



Effects of loading and synthesis method of titania-supported cobalt catalysts for Fischer–Tropsch synthesis



Thomas O. Eschemann, Johannes H. Bitter¹, Krijn P. de Jong*

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterial Science, Utrecht University, P.O. Box 80083, 3508 TB Utrecht, The Netherlands

ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form 2 October 2013

Accepted 9 October 2013

Available online 10 November 2013

Keywords:

Fischer–Tropsch

Cobalt

Titania

Incipient wetness impregnation

Deposition precipitation

ABSTRACT

Because of their high activity and selectivity to C_{5+} hydrocarbons in the Fischer–Tropsch process, titania-supported cobalt catalysts have received great interest from industrial and academic institutions. Here, we report on three catalyst preparation procedures, incipient wetness impregnation (IWI), deposition precipitation using urea hydrolysis (DPU) or ammonia evaporation (DPA) to prepare, Co/TiO_2 catalysts with 4–24 wt.% Co. The results reveal a strong impact of the catalyst preparation, procedure on dispersion and distribution of cobalt over the titania surface. IWI led to clustered cobalt, oxide particles of ~ 10 nm, while for the DPA catalysts, similarly sized nanoparticles were found to be, well-distributed over the support surface. Co/TiO_2 catalysts prepared by DPU showed the presence of, ~ 2 nm supported cobalt oxide particles beside large unsupported particles. Catalytic tests under, industrially relevant conditions show that the DPA catalysts displayed a superior activity and C_{5+} , selectivity for the entire cobalt loading range studied.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Ever since its invention in the 1920s the Fischer–Tropsch (FT) reaction, the catalytic conversion of synthesis gas into hydrocarbons, has been a topic of great interest for both academic and industrial research. Depleting reserves and increasing prices of crude oil have been a driving force for a growing number of large scale FT applications, as synthesis gas can be generated from alternative feedstock such as coal, biomass or natural gas. In the low temperature FT process, synthesis gas is converted to a mixture of linear high molecular mass hydrocarbons, which is further converted to fuels, lubricants and chemicals [1–3]. For the economic viability of FT plants a good catalyst performance in terms of high activity, selectivity and stability at affordable costs is essential, which makes supported cobalt catalysts the material of choice for modern plants [4–7]. Titania-supported cobalt catalysts have the benefit of particularly high selectivities to heavy (C_{5+}) hydrocarbons [8,9], although it should be noted that the support is a reducible oxide and, therefore, catalysts are potentially prone to strong metal support interactions (SMSI) [10].

Previous research has shown that particle sizes of supported cobalt nanoparticles have a strong impact on the activities and selectivities in the FT reaction. Turnover frequencies (TOF) and selectivities to higher hydrocarbons are reported to be constant for larger cobalt particles. However, both the TOF and the selectivity to C_{5+} products decrease below a critical particle size [11–14]. Aside the well-studied metal dispersion effects on activity and selectivity in case of cobalt FT catalysts, it has very recently been shown for methanol synthesis catalysts, that the distribution of the active metal species over the support material strongly affects catalysts stability [15]. Furthermore, the chemical nature of the compounds used in the catalyst synthesis can have a strong influence on reducibility and catalytic properties [16].

Catalyst synthesis methods that have been applied for supported cobalt catalysts for the FT reaction include impregnations with different precursors, co-precipitation, deposition precipitation, sol–gel methods, chemical vapor deposition and colloidal methods. The theoretical background and the obtained results for various combinations of support materials and synthesis methods have been reviewed extensively before [6]. SiO_2 and $\gamma-Al_2O_3$ are by far the most widely used support materials for the preparation of cobalt-based FT catalysts. These supports feature large specific surface areas and appreciable pore volumes and are suitable for Incipient Wetness Impregnations (IWI), in which the metal precursor is deposited within the pores upon drying [17]. Modifications in both drying [18] and the subsequent decomposition of the metal precursor [19] have led to highly active and selective catalysts. For commercially available TiO_2 support materials, however,

* Corresponding author. Visiting address: Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterial Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands. Tel.: +31 30 253 6762; fax: +31 30 251 1027.

E-mail addresses: t.o.eschemann@uu.nl, k.p.dejong@uu.nl (K.P. de Jong).

¹ Present address: Wageningen UR, Bornse Weiland 9, 6700 AA Wageningen, The Netherlands.

the maximum applicable metal loadings by IWI are limited by relatively low pore volumes.

A potential solution to this problem is using deposition precipitation (DP), in which the support material is suspended in excess solution of the metal precursor, which can be precipitated on the solid–liquid interface, e.g. upon change of pH of the suspension [20]. The method allows the preparation of highly loaded catalysts with highly dispersed supported nanoparticles. For the deposition of small nanoparticles with narrow size distributions nucleation at the support must outweigh that in solution. This can either proceed via epitaxial growth of support oxide compounds, as has been well studied for the formation of cobalt phyllosilicates [21]. Alternatively, in the case of nickel deposition on oxidized carbon nanofibers [22], ion-adsorption can precede the nucleation of a hydroxide. In case that an attractive electrostatic interaction between the metal precursor and the support surface prevails, concentration and charge of the metal precursor need to be considered as well as the net surface charge of the oxidic support material [23,24]. In case of pH values above the point of zero charge (PZC, 6.5 for TiO₂), the surface of the oxide is deprotonated and negatively charged, thus adsorption of cations is favored. For pH values below the PZC the surface is positively charged and anions will adsorb. For titania-supported cobalt catalysts, two different DP methods have been put forward in the literature. The first method uses cobalt nitrate as metal precursors and hydrolysis of urea to increase pH such that deposition of cobalt hydroxy species occurs [25]. The second method [26,27] involves a cobalt ammine complex in alkaline solution as metal precursor, which is decomposed by evaporation of ammonia to bring about precipitation.

In this study, we have investigated three catalyst preparation methods, being incipient wetness impregnation (IWI) and the two DP methods described above. We have prepared titania-supported cobalt catalysts in the range of 4–24 wt.% metal loading and show that the preparation method has a strong impact on both the physicochemical properties and the activities and selectivities during FT synthesis under industrially relevant conditions.

2. Materials and methods

2.1. Catalyst synthesis

For incipient wetness impregnation (IWI), TiO₂ (Aeroxide P25, Evonik Degussa) was pre-sieved to 75–150 μm and dried under vacuum. The support material was impregnated with an aqueous solution of Co(NO₃)₂·6H₂O (Acros, p.a.). Subsequently, the material was dried in an oven under static air at 60 °C overnight. After that, the catalyst was heat-treated at 350 °C (2 h, 2 °C/min) in a fluidized bed under a flow of N₂. Note that for higher loadings up to three subsequent impregnations and heat-treatments were required. The catalysts are labeled IWI-XX, XX being the weight percentage of Co, assuming Co to be in the form of Co₃O₄.

In order to prepare Co/TiO₂ catalysts by urea hydrolysis DP (DPU) [25,27] with loadings of 4–24 wt.% Co, 2 g of TiO₂ powder were suspended in 150 mL of an aqueous solution of an appropriate amount of Co(NO₃)₂·6H₂O (0.5–4.0 g) in a double-walled thermostated vessel, which allows pressure release along the axis of the overhead stirrer. The pH was adjusted to 3 using HNO₃ and the suspension was heated to 90 °C under vigorous stirring, then 10 mL of an aqueous solution of urea (Acros, p.a., threefold molar amount of Co²⁺) were added. The suspension was stirred for further 20 h, before it was left to cool to ambient temperature. The solid was filtered off, washed thoroughly with water and dried at 60 °C overnight. The obtained filter cake was crushed and sieved to 75–150 μm and then heat-treated in a flow of N₂ at 400 °C (4 h, 5 °C/min). The catalysts are labeled DPU-XX.

For the preparation of Co/TiO₂ catalysts by ammonia evaporation DP (DPA) [26,27] with loadings of 4–24 wt.% Co, 24.75 g of CoCO₃ (Acros, p.a.) were dissolved in 255.6 g of 25 wt.% ammonia solution (Merck, p.a.). 24.75 g of (NH₄)₂CO₃ (Acros, p.a.) were added and the mixture was diluted to give a total of 500 mL. 8 mL of this stock solution were mixed with 70 mL of 9 wt.% ammonia solution and used to suspend an appropriate amount of TiO₂ powder (0.5–4.0 g) in a PTFE round-bottom flask. The flask was equipped with a reflux cooler and the suspension was stirred and heated to 100 °C for 3 h while air was not excluded. After cooling to ambient temperature, the material was filtered off, washed thoroughly with water and dried at 60 °C overnight. The obtained filter cake was crushed and sieved to 75–150 μm and then heat-treated in a flow of N₂ at 400 °C (4 h, 5 °C/min). The catalysts are labeled DPA-XX.

For selected catalysts prepared by the DPA or DPU method, the vessel was equipped with a pH electrode to record the pH as a function of time during the first hours of precipitation. For comparison, pH curves were also recorded for analogous experiments in absence of the support material.

Elemental analysis using AAS was performed on selected catalysts. The results show that the experimentally determined cobalt loadings are in good accordance with the nominated metal loadings. For the experimental procedure and results the reader is referred to the supporting information.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) was performed on a Bruker D2 Phaser with a Cu Kα (λ = 1.789 Å) source. Co₃O₄ crystallite size estimation was performed using the Co₃O₄ peak at 37° 2θ with an automatic calculation routine in DiffractionEvaluation V2.0 software by Bruker, which is based on the Debye–Scherrer-equation.

For transmission electron microscopy (TEM), the heat-treated catalysts were ground with a mortar, suspended in ethanol using an ultrasonic bath and dropped onto a copper grid with holey carbon film. Alternatively, the catalyst particles were embedded in a two component resin (Epofix, EMS) and cured at 60 °C overnight. The embedded samples were cut into slices of 50 nm using a Diatome Ultra 35° diamond knife mounted on a Reichert-Jung Ultracut E microtome and then transferred to a copper TEM grid. The samples were analyzed using a Tecnai T10/Tecnai T12 microscope, with electron beam voltage of 100 kV, 120 kV, respectively.

Temperature-programmed reduction (TPR) was carried out using a Micromeritics Autochem II ASAP 2920. Typically, 50 mg of the sample were dried in a flow of Ar at 120 °C for 1 h and then reduced in a flow of H₂/Ar (1:19, v/v) at a temperature ramp of 5 °C/min.

2.3. Hydrogen chemisorption

Hydrogen chemisorption was carried out on a Micromeritics Autochem ASAP 2020. Typically 100 mg of catalyst were dried in a flow of He at 120 °C for 2 h and then reduced in a flow of H₂ at 350 °C for 2 h. After evacuation hydrogen chemisorption was measured at 140 °C.

2.4. Fischer–Tropsch synthesis

Fischer–Tropsch synthesis was carried out in a 16 reactor catalytic testing setup (Flowrence, Avantium). The catalysts were diluted with SiC (200 μm) to arrive at the same amount of Co in every reactor, giving a catalyst bed volume of 200 μL. The catalysts were dried in a flow of He for 2 h and then reduced in situ in a flow of H₂/He (1:3, v/v) at 350 °C (8 h, ramp 1 °C/min). Subsequently, the reactors were cooled to 180 °C and pressurized to 20 bar under a flow of H₂. After switching to H₂/CO (2:1, v/v) the temperature was

Download English Version:

<https://daneshyari.com/en/article/54131>

Download Persian Version:

<https://daneshyari.com/article/54131>

[Daneshyari.com](https://daneshyari.com)