Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Applied Catalysis A: General 288 (2005) 1–9

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Cobalt oxide/γ-alumina catalysts prepared by equilibrium deposition filtration: The influence of the initial cobalt concentration on the structure of the oxide phase and the activity for complete benzene oxidation

Theodora Ataloglou [a], Christina Fountzoula [a], Kyriakos Bourikas [b], John Vakros [a,b], Alexis Lycourghiotis [a], Christos Kordulis [a,c,*]

[a] *Department of Chemistry, University of Patras, GR-265 00 Patras, Greece*
[b] *School of Science and Technology, Hellenic Open University, Sahtouri 16, GR-262 22 Patras, Greece*
[c] *Institute of Chemical Engineering and High Temperature Chemical Processes, FORTH/ICE-HT, P.O. Box 1414, GR-265 00 Patras, Greece*

Received 9 August 2004; received in revised form 15 November 2004; accepted 15 November 2004
Available online 31 May 2005

Abstract

In the present work we studied the influence of the initial concentration of the impregnating solution used for mounting Co(II) species on the γ-alumina surface by equilibrium deposition filtration method (edf) on the physicochemical properties and the catalytic activity of the "cobalt oxide"/γ-alumina catalysts. The complete oxidation of benzene has been used as a model reaction.

Two series of catalysts (edf-X-A and edf-X-B) of varying Co content (X: up to 21 wt.% Co) were prepared using the above-mentioned method and tested at various temperatures in the range 200–300 °C using a fixed-bed reactor. In the first series (A) various Co loadings were obtained by varying the initial Co(II) concentration of the impregnating solution. In the second series (B) the corresponding Co loadings were obtained by using the impregnating solution used for the preparation of the catalyst of A series with the maximum Co(II) content and varying the impregnation time. All catalysts were characterized using various techniques, X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS), X-ray powder analysis (XRD), nitrogen adsorption (BET) and temperature-programmed reduction (TPR).

It was found that the initial Co(II) concentration of the impregnating solution used for depositing the corresponding species on the γ-alumina surface by edf influences the catalytic activity of the "cobalt oxide"/γ-alumina catalysts with respect to the complete oxidation of benzene. The increase of the initial Co(II) concentration of the impregnating solution brings about a change in the composition of the *deposited phase* formed in the impregnation step by decreasing the ratio "Co(II) surface inner-sphere complexes/surface Co(II) precipitates". Upon calcination, the Co(II) surface inner-sphere complexes are transformed to well-dispersed "cobalt oxide" phase strongly interacting with the support surface while the surface Co(II) precipitates are transformed to Co_3O_4 crystallites loosely interacting with the support surface. The former phase is responsible for the relatively high dispersion of Co observed in the A series of catalysts but it is rather inactive, while the latter exhibits lower dispersion but higher activity. Thus, the edf catalysts prepared using high initial Co(II) concentration exhibited higher catalytic activity than the corresponding ones prepared using low initial Co(II) concentration.

Keywords: Cobalt oxide catalysts; Preparation method; Equilibrium adsorption; VOCs combustion; Benzene oxidation; DRS; XPS; TPR

---

1. Introduction

Cobalt oxide supported on alumina catalysts are quite promising, among metal oxide supported catalysts, for the catalytic combustion of the volatile organic compounds (VOCs) [1,2]. It is well known that the physicochemical characteristics of the supported cobalt phase are crucial for the catalytic behavior of such catalysts. The latter depends mainly on the dispersion of the active species, their structure and their interaction with the support surface. In other words, the catalytic performance of alumina-supported

---

[*] Corresponding author. Tel.: +30 2610 997 125; fax: +30 2610 994 796.
E-mail address: kordulis@chemistry.upatras.gr (C. Kordulis).

doi:10.1016/j.apcata.2004.11.022

cobalt depends on the support properties and the nature of the surface species formed after the catalyst preparation [3–14].

In a recent work [15] we have studied the influence of the methodology used for depositing Co(II) species on the γ-alumina surface on the physicochemical properties and the catalytic activity of the "cobalt oxide"/γ-alumina catalysts. The oxidation of benzene, a typical reaction for the catalytic combustion of VOCs, has been used as a model reaction. We have compared the catalytic activity of the "cobalt oxide"/γ-alumina catalysts prepared by three different preparation methodologies, namely the simple pore volume impregnation (pvi), the pore volume impregnation adding in the impregnating solution nitrilotriacetic acid (nta-pvi) [16] and the equilibrium deposition filtration (edf) [17–23]. It was found that the catalytic activity for low, medium and high Co content follows, respectively, the orders, nta-pvi $\gg$ pvi $\gg$ edf, nta-pvi $\gg$ edf $\approx$ pvi and edf > nta-pvi > pvi. Therefore, it was concluded that the substitution of the conventional pvi technique either by adding nta in the corresponding impregnating solution or by the edf results to greater activity of the "cobalt oxide"/γ-alumina catalysts with low/medium or high Co content, respectively.

Detailed characterization of the catalysts studied indicated that the most active sites are located on Co_3O_4 supported crystallites loosely or moderately interacting with the γ-alumina surface. Two critical parameters, related with the method followed for mounting Co(II) species on the γ-alumina surface, control the characteristics of the supported phase and thus the amount and the size of the above-mentioned Co_3O_4 crystallites: the ratio "amount of Co(II) deposited in the impregnation step to that remaining in the liquid phase inside the pores precipitating thus in the drying step" closely related with the ratio "amount of Co(II) in the *deposited phase* (isolated Co(II) surface inner sphere complexes and Co(II) surface precipitates)/amount of Co(II) in the *precipitated phase* formed in the drying step" as well as the composition of the *precipitated phase*.

The application of the pvi technique resulted to low values for the above ratios. Therefore, in the pvi catalysts a rather unstable precipitated phase of $Co(H_2O)_6^{2+} \cdot 2NO_3^-$ predominates after drying. Upon calcination it is transformed into Co_3O_4 crystallites of relatively big size loosely interacting with the support surface. This is related to low Co dispersion and thus to low catalytic activity.

The application of the edf resulted to high values for the above-mentioned ratios. Therefore, the *deposited phase* is predominant. Upon calcination it is transformed to well (very well) dispersed cobalt phases strongly (too strongly) interacting with the support surface. Although these phases are responsible for high Co dispersion they do not contribute to the catalytic activity unless the *deposited phase* is mainly comprised from a Co(II) surface precipitate with relatively large number of layers as it is the case for the sample with the maximum Co content (21 wt.% Co).

The application of the nta-pvi technique resulted to very low values for the ratios mentioned above. This is because the [Co(II)-nta]- and $[Co(II)\text{-}2nta]^{4-}$ complexes, in which the $Co(H_2O)_6^{2+}$ complex is completely transformed, are not practically adsorbed on the support surface. Therefore, in the nta-pvi catalysts a *precipitated phase* containing the $[Co(II)\text{-}nta]^- \cdot NH_4^+$ (or H^+) and $[Co(II)\text{-}2nta]^{4-} \cdot 4NH_4^+$ (or $4H^+$) complex salts predominates. Upon calcination these salts are transformed into Co_3O_4 crystallites of small size, which are moderately interacting with the support surface. This is related to relatively high Co dispersion, mainly that for the catalytically active species, and thus to high catalytic activity.

Based on the above-mentioned findings and taking into account the carcinogenic action of the nta and the difficulties encountered following nta-pvi technique [14] we tried in the present work to ameliorate more the edf technique. The main goal is to prepare "cobalt oxide"/γ-alumina catalysts having Co_3O_4 crystallites of relatively small size (high Co dispersion), but moderately interacting with the support surface even at low and medium Co loading.

A reasonable approach towards this target seems to be related to the change of the composition of the *deposited phase* obtained upon equilibration. More precisely, the increase of the amount of the Co(II) surface precipitates at the expense of the isolated Co(II) surface inner sphere complexes formed could be proved beneficial for the catalytic activity. Such a change in the composition of the *deposited phase* is attempted by using high initial concentration for the impregnating solution.

In the present paper we studied two series of "cobalt oxide"/γ-$A1_2O_3$ catalysts, each one with varying Co(II) surface concentration. Both series were prepared by the edf methodology. In the first series (A) various Co loadings were obtained by varying the initial Co(II) concentration of the impregnating solution. In the second series (B) the corresponding Co loadings were obtained by using the impregnating solution used for the preparation of the catalyst of A series with the maximum Co(II) content and varying the equilibration time. All catalysts were characterized using various techniques, X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS), X-ray powder analysis (XRD), nitrogen adsorption (BET) and temperature-programmed reduction (TPR). Moreover, the catalytic activity of these catalysts was determined using the combustion of benzene as a model reaction, characteristic of the catalytic combustion of VOCs.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Materials

Cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$, 99% of purity] purchased from Merck has been used for the preparation of the solutions used in the preparation of the