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# Cobalt particle size effects on catalytic performance for ethanol steam reforming – Smaller is better



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Andre L.M. da Silva<sup>a</sup>, Johan P. den Breejen<sup>b</sup>, Lisiane V. Mattos<sup>a,1</sup>, Johannes H. Bitter<sup>b,2</sup>, Krijn P. de Jong<sup>b</sup>, Fábio B. Noronha<sup>a,\*</sup>

<sup>a</sup> Instituto Nacional de Tecnologia – INT, Av. Venezuela 82, 20081-312 Rio de Janeiro, Brazil <sup>b</sup> Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, Sorbonnelaan 16, 3508 CA Utrecht, The Netherlands

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#### ABSTRACT

The effect of the cobalt particle size in the ethanol steam reforming reaction at 773 K for hydrogen production was investigated using cobalt on carbon nanofiber catalysts. It was found that the turnover frequency increases with decreasing Co particle size, which was attributed to the increasing fraction of edge and corner surface sites with decreasing size. Regarding catalyst stability, a decrease in deactivation rate was observed with decreasing cobalt particle size. This was caused by a significantly lower amount of carbon deposition on the smallest Co particles than on larger ones, as concluded from transmission electron microscopy measurements. The reduced amount of carbon deposition is ascribed to a lower fraction of terrace atoms, proposed to be responsible for initiation of carbon deposition on catalysts with large (>10 nm) Co particles. Therefore, it was concluded for this non-noble metal that the smallest particles perform best in catalysis of ethanol steam reforming.

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#### 1. Introduction

The understanding of particle size and shape effects on catalytic activity and selectivity requires a fundamental insight in the relation between surface structure and catalyst performance [1-5]. This relation does also depend on the type of bonds of reactants involved. For example, for  $\pi$ -bond activation an optimum particle size is generally found, below which the surface-specific activity drops. Examples are provided in the ammonia synthesis [6] and Fischer–Tropsch catalysis [7–9] in which the N<sub>2</sub> and CO bonds have to be activated, respectively. In case of the ammonia synthesis, an optimum metal particle size could be attributed to a maximum in the number of specific surface sites facilitating  $\pi$ -bond activation [6]. For  $\sigma$ -bond activation, e.g., in hydrogenolysis and CH<sub>4</sub> activation reactions, the particle size-performance relations are less unambiguous. For noble metals both a decrease [10,11] and an increase [12–18] in surface-specific activity with decreasing particle size has been observed. For non-noble metals, however,

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information on the effect of particle size on catalyst performance in  $\sigma$ -bond activation reactions is scarce [19,20]. This is most likely related to the hampered reducibility of small non-noble metal particles. Moreover, the small particles may interact strongly with an oxidic support, which may result in the formation of stable mixed oxides during calcination, reduction or reaction. With the advent of inert nanostructured carbon support materials such as carbon nanofibers [21] and carbon nanotubes [22]; however, a possibility to study the intrinsic effects of the particle size of non-noble metals on activity and selectivity is provided. In the current study carbon nanofibers (CNF) were chosen as support material to study the effect of cobalt particle size on activity and selectivity in  $\sigma$ -bond activation in the steam reforming (SR) of ethanol reaction. In this case, the use of an inert support such as CNF or other carbonaceous materials [23] is fundamental since the majority of oxides are active for SR of ethanol. This approach using an inert CNF material is similar to the one applied in the study of the Co particle size effects in the  $\pi$ -bond activation in Fischer–Tropsch catalysis [7,24].

The SR reaction comprises a complex reaction network, including several reaction intermediates [25–29]. Recently, Ferrin et al. [30] showed using density functional theory (DFT) calculations for ethanol hydrogenolysis that the C–C bond cleavage, proposed to be the rate-determining step (RDS), of the CH–CO intermediate was facilitated on step sites. As the number of step sites increases



<sup>\*</sup> Corresponding author. Fax: +55 (21) 2123 1166.

*E-mail addresses:* k.p.dejong@uu.nl (K.P. de Jong), fabio.bellot@int.gov.br (F.B. Noronha).

 <sup>&</sup>lt;sup>1</sup> Present address: Universidade Federal Fluminense (UFF), Departamento de Engenharia Química e de Petróleo, Rua Passo da Pátria 156, 24210-240 Niterói, Brazil.
<sup>2</sup> Present address: Wageningen University, Wageningen, The Netherlands.

with decreasing particle size, a particle size effect in SR catalysis is therefore expected. However, experimental studies about the intrinsic effects of the particle size on the SR reaction are scarce and contradictory. A study by Ribeiro et al. [31] showed an indicative trend of an increasing surface-specific activity (TOF) with decreasing Co particle size (<8 nm) for the SR of ethanol over Co/ SiO<sub>2</sub> under mild conditions where ethanol was mainly dehydrogenated to acetaldehyde. Song and Ozkan [32] studied the performance of Co/ZrO<sub>2</sub>, Co/CeO<sub>2</sub>, and Co/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts on the SR. The TOF calculated at 723 K for the three catalysts increased in the order:  $Co/ZrO_2$  (0.054 s<sup>-1</sup>) <  $Co/CeO_2$ -ZrO<sub>2</sub> (0.214 s<sup>-1</sup>) < Co/ $CeO_2$  (0.476 s<sup>-1</sup>). Cobalt crystallite size determined by XRD for the reduced and passivated catalysts revealed a correlation between intrinsic activity and crystallite particle size, which followed the order:  $Co/ZrO_2$  (15 nm) <  $Co/CeO_2$ -ZrO<sub>2</sub> (20 nm) < Co/ $CeO_2$  (25 nm). However, the supports used are significantly active for SR. Therefore, the careful elimination of the effect of the support is fundamental to determine the intrinsic cobalt particle size effects on the SR reaction.

Even more important than activity is catalyst stability which might be dependent on particle size or number of surface ensemble sites too. The effects of particle size on for example carbon deposition in  $CH_4$  reforming or decomposition over Ni-based catalysts have been demonstrated, showing that the lowest amount of coke is formed on the smallest particles [33–35]. The number of studies toward an understanding of the effect of particle size on catalyst stability for SR of ethanol, though, is rather limited.

Here, we report on the effects of cobalt particle size and related surface structure on the activity, selectivity, and stability in the SR of ethanol reaction using Co/CNF catalysts. The aim of this research was to obtain a quantitative understanding of the relation between the number of specific sites on the surfaces of Co particles, using a geometrical model, and their activity and stability.

### 2. Experimental

### 2.1. Catalyst preparation

The carbon nanofiber support material (SA =  $200 \text{ m}^2 \text{ g}^{-1}$ ,  $PV = 0.65 \text{ mL g}^{-1}$ ) was obtained from synthesis gas using a 5 wt% Ni/SiO<sub>2</sub> growth catalyst. The obtained material was purified in subsequent reflux treatments of 1 M KOH and concentrated HNO<sub>3</sub>. In the latter step, oxygen-containing groups required to achieve high metal dispersions were introduced [36]. The cobalt catalysts were obtained using incipient wetness impregnation of cobalt acetate tetrahydrate or cobalt nitrate hexahydrate solutions in either water or ethanol, aiming for various Co loadings (0.9-22 wt%) [7]. After impregnation, the samples were dried in static air at 393 K. Subsequently, a reduction was conducted at 623 K for 2 h, in a flow of 30 vol% H<sub>2</sub> in N<sub>2</sub>, followed by a passivation at room temperature by exposure of the catalyst to air. The cobalt particle sizes were determined using H<sub>2</sub>-chemisorption, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) analysis. Co/CNF catalysts with cobalt particle sizes ranging from 2.6 to 16 nm were obtained.

#### 2.2. Catalyst characterization

Cobalt particle sizes were determined by H<sub>2</sub>-chemisorption using a Micromeritics ASAP 2010C. Before each measurement, the samples were dried in vacuum at 393 K for 2 h followed by a reduction (5 K min<sup>-1</sup>) in H<sub>2</sub> flow at 623 K for 2 h. Subsequently, the samples were evacuated at that temperature for 30 min. The H<sub>2</sub> adsorption isotherms were measured at 423 K. From extrapolation of the linear part of the isotherm to zero pressure, the total hydrogen uptake was determined. Based on that, the cobalt particle sizes were calculated assuming a hemispherical particle geometry and an H/Co<sub>s</sub> adsorption stoichiometry of 1 [37].

XPS measurements were carried out on passivated Co/CNF samples in a Vacuum Generators XPS spectrometer using Al K $\alpha$  radiation. The surface atomic ratios were calculated from photoelectron peak areas after correcting for photoionization cross sections and photoelectron mean free paths. Subsequently, the Co particle size was calculated from the XPS intensity ratios of the Co 2p<sub>3/2</sub> and C 1s peaks ( $I_{Co}/I_C$ ) using a model based on the work described by Kuipers et al. [38].

TEM analysis was used to study the cobalt particle sizes of the fresh and spent catalysts. The catalysts were suspended in ethanol, and brought onto a carbon support film on a copper TEM grid. The TEM measurements were conducted with a Tecnai 20 FEG microscope operating at 200 kV.

Thermogravimetric analysis of the fresh and used Co3 and Co16 catalysts was carried out in a TA Instruments equipment (SDT Q600). The sample was heated under air from room temperature to 1273 K at a heating rate of 20 K/min.

Temperature-programmed surface reaction (TPSR) was performed in a microreactor coupled to a quadrupole mass spectrometer (Omnistar, Balzers). The sample (50 mg) was reduced under flowing  $H_2$  (30 cm<sup>3</sup>/min) up to 623 K (5 K/min) and maintained at that temperature for 1 h. After reduction, the system was purged with helium at the reduction temperature for 30 min and cooled to room temperature. A mixture containing  $H_2O/He$  (60 cm<sup>3</sup>/min) was passed through the sample as the temperature was raised at 10 K/min to 773 K, and it was kept for 1 h. The reaction products were monitored with a quadrupole mass spectrometer.

## 2.3. SR reaction

The SR of ethanol reaction was performed in a fixed-bed reactor at atmospheric pressure. Prior to reaction, the Co/CNF catalysts were reduced at 623 K for 1 h and then purged under N<sub>2</sub> at the same temperature for 30 min. All reactions were carried out at 773 K and H<sub>2</sub>O/ethanol molar ratios of 3.0 and 10.0 were used. The reactant mixtures were obtained by flowing two N<sub>2</sub> streams (30 mL min<sup>-1</sup>) through two saturators, one containing water and the other one containing ethanol, which were maintained at the temperature required to obtain the desired H<sub>2</sub>O/ethanol molar ratios. The partial pressure of ethanol was maintained constant for all experiments. The variation of partial pressure of N<sub>2</sub>.

Two different series of experiments were carried out to determine the intrinsic activity and to study the catalyst deactivation. In the first series, different amounts of catalyst (2.5–5.0 mg) and N<sub>2</sub> flow rates (120–180 mL min<sup>-1</sup>) were used in order to obtain low ethanol conversions (iso-conversion). Then, reaction rate  $(mol_{EtOH} g_{Co}^{-1} s^{-1})$  and Turnover Frequency (TOF;  $mol_{EtOH} mol_{surf,Co}^{-1} s^{-1})$  were calculated taking into account the initial ethanol conversion that was taken after 0.2 h TOS. For the calculation of TOF, the cobalt particle size determined by H<sub>2</sub>-chemisorption or XPS was used. In the second series, 20 mg of catalyst and a total flow rate of 60 mL min<sup>-1</sup> were used for all catalysts in order to observe the catalyst deactivation within 24 h time-on-stream (TOS).

The catalysts were diluted with inert SiC. The reaction products were analyzed by a gas chromatograph (Micro GC Agilent 3000 A) containing three channels for three thermal conductivity detectors (TCD) and three columns: a molecular sieve, a Plot Q, and an OV-1 column. The ethanol conversion and product distribution were determined from:

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