Catalysis Communications 71 (2015) 88–92

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Effect of pH on catalyst activity and selectivity in the aqueous Fischer–Tropsch synthesis catalyzed by cobalt nanoparticles

Jorge A. Delgado [a,b], Sergio Castillón [c], Daniel Curulla-Ferré [d], Carmen Claver [a,b], Cyril Godard [b,*]

[a] *Centre Tecnòlogic de la Química de Catalunya, C/ Marcel.li Domingo s/n, 43007 Tarragona, Spain.*
[b] *Departament de Química Física I Inorgànica, Universitat Rovira I Virgili, C/ Marcel.li Domingo s/n, 43007 Tarragona, Spain*
[c] *Departament de Química Analítica I Orgànica, Universitat Rovira I Virgili, C/ Marcel.li Domingo s/n, 43007 Tarragona, Spain*
[d] *Total Research and Technology Feluy, Zone Industrielle Feluy C, B-7181 Seneffe, Belgium*

ARTICLE INFO

Article history:
Received 24 March 2015
Received in revised form 31 July 2015
Accepted 4 August 2015
Available online 8 August 2015

Keywords:
Cobalt nanoparticles
Fischer–Tropsch
Aqueous phase
pH effect

ABSTRACT

Cobalt nanoparticles of 2.6 nm were synthesized in water using $NaBH_4$ as the reducing agent and PVP as stabilizer. The nanoparticles were fully characterized and their catalytic performances evaluated in the aqueous phase Fischer–Tropsch synthesis (AFTS) at various pH values. The pH of the catalytic solution was shown to affect both the activity and selectivity of the AFTS reaction since side reactions such as WGS and formation of formate from CO_2 were favored at basic pH.

1. Introduction

The increasing worldwide energy demand has made major companies to consider alternative feedstocks such as natural gas, coal and biomass to replace fossil fuels [1]. In this context, the Fischer–Tropsch synthesis (FTS) has been considered a key process of the biomass-to-liquid (BTL), gas-to-liquid (GTL) and solid-to-liquid technologies (STL) [2] since through this catalytic reaction, syngas can be transformed into high quality synthetic fuels [3–5]. FTS is catalyzed by several transition metals including Ru, Co and Fe. However, Co-catalysts are more attractive from an industrial point of view due to their higher hydrocarbon productivity, good stability and commercial availability [1].

Currently, the control of the selectivity is one of the main goals in FT investigation [6]. In this context, the use of unsupported nanoparticles is of high interest as they mimic metal surface activation and catalysis at the nanoscale, and shed some light on the effect of the support on catalysis [7]. The first report of the aqueous phase FT synthesis (AFTS) was performed using ruthenium nanoclusters stabilized with poly(N-vinyl-2-pyrrolidone) (PVP) as catalysts [8]. Recently, the effect of the polymer stabilizer was also studied in our group in the AFTS catalyzed by RuNPs [9]. PVP stabilized RuNPs were more active and selective towards hydrocarbons than those stabilized by lignins, indicating that the nature of the stabilizing polymer does affect the catalytic performance in AFTS, strongly influencing the production of CO_2 by Water Gas Shift (WGS) reaction.

One of the earliest studies on colloidal cobalt nanocatalysts applied in the AFTS was published by Kou et al. who reported activity of 0.12 $mol_{CO}\ mol_{Co}^{-1}\ h^{-1}$ at 170 °C. In this study, the CoNPs were synthesized by chemical reduction using sodium borohydride as reducing agent in water [10]. More recently, the same author compared Co nanoparticles reduced by $LiBEt_3H$ and $NaBH_4$, in the aqueous-phase Fischer–Tropsch synthesis [11]. Higher catalytic performance was observed for the former case, and comparing the particle size distribution of the catalysts before and after reaction, it was suggested that catalyst reconstruction occurs during the reaction. In addition, the authors proposed that B-doping could affect the catalytic performance of these NPs. They also reported the use of cobalt/platinum alloy nanoparticles stabilized by PVP as catalysts of the AFTS [12], reaching activity up to 1.1 $mol_{CO}\ mol_{Suf\text{-}Co}^{-1}\ h^{-1}$ with a growth factor (α) of 0.8 at 160 °C. This outstanding activity was rationalized by the formation of Co overlayer structures on Pt NPs or Pt–Co alloy NPs. Finally, the synthesis of CoNPs by thermal decomposition of $Co_2(CO)_8$ was also reported using a modified lipophilic C_8-PVP stabilizing agent and squalane as solvent [13]. The resulting CoNPs with a size of 3.54 ± 1.63 nm displayed a FT activity of 0.022 $mol_{CO}\ mol_{Co}^{-1}\ h^{-1}$. Other colloidal Co nanocatalysts for FTS were reported in ionic liquids [14,15] and squalane [13] although in these cases, low activity and agglomeration issues were described.

In the present work, we describe the synthesis and characterization of colloidal CoNPs stabilized with poly(N-vinyl-2-pyrrolidone) and their evaluation as nanocatalysts in the aqueous phase FT synthesis with a

---

[*] Corresponding author.
E-mail address: cyril.godard@urv.cat (C. Godard).

http://dx.doi.org/10.1016/j.catcom.2015.08.003
1566-7367/

particular focus on the effect of the pH on the catalysts activity and selectivity.

2. Experimental section

2.1. Synthesis of cobalt nanoparticles by chemical reduction method

Cobalt nanoparticles (Co1) were synthesized by chemical reduction of cobalt(II) chloride in the presence of polyvinylpyrrolidone as stabilizer (PVP:Co ratio of 20) using sodium borohydride as reducing agent. As a standard procedure, 0.226 g of $CoCl_2·6H_2O$ (0.93 mmol) was dissolved in 50 ml of H_2O containing the 2.066 g of PVP-K30 (18.6 mmol based on monomer units, PVP:Co ratio of 20). Then, a solution of 0.358 g of $NaBH_4$ (9.30 mmol) in 16 ml of H_2O was added at room temperature during 5 min. The solution was maintained under vigorous mechanical stirring for 2 h. Then 100 μl of the colloidal solution was centrifuged, washed with water and re-dispersed by sonication. Three drops of the obtained colloidal solution were deposited on a Cu-formvar or holey carbon grids for TEM and HR-TEM analysis. For the isolation of the CoNPs, the freshly prepared NPs were initially precipitated by a strong magnet and the supernatant was decanted. Then, the precipitated NPs were washed with water to remove the excess of salts and PVP. The decantation and washing process was repeated three times with water, then three times with ethanol and three times with hexane. The resulted CoNPs were finally dried under vacuum and stored in a glove-box.

2.2. Fischer–Tropsch catalytic experiments

The FT experiments were performed according to reported methods [8,9]. Freshly synthesized CoNPs (0.93 mmol Co, as described above) were magnetically decanted and washed three times with water and then re-dispersed in 66 ml of water. The obtained suspension of CoNPs was transferred into the autoclave equipped with a Teflon liner. The autoclave was then purged three times with Ar, and pressurized with an Ar pressure of 1.5 bar. 10 bar CO and 20 bar H_2 were further added giving a final pressure of 31.5 bar (H_2:CO:Ar = 2:1:0.15). The autoclave was heated to 180 °C under mechanical stirring at 1000 rpm during 12 h. After the reaction, the autoclave was cooled to room temperature prior to gas analysis. All the components contained in the gas phase (CO, H_2, Ar, CO_2, and C_1–C_8 hydrocarbons) were analyzed by GC-TCD and the quantification was performed using calibration curves for each component. The compounds present in the aqueous phase were extracted with dichloromethane (10 ml) containing 1 μl of bicyclohexyl as internal standard. The organic phase containing the hydrocarbon and oxygenated products were analyzed by GC–MS. The identification and quantification of products was performed by comparison with standards using calibration curves for each compound.

3. Results and discussion

3.1. Synthesis and characterization of CoNPs

The CoNPs Co1 were synthesized by chemical reduction of cobalt chloride in the presence of polyvinylpyrrolidone (PVP) as stabilizer and sodium borohydride as reducing agent (Scheme 1).

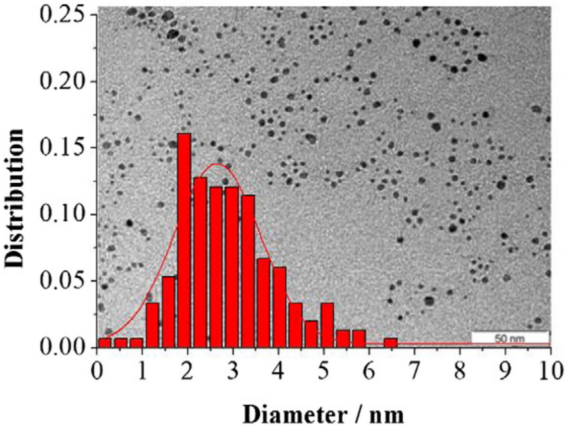


Fig. 1. Size histograms and TEM micrographs of Co1.

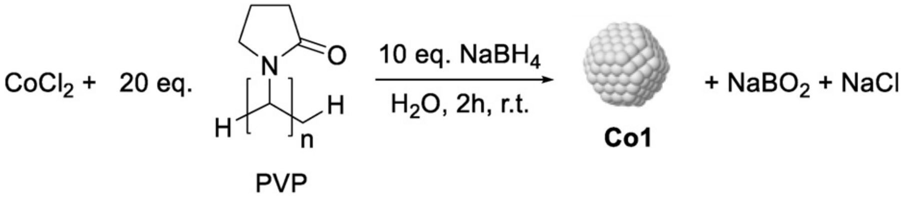
The TEM micrograph and size histogram of Co1 displayed in Fig. 1 show the formation of spherical cobalt nanoparticles of 2.64 ± 0.92.

The fine structure of Co1 was also studied by high-resolution transmission electron microscopy (HR-TEM, Fig. 2). In the micrograph, single particles of *ca.* 2.6 nm size were observed, in agreement with the size previously obtained by TEM. The presence of diffuse rings in the electron diffraction pattern of Co1 also suggested an amorphous structure of the cobalt phase, as previously reported for CoNPs synthesized through similar colloidal methods [16–18].

Analysis of the XRD patterns obtained for Co1 revealed the presence of at least three broad bands centered at 34°, 45° and 60° (Fig. 3), which could not be unambiguously attributed to a specific metallic or oxide phase. Similar XRD patterns were reported for CoNPs synthesized by chemical reduction using $NaBH_4$ as reducing agent [18,19]. For instance, Torres et al. reported the synthesis of CoNPs of *ca.* 1 nm exhibiting XRD patterns with broad bands and attributed this effect to the small size of the CoNPs [19]. In contrast, Pileni et al. attributed the broadness of XRD patterns of 7 nm CoNPs (also synthesized by chemical reduction) to their amorphous structure [18]. Therefore, in view of these reports, the broad bands observed here could arise from the amorphous structure (in agreement with HR-TEM) and/or due to the small size of the CoNPs.

A sample of Co1 was subjected to a thermal treatment with the aim to force the crystallization/sintering of the NPs thus revealing a more defined crystalline pattern [20]. Co1 was heated to 500 °C within 2–5 min under argon flow and kept at this temperature for 2 h, after which the solid was allowed to rapidly cool to ambient temperature (5–10 min). The diffraction pattern of the thermal treated sample exhibited only fcc and hcp cobalt crystalline phases (Fig. 3). A well-defined pattern of $B(OH)_3$ was also observed at low angles ($2\theta = 27°$). It was therefore concluded that Co1 is mainly composed by metallic cobalt and $B(OH)_3$. The presence of boron was therefore hold responsible for the distortion of the crystalline structure of the CoNPs, as previously reported [20].

Quantification of the content of cobalt and boron in Co1 was performed by ICP. The content of Co and B resulted to be 90 and 10 wt.% corresponding to a Co/B atom ratio of 2.8. In contrast to our findings, Kou et al. reported Co/B values of *ca.* 0.2 for CoNPs of 14 ± 6 nm



Scheme 1. Synthesis of Co1 by chemical reduction method.