PREPARATION, CHARACTERIZATION AND CATALYTIC ACTIVITY OF ALUMINA-SUPPORTED COBALT OXIDE FOR DESTRUCTIVE OXIDATION OF ORGANIC COMPOUNDS IN GASEOUS PHASE

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ABSTRACT

Complete oxidation of different volatile organic compounds (VOCs) and CO into harmless water and carbon dioxide using ozone and air as oxidizing agents was investigated over alumina-supported cobalt oxide catalyst. The synthesized catalyst has been characterized by a variety of methods including chemical analysis, IR spectroscopy, X-ray photoelectron spectroscopy, magnetic measurements. The results obtained reveal that the synthesized catalytic system is suitable for catalytic neutralization of exhaust gases from toxic compounds. A significant increase of the catalytic activity and decrease of the reaction temperature was observed using ozone as an oxidant.

Keywords: cobalt oxide, ozone decomposition, CO oxidation, VOCs complete oxidation.

INTRODUCTION

Volatile organic compounds (VOCs) represent a large class of substances emitted from chemical, petrochemical, and allied industries that contribute to both indoor and outdoor air pollution. The damaging effects of VOCs are numerous, ranging from minor annoyances such as eyes, nose, and throat irritation, headaches, and nausea to serious dangers such as damage to the kidneys, liver, and central nervous system. The treatment of such hazardous waste gases in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance.

An effective, economic and environmentally friendly method for abatement of VOCs is based on heterogeneous catalytic reactions providing complete oxidation. Compared to thermal oxidation, catalytic oxidation can be done at much lower

temperatures. Both noble metal catalysts and metal oxides have been studied extensively for the destruction of VOCs [1-6]. The development of more active metal oxide catalytic systems and using suitable oxidants would be advantageous to provide a low-cost alternative to noble metals for oxidative destruction of VOCs at mild conditions. Cobalt oxides, both unsupported and supported on different oxide support materials (including alumina), have proven their high catalytic activity in the field of air pollution control of CO [7,8] and organic pollutants from effluent streams [9, 10]. In previous papers [11,12] we have described the preparation of a bulk unsupported cobalt oxide system using the oxidation-precipitation method. It has been found that the obtained system has a high catalytic activity in some oxidation reactions, carried out in an aqueous and in a gaseous phase [13,14]. 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 important to investigate the catalytic properties of this oxide system upon deposition on support materials.

The present study aims to synthesize and characterize an alumina-supported cobalt oxide system (denoted as CoO_x/Al_2O_3), designed as catalyst for low-temperature complete oxidation and to investigate its catalytic activity and selectivity for oxidation of CO and volatile organic substances, using two different oxidants (ozone and oxygen).

EXPERIMENTAL

The CoO_x/Al_2O_3 catalyst was prepared by deposition oxidation-precipitation method in an aqueous solution. A required amount of $Co(NO_3)_2 .6H_2O$ was dissolved in 150 ml of deionised water. An aqueous solution of $Co(NO_3)_2$ was heated up to 70^oC and then, the support - γ-Al_2O_3 was added and kept under continuous stirring for 4 hours. The impregnated catalyst precursor was separated from the solution and subsequently added to a mixture of aqueous solutions of NaOH (4M) and NaOCl (1M). The solid was kept digesting for 24 hours, washed several times (until disappearance of the chlorides), and then dried in an oven at 110^oC for 12 h.

The catalytic activity of the samples was investigated in an isothermal plug flow reactor. 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. The inlet concentration of ozone for the reaction of ozone decomposition varied between 22.0 to 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 catalytic oxidation of CO and VOCs were carried out within the range of 25 to 110ºC and 25 to 250ºC, respectively. The amounts of CO and VOCs were dosed by an Ismatex MS2/6 (Switzerland) pump. The oxidizing agent being 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 VOCs - 0.09 vol.% . 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 $\pm$ 2 ppm.

RESULTS AND DISCUSSION

The results of chemical analysis and textural characterization of the supported catalyst are listed in Table 1.

Table 1. *The results of chemical analysis, magnetic measurement and textural characterization of the supported CoO_x/Al_2O_3 catalyst*

Co loading in the catalyst [% w/w]	5.16
Co surface density of the catalyst [atoms/nm^2]	2.55
O*/Co atomic ratio of the catalyst	1.51
BET surface area of the catalyst [m^2/g]	207
Total pore volume of the catalyst [cm^3/g]	0.36
Pore size (mean diameter) [nm]	4.8
Magnetic susceptibility of the catalyst χ (.10^6)	-0.12

The supported CoO_x/Al_2O_3 catalyst has a larger surface area than the unsupported one and can be expected to show a higher activity. On the other hand the CoO_x deposition induces a slight decrease of the BET surface area of the initial support, indicating partially blocking of the pores with a smaller diameter of the alumina. The applied synthesis yields mesoporous CoO_x/Al_2O_3 catalyst with mean pore diameter of 4.8 nm.

The IR spectra of the γ-Al_2O_3 support (a), the bulk phase CoO_x (b), the freshly prepared CoO_x/Al_2O_3 catalyst (c) and the used catalyst after ozone decomposition (d) are presented in Fig 1.

As seen from Fig. 1 the spectra of (c) and (d) do not differ essentially, showing that the catalyst structure is not altered during the catalytic reaction. A broad band centered at 3410 cm^{-1} can be attributed to the lattice modes of hydrogen bonded hydroxyl groups, whereas the band at 1640 cm^{-1} corresponds to adsorbed molecular water thus indicating that all the samples are hydrated/hydroxylated.

An intense absorption band at 580 cm^{-1} are observed in both spectra of the (c) and (d) samples. In accordance with the literature data [15], it is assigned to the stretching vibration of the surface cobalt-oxygen bond and also accounts for the presence of active oxygen in the samples. The indicated band is similar to the OB$_3$ vibrations in the spinel lattice of Co_3O_4 (where B denotes the Co (III) ions in an octahedral coordination), suggesting that the cobalt in CoO_x/Al_2O_3 is situated in an octahedral oxygen environment.
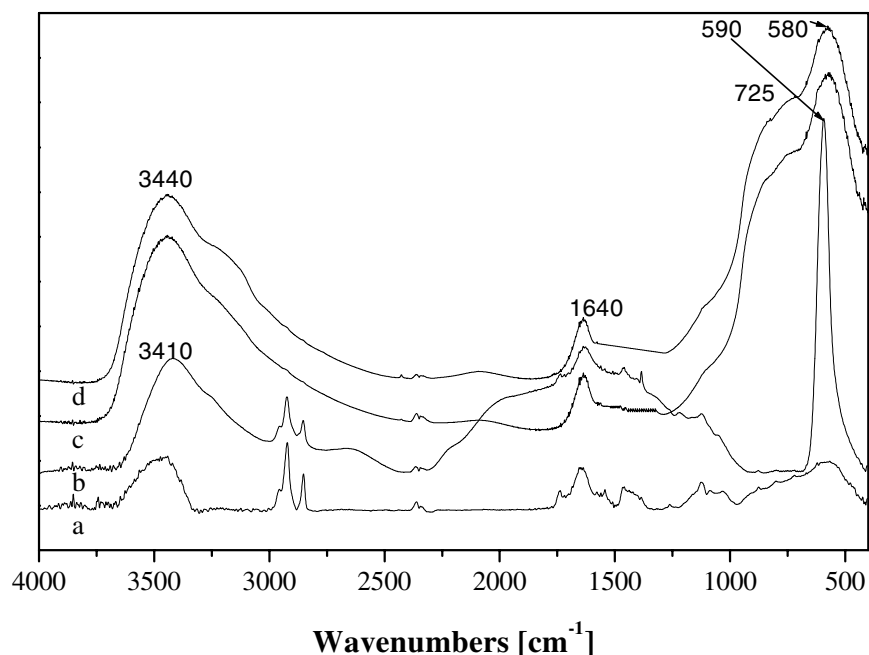
Figure 1. *Infrared spectra of γ-Al$_2$O$_3$ support (a), bulk phase CoO$_x$ (b), freshly prepared CoO$_x$/Al$_2$O$_3$ catalyst (c) and used catalyst after ozone decomposition (d).*

The Co2p XPS spectra of fresh and ozonated CoO$_x$/Al$_2$O$_3$ catalysts are shown in Fig. 2 curves *a* and *b*, respectively. The spectra of both samples show similar features, indicating that upon catalytic reaction there is no change in the electronic density of the cobalt atoms. The XPS spectra contain the spin-orbital components Co2p$_{3/2}$ at 780.3 eV and Co2p$_{1/2}$ at 795.3 eV. The measured binding energy values, spin orbit splitting of 15.0 eV and ambiguous satellites imply that the studied samples contain cobalt in a Co^{3+} oxidation state only, present as Co$_2$O$_3$. This assumption is confirmed by the magnetic measurement results (Table 1), according to which the CoO$_x$/Al$_2$O$_3$ contains Co(III) (octahedral) ions having t$^6_{2g}$ configuration and being diamagnetic ($\chi = -0.12.10^{-6}$).

Fig. 3 presents the time – conversion dependence of the CoO$_x$/Al$_2$O$_3$ catalyst in ozone decomposition measured at 700 min at three different temperatures: 25ºC, 0ºC and -45ºC. The activity of the catalyst towards ozone decomposition is very high even at temperatures below -40°C and reaches almost 100% at room temperature. Moreover, at each temperature in the beginning the activity is lower and with time followed by increase and stabilization. This behaviour reveals that active species are formed on the surface of the CoO$_x$/Al$_2$O$_3$ catalyst during the catalytic ozone decomposition, which leads to enhancement of the initial activity.

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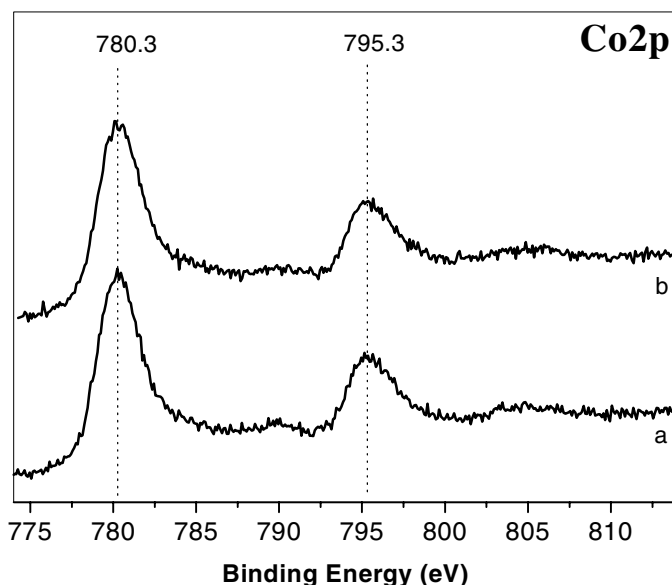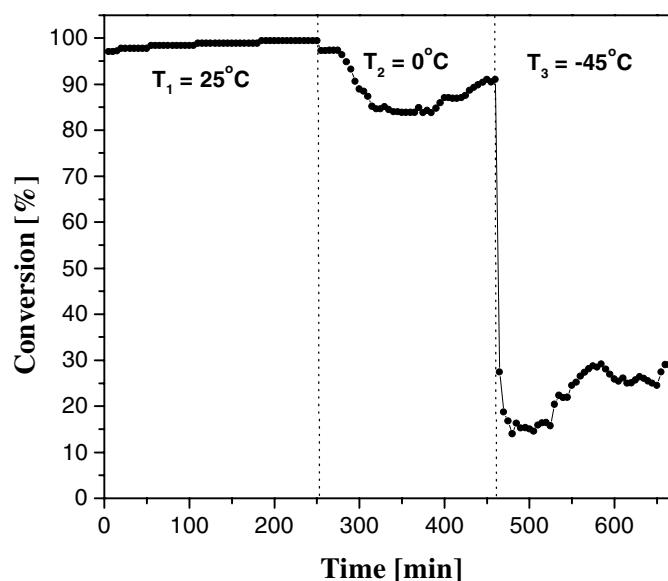**Figure 2.** *XPS spectra of fresh (a) and used (b) in reaction of ozone decomposition samples of the CoO_x/Al_2O_3 catalyst*

Figure 3. *Conversion – time dependence of the CoO_x/Al_2O_3 catalyst in ozone decomposition at different temperatures*

A significant increase of the catalytic activity of CoO_x/Al_2O_3 catalyst in complete oxidation of different VOCs and CO was observed using ozone as an oxidant instead of air (Figs. 4,5). In fact, the light-off temperature of iso-propanole conversion in presence of ozone is lower with 185^oC compared with the case of oxidation in air. Using ozone as oxidant allows carrying out the reaction in low-temperature region (below 80°C) which is extremely substantial in catalytic oxidation of toxic VOCs, because permits saving of energy.
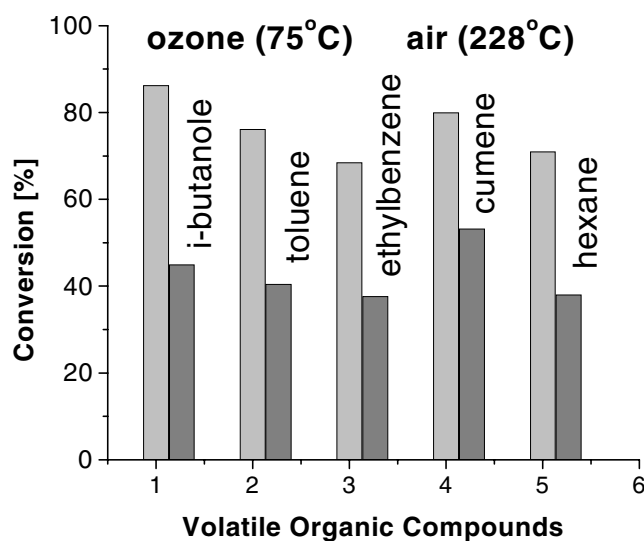
Figure 4. *Comparative study on the catalytic oxidation of different VOCs with ozone and air over CoO$_x$/Al$_2$O$_3$ catalyst*
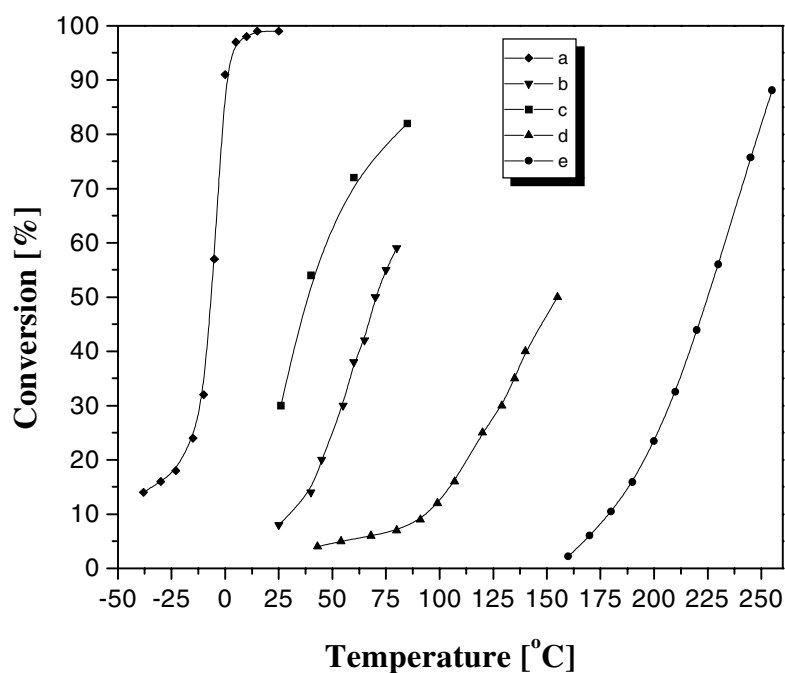

Figure 5. *Conversion - temperature dependences for: (a) - ozone decomposition, (b) - CO oxidation with O$_3$, (c) - i-propanol complete oxidation with O$_3$, (d) - CO oxidation with O$_2$ and (e) - i-propanol complete oxidation with O$_2$ over CoO$_x$/Al$_2$O$_3$ catalyst*

Two main reasons for the high catalytic activity are found: (i) high content of active and mobile oxygen obtained during the synthesis on the catalyst's surface; (ii) catalytic active complex of O-[Co^{4+}], which is formed during the reaction of ozone decomposition and it is able to oxidize VOCs at room temperatures.

Very important feature of the CoO_x/Al_2O_3 catalyst is that it possesses both activity toward ozone decomposition and ozone oxidation which lead to removing the residual ozone from waste gases. Hence the CoO_x/Al_2O_3 catalyst is very suitable for application in environmental catalysis.

ACKNOWLEDGEMENTS

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