Fig. 3. Correlation between the initial EG concentration (1-50 wt.%) and the Ni crystallite size (XRD) of the spent catalyst for reaction at 230 °C for 6 h under initial Ar (\Box no KOH, \blacksquare 0.5 M KOH) and H₂ atmospheres (\bigcirc no KOH, \spadesuit 0.5 M KOH). Lines added to guide the eye.

The effect of the pH on the Ni particle growth was further investigated over a wide range of KOH concentrations (0-1.2 M) both in water and in EG solutions. Fig. 4 shows the correlation between the crystallite sizes of the spent catalysts and the final pH of the reaction solutions. The latter is representative of the pH during the reaction, as shown in Fig. S3. For aqueous solutions of EG and KOH, we observed that below approximately pH 8 increasingly large Ni crystallites were formed during reaction, whereas above this pH the crystallite size remained unchanged and was close to that of the parent catalyst. A similar observation was made for



Fig. 4. Correlation between the crystallite size of the spent catalysts and the pH of the final reaction mixture (lines added to guide the eye). The pH of the feed solutions was adjusted by addition of KOH (0–1.2 M) to aqueous solutions of 1 wt.% (\bigcirc) and 10 wt.% EG (\bullet) and to water (\blacksquare). Reactions were performed at 230 °C for 6 h under inert gas.

aqueous solutions of KOH (i.e., without EG); however, at very high pH (>13), we observed again an increase in the particle size. Since the pH was measured at room temperature, we acknowledge that the values are overestimated with respect to the pH at the reaction temperature (230 °C) due to the increase in self-ionization of water at higher temperatures (pK_w = 11.3 at 230 °C); however, this deviation is expected to be equal for all experiments.

The effect of the pH of the solution on the stability of the Ni nanoparticles is twofold, as it influences both the redox potential and the solubility of Ni species. Both these effects are traditionally visualized using Pourbaix (potential versus pH) diagrams. Beverskog et al. have calculated Pourbaix diagrams for the Ni–water system at elevated temperatures $(200–300 \,^{\circ}\text{C})$ and shown that at a pH below neutral, bulk Ni⁰ can be oxidized by water or acids [28]. In an acidic medium the oxidized Ni species dissolve and Ni²⁺ ions are predominantly formed [29]. This explains the leaching we observed during APR under standard conditions, which, as a result of reaction products, took place in an acidic medium.

At a pH above neutral, oxidation of bulk Ni is prevented because the redox potential of the $H^+/H_2(g)$ couple decreases with increasing pH (as follows from the Nernst equation, $E_{\rm h} = -0.1$ pH at 230 °C) [30] and falls below that of the Ni/Ni²⁺ couple. While oxidation and leaching of Ni are linked in acid media, this is not the case under alkaline conditions. Even though the bulk Ni phase is thermodynamically stable under alkaline conditions. surface oxidation can still occur. As a result of water dissociation, Ni-OH or Ni-O species form on the Ni surface or at low-coordination sites [31]. However, under alkaline conditions, oxidized nickel species are not soluble [28]. The prevention of Ni leaching is essential for the stability of the Ni nanoparticles because the formation of mobile Ni species is a prerequisite for Ostwald ripening, since they enable mass transfer from the smaller to the larger Ni particles. We observed that nickel particle growth occurred already at neutral pH, in contrast to what was expected from the previous discussion, and alkaline conditions were required (pH > 8) to stabilize our catalyst (Fig. 4). This is most likely because we used Ni nanoparticles, which can be oxidized more easily than the bulk phase [32,33], thus explaining the need for a higher pH than for the bulk phase. In very alkaline solutions (pH > 13), the formation of anionic soluble Ni species (e.g., Ni(OH) $_{3}^{-}$) becomes favorable [28], which can explain the increase in particle size observed at very high pH (Fig. 4).

Besides the pH, the partial hydrogen pressure also affects the oxidation and solubility of Ni. In acidic media, the extent of particle size growth was shown to be diminished with an H₂ gas atmosphere compared to that with an inert gas (Table 1, entries 2 and 3). Lower levels of Ni leaching were measured for reactions with 1 wt.% EG under H₂ versus Ar, 3.8 ppmw and 6.4 ppmw, respectively. As expected with the use of H₂ gas, the Ni-ion solubility (Ni(s) + 2H⁺ (aq) \leftrightarrow Ni²⁺(aq) + H₂(g)) was suppressed [34], resulting in a lower Ni crystallite growth rate.

Finally, the presence of organic species also plays an important role in the Ni particle growth mechanism. Fig. 4 shows that Ni crystallites are more stable in EG mixtures than in water. Also, without KOH, in acidic media, a decrease in the extent of particle growth was accomplished by increasing EG concentration from 1 to 50 wt.% (Table 1, entries 10–14). However a straightforward relation between the concentration of dissolved Ni species and the initial EG concentration was not observed. The amount of leached Ni increased from 3.8 for 1 wt.% EG to 7.1 and 6.6 ppmw for 10 and 20 wt.%, respectively, and decreased again for 50 wt.% solutions (1.6 ppmw). Shabaker et al. also showed that leaching of Ni from Sn-modified Raney Ni catalyst during APR can be reduced by a factor of 5 when the feed concentration is changed from 5 to 63 wt.% EG. This resulted in higher catalyst stability, and the authors concluded that the presence of excess water is partly responsible for the deactivation [35]. Increasing the reactant concentration might have a stabilizing effect by decreasing the surface coverage of adsorbed water and increasing the coverage of the reactant and products, thereby minimizing oxidation and slowing down the Ostwald ripening process. This is in agreement with our observation that the stabilizing effect of externally added H₂ pressure becomes less significant with increasing feed concentration (see Fig. 2). In addition, Sievers et al. [36] have shown that increased coverage of the catalyst by organic species (substrate and/or intermediates) has a stabilizing effect. To investigate whether the initial EG concentration influences the nickel particle growth via the formation of liquid phase products, we measured the concentrations of the latter (Table S1). Increasing concentrations of ethanol (0–21 mmol/L) and methanol (0–16 mmol/L) were observed as functions of the EG feed concentration (1–50 wt.%). The concentration of glycolic acid, expected to have a negative effect on the stability, was between 1.6 and 2.0 mmol/L and was not a strong function of the reactant concentration (see Fig. S2). Therefore we speculate, in analogy with work of Sievers et al. [36], that coverage of the catalyst by organic species (substrate and/or intermediates) can play an essential role in stabilizing the Ni nanoparticles, in our case by slowing down the Ostwald ripening process.

3.2. Effects of gas atmosphere and pH on catalytic performance

The effect of reaction conditions on the catalytic performance of Ni/CNF in reforming EG was evaluated using a slurry batch reactor. The conversion over time was followed by taking intermittent liquid phase samples, whereas the composition of the gas phase was measured at the end of the reaction. In addition, the H_2 and CH_4 productivity, expressed as turnover frequencies, was measured in a continuous flow reactor.

3.2.1. Slurry batch experiments

Fig. 5 displays the conversion profiles for EG reforming in a slurry batch reactor. Batch reaction time t = 0 is defined as the moment the reactor reached 230 °C; however, during the heating period of approximately 30 min, substantial conversion was realized. With standard APR conditions, 80% conversion was realized after 1 h. When the initial gas phase was changed to H₂, only 48% conversion was obtained in the first hour, indicating that the initial rate for EG conversion decreases under H₂. The decreased activity can be explained by a negative effect of H₂ on the reaction kinetics [37,38]. Fig. 5 further shows that the rate of EG conversion is considerably increased by the addition of KOH, as full conversion is now reached within 1 h. A similar observation was made by Liu et al. [41], who found that during APR of glycerol the activity progressively increased by up to a factor of 4 when the KOH concentration increased from 0 to 1.6 M. This could be related to the shift in redox potential, which predicts that Ni is less likely to be oxidized under these conditions and the Ni particles are thus more metallic in nature under alkaline conditions. Also, KOH can act as a co-catalyst, and the mechanism might be different at high pH, as can be inferred from the work of Zope et al. [39] on the alkalineenhanced oxidative dehydrogenation of glycerol. The authors showed that in alkaline media the oxidative dehydrogenation of glycerol is facilitated over a Pt surface. They elaborate by means of DFT calculations that the activation barrier for O-H dissociation and subsequent activation of C-H bonds is significantly reduced in alkaline media over a Pt catalyst, resulting in enhanced reaction rates. Finally, the addition of base leads to capture of CO_2 (Table 2) and thus may enhance kinetics if CO₂ inhibits the APR over nickel.

The effect of the reaction conditions on the gas phase compositions is shown in Table 2. The main components detected were H_2 , CO_2 , and CH_4 , together with small amounts of CO and higher alkanes (C_2H_6 and C_3H_8). As proposed by Dumesic [10], the APR of EG proceeds through reforming,

$$C_2H_6O_2(l) \rightarrow 2CO(g) + 3H_2(g), \tag{1}$$

and subsequent WGS (water-gas shift) reaction,

$$CO(g) + H_2O(l) \leftrightarrow CO_2(g) + H_2(g), \tag{2}$$

while especially for Ni-based catalysts, methanation of CO,

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(l), \tag{3}$$

or
$$CO_2$$
,



Fig. 5. Conversion versus time for reforming 1 wt.% EG in a batch reactor (a) without and (b) with the addition of KOH under initial (\blacksquare) Ar and (\bullet) H₂ at 6 bar. Conditions: 230 °C, 6 h, 100 ml 1 wt.% EG, and 2.0 g Ni/CNF. The moment that the reactor reached 230 °C has been defined as *t* = 0.

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O,$$
 (4)

can occur as side reactions [40]. Additionally, under alkaline conditions, CO_2 capture takes place:

$$\operatorname{KOH}(a) + \operatorname{CO}_2(g) \to \operatorname{KHCO}_3(a).$$
 (5)

The CO₂ concentration reached up to 31% and 23% v/v for 1 and 10 wt.% EG solutions, respectively (Table 2, entries 1 and 3). With KOH added to the feed, this was reduced to 9.7% v/v for substoichiometric amounts of KOH (KOH:EG 0.31, Table 2, entry 2), while CO₂ was absent for excess amounts of KOH (KOH:EG 3.1, Table 2, entry 4), which demonstrates the complete capture of CO₂ in the form of (bi)carbonates. Interestingly, the formation of CH₄ was also affected by the addition of KOH. In the absence of KOH, high concentrations of CH₄, 19% and 38% v/v, were formed for both the reactions with 1 and 10 wt.% EG, resulting in low H₂ selectivities (52% and 31%, respectively, Table 2, entries 3 and 1). In contrast with alkaline feed solutions of 1 and 10 wt.% EG, much higher H₂ selectivities (96% and 94%, Table 2, entries 2 and 4) were obtained. Even in the presence of an initial H₂ atmosphere, the CH₄ concentration was still rather low (4.3% v/v, Table 2, entry 5).

The increase in H₂ selectivity in the presence of KOH corroborates previously published results [27,41,42] and can be explained by several factors. Due to the CO₂ capture in the form of (bi)carbonate (4) [41], the thermodynamic limitations of the WGS reaction can be circumvented [43]. As the WGS reaction becomes irreversible, this effectively decreases the CO concentration while simultaneously eliminating the possibility of methanation of CO₂. This is evident from the low CO₂ concentration in the gas phase (Table 2). The selectivity is then controlled by the relative WGS and methanation rates. The base can affect the rate of the individual reactions differently; i.e., an increase in H₂ selectivity can be the result of either an increase in the reforming and WGS reaction rate or a decrease in the methanation rate, or even change the nature of the catalytic site. Since H₂O dissociation is a necessary step in the WGS mechanism, Liu et al. speculate that KOH addition increases the rate of the WGS reaction by increasing the hydroxyl concentration on the catalyst surface [41]. Also, the active sites might change, or new sites might be formed, in the presence of the base. First of all, the (potassium) bicarbonate formed during the reaction is known to act as a homogeneous catalyst for the WGS reaction even at the temperatures in this study [44]. This can only explain the higher H₂ production rates in the presence of the base provided that the WGS is the rate-determining step in the overall process, as has been suggested based upon the increased reaction rates for Pt and Pd catalysts upon addition of a WGS promoter [45,46]. Second, Ni(OH)₂ species might be formed under alkaline conditions, which are also known to be a highly active catalyst for the WGS reaction [47]. It has also been suggested that the increase in hydrogen selectivity is the result of a suppression of CO methanation by blockage of Ni defect sites or a disruption of ensembles required for methanation. This has, for instance, been demonstrated by doping Raney Ni catalyst with Sn in the APR of polyols [12,48], and potassium ions can play a similar role in the blockage of the methanation activity of Ni catalysts [41].

3.2.2. Fixed-bed reactor experiments

To evaluate the catalyst stability with respect to H₂ production and to eliminate the negative influences of the pressure build-up in the batch reactor on the reaction kinetics, we performed catalytic tests under continuous-low conditions in a fixed-bed reactor. Fig. 6 shows the catalytic activity of Ni/CNF with time on stream, expressed as the H₂ production rate for the reforming of 10% EG solutions optionally containing 0.5 M KOH. The result of a benchmark 5% Pt/CNF without KOH added is included for comparison [11]. The H₂ production rates for all catalysts increased in the first few hours (due to transient phenomena in the reactor and gasliquid separator) before reaching the steady state. With Ni/CNF, a maximum H_2 production of 194 µmol min⁻¹ g_{cat}^{-1} was observed after about 2 h, followed by a sharp decline between 2 and 8 h, indicating that significant deactivation occurred already during the first few hours. After this period, the activity continued to decline more slowly. The deactivation, expressed as the relative difference between the maximum activity and the activity after 50 h on stream, is given in Table 3 and shows that the Ni/CNF catalysts lost 93% of their initial activity. The loss of active surface area for Ni/CNF, measured by H₂ chemisorption after 6 h, was 91%. This shows that the deactivation of Ni/CNF can be ascribed to the loss of surface area as a result of particle growth.

Stable H₂ productivity was observed for Pt/CNF and for Ni/CNF with KOH after approximately 10 h. The H₂ production rate was highest, 646 μ mol min⁻¹ g⁻¹_{cat}, for the Pt/CNF catalysts and was not likely controlled by mass transfer, since the volumetric productivity of our most active catalysts (439 μ mol min⁻¹ cm⁻³_{cat} for Pt/CNF with a bed density of 0.71 g cm⁻³) is comparable to that of Pt/Al₂O₃, for which it was shown that transport limitations were not significant [37,48]. For the Ni/CNF, an increase in activity to



Fig. 6. Activity with time on stream for Ni/CNF and Pt/CNF in the continuous aqueous phase reforming of 10% EG at 230 °C, 29 bar, and WHSV = $3 h^{-1}$.

Table 3 Steady state catalytic performance in the APR of 10% EG at 230 °C, 29 bar, 10 h TOS, and WHSV = 3 h^{-1} .

Catalyst system	TOF_{H2} (min ⁻¹)	TOF_{CH4} (min ⁻¹)	Conversion (%)	H_2 selectivity $(v/v\%)^a$	Deactivation (%) ^b
Ni/CNF ^c	0.16	0.009	3.5	90	93
Ni/CNF + 0.5 M KOH	1.34	0.009	22.4	99	<2
Pt/CNF ^d	5.1	0.018	27.0	99	<2

^a Hydrogen gas phase selectivity with respect to the formation of gas phase alkanes.

^b Deactivation expressed as the percentage of decrease in H₂ production rate between the maximum and final production rates (50 h TOS).

^c Catalyst underwent deactivation.

^d Catalyst from Ref. [11].

455 μ mol min⁻¹ g_{cat}^{-1} in H₂ production was observed when KOH was present. The H₂ productivity of that catalyst approached that of the benchmark Pt/CNF catalyst and, in contrast to the reaction without KOH, did not decline over time. This stability is in agreement with the observations from TEM and XRD, which show that the Ni particles were stable in the presence of KOH.

Table 3 also lists the H₂ selectivity and the activity of the Ni/CNF and Pt/CNF catalysts for the formation of H₂ and CH₄, expressed as turnover frequencies (TOF). For the sake of simplicity, the number of surface metal sites of the fresh catalysts has been derived from the total H₂ uptake, measured by H₂ chemisorption (using H/ Ni = 1), 361 μ mol/g for Ni/CNF and 138 μ mol/g for Pt/CNF. The H₂ selectivity increased from 90% to 99% with KOH in the feed solution, which is in agreement with the result for batchwise reforming, which also showed an increase in H₂ selectivity with the addition of KOH. The CH₄ TOFs at 10 h TOS were comparable (0.009 min⁻¹) for Ni/CNF in the presence and absence of KOH, but since significant deactivation had occurred without KOH addition, we conclude that the initial rate of CH₄ production is reduced in the presence of KOH. It should also be noted that in batch mode the H₂ selectivity for Ni/CNF was much lower (31% versus 90%) than in plug flow mode. The higher H₂ selectivity in the continuous reforming of EG can be explained by lower system pressure (29 bar) under continuous operation compared to batchwise reforming (Table 2), where the H₂ and CO₂ accumulate in the reactor. Consequently, the H₂ and CO₂ pressures were lower in the fixed-bed reactor, which resulted in a lower methanation rate [40,49] than in the batchwise experiments. However, further research is needed to elucidate the effect of base addition and gas phase compositions on the reforming, methanation, and WGS reaction in more detail.

4. Conclusion

The hydrothermal stability and performance of Ni/CNF catalysts were investigated for the production of H_2 via aqueous phase reforming of ethylene glycol at 230 °C. Results from spent catalyst characterization with XRD, TEM, and chemisorption showed that during APR the Ni/CNF catalyst deactivated due to loss of Ni surface area as a result of Ni particle growth. Our results suggest that this particle growth correlates with Ni leaching, which is a result of the acidic APR conditions. The extent of this growth could be controlled by tuning the reaction conditions, for which the effectiveness can be summarized as follows; increase in pH > increase in reactant concentration > increase in H₂ pressure. When a gas atmosphere containing H₂ or a high concentration of EG was used, the particle growth was suppressed. Modifying the pH of ethylene glycol solutions with KOH was most effective in stabilizing the Ni nanoparticles, and at pH > 8, the nickel particle growth was almost completely prevented. Under these conditions, Ni oxidation and leaching were inhibited, which is crucial to prevent the subsequent growth of Ni particles via Ostwald ripening. With addition of KOH, the H₂ selectivity was also increased, and by performing APR of EG with KOH in a fixed-bed reactor, a H₂ selectivity of 99% was

achieved. The H_2 production remained stable with KOH addition, whereas the catalyst lost 93% of its initial activity during 50 h time on stream without KOH.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.07.014.

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