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Influence of the preparation method on the structure–activity of cobalt oxide catalysts supported on alumina for complete benzene oxidation

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Abstract

In the present work we studied the influence of the methodology used for mounting Co(II) species on the γ-alumina surface on the physicochemical properties and the catalytic activity of the 'cobalt oxide'/γ-alumina catalysts for complete oxidation of benzene.

Three series of catalysts of varying Co content (up to 21 wt.% Co) were prepared using three preparation methods: pore volume impregnation (pvi), equilibrium deposition filtration (edf) and pore volume impregnation adding nitrilotriacetic acid (nta) in the impregnation solution. 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.

The catalysts prepared were characterized using various techniques (BET, UV–vis/DRS, XRD and XPS) at each step of the preparation procedure, namely after the Co(II) mounting on the support surface, after drying as well as after calcination. It was inferred 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 and thus to the formation of a rather unstable precipitated phase consisted mainly by $Co(H_2O)_6{}^{2+}\cdot 2NO_3{}^-$. Upon calcination it is transformed into loosely bounded Co_3O_4 crystallites of relatively big size. This is related with the low Co dispersion and thus with the low catalytic activity exhibited by these catalysts.

The application of 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) bounded with the support surface and thus reducible at high temperatures (non reducible up to 800 °C). Although these phases are responsible for the high Co dispersion achieved they do not contribute to the catalytic activity unless the *deposited phase* mainly comprises a Co(II) surface precipitate with relatively large number of layers as it is the case for the sample with the maximum Co content.

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 $[Co(II){-}2nta]^{4-}$ 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 $[Co(II){-}nta]^-\cdot NH_4{}^+$(or H^+) and $[Co(II){-}2nta]^{4-}\cdot 4NH_4{}^+$ (or $4H^+$) complex salts predominates. Upon calcination these are transformed into Co_3O_4 crystallites of small size, which are moderately interacting

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with the support surface. This is related with the relatively high Co dispersion, mainly that for the catalytically active species, and thus with high catalytic activity.

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

1. Introduction

It is well known that the dispersion and the physicochemical characteristics of the active species are the key factors determining the activity and the selectivity of the supported catalysts. Therefore, the maximization of the dispersion and the achievement of proper characteristics for the active species are challenges for heterogeneous catalysis. A reasonable approach towards the solution of this problem is related with the selection of an appropriate methodology of preparation. The deposition of the active species on the surface of catalytic supports, the most critical preparation step, usually takes place from electrolytic solutions. The pore volume impregnation (pvi), the wet impregnation, the deposition–precipitation [1] and the equilibrium deposition filtration (edf), otherwise called equilibrium adsorption [2–8] are the most popular methodologies which have been reported so far.

Following pvi or wet impregnation the deposition takes place mainly in the step of drying, which follows the impregnation step, by uncontrolled precipitation in the liquid phase inside the pores of the support due to water evaporation. In contrast, following deposition–precipitation the deposition takes place in the step of impregnation by controlled precipitation brought about by a precipitation agent added into the impregnating suspension. Finally, following edf the deposition also takes place in the step of the long time equilibration of quite dilute impregnating suspensions via adsorption, which in certain cases is followed by surface oligomerization, polymerization or surface (more precisely interface) precipitation [9–28].

Following the conventional pvi technique the dispersion of the active species usually achieved is not sufficiently high. In contrast, quite small supported crystallites of the active phase are usually obtained when edf or deposition–precipitation are used. In spite of the above, pvi is a very simple technique well fitted to the industry requirements. Sporadical studies have been reported dealing with the efforts done to improve the dispersion achieved following this technique. This is usually achieved by adding to the impregnating solution several substances which are presumably complexed with the active ion to be deposited, though the mechanism by which these substances act have not been elucidated in the most of cases [29]. On the other hand, it has been recently shown that a modified version of the edf technique may meet industrial demands [6].

In view of the above, a study devoted to the comparison of the above-mentioned methodologies for obtaining high dispersion of the active species is perhaps quite interesting from the preparative point of view. In this respect the selection of the 'cobalt oxide' supported on γ-alumina catalysts is quite promising for the following reasons. First, because it has been recently reported that the dispersion achieved by the pvi technique may be increased either by applying the edf technique [17] or by adding nitrilotriacetic acid [$N(CH_3COOH)_3$, nta] in the pvi solutions [29]. Second, because the above-mentioned catalysts are quite promising, among metal oxide-supported catalysts, in the catalytic combustion of the volatile organic compounds (VOCs) [30,31]. Third, because considerable progress has been pointed out concerning the deposition mechanism of the $Co(H_2O)_6^{2+}$ species, usually being in the impregnating solution, on the 'oxidic supports/electrolytic solution' interface related to the edf technique.

A review article dealing with this subject has been recently reported by our group [9]. It was concluded that the deposition mechanism depends on two factors: The acid–base properties of the support surface (γ-Al_2O_3, α-Al_2O_3, SiO_2, TiO_2) and the surface Co(II) concentration. Concerning γ-alumina it was concluded that mononuclear (monodentate, bidentate) or hydrolyzed mononuclear inner sphere surface Co(II) complexes are rather formed for Co(II) surface concentrations corresponding to lower than 0.33 theoretical $Co(H_2O)_6^{2+}$ surface layers. Above this value, the mechanism changes progressively, as the Co(II) surface concentration increases, from binuclear, oligonuclear, multinuclear inner sphere Co(II) surface complexes into surface $Co(OH)_2$-like precipitate at relatively high Co(II) surface concentrations though at lower pHs than those required for bulk precipitation. In all cases cobalt forms surface species with Co(II) in octahedral symmetry. A recent kinetic study of the $Co(H_2O)_6^{2+}$ deposition on the 'electrolyte solution/γ-alumina' interface has shown that even for Co(II) surface concentration corresponding to 0.03 theoretical $Co(H_2O)_6^{2+}$ surface layers at least binuclear or hydrolyzed binuclear inner sphere Co(II) surface complexes are formed [32].

In the present paper, we prepared three series of 'cobalt oxide'/γ-Al_2O_3 catalysts, each one with varying Co(II) surface concentration. The first series was prepared by pvi, the second by pvi in the presence of nta and the third by edf. These 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.