

## Effect of cobalt precursors and ceria support modification for the design of VOC oxidation catalysts

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### Introduction

Volatile organic compounds (VOC) are directly (toxic or malodorous nature) or indirectly (ozone precursors) harmful to human health. Catalytic oxidation is one of the most promising options for VOC elimination, since the reaction operates at temperatures much lower than those required for thermal incineration. The advantage of low oxidation temperature is a reduction of the fuel consumption, particularly for the treatment of large volumes of air containing VOC in low concentrations. Generally, noble metal catalysts present higher activities than other metal catalysts, but their manufacturing cost is high and their resistance to poisoning is low. Thus, efforts have been made to develop transition metal based catalysts with high catalytic activity. For high metal loadings, Co dispersion enhancement can be achieved by using organic complexes [1]. Moreover the ability of the support material to supply oxygen during the process can significantly enhance the catalytic activity.  $\text{Ce}_x\text{Gd}_{1-x}\text{O}_2$  solid solutions appear as promising candidates to be used as support since in comparison with  $\text{CeO}_2$ , such system present high oxygen mobility and redox properties [2]. This study examines the effect of the ethylenediamine use at the stage of cobalt impregnation and of the gadolinium addition to the ceria support on the catalytic performances of cobalt-ceria based catalysts devoted to the destruction of VOC(s) emitted by stationary source. Butanol has been chosen as VOC probe molecule, because alcohol concentration in the atmosphere is increasing.

### Materials and Methods

The starting ceria powder (calcined at 600°C) was first synthesized by hydrolysis of  $\text{Ce}(\text{NO}_3)_3$  with ammonia. Impregnation of  $\text{CeO}_2$  using cobalt nitrate or cobalt complex solutions obtained by dissolution of cobalt nitrate and ethylenediamine ( $\text{en}/\text{Co} = 1$ ) with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution was performed. After impregnation, the solids were dried at 100°C for overnight and calcined in air at 450°C (2°C/min) for 4 hours. Final products were noted  $\text{Co}(\text{en})$  or  $\text{Co}(\text{nit})/\text{CeO}_2$ . The same procedure has been performed on  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  support supplied by Rhodia. The powders were characterized by Raman spectroscopy, X-ray diffraction (XRD), specific surface areas (SSA) measurement, differential thermal and thermogravimetric analyses (DTA/TG),  $\text{H}_2$ -Temperature-programmed reduction (TPR) and conductivity measurements were performed on dense pellets by AC impedance spectroscopy. Butanol oxidation test was carried out in a fixed bed reactor and studied between 25 to 450°C. After a step of activation, the catalyst was submitted to 1000 ppmv of butanol diluted in air ( $10\text{ L}\cdot\text{h}^{-1}$ ).

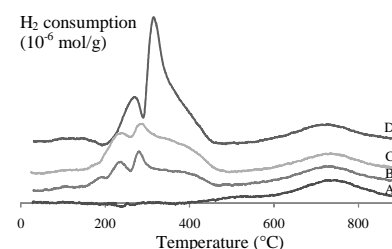
### Results and Discussion

A decrease in the SSA is observed after the impregnation of Co-precursor on  $\text{CeO}_2$  and  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  supports. This phenomenon is emphasized when ethylenediamine is used during the synthesis due to the size of the Co-ethylenediamine complex. After activation at

450°C, specific surface areas are close to that of support, in agreement with thermogravimetric analyses which revealed a complete Co precursor decomposition at this temperature.

XRD patterns obtained for the activated samples showed that (i) cobalt content increase from 2.5 to 7.5wt% leads to the detection of  $\text{Co}_3\text{O}_4$  and  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  phases (ii) for  $\text{Co}(5\text{wt}\%)/\text{Ceria}$ , the fluorite  $\text{CeO}_2$  structure is only observed whatever the precursor used. These results suggested the possible insertion of  $\text{Co}^{3+}$  in the ceria and the best dispersion of  $\text{Co}_3\text{O}_4$  using ethylenediamine during the synthesis. Indeed since the cobalt atom is surrounded by the ligands, cobalt atoms are forced to be far apart one from another leading to highly dispersed cobalt oxides [3].

According to the literature data, the  $\text{H}_2$ -TPR of ceria (promoted or not by Gd) exhibit two peaks corresponding to reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  (surface ( $T_{\text{max}} = 500^\circ\text{C}$ ) and bulk ( $T_{\text{max}} = 750^\circ\text{C}$ )). Cobalt introduction to  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  strongly modifies the TPR curve profiles (Figure 1). The main results are (i) reduction of surface ceria for  $\text{Co}(\text{nit})$  samples at lower temperature which can be explained by a spillover effect on metallic cobalt and (ii) presence of two types of cobalt species in relation to the anionic vacancies of the support.



**Figure 1.**  $\text{H}_2$ -TPR profiles of  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  (A) and  $\text{Co}(\text{nit})/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  (B) = 2.5wt% (C) = 5wt% and (D) = 7.5wt% of cobalt

The introduction of Co and Gd to  $\text{CeO}_2$  promotes the activity and the selectivity by respectively lowering the light-off temperature and by suppressing the CO formation observed in the presence of pure  $\text{CeO}_2$ . According to a redox mechanism, the differences in the catalytic performance of the butanol oxidation over cobalt ceria catalysts can be explained by a higher reducible quantity of metal oxides ( $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$ ) when ethylenediamine is used at the stage of impregnation or when the support is promoted by gadolinium.

### Significance

This work deals with the study of the potentiality of new modified cobalt ceria based catalyst for the destruction of VOC(s) emitted by stationary source.

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