



# Cyclodextrin-cobalt (II) molecule-ion pairs as precursors to active $\text{Co}_3\text{O}_4/\text{ZrO}_2$ catalysts for the complete oxidation of formaldehyde: Influence of the cobalt source



Lei Bai<sup>a</sup>, Frédéric Wyrwalski<sup>b</sup>, Maryam Safariamin<sup>b</sup>, Rudina Bleta<sup>b</sup>, Jean-François Lamonier<sup>b</sup>, Cédric Przybylski<sup>c</sup>, Eric Monflier<sup>b</sup>, Anne Ponchel<sup>b,\*</sup>

<sup>a</sup> College of Chemistry and Materials Engineering, Anhui Science and Technology University, Donghua Road, Fengyang, Eastern Bengbu, Anhui 233100, China

<sup>b</sup> Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), F-62300 Lens, France

<sup>c</sup> Univ. Evry Val d'Essonne, Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement (LAMBE), CNRS UMR 8587, Bld F. Mitterrand, F-91025 Evry, France

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## ABSTRACT

The present paper reports on the use of  $\beta$ -cyclodextrin ( $\beta$ -CD) during the preparation of zirconia-supported cobalt oxide catalysts by impregnation and their performances in the complete oxidation of formaldehyde. The effect of  $\beta$ -CD was carefully characterized at different stages of the preparation with respect to three cobalt precursors (i.e. cobalt nitrate, acetate and acetylacetonate) by UV-Vis spectroscopy, dynamic light scattering, mass spectrometry, TG-MS analysis, X-ray diffraction and temperature-programmed reduction. It was found that  $\beta$ -CD had a strong impact on the final properties of catalysts, both in terms of reducibility and dispersion of active species. The results were rationalized to the occurrence of complexation between the cobalt precursor and  $\beta$ -CD and highlighted the pivotal role played by the counteranion. The best combination was obtained using cobalt nitrate with a  $\beta$ -CD/cobalt ratio 0.1 while the beneficial impact of cyclodextrins for the impregnation method was successfully extended to other cyclodextrins ( $\alpha$ -CD and  $\gamma$ -CD).

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## 1. Introduction

Formaldehyde is a well-known volatile organic compound (VOC) used for its disinfectant and biocide properties but also as a precursor for the synthesis of various resins in the textile, automobile and wood industries. However, this VOC is highly toxic and regulations on its emissions will become more drastic in a near future [1]. Currently, no viable alternative to this compound has been found for its use in the industry. Among the different possible technologies to control HCHO emissions, heterogeneous catalysis processes occupy a prominent place with their intrinsic characteristics, including a limited energy consumption, a complete and selective elimination of pollutant, and possibly the use of renewable active materials [2,3]. The available literature on formaldehyde removal (process, mechanism or catalysts) is very limited compared to that devoted to other VOC molecules including alcohols, BTX and chlorinated compounds [4–11]. Supported noble

metals and bulk transition metal oxide are the two classes of catalysts studied in the total formaldehyde oxidation. Thus, room temperature oxidation of formaldehyde is possible using noble metals (e.g., Pt, Au, Pd) as active phases [12–17]. However the replacement of these elements in environmental process is challenging, due to the well-known limitation of their use, e.g. high price and limited resource. Transition metal oxide based materials offer a low-cost alternative to noble metal catalysts which have been investigated, mainly using manganese oxides [2,18–25]. The design of these materials through the improvement of the specific surface area, porosity, surface reducibility and dispersion is a way to improve their activity in the formaldehyde oxidation. Only a few number of studies have been addressed to the use of cobalt oxides in the formaldehyde oxidation [26–28], though the typical spinel structure of  $\text{Co}_3\text{O}_4$  has received a great interest for the oxidation of  $\text{CH}_4$ , CO and VOC thanks to its versatile redox properties and stability in air [9,10,29,30].

Over the past decade, significant efforts have focused on the enhancement of the efficiency of cobalt catalysts. Indeed, activities for catalytic oxidation are known to be influenced by a number of factors, including cobalt particle size, dispersion and reducibility of the metal species. In line with this, the preparation of nanostruc-

\* Corresponding author. Present address : Université Pierre et Marie Curie, Institut Parisien de Chimie Moléculaire, CNRS UMR 8232, 4 place Jussieu, 75252 Paris Cedex 05.

E-mail address: [anne.ponchel@univ-artois.fr](mailto:anne.ponchel@univ-artois.fr) (A. Ponchel).

tured  $\text{Co}_3\text{O}_4$  materials with different sizes and morphologies, such as nanorods, nanosheets or nanospheres [31,32] has been described and studied for complete oxidation reactions. Ordered mesoporous  $\text{Co}_3\text{O}_4$  has also been synthesized by nanocasting using porous carbons [33] or silica hard-templates, such as KIT-6 and SBA-15 [34,35]. These porous  $\text{Co}_3\text{O}_4$  replica were generally found to have surface areas in the range of 50–100  $\text{m}^2/\text{g}$  while their mesoporous characters facilitate the diffusion of the substrate during the catalytic oxidation of CO or VOCs [36–38].

From an industrial application point of view, the utilization of cobalt oxide nanoparticles in the supported form is still preferred over pure cobalt oxide nanomaterials because of their higher resistance to sintering and deactivation [39]. The most common method is probably aqueous impregnation of porous inorganic supports with cobalt nitrate, despite the fact that it can have the drawback of a premature aggregation of the active sites during the evaporation of the impregnation solvent. In order to affect the metal dispersion in cobalt catalysts, alternative impregnation preparations involve the use of various types of cobalt precursors [40], including specifically cobalt acetate [41,42] or organic chelating agents with a suitable stoichiometry. The latter are usually chemicals that can complex the cobalt ions while being readily eliminated during the further steps of the catalyst preparation (e.g. oxidative treatments). Thus, the employment of carboxylic acids, amino acids, amines carbohydrates [43–48] and water-soluble saccharide derivatives (e.g. sucrose or sorbitol) [49–51] has been the subject of several investigations to facilitate the formation of smaller oxide ( $\text{Co}_3\text{O}_4$ ) particles in cobalt catalysts. However, it should be noted that their amount should be controlled appropriately as their decomposition can result in a significant exothermic effect and alteration of both catalyst and support structures. Beyond the metal dispersion, the reducibility of the active cobalt species, and in particular that of the Co(III)/Co(II) redox couple, is another important factor that may affect the oxidation activity of the catalyst [52]. Thus, it is commonly accepted that, for comparable levels of metal dispersions, the easier the reduction of the dispersed  $\text{Co}_3\text{O}_4$  species, the higher the oxidation activity of the catalyst. The reducibility is generally dependent on several variables such as the type of Co precursor, the type of promoter and its loading, and the type of support [40,53]. In line with this, the use of supports (e.g. alumina) that strongly interact with cobalt oxide results in an increase in the fraction of hard-to-reduce cobalt species whereas supports (e.g. zirconia) with weak metal-support interactions facilitate the reduction of the cobalt oxide particles [54].

Cyclodextrins (cyclic oligosaccharides constituted of D-glucopyranose units) have emerged in recent years as interesting candidates for the stabilization of colloidal metallic nanoparticles [55,56] and synthesis of materials or catalysts [57–61] thanks to their ability to form host-guest complexes with molecules or adducts with metal salts [62,63]. Thus our group has previously established that the controlled addition of  $\beta$ -cyclodextrin during the impregnation step could have a significant beneficial impact on the dispersion and reducibility of supported cobalt species and on their catalytic behavior in the complete oxidation of formaldehyde [26] and Fischer-Tropsch synthesis [64]. Optimization of the ratio of  $\beta$ -CD to cobalt in the impregnating solution showed that the most effective  $\text{Co}_3\text{O}_4/\text{ZrO}_2$  catalyst was obtained using a ratio of 0.1, exhibiting a drop in light-off temperature of ca. 15 °C ( $T_{50}$ ) in the oxidation of formaldehyde [26]. This optimal ratio of 0.1, which in other words corresponds to approximately 2 OH groups per cobalt ion (on the basis that the  $\beta$ -CD has 21 OH groups in total), was linked to the formation of adducts of  $\text{Co}^{2+}$  with  $\beta$ -CD, in which the cobalt center would be coordinated to two O atoms of adjacent hydroxyl groups of  $\beta$ -CD. These complexes allowed to reduce the risk of particle aggregation by preventing the

interactions of cobalt ions together and their subsequent decomposition yielded the formation of smaller and more reducible supported cobalt oxide particles.

In the present paper, and in order to further examine the scope of cyclodextrins in the preparation of cobalt zirconia-supported catalysts, we have extended the investigation to other cobalt precursors. In particular, we have sought to compare the effects of the  $\beta$ -CD addition with respect to three different cobalt salts (i.e. cobalt nitrate, cobalt acetate and cobalt acetylacetonate) on the structure of the final  $\text{Co}_3\text{O}_4/\text{ZrO}_2$  catalysts (5 wt.% Co) prepared by impregnation and on their resulting catalytic performances in the complete oxidation formaldehyde (HCHO), viewed here as a major indoor pollutant with harmful effects on the human health [65]. The so-prepared materials have been carefully characterized by UV-Vis spectroscopy, dynamic light scattering, mass spectrometry,  $\text{N}_2$  adsorption/desorption, thermal analysis, X-ray diffraction and temperature-programmed reduction and then tested for the oxidation of formaldehyde. Interestingly, a correlation between the cyclodextrin-cobalt interactions and the dispersion, reducibility and catalytic activity of the cobalt oxide species has been found, supporting the important role of the combination between the cyclic oligosaccharide (with its large number of hydroxyl groups) and the cobalt precursor during the different steps of the catalyst preparation. Finally, the impact of other native cyclodextrins ( $\alpha$ -CD and  $\gamma$ -CD) on the catalytic behavior of cobalt zirconia-supported catalysts has also been investigated under optimized preparation conditions.

## 2. Experimental part

### 2.1. Chemicals

Native  $\beta$ -cyclodextrin ( $\text{C}_{42}\text{H}_{70}\text{O}_{35}$ ; MW = 1134  $\text{g mol}^{-1}$ ), abbreviated as  $\beta$ -CD, was kindly supplied by Roquette Frères (Lestrem, France).  $\alpha$ -cyclodextrin ( $\text{C}_{36}\text{H}_{60}\text{O}_{30}$ ; MW = 942  $\text{g mol}^{-1}$ ) and  $\gamma$ -cyclodextrin ( $\text{C}_{48}\text{H}_{80}\text{O}_{40}$ ; MW = 1297  $\text{g mol}^{-1}$ ), denoted as  $\alpha$ -CD and  $\gamma$ -CD respectively, were purchased from Wacker Chemie. All other reactants were purchased from Sigma-Aldrich, Strem Chemicals and Acros Organics in their highest purity and used without further purification. Distilled deionized water was used in all experiments.

### 2.2. Catalyst preparation

The starting support ( $\text{ZrO}_2$ ) was prepared according to a coprecipitation procedure previously described [59]. The support was calcined under air flow at 600 °C before use. The resulting zirconia has the following feature: specific surface area 62.6  $\text{m}^2 \text{g}^{-1}$  and BHJ pore size 6.6 nm. It is composed mainly of monoclinic- $\text{ZrO}_2$  with a small fraction of tetragonal phase (<15 wt.%). Cobalt oxide zirconia-supported catalysts were prepared by wet impregnation method using aqueous solutions of cobalt nitrate [ $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ ], cobalt acetate [ $(\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O})$ ] and cobalt acetylacetonate hydrate [ $(\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O})$ ] in the presence or absence of cyclodextrins. The concentration of the impregnating solutions was calculated to obtain 5 wt.% cobalt in the final catalyst while the amount of cyclodextrin was adjusted in order to have an initial molar ratio of cobalt to cyclodextrin of 0.1 or 1. After the impregnation step, the materials were dried overnight in an oven at 100 °C and calcined at 400 °C for 4 h in a flow of air (heating rate of 2 °C  $\text{min}^{-1}$  and 2 L  $\text{h}^{-1}$ , respectively). The so-obtained catalysts were denoted  $(\text{Anion})\text{-CD}_x/\text{Zr}$  where *Anion* designates the anion of the cobalt (II) precursor employed during the impregnation (N = nitrate, AC = acetate and acac = acetylacetonate) and *x* corresponds to the initial molar ratio of cobalt to cyclodextrin. Control

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