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Sol–gel synthesis of silica–cobalt composites by employing Co_3O_4 colloidal dispersions

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ABSTRACT

Silica–cobalt composites with cobalt contents (w/w) around 10% were synthesized by employing the sol–gel method, tetraethylorthosilicate as the silica precursor and either a solution of cobalt nitrate or a colloidal dispersion of Co_3O_4 or $Co(OH)_2$ nanoparticles as the cobalt precursors. Cobalt oxide was obtained by the precipitation of Co^{2+} ions in alkaline medium and by subsequent thermal treatment. Stable colloidal dispersions of cobalt oxide were prepared by using high power ultrasound and by covering nanoparticles with lauric acid bilayers. All materials were characterized by X-ray diffraction, infrared and Raman spectroscopy, transmission electron microscopy, and adsorption/desorption of nitrogen. Further, the reducibility of cobalt species was studied using the thermal-programmed reduction technique. All the Co_3O_4/silica composites were mesoporous (3.9–5.4 nm) with considerably high porosity (321–567 $m^2\,g^{-1}$). The TEM mean size of Co_3O_4 nanoparticles within the calcined composites varied from 10 to 18 nm, according to the cobalt precursor employed in the synthesis. The reducibility of cobalt species also depended on the employed cobalt precursor, as shown by the thermal programmed reduction experiments. The composites which were prepared from the Co_3O_4 colloidal dispersions were reduced at lower temperatures; 80% of the total Co amount was reduced in the range of 300–500 °C. On the other hand, only 53% of total Co in the sample prepared from cobalt nitrate solution was reduced from 200 up to 900 °C. The difference on the reducibility was attributed to morphological characteristics of the composite samples.

1. Introduction

Nanocomposites based on cobalt oxide nanoparticles supported on silica matrix were widely investigated and employed as catalyst precursors for several reactions, the Fischer–Tropsch synthesis [1–7] being of great importance due to their significance in the conversion of biomass into liquid biofuels [8].

Different methods for the synthesis of cobalt/silica composites have been described and can be roughly split into two classes: one that cobalt is incorporated within a pre-synthesized silica matrix, including the impregnation [9,10], ionic exchange [11,12] and grafting [13] methods and the another which cobalt is incorporated in during the synthesis of the silica matrix, such as the precipitation [14] and the sol–gel [15,16] methods. According to this, the composite properties are strongly influenced by the employed preparation method [17], the sol–gel method appearing to be an important method which allows a good control of the textural characteristics of the material and a better dispersion of cobalt oxide into the silica matrix [18]. Generally, a solution of a cobalt salt is incorporated into a sol–gel mixture containing the silica precursor and, after gelation, aging and drying, the resulting xerogel is calcined to produce Co_3O_4 nanoparticles together with cobalt silicates which are species usually not desired [18]. On the other hand, the incorporation of previously synthesized nanoparticles into sol–gel mixtures is not a very common procedure, but it can be very advantageous for concerning the control of nanoparticle size [19] and the possibility of changing the interactions between both silica and cobalt species. Therefore, a good choice of investigations can be made because several synthetic methods for the preparation of cobalt oxide particles are available, such as pulsed laser deposition [20], sol–gel [21] reduction–oxidation [22], hydrothermal oxidation in gel [23] and cobalt salt decomposition [24–26], among others.

The aim of this work is to synthesize cobalt oxide/silica composites by the sol–gel method with tetraethylorthosilicate as the silica precursor and either an aqueous solution of cobalt nitrate or

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colloidal dispersions of cobalt hydroxide and cobalt oxide nanoparticle as cobalt precursors. All materials are characterized regarding composition, structure and texture using atomic absorption analysis, powder X-ray diffraction, infrared and Raman spectroscopy, nitrogen adsorption/desorption analysis and transmission electron microscopy. In view of the possible applications of these materials as metal catalysts, the reducibility of the cobalt species within the composites is also studied applying the thermal-programmed reduction technique.

2. Experimental

2.1. Materials

The materials being used in this work are: tetraethylorthosilicate 98%, TEOS, from Aldrich, USA; cobalt (II) nitrate hexahydrate from Nuclear, Brazil; sodium hydroxide, ammonium hydroxide and lauric acid from Vetec, Brazil, and ethanol 99% from Synth, Brazil. All reagents and solvents were used as received.

2.2. Synthesis and characterization

2.2.1. Synthesis of cobalt hydroxide and cobalt oxide nanoparticles

The cobalt hydroxide ($Co(OH)_2$) nanoparticles were synthesized by precipitation of Co^{2+} ions in alkaline medium. 50 mL of a 0.27 mol L^{-1} aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ was added drop wise to 300 mL of a 1.25 mol L^{-1} sodium hydroxide solution with vigorous mechanical stirring (2400 rpm) at room temperature [27]. The black colored solid sample was precipitated, which was isolated by centrifugation and then washed three times with 300 mL distilled water. A small portion of this solid sample was dried at 70 °C and kept in a desiccator for characterization. The majority of the solid sample was stored in water (50 mL) and employed afterwards for the preparation of the colloidal dispersion.

The cobalt oxide (Co_3O_4) nanoparticles were obtained by thermal treatment of a cobalt hydroxide sample which was previously synthesized as described above. After washing the $Co(OH)_2$ sample, the solid sample was dried at 70 °C for 24 h and then heated in air up to 350 °C during 60 min. A small portion of the solid was kept in a desiccator for further characterization and the other part was used for the preparation of colloidal dispersions.

2.2.2. Preparation of colloidal dispersions of cobalt oxide nanoparticles

The $Co(OH)_2$ which had been kept in water was sonicated during 10 min employing an immersion ultrasonic probe (750 W, 20 Hz, 30% amplitude), the resulting colloidal dispersion named ionic fluid of $Co(OH)_2$ nanoparticle, IFOH.

Two types of cobalt oxide dispersion were obtained; the preparation began by grinding the Co_3O_4 solid sample in an agate mortar and then passing it through a 200 mesh steel sieve. One of the dispersions was prepared by simply sonicating 0.73 g of the Co_3O_4 sample in 50 mL distilled water for 10 min, resulting in a colloidal dispersion which was named ionic fluid of Co_3O_4 nanoparticles, IFO. The procedure to obtain the other type of Co_3O_4 dispersion started with the preparation of an ionic fluid of Co_3O_4 nanoparticles which was heated at 60 °C and stirred vigorously while adding lauric acid (0.90 g). After a few minutes, phase separation was observed indicating that Co_3O_4 nanoparticles had been covered with a monolayer of lauric acid. Immediately, the pH of the mixture was adjusted to 8 with a dilute solution of ammonium hydroxide and the temperature was raised to 75 °C in order to increase the solubility of lauric acid. After stirring 30 min, a very stable colloidal dispersion of Co_3O_4 nanoparticles arose, suggesting that a bilayer of lauric acid had been formed on the nanoparticles' surface. This dispersion was named lauric acid fluid of Co_3O_4 nanoparticles, LFO.

2.2.3. Preparation of cobalt oxide–silica-based composites from different cobalt precursors

The cobalt oxide–silica-based composites were prepared by the sol–gel method in basic conditions [28–30], using TEOS as the silica precursor and either an aqueous solution of cobalt nitrate or the colloidal dispersions of cobalt hydroxide (IFOH) and cobalt oxide (IFO and LFO) as the cobalt precursor.

Initially, 20 mL TEOS and 190 mL ethanol were added together in a round bottom flask coupled to a reflux system. The mixture was heated up to 50 °C and stirred magnetically, while 86.5 mL of 0.14% ammonium hydroxide solution was added drop wise. By the time the addition was completed, stirring and heating were maintained during 3 h. After this, silica sol was poured into a glass container and again stirred and heated at 70 °C for the 3 following hours, allowing the ethanol to evaporate. Every 15 min the volume of the silica sol was adjusted to the initial amount, using distilled water. The pH of the medium was adjusted to 8 and either 20 mL of 0.46 mol L^{-1} cobalt nitrate solution or 50 mL of the colloidal dispersion of cobalt oxide nanoparticles (IFOH, IFO or LFO) were incorporated into the silica sol. After stirring the resulting colloidal dispersion for a few minutes, the pH was adjusted to 9. The resulting sol was poured into a polyethylene recipient and heated to 70 °C during 48 h in order to gelate and dry. At this point the following dried gels (xerogels) were obtained: SiCo(IFOH), SiCo(IFO), SiCo(LFO) and SiCo(S), the latter being prepared by employing cobalt salt. The final composites were obtained after calcination of the xerogels at 700 °C for 2 h. A reference SiO_2 sample was also prepared using the same method.

2.2.4. Characterization of cobalt oxide nanoparticles and composites

The amount of cobalt in the composites was determined by atomic absorption analysis, using a Perkin Elmer instrument, Analyst 200. The powder X-ray diffractograms (XRD) of the samples were recorded in a Shimadzu/XRD 6000, using CuKα radiation ($\lambda = 1.54056$), 40 kV, 30 mA and 2θ in the range of 10–80 degrees. The crystalline phase was identified by using the JCPDS (Join Committee on Powder Diffraction Standards) data and the crystallite diameters were estimated by using the Scherrer's equation [31].

Fourier transform infrared spectra (FTIR) of non-calcined and calcined samples were recorded in a Bomem/MB100 spectrometer in the region of 4000–400 cm^{-1}. Potassium bromide was used to prepare the 1% sample pellets. The Raman measurements were obtained in a triple spectrometer (Jobin Yvon, model T64000) equipped with a liquid nitrogen cooled CCD detector and Argon ion laser ($\lambda = 514$ nm). Samples were also analyzed by transmission electron microscopy (TEM) in a Jeol JEM 1011 instrument. All measurements were performed at room temperature.

Nitrogen adsorption–desorption isotherms were performed in a Micromeritics ASAP 2010 instrument, on samples previously degassed at 120 °C for 24 h, under vacuum. The specific surface areas were calculated based on the adsorption curve (BET method) and the pore size distribution curves were obtained from the desorption branch, using the Barrett–Joyner–Halenda (BJH) method.

The TPR experiments were carried out in a Micromeritics Pulse Chemisorb 2900 equipment with a thermal conductivity detector. Samples (0.035–0.055 g) were previously heated under nitrogen at 200 °C for 1 hour in order to remove adsorbed water. After cooling down to room temperature, the measurements were performed from 30 °C to 1000 °C at a rate of 10 °C min^{-1} using a 5% H_2/N_2 mixture.

Previously to the analysis, samples were grinded in an agate mortar and passed through a 100 mesh steel sieve.