Effect of initial nickel particle size on stability of nickel catalysts for aqueous phase reforming☆

Tomas van Haasterecht [a], Marten Swart [a], Krijn P. de Jong [a], Johannes Hendrik Bitter [a,b,*]

[a] Inorganic Chemistry and Catalysis, Utrecht University, 3508 TB Utrecht, The Netherlands
[b] Biobased Chemistry and Technology, Wageningen University, 6708 WG Wageningen, The Netherlands

ARTICLE INFO

ABSTRACT

The deactivation behavior by crystallite growth of nickel nanoparticles on various supports (carbon nanofibers, zirconia, SiC, α-Al$_2$O$_3$ and γ-Al$_2$O$_3$) was investigated in the aqueous phase reforming of ethylene glycol. Supported Ni catalysts of ~10 wt% were prepared by impregnation of carbon nanofibers (CNF), ZrO$_2$, SiC, γ-Al$_2$O$_3$ and α-Al$_2$O$_3$. The extent of the Ni nanoparticle growth on various support materials follows the order CNF ~ ZrO$_2$ > SiC > γ-Al$_2$O$_3$ >> α-Al$_2$O$_3$ which sequence, however, was determined by the initial Ni particle size. Based on the observed nickel leaching and the specific growth characteristics; the particle size distribution and the effect of loading on the growth rate, Ostwald ripening is suggested to be the main mechanism contributing to nickel particle growth. Remarkably, initially smaller Ni particles (~12 nm) supported on α-Al$_2$O$_3$ were found to outgrow Ni particles with initially larger size (~20 nm). It is put forward that the higher susceptibility with respect to oxidation of the smaller Ni nanoparticles and differences in initial particle size distribution are responsible for this behavior.

© 2016 Science Press and Dalian Institute of Chemical Physics. All rights reserved.

1. Introduction

The use of biomass as a resource for the production of renewable fuels and especially chemicals is of increasing interest because of its potential role in the transition towards a more sustainable use of our natural resources. In order to efficiently process biomass (derived) resources into useful chemical and fuels the use of catalytic processes is invaluable. This requires the design of catalyst stable under the conditions typically employed for such process. For example the oxidation, hydrogenation, hydrogenolysis and reforming or biomass derived sugars all take place in the aqueous phase at elevate temperatures and pressures using supported metal catalysts. Platinum based catalysts are often employed in these processes but, because of the high cost and low abundance of Pt, alternatives are highly sought-after. Nickel has been proposed as alternative to Pt for the production of renewable hydrogen via the aqueous phase reforming of sugars and sugar like substrates (poly-ols) [1–3]. Although it was found that Ni is less selective toward H$_2$ production due to methanation [1], this can be suppressed by alloying with e.g. Sn [4]. The stability of nickel is however still an issue for these catalysts and the loss of dispersion due to nickel particle growth is the main reason for the deactivation of carbon nanofiber (CNF) supported nickel catalyst in the aqueous phase [1].

Understanding the growth process of supported metal particles is of vital importance in order to develop strategies to improve catalyst stability. The growth of Ni [5] and other metal particles [6–8] has been investigated extensively in gas phase reactions [9]. Much less attention has been devoted to the growth of metal particles in the liquid or aqueous phase. Deactivation of Cu [3,10] and Ni [2,11] in the aqueous phase as a result of particle growth has been reported but studies on the growth kinetics of metal particles in the liquid phase have mainly focused on supported platinum catalyst [12–17] at low temperatures [15–17]. The growth of supported metal particles is also of interest in the design of stable fuel cell electrodes, especially low temperature PEM cells. Here significant work has been done focusing on the particle growth mechanism for the synthesis of stable electrodes, although again with a focus on Pt as the active phase. This often involves investigation of the growth characteristics of supported Pt nanoparticles in water or electrolyte solutions under induced accelerated aging with via a potential sweep. Morgan et al. reviewed the literature on mechanisms of surface area loss of platinum electrodes [18]. They

concluded that platinum loss occurs due to platinum dissolution and platinum particle growth occurs due to Ostwald ripening (OR) but the role of particle migration and coalescence (PMC) is uncertain. Like in the gas phase the growth of metal particles in the liquid phase might proceeds via two very different mechanisms, i.e. via Oswald ripening (OR) or particle migration and coalescence (PMC) [19]. The driving force for the growth of (metal) particles via both mechanisms is the minimization of the total surface free energy of the system.

The growth of supported metal nanoparticles via migration and coalescence, also called sintering (sintering is used by some authors to exclusively denote particle growth via the particle migration and coalescence mechanism while others have used it as an umbrella term that encompassed both particle growth via Ostwald ripening and growth via particle migration and coalescence, Ostwald ripening is then referred to as chemical sintering while migration and coalescence is referred to as thermal sintering) or thermal sintering, involves the random motion of particles over the support resulting in collision with other mobile or immobile particles and their subsequent merger into a larger particle (coalescence). The migration of the particles does not necessarily occur as a concurrent movement of the entire particle, but probably results from an overall but random mass transfer of (ad)atoms from the particle to the support surface [19]. This mechanism generally occurs at high temperatures since a high mobility of the atoms is required for this mechanism. In other words this is a highly activated process and for gas phase reactions this generally occurs around temperatures of about half the melting point of the bulk metal (Tammann temperature), e.g. 590 °C for nickel. While the temperature in aqueous phase processes is substantially lower (e.g. 200 °C this study) this does not exclude thermal sintering as a particle growth mechanism a priori, since (liquid) water can affect the properties of metal nanoparticles and the mobility of the particles on the support differently than a gaseous environment.

The second mechanism, called Ostwald ripening or particle coarsening, is a mechanism of inter-particle migration by which molecules or atoms migrated from the smaller particles fixed on the support to the larger particles. The molecular or atomic species migrate either though a second phase (gas phase/solution, i.e. gaseous or ionic species) or via the support (adatoms). These different transport modes are denoted three dimensional (3D) and two dimensional (2D) Ostwald ripening respectively. The different mechanisms, PMC and 3D or 2D OR, are not mutually exclusive [20] and the dominating mechanism might even change during the growth process [19]. This makes the determination of the mode by which supported metal particles grow a daunting task.

Here we investigate the particle growth behavior of supported nickel catalyst as function of the support type and the size of the Ni nanoparticles in the aqueous phase using the reforming (APR) of ethylene glycol as a model reaction These conditions, hot (230 °C) compressed water with a carbohydrate model compound, are relevant to the catalytic processing of biomass feedstock. The supports were selected based on their known stability under these conditions with the addition of γ-Al_2O_3 which was included since it is one of the most used supports in APR. We show that the particle growth observed under these conditions is best described by an Ostwald ripening mechanism with migration of dissolved nickel species through the aqueous phase. Besides the support type, the initial particle sizes as well as the initial particle size distribution are shown to be important parameters that affect the particle growth characteristics.

2. Experimental

The support materials used in this study were α-Al_2O_3 (BASF Al-4196E 1.8 mm), γ-Al_2O_3 (Engelhard, BN 245), ZrO_2 (Degussa, BN132), β-SiC (SiCAT CtS-56) and surface-oxidized carbon nanofibers (CNF, prepared in-house). The catalyst were prepared by incipient wetness impregnation of the support materials with aqueous solutions of $Ni(NO_3)\cdot6H_2O$ to obtain a metal loading of approximately 10 wt%. Catalyst characteristics and preparation conditions are shown in Table 1. After impregnation the catalysts were dried in vacuum at room temperature or overnight in air at 80 °C. Next, the catalyst precursor was activated by direct reduction or by calcination in static air or in N_2 flow followed by reduction in 33% H_2 in N_2 (150 mL/min). After the reduction treatment part of the sample was passivated by controlled exposure to air before characterizing with XRD and TEM.

The stability of the supported Ni catalysts was investigated during the aqueous phase reforming of ethylene glycol. Typically 100 mg catalyst (90–220 μm sieve fraction) was loaded into a 10 mL batch autoclave reactor (Swagelok union mini-reactors similar to those reported in [21,22]) and 4 mL of 1 wt% aqueous ethylene glycol solution was added using a volumetric pipet. The reactor was filled in a glove box under inert atmosphere. The reactant solution was degassed with argon gas prior to its introduction into the glove box in order to prevent oxidation of the freshly reduced catalyst by dissolved oxygen. Next the reactor was placed in a preheated (230 °C) tumbling oven (4 rpm) as previously reported [23].

Fresh and spent catalysts were characterized by X-Ray powder diffraction (XRD), H_2 chemisorption, and Transmission Electron Microscopy (TEM). Powder X-ray diffraction (XRD) was measured using an D2 PHASER X-ray Diffraction Analyzer from Bruker with Co $K\alpha$ radiation ($\lambda = 1.789$ Å). Nickel crystallite sizes of the reduced and passivated catalysts were estimated with the Scherrer equation using a shape factor of 0.89. Values for the full width at half maximum for Ni (111) were obtained from a least squares fit of the experimental data with a pseudo-Voight function by

Table 1. Overview of catalyst preparation conditions and sample treatment history with resulting nickel particle sizes obtained from XRD and H_2-chemisoption.

Sample code	Ni[a] (wt%)	Drying (°C)	Cal[b] (°C)	Red[c] (°C)	BET area[d] (m²/g)	Ni particle size (nm)		
						d_{XRD}[e]	d_{H2C}[f]	d_{TEM}
Ni/γ-Al_2O_3	9.2	80	600 (air)	500 (2 h)	185	4	14	~5 to 10
Ni/ZrO_2	9.5	80	600 (air)	500 (2 h)	81	10	8.7	–
Ni/SiC	9.8	80	600 (air)	500 (2 h)	23	16	–	–
Ni/CNF	9.8	80	–	300 (2 h)	173	6	4	–
20Ni/α-Al_2O_3	9.8	80	500 (air)	500 (2 h)	7	20	24	22
12Ni/α-Al_2O_3	9.8	vacuum	400 (N_2)	400 (1 h)	7	12	9.1	12
2%Ni/α-Al_2O_3	2.0	vacuum	–	500 (1 h)	7	13	–	–

[a] Nominal nickel loading.
[b] Calcination (cal) treatment in static air or N_2 flow (150 mL/min) at the designated temperature with a 5 °C/min heating ramp for 2 h.
[c] Reduction treatment (red) in 30% H_2 in N_2 (total flow 150 mL/min) at the designated temperature with a 5 °C/min heating ramp.
[d] Specific surface area of the support material according to the BET method.
[e] Average nickel crystallite sizes as determined by XRD (d_{XRD}).
[f] Average nickel particle sizes as determined by hydrogen chemisorption (d_{H2C}).