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Synthesis of cobalt nanodumbbells and their thermal stability under H_2, H_2/CO and O_2 atmospheres

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ABSTRACT

Hexagonal close packed dumbbell-shaped cobalt nanoparticles (Co^0-hcp) have been fabricated by the polyol method. The thermal stability of these Co^0-hcp nanoparticles has been studied under Fischer-Tropsch Synthesis (FTS) relevant environments such as H_2 and H_2/CO by using SiO_2/SiN_x TEM grids which allowed the structural changes of individual particles to be followed after each *off line* treatment. The TEM analyses demonstrated that the Co^0-hcp nanodumbbells are very stable when thermally treated in H_2 at 250 °C for 9 h followed by H_2/CO at 230 °C, 16 bar for 5 h. These studies indicate that the hcp phase of Co is retained after FTS. Furthermore, subjecting the cobalt nanodumbbells to regeneration conditions such as reduction followed by oxidation led to hollow nanodumbbells with a polycrystalline cobalt oxide (Co_3O_4) shell (so-called Kirkendall effect) which disintegrated to smaller face centered cubic metallic cobalt (Co^0-fcc) particles after further reduction.

1. Introduction

Interest in synthesizing well defined metallic nanoparticles (NPs) with different sizes and shapes has grown massively in recent years, mainly due to their potential industrial application exploiting different optical, electronic, magnetic and catalytic properties [1,2]. Metal and metal oxide NPs with different shapes have been prepared following a wide range of methodologies [1,3–8].

These routes allow catalyst preparation with more control over the active sites [9]. Several studies have shown that the performance of different metals in terms of reactivity and selectivity can be tailored by controlling the shape of the nanocrystals. This is because the shape dictates the number and assembly of atoms located at edges or corners, which can have a critical impact on the catalytic performance [10]. In this regard, structure-activity relationships have been evaluated for platinum in a wide range of reactions such as aromatization [11], Suzuki cross-coupling reaction [12], hydrogenation of benzene [13] and oxygen reduction reaction [14], in which the relevance of the Pt {111} and the Pt {100} surfaces have been described.

Cobalt based catalysts are the preferred option for obtaining liquids fuels from syngas (H_2 + CO), via so-called Fischer-Tropsch Synthesis (FTS) [15–19]. They display high activities and selectivity to long-chain hydrocarbons, low activity to the competitive water-gas shift reaction (WGS) and good resistance toward deactivation. The performance of Co-based catalysts has been widely studied and reported to be highly influenced by the mean cobalt particle size [20–24], the support, the use of promoters and the polymorphic phase of Co [14,18]. However, studies of the reactivity of Co nanoparticles in terms of their shape are scarce.

Colloid chemistry offers a direct route to control the size, the shape and the structure of the cobalt nanoparticles which makes them a very valuable tool for studying heterogeneous catalysis in general, and the FTS process in particular [25]. Thus, cobalt nanoparticles with controlled size distribution prepared by hot injection or microemulsion methods have been already used to study the particle size effect on the FTS process [20,23]. A recent paper reports the relevance of the shape and therefore the crystallographic orientation of cobalt oxide (Co_3O_4) at the surface of nanorods [26]. This appears to promote the reduction of the catalyst, negating oxidation during FTS. The authors have introduced the novel concept of "self-healing catalysts" which eliminates the need for periodic regeneration. This phenomenon originates from the exposure of {110} surfaces on the nanorods, which present the readily reducible Co^{3+} on the surface thus promoting reduction of the catalyst. Similarly, the crystal plane effect of CoFe nanostructures has also been studied [27]. The authors fabricated CoFe nanowires and nanosheets which displayed different catalytic properties in FTS. Thus, the CO conversion was 44% over the nanowires and 13% over the nanosheets. The superior performance of the CoFe nanowires was ascribed to the large fraction of active {110} crystal planes. However, in both cases it would have been interesting to monitor the size/shape of the nanorods after the different thermal treatments and reaction in order to discard shape changes (if any) and a misinterpretation of the results. The Co^0-hcp nanorods with mainly {10-10} planes exposed have been

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investigated in the glycerol hydrogenolysis and found to be more active than Co^0-fcc spheres, demonstrating the facet-dependent performance [28]. The authors showed TEM micrographs of spent cobalt materials and observed that the surface of the rods became rough although their 1D shape was retained, evidencing the robustness of the materials dispersed in a 10% glycerol solution under 200 °C and 3.0 MPa of H_2 for 16 h.

Co^0-hcp nanocrystals with different shapes and hence, different exposed faces have been prepared following a great variety of routes. Co^0-hcp nanoplatelets have been synthesised through the reduction of $CoCl_2$ by NaH_2PO_2 in an aqueous solution in the absence of any surfactant [29]. Disk-like Co^0-hcp has been made by sonication of aqueous Co^{2+} and hydrazine [30]. Co^0-hcp nanodisks were also prepared by decomposition of $Co_2(CO)_8$ in a hot mixture of coordinating solvent and amines [31]. Co^0-hcp nanoflowers have been prepared by the reduction of Co^{2+} as $Co(CH_3COO)_2$ in 1,2-propanediol in the presence of hexadecylamine and $RuCl_3$ (polyol method) [32]. Co^0-hcp nanowires have been prepared by the decomposition of cobalt carboxylates or the organometallic $Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})$ in the presence of acid/amine mixtures [33]. Co^0-hcp nanorods have also been produced by the polyol method [34]. The Co^0-hcp nanorods are formed by reducing cobalt(II) laurate in 1,2-butanediol containing NaOH and $RuCl_3$. The influence of the concentration of NaOH, the carboxylate chain length, the cobalt precursor and the formation mechanism has been discussed in the literature [30,35,36]. Noble metals such as Ru are used as seeding agent to control the nucleation step in the formation of the particles, which finally translates into a control of the size of the particle. During the process, the alcohol firstly reduces Ru^{3+} (which is easier to reduce than Co^{2+}) forming small Ru clusters which facilitate the reduction of Co^{2+} to nanocrystals [34]. The formation of bimetallic Ru and Co particles can occur where, taking into account the high Co:noble metal ratio, noble metals are present as isolated atoms or small clusters embedded within the Co particles structure [34].

Co nanoparticles with preferentially exposed defined crystal planes, might be useful materials to investigate the crystal plane sensitivity of cobalt in FTS but the thermal stability of the nanomaterials under different conditions such as temperature, pressure and atmosphere needs to be confirmed. In a first step, herein we report the fabrication of Co^0-hcp nanorods and the stability of these nanostructures under FTS relevant conditions and atmospheres such as H_2, H_2/CO as well as O_2.

2. Materials and methods

2.1. Synthesis of cobalt nanoparticles

The Co^0-hcp nanorods are prepared following the procedure previously reported elsewhere [37]. Thus, 6 mmol of cobalt laurate (prepared *in house*, see details below), 36 mmol of sodium laurate (Sigma-Aldrich 99–100%), 0.15 mmol of $RuCl_3$ (Aldrich), and 6 mmol of NaOH (Fisher Chemical) are added to a flask containing 75 mL of 1,2-butanediol (Sigma-Aldrich purum, ≥98.0%). The mixture is heated under Ar atmosphere to 175 °C with a ramp rate of 13 °C/min for 20–30 min until the colour of the solution turned from purple to black, evidencing the reduction of Co^{2+} to Co^0. After cooling to room temperature, the cobalt particles were recovered by centrifugation and washed thoroughly with absolute ethanol (VWR Chemicals) and subjected to further centrifugation (3 cycles). The Co NPs were stored in ethanol until further used.

Cobalt laurate was prepared *in house* according to the following procedure [38]; 37 mmol of sodium laurate (Sigma-Aldrich 99–100%) were dissolved in 100 mL of distilled H_2O at 90 °C. In another flask, 37 mmol of $CoCl_2$ (Alfa Aesar, anhydrous 99.7%) was dissolved in 100 mL of distilled H_2O at 90 °C. The $CoCl_2$ solution was added dropwise to the sodium laurate solution and stirred for 5 min at 90 °C. A purple solid was quickly formed which was cooled and washed thoroughly with 100 mL of distilled H_2O (×2) and then with 100 mL of methanol (Sigma-Aldrich ≥99.7%). Finally, the cobalt laurate was dried in the vacuum oven at 60 °C for 3 h. The cobalt content on the precursor has been estimated using thermogravimetric analysis and found to be ca. 16.5 wt.% Co.

2.2. Characterization of the cobalt particles

Transmission electron microscopy (TEM) was used to determine the size and the shape of the cobalt nanoparticles. The micrographs were recorded using JEOL JEM-2011 operated at 200 kV. The samples were dispersed in toluene in an ultrasound bath for 1 h and a drop of the suspension deposited onto carbon coated copper grids. The dimensions of the cobalt nanoparticles and the standard deviation were obtained after measuring 100 nanoparticles.

Powder X-ray diffraction (PXRD) patterns were recorded with a Panalytical X'Pert PRO Multipurpose Diffractometer, using Co Kα irradiation ($\lambda = 1.790307$ Å). Diffraction patterns were collected from 20° to 100° (2θ) with a step size of 0.02°.

Temperature Programmed Reduction (H_2-TPR) experiments were carried out over a Co/Al_2O_3 (Sasol, Puralox) catalyst in order to evaluate the hydrogenation of the organics stabilizers adsorbed on the surface of the cobalt nanoparticles and establish the temperature necessary to remove them under H_2 environment. The Co/Al_2O_3 catalyst was prepared by dispersing the cobalt nanoparticles in toluene and contacting with Al_2O_3 for 1 h in the ultrasound bath. Then, the solid was centrifuged and dried at 60 °C for 1 h. The H_2-TPR experiment was carried out in a Micromeritics Autochem 2920 coupled to Balzers Thermostar quadrupole mass spectrometer. The sample was loaded into a U-shaped quartz reactor and dried at 120 °C (10 °C/min) for 10 min under Ar. Then, the system was cooled down to 0 °C and the gas switched to 10 vol.% H_2 in Ar. The sample was heated up to 800 °C (5 °C/min) and the products monitored by MS.

2.3. Thermal stability of the cobalt nanoparticles under H_2, H_2/CO and O_2

The thermal stability of the cobalt particles was studied by using SiO_2/SiN_x grids which allow observing the same particles after *off line* treatments [39,40]. These special grids have only one square window through which electron beam can pass. The particles deposited on this square window are analysed and using the corners of the square and the particles deposited at the corners as markers, it is possible to look at the same area before and after exposure to reactive atmosphere.

The cobalt particles were deposited on the SiO_2/SiN_x TEM grid as described on the Section 2.2. The morphology and structure of the as prepared cobalt nanoparticles were analysed by TEM. The grid was then removed from the microscope and subjected to H_2 treatment at 250 °C (1 °C/min) for 9 h. The sample was cooled to room temperature in hydrogen, and then helium, straight from a cylinder, with no further purification, was flowed through the reactor for 1 h. Residual oxygen in this gas (assumed to be at ppm levels), is found sufficient to passivate the cobalt nanoparticles on the TEM grid. The morphology and structure of the cobalt nanoparticles were again analysed by TEM. The grid was then removed again from the microscope, re-reduced with H_2 at 250 °C (1 °C/min) for 1 h and subjected to FTS conditions at 230 °C and 16 bar for 5 h under a flow of 28 mL/min (feed composition 50–60 vol.% H_2, 30–40 vol.% CO) [41]. After cooling to room temperature in syngas, helium was flowed over the sample for 1 h as above, and then analysed again by TEM.

Using the same batch of Co particles a second SiO_2/SiN_x grid was coated with cobalt nanoparticles following the method described in Section 2.2. This sample was subjected to a reduction-oxidation-reduction (ROR) cycle. Firstly, the grid was heated to 250 °C (1 °C/min) for 9 h in flowing H_2 (R). Then, the H_2 flow was switched to He for 1 h to evacuate the system. Then, the He flow was switched to air and the system heated to 350 °C (5 °C/min) for 3 h, cooled to room temperature and analysed by TEM (RO). Finally, the same grid was submitted to a second reduction step by heating to 350 °C (1 °C/min) for 6 h in flowing