



Cobalt oxide supported on alumina catalysts prepared by various methods for use in catalytic afterburner of PEM fuel cell

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ABSTRACT

In the present work we have investigated the influence of the preparation method on the physicochemical and activity features of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts used for the combustion of anode tail gas produced in a proton-exchange membrane (PEM) fuel cell. The catalysts prepared contain 21% (w/w) Co and have been calcined at 850 °C. Three different impregnation methodologies have been followed: incipient wetness impregnation (IWI) using a cobalt nitrate aqueous solution, incipient wetness impregnation using a mixed cobalt nitrate–nitrilotriacetic acid (IWI-nta) aqueous solution and equilibrium deposition filtration (EDF) using a cobalt nitrate aqueous solution. The catalysts were characterized using nitrogen adsorption for determining the specific surface area, the pore volume and the mean pore diameter as well as using X-ray powder diffraction (XRD), diffuse reflectance spectroscopy (DRS; UV–vis), LRS, X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR). Catalytic activity measurements were performed in the temperature range 250–850 °C using a continuous flow fixed-bed micro-reactor working under atmospheric pressure and fed with a reaction mixture consisted of 15% H_2 /3% CO /1.1% CH_4 /20% O_2 balanced in He.

The EDF methodology imposed interfacial deposition and resulted to the formation of an almost bi-dimensional surface precipitate. Upon calcination, this surface precipitate provided a very well-dispersed CoO_x amorphous species strongly interacted with the support surface and thus hardly reducible as well as relatively small Co_3O_4 supported nanocrystals (14.3 nm). The first phase is the predominant one. Therefore, EDF resulted to a catalyst with the highest cobalt surface and specific surface area. The conventional IWI imposed bulk (solution) precipitation and thus induced relatively large supported crystallites which upon calcination provided relatively large supported Co_3O_4 nanocrystals (19.8 nm) and CoAl_2O_4 as well. The formation of the relatively large nanocrystals and the insertion of cobalt inside the γ -alumina lattice to form CoAl_2O_4 may be responsible for the lowest cobalt surface obtained in this catalyst. The presence of the nitrilotriacetic acid in the impregnating solution induced the exchange of the water ligands of the Co(II) aqua complex present in the cobalt nitrate solution with organic ligands and thus the bulk precipitation of an organometallic complex. The more bulky organic ligands decreased the cobalt–support interactions. Thus, the insertion of cobalt inside the γ -alumina lattice and the formation of CoAl_2O_4 are inhibited upon calcination of the IWI-nta sample. This may be responsible for the relatively higher cobalt surface obtained with respect to that achieved in the IWI sample though the size of the Co_3O_4 nanocrystals is larger in the IWI-nta sample (25.8 nm). At relatively high reaction temperatures all catalysts exhibited almost the same activity for oxidation reactions. In contrast, at low reaction temperatures the EDF catalyst proved to be more active for the CH_4 production as well as for the oxidation of H_2 and CO . This behaviour may be attributed to the favourable physicochemical characteristics of this catalyst.

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1. Introduction

The rapid development in recent years of the proton-exchange membrane (PEM) fuel cell technology has stimulated research in all areas of catalysts used for generation of pure hydrogen (fuel reforming, water–gas shift and carbon monoxide preferential oxidation) as well as of anode tail gas combustion catalysts [1,2]. The principal aim in the latter case is the efficient use of the fuel cell effluents (CO, H₂ and CH₄) to produce via oxidation reactions the energy necessary for the hydrogen generation reactors and to minimize the CH₄ and CO emissions. Catalytic or non-catalytic burners are generally used for this purpose [2]. It should be noted that CH₄ is much more powerful greenhouse gas than CO₂.

Among the components of the effluent of a fuel cell, hydrogen is the most easily combusted. The opposite is true for the complete oxidation of any CH₄ present. Methane is, in effect, the least reactive of the hydrocarbons and therefore the most difficult to oxidise. It has been found that conventional three-way catalysts (containing Pd–Pt–Rh), currently used for gasoline-vehicle emissions control, show relatively poor methane conversion, when operating in stoichiometric air/fuel ratio [3]. In contrast, Pd–Pt catalysts are quite effective for methane oxidation [4]. On this basis, new catalysts containing Pd or Pd–Pt have to be designed in order to replace the conventional Pd–Pt–Rh catalysts [5]. Thus, a lot of research effort is addressed to this subject [6–13]. On the other hand, current commercial catalysts for cleaning exhausts from *natural gas vehicles* have three times higher noble metals (Pd–Pt) content (up to 300 g/ft³) than the standard gasoline three-way catalysts in order to oxidise methane efficiently [14].

Considering the relevant cost of precious metals the design of alternative and cheaper systems would be highly desirable [5]. Non-precious metal catalysts supported on various carriers seem to be a good alternative, especially for feeds without sulfur, as in the case of PEM fuel cell [15–22]. Cobalt oxide supported, mainly, on alumina as well as on other oxide supports is one of the most popular candidates studied for methane combustion [21–24]. The supported species formed on the surface of these catalysts, their dispersion and the strength of their interaction with the support as well as the nature of the latter influence drastically the activity of the above-mentioned catalysts.

We have recently studied cobalt oxide catalysts supported on γ -alumina [25–28]. It has been found that the preparation method followed has remarkable influence on the structural and activity features of these catalysts. A relatively large size of the supported “cobalt oxide” nanocrystallites is imposed by *bulk precipitation*. This is mainly realized by incipient wetness impregnation (IWI). In contrast, a quite small size of the supported “cobalt oxide” nanocrystallites, not strongly interacted with the support surface, is imposed by *interfacial precipitation*. This is realized by equilibrium deposition filtration (EDF) [29,30]. This phase has been found to be the optimum supported phase for complete oxidation reactions (e.g. benzene oxidation) [30].

In the above-mentioned studies [25–30] the calcination temperature did not exceed 650 °C. On the other hand in an “afterburner” the temperature reaches, and in some cases exceeds, 800 °C. For this reason in the present work we have investigated the influence of preparation method on activity features of CoO_x/ γ -Al₂O₃ catalysts *calcined at 850 °C*. Specifically, we have compared the catalytic activity of three “cobalt oxide”/ γ -alumina catalysts prepared by three different preparation methodologies: conventional IWI using a cobalt nitrate aqueous solution, incipient wetness impregnation using a mixed cobalt nitrate–nitrilotriacetic acid aqueous solution (IWI-nta) [31] and EDF using a cobalt nitrate aqueous solution [32–36].

The second, *also principal*, goal of the present work is to examine whether the change in the impregnation method could influence the final physicochemical characteristics of cobalt-supported γ -alumina catalysts calcined at relatively high temperature (850 °C). This will allow interpreting eventual differences in the catalytic activity by taking into account the changes in the physicochemical characteristics of the supported catalysts brought about by replacing the conventional IWI technique with the aforementioned impregnation methods. Thus, the catalysts prepared have been characterized using, jointly, various physicochemical techniques (BET, XRD, UV–vis DRS, XPS, Raman and TPR).

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Materials

Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O, 99% of purity] purchased from Merck has been used for the preparation of the solutions used in the preparation of the catalysts. Ammonium nitrate stock solutions, used for regulating the ionic strength, were prepared from the respective solid (Merck, 99% of purity). Nitrilotriacetic acid 2 M solution was used in the preparation of the IWI-nta catalyst. γ -Alumina powder, 90–150 μ m, was used as support. This is obtained by crushing AKZO γ -alumina extrudates (HDS-000-1.5mm E).

2.1.2. Preparation of the IWI sample

The IWI sample was prepared using successive dry impregnations of the support with suitable Co(NO₃)₂ aqueous solutions in order to obtain a final catalyst containing 21% (w/w) Co. After each impregnation step the sample was dried at 120 °C for 2.5 h and the final sample was calcined at 850 °C for 3 h.

2.1.3. Preparation of the IWI-nta sample

The IWI-nta sample, containing also 21% (w/w) Co, was prepared using successive dry impregnations. The solutions used in the impregnations were prepared by dissolving a given amount of the Co(NO₃)₂·6H₂O in an aqueous solution of nitrilotriacetic acid 2 M. The pH of this solution was regulated to be equal to seven. The impregnated material had a gel-like appearance and after drying at 120 °C for 2.5 h was transformed into a hard solid. The latter was crushed before the next impregnation. The final sample was calcined at 850 °C for 3 h.

2.1.4. Preparation of the EDF sample

The EDF sample was prepared at 25.0 ± 0.1 °C and pH 7.0 under N₂ atmosphere. A thermostated vessel (10 L) equipped with a pH control system involving a glass/saturated calomel electrode (Methrom) and a dosimat has been used. A volume of 5.0 L of cobalt nitrate solution (25 × 10^{−3} M) was poured in this vessel and its ionic strength was adjusted at 0.1 M by using NH₄NO₃. The pH was adjusted by adding NH₄OH 0.1 M aqueous solution under stirring. Ten grams of γ -alumina powder was added into the stirred solution. As the deposition of the Co(H₂O)₆²⁺ ions onto the alumina surface caused a decrease in the pH of the suspension, the pH control system fed a suitable amount of the NH₄OH solution to keep pH 7. When the pH control system stopped to feed NH₄OH solution, the suspension was filtered. The solid sample was dried in air at 120 °C for 2.5 h and calcined at 850 °C for 3 h. The Co(II) concentration in the solid was 21% (w/w). This was determined by measuring photometrically its concentration in the corresponding impregnating solution before and after deposition using a Cary 3 Varian spectrophotometer. The above measurements were based on the Nitroso R-Salz procedure [37].

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