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Catalytic oxidation of VOCs and CO by ozone over alumina supported cobalt oxide

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Abstract

An alumina-supported cobalt oxide system with overstoichiometric oxygen (CoO_x/Al_2O_3) was investigated with respect to heterogeneous catalytic decomposition of ozone, complete oxidation of volatile organic compounds (VOCs) and oxidation of CO. The experiments were performed in the temperature range of −45 to 250 °C in an isothermal plug-flow reactor. The characterization of the CoO_x/Al_2O_3 catalyst was performed by chemical analysis, XPS, XRD, IR techniques, magnetic and adsorption measurements.

A very high activity of the catalyst towards ozone decomposition was observed even at temperatures below −40 °C, the catalyst remaining active for a long time. The activity of the catalyst with respect to complete oxidation of VOCs and oxidation of carbon monoxide was studied in presence of different oxidizing agents (ozone or oxygen). A significant increase in the catalytic activity and decrease in the reaction temperature was observed using ozone as an oxidant.

Two main reasons for this behaviour were found: (i) the high content of active and mobile oxygen obtained during the synthesis on the catalyst surface; (ii) the catalytically active complex of $O^-[Co^{4+}]$, formed during the reaction of ozone decomposition and able to oxidize VOCs at room temperature.

Keywords: Cobalt oxide; Ozone decomposition; CO oxidation; VOCs complete oxidation

1. Introduction

Catalytic processes are used for removing harmful components from waste gases. It is important to reduce the temperature of the catalytic reactions with a view to saving energy, at the same time keeping a high catalytic activity. Therefore, investigations are aimed at finding effective low-temperature catalysts or new catalytic processes. Such an appropriate process is ozone catalytic oxidation (OZCO method), which uses ozone as an oxidant in catalytic oxidation reactions. Ozone is known as a strong oxidizing agent for waste and drinking water treatment, sterilization and deodoration [1–3]. During the exploitation of copiers and laser printers, ozone is released into the office air [4]. Due to the fact that ozone itself is toxic, the residual ozone from these processes must be removed. The main method for neutralization of waste gases containing residual ozone is the heterogeneous catalytic decomposition. The catalytic ozonation is a promising method ensuring the purification of waste gases [5–10] and waters [11–13] from organic contaminants. The main hypothesis is that the catalytic ozone decomposition yields a highly reactive oxygen species, which completely oxidize the toxic compounds at lower temperatures [5,7–10].

The activity of various types of catalysts has been investigated with respect to both catalytic decomposition of ozone and catalytic oxidation of CO and VOCs with ozone. In many cases, alumina-supported metal oxides of Fe, Ag, Co, Ni, Mn, and Cu have shown high activity for ozone decomposition at ambient temperature [14,15]. The observed higher ozone decomposition activity of MnO_x/Al_2O_3 compared to the other catalysts has been explained by the ability of the manganese species to reach several different oxidation states [16]. However, the catalytic activity of these metal oxides in reaction of ozone decomposition decreases with time [17].

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Among transition metals oxides, cobalt oxides, both unsupported and supported on different oxide support materials (including alumina), belong to the most important catalysts for complete oxidation [18]. Their high catalytic activity in air pollution control of CO [19–22], NO_x [23–26] and control of organic pollutants from effluent streams [27,28] has been reported in a large number of papers. In previous publications [29,30], we have investigated a cobalt oxide system, prepared by the oxidation–precipitation method, which contained an overstoichiometric amount of oxygen and Co ions in a high oxidation state. It has been found that the obtained system, denoted as CoO_x, has a high catalytic activity towards some oxidation reactions taking place in aqueous and in a gaseous phase [31–33] as well as towards ozone decomposition (our unpublished data). According to the results obtained, the synthesized cobalt oxide system is prominent and useful in a wide field of applications in environmental protection. From a practical point of view, it is of interest to investigate the catalytic properties of this oxide system upon deposition on support materials.

The aim of the present work is to investigate the catalytic activity of an alumina-supported cobalt oxide system with overstoichiometric oxygen (denoted as CoO_x/Al_2O_3) during heterogeneous catalytic decomposition of ozone. Based on the high oxygen content in this catalyst, the oxidation of CO and organic substances, using two different oxidants (ozone and oxygen) will be studied.

2. Experimental

2.1. Sample preparation

The CoO_x/Al_2O_3 catalyst was prepared by deposition oxidation–precipitation method in an aqueous solution. The active phase of the supported catalyst (CoO_x) was synthesized according to the procedure described in detail in Refs. [29,30]. The required amount of $Co(NO_3)_2\cdot 6H_2O$ was dissolved in 150 ml of deionized water. The solution was heated up to 70 °C and then, the support—γ-Al_2O_3 was added and kept under continuous stirring for 4 h. After cooling to room temperature, the impregnated catalyst precursor was separated from the solution and was added to a mixture of aqueous solutions of NaOH (4 M) and NaOCl (1 M). The solid was kept digested for 24 h, washed several times (until disappearance of the chlorides), and then dried in an oven at 110 °C for 12 h.

2.2. Sample characterization

The bulk unsupported CoO_x catalyst was characterized by means of IR, XPS, ESR, XRD, DTA and chemical analyses. The specific surface areas of the supported catalyst and the γ-Al_2O_3 support were determined by the BET method using low-temperature nitrogen adsorption. Pore size distribution was evaluated from the adsorption curve of the isotherm, using the procedure developed by Orr and Dalla Valle [34]. The chemical composition was determined by atomic absorption spectrometry with Pye Unicam SP90V. The total overstoichiometric oxygen or so-called active oxygen content, O^* (the active oxygen content is considered to be the amount of oxygen above the stoichiometric content in the oxide, corresponding to the lowest stable valence state [35]) was determined by a direct iodine method [36]. The infrared spectra in the region of 4000–400 cm^{-1} was recorded on a Bruker model IFS 25 Fourier transform interferometer (resolution < 2 cm^{-1}) using KBr discs as matrices. The XPS studies were performed in a VG Escalab II electron spectrometer using Al Kα radiation with energy of 1486.6 eV. The residual gas pressure in the analysis chamber was 10^{-7} Pa. Binding energy values (BE $\pm$ 0.2 eV) were referenced to the C 1s line at 285.0 eV as well as to the Al 2p line of the alumina support at 74.3 eV. The integrated peak area of the Co 2p line was normalized to that of the relevant Al 2p line corrected by the corresponding photoionization cross sections. X-ray powder diffraction (XRD) measurements were carried out using a DRON-3 apparatus with a Co Kα radiation with scintillation calculation. Magnetic measurements were carried out in air with a magnetic apparatus constructed according to the Faraday method. The magnetic susceptibility (χ) was measured in the temperature range of 290–490 K with a magnetic field intensity varying from 2×10^3 to 10×10^3 Oe.

2.3. Catalyst activity measurements

The catalytic activity of the samples was investigated in an isothermal plug flow reactor. A catalyst particle size of 0.3–0.5 mm was chosen taking into account the reactor diameter (6.0 mm) and the volume rate (mean value 22 000 h^{-1}, calculated with respect to the total catalyst bed volume) in order to reduce the effect of external diffusion. The preliminary treatment of the catalysts included heating at 120 °C for 1 h in air flow. The rate of the gas flow was 4.4 l/h, the catalyst volume—0.2 cm^3, and the mass of the catalyst under consideration—0.15 g.

Ozone was synthesized in an oxygen flow (99.7% dried over silica gel) using an ozone generator with a silent discharge of 4–6 kV between the electrodes. The inlet concentration of ozone for the reaction of ozone decomposition varied between 22.0 and 24.0 g/m^3. The ozone concentration was analyzed with an Ozomat GM (Germany) ozone analyzer with an accuracy of ± 0.1 g/m^3. The reaction temperature varied between −45 and 25 °C and was maintained with an accuracy of ±0.2 °C.

The catalytic oxidation of CO and *iso*-propanol were carried out within the range of 25–110 °C and 25–250 °C, respectively. The amounts of CO and *iso*-propanol were dosed by an Ismatex MS2/6 (Switzerland) pump. The oxidizing agent was oxygen from synthetic air (gas mixture of 80% nitrogen and 20% oxygen) or ozone produced in oxygen. The inlet concentration of carbon monoxide was 0.18 vol.% and that of *iso*-propanol—0.095 vol.%. The inlet concentrations of ozone for CO and *iso*-propanol oxidation were chosen in stoichiometric ratios, considering that only one oxygen atom from the ozone molecule is consumed. The rate of complete oxidation was evaluated by measuring the amount of CO_2 formed during the reaction with a Maihak (NDIR) gas analyzer. The CO and CO_2 concentrations were determined with an accuracy of ±2 ppm. The same analyzer measured the oxygen with an accuracy of ±100 ppm.