

The key role of support surface tuning during the preparation of catalysts from reverse micellar-synthesized metal nanoparticles

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Abstract

Silica-supported cobalt catalysts have been prepared by depositing cobalt nanoparticles synthesized in reverse micellar systems. Two different reverse microemulsions comprising both a neutral (Triton X114) or an ionic (AOT) surfactant were used for the synthesis of nanoparticles. The materials have been characterized by ^{29}Si MAS NMR, XRD, FTIR, H_2 -TPR, and TEM. Protection of the hydroxyl groups on the silica surface by silylation prior to loading of the cobalt nanoparticles has been found crucial for attaining the desired metal dispersions in the final catalyst owing to a higher chemical compatibility between the hydrophobic support surface and the microemulsion during the deposition step.

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1. Introduction

Reverse micellar synthesis (also known as w/o or reverse microemulsions) of metal nanoparticles is an attractive route to prepare materials with applications in a wide range of disciplines, such as optics, magnetism, electrochemistry, and heterogeneous catalysis [1,2]. The microemulsion parameters and the concentration of the metal precursor in the aqueous phase can be used to finely tune the metal particle size with a very narrow size distribution [3]. These features are of major importance in heterogeneous catalysis on supported metal catalysts, since in many cases the final metal dispersion determines the overall catalyst activity and, sometimes, the product selectivity. The deposition of the metal nanoparticles from the aqueous cores of the microemulsion onto the surface of a suitable carrier is a crucial step in the preparation of supported metal catalysts by this methodology. Two main approaches have been

developed for this purpose. In one of them, the oxidic carrier (e.g. SiO_2 , Al_2O_3 , TiO_2 , and ZrO_2) is generated in situ after the synthesis of the metallic nanoparticles in the micellar medium, for instance, by hydrolysis and condensation of alkoxide-type precursors [4,5]. This approach, however, suffers from two main limitations. On one hand, the yield at which the carrier is obtained (and thus the final metal loading) can not be easily controlled, and even more important, some of the metal particles become totally or partially embedded in the supporting phase [4]. Even if the later feature may be favorable when preparing shell-protected metal-oxide composites, it is undesirable for catalytic applications as it reduces the accessible metallic surface in the final catalyst.

In a second approach, the metal nanoparticles are transferred to the outer surface of the carrier by contacting the solid with the reverse microemulsion and subsequent destabilization of the micellar medium, for instance by addition of a solvent such as tetrahydrofuran (THF) [6]. Although this methodology overcomes the problem of metal embedding by the carrier, the final metal dispersions obtained are usually much poorer than those expected from the metallic

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particle size determined by directly loading the nanoparticles from the micelles onto a carbon covered TEM grid, indicating the occurrence of extensive particle agglomeration [7]. Although the rate of addition of THF during the particle deposition has been claimed to be crucial for avoiding particle coalescence [7], sizes above 15 nm are commonly obtained for Pt [7], Pt–Pd [8] or Pt–Ir [9] particles loaded on oxidic carriers even when using extremely low THF addition rates. Therefore, the final dispersion levels obtained by this route do not seem to offer any advantage with respect to more conventional preparations, such as impregnation.

In this communication, we show that the loss of metal dispersion during the loading of metal nanoparticles synthesized in reverse microemulsions on oxidic carriers can be avoided by increasing the hydrophobicity of the support through silylation of its surface hydroxyl groups owing to an enhanced chemical compatibility between the surface of the support and the micellar medium. The relationships between the nature of the support-microemulsion interface and the final metal dispersion are shown here for the important case of Co/SiO₂ catalysts, which are widely applied for the production of ultra-clean synthetic fuels from syngas (mixture of CO and H₂) through the well-known Fischer–Tropsch (FT) process [10].

2. Experimental

2.1. Preparation of the silica supports

Amorphous spherical-shaped silica (silica gel 100, Fluka) either as purchased or after a surface silylation treatment was used as support for the preparation of Co/SiO₂ catalysts by the reverse microemulsion method. The untreated SiO₂ sample has a BET surface area of 387 m²/g and a total pore volume of 0.81 cm³/g as determined by N₂ physisorption. Silylation of the commercial silica was accomplished by degassing the sample at 300 °C under vacuum for 2 h and then mixing the solid with a solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Aldrich, 97%) in toluene in a molar ratio of 1 SiO₂:0.15 HMDS:10 toluene. The slurry was refluxed at 120 °C for 2 h under dry nitrogen atmosphere. Finally, the solid was recovered by filtration, washed with toluene, and dried at 60 °C overnight.

Prior to the deposition of cobalt nanoparticles from the microemulsion, the non-silylated silica sample was dehydrated at 150 °C for 2 h and then cooled down to room temperature in a vacuum-desiccator.

2.2. Synthesis of cobalt nanoparticles

Reverse microemulsions were prepared by mixing an organic solution of the surfactant in *n*-hexanol (HPLC grade, Aldrich) with an aqueous solution of Co(NO₃)₂ · 6H₂O (Aldrich) under stirring. Two different surfactants, sodium bis(2-ethylhexyl) sulfosuccinate (AOT, Fluka) and polyoxyethylene (8) octylphenyl ether (Triton

X114, Aldrich), were used as representative of the ionic and non-ionic surfactants, respectively. Ionic surfactants are commonly used to prepare stable metal colloids very small in size, while non-ionic surfactants are generally employed when trying to avoid counterion interactions at the inner boundary of the reverse micelles [11]. Unless otherwise specified, the molar water-to-surfactant ratio (ω) was set at a value of 8. The cobalt concentration in the aqueous phase was 0.3 M, and the surfactant concentration in the organic phase was 1 M. Thermodynamically stable, reddish transparent microemulsions were obtained in all cases.

Hydrazine hydrate (N₂H₄ · 1H₂O, Aldrich, 98%) was directly added to the microemulsions in a 20-fold molar excess with respect to the stoichiometric amount according to the following reduction equation: 2Co²⁺ + N₂H₄ + 4OH⁻ → 2Co⁰ + N₂ + 4H₂O. Even if it is likely that hydrazine is not a strong enough reductant to completely reduce the Co²⁺ cations to Co⁰ at room temperature [1], the goal of adding hydrazine here is just nanoparticulating the cobalt phase. Since the supported catalysts are submitted to calcination in air to remove the organic material and subsequent reduction in H₂ to obtain the metallic cobalt particles, the state of the cobalt upon addition of hydrazine becomes less relevant from the point of view of the properties of the final catalysts.

2.3. Preparation of Co/SiO₂ catalysts

The silica support (silylated or non-silylated) was immediately added to the microemulsion and the slurry was thoroughly stirred for 3 h. Afterwards, THF was added at a rate of 0.33 mL/min in an amount of 100 mL per gram of support. Then, the solid was decanted, vacuum-filtered, exhaustively washed with ethanol and dried at room temperature overnight and at 60 °C for 10 h. Finally, the solid was calcined in flowing air at 500 °C for 3 h in order to remove the organic material, including the anchored trimethylsilyl groups in the case of the silylated silica support. In all cases, the carbon content after calcination as determined by elemental analysis was very low (<0.4 wt%). The nominal cobalt content in all catalysts was 5 wt%.

The prepared Co/SiO₂ catalysts were denoted as Co_X_Y, where X refers to the surfactant (TT for Triton X114 and AOT) and Y indicates the silica support used (US for the untreated silica and SS for the silylated one). For instance, the catalyst prepared using the microemulsion with Triton X114 and the silylated silica is denoted as Co_TT_SS.

2.4. Characterization techniques

The cobalt loading in the calcined catalysts was determined by atomic absorption spectrophotometry (AAS) in a Varian Spectra A-10 Plus apparatus. X-ray diffraction (XRD) patterns of calcined samples were obtained in a

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