



# Hydrogen from steam reforming of ethanol over cobalt nanoparticles: Effect of boron impurities



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## ABSTRACT

Cobalt nanoparticles have been prepared by reduction of cobalt chloride by sodium borohydride. They are very active catalysts for ethanol steam reforming at moderate temperature. The best catalytic materials show full ethanol conversion and hydrogen yields of the order of 83% and stable activity for 8 h when tested at 773 K, GHSV 324,000 h<sup>-1</sup> with diluted 1:6 ethanol:water feed in He 41.6%. The amount of coproduced methane is very low (yield <0.05%). Experiments performed at different space velocities provide evidence of the intermediate formation of acetaldehyde in the ethanol steam reforming path. The fresh Co nanopowders are amorphous and are actually contaminated mainly by Boron species and traces of Na, Cl and C. During reaction, Cobalt nanoparticles are transformed into cubic metallic Co crystallites. The surface properties of these materials are very sensitive to: (I) the separation procedure from the reaction medium at the end of the preparation step, and (II) the conditions of ageing and storage in the laboratory. An increasing time of ageing seems to favor the formation of borates species and the observed oxidation of metallic cobalt to cobalt oxides. These phenomena could be associated to the loss in the catalytic activity that results in a lower ethanol conversion, lower hydrogen yield and sometimes, higher selectivity to acetaldehyde.

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## 1. Introduction

Bio-ethanol steam reforming is a possible way for producing renewable hydrogen and syngas [1–9]. In spite of the many studies undertaken recently on Ethanol Steam Reforming (ESR), no consensus was still obtained on the best conditions for performing ESR nor on the best catalyst formulation.

In the era of nanotechnology, catalysis by metal nanoparticles became a relevant field of investigation. In fact, a number of methods were developed allowing the preparation of well-characterized and shaped metal nanoparticles [10]. This allowed to test the effect of the size and shape of particles on catalytic activity. As for example, Alayouglu et al. [11] investigated monodisperse platinum nanoparticles with the shapes of octahedron, cube, truncated

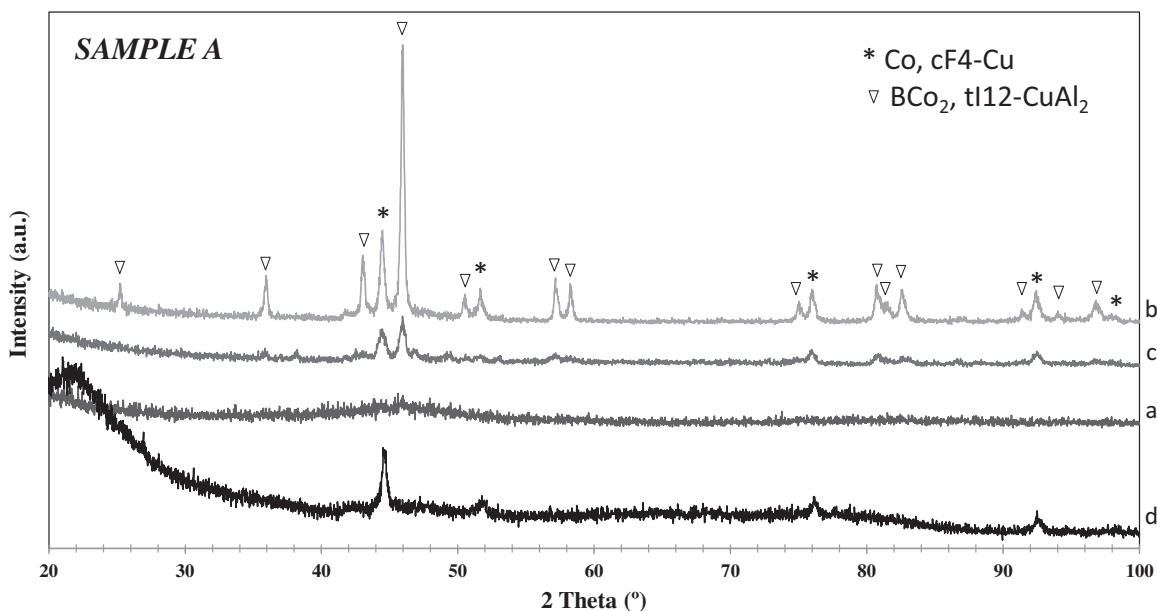
octahedron, and sphere, and tested them in methyl-cyclopentane ring opening in the presence of hydrogen. These studies could also allow to compare the catalytic data with those arising from monocrystal data, thus attributing the catalysis on nanoparticles to the activity of the exposed faces or, alternatively, of corners and edges. On the other hand, metal nanoparticles are indeed very efficient catalysts for a number of organic reactions, as shown in the case of Pd nanocrystals [12]. However, the thermal stability of unsupported metal nanoparticles is generally weak, their applicability being usually limited to liquid phase reactions performed at low temperature; alternatively they may be essentially regarded as model catalysts, whose activity is limited to small time on stream experiments.

Cobalt is an active catalyst for a number of hydrogenation reactions. It has been used, mostly supported such as e.g., the Co/Al<sub>2</sub>O<sub>3</sub> or Co/SiO<sub>2</sub>-ZrO<sub>2</sub> catalysts, in the low-temperature Fischer Tropsch process [13], CoO/SiO<sub>2</sub> and CoO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CoO/ZrO<sub>2</sub>-Kieselguhr catalysts for hydrogenation of oxoaldehydes and amination of alcohols and the reductive amination of aldehydes and ketones for the manufacture of ethylamines and propylamines [14–17].

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**Fig. 1.** XRD of catalyst A: fresh (a); after annealing at 773 K for 3 h in Ar (b); aged sample after annealing at 773 K for 3 h in Ar (c); exhaust sample after catalysis at 51,700 h<sup>-1</sup> (d).

Unsupported cobalt has been used in the past for Fischer Tropsch synthesis [18], while Raney-type “sponge” cobalt is commercially available for use in the hydrogenation of nitriles and nitro compounds to amines [19].

Unsupported cobalt catalysts produced by reducing Co oxide where found to be very active for ESR [20–22]. Recently, we found that unsupported cobalt nanoparticles (NPs), prepared by reducing Co chloride with NaBH<sub>4</sub>, may act as very good catalysts for ESR at least upon short time on stream experiments [23]. In particular, they allowed high hydrogen yield (over 85%) at moderate temperatures with low CO and CH<sub>4</sub> coproduction. XRD analysis did not show any crystalline phase in case of the fresh catalyst and the characteristic pattern of cubic metallic Co after its use. However, the fresh catalyst after annealing at the reaction temperature (773 K) also shows, besides the pattern of cubic Co metal, some reflections attributed to poorly crystallized cobalt boride Co<sub>2</sub>B, showing the presence of boron impurities and their strong interaction with cobalt. Indeed, the presence of impurities arising from the preparation procedure and from the precursor salts and their roles in modifying the catalyst behavior is a relevant point in the field of heterogeneous catalysis. With the preparation adopted, boron and sodium impurities arising from the reductant as well as chlorine arising from the cobalt source can be expected.

As a development of our previous work, we wanted to investigate whether the contamination of the nanoparticles could affect the catalytic activity of the resulting Co nanoparticles. In particular we will focus our attention on contamination by boron, the main contaminant residue of the reducing agent.

## 2. Experimental

### 2.1. Preparation of cobalt nanoparticles

Co-based nanoparticles were prepared using a reduction method in aqueous solution. In a typical synthesis procedure, a controlled excess of sodium borohydride is added as reducing agent to a 10<sup>-2</sup> M solution of CoCl<sub>2</sub>·6H<sub>2</sub>O maintained at room temperature under mechanical stirring and argon flux as described elsewhere [23,24]. The addition of the reductive agent is quickly followed by the appearance of a black precipitate. The reaction is then main-

tained for 15 min under the inert flux and stirring. The separation from the reaction medium and as well the washing procedure were carried out in different ways for the different samples prepared. Four samples, hereinafter denoted A–D, will be considered here. The different separation procedures will be described in the corresponding section. Depending on whether the sample has been tested and characterized few days after the preparation, several weeks or months after the preparation, or after catalytic runs, they will be denoted as “fresh”, “aged” or “exhaust”, respectively.

### 2.2. Characterization techniques

X-ray diffraction patterns on dried nanoparticles, annealed at 773 K for 3 h, and on the exhaust samples (after the ESR experiment) were carried out by using a vertical powder diffractometer X’Pert with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The patterns were usually collected in the 25–100°  $2\theta$  range with a step of 0.02° and a counting time for each step of at least 12 s. Powder patterns were indexed by comparing experimental results to the data reported in the Pearson’s Crystal Data database [25].

IR spectra were recorded with ThermoFisher Instrument using KBr pressed disks (1% wt/wt of sample, total weight 0.8080 g).

A scanning electron microscope ZEISS SUPRA 40 VP, with a field emission gun, was used to study the morphology of all the prepared catalysts (FE-SEM measurements). This instrument is equipped with a high sensitivity “InLens” secondary electrons detector and with an EDX microanalysis OXFORD “INCA Energie 450  $\times$  3”. Samples for SEM analysis were suspended in ethanol and exposed to ultrasonic vibrations to decrease the aggregation. A drop of the resultant mixture was finally laid on a Lacey Carbon copper grid.

XPS measurements were performed using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K $\alpha$  radiation (300 W, 15 kV, and 1253.6 eV) and Al K $\alpha$  radiation (300 W, 15 kV, and 1456.6 eV) with a multi-channel detector. Spectra of fresh, aged or exhausted samples were recorded in the constant pass energy mode at 29.35 eV, using a 720  $\mu$ m diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHIACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted

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