

# Stability and activity of carbon nanofiber-supported catalysts in the aqueous phase reforming of ethylene glycol

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## Abstract

Nickel, cobalt, copper and platinum nanoparticles supported on carbon nano-fibers were evaluated with respect to their stability, catalytic activity and selectivity in the aqueous phase reforming of ethylene glycol (230 °C, autogenous pressure, batch reactor). The initial surface-specific activities for ethylene glycol reforming were in a similar range but decreased in the order of Pt (15.5 h<sup>-1</sup>) > Co (13.0 h<sup>-1</sup>) > Ni (5.2 h<sup>-1</sup>) while the Cu catalyst only showed low dehydrogenation activity. The hydrogen molar selectivity decreased in the order of Pt (53%) > Co (21%) > Ni (15%) as a result of the production of methane over the latter two catalysts. Over the Co catalyst acids were formed in the liquid phase while alcohols were formed over Ni and Pt. Due to the low pH of the reaction mixture, especially in the case of Co (as a result of the formed acids), significant cobalt leaching occurs which resulted in a rapid deactivation of this catalyst. Investigations of the spent catalysts with various techniques showed that metal particle growth is responsible for the deactivation of the Pt and Ni catalysts. In addition, coking might also contribute to the deactivation of the Ni catalyst.

## Key words

carbon nano-fiber; catalyst deactivation; aqueous phase reforming; non-noble metal catalyst

## 1. Introduction

Research efforts on renewable alternatives to fossil resources for the production of energy carriers and chemicals are ever increasing. Non-edible renewable lignocellulosic biomass, especially the carbohydrate fraction, is widely regarded as a sustainable replacement for part of the current fossil fuel use [1]. Carbohydrates are conveniently available and largely CO<sub>2</sub> neutral. Like in the current fossil fuel based infrastructure, heterogeneously catalyzed processes are expected to play a key role in the thermochemical conversion of this carbohydrate feedstock into chemicals and fuels.

Due to the presence of water in biomass and the high solubility of carbohydrate derivatives in water, the processing of lignocellulosic (derived) feedstocks in an aqueous environment is preferable. Unfortunately, the stability of the currently available heterogeneous catalysts in this media is limited and has to be addressed.

A promising process is the catalytic conversion of biomass derived polyols and sugars into hydrogen by aqueous phase reforming (APR) [2]. APR takes place at elevated temperatures (200–250 °C) and pressures (16–40 bar) high

enough to keep water in the liquid phase. Thermodynamics predict that under these conditions it is possible to produce H<sub>2</sub> with low CO content, which makes this process especially attractive for use in combination with PEM fuel cells [3]. The essential surface chemistry of APR is believed to involve dehydrogenation and the cleavage of C–C bonds over a metallic catalytic site (1) followed by the water-gas shift reaction (WGS) of the adsorbed CO (2) (as shown here for ethylene glycol) [2].



APR has previously been described for substrates like glycerol, sorbitol [4] and cellulose [5]. Ethylene glycol (EG) is often used as model substrate for fundamental studies since it contains the same functionality as the larger polyols but gives fewer by-products [6].

Supported (promoted) platinum-based catalysts have been investigated extensively for the production of hydrogen via APR. These catalysts display a high surface-specific activity and high molar hydrogen selectivity [6,7].

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It has been acknowledged that the development of a catalyst based on more abundant and less expensive base metals is desired [8]. Metals like nickel, cobalt, and copper are of interest in this regard because of their activities in the (steam) reforming of methane, methanol and ethanol. Of these, nickel has been investigated most intensively for APR, mainly supported on alumina [7,9–15], silica [3], ceria [16] or hydrotalcite [17]. The use of bulk (modified) Raney nickel [4,6,18–21] catalysts has also been described in literature while cobalt [7,21–24] and copper [21] have received less attention.

Cobalt, nickel, copper are more susceptible towards oxidation and, as a result, leaching than noble metals like platinum. Thermodynamic analysis predicts that bulk metallic cobalt [25] and nickel [26,27] cannot be oxidized by water at temperatures and pressures ( $<250\text{ }^{\circ}\text{C}$ ,  $P_{\text{H}_2} >1\text{ bar}$ ) typically encountered in APR [6]. Indeed it has been reported that nickel and copper catalysts remain metallic under even more severe conditions ( $T, P$ ) of hydrothermal gasification [28]. Nevertheless, their oxidation resistance is also expected to decrease with decreasing pH. Under APR conditions the pH might be low due to the presence of acid products in liquid phase such as alcohols, aldehydes, carboxylic acids and carbonic acid [3,29–31]. This increases the driving force for water to oxidize the metal and thus will increase the risk of catalyst leaching, as was observed for nickel-based catalysts [4,32,33].

For nickel on silica coke formation [3] and particle growth [4] were identified as deactivation mechanisms. Oxidation was suggested as the deactivation mechanism for nickel supported on alumina [12]. A combination of sintering and oxidation was observed for nickel on ceria [16].

Besides the stability of the active phase, the stability of the support is also of crucial importance. Conventional high surface area supports, e.g. silica and alumina, are unstable in hot liquid water [28]. It has been shown by several authors that under hydrothermal conditions  $\gamma$ -alumina is transformed to boehmite [13,34] while partial dissolution of silica takes place [35]. Since structural changes of the support can enhance deactivation [36], the choice of support material is critical for the stability of the catalyst. Carbonaceous materials are stable under hydrothermal and even supercritical conditions [37] and are preferred as support material for APR catalyst. Different types of carbon like carbon nano-tubes [22], carbon black [38], activated carbon [39,40] and mesoporous carbon [41] have previously been used as supports for platinum-based catalyst in APR.

In the current work we use carbon nano-fibers (CNF), a well characterized, high surface area, mesoporous and inert support which has been proven to be very promising for multiple different catalyst systems [42–45]. To the best of our knowledge, base metals supported on carbon have not been explored for APR yet. Therefore in the present study we have compared cobalt, nickel, copper and platinum supported on CNF with respect to their stability and activity in the aqueous phase reforming of ethylene glycol. A Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is included in this study as the benchmark since this catalyst

is often studied and shows good performance [6,7,9]. Characterization of the parent and spent catalysts is carried out to describe the role of deactivation due to oxidation, leaching, sintering and carbon depositions. We show that besides reforming, additional reaction pathways exist depending on the metal component.

## 2. Experimental

### 2.1. CNF synthesis

Carbon nano-fibers were prepared by chemical vapor deposition of diluted synthesis gas (266 mL/min CO, 102 mL/min H<sub>2</sub>, and 450 mL/min N<sub>2</sub>) over a 5%Ni/SiO<sub>2</sub> catalyst (5 g) under 4 bar and 550 °C for 24 h. This procedure yielded 35 g of raw CNF. To remove SiO<sub>2</sub> from the raw CNF, they were suspended in a 400 mL 1 M KOH (Acros 85%) solution and refluxed for 1 h. Then the solution was decanted and the procedure was repeated three times. After that the fibers were washed with copious amounts of demineralized water and recovered by filtration. Subsequently the fibers were treated in 65% boiling nitric acid for 1.5 h to remove exposed nickel and introduce surface oxygen groups (0.21 mmol/g [46]). The surface oxidized fibers (CNF-ox) were washed with copious amounts of demineralized water and dried at 60 °C in air for 16 h prior to being used as a support material. This method has been described previously in more detail [47].

### 2.2. Catalyst preparation

Samples with nominal loadings of 5 wt% for platinum and 15 wt% for cobalt, nickel or copper were prepared by incipient wetness impregnation of CNF-ox aqueous solutions containing respectively 0.45 M Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Sigma-Aldrich 99.995%), 5.0 M Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Acros 99%), 5.0 M Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Acros 99%) or 4.6 M Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Acros 99.5%). Typically 2 g of CNF-ox (sieve fraction 90–150  $\mu\text{m}$ ) were dried under vacuum at 80 °C for 2 h. After cooling to room temperature the support was impregnated with 1.2 mL of the aqueous metal precursor solution. The impregnated samples were then dried for 16 h at 120 °C. Next the samples were reduced for 2 h at 300 °C (Co, Ni and Pt) or 400 °C (Cu) in a flow of 30 (v/v)% H<sub>2</sub>/N<sub>2</sub> (100 mL/min) with a heating ramp of 5 °C/min. The reduced catalysts were cooled to room temperature and the reactor was opened. This allowed air to diffuse into the reactor, resulting in slow passivation of the catalysts. The catalysts were labeled as Ni/CNF, Co/CNF, Cu/CNF and Pt/CNF. A commercially available 5% platinum on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Sigma Aldrich) was used as a benchmark catalyst (this sample was labeled as Pt/Al<sub>2</sub>O<sub>3</sub>).

### 2.3. Catalyst characterization

Both parent and spent catalysts were characterized by X-ray powder diffraction (XRD), H<sub>2</sub> chemisorption, N<sub>2</sub>-physisorption, atomic absorption spectroscopy (AAS) and thermo gravimetric analysis (TGA).

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